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Wastewater Resource Recovery and Biological Methods

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Contents

Chapter 1
New Scope in the Field of Wastewater Treatment: Biopolymer Production and Its Uses

Archna Kumar, Deepika, Kashika Kapoor, Tarkeshwar, and Kapinder

Abstract The generation of a large amount of wastewater through industries and other sources could not be avoided due to fulfilment of daily needs which exhibit major global concern. Wastewater (WW) released from industries such as paper, distilleries, textiles, food and municipal waste consists of various organic and inorganic pollutants, when released into the environment, leads to a significant footprint such as eutrophication. There are several microorganisms present in the wastewater that can utilize biodegradable organic pollutants to synthesize various biopolymers of human interest as well as also help in the reduction of biological oxygen demand (BOD). Microorganisms such as Purple phototrophic bacteria (PPB) adapted to survive in the different complex environment due to the accumulation of various polymers internally for balancing the carbon/nutrient reserve or electron/energy balance during adverse conditions. Wastes from different industries have high potential as primary as well as secondary feedstocks through extraction, fermentation and various other techniques to produce biopolymers. Biopolymers obtained from these wastes are even categorized on the basis of the nature of the substance produced or its solubility. Polyhydroxyalkanoates (PHAs), bacterial cellulose, glycogen and polyphosphate are few examples of biopolymers derived from various micro-organisms present in the wastewater. In the present chapter, categories of biopolymers, their structure, types and their significance are discussed in details.

Keywords Biopolymers · Polyhydroxyalkanoates · Purple phototrophic bacteria · Bacterial cellulose

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1.1 Introduction

Rapid increases in human population, urbanization and industrialization, create great pressure on natural resources. Various statistical studies indicate that the injudicious exploitation of natural resources and the elevation of the above-mentioned factors are the major cause of the generation of high amounts of waste material. Among all the wastes, Wastewater can be explained as "Water that is being used and is obtained from various sources and is a combination or result of domestic, industrial, commercial or agricultural activities" (Carley and Christie 2017).

Wastewater has a great potential and may be an important and valuable asset if it is used and treated judiciously. However, wastewater generated from various sources such as industries, households' agriculture and other human activities consists of various pollutants as well as varying amounts of several nutrients such as proteins, starch, phosphates, fats, sulphates, nitrate and many more nutrients which can damage the aquatic environment's life if they are released in untreated form (Perera et al. 2019).

Recovered nutrients from wastewater can be further used as biofertilizers (Oliveira et al. 2021) and in many other useful products. Along with these nutrients wastewater also has microbial consortium that can be utilized as biodegradable organic pollutants to synthesize various biopolymers that are used for the humans welfare and reduce the biological oxygen demand (BOD). Polyhydroxyalkanoates (PHAs), bacterial cellulose, glycogen and polyphosphate are a few examples of biopolymers derived from various micro-organisms present in the wastewater (Fig. 1.1) (Fradinho et al. 2021). The utilization of biopolymers obtained from diversified sources has been explored in past years for biomedical and pharmaceutical enterprises. Generally, the degradation of biopolymers is simple in the ecosystem thus they are considered eco-friendly. Their application is prominently reflected in several industries like pharmaceutical, food, manufacturing, packaging and biomedical engineering industries. Several unique properties of biopolymers like abundance, eco-friendly, biocompatibility and non-toxicity etc. make them a promising material (Fig. 1.1). Recent advancement in nanotechnology is capable to enhance valuable properties and practical applications of biopolymers which open more and more possible ways for its commercial utilization. A few examples of biopolymers are protein, cellulose, starch, DNA, RNA, lipids, collagen, carbohydrates, etc. Numerous biopolymer products and possible applications are given in this chapter.

1.2 Biopolymer

The new generation or new era of polymeric material can be a promising tool in the form of a Biopolymer. These are also known to be "The building blocks of nature" because of their presence in all the living matter whether it is a microbe, higher and lower animal, or a plant in origin.

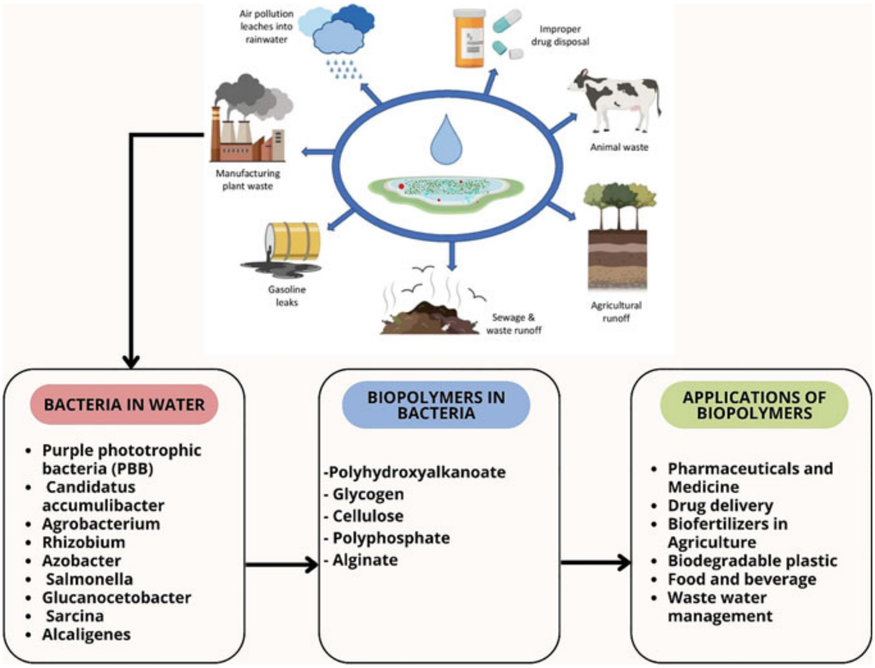


Fig. 1.1 Wastewater treatment using bacteria by the production of biopolymer

The term "biopolymer" is derived from two words bio and polymer; bio (prefix) means that the origin is made naturally (Pandey 2020) and it means that the nature of biopolymers is biodegradable. Biopolymers are monomers of covalently bonded units that form chain-like structures. These are degraded naturally by animals or microorganisms. From the, carbon dioxide and water are generated as by-products for the environment. Characteristics like renewability, abundance and biodegradability make it a good option to choose.

Biopolymers consist proteins polymers of amino acids, genetic material RNA and DNA polymers of nucleic acids, glycoforms-carbohydrates and glycosylated molecules, various metabolites, and other structural molecules (Fig. 1.2).

1.2.1 Types of Biopolymers Based on Repeating Units

1.2.1.1 Homopolymer

The polymers those are made by the repeating units of any one type like AAAAAA, BBBBBB etc., e.g. poly (ethylene terephthalate), poly (vinyl chloride), polyethylene.

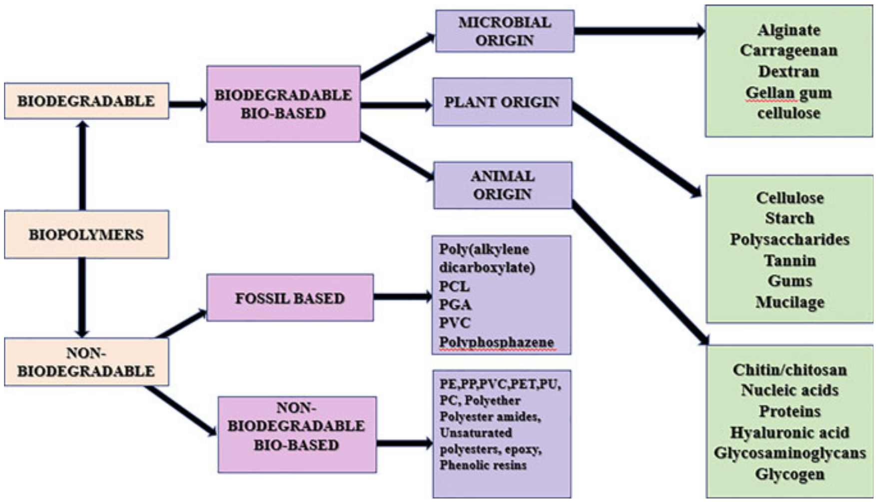


Fig. 1.2 The broad classification of biopolymers. *PE* polyethylene, *PP* polypropylene, *PVC* polyvinyl chloride, *PET* polyethyleneterephthalate, *PC* polycarbonate, *PCL* polycaprolactone, *PGA* polyglycolic acid, *PU* polyurethane polymers are classified into two main types on the based on the repeating units

1.2.1.2 Copolymer

Copolymers are also known as heteropolymers. These are made by the repeating units of more than one type in their structure e.g. poly (styrene-co-butadiene), poly (ethylene-co-propylene) etc.

Further Copolymers are subdivided into four main types.

1. **Random Copolymer** = These polymers have two or more than two numbers of repeating units. (A and B) such as ABBBBABBAAAA.
2. **Alternating Copolymer** = Repeating units (two (A and B) or more than two) are alternatively arranged in the chain. A-B-A-B-A-B-A-B-A-B.
3. **Block Polymer** = Repeating units are arranged in groups like AAAAA-BBBBB-AAAAAAA-BBBBBB.
4. **Graft Polymer** = Two homopolymers are covalently arranged where one homopolymer is grafted on the other homopolymer.

1.2.1.3 Purple Phototrophic Bacteria (PPB)

PPB are those bacteria which have an exclusive metabolism that helps them to survive in the diverse environment including waste water. PPB includes various biopolymers which help them to adapt in unfavorable and unstable conditions like starvation etc., Energy and Nutrients are necessary for the formation of such biopolymeric compounds but these also serve for storage electron/energy balance/carbon and nutrient reserve for adverse conditions. Glycogen, Polyhydroxyalkanoates (PHA) sulphur and polyphosphate are some biopolymers which are synthesized by PPB and can be used in various sectors such as the manufacturing of bioplastics and fertilizers sectors (Fradinho et al. 2021).

1.2.1.4 Occurence of Biopolymeric in PPB

Mainly there are four types of compounds that are synthesized by PPB and it depends on the condition in which PPB are growing. These compounds are PHA, Sulphur, polyphosphate and glycogen.

1.2.1.5 Poly-P

Polyphosphate is important in many features of bacterial metabolism like response in stationary growth phase, anxiety quorum sensing, pathogenicity or biofilm formation. Poly-P kinase (PPK), is the enzyme responsible for the biosynthesis of polyphosphate (Lai et al. 2017). Polyphosphate is formed by the repeating $PO_4{}^3$ which are attached by high-energy input anhydride bonds (Liang et al. 2010). Poly-P accumulates phosphate in respond to lack of phosphate however some organisms such as microalgae (Solovchenko et al. 2016), PPB (Lai et al. 2017; Liang et al. 2010) and Poly-P accumulating organisms (PAOs) (Desmidt et al. 2015). Uses Poly-P in place of energy storage (ATP) (Solovchenko et al. 2016), PPB (Lai et al. 2017; Liang et al. 2010) and Poly-P accumulating organisms (PAOs) (Desmidt et al. 2015). The presence of high intensity light is required for Poly-P in PPB. Similar kind of phenomenon also occurred in more photosynthetic microorganism (Carvalho et al. 2019).

Phosphorus is used as a biofertilizer in agriculture but it also has great applications in various industries such as food, pharmaceuticals etc., (Solovchenko et al. 2016) but the formation of bacterial Poly-p is not used commercially because of low-priced chemical synthesis process of phosphate (Iliescu et al. 2006).

For the maintenance of a sustainable aquatic environment, biotic seizure and recovery of Phosphate are crucial. In the coming future PPB biomass also can be utilised as N/C/P based biofertilizers but currently PPB are under trials for phosphate recovery processes (Sakarika et al. 2020).

1.2.1.6 Glycogen

Glycogen is a is a polysaccharide composed by glucose units and it is the mode of energy carbon and carbon storage which encourage existence inadverse conditions (Sekar et al. 2020).

1molecule of glycogen requires $2CO_{2,}$ 4 ATP, and 4 reducing equivalents and one molecule of PHB only involves 1 reducing equivalent and 2 ATP (Fradinho et al. 2014). It means glycogen needs more energy for their synthesis as compared to

PHA but the glycogen is necessary for polysaccharides biosynthesis during growth conditions. It acts as a natural carbon storage process. PHA regulates the electron balance and requires less energy (Bayon-Vicente et al. 2020).

1.2.1.7 PHA

PHA is the biopolymer synthesized in bacteria which provide them to survive in unfavourable conditions such as nutrition deficiency and to use it in carbon source and energy storage (Monroy and Buitron 2020). There are mainly two types of PHA one is medium-chain-length PHA (mcl-PHA) containing 6–14 carbons and other is short chain length PHA (scl-PHA) consist of 3–5 carbons.

1.2.1.8 Sulfur

Purple Phototrophic Bacteria (PPB) may flourish by using sulfur compounds in reduced form, especially Hydrogen sulphide. H_2S act as an electron donor in the biosynthesis mechanism of sulfur compounds (Pokorna and Zabranska 2015). Sulfide is converted to sulphate through an oxidization process. In this pathway, an intermediate, elemental Sulfur oxide is produced. Sulfur oxide gets collected in the form of droplets outside or inside the PPB. Sulfur oxide works as an electron acceptor (in accumulated form) and as a donor also (Trüper 1984), therefore sulfur compounds, specifically SO, are anticipated to have a substantial effect on the production and/or consumption of hydrogen by PPB (Laurinavichene et al. 2007). Surpluses of sulfur in the environment may be a cause for the induced accumulation of sulfur up to 30% of the dry weight of the bacterial cell (Pedrós-Alió et al. 1985). Studies indicated that there is no commercial production plant available for sulfur removal by PPB, But this seems like a promising technology for the future for example, for biogas desulphurization. A study executed in the laboratory and transformed at a Pilot scale indicated complete oxidation of H_2S of the biogas by exploiting the purple sulfur bacterium *Ectofhiorhodospira shaposhnikovii* (Vainshtein et al. 1994). Record also evidenced the success story of PPB amplified from domestic wastewater grown photoautotrophically. In this process inorganic carbon and sulfide act as electron donors for mixed culture. Recent studies also offer lead towards the probable capability of mixed cultures in photoautotrophic sulfide elimination. In this ascendency of purple sulfur bacterium Allochromatium sp. was detected (Egger et al. 2020). These all indicated mixed cultures of Purple Phototrophic Bacteria may be a key budding tool for synchronized wastewater management and biogas upgrading process, including the removal of carbon dioxide biogas desulphurization, organic matter, and nutrients removal (Marín et al. 2019).

1.3 Some Major Biopolymers that Are Extracted from Micro-organisms

1.3.1 Polyphosphate

1.3.1.1 Retrieval of Phosphorus in Form of Polyphosphates from Waste Water

Phosphorus retrieval from wastewater is an important topic as it is a non-renewable resource and its utilization in agriculture and many industries is very crucial (Chu et al. 2022). To overcome eutrophication in water bodies, some nutrients such as nitrogen and phosphorus need to be removed from the wastewater (Carey and Migliaccio 2009). Technologies which remove phosphorus from wastewater are of great interest. Enhanced Biological Phosphorous Removal (EBPR) is one such technology that removes phosphorus from waste water (Gautam et al. 2014).

In EBPR, organisms called Polyphosphate Accumulating Organisms (PAOs) play a major role. PAOsare the bacteria that remove phosphorus from waste water. PAOsachieve phosphate removal by the accumulation of polyphosphate (Poly-P) within themselves. (Tarayre et al. 2016). *Candidatus Accumulibacter phosphatis* is one of the important PAOs discovered (Hesselmann et al. 1999).

1.3.1.2 Methods for the Isolation of PAOS

Poly-P and poly-β-hydroxyalkonic acid (PHA) are mainly used to detect and identification of PAOs whereas Poly-P is mostly used for identification. First of all, the original samples are collected from wastewater treatment plants where free phosphate is removed from wastewater by collecting it as Poly-P (Bao et al. 2007).

Morohoshi et al. (2003) established a way by the visualization of blue colour on agar plates with the help of hydrolysis of 5-bromo-4-chloro-3-indolyl phosphate for PAOs detection. One another method was developed by Chaudhry and Nautiyal (2011) in agar plates by the use of Toluidine blue-O dye. However, it should be remembered that it has not been possible to isolate the pure culture of PAOs.

1.3.1.3 Phosphate Accumulation in PAOS

In EBPR process primary phosphorus storage compounds may be mineral or organic. For example, Cyanobacteria synthesize Phosphorus in their sheets with calcium and other bacteria accumulate teichoic acid which is made up of glycosyl and polyol residues linked by phosphodiester bonds (Kulakovskaya et al. 2012).

1.3.1.4 Isolation Mechanism of EBPR Process

The isolation process is directly influenced by anaerobic and aerobic mechanisms. The PAOs accumulate phosphate by switching between anaerobic and aerobic conditions, which are then isolated.

Anaerobic Condition: Before performing phosphate uptake assays, an anaerobic step is required to remove the nitrate, nitrites, and dissolved oxygen from the Poly-P. PAOs absorb Volatile Fatty Acids (VFA) from the wastewater. Simultaneously, the PAOs degrade glycogen to produce ATP and poly-β-hydroxyalkanoic acid (PHA). ATP is required for organic matter absorption and PHA synthesis. During the aerobic stage, the deposited PHA serves as a C-source and provides energy for phosphate accumulation and synthesis (Fig. 1.3).

Aerobic Condition: PHAs are degraded in aerobic conditions to allow for cell growth and the replenishment of glycogen and Poly-P reserve material. It is oxidatively phosphorylated to produce ATP. Soluble phosphorous is taken away from the environment and incorporated into Poly-P. Phosphate is then removed from the system when the PAOs are settled as P-rich sludge from the EBPR system after the aerobic stage (Fig. 1.4).

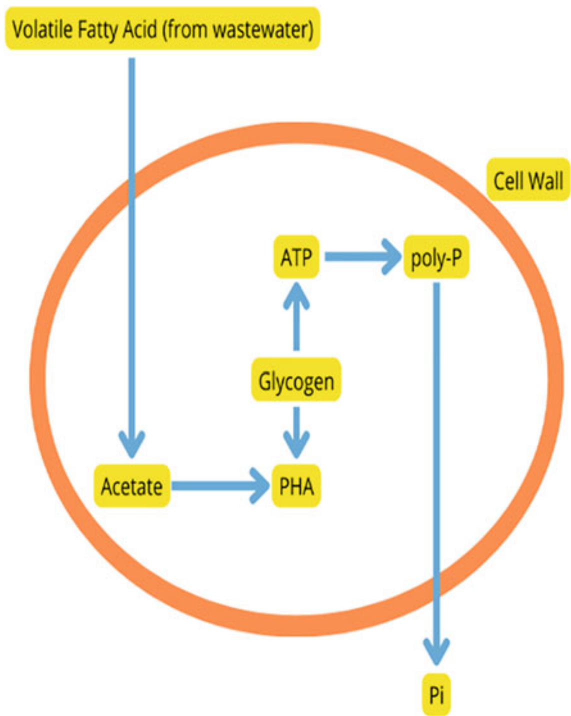


Fig. 1.3 Anaerobic mechanism

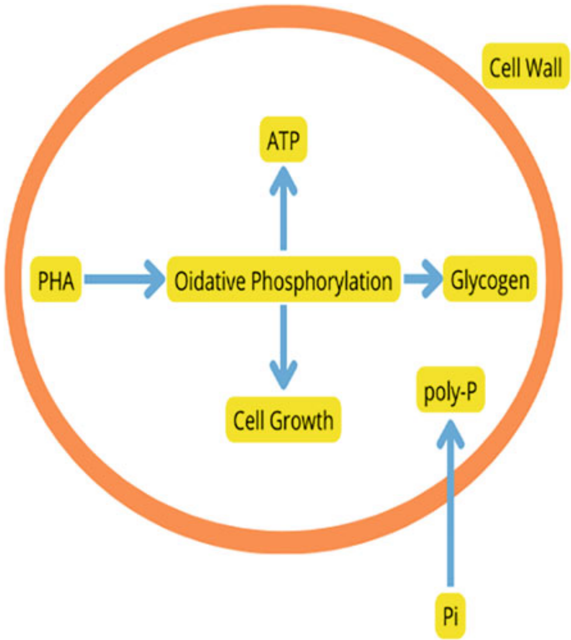


Fig. 1.4 Aerobic mechanism

1.3.2 Cellulose

Cellulose is mainly extracted from plants and bacteria. This naturally occurring phenomenon of cellulose makes it the most abundant biopolymer on earth. The highest pure form of bacterial cellulose creates the interest of many researchers and industrial sectors (Gorgieva and Trček 2019).

Bacterial Cellulose (BC) is a biocompatible, extremely natural and pure, adjustable material which is very useful. BC derived materials are in demand nowadays because of their applications such as skin related diseases such as ulcers, burn, and wounds etc., (Sulaeva et al. 2015). Studies also reflect that BC is the future of regenerative medicine material designed specially which offers us cell adhesion, migration, proliferation, differentiation etc.

The membranes of bacterial cellulose speed up the process of epithelization in order to avoid infections. BC bio composites hold the potential for regulating cell adhesion. Materials derived from BC promises the enhancement of quality along with the functionalities of the current generation of biomedical materials (Portela et al. 2019).

1.3.2.1 Structure of Bacterial Cellulose

A translucent and gelatinous film is formed around the BC. This layer is formed by interwoven of indefinitely very long cellulose microfibrils which is distributed in very random directions. Also, bacterial cellulose is formed by gram-negative bacteria cultures of *Agrobacterium, Gluconacetobacter, Acetobacter, Achromobacter, Azobacter, Pseudomonas, Rhizobium, Salmonella, Aerobacter, Alcaligenes, Sarcina* extracellularly (Sheykhnazari et al. 2011).

Gluconacetobacter genus has the highest efficacy of BC producer. At the time of formation of BC *Gluconacetobacter* forms a pellicle. This pellicle has microfibrillar grid of cellulose chains that too in parallel orientation. The chemical structure of BC is made up of (1 → 4)-D anhydroglucopyranose chains bounded through -glycosidic linkages 1. Intra and inter hydrogen bonding networking, forming parallel chains, van der Waals and hydrophobic interactions are responsible for determining the geometry of the material. For the making of anti-parallel packing, BC is treated with 5–30 wt% of sodium hydroxide has a small diameter or we can say that due to its reduced diameter it posses higher surface area than the cellulose obtained from different sources (Kolpak et al. 1978).

1.3.2.2 Application of Bacterial Cellulose

Because of the high in vitro biocompatibility BC membranes are found as ideal wound dressing material, a good choice for providing optimal three-dimensional substrate attachments for the cells. BC is flexible, can exchange gasses and has water retention capability. Not only this BC membranes can sustain a protective layer which helps in reducing bacterial infection, pain etc. BC is commercialized as many trademarks, such as Xcell®, Bionext® and Membracell® that mimic the extracellular barrier to increasing epithelialization.

BC also has innovative and very interesting utilization in the field of Biosynthetic grafts i.e. in ophthalmic scaffolds and contact lenses. Also, BC is used as emulsion and hydrogel stabilizers so that it can help in the reduction of the use of surfactants in Pickering emulsions.

BC is also used in drug-delivery systems to ameliorate drug uptake by targeted cells. Thus, we can say that BC and materials derived from it help in the diagnosis and treatment of a wide variety of diseases (Picheth et al. 2017).

1.3.3 PHA (Polyhydroxyalkanoates)

The PHA is the biopolymer created by the microorganism for using it during stress-full periods such as lack of nutrition etc., and to utilize them as a energy and carbon storage. The best part of the PHA is the they are biodegradable polymer or form of plastic and the reason is that they are made by naturally produced (Mannina et al.

2020). Both kinds of bacteria gram-positive as well as gram-negative have ability to produce PHA. Bacteria like *pseudomonas. Halomonas, Bacillus magaterium* and *Cupriavidusnecator* have the ability to produce various PHA (Muneer et al. 2020). Both the positive and negative bacteria have 40% of the dry weight of PHA (Zinn et al. 2001). Nowadays various industries and researchers and industries looking forward to making a biodegradable plastic through this but it takes a lot of monomer units to make as single polymer and that is why this method is kind of expensive and time consuming. The First PHA was discovered in 1925 by Limoigne. When further researchers go on came to know that plastic which is produced by PHA is thermoplastic and the plastic of PHA is produced when we treat the PHA chemical with temperature. Some good examples of PHA are *Lactobionic acid, Glucanolactone*and *polyhydroxybutanic acids.*

1.3.3.1 Properties of PHA

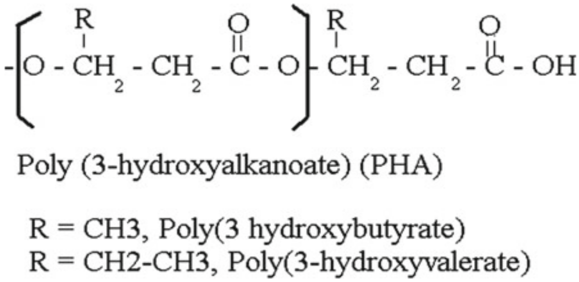
One of the most salient properties of PHA is they have a dual nature which shows the nature of carbohydrates as well as the nature of lipids. Their weight property is more identical to carbohydrates while their solubility in water is very similar to lipids.

Evidence indicated that it is an organic polymer which is biodegradable, natural and organic, nontoxic and easily renewable and replenishable material.

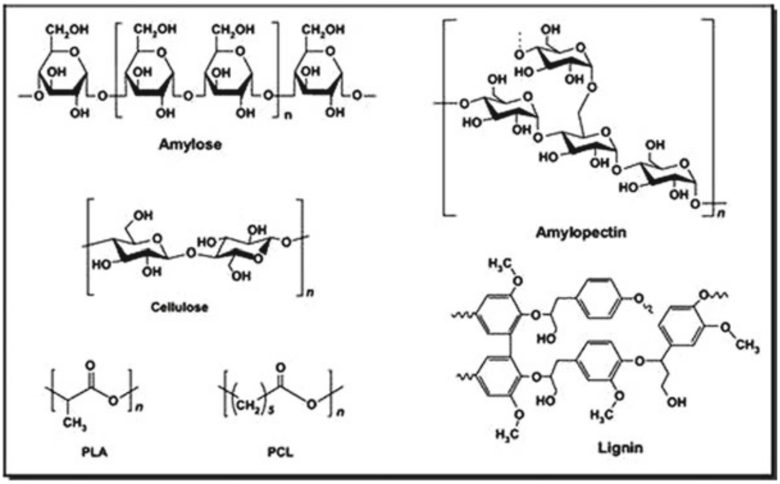
- PHB (polyhydroxybutanate) a type of PHA has additional properties than other PHA chemicals. Such as PHB have highly air impermeability and it does not let gases in or out easily
- PHB has water insolubility as well as PHB is the thermoplastic
- PHA has really good resistance to UV rays
- They are usually stiff in physical property
- A High degree of polymerization
- They show the modification for polymerization such as block copolymerization and graft copolymerization.

1.3.3.2 Structure

PHA hasround granules 0.1–0.2 mm diameter in size. Mostly accumulated in the cytoplasm of bacteria. PHA monomers give rise to the PHA polymer such as polyhydroxybutanate where 600 repetition of the PHA monomer gives rise to the simplest PHA polymer while the limit can be extended to 35,000 monomers in structure the CH_2 can be repeated 1, 2 or 3 times in the chain of the PHA while the functional group which is denoted by the R in chain can be used from 1 to 3 as a acyl (Zinn et al. 2001).



Monomer unit of PHA



https://tse4.mm.bing.net/th/id/OIP.xmvo5q-uxmR-E-t8LJeqswHaEj?pid=ImgDet&rs=1

This fig is an example of the various chemical structure which belongs to polymers of PHA.

Production of PHA

PHA is naturally produced by various gram-positive and negative-bacteria. For commercial industry level production tons of bacterial culture is required.

For this much quantity production a lot of such as sulfur, nitrogen, oxygen and carbon is needed. It need a lot of time and capital. At least 600 monomers are required to make a single polymeric unit. Several researchers are working on the development of a special strain of such microorganisms which can produce a lot PHA monomers. This may be useful for industry level production and can increase the manufacture of biodegradable plastic.

1.3.3.3 Biosynthesis of PHA

The Above description reveals the path of PHA production in laboratories and in industries. In further discussion, the biology behind PHA production is discussed.

Bacteria have three Pathways of producing PHA (Fig. 1.5):

1. The glycolysis of the stored sucrose and producing enzymes like PHAA, PHBB and PHAC that glycolysis its inner previous stored nutrition and produce PHA.
2. Breaking down of fatty acid in the bacterial cell that also takes place through the same enzymes.
3. Through carbon sources while the enzyme remains the same but the pathways will be different.

1.3.3.4 Applications of PHA

According to the recent data, the plastic production has reached around 360 million tons in 2018 worldwide (Plastics Europe 2019) and only 2.01 millions tons bioplastic is produced worldwide i.e. 0.56% of world's plastic production (European Bioplastics 2020).

However, the high input values in terms of economy to maintain a pure microbial fermentation process for the invention of industrial PHA is the major problem. The cost of PHA production is around (7–12 € PHA kg^{-1}) which is extremely high as related to other biopolymers such as polylactic acid (2.5–3.0 € kg^{-1}). This creates a hurdle in further research activities and their utilization for commercial applications such as the medical and pharmaceuticals sector (Koller et al. 2017). The PHA can be used as a biodegradable plastic which is environmentally friendly and will reduce environmental pollution.

1.4 Conclusions

Wastewater comes from various sources like the food and pharmaceutical industry, agriculture, sewage, domestic and other human activity consists of various nutrients and harmful pollutants also. From wastewater, organic pollutants may be converted into biopolymers through microbes like PPB. The Significance and categories of biopolymers are discussed in this chapter elaborately. Mechanism of Glycogen, PHA, sulphur and polyphosphate and their applications such as biodegradable plastic, drug delivery, biofertilizer in agriculture, pharmaceuticals and medicine etc., Along with this a critical review is constructed on retrieval of polyphosphate and cellulose from wastewater. However, the cost, technologies and interdisciplinary approach for biopolymer formation provide a hurdle in the current century but it will become an eco-friendly and biocompatible approach in the coming future.

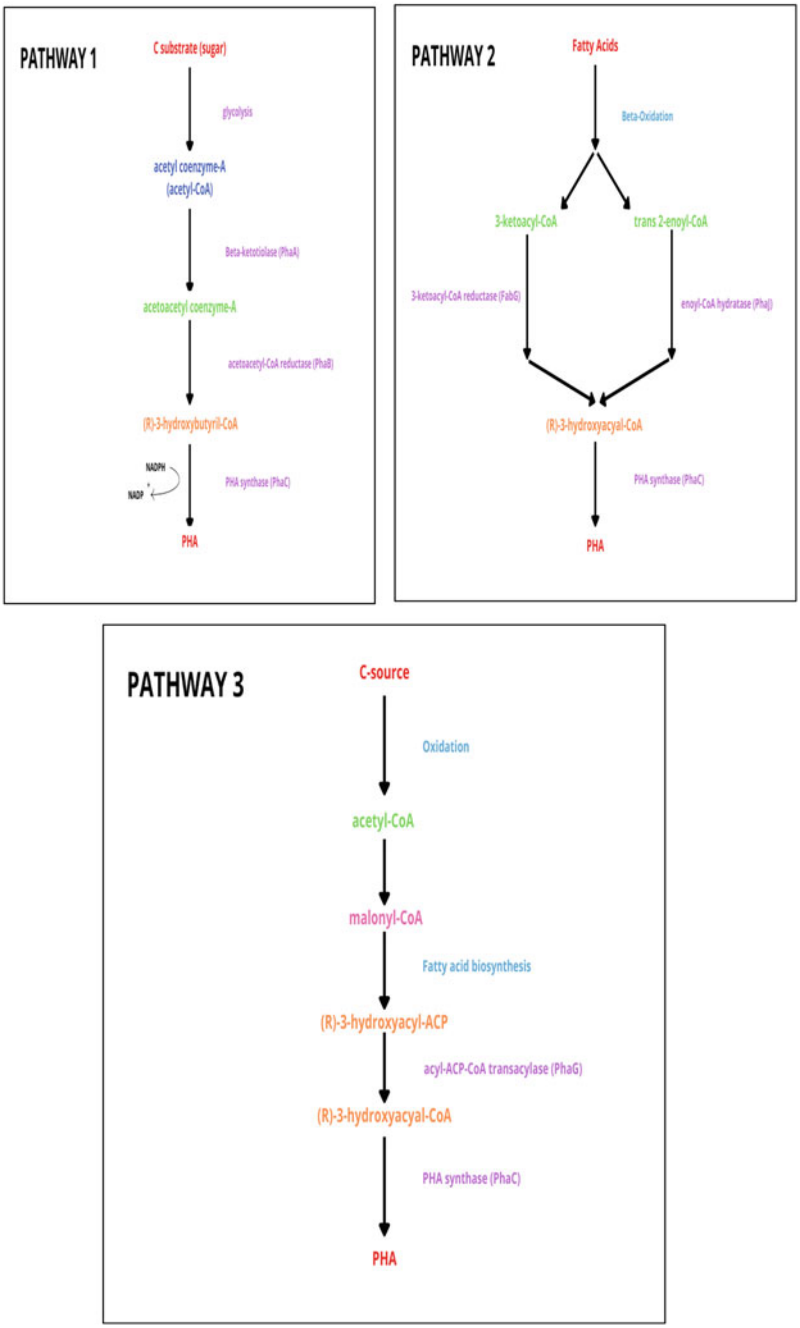


Fig. 1.5 Pathways of producing PHA

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Chapter 2
Recovery of Nutrients from Wastewater

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Abstract Macronutrients like phosphorous (P) and Nitrogen (N) or nutrients like Calcium (Ca) and Potassium (K) could be recovered from wastewater. Recently, several technologies like enhanced biological phosphorous removal, chemical and electrical precipitation of nitrogen, microalgae-based methods to recover nitrogen, struvite transformed into fertilizer, use of UV light, and others have been proposed to recover nutrients from wastewater. The depletion of phosphoric rock and the escalating prices of obtaining Ca, K, and N, and the advances in wastewater treatments have paved the way to develop new technologies or to improve the efficiency of the current ones. This is a worldwide trend encompassing industrial powerhouses, and third world countries economies. We discuss: (a) the conditions that brought the world to this emerging situation, (b) the technologies that used, modified, or recently emerged to cope with this situation, (c) the economics of nutrient recovery from wastewater, (d) suggest new proposals for future research.

Keywords Nutrient depletion · Eutrophication · Environmental pollution · Fertilizers · Emerging technologies · Wastewater treatment plants

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2.1 Introduction

This chapter is intended to update researchers, managers, administrators, politicians, and public in general about the new paradigm that face the water treatments plants (WTPs) nowadays. We pass from a culture of removal to a culture of recycling, and to no doubt the easiest and most likely component of wastewater and general waste in general are nutrients. Therefore this chapter is dedicated to the recovery of the main nutrients present mainly in wastewater of all kinds.

2.2 Recovery of Macronutrients Phosphorous and Nitrogen and Their Salts

The main nutrients recovered from wastewater are phosphorous (P) and nitrogen (N) in different salts and under a great variety of conditions and procedures. These elements and their salts are essential compounds of genetic material, amino acids and chlorophyll. Besides, P is an important component of the energy budget of organisms as part of Adenosine Triphosphate (ATP). The most common form of P on earth is found in sedimentary and igneous rocks where mining is the most viable extraction option (Sengupta et al. 2015). However, P is a non-renewable resource with high probability of exhaustion (Sengupta et al. 2015; Perera et al. 2019). On the other hand, N is abundant in the atmosphere (78%), but its presence in soil is limited. In soil its bioavailability is due to N fixation in reactive forma like amino acids, nitrates, and ammonium. However, N in soil is insufficient to satisfy the food and energetic demand of the world population, even as of today, when the anthropogenic production of reactive nitrogen is increasing (Sengupta et al. 2015). One strategy is the partial substitution of fertilizers by manure which could increase crop production and decrease the emission of NH_3 and N_2O depending of the local environmental conditions (Zhang et al. 2019).

Most of the nutrients found in wastewater are carbon, N and P (Sengupta et al. 2015). Different types of animals, domestic, and industrial residues contain N and P generating contamination of water. These residues could be discharged in aquatic systems untreated. However, even wastewater treatment plants (WWTPs) contribute to the N load in both superficial and underground water. Therefore, removing these contaminants is crucial for protection of the water resource (Rahimi et al. 2020). The conventional WWTPs ordinarily remove nutrients from wastewater with phosphate-enriched sludge and convert nitrogenated compounds in nitrogen gas via denitrification/nitrification to control eutrophication. However, the energy incorporated from nitrogen compounds can be lost during the conversion to nitrogen gas; the phosphate in the sludge is relatively diluted and can sometimes get lost in the receptor aquatic systems making it difficult its recovery (Perera et al. 2019).

The different oxidation states of N make its removal process complex and daring. Treatments with absorption or coprecipitation sometimes are not adequate due to the stability and solubility of nitrate resulting in high energy and cost. Most of the WWTPs include only the physical sedimentation of solids (primary treatment) and diverse forms of biological oxidation (secondary treatment). The removal of nutrients and disinfection (tertiary treatment) is the treatment that enhances the quality of the effluent before its reuse, recycling or discharge. However, its implementation depends on environmental legislation (Rahimi et al. 2020).

The discharge of nutrients containing N and P could provoke eutrophication in aquatic systems (Sengupta et al. 2015; Perera et al. 2019). In freshwater ecosystems, eutrophication is the result of big loads of N, which alters the structure and dynamics of the ecosystem causing algal blooms with the possibility of producing cyanotoxins causing proliferation of aquatic plants, oxygen depletion, put at risk the species belonging to that particular ecosystem, and even affectations to human health (Rahimi et al. 2020).

Intense agricultural and animal husbandry practices is associated with diverse environmental impacts including the increase in the emission of greenhouse gases and reactive N due to the change of soil use, the demand of synthetic fertilizers and husbrandy; agriculture is the main source of emission of nitrous oxide (N_2O) due to the use of synthetic fertilizers and manure (Zhang et al. 2019). The use of fertilizers based on N and P is fundamental to fight worldwide nutrition. Approximately 170 Tg (Teragrams) of reactive N (NH_4^+) are applied in crops annually, accumulating only 4 Tg, and the rest is lost through air or water altering their quality affecting human health and biodiversity. Besides, 2% of global reactive N is liberated as N_2O contributing to global warming and affecting the ozone layer; 12% of that global reactive N is dissipated as NO_x and NH_3 affecting the atmosphere (Sengupta et al. 2015).

Recovery of nutrients is fundamental, its reintegration as fertilizers decrease their cost and accumulation in the atmosphere contributing to food production. This recovery is part of the 3R's strategy (reduce, reuse, recycle). Therefore, the use of nutrients that generates lesser environmental impact can contribute to the burden reduction of the N and P production decreasing their entrance to the environment (Sengupta et al. 2015).

The N and P obtained by microalgae can be used to produce fertilizers, bioenergy, food, animal feed, and pharmaceuticals. Besides, treatment of residual water with microalgae includes assimilation of organic contaminants, which are converted into cellular constituents (carbohydrates and lipids), becoming a good alternative for WWTPs with less environmental impact (Rahimi et al. 2020). There are diverse methods for nutrient recovery, depending on the availability of material, costs and efficiency of recovery. The next sections will summarize the most important methods used for N and P recovery.

2.3 Phosphorous Recovery

2.3.1 Ionic Exchange and Adsorption

Absorption and the interchange of ions can be used as columnar systems in a fixed bed through which residual water passes through or can be dispersed through the residual water settlement in a clarifier. Depending on the sorbent material, the attraction between the sorbent and the sorbato could be physical or chemical; physical absorption usually uses Van der Waals forces to attract the target solute, while chemical absorption removes the target solute through a chemical reaction (Sengupta et al. 2015). The PO_4^{3-} is absorbed in a porous selective medium of P interchanged with Cl^- cations to reduce the P from the effluent maintaining neutrality (Perera et al. 2019). When the sorbent is used, the columnar system of fixed bed has many advantages over other methods of removal and recovery of P. The sorbent could be regenerated and recovered several times, and P can be recovered easily through the regenerating agent as struvite. Different materials have been suggested as P adsorbents with the limiting factor of their specific chemical composition, which make it difficult to determine the efficiency of regeneration and removal. Among the most common absorbents are iron and aluminum hydroxides given their great capability of forming ligands with oxyanions like P. The most common limitations to this kind of absorption are the high cost of regenerating agents and sorbents for the pretreatment of residual water for the correct function of the system according to the specific capacity of the sorbent and the safe elimination of the wasted regenerating agent. Phosphorous precipitation outside the regenerating agent allows to continue with recycling and reuse of the solutions. Some systems use non-hazardous regenerating solutions like sea water at neutral pH, reducing the disposal of hazardous wastes (Sengupta et al. 2015).

There are many commercial ion exchangers such as Purolite A500P, A520E. Hybrid anionic exchangers like (HAIXs) and Amberlite IRA-410 composed of hydrotalcite. There are also synthetic media with good removal capacity like DOW-Cu, DOW-FeCu, and DOW-HFO. Regardless of the exchangers and regenerating media the systems are adequate to remove trace concentrations of P in effluents with low solid concentrations (< 2000 mg/L). Besides, it is possible to regenerate the medium using a similar amount of alkaline solution or brine or their mixture. The desorption solutions (regenerating agents) include NaCl (1–6%), $MgCl_2$, and mixtures de NaCl e NaOH. However, the amount of P desorbed depends on the type and volume of the desorption solution used, as well as in the process of regeneration. Phosphorous extraction through the regenerating solution is very important from the perspective of nutrient recovery, as well as the cost of the process. A common system is when P is recovered as struvite or calcium phosphates. Precipitation of P is conveyed through addition of calcium salts [$Ca(NO_3)_2$] or a mixture of $MgSO_4.7H_2O$ and NH_4Cl. In spite of the fact, that the precipitation can produce high purity fertilizers with HAIX medium, liberating metal ions (Al^{3+} and Ca^{2+}) can reduce the purity of the production (Perera et al. 2019).

2.3.2 Magnetic Microsorbents

The nutrients absorbed in a magnetic medium are recovered by capturing medium suspended using magnetic dividers of great gradient with the subsequent regeneration and precipitation of the desorption medium. Among the most common magnetic microsorbents, we found ferromagnetic zirconium ferrite ($ZrFe_2(OH)_8$), particles of carbonyl iron, particles of iron and magnetite, and nanoparticles of Fe_3O_4 soaked a matrix of SiO_2 coated with selective phosphorous. The magnetic ion exchangers used typically to remove organic compounds, can be used to remove P from secondary effluents. Most of these materials are capable of reducing levels of P under 0.05 mg/L of total P (< 0.005 mg/L PO_4-P). The regeneration can be done with several solutions or mixtures like of MgFe–Zr with 88% and 95% absorption and desorption, respectively. Desorption can be carried on with a solution of NaOH 1M + NaCl 1M (Perera et al. 2019).

2.3.3 Filtration

Phosphorous in residual water can exists as organic solids and dissolved phosphates, the latest ones related directly with the BOD_5 concentrations, total suspended solids, and volatile suspended solids of residual water. Removal of dissolved P and solid P through rapid sand filtration with a membrane offers a practical and simple solution for the reduction of tertiary P, in recent years, it has been improved in efficiency and its price reduced. Among the most common sand filters, there are the membrane tertiary filters, reverse osmosis filters, and membrane bioreactors, which use a system of auxiliary suspended growth for the removal. However, despite the good results, these systems are costly and it is not easy to recover P (Sengupta et al. 2015). Orthophosphates and P particles are removed due to different mechanisms. Activated zeolite is a good matrix for recovery of P and ammonia simultaneously via calcium and magnesium precipitation to form brushite and struvite and a superficial complex containing Al and Fe; these zeolites can potentially be used as slow-release fertilizers (Perera et al. 2019).

2.3.4 Urine Separation

The domestic residual waters can contain 50–80% of P and 80–90% of N from the urine, which represents 1% of the total volume of domestic residues. It is possible to recover N and P simultaneously using coprecipitates of struvite with $MgK(PO_4)$ and $MgNa(PO_4)$ from a divided source of urine. In fact, urine could be used as fuel of microbial cells after the pre-precipitation with struvite using $MgSO_4$, MgO, $Mg(OH)_2$, $MgCl_2$ or synthetic marine water as a rentable source of Mg. Phosphorous recovery increases proportionally to the increase in Mg. However, typical urine has a proportion of Mg:P of 0.1:1, which creates a necessity of adding Mg^{2+} as $MgCl_2$. Regardless of the precipitated form of struvite, the recovery of nutrients from divided sources of urine has the inconvenient of the necessity of adding Mg and adjust pH which represents 97% of the costs are attributed to NaOH and pH adjustment (Perera et al. 2019).

2.3.5 *Struvite Precipitation*

The struvite is considered a good slow release that increases the agronomic properties when combined with complex fertilizers. Struvite is known as magnesium ammonium phosphate, is of prolonged release, low frequency application and lacks fertilizers and avoids burning crops at high application rates. Recovery of P by crystallization of struvite has advantages over other technologies in terms of purity, crystalline form, and the characteristics of desiccation of the product, efficiency of P removal, and the presence of Mg in struvite, the capacity of simultaneous removal of ammonium and low loss of N due to evaporation when compared with other fertilizers with N. Struvite is crystallized when the concentration of PO_4^{3-}, NH_4^+, and Mg^{2+} exceeds the solubility index of struvite. The recovery of P as struvite is a common process of separation applied to sources rich in nutrients such as urine divided from the original source, lixiviates from landfills, swine residual water, supernatant from anaerobic sludge from digestors, and regenerating solutions of ion exchangers (Perera et al. 2019).

2.3.6 *Electrodialysis*

Electrodialysis is a process in which anions (PO_4^{3-}, SO_4^{2-} y Cl^-) and cations (NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}) are divided using membranes of anionic or cationic exchangers in the presence of an electric field. During this process the concentrated solutions of anions and cations can be obtained in different compartments. This process is typically used in the recovery of N and K, but it can also be used to concentrate P, which can be then by recovered as struvite (Perera et al. 2019).

2.3.7 *Chemical Precipitation*

Chemical precipitation is considered an efficient and stable process in which 0.1 mg/L of P can be obtained from effluents with high chemical concentrations. Chemical costs can be reduced by combining the technology processes of advanced filtration to remove fine precipitates from P. Among the metallic ions commonly used in chemical precipitation are Fe^{3+}, Al^{3+} and Ca^{2+} to remove P from residual water with precipitates removed together with waste sludge. However, this process increases the volume of sludge up to 35%, which becomes a problem during its handling and disposal (Perera et al. 2019). The cheapest and easiest way to remove the excess of dissolved P from residual water effluents is through chemical precipitation using Al, Ca or Fe. The most common precipitates used for WWTPs are clays [$Ca(OH)_2$], alum [$Al_2(SO_4)_3.18H_2O$], and ferric chloride ($FeCl_3$). The use of these chemicals can produce trace amounts of soluble hydroxide and complexes of P that do not interfere with precipitation. Alkalinity, pH, and hardness are the main factors tom consider when chemical precipitation is used to remove P from residual water. Iron phosphates and its oxyhydroxide complex are close to minimum solubility in the pH range of 4–6. On the other hand, aluminum phosphates and the complexes of hydroxide reach minimum solubilities at pH ranges of 5–7. Therefore, precipitation will reduce disolved P, the reuse and recovery of P in sludge is impractical, unless tertiary infrastructure is located in place to carry on the chemical reduction (Sengupta et al. 2015).

Chemical precipitation without recovery has negative effects of drastic increase in the amount of sludge formed during primary and secondary treatments, especially when precipitation is based on alum and clays. Perhaps when most of P has been precipitated outside the solution, the residual calcium, aluminum and iron salts would continue the precipitation with hydroxide increasing the sludge up to 35%. Many WWTPs have showed the natural formation of struvite as Mg ($MgNH_4PO_4$) or K (KNH_4PO_4). This precipitate is spontaneously formed at pH > 8.0 when all equal parts of dissolved P, ammonium, and Mg or K enter to a high turbulence system. Struvite is problematic for certain ways of P production due to its capacity of releasing ammonia gas producing high levels of N emissions. However, struvite can be used as a prolonged release fertilizer, making it ideal to prevent excessive concentrations of P in run offs. Struvite could also reduce the hardness caused by Mg. In many cases where agricultural and animal wastes are the main sources of Mg, N and P must be supplemented in the systems to promote crystallization. In cases where struvite recovery has been implemented in WWTPs after Mg introduction struvite recovery reached levels of 85–97% (Sengupta et al. 2015).

2.3.8 Biological Recovery

Phosphorous can be removed through microbial and plant assimilation, precipitation with di or tri-valent cations in the soil or sediment, or adsorption in clays and organic material. Phosphorous can be accumulated in peat. Microbial assimilation of P sometimes is high, but it represents a short-term solution due to the high rate of microbial conversion in the constructed wetlands. Biological assimilation through plants and algae is one of the most trustworthy long-term methods for P removal in wetlands. The plant species more commonly used are: *Eichhornia crassipes*, *Pistia stratiotes* and several species of Lemnaceae, which can remove up to 83–87% of total N, and

70–85% of total P in residual waters that can be used as fertilizers (Sengupta et al. 2015).

Phosphorous can also be removed by "Enhanced biological phosphorous removal" (EBPR) when no strict limits of P are applied together with the use of Phosphate Accumulating Organisms (PAOs), which result in P enrichment in the sludge removing up to 80–90% of total P; besides, the addition of an anoxic tank can remove N simultaneously. However, EBPR is a very sensitive biological process that requires control of pH, temperature, content of volatile fatty acids, cationic concentration, nutrient proportion for microorganisms, time of hydraulic retention, time of solid retention and the composition of residual water. Although EBPR is capable of removing P in residual sludge, the reuse of P implies the direct application of earth or the separation of concentrated currents. However, the product is voluminous and with risk of contamination (Perera et al. 2019).

2.3.9 Electrochemical Recovery

Electrochemical recovery can be divided in the following processes:

1. Processes that use sacrificial anodes, which operate using doses of Mg^{2+}, Al^{3+}, Fe^{2+} o Fe^{3+} to assist the chemical precipitation.
2. Processes that use dimensionally stable anodes (DSAs), which alter the water matrix which in turn precipitates P compounds. This changes pH provoking P precipitation against cations in solution with recovery efficiencies of 90% of P at pH higher than 9 in precipitates of calcium phosphate and/or amorphous calcium carbonate, which is a simple and of low cost method (Perera et al. 2019).

2.3.9.1 Acid Hydrolysis at High Temperature

When amounts of 2–3% of P is found in organic solids in the typical primary and secondary treatment of residual sludge, the acid hydrolysis at high temperature and P extraction is a viable option. The treatment of residual water sludges after dehydration and incineration, can be digested in HCl to release P as phosphoric acid (H_3PO_4) with an 85% production. This is a key element to the process of extraction of the modified solvent, which is essential for the development of raw material (Sengupta et al. 2015).

2.4 Nitrogen Recovery

Two biological techniques for N recovery are the bioelectrochemical processes and the use of photosynthetic microorganisms. The bioelectrochemical system (BES) includes the removal and recovery of N from residual waters producing electricity. Photosynthetic microorganisms can assimilate N and P and recycled them as microalgal biomass to produce fertilizers from residual water (Rahimi et al. 2020).

2.4.1 Adsorption and Ion Exchange

Reactive N exists as NH_4^+ in the typical residual water, being a significant contaminant of domestic wastewater and urine. Since NH_4^+ is a cation, the process based in adsorption and ion exchange is very relevant due to the unique properties such as: high selectivity, high removal, fast kinetic of attainment and regeneration, lesser requirement of space, and simplicity in application and operation. This method is environmentally friendly due to the use of zeolite as ion exchanger releasing non-toxic cations interchangeable (Na^+, K^+, Ca^{2+}, y Mg^{2+}) (Sengupta et al. 2015). Zeolite is a very attractive adsorbent for NH_4^+ removal, because is efficient, economically competitive, and easy to use, and with capabilities of withstand shock loads (Perera et al. 2019). Therefore, zeolite is the ion exchanger sorbent more popular for N recovery. Zeolite has a tetrahedral structure where the aluminum and silicon atoms are covalently united to the oxygen atoms forming interconnected jails and channels. The substitution of Si^{4+} with Al^{3+} generates a negative net charge in the isomorphous structure, The small atoms occupy sites previously occupied by big atoms. The greater the substitution the greater is the negative charge in zeolite. These negative charges inside the pores are balanced by cations like Na^+, K^+, Ca^{2+}, and Mg^{2+} in the surface of zeolite. These cations are retained by weaker electrostatic forces and are exchanged with NH_4^+ in the solution. There are zeolites with diverse characteristics according to the regional geological formation, and even some zeolites can be modified to obtain an optimal performance with respect to their homoionic form, size of the grain, pH, NH_4^+ concentration in the influent, time of hydraulic retention, force of ionic competence with respect to cations, and temperature. These modifications improve the adsorption capacity and the purity of zeolites. The treatments with acids, alkali and alkali metal salts, integral calcinations, and treatment with microwaves are among the most popular modification techniques (Sengupta et al. 2015).

Once the ion exchangers/adsorbents are depleted, the recovery of N and the opportunity of reuse is performed. Charged zeolites can be directly applied to agricultural fields as slow-release fertilizers. The most common regeneration technique employs a NaCl solution where NH_4^+ is desorbed and exchanged with Na^+ in solution. This provides a concentrated current of NH_4^+. Another technique is acid, heat and biological regeneration depending on the process of recovery used. The regeneration results in a concentrated current of NH_4Cl in chemical regeneration or $NaNO_3$ in biological regeneration. Posteriorly, is possible to use these solutions as fertilizers; the zeolite can be also used as fertilizer (Sengupta et al. 2015). Natural and modified zeolites and clinoptilolite are among the absorbents more commonly used to remove ammonium. The capacity of natural absorption of clinoptilolite can increase by addition of NaCl (Perera et al. 2019). This process of ionic exchange between cations and anions results in the concentration and precipitation of phosphate of ammonium magnesium known as struvite (Liberti et al. 2001; Sengupta et al. 2015). Zeolites can be also used to simultaneously remove N and P from residual waters with capacity of being used as fertilizers of prolonged release (Perera et al. 2019). There are alternative absorbents more efficient for ammonium removal than zeolite; carbon nanotubes, hydrogels, and natural substances like wheat straw or volcanic tube for ammonium removal (Sengupta et al. 2015; Perera et al. 2019). Recently, palygorskite has showed a great capacity for removal of NH_4^+ (Perera et al. 2019), being capable of removal efficiencies of 100% after treatment with NaCl at low ammonium concentrations (Gianni et al. 2021). The hydrogel loaded with ammonium, with its characteristic high-water retention and multifunctionality can be used as fertilizer in agriculture. Wheat raw have also great capacity to retain ammonium that together with a super absorbent resin (SAR) optimizes its execution and use as a late fertilizer (Sengupta et al. 2015).

2.4.2 Struvite Precipitation

This chemical technology is one of the favorites for P and NH_4^+ removal from residual waters with a significant potential for N recovery, because is simple, effective and environmentally friendly with N recover as fertilizer (Rahimi et al. 2020). This technology can be redirected to N recovery. However, Mg^{2+} and PO_4^{3-} need to be added, because sometimes there is excess NH_4^+ for the stoichiometric requirement needed for struvite precipitation, and the amount of P is insufficient for removing all the N in the medium (Perera et al. 2019). Struvite precipitation with a $Mg:NH_4:PO_4$ (1:1:1) proportion is capable of removing up to 95% of NH_4^+ from anaerobic effluents; in these effluents there are great amounts of ammonium and P (from manure), and great amounts of Mg salts for struvite precipitation, which increases the cost and modifies pH. However, Mg oxide is an optional source for struvite crystallization, decreasing the cost, with good availability, maintaining the alkalinity and capacity of absorption to remove organic and polymeric substances (Rahimi et al. 2020).

2.4.3 Electrodialysis

This method is used to concentrate and recover ammonium, in contrast with P recovery. Ammonium is concentrated in the cathode of the electrodialysis cell. Typically, ammonium recovery implies the posterior extraction and adsorption of the concentrated ammonium solution, which can reach up to 100% efficiency. However, its recovery rate is limited by the amount of Na^+ and K^+ in the influent. It is possible that NaCl addition to the cationic solution increases the flux of ammonium reducing the gradient of concentration of Na (Perera et al. 2019).

2.4.4 Electrochemical Separation

It is similar to electrodialysis. However, ammonium can be recovered via extraction and adsorption in H_2SO_4 to produce ammonium salts. However, is important to maintain the actual efficiency of NH_4^+ in the influent. The electromigration depends on the valence, concentration, diffusion coefficient of the ionic species and the force of the electric field (Perera et al. 2019).

2.4.5 Bioelectrochemical Systems (BES)

This methodology is based on the same principle that electrochemical separation, but can generate the energy required for the process when the influent contains enough organic matter. In BES, the oxidation catalyzed biologically from the organic substrate occurs in the anode and liberates electrons that travel through internal resistors to reduce O_2 to OH^- in the cathode. Due to this reaction the cations H_3O^+, Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+ are transported to the cathode through an ion exchange membrane to maintain neutrality. Due to the fact that the cathode is continuously aerated, NH_4^+ is concentrated in the cathode and released with the air as $NH_{3(g)}$ at high pH in the cathodic compartment. Ammonium released in the gas could be subsequently absorbed for its recovery (Perera et al. 2019). The biological oxidation of the organic matter in the residual waters of the anodic compartment contributes to the energy recovery. At the same time, the ammonium/ammonia in residual water is transported through the ion exchange membrane to the cathodic compartment with a high pH catholyte, leading to ammonium recovery by liberation. The electric field induce migration of ammonium/ammonia through the ion exchange membrane. This process allows recovery of ammonium/ammonia from residual water in a Bioelectrochemical System (BES). Ammonium recovery can be achieved through urine with a pre-treatment for P recovery via struvite precipitation (Rahimi et al. 2020).

2.4.6 Aereal Separation of Ammonia

This technology is a process of chemical removal of ammonia that promotes the conversion of NH_4^+ to NH_3 via the entrance of air or other gas in residual water to obtain in aqueous NH_3 phase (Rahimi et al. 2020). This method has been used to remove N under conditions dependent of pH, which must be close to 9.3. The N in ammonia in solution is converted to ammonia gas where a solution of lime or caustic soda is applied to maintain pH at 10.8–11.5 (Sengupta et al. 2015). The kinetics of ammonia release is control by pH, temperature, and the mass transfer area, but pH is by far the most important factor (Perera et al. 2019; Rahimi et al. 2020). This converts the ammonia ions to ammonium in a solution and provides air simultaneously converting it to ammonia gas according to the following reaction:

$$NH_4^+ + OH^- - \text{air}- \rightarrow H_2O + NH_3(g)$$

To achieve a higher efficiency of separation, the process is carried out in a packed column, which offers a greater mass transfer area. This process is affected by factors like ammonium concentration, the hydraulic load, the rate of air flux, the packaging, etc. Separation of ammonia has been successful in many municipal WWTPs. However, the columns get dirty easily. Some WWTPs have implemented a water-sparged aerocyclone with a higher separation efficiency and mass transfer that consumes less air when compared with the separation tanks and packed columns (Sengupta et al. 2015).

2.4.7 Schemes of N Recovery Based on Membranes

The processes of separation based on membranes have been used in residual water operations with microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) as the predominant technologies. This processes offers several advantages for ammonia recovery like being independent of the gas or the liquid flux rate, absence of secondary contaminants, these characteristics means that the ammonia concentration does not affect the removal efficiency (Sengupta et al. 2015). The NH_3 is recovered as $(NH_4)_2SO_4$ in tubular membranes submerged in residual waters containing ammonium and vice versa, where pH higher to 9 is required for a high efficiency of ammonium removal (Perera et al. 2019).

2.4.8 Biological Assimilation

The biological treatment of residual waters for N removal consists of microbial communities involved in the N cycle, which includes Actinobacteria, Bacteroidetes, Chloroflexi, Planctomycetes, Proteobacteria, Firmicutes etc. (Rahimi et al. 2020). In the landfills built to assimilate the nutrients, the soluble organics are degraded aerobically and anaerobically via the suspended microbial growth, and oxygen is added through the air–water interphase and the plants present in the landfills. N is removed through nitrification and denitrification in aerobic and anaerobic zones; ammonia is oxidized in aerobic zones and nitrate is converted to N gas and nitrous oxide in anoxic zones (Sengupta et al. 2015). Microalgae and cyanobacteria have been considered as an alternative system for the biological treatment of residual water. They generate oxygen through photosynthesis, which is consumed by the bacterial populations to degrade organic residues to simpler organic nutrients. Besides, microalgae and cyanobacteria remove inorganic nutrients in tertiary treatments before the discharge to receptor waters. N and ammonia assimilated by microalgae and cyanobacteria is converted to biomass instead of being released to the atmosphere, which becomes an advantage for N recovery. The N removal capacity is based on ammonification and the assimilatory reduction of nitrite to ammonium (Rahimi et al. 2020).

2.4.9 Direct Conversion on Feed and Protein for Livestock

The N in residual water can be converted directly to protein-rich alimentary sources through the use of heterotrophic microorganisms. This emerging technology shortens the N cycle, reducing losses of N through food production. In the Biofloc technology microorganisms assimilated residues including reactive N in biomass, which then is food for fishes in an innocuous way; even aquaponics contributes to the direct conversion of N residues to plant proteins used as food (Perera et al. 2019).

2.5 Potassium Recovery from Wastewater

Potassium is an element of the periodic table whose chemical symbol is K with atomic number of 19. As a chemical element can be found in nature mainly in saline water and other sources like salt flats and salty lakes. Potassium is an alkaline metal with a whitish/silver color. Potassium oxidizes quickly in the air, is too reactive specially in water and with chemicals properties similar to sodium. One of the most frequent uses of potassium is in photoelectric cells. In the case of chlorides and nitrates it can be used as fertilizer. Some industries use potassium in the ellaboration of photovoltaic crystals and diffusors used in the heat transference between NaK (sodium and potassium). Potassium is an essential element for the metabollic proccesses of the flora. Potassium participates in the maintenance of the osmotic pressure and the celular size; in photosynthetic proccesses and energy production (stoma apperture, carnosity of plants and carbón dioxide interchange). Low concentrations of K in organisms are manifested in symptoms like growth restriction, low harvest crops and bad quality of crop production. However, high amounts of K are also detrimental that can cause damage to seeds inhibiting other minerals and decreasing the quality of crops.

Potassium is obtained through mining in potassium deposits like camalita. Oceans are also sources of K extraction. However, K is found in low concentrations in oceans, which make its extraction costly and complicated. The mechanism of K attaintment was created in 1808 by Gay-Lussac and Thénard. The method conists in melting of potash in its natural state and pass it through hot iron. This proccess produces a detachment of potassium atoms from other elements. This method was substituted in 1823 by the Brunner Method. The new proccess of K attaintment consist in the heating of a mixture of potassium carbonate and carbón, which later was replaced for calcium carbonate. Today, the methods to obtain potassium are through electrolysis of potassium hydroxide, which produces potassium with 98% purity. However, this procedure is expensive.

2.6 Calcium Recovery from Wastewater

In North America, the pulp and paper industry are one of the most important industries (Nemerow and Dasgupta 1991). Paper product production and wood pulping generates a considerable amount of pollutants characterized by biochemical oxygen demand, chemical oxygen demand, suspended solids, toxicity and color when untreated or poorly treated effluents are discharged receiving waters. Wastewater effluent from paper manufacturing is characterized by a bad odor, dark color, low biodegradability and high organic load, with unsaturated fatty acids, lignin, lignin derivatives, resin acids, metals, chlorinated phenols and unsaturated aromatic compounds such as principal components (Lindholm-Lehto et al. 2015). It is estimated that this industry consumes between 76,000 and 23,000 L of water per ton of product, (Nemerow and Dasgupta 1991) resulting in the generation of large amounts of wastewater. Industry effluents increase the amount of toxic substances in the water, causing the death of zooplankton and fish, as well as profoundly affecting the terrestrial ecosystem.

One of the processes for the manufacture of paper is Kraft pulping. Kraft pulp (KP) is a widely used type of chemical pulp (CP), which is an alkali process for producing chemical pulp. To remove the lignin, the wood chips are cooked in a solution of sodium hydroxide and sodium sulfide, called white liquor, (Sainlez and Heyen 2013). In addition, some other inorganic compounds, such as Na_2CO_3, Na_2SO_4, Na_2SO_3 and $Na_2S_2O_3$, may be present in the liquor (Ekstrand et al. 2013). The resulting black liquor can be concentrated and burned in a recovery furnace to produce an inorganic melt of Na_2CO_3 and Na_2S to reproduce the chemicals needed for cooking (Sainlez and Heyen 2013). Calcium is not a processing element in chemical pulping and bleaching (paper). The cause of hard scale deposits on heating surfaces and screens in pulping digesters, bleaching tanks, and black liquor evaporators is the residue left over from the pulping process (Rudie 2000).

Calcium in black liquor comes from three main sources: it comes from wood; water and it can also come from the white liquor from the recausticizing process if there is overliming (Keitaanniemi and Virkola 1978; Erickson and Holman 1986). The concentration of Ca is higher in the black liquor than would be expected from its solubility product. Calcium would normally precipitate immediately in the black liquor due to the high carbonate content. However, the organic compounds in black liquor allow much higher levels of calcium to remain dissolved. It is difficult to limit Ca levels in black liquor because most of it comes from wood chips. Stemwood contains approximately 500–1000 mg Ca/kg dry solids or more and accounts for the majority of the soluble calcium in the pulping and bleaching process (Werkelin et al. 2005; Wistara and Yustiana 2014).

2.7 Pulp and Paper Wastewater Treatments

The application of various physicochemical treatment methods, including the removal of suspended solids, colloidal particles, floating matter, colors and toxic compounds through sedimentation, flotation, adsorption, coagulation (Pokhrel and Viraraghavan 2004; Kamali and Khodaparast 2015).

2.7.1 Coagulation and Precipitation

The basis of these methods is the addition of metallic salts to the current to generate larger flocs from small particles.

2.7.2 Sedimentation and Flotation

Suspended matters present in the pulp and paper wastewater are composed primarily of bark particles and fiber debris (Thompson et al. 2001).

2.7.3 Adsortion

Various adsorbents such as activated carbon, coal ash, fuller's earth, silica, etc. have been previously tested and shown acceptable performances for decolorization and removal of pollutants from wastewater (Pokhrel and Viraraghavan 2004).

2.7.4 Microbial $CaCO_3$ Precipitation

The microbial carbonate precipitation (MCP) process is a natural microbial process and the mechanism of MCP is defined as the ability of microorganisms to alkalinize an environment through various physiological activities (Erkan and Engin 2019).

2.7.5 Wastewater from Paper Production

There are different methods for the treatment of wastewater from paper production (Table 2.1). However, one of the main problems is the amount of calcium that is produced. Therefore, more studies are required to determine what treatment (primary, secondary or tertiary) is the one that can give the best results.

Table 2.1 Wastewater treatment for the paper industry

Process	Removal percentage	Reference
Coagulation and precipitation		
Aluminum chloride	Turbidity, 95.7 Lignin, 83.4 Water recovery, 72.7	Wang et al. (2011)
CaO	COD, 90	Eskelinen et al. (2010)
$CaSO_4$ $2H_2O$	Dissolved solids, 63	Sheela and Distidar (1989)
Sedimentation and flotation		
Sedimentation	TSS, 70–80	Rajvaidya and Markandey (1998)
Flotation	TSS, 65–95	Gubelt et al. (2000)
Flotation	TSS, 95	Wenta and Hartmen (2002)
Adsortion		
Ion exchange resin	Hydrophobic and high molecular weight fractions, 72	Ciputra et al. (2010)
Activated carbon	Hydrophobic and high molecular weight fractions, 76	Ciputra et al. (2010)
Activated petroleum coke	Removal of color, COD, DOC, 90	Shawwa et al. (2001)
Microbial $CaCO_3$ precipitation		
MCP and urea	$CaCO_3$, 90	Erkan and Engin (2019)

2.8 Recovery of Other Nutrients from Wastewater

Besides recovering macronutrients like P and N (and their different salts and mixtures), calcium and potassium from wastewater, many other nutrients are removed either experimentally or in real wastewater treatment plants. For instance, Chitosan and chitosan-EGDE beads removed acid dyes; they were favorable adsorbers and could be employed as low-cost alternatives for the removal of acid dyes in wastewater treatment (Azlan et al. 2009). In fact, Sulfur (S), sodium, potasium, magnesium, H, Cl, and NH_4 (ammonium ion) have been recover from municipal wastewater using chitosan beads (Shahid et al. 2021). Microalgae are efficient collectors of macronutrients; other nutrients like CO_2 and carbon were recovered using microalgae (Acién Fernández et al. 2018). Ammonia (NH_3) recovered using experimental set up (Kumar et al. 2013). Recovery of ions PO_4^{3-}, SO_4^{2-}, NH_4^+, K^+, Mg^{2+} and Ca^{2+} from swine wastewater using electrodialysis has been achieved (Ye et al. 2019). Recovery of NH_4-N, PO_4-P, Na^+, and K^+, Zn, Mn, Cu, Fe, S, Mg, Ca using bio-electroconcentration (Monetti el al. 2019). Low values of N and P recovery in Australia. Pellet reactor combined with selectrodialysis is an appropriate method to recover phosphate from wastewater as calcium phosphate (Tran et al. 2014). Cañadas et al. (2021) highlighted 2-methyltetrahydrofuran as a promising bio-based extraction solvent for sustainable recovery of vanilla compounds. Vanillin and vanillic acid were recovered in percentages of up to 95.37%. Calcium (Ca), magnesium (Mg), phosphate and (bi)carbonate are removed simultaneously in electrochemical recovery of phosphorus (P) from wastewater. $32 \pm 1\%$ Mg were removed in 24 h (Lei et al. 2019). Itakura et al. (2005) recovered boron using a hydrothermal treatment technique as recyclable precipitate $Ca_2B_2O_5 \cdot H_2O$ from aqueous solutions. Chemical principle of magnesium ammonium phosphate (MAP) precipitation, factors influencing MAP crystallization, and various developments achieved through bench, pilot and full-scale MAP reactors. A brief description is given of MAP purification and dissolution to economically exploit MAP as a phosphate and magnesium source (Liu et al. 2013).

2.9 Conclusion and Prospects

The recent thinking in WWTPs is not only the removal of contaminants, but rather the recovery and reuse of all contaminants. Macronutrients like N and P are the best candidates to be recover from WWTPs worldwide. In fact, recovery of N and P is nowadays achieved in many WWTPs worldwide. Many more WWTPs that today remove N and P are suited with a few modifications to recover N and P. In the case of N that includes also ammonia and ammonium. Most of the recovery is via struvite conversion which is then used as a slow-release and prolonged fertilizer. Many biological systems (landfills) represent a sustainable alternative for N and P recycling. The direct conversion of N and P into protein via: (a) Biofloc technology, (b) microbial (microalgae and cyanobacteria), and plant assimilation, (c) Enhanced biological phosphorous removal and then recovery, (d) direct conversion of N and P residues to plant proteins used as food. All these technologies are low-cost sustainable technologies that are already being implemented in many agricultural, industrial and municipal WWTPs. However, there are other technologies like chemical precipitation, electrochemical systems (including bioelectrochemical systems) which are costly and adequate for selected discharges. Several of these systems have been developed only at the experimental stages and need further research to make them economically suitable to be implemented in selected WWTPs worldwide.

Potassium and calcium are also recovered in several WWTPs worldwide, but its recovery sometimes include a cost that prevents many WWTPs to implement such technologies. Some industries like the pulp and paper industry might be well suited for calcium recovery given the enormous amounts of calcium produced as by-product. Research in these areas is still needed.

Sulfur, sodium, potasium, magnesium, H, Cl, and NH_4 have been recovered from municipal WWTPs via chitosan beads. This is an expensive treatment for selected discharges. However, recovery of other nutrients is just in a preliminary and experimental phase. More experiments need to be conducted to unveil new alternatives that can be adapted to WWTPs worldwide to establish selected WWTPs for selected discharges that allow recovery and reuse of other nutrients apart from Ca, N, K, and P.

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Chapter 3
Recent Update on the Recovery of Various Metals from Wastewater

Isidoro Rubio-Franchini, Jesús Alvarado-Flores, and Roberto Rico Martínez

Abstract Recovery of metals from wastewater is a reality in selected wastewater treatment plants worldwide. Several low-cost techniques have been already implemented in wastewater treatment plants in industry to recover specific metals. Adsorption, coagulation, flocculation, and precipitation techniques are relatively low-cost techniques already implemented in wastewater treatment plants for the removal of contaminants. Electrochemical and photocatalysis techniques are more expensive and their inclusion as part of wastewater treatment plants is more complex. However, scientific literature is full of reports on experimental set ups and conditions that improve the current techniques for metal recovery. The goal is to allow the adaptation of selected wastewater installations for particular discharges where metal recovery could be feasible in economic, environmental and technological terms.

Keywords Bioelectrochemical systems · Electrochemical deposition · Ion exchange · Adsorption · Photocatalysis

3.1 Introduction

The World Health Organization (WHO) published an account of the ten pollutants of major concern for public safety; among them we found arsenic, cadmium, lead, and mercury (WHO 2010). It is well known that mining is the main source of contamination by heavy metals regarding water reservoirs, except for arsenic which comes from

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natural sources (Ministerio de Salud Peru 2019). The development of new processes and technologies have improved recovery of metals. Great amounts of metals potentially toxic are emitted to the atmosphere and due to the geochemical cycles; these metals are deposited in terrestrial and aquatic ecosystems (Fu and Wang 2011).

Water is an indispensable resource for humans, and consequently municipal, industrial, and agricultural wastewater is generated. In these three types of wastewaters the presence of heavy metals has been detected. Due to the intensity of mining industries, technological manufacturing, battery industries, paper industry, pharmaceuticals, tourism, and agricultural activities. Due to the above, the metals zinc, copper, nickel, mercury, cadmium, lead, and chromium have increased in concentration, even above the maximum values allowed by environmental legislation in wastewater, all this represents a problem in the aquatic ecosystems where effluents are discharged, even reaching concentrations dangerous to human health, by contaminating groundwater reserves. Therefore, it is important and a priority to remove heavy metals in wastewater, to avoid environmental disasters, lethal effects, bioaccumulation, bio magnification of metals in food webs, and irreparable damage to human health. This section discusses recovery processes in the removal of metals in wastewater such as: (A) Adsorption, (B) Ion Exchange, (C) Membrane Filtration, (D) Chemical precipitation, coagulation and flocculation, (E) Electrochemical Treatment and Photocatalysis. According to Azimi et al. (2017), removal efficiencies vary from 12 to 100%, the surface functional group (thiol, amine, carboxylic groups), pH (2.85–8), temperature, organic matters and type of metals, decrease or increase efficiencies. These methods have removed the metals: Hg, Ag, Pb, Cd, Cr, Co, As, Ni, Cu, Zn, and Fe.

3.2 Recovery of Metals by Adsorption

Adsorption removal processes have the following characteristics, are of low operating cost, their design is simple and adaptable, and little toxic waste is produced. In principle, the adsorption method is characterized by having multifunctional groups to perform the processes of adsorption of metals in wastewater. The functional groups will determine the adsorption capacity, as well as the metal to be removed or the metals present in the wastewater.

There are several adsorption materials, in general, adsorption processes can be reversible and irreversible, reversible ones are physical processes, while irreversible ones are chemical processes, because metals are joined by ionic covalent bonds to materials (Burakov et al. 2018). The adsorption process depends on the concentration of the metal in the wastewater, as well as on physical and chemical variables such as temperature, pH, contact time with the adsorbent material and stirring speed.

The most commonly used materials are for example Graphene Oxide membranes, activated carbon, minerals such as zeolite, clay minerals, biomaterials, industrial solid waste, fullerenes, and carbon nanotubes, Table 3.1 shows some examples of their adsorption capacity and the metals that are adsorbed.

Table 3.1 Adsorbent materials

Type de material	Active group	Adsorption capacity	Metal adsorption	References
Chitosan/ sulfhydryl-functionalized graphene oxide composite	–OH, –COOH, –SH, and $–NH_2$		Cd, Cu, Pb	Pan and An (2019)
4-aminothiophenol modified GO and 3-aminopropyltriethoxysilane modified GO	GO-SH, GO-N	99.17–103.28 mg/g	Cd, Cu, Pb	Pan and An (2019)
Pristine GO	GO	32.91 mg/g	Cd, Cu, Pb	Pan and An (2019)
GO/Fe–Mn composite	GO/ Fe–Mn	32.9 mg/g	Fe, Mn	Pan and An (2019)
Chitosan/poly(ethylene oxide)/activated carbon (AC) nanofibrous membrane (CPANM)		176.9, 186.2, 195.3, 217.4, and 261.1 mg/g respectively	Pb, Zn, Cu, Fe, Cr	Pan and An (2019)
Active carbon-eucalyptus		0.45 and 0.53 mmol/g	Cu, Pb	Burakov et al. (2018)
Active carbon-rubber wood		44 mg/g	Cr	Burakov et al. (2018)
Active carbon-hazelnut shell		170 mg/g	Cr	Burakov et al. (2018)
Bentonite clay		11.89 mg/g	Cu	Burakov et al. (2018)
Algae: *Chaetomorphalinum*			Cu, Cd, Pb, Zn	Burakov et al. (2018)
Algae: *Caulerpa lentillifera*			Cr	Burakov et al. (2018)
Algae: *Ulvalactuca*			Pb	Burakov et al. (2018)
Waste sludge		168 mg/g	Zn	Burakov et al. (2018)
Carbon nanotubes		2.88 min to max 47.86 mg/g	Cu, Ni, and Pb	Burakov et al. (2018)

3.3 Recovery of Metals by Ion Exchange

In principle, the removal of metals by Ion Exchange from water is based: an ion present in water can be exchanged for another ion on a surface, in this case from a resin (Al-Enezi et al. 2004). Materials can be resins, hummus, cotton, soils, and even bacterial cells. The removal efficiency will depend on the concentration of the metals in the water, the temperature and pH of the water, the physical–chemical factors of the metals, and the sites or loads of the material or resin. Resins can be classified as cation exchange resins and anion exchange resins.

For example, a commercial sulfonated polystyrene-divinylbenzene resin with a porosity of 18.98% removed 34 ppb of mercury in water Monteagudo and Ortiz (2000). While the results of Rao et al. (2005), showed that using a commercial resin called Duolite ES 467 (amino-phosphonic functional groups), the maximum removal for Pb was 11.63 g dm^{-3} while for Fe it was 33.96 g dm^{-3}. In context, the USEPA and WHO has as maximum allowable values of Pb in water for human consumption of 10 and 50 ug g dm^{-3}. This means that resin removal processes can be very efficient, as long as the concentrations are not above the maximum allowable values. Ion Exchange removal processes are ideal for adsorbing metal mixtures, including insulating or separating metals, adsorption efficiency, and recovery efficiency, for example, can be up to 100%, as done by Koliehova et al. (2019), to remove metals in a mixture of Cu, Zn, and Ni, in a strong-acid KU-2-8 ion exchange column.

With the passage of influents and effluents through ion exchange resins, the organic matter must be reduced, to avoid saturation of the column. When water passes through the anionic exchange columns (OH–) they regenerate with sodium hydroxide (NaOH), and cationic (H–) with sulphuric or hydrochloric acid (Kansara et al. 2016). In addition, the authors Kansara et al. (2016) mention that there are factors to consider in the optimization processes of ion exchange columns such as calcium sulfate fouling, iron fouling, and adsorption of organic matter, bacterial contamination, and chlorine contamination.

Finally, the removal of metals by ion exchange is used followed by a Fenton process, which uses Iron, when combining both treatments, in wastewater processes, the resins can maintain their iron adsorption efficiency for up to three cycles according to the results of Domínguez et al. (2022). Demonstrating then that Fenton's process followed by Ion Exchange can be used for wastewater treatment (olive oil extraction industry wastewater).

Another example of the application of joining processes of treatment and removal of contaminants is the one carried out by Raghu and Basha (Raghu and Basha, 2007), where they use Ion Exchange and chemical and electrocoagulation treatment, to improve the water quality of effluents in the textile industry. In this study, divinylbenzene-polystyrene resins Amberlite IR 120 (cationic) and Amberlite IR 400 (anionic) were used.

3.4 Recovery of Metals by Membrane Filtration

Membrane filtration processes for wastewater treatment are considered secondary processes and have great potential, for example, efficiency in recovering nutrients, sustainable operation, low costs, and good performance in reducing energy costs (Hube et al. 2020). It is important to note that a limitation of the use of membranes is fouling, specifically in high contents of organic matter. Membrane filtration processes can be (a) pressure, (b) osmotic, (c) thermal and (d) electrical-driven.

The processes of removal of metals by membranes are direct, they do not require biological or chemical processes, only physical: by removing particles, nutrients, and pathogens. Membrane characteristics such as pore size, water pretreatment, and fouling, pH affect metal removal processes, for example, in Direct electrical-driven membrane processes, pH affects and/or favors ion transport, in phosphate-enriched wastewater, a pH of 6 significantly removes fluoride (Hube et al. 2020). The membrane filtration process for the removal of contaminants in wastewater, due to its low cost of operation, is suitable for communities, in undeveloped countries.

There are several types of organic, ceramic, and metallic membranes: organic membranes are the most used, however, their cost–benefit is low, compared to ceramic and metallic membranes, according to the author Du et al. (2020), there are factors that affect membranes, such as the structure and properties of the membranes, the material, and the operating conditions.

According to Yu et al. (2022), mixed matrix membranes (MMMs) are technology with great potential for metal removal compared to more commonly used commercial membranes: polysulfone (PSF), polyacrylonitrile (Pan), polyvinylidene fluoride (PVDF), and polyethersulfone (PES). Mixed matrix membranes (MMMs) are essentially the mixture of membranes with adsorbent materials, which possess abundant adsorption sites, however, these materials are powders and must be fixed to the membranes. On average the rejection percentage of MMMs based on inorganic materials is 85.81%, while MMMs of organic materials the average value is 80.4%. The metals that remove this type of membrane are Cu, Cr, Fe, Cr, and Pb.

3.5 Recovery of Metals from Chemical Precipitation, Coagulation, and Flocculation

The method of flocculation/coagulation/precipitation consist in the use of substance known as a flocculant, which has the propriety of producing aggregation of colloidal particles, allowing a fast solid–liquid separation with the complex precipitating at the bottom, which is posteriorly recuperated for further treatment (Navratil 2000). Flocculants agents destabilized the colloidal and favor agglomeration of greater particles. In the first step, coagulation eliminates the double electric coat that characterizes colloidal substances, and with flocculation colloids are agglomerated thanks to the attraction of particles with the agglomeration of flocculants. The most important factors to take into account for this method are: (a) appropriate doses of flocculent, (b) the contact time of flocculants, (c) time in which agglomeration and precipitation of the complexes formed takes place. The chemical substances employed in flocculation and precipitation are: calcium hydroxide, ferric sulphate, ferrous sulphate, ferric chloride, and aluminum sulphate. These compounds have in common the fact that they have free electrons or not paired in the atoms of oxygen (Ismail et al. 2012).

Flocculants can be classified by their nature (mineral or organic), origin (synthetic or natural), the sign of their electrical charge (anionic, cationic or non ionic). The first flocculants used were inorganic polymers (activated silica or aluminum sulphate), and natural polymers (starches, alginates) (Azmi et al. 2018). Today, there are great amounts of synthetic flocculants, of great effectivity, which often result in a minimal amount of sludge. Cobalt and Li can be recovered from spent batteries by chemical precipitation (Zhu et al. 2012). Metals Cd, Cr, Cu, Fe, Ni, and Pb, can be recovered from aqueous solutions by chemical precipitation (BrbootI et al. 2011).

Heavy metals Cd, Cu, Fe, Hg, Ni, Pb, and Zn can be efficiently recovered from wastewater by sulfur-containing precipitation agents (Pohl 2020). Ag, Cr, and Hg can be removed by precipitation from hazardous liquid waste with efficiencies above 99% (Pitalúa-Sánchez et al. 2019); these metals could in theory be recovered with further treatment. Precipitation with lime (calcium oxides and hydroxides), is one of the cheapest and simplest techniques with precipitation of metals: Co, Cu, Fe, Mn, Ni and Zn (Murnane et al. 2019).

3.6 Electrochemical Treatment and Photocatalysis to Recover Metals

Electrochemical treatment is a methodology that encompasses many procedures that allow separation and recovery of metals. Several electrochemical conditions can be used for better separation of metals. Varun et al. (2021) classified the electrochemical conditions necessary for the recovery of metals. In here, we will only discuss those that might be important for wastewater recovery:

(a) Potential controlled electrodeposition (or potentiostatic process), where a constant voltage is applied, and the current density may change as a function of time. The advantage of this technique is that the potential is the driving force that determine which electrochemical reaction occurs, allowing high selective metal recovery.
(b) Pulsed current/electrochemical deposition generates a constant current or voltage during the on-time pulse, followed by a pause when switched to the off-time pulse.
(c) Electrowinning and electrorefining. In electrowinning, a direct current is applied between the anode and cathode electrodes and the targeted metal species can be reduced at the cathode and extracted in their metallic form. In Electrorefining takes the unrefined metals of electrowinning to purify them.
(d) Aqueous Electrolytes Based Electrochemical Methods. Aqueous solutions are excellent electrolytes for electrodeposition and this is the preferred technique for wastewater recovery of metals at industrial scales. Nevertheless, several challenges still persist to improve its selectivity and metal recovery effectiveness.
(e) Non-Aqueous Electrolytes Based Electrochemical Methods. When compared to aqueous electrolytes, metal recovery through electrodeposition from non-aqueous electrolytes have many advantages like wide electrochemical windows

and high stability. Among non-aqueous electrolytes there are organic solvents, molten salts, ionic liquids, and deep eutectic solvents. However, excepting the classical organic solvents, other non-aqueous electrolytes are costly.

Varun et al. (2021) also includes Electrodeposition in Supercritical Fluids and Electroplating with the Aid of Supercritical Fluids. However, these techniques might be used for specific liquid waste scenarios and not for the typical urban wastewater plants.

3.7 Electrochemical Deposition

Electrochemical deposition (ED) is by far the treatment most likely to be used (or already being used) to recover metals from wastewaters. For instance, O'Connor et al. (2018) reported that the metals and or metalloids: Cu, As, Eu, Nd, Ga, and Sc, can be efficiently recover from electronic end-of-life and manufacturing derived wastewaters by ED using carbon nanotube-enabled filters. Figueroa and Wolkersdorfer (2014) conclude that Cu is the only metal that can be economically recovered of acidic mining wastewater using ED. Chen and Lim (2005) using ED showed that Ag, Cu and Pb can be recovered from experimental wastewater containing humic acids. Uranium can be recovered efficiently by ED in experimental wastewater (Jang et al. 2019).

3.8 Bioelectrochemical Recovery of Metals

Bioelectrochemical Systems (BES) consist in microorganisms converting chemical energy stored into biodegradable substances and eventually into electrical energy. Metal recovery of BES oscillates between 44.2 and 100% (Wang and Ren 2013). In many cases metals are recovered by a combination of different bacteria. Biolectrochemical recovery of metals include: chromium, copper, gold, iron, mercury, selenium, silver, and vanadium (Wang and Ren 2013). Many other metals have been recovered from wastewater (at least experimentally, see Table 3.2).

3.9 Photocatalysis

Photocatalysis is an emerging advanced catalytic oxidation technology that has many advantages: (a) light is the only energy source, (b) it is a clean new technology that can remove heavy metals (Gao and Meng 2021). Recently a few publications documented the recovery of metals using this novel technique. For instance, Ag has been efficiently recovered via photocatalysis under experimental conditions (Ding

Table 3.2 Microbial species used in biolectrochemical systems (BES) for metal recovery

Bacterial species	Metal	Sources
Acinetobacter calcoaceticus	Mo(VI)	Shukor et al. (2010a)
Anaeromyxobacter dehalogenans	Se(IV)	Combs et al. (1996)
Anoxybacillus sp.	Hg(II)	Kritee et al. (2008)
Aspergillus niger	Co(III), Cr(VI), Ni(II)	Shugaba et al. (2012), Yang et al. (2020)
Aspergillus parasiticus	Cr(VI)	Shugaba et al. (2012)
Bacillus cereus	Cr(VI)	Moreno-Benavides et al. (2019)
Bacillus megaterium	Cr(VI)	Aslam et al. (2016)
Bacillus sp.	Se(VI)	Kashiwa et al. (2000), Tomei et al. (1995)
Bacillus subterraneus	Fe(III), Mn(IV)	Kanso et al. (2002)
Bacillus subtilis	Cr(VI), Se(IV)	Combs et al. (1996), Liu et al. (2020)
Bacteroides facilis group	Ag(I)	Dao (2018)
Castellaniella spp.	Cd(II), Cr(VI), Cu(II)	Amanze et al. (2022)
Cellulomonas	Cr(VI), Fe(III), U(VI)	Sani et al. (2002)
Chrysiogenes arsenates	As(V)	Macy et al. (1996)
Clostridium spp.	U(VI)	Suzuki et al. (2003)
Corynebacterium hoagie	Cr(VI)	Viti et al. (2003)
Cupriavidus metallidurans	Pd(II), Au(III)	Reith et al. (2009)
Cupriavidus necator	Pd(II)	Reith et al. (2009)
Desulfovibrio desulfuricans	Au(III), Se(IV), Se(VI)	Deplanche et al. (2012), Deplanche and Mackaskie (2008)
Desulfotomaculum auripigmentum	As(V)	Newman et al. (1997)
Desulfoporosinus spp.	U(VI)	Suzuki et al. (2003)
Escherichia coli	Au(III)	Deplanche and Mackaskie (2008)
Enterobacter sp.	Mo(VI)	Shukor et al. (2009)
Geobacillus sp.	Au(III)	Correa-Llantén et al. (2013)
Geobacter berridijiensis	Fe(III)	Nevin et al. (2005)
Geobacter psychrophilus	Fe(III)	Nevin et al. (2005)
Geobacter sulfureducens	Pd(II)	Tuo et al. (2013)
Klebsiella sp.	Mo(VI)	Lim et al. (2012)
Microbacterium arborescens	Se(IV)	Combs et al. (1996)
Plectonema boryanum	Ag(I)	Lengke et al. (2007)
Pseudomonas aeruginosa	Cr(VI)	Tandukar et al. (2009)
Pseudomonas fluorescens	Se(IV)	Nancharaiah et al. (2016)

(continued)

Table 3.2 (continued)

Bacterial species	Metal	Sources
Pseudomonas sp.	Cr(VI), Mo(VI)	Rahman et al. (2007), Viti et al. (2003), Shukor et al. (2010b)
Rhodospirillum rubrum	Se(IV)	Kessi et al. (1999)
Serratia sp.	Mo(VI)	Rahman et al. (2009)
Shewanella algae	Au(III)	Konishi et al. (2006)
Shewanella oneidensis	CrVI, V(V)	Carpentier et al. (2003)
Shewanella putrefaciens	Fe(III), Mn(IV)	DiChristina et al. (2002)
Trichococcus pasteurii	Cr(VI)	Tandukar et al. (2009)
Verticillium luteoalbum	Pd(II), Au(III)	Gericke and Pinches (2006)

et al. 2015). Several metals: Al, Cd, Cu, Co, Li, Mn, Ni, Pb, Sn, and Zn have been recovered via photocatalysis (Bahadoran et al. 2022). Gold can be recovered via photocatalysis under experimental conditions (Kunthakudee et al. 2022).

3.10 Conclusions and Perspectives

Recovery of metals from wastewater is a reality in selected WWTPs worldwide. Several low-cost techniques have been already implemented in WWTPs in industry to recover specific metals. Adsorption, coagulation, flocculation and precipitation techniques are relatively low-cost techniques already implemented in WWTPs for the removal of contaminants. In many cases small changes can be implemented in WWTPs to recover metals in a sustainable way. Already some selected municipal WWTPs worldwide have been adapted to recover metals. Electrochemical methods and photocatalysis are expensive methods that require either expensive set ups or maintenance to be adapted to current WWTPs. However, many experiments are being conducted worldwide to improve these techniques and some of these techniques can be now applied at industrial scales to remove precious metals (and metals in general) at selected discharges. The development and improvement of such techniques would thrive in the following years with the concomitant advantage of closing the economic and technological gap that currently impedes the application of these techniques to municipal WWTPs.

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Chapter 4
Chemical, Physical and Biological Techniques for Recovery of Heavy Metals from Wastewater

Deeksha Ranjan

Abstract With the ever-increasing population, industrialization, and urbanization there has been rapid rise in the demand of water resources. This has resulted in issues like inadequate supply of water, degradation in the quality of water. Contamination of water resources with metals has become a serious concern these days. Metals, themselves being non-renewable resource are discarded in the aqueous environment, thus are not only wasted but also impose serious health issues to every form of life. Besides the inherent concern of water contamination through metals, it is also seen as an opportunity to regain and recover the metal resource from wastewater. The current emphasis to achieve sustainable development goals, which includes circular economy i.e., circular utilization of resources, has opened up challenges and opportunities where wastewater is considered as a resource and its treatment is done for removing pollutants as well as recovering valuable resources from it. The current chapter elaborates the conventional, as well as novel and emerging chemical, physical and biological techniques used for the recovery of heavy metal resources from wastewater.

Keywords Heavy metal · Recovery · Precipitation · Filtration · Ion exchange · Adsorption

4.1 Introduction

Water, a natural renewable resource, is essential for every form of life for their sustenance and general well-being. For a healthy and prosperous society, fresh and clean water supply and proper sanitation is essential. Water is an important factor for every sustainable development goal as it is essentially required for socioeconomic development. It supports a healthy ecosystem and biodiversity (Singh and Gupta

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2016). Hence, lack of access to freshwater resources can cause a decline in countries' economic growth as it is needed to sustain critical human activities like food and energy production, and industrial operations. Water is gift of nature to the mankind and it is impossible to find an alternative for it for most of its uses. It is considered to be one of the most manageable natural resources, as it can be transported, stored and even recycled with comparative ease (The 2030 water resources group 2016). Various sources of water, such as surface and groundwater, play a major role in agriculture, livestock, hydropower generation, industrial activities, forestry, navigation, recreational activities etc. However, in the last few decades, there is rapid intensification in the demand of water resources, owing to ever rising population, growing economies and shift in pattern of consumption. There is a decrease in per-capita availability of fresh water resources (The 2030 water resources group 2016). With increasing urbanization especially in developing and under developed countries, there is a continuous stress on freshwater resources because of high water demands, which leads to inadequate water with degraded quality. Climate change has affected the water cycle and thus has led to alteration in the availability and distribution of water, resulting in further straining the water resources. Anthropogenic activities causing water pollution have further threatened the sustainability of water supply, damaging the water quality, human health and environment. Degraded water quality is caused by poor sanitation, agricultural run offs and unregulated industrial effluents discharge. Most of the wastewater generated enters back into the nature untreated and causes serious health and environmental issues (The 2030 water resources group 2016; Delgado et al. 2021).

4.1.1 A Shift Towards Wastewater Treatment and Circular Economy

With all these challenges, it is becoming difficult for the policy makers to fulfil demands of fresh and clean water resources for the rising population food, energy and economic growth. These demands are to be satisfied keeping the public health and environmental concerns in mind. The scarce availability of natural freshwater resources has creates a paradigm shift from waste treatment to resource recovery i.e., from 'use and throw' to 'use, treat and reuse approach'. Wastewater treatment, in future, thus, can grow as a profitable investment. Instead of considering wastewater as a waste to be discharged and disposed off, it should be treated as a valuable resource to be recycled and reused, from which other resources like water, food, energy etc. can be extracted. Wastewater is a mixture composed of many valuable metals, nutrients and many chemicals, which if extracted can help in fulfilling the demand of natural resources and thus socioeconomic development of a country and water after treatment can be reused for many other purposes like groundwater discharge, irrigation and recreational purposes leading to a closed-cycle (The 2030 water resources group 2016; Delgado et al. 2021).

This kind of a closed loop system is considered as a part of circular economy, which is the current emphasis in sustainable development goals. Circular economy is aimed to tackle the wastes in a more sustainability, inclusive, efficient, and resilient way. According to the concept of circular economy, the material may it be a raw material or a product, should remain in the economic cycle for as much time as it can and the generated waste should be considered as a secondary raw material to be recycled and reused. However, the linear economy concept, is based on using and disposing and waste is the last phase of the any process. Shifting to a circular economy could be beneficial in growing economic, providing opportunities and competitiveness for innovations, reducing stress on environment, and also improving the security of raw materials (Delgado et al. 2021). It promotes the sustainable management of materials and energy by not only minimizing the generation of waste but also using them as a secondary material to recover resources from it (The 2030 water resources group 2016). However, the major challenges to resource recovery and wastewater treatment arise due to contamination from industries and other human activities.

4.2 Presence of Metals in Aqueous Environment

Contamination and toxicity caused by heavy metals and their compounds is of major concern globally. Heavy metals Hg, Pb, Cr, Cd, As, Ag, Au etc. and their compounds are used in industries like textile, pulp and paper, leather, cosmetics, electronics, food and agricultural. From these industries heavy metals enter into the soil as well as aqueous environment and also into the food chain through discharge of hazardous industrial waste effluents. Heavy metals are bio-accumulative and can also be biomagnified in nature. Heavy metals are hazardous to almost every form of life and environment and thus need to be treated and removed from the system. Precious metals like Ag, Au, Pt etc. also come under the category of heavy metals. They are precious as they are rare and chemically inert in nature. Usually these do not get oxidized, corroded, and tarnished naturally, and are used extensively in the manufacturing of jewellery, fabrication of electronic devices and as catalyst in industries. Ir and Rh are capable of performance under very harsh and unfavourable conditions. Thus, precious metals have also become a necessity for the human life. The demand of rare and precious metals has increased with the advancement of science and technology and rise in economies and population globally. The high demand results into more mining of these precious metals polluting the soil as well as water systems and thus imposing risk to human health and environment. Activities like construction, demolition, industrial, commercial and domestic add up to huge amount of waste generated every day, leaving its footprints in the forms of wastes containing different non-recycled organic and inorganic chemicals including metals. Thus, precious metals along with other heavy metals are found in waste and wastewater systems (He and Kappler 2017; Qasem et al. 2021). Few common heavy metals, their sources, health hazards and permissible limits have been shown in Table 4.1 (Mahmud et al. 2016):

Table 4.1 Common heavy metals, their sources, hazards, and permissible limits

Common heavy metals	Sources	Effects	Parmissible limit (WHO) (mg/L)
Cr(III), Cr(VI)	Leather tannic, chrome plating, textile manufacturing and pulp processing, petroleum refining, electroplating industry	On human: headache, nausea, vomiting, diarrhoea, carcinogenic, chronic bronchitis, irritation in eyes On plants: chlorosis, wilting, biochemical lesions, reduced biosynthesis germination	0.05
Pb	Metal plating and finishing operations, wastes from batteries industries, soil wastes, exhaust from automobiles, additives in gasoline and pigment, factory chimneys, smelting of ores, fertilizers, and pesticides, bangle industry	On human: damaging foetal brain, anorexia, damaging renal system, nervous system and circulatory system, insomnia, reduced fertility On plants: affects photosynthesis and growth, chlorosis, inhibit enzyme action and seed germination	0.05
Cu	Mining, electroplating, smelting operations, plastic industry	On human: Wilson disease, abdominal pain, headache, liver and kidney damage, nausea, vomiting On plants: chlorosis, oxidative stress, growth retarder	1.5
Cd	Paint pigments, pesticides, plastic industry, battery industry, e-wastes, incineration and fuel combustion	On Human: renal disorders, carcinogenic, bone disease, itai-itai, emphysema, hypertension On plants: chlorosis, disease in plant nutrients, growth inhibition, reduced seed germination	0.005

(continued)

Table 4.1 (continued)

Common heavy metals	Sources	Effects	Parmissible limit (WHO) (mg/L)
Ni	Smelting operations, thermal poers plants, paint and powder, batteries processing units, galvanization, metal refining, super phosphate fertilizers	On human: headache, dizziness, dermatitis, nausea, chronic asthma, cardiovascular disease, chest pain, coughing, carcinogenic On plants: decrease chlorophyll content, inhibit enzyme growth and activity, reduced nutrient uptake	0.02
Zn	Smelting, electroplating, rubber industry, paints and dyes, batteries, phaophate fertilizer and detergents, wood preservatives	On human: depression, ataxia, lethargic, neurological disorders, kidney and liver failure, prostate cancer, seizers, vomiting On plants: affects photosynthesis, growth inhibitor, reduced chlorophyll, reduced seed germination and plant biomass	5.0

(continued)

Table 4.1 (continued)

Common heavy metals	Sources	Effects	Parmissible limit (WHO) (mg/L)
As	Geogenic processes, smelting, thermal power plants, fuel burning, wood preservatives, dyes	On human: brain damage, dermatitis, skin cancer, cardiovascular and respiratory disorder, conjunctivitis On plants: growth inhibition, damage cell membrane, physiological disorders, loss of fertility	0.05
Hg	Chlor-alkali plants, thermal power plants, wastes of damaged thermometers, barometers, electric appliances, fluorescent lamps industry	On human: ataxia, blindness, reduced fertility, dementia, dizziness, gastrointestinal disorder, gingivitis, memory loss, reduced immunity On plants: affects photosynthesis and antioxidative system, reduced plant growth, yield, nutrient uptake	0.001

4.3 Need for Recovery of Metals from Wastewater

Heavy metals enter the aqueous environment through various sources as discussed above. Besides their economic value, use in different processes and components, they pose a serious hazard to human life as well as ecological system. Moreover, the traditional process of mining of precious metals is also quite costly as huge amount of energy and chemicals are used for extracting metals. High grade ores are used as raw materials so the whole process becomes cost effective and profitable. However, mining activities are being limited to protect the natural resources of high-grade ores (He and Kappler 2017). The import–export of precious metals is also restricted in many of the countries because of strict laws and regulations. To this, the recovery of heavy metals along with precious metals from wastewater may come as a possible solution that can help in boosting the economy also (Qasem et al. 2021).

4.4 Methods for the Recovery of Metals from Wastewater

Keeping in mind the sustainable development goals, attention is given to reuse the wastewater, generated from various point and nonpoint sources, as a resource to recover heavy metals including precious metals. This is done toto preserve valuable natural resources and to protect ecological system from the damage, the metals may cause. Resource recovery also makes the whole process cost effective and thus helps in overall economic growth and achieving the sustainable development goals. The techniques and methods used to remove and recover these metals present in wastewater include conventional techniques as chemical precipitation, coagulation and flocculation, ion exchange, adsorption, electrochemical and biodegradation methods. The novel and advanced techniques include membrane technology, photocatalysis technology and nanotechnology (Fu and Wang 2011; Zhang et al. 2013; Azmi et al. 2017; Huang et al. 2018). Overall, the techniques are categorised as chemical, physical, and biological and hybrid methods (Fig. 4.1) (Fu and Wang 2011; Azmi et al. 2017). These techniques are discussed in detail one by one in following sections.

4.4.1 Chemical Precipitation for Metal Recovery

Chemical precipitation is an effective and mature method that is commonly employed to treat effluent wastewater from various industries and mining. It involves pretreatment, adjustment of initial pH, coagulation-flocculation and clarification, sludge thickening, sludge watering and polishing of effluents. Generally, it works on the principle of lower metal ions solubility i.e., dissolved metal ions are converted to their insoluble forms by addition of precipitating agents as hydroxides, carbonates and sulphides, in order to facilitate sedimentation. Efficiency of this method depends

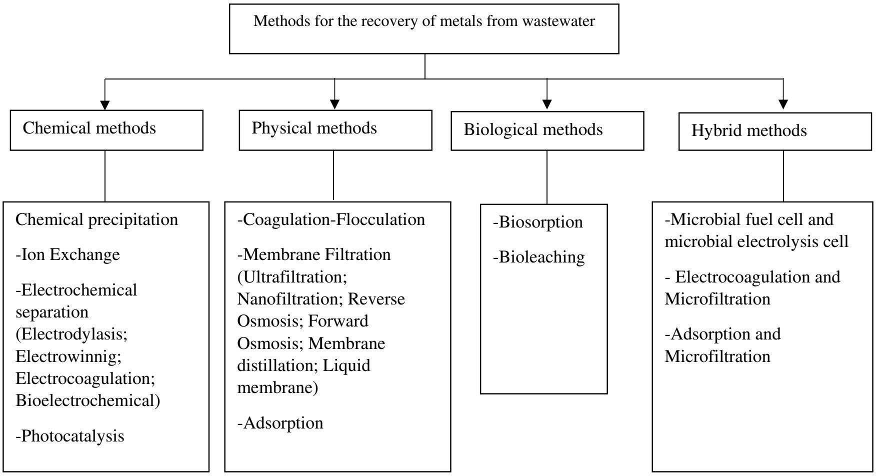

Fig. 4.1 Categorization of methods for the recovery of metals from wastewater

on precipitate formation and settling rates. Metal precipitation in hydroxide form is most common of all because it is comparatively cheap, simple and pH is easily adjustable (Kurniawan et al. 2006; Fu and Wang 2011; Azmi et al. 2017). Alkalis mainly used for hydroxide precipitation are NaOH (caustic soda) and $Ca(OH)_2$ (lime). Metal ion precipitates as shown below,

$$M^{n+} + n(OH)^- \rightleftharpoons M(OH)_n \downarrow \tag{4.1}$$

It is reported that pH between 9–11 is the most suitable for precipitation. Wastewater with low metal concentrations and high pH require high amount of lime and caustic soda. The process in simple, easy, involves low investment and has high degree of automation. However, large quantity of sludge formation during the process, which needs to be dewatered, stabilized and/or disposed; lower speed of precipitation; inadequate settling and aggregation of metal ions are the main drawbacks of this process (Grad et al. 2021a, b). Calcium hydroxide has been used for the precipitation of Zn and Cd in wastewater and reported to reduce the solubility to as low as 5 mg/L. Hydroxide precipitation is also done to reduce the concentration of Cu^{2+}, Ni^{2+}, Pb^{2+}, Cr^{3+}.

Precipitation in the form of sulphide is characterized by high metal removal efficiencies as there are lesser dissolved solids. It is reported to reduce and remove metal ions from wastewater. A lower concentration of sulphides will enhance the metal ion concentration in wastewater, while a higher sulphide will form hydrogen sulphide which is malodorous and hazardous. Precipitation using sulphide is recommended to be carried out in neutral pH. The general reaction is as follows:

$$M^{n+} + S^{2-} \rightleftharpoons M_nS \downarrow \tag{4.2}$$

Toxicity caused by sulphide precipitation and comparatively high cost are drawbacks of sulphide precipitation (Anotai et al. 2007; Al-Hemaidi 2012).

As an alternate to hydroxide precipitation, carbonates are used. It is effective at precipitation at lower pH. Sodium carbonate and calcium carbonates are used for precipitation as follows:

$$M^{n+} + n\,CO_3^{2-} \rightleftharpoons n\,M(CO_3) \quad (4.3)$$

$$nM(CO_3) \rightleftharpoons CO_2 + M(OH)_nCO_3 \downarrow \quad (4.4)$$

As compared to other precipitating agents, lesser quantity of sludge is produced. However, it is associated with CO_2 generation and high precipitating agents are required for effective precipitation. Cu, Mn, Zn, Pb have been efficiently removed using carbonate precipitation (Patterson et al. 1977; Al-Hemaidi 2012).

Though precipitation method is industrially proven, however in general it is associated with some drawbacks (Grad et al. 2021a, b):

- A large quantity of sludge production in comparison to other traditional methods.
- In case of presence of chelating agents, sequestering agents, bath additives, cleaners and electroless formulations, additional precipitating agents are to be added to precipitate metal ions in wastewater, which adds up to the amount of sludge generated.
- If the concentration of suspended solids is lower than 5–10 mg/L, then it is not removed by precipitation.
- Some of the metal hydroxide precipitates are amphoteric in nature and are minimum soluble i.e., they are increasingly soluble with the increase and decrease of pH. The optimum pH at which a metal precipitates varies with metals. That means at a certain pH, one metal hydroxide may have maximum and other may have minimum solubility. This will cause few of the metal hydroxide to be dissolved back to the wastewater with the change in pH.
- It is difficult to set an optimum ideal pH in case of multi metal wastewater. As wastewater from different industrial processes generally consists of various metals, this means at optimum pH of one metal other metals will dissolve back into wastewater.

4.4.1.1 Metal Recovery from Sludge

Metals from the precipitate are recovered by solid–liquid separation, and then further purification via chemical extraction. The sludge which is settled in the clarification tank has around 1–2% of solids. It is difficult to dewater the hydroxide sludge as these are generally gelatinous as compared to the sludge produced by adding lime. Also, specific attention has to be paid and recovery methods may change as the composition of produced sludge might be different from different wastewater treatment plants (Andreoli et al. 2007). From sludge metals can be recovered by electrolytic recovery after digesting the sludge in acidic medium and then neutralized. Metals like Cu. Ni and Cr are recovered with the recovery cost of around \$13.25 per kg which is high in comparison to its market value. The metal loaded sludges can be stockpiled for future economical metal recovery (Krishnan et al. 1993; Sreekrishnan et al. 1993). The metals can be leached from sludge both chemically and biologically. Metals are chemically leached by using various organic and inorganic acids. Most commonly used inorganic acids are hydrochloric acid, nitric acid, sulfuric acid, and phosphoric acid, while common organic acids used are acetic acid, citric acid and oxalic acid. Although, chemical leaching is associated with producing a high concentration of metals. It is a costly affair as large amounts of acids and then alkalis (for neutralization) are used, making the process impractical (Marchioretto 2003).

A more eco-friendly and economic way for metal leaching and further recovery is by microbiological digestion of the sludge. Bioleaching, which is a biohydrometallurgical process, insoluble forms of metal are converted to water soluble forms by employing microbes. This process usually does not require harmful chemicals. Two types of microbial leaching processes are reported. One, with the help of iron oxidizing bacteria like *Acidobacilus ferroxidans*, and *Leptospirilium ferooxidans* which requires ferrous sulphate as substrate and initial pH of sludge to be lowered to approx. 4.0 (Erust et al. 2013).

$$Fe^{2+} + H^{+} + O_2(\text{bacteria}) \rightarrow Fe^{3+} + H_2O \tag{4.5}$$

$$\text{Metal} - X + Fe^{3+} \rightarrow \text{Metal}^{2+} + Fe^{2+} \tag{4.6}$$

Other, is microbial leaching with the help of bacteria like *Acidobacillus thioxidans*, which requires elemental sulphur as substrate and no initial lowering of pH (Erust et al. 2013).

$$\text{Metal} - S + O_2(\text{bacteria}) \rightarrow \text{Metal}^{2+} + SO_2 \tag{4.7}$$

The metal leachates obtained from sludge have complex composition and it is difficult to recover metals directly from it. Sometimes these also have a low metal concentration, presence of other organic and inorganic chemicals, and high ionic strength. Thus, the leaches are first purified and then concentrated to recover pure single metal from it (Gerardo et al. 2013).

Leachates are purified using methods like sedimentation, cyclone and various membrane filtration techniques. Some of the metal separation techniques used are solvent extraction using liquid–liquid extraction (LLE), electrodialysis, membrane filtration (Visser et al. 2001; Gerardo et al. 2013). During LLE, two immiscible phases are the organic phase and aqueous phase. Organic phase consists of a dilute solution of organic extractants, while the aqueous phase consists of aqueous solution of metal to be extracted. The metal present in aqueous phase is transferred to the organic phase and an equilibrium is established between two immiscible phases. Specific organic extractants are required for specific metal extraction. LLE efficiency is affected by pH and concentration of organic phase. Extracted metal is then stripped and recovered into the aqueous medium from the organic phase. Usually, electrowinning is used then used to remove metals from the organic solutions, which is then again reused after recycling (Visser et al. 2001). The other methods and techniques used for the metal recovery will be discussed one by one.

4.4.2 Coagulation—Flocculation for Metal Recovery

The process is carried out by adding chemicals which helps in agglomerating and sedimenting the colloidal suspended particles of metals in wastewater by destabilizing and flocculating them. Destabilization of colloidal suspended particles is done by neutralizing them by addition of coagulants to wastewater. Colloidal particles are negatively charged particles, and thus positively charged coagulants like aluminium sulphate, ferrous sulphate and ferric chloride, are added to neutralize the ionic charges. Flocculants, like polyaluminum chloride, polyferric sulfate, polyacrylamide, polydiallyldimethylammonium chloride, polyethyleneimine-sodium xanthogenate, mercaptoacetyl polyethyleneimine and other neutral or anionic macromolecules, then agglomerates and brings the neutralized particles together by binding them and forming larger particles known as flocs. The heavier metal flocs then settle to the bottom and are either recovered by sedimentation or filtration (Chang et al. 2009; Fu and Wang 2011).

Advantages of coagulation and flocculation method includes low capital investment, simple operation, improved stability and settling of sludge, improved rates of sedimentation, dewatering characteristics, microbial inactivation. Drawbacks of this method are high cost of operation due to high chemical usage, toxicity and hazards of coagulants and flocculants, selectivity for some metals, generation of high amount of sludge and further treatment of generated sludge for recovery of metals, additional cost for sludge treatment (Chang et al. 2009).

Coagulation-flocculation has been employed for the removal and subsequent recovery of metals from wastewater. Few precious metals have also been recovered from industrial wastewater (Kawakita et al. 2008; Folens et al. 2017). Metallic salts present in wastewater are hydrolysed by the addition of coagulants and form cations which adsorbs with the help of negatively charged colloidal particles.

4.4.3 Ion Exchange for Metal Recovery

It is also one amongst the most studied methods used to remove and recover metals present in wastewater. In this regard the attempts were started in 1990s. The process is based on reversible ion exchange chemical reaction between the solid phase which is immobile and liquid phase which is mobile. Solid ion exchangers are insoluble granular substances containing exchangeable ionic radicals that are bound with acidic or basic groups.. These radicals actually exchange metal ions from liquid phase, without modifying and damaging the structure of ion exchangers. The first ion exchanger used was zeolites (the natural earth). Thereafter, ion exchangers produced synthetically as inorganic aluminosilicates and organic resins. Resin term is now being generally but wrongly used for all kinds of ion exchangers (Els et al. 1997; Kurniawan et al. 2006).

General reaction showing mechanism of ion exchange is shown below:

$$\text{M-EC}^{+} + \text{WC}^{+} \rightleftharpoons \text{M-WC}^{+} + \text{EC}^{+} \tag{4.8}$$

where, M-EC^+ represents the cationic ion exchanger (M represents fixed anionic part and EC^+ represents exchangeable cation, which is generally H^+ or Na^+) and WC^+ represents the wastewater cation.

4.4.3.1 Types of Resins

Ion exchange resins are three-dimensional covalent networks hydrocarbon chains carrying exchangeable ions. These are basically of two types: those which exchange cations are called cationic exchange resins or cation exchangers and those which exchange anions are the anionic exchange resins or anions exchangers. The functioning of ion exchangers depends upon initial pH, flow rates, turbidity, regenerant type and wastewater complexity. The cation exchangers may be categorized as strong and weak acid and like-wise the basic exchangers may be strong or weak base. Also, resins which are useful for removing a specific metal ion are referred as chelating ion exchangers (Pendias and Kabata-Pendias 1992; Yang et al. 2001).

Cation Exchangers

Strong acid cation exchangers are sulphonated polystyrene and have HSO_3 radicals (sulfonic radicals). The acidity is close to that of sulfuric acid. The ion exchange reaction occurs as follows:

$$\text{RSO}_3 - \text{H}^{+} \rightleftharpoons \text{RSO}_3 - \text{Na}^{+} + \text{H}^{+} \tag{4.9}$$

These resins are selective to metals in the following order:

$$\begin{aligned} &\text{Fe}^{3+} > \text{Al}^{3+} > \text{Ca}^{2+} > \text{La}^{3+} > \text{Y}^{3+} > \text{Ba}^{2+} > \text{Th}^{4+} > \text{Hf}^{4+} > \text{Zn}^{2+} \\ &\quad > \text{Ac}^{3+} > \text{La}^{3+} > \text{Th}^{4+} > \text{La}^{3+} > \text{Ce}^{2+} > \text{Na}^{+} > \text{Mg}^{2+} > \text{Be}^{2+}. \end{aligned}$$

Weak acid cations are polyacrylic resins having HCO_3 radicals (carboxyl radicals) and acidity is close to weak organic acids like formic acid and acetic acid. These can be regenerated easily as compared to strong acid cation exchangers. The general reaction of ion exchange is as follows:

$$RCO_2H \rightleftharpoons RCO_2^- + H^+ \quad (4.10)$$

$$RCO_2H + HCO_3^- + Na^+ \rightleftharpoons RCO_2 - Na^+ + H_2O + CO_2 \quad (4.11)$$

Metal selectivity for these resins is following order:

$$H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+.$$

Anion Exchangers

Strong base anion exchangers are composed of simple quaternary ammonium radicals have strong basicity but low capacity and poor regeneration as compared to those having radicals of quaternary ammonium and alcohol.

Weak base anion exchangers contain mixed primary, secondary, tertiary and quaternary amines having nucleus of aliphatic, aromatic or heterocyclic compounds. General reaction showing ion exchange is as follows:

$$R_4N^+OH^- + H^+ + A^- \rightleftharpoons R_4N^+A^- + H_2O \quad (4.12)$$

It follows the selectivity order given below:

$$NO_3^- > CrO_4^{2-} > Br^- > SCN^- > Cl^-.$$

Weak base exchangers show ion exchange as follows:

$$R_3N + H^+ + A^- \rightleftharpoons R_3NH^+A^- \quad (4.13)$$

The selectivity order is given below:

$$OH^- > SO_4^{2-} > CrO_4^{2-} > NO_3^- > PO_4^{3-} > MoO_4^{2-} > HCO_3^- > Br^-.$$

Adsorbent Resins

These resins work on reversible adsorption of non-ionic organic compounds dissolved in polar and nonpolar solvent. The interaction between metals present in wastewater and adsorbent resin may be physical or chemical and depends on types of functional groups present on adsorbent, its hydrophilic nature, polarity, porosity and specific surface area of resin. Resins may be regenerated by eluants like pure water or steam, acids, bases or salts.

Polyfunctional Resins

These have combined properties of that of weak as well as strong resins. They have high exchange capacity and can be easily regenerated.

Chelate Resins

They are composed of special functional groups, like aminophosphoric, aminodiacetic, Aminodioxime and mercaptan, which remove metal ions by chelating them. Further metals can be separated by gas chromatography and electrolysis process.

4.4.3.2 Metal Recovery from Resins

The metal ions in wastewater are exchanged with positively charged groups of cation exchanger. The exchangers are then separated from water and recovery of metal is done by elution with acidic regenerant. This allows concentrations of dissolved metals in the acid regenerant from cation exchanger. The regenerant is free from organic impurities and have a high metal concentration of up to 4–6 g/L which further requires evaporator, electrodialysis or hydrometallurgically processed to recover metal from it. The removal and recovery of Au and Ag was studied. A weak base anion spent resin from a dimineralisation plant, Purolite A- 100—was used, in order to reduce cost of whole operation. It is reported to recover 25 times Au concentration after elution. Resin also showed high recovery of Ag after elution. Another study reports recovery of Au(III) by eluting with solution of Au-HCl from anion exchange resin Lewatit MP-64. It was affected by concentration of HCl and Au(III), temperature and amount of resin also. Gold particles were recovered from solution after processing the solution with sodium borohydride. Other researches were also done to remove and then recover precious metals Pt(II) and Pt(IV) from chloride solution, other members of platinum group, and Au from different effluents of precious metal refineries. In another study, Amberjet™ 4200 resin showed adsorption capacity of more than 98% for Au removal and recovery form wastewater generated from bioleaching. Heavy metals Cu and Au are reported to be removed and recovered more than 98% and 78% respectively using Amberlite IRC-86 resin from bioleaching wastewater. Recently, Au and Ag recovery from wastewater was done through reductive ion exchange using a faradaic electrode material $NaTi_2(PO_4)_3$ (Alguacil et al. 2005; Nikoloski and Ang 2014; Yahorava and Kotze 2014; Choi et al. 2020; Dong et al. 2021).

4.4.3.3 Advantages and Disadvantages of Ion Exchange

Ion exchange and then elution to recover metal ions has gained popularity because of its future certainty. It offers advantages of simple operation, high loading capacity and efficiency, highly economic, energy efficient, no sludge generation, mechanical stability, selectivity for some pollutants, high binding capacity for metals from leachate solutions with even low concentration. The drawbacks on the other hand are high capital and operational expenses; requirement of large amount of chemicals for resin regeneration which is associated with problem of secondary effluent generation again requiring a pre-treatment, unsuitability for all metal types. Other disadvantages include risk of clogging, chances of resin degradation, limited adsorption capacity of resins, not effective for emerging pollutants (Kurniawan et al. 2006; Nikoloski and Ang 2014).

4.4.4 Membrane Filtration for Metal Recovery

It is a physical method for separation of particles of different sizes and characteristics. Treatment of wastewater using membrane technology is highly promising, effective and might help the effluents to be within the permissible limits. Depending upon the driving forces, membrane filtration methods are of different types. Microfiltration, Ultra filtration, Nano filtration and Reverse osmosis or hyper filtration are pressure driven techniques. Pervaporation, Per-traction, Dialysis are driven by chemical potential difference, while Gas separation vapour permeation, Liquid membranes, Electro-dialysis, Membrane electrophoresis are driven by electrical potential difference. Ultrafiltration, nanofiltration, and reverse osmosis have been lately employed in efficiently removing and recovering heavy metals from various wastewater effluents. In membrane separation, the concentrate or retentate is the solution which is retained by the membrane while, filtrate or permeate is that solution that passes through the membrane (Azmi et al. 2017; Rahmati et al. 2019).

The membrane separation method is associated with various advantages and disadvantages such as low consumption of energy as compared to other processes, less quantity of retentate is to be taken care of, selective retention of metal ions with complexing agent, permeated water and can be reused after recovering other resources from it, with modular design the operation is easy and minimum requirement of labour, continuous operation (Azmi et al. 2017).

4.4.4.1 Ultrafiltration

Ultrafiltration requires low transmembrane pressure. It utilises permeable membrane of pore size 5–20 nm for segregating suspended particles, metal ions as well as macromolecules present in inorganic solution. Efficiency of ultrafiltration to retain heavy metal ions is enhanced when the ions are complexed with micelles or macromolecules. These are referred to as Micellar enhanced ultrafiltration (MFUF) and Polymer enhanced ultrafiltration (PEUF). Metal ions are bonded with additives to enhance their size to be retained by the membrane, thus increasing the performance of ultrafiltration. Water soluble polymers like polyacrylic acid and polyethylenimine had been used to recover Copper from wastewater (Chhatre and Marathe 2006; Ghosh and Bhattacharya 2006).

There are two procedures, diafiltration and concentration. Diafiltration involves complexing polymer agent in solution with continuous renewal of filtrate by fresh input. When the polymer becomes loaded after sometimes, the metal ions start appearing in the solution. A large excess of complexing agents would cause a loss of metal ions in the filtrate. In the concentration method, premixed volume of metal-polymer complex is batch concentrated by retentive membrane. Recovery of metal ions can be done by a shift in pH or by electrolysis for both diafiltration and concentration procedures (Nguyen et al. 2015; Rahmati et al. 2019).

MEUF technique is employed successfully for recovering metals which are present in low concentration in wastewater. It is associated with low consumption of energy because of high flux and selectivity. Less space is required, and it is efficient in removing and recovering metal ions. During MEUF addition of surfactants is done equal to or more than the critical micellar concentration. The hydrophopic core of micelles solubilizes organic matter while the outer hydrophilic tail comprising surface adsorbs the metal ions via electrostatic forces. Heavy metals bound with micelles are retained by ultrafiltration membrane easily. Usually, surfactants having opposite charges than metal, attain highest retention. Cationic surfactant, polyelectrolytes and anionic surfactant, sodium dodecyl sulphate are used generally in recovering heavy metals from wastewater.

Efficiency of MEUF depends upon factors including operating conditions as pH, pressure, feed temperature and concentration, surfactant concentration, flow rate. Factors also includes type of surfactants, added solutes, kind of ultrafiltration membrane used. The pressure applied should be less than the maximum pressure the membrane can tolerate. At a particular concentration the permeate flux varies with pressure. A high percentage of rejection coefficient can be obtained when surfactant to metal molar ratio has been maintained above 5. Some studies report that the concentration of permeate increased with concentration of feed. The thermal expansion and viscosity of the solution depends on the feed temperature. Critical micellar concentration also depends upon feed solution temperature.

PEUF is also referred to as complexation enhanced, size enhanced, polymer assisted, or polymer supported ultrafiltration. This process involves binding of metal ions with water soluble polymers, thus forming a macromolecule, which helps retaining the metal ions by the ultrafiltration membrane. Examples of polymers used for binding are Polyvinylamine (PVA), Polyethyleneamine (PEI), Polyacrylic acid (PAA) etc. The polymers bind to the metal ions via chelation or ionic bonds with the help of functional groups which are sulfonated, carboxylated, amine or phosphonic.

The efficiency of PEUF depends upon pH and concentration of feed solution, types of metal ions to be recovered and the nature of binding polymers. Percentage of rejection coefficient was found to be decreased as concentration of chromium increased in feed solution. Optimum ratio of PEI polymer and metal ions was reported to be 6 and 3 for selectively removing and recovering Ni(II) and Cu(II). PEUF requires low energy and low cost to operate, it is well efficient in recovery and reuse of metal ions and complexation polymer of retentate. The major challenge is the selection of suitable water-soluble polymer for specific metal ions.

Overall, advantages of ultrafiltration are that this method is extensively used on large scale, equipment is easily scalable, compact and modular, easy operation and requires low energy, no sludge production, low capital and operational cost, almost no effect on water chemistry. The disadvantages on the other hand are requirement of extra cost for concentrate treatment, limited to certain particle size, and membrane fouling Samper et al. 2009; Fu and Wang 2011; Rafique and Lee 2014.

4.4.4.2 Nanofiltration

This is a pressure driven membrane separation process, properties of which lies between ultrafiltration and reverse osmosis. The presence of functional groups and their dissociation may provide membrane surface the residual charges, which is dependent on pH of solution. Membrane has pore size from 1 to 4 nm diameter. The method is used in concentrating those constituents having molecular weight more than 1000 Da and in removing solutes having molecular weight more than 200 Da and size between 0.0005–0.007 μm. The mechanisms which are involved in the rejection of solute metal ions from wastewater are charge (coulombic) interaction, size exclusion via hydrated ions, and dielectric interaction and it has been found during studies that the charge and hydration mechanisms are dominating in rejection of ions while dielectric interaction playing a minor role. Ions having same charges as that of the membrane are called co-ions and these used to characterize the rejection charge pattern. If the co-ions may increase the rejection, indicating the charge pattern. The counter ions can actually decrease the rejection if having multiple valency, while the co-ions having low charge and mono-valency can increase the rejection. The charge interaction lowers with rise in concentration of electrolyte and is more significant with dilute solutions like rinse waters. The hydrated pattern is that the larger the size of hydrated ion, the more it is rejected. Hydration effect decreases with increase in concentration of ions which favours its significance for dilute solutions such as rinse waters. Hydration is also reported to be decreased by presence of water structure breakers like $NO_3^{=}$, however, it is increased by presence of structure forming ions like Na^+ and Cl^- (Chhatre and Marathe 2006; Ghosh and Bhattacharya 2006; Fu and Wang 2011; Rafique and Lee 2014). Nanofiltration is reported to be employed for removing and recovering metals like Co, Cu, Ni, Pb, Zn,, Cd, Cr, As, Hg, Li (Murthy and Chaudhari 2008; Muthukrishnan and Guha 2008; Boricha and Murthy 2009; Cséfalvay et al. 2009; Urgun-Demirtas et al. 2012; Gherasim et al. 2013; Yu et al. 2013; Gherasim et al. 2015; Gao et al. 2016; Thabo et al. 2021; Wang et al. 2021).

Nanofiltration has associated advantages of widely used method on large scale, no need of chemicals and additives, no generation of sludge, compact, modular and scalable equipment, selective removal of monovalent and multivalent ions. The disadvantages are relatively high capital cost, low remotion of monovalent ions, pre-treatment is required, extra cost of treatment of concentrate, fouling of membrane.

4.4.4.3 Reverse Osmosis

Reverse osmosis utilises semipermeable membrane of pore size 10^{-4} μm. The pore size is less than the metallic size, so that water can pass and metal ions are retained. It is useful for rinse waters which are relatively dilute. By applying high pressure on the feed side, water is forcibly allowed to enter the permeate side through membrane, while retaining the metal ions on the feed side, where they concentrate. Care should be taken that the membrane does not get clogged and fouled. The pH of wastewater containing metal ions is first lowered by adding acid to it, in order to redissolve the metal ions, which got precipitated because dilution has raised the pH of wastewater. Filtration is needed before performing reverse osmosis in order to prevent clogging of membrane. Hydrostatic pressure of approx. 20–70 bar, which is higher than the osmotic pressure of feed solution is exerted on feed side in order to revert the natural osmotic diffusion (Naja and Volesky 2009; Fu and Wang 2011; Wang et al. 2011; Azmi et al. 2017).

$$\pi = \Delta C^{*} R^{*} T \tag{4.14}$$

where, Π = osmotic pressure (Pa), ΔC = concentration difference in mol/m^3, R = ideal gas constant (8.314 J/mol/K), T = temperature in Kelvin.

This equation shows that for smaller molecules greater osmotic pressure is to be applied for same difference in concentration. This method has been adopted for recovering Nickel, Chromium, Copper ions from wastewater generated by electroplating and showed above 98% removal efficiency (Ozaki et al. 2002). It is also reported recovering metal ions and purify wastewater from mining industries also (Samaei et al. 2020). Metals like Mn, Fe, Zn, As, Cd etc. were also recovered by employing Volume retarded osmosis low-pressure membrane (VRO-LPM) and around 95% rejection has been obtained (Choi et al. 2019). Ultra-low pressure reverse osmosis (ULPRO) along with nanofiltration has been used for achieving rejection of heavy metals above 97% (Zhong et al. 2007). Reverse osmosis and nanofiltration were hybridized using cyanidation and were tested in recovering Ag from mining wastewater (Koseoglu and Kitis 2009).

Reverse osmosis is efficient for recovery of heavy metals including precious and noble metals. The permeate obtained is of high quality and can be reused for leaching. It is a compact process and attains high rejection efficiency. It requires small space as the equipment is compact. However, the associated high energy requirement, high operational and capital cost and membrane fouling are some drawbacks of it.

4.4.4.4 Forward Osmosis

In this process the feed and draw solution are separated by a semipermeable membrane. Water from feed side passes through the membrane towards draw side, driven on natural energy of osmotic pressure difference between draw and feed solution. Thus, metal solute is rejected, retained and recovered at feed side while treated water at the draw side. Forward osmosis has already been in use for recovering various heavy metal ions from wastewater, however, its use in processing of precious metals is recent. This method can be hybridized with other methods like membrane distillation for overall recovery of resources from wastewater thus making it an environment friendly approach (Chekli et al. 2016; Gwak et al. 2018; He et al. 2020; Chia et al. 2021).

4.4.4.5 Membrane Distillation

This technique is thermally driven and is widely used for desalination. A hydrophobic membrane is used to separate the two streams of hot i.e., feed side and cold i.e., permeate side and only vapours are allowed to pass through the membrane pores while other molecules are retained. At the feed side volatile compounds are evaporated and towards the permeate side diffused vapours condense. This vapour pressure difference is the driving force for the process. Low grade or renewable energy sources as solar, wind, waste heat can be used for this process. This technique is highly selective and shows almost 100% solute rejection for contaminants which are non-volatile. The operating conditions are mild and have excellent sealing properties. There are lesser chances for membrane fouling. Membrane distillation has four types which are direct contact, air gap, sweeping gas and vacuum membrane distillation. This process is more efficient in removing and recovering metal ions when used in combination with techniques like electrodialysis. It has been found to highly efficient in removing various heavy metals (Chin et al. 2020; Naidu et al. 2020; Foureaux et al. 2020; Chen et al. 2020a, b, 2021a, b).

Membrane distillation has the advantages which includes requirement of low operating pressure, excellent recovery potential, smaller carbon footprints, can use waste heat. However, high energy intensiveness, unwanted volatile compounds, high capital and operational cost, high pre-treatment cost are few drawbacks associated with it (Chin et al. 2020; Naidu et al. 2020).

4.4.4.6 Liquid Membrane

This membrane separation process is used as a substitute of solvent extraction process. The two liquid phases, feed and permeate solutions, are separated by another liquid phase membrane. The membrane comprises of an organic liquid phase and is immiscible with both other solutions. The extraction and stripping occur in single step. The process is carried out by supported liquid membrane (SLM), emulsion liquid membrane (ELM), bulk liquid membrane (BLM) and polymer inclusion membrane (PIM). SLM is the most adopted of all these techniques. In SLM a microporous substrate is used to support the thin liquid phase to immobilized within membrane wall. In 1986 SLM has been employed for metal ion transport by Babcock et al. ELM, on the other hand, is a three-phase dispersion and includes internal phase, liquid membrane phase and external phase. Liquid phase of ELM comprises of surfactant and extractant are recycled and used in generating emulsion, however, internal phase is purified for recovering precious metals (Babcock et al. 1986; Fane et al. 1992; Othman et al. 2004; Rahmati et al. 2019; Noah et al. 2020). The recovery of heavy metals especially precious metals was started during 1990s. Recovery of Pd, Pt, Cu, Au have been studied using the SLM techniques. Au recovery was also studied with the help of ELM using biodegradable emulsifier. A highly selective ELM has been reported to recover Pd from electroplating industry discharge. ELM has also been employed to recover Ag from diluted aqueous solution. Nano-ELM are also being recently utilized for Ag metal recovery. Some heavy metals have also been reported to be recovered using ELM (Fu et al. 1997; Weerawat et al. 2003; Kargari et al. 2004a, b, 2006a, b; Nabieyan et al. 2007; Mohammadi et al. 2008; Reddy et al. 2013; Noah et al. 2016; Laki and Kargari 2016; Masry et al. 2021).

Liquid membranes are highly selective and are quite efficient in recovery of metals from wastewater. Specific molecular recognition can be achieved using this process. However, as it is an emerging technique, there are few industrial application-based challenges also related to equipment and its installation. Stability of emulsion and failure of membrane in EMP technique. Membrane leakage and rupturing can be eliminated to some extent by improving elasticity by the use of bifunctional surfactants. In SLM technique loss of solvent occurs and it comes out through supporting membrane pores because of its dissolution and large pressure gradient (Babcock et al. 1986; Othman et al. 2004; Rahmati et al. 2019; Noah et al. 2020).

4.4.5 Adsorption and Desorption for Metal Recovery

Amongst the hydrometallurgical techniques utilized to extract and recover heavy metals including precious metals from wastewater as well as leaching solutions, solid phase extraction (SPE) or Liquid–solid extraction is advantageous over other techniques in many terms specially over liquid–liquid extraction. The technique is used to isolate and then separate analytes from liquid phase. SPE utilizes adsorbents, which are solid materials having various functional groups present at its surface. Extraction of desired or targeted metals from liquid phase occurs when the metal adheres or binds the functional groups at adsorbent surface. Adsorbents may have specific functional groups that may be used to bond and thus remove specific desired chemicals. Thus, there is selective extraction, identification, and quantitation of specific chemicals. Depending upon the objective of extraction, the immobilized analyte is recovered from adsorbent surface. The need of recovering and regenerating the analyte is depended on the many factors as solute and adsorbent cost, recovery cost and the hazardous effects of the solute that it may cause to the environment if it is disposed-off in aqueous environment or atmosphere. Thus, the recovery of adsorbed solute by stripping adsorbent with the help of eluant and then subsequent regeneration and reusing the adsorbent are important aspects of adsorption process from the environment and economic point of view (Urasa et al. 1997; Neyestani et al. 2017).

Adsorption is commonly utilized to treat wastewater to remove and recover metal ions because of several advantages which involves simple operation, highly removal efficiency, faster rate, less consumption of chemicals, economic as well as environment friendly. Also, by carefully choosing adsorbents the possibility of complete metal recovery and high enrichment can be achieved. The metal ions are finally recovered by desorbing it from adsorbent surface, thus regenerating the adsorbent. Various methods are available for the regeneration of adsorbent like thermal, electrochemical, ultrasonic and chemical methods. The chemical regenerating agents may be acids, alkalis, chelating agents or simply water. Many researchers have studied adsorption–desorption of metal ions from wastewater samples for several cycles (Kulkarni and Kaware 2014; Lata et al. 2015).

The complex process through which metal ions interact with the adsorbent is governed by several mechanisms like chemisorption, physisorption (adsorption via physical forces like intermolecular forces). Also, complexation, ion exchange, chelation and diffusion through adsorbent surface are also involved (Basso et al. 2002; Qaiser et al. 2007). Adsorption–desorption has many advantages as it is economic as compared to other techniques, has high metal binding capacities, potential regeneration capacity, sludge free operation, high efficiency of removal (Fu and Wang 2011; Kulkarni and Kaware 2014).

Adsorbents all together can be categorised into: carbon-based adsorbents, chitosan-based adsorbents, mineral adsorbents, nanoadsorbents, magnetic sorbents, biosorbents, metal–organic framework adsorbents (Qasem et al. 2021). Various adsorbents which have been tested and employed in metal removal and recovery from various sources of wastewater include activated carbon, biosorbents and other low-cost adsorbents like industrial and agricultural by-products and wastes, nanoadsorbents including carbon nanotubes, chitosan derived biopolymers etc. (Li et al. 2003; Bhatnagar and Sillanpää 2009; Sousa et al. 2009; Machado et al. 2010; Khorasgani 2013).

A novel adsorption technique which is tested lately is magnetic solid phase extraction (MSPE). During MSPE magnetic adsorbent is added to the aqueous sample containing targeted metal ions. When metal ions get adsorbed on magnetic adsorbent surface an external magnetic field is applied to collect t adsorbent containing metal ions. Metal ions then are eluted from the magnetic adsorbent and recovered using suitable eluant and the treated water is reused. Use of magnetic adsorbent offers advantages as having simple sample pre-treatment, separation of metal ions is fast and simple, high selectivity of magnetic adsorbents towards various environmental chemicals and biochemicals even in presence of suspended solids, repelling of impurities by magnetic adsorbent hindering adsorption of targeted metal ions (Ghanei-Motlagh et al. 2016).

Amongst many adsorbents activated carbon has been widely utilized to study the adsorption of heavy metal ions. It is highly efficient for a range of water pollutants in comparison to some of the chemical as well as physical techniques. It is simple to use and has fast adsorption kinetics. Also, adsorption using activated carbon, activated alumina, silica gel, heamatite, feldspar, limestone are associated with high cost, low adsorption capacity, loss during regeneration which makes it practically not possible to use in developing and poor countries. Thus, desorption needs to be carried out with the help of suitable regenerants which makes this process economic and eco-friendly. Biosorption, is a technique where biological materials are utilized for adsorptive removal of metal ions. It offers advantage over using activated carbon and other chemical adsorbents; however, it is also dependant on the continuous and easy supply of biosorbents. Desorption during treatment of wastewater using adsorption technique become a necessary step to regenerate the adsorbent and recovering the heavy metal ions from adsorbents, and thus making the whole process economic and eco-friendly. A successful desorption requires a good regenerant and that should be properly selected. Selection of regenerant depends on the type of the adsorbent used, the mechanism of adsorption, and also that the regenerant should not damage the biosorbents or biomass and it should be economic and environment friendly too (Kulkarni and Kaware 2014; Lata et al. 2015).

There are many studies on removing and recovering heavy metals from aqueous environment. Literature reports desorption has been carried out with the help of distilled and deionized water, various acids like hydrochloric acid, nitric acid, sulfuric acid, acetic acid etc., alkalis like sodium/potassium hydroxide, sodium/potassium carbonate, sodium bicarbonate etc., salts like sodium/potassium/calcium chloride, ammonium sulphate, ammonium/potassium nitrate etc., different chelating agents, buffer solutions (like bicarbonates, phosphates, tris etc.), mixture of various chemicals like H_2O_2 in HNO_3 solution. The regenerating eluants are used in different concentrations to desorb and recover maximum metal ions from adsorbents. Also, it has been reported in various studies that desorption, regeneration and reuse of adsorbents has been done for more than one cycle achieving maximum metal recovery without damaging the properties of adsorbents (Manju et al. 1998; Bajpai and Chaudhari 1999; Ranjan et al. 2009; Das 2010; Koon et al. 2011; Li et al. 2013; Kulkarni and Kaware 2014; Lata et al. 2015; Aghaei et al. 2017; Takaluoma et al. 2018; Chang et al. 2021; Grad et al. 2021a, b).

4.4.6 Electrochemical Separation Methods for Metal Recovery

Recently, remarkable attention has been paid for recovering metals through electrochemical separation method in order to attain sustainability and enable circular economy. In electrochemical process, the electric potential is applied to the charged ionic species to transport it from one medium to the other. From wastewater contaminated with positively charged metal ions, the metal recovery is done by applying electric potential in an electrolytic solution thus plating out the metal on an electronegative cathode. Electric potential is created by performing oxidation at anode and reduction at cathode and by varying the potential selective plating out of metal can be achieved. The redox reaction leads to the purification of water though metal removal. This method helps in removing and recovering metal ions from even very low concentration of wastewater, thus sometimes reducing metal concentration below the permissible guidelines of government (Naja and Volesky 2009).

Currently, electrodeposition (electrowinning), electrodialysis, electrocoagulation, bioelectrochemical are the most adopted electrochemical methods for recovering heavy metals including precious and noble metals from wastewater. The problems associated with dilute electroplating are decreased rate of mass transfer with decrease in concentration gradient which results in lower plating out of metal thus decreasing process efficiency. Moreover, hydrogen gas formed at cathode creates a barrier in plating out metals. Both the issues are solved by maintaining large cathodic area, i.e., flow-through process, and by rising the turbulence in solution, i.e., flow-by process. Example of flow-through processes are mesh cathode, packed bed cathode and fluidised bed cathode, whereas flow-by processes include forced flow cathode and rotating cathode. For better performance of metal recovery the electrochemical processes are combined with other techniques as ion-exchange, precipitation etc.

Over the other methods and process used for metal recovery electrochemical approaches have several advantages like: uniform metal deposition, high purity, simple and well controlled, faster kinetics achieving high purity. It avoids the use of highly toxic chemicals, avoids large swings in pH and heat, there is no generation of secondary waste. Moreover, the design and features of this process are versatile, modular, reversible, and scalable making it a highly economic and efficient approach. Disadvantages of electrochemical process includes high initial as well as operational cost because of the requirement of large amount of energy in the form of electricity (Fu and Wang 2011; Azmi et al. 2017).

4.4.6.1 Electrodialysis

Electrodialysis, a very effective process used for concentrating heavy metals present in wastewater while purifying the water. An ion selective membrane separates the contaminated water or metal containing leachate, and only cations (metal ions) are allowed to permeate through the membrane on application of an electric potential. Cations thus migrate towards cathode while anions migrate towards anode. Metal ions are thus removed from the feed stream side i.e., diluate and concentrated on the receiving stream side i.e., concentrate. Thus, on the feed side almost purified water is obtained which can be reused. The concentrates solution containing metal ions is then returned to the electroplating cell. Traditional electrodialysis had certain limitations of high cost, strength and efficiency of cation selective membrane. In present days, selectivity of the membrane towards metal extraction has become the most attractive aspect of the process. However, relatively high-power consumption and high removal limits are few drawbacks which makes the industrial application of this process rare.

4.4.6.2 Electrowinning

It is one of the most traditional and environment friendly electrochemical metal recovery techniques in which the soluble and mobile metals ions are immobilized as metallic coatings with the help of electrochemical reactions. This method has been reported to be in use for metal recovery since 1970s and electroplating of rather electropositive metals like Cu and Ag was studied. The fundamental process of electrowinning is electrodeposition in which cathodic reduction takes place on applying a direct current between anode and cathode allowing targeted metal ions to be reduced and extracted in its metallic form at the cathode.

$$M_e^{n+}(soluble) + me^- \rightarrow M_e \tag{4.15}$$

A competing cathode reaction in aqueous solution occurs with evolution of hydrogen:

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \tag{4.16}$$

The turbulence created with production of hydrogen gas in the system, facilitates in enhancing the mixing. Bubbles of hydrogen gas also serves as a means of transferring insoluble suspended particles to the surface of wastewater, which forms a floating layer on the surface. During this process of electrolysis, where the metal ions are reduced at cathode, electrochemical oxidation occurs at anode which usually comprises of oxygen evolution. Under acidic conditions the anodic reaction occurs as follows:

$$2H_2O \rightarrow O_2 + 4H^+ \tag{4.17}$$

In basic medium, however, the following anodic reaction occurs:

$$4OH^- \rightarrow O_2 + H_2O + 4e^- \tag{4.18}$$

Various electrochemical parameters which govern the process of electrowinning are applied voltage, current and current density. Other parameters are concentration, mass transfer, current efficiency, overpotential, space–time yield. In presence of competing metal ions, the metallic species with high standard electrode potential is reduced and deposited on cathode.

Electrowinning is applied following a series of purification and concentration steps to allow efficient application in terms of mass transfer rate. By controlling the applied potential, the process can be made selective. A form of electrowinning is membrane electrowinning. It can also be used in conjunction to other hydrometallurgical and pyrometallurgical methods for the recovery of desired metal ions. Electrodeposition is carried out only using a simple system consisting of an electroplating bath and inert anode and cathode. Electrodeposition has been carried out for the recovery of Cu achieving approx. 93% extraction, for Cd approx. 95% recovery was achieved, and for Co, Ni, Mn, Ag (Armstrong et al. 1996; Chen and Lim 2005; Martins et al. 2012; Jin et al. 2017).

Various associated advantages of electrowinning are a well-controlled process with excellent selectivity, requirement of lesser amount of chemicals and generation of almost no sludge. The limitations of this technique, however, are high initial as well as operational cost because of high usage of electricity and maintenance or replacement of electrode and labour. At lower wastewater concentrations electrowinning becomes very expensive because of application of high ohmic resistance.

4.4.6.3 Electrocoagulation

Electrocoagulation, one of the most considered processes employed for metal recovery. It involves destabilization of suspended and dissolved particles when current is passed through the medium. In situ coagulants are generated by oxidation at sacrificial anode, which is generally made of aluminium or iron. Selection of aluminium and iron as anode is done because of its easy availability and low cost. When current is passed the oxidation occurs at anode and generates Al^{3+} or Fe^{2+} cations continuously, and water is converted to oxygen and H^+ cations, however, at cathode water converts to hydrogen gas and OH^- anions. These hydroxide ions hydrolyse the Al^{3+} or Fe^{2+} cations immediately and spontaneously forming iron or aluminium hydroxides, which acts like coagulants. A sequence of following reactions takes place (taking iron as anode):

At anode:

$$4\,\mathrm{Fe}(s) \rightarrow 4\,\mathrm{Fe}^{2+}(\mathrm{aq}) + 8\mathrm{e}^-(\mathrm{aq}) \tag{4.19}$$

$$4\,\mathrm{Fe}^{2+}(\mathrm{aq}) + 10\,\mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow 4\,\mathrm{Fe(OH)_3}(s) + 8\,\mathrm{H}^+(\mathrm{aq}) \tag{4.20}$$

At cathode:

$$8\,\mathrm{H}^+(\mathrm{aq}) + 8\mathrm{e}^- \rightarrow 4\,\mathrm{H_2}(g) \tag{4.21}$$

$$\text{Overall: } 4\,\mathrm{Fe}^{2+}(s) + 10\,\mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow 4\,\mathrm{Fe(OH)_3}(s) + 4\,\mathrm{H_2}(g) \tag{4.22}$$

The formation of hydrogen assists in physically separating the flocculated metal ions by floating them to the surface of water. Formation of various hydroxide species, by combinations of the metal cations generated at anode and hydroxide anions generated at cathode depends upon the pH of the solution. The hydroxides coagulate and finally precipitate at the bottom of the system. The precipitated sludge is dissolved in leaching solution to dissolve the metal ions and recover it with either electrowinning or other processes.

The whole process of electrocoagulation depends upon the material of electrode and its area, solution pH, current density and treatment time, presence of contaminants, and distance between the electrodes. The advantages of this process are its potential of treatment of oily water, in-situ generation of coagulants, easy removal of flocs which are large and stable, formation of non-toxic and easily removable sludge, hydrogen gas assists in removal of flocs, complete automation of process is possible, operation is simple, no chemicals are required, purified water is colourless, odourless. The drawbacks are high possibility of cathode passivity resulting in low efficiency, high usage of energy, as anode is sacrificial its periodic replacement is required, generation of harmful secondary pollutants (Naja and Volesky 2009; Fu and Wang 2011; Azmi et al. 2017).

4.4.6.4 Bioelectrochemical

Bioelectrochemical systems is a novel and emerging technology used to recover various resources including energy. In this system microbes facilitate the conversion of chemical energy to electrical energy and chemicals. Chemical energy is produced by biodegradation of organic materials. This method provides a flexible platform for both oxidation and reduction reactions. It consists of varied configurations of an anode, a cathode and a separator, which is optional. Biodegradation of organic compounds present in wastewater usually occurs in the anodic chamber by microorganisms, generating electron flow from anode to cathode. At the cathodic chamber the electrons are either utilized directly to produce electricity (microbial fuel cell), or are taken up for the reduction of water, other organic chemicals (microbial electrolysis cell or microbial electrosynthesis), oxidized chemicals like CO_2 and metal ions. Thus metals are usually recovered at cathode by reduction. The metals can be selectively recovered by finely tuning the electric potential at which reduction or oxidation takes place. The electroactive biofilm, at carbon anodes, generally comprises of a mixed culture of exoelectrogenic bacteria inoculated from activated sludge. Most of the reports have mentioned the use of acetate as organic matter to be biodegraded at anode and donate electron for complementing reduction reaction at cathode (Heijne et al. 2010; Choi and Cui 2012). Uranium (U) was recovered in 2005 by bioelectrochemical method, followed by recovery of other metals like Fe, Cd, Zn, Ag, Cu and Pb from dilute solution. The method has also been used for the leaching Co(II) from $LiCoO_2$ particles, and recovery of Co, Cr, Cu, Hg, Ag, Se, and Cd from water (Gregory and Lovley 2005; Modin et al. 2012).

Bioelectrochemical metal reduction and thus recovery mainly adopts four pathways. The first pathway includes metals like Au(III), V(V), Cr(VI), Ag(I), Cu(II), Fe(III), and Hg(II), etc., having higher potential than the anodic. These metals are directly used as electron acceptor and reduced at abiotic cathode. The reduction is thermodynamically favoured and occurs in absence of any external energy source. Second pathway includes metals having reduction potential lower than anode potential (e.g., Ni(II), Pb(II), Cd(II), and Zn(II), etc.) and requires an external energy source for forcibly transferring anodic electrons to abiotic cathode. Third pathway is the reduction of metal oxides at cathode by microbes. Reduction of Cr(VI) at biocathode is reported to be assisted by microbial metabolism. Fourth pathway includes both second and third pathways and is the reduction of metal by microbes at controlled potential. Cr(VI) is the only tested and reported example for third and fourth pathways (Wang et al. 2008; Choi and Cui 2012).

The technology is proven to be a sustainable one for it generates electricity as well as treats sewage discharged by industries. It employs microbes for a clean and efficient fuel along with recovery of high value chemicals. Electrodes used are infinite donors and acceptors of electrons, requires minimum external source of energy while producing electricity for on-site usages. The method is advantageous in terms of saving aeration energy and sludge disposal. It is used for treatment of lower concentration wastewater (McCarty et al. 2011; Huggins et al. 2013; Zhang and He 2013).

4.4.7 Photocatalysis for Metal Recovery

Photocatalysis is a chemical process which requires combined action of both light and a photocatalyst. Commonly used photocatalysts are transition metal oxides or semiconductors like TiO_2, ZnO, ZnS, WO_3, WS_2, CdS etc., as these have no energy levels for the promotion of recombination of photogenerated electrons or holes in their structure. For metal recovery the photogenerated electrons by low energy ultraviolet light with semiconductor catalyst are utilized to reduce metal ions present in water. Generally, photocatalytic process involves these steps: photogeneration and separation of charge carriers under low energy ultraviolet light and then diffusion and reduce on the photocatalyst surface.

$$\text{Semiconductor} + h\nu \rightarrow e^- + h^+ \tag{4.23}$$

$$M^{n+} + e^- \rightarrow M \tag{4.24}$$

$$D + h^+ \rightarrow D^+ \tag{4.25}$$

where, M^{n+} represents metal ions which act as electron acceptor, D is the donor species. Heavy metals including precious metals, accepts electrons and get reduced to their metal crystallites forming precipitates from where it is finally recovered (Avid 2019; Zhang et al. 2019; Li et al. 2021).

Factors affecting process efficiency are pH of solution, relative reduction potential of the dissolved metal and the semiconductor, presence of scavengers of electron and/or holes, intensity of light, type and loading of semiconductors (Avid 2019; Zhang et al. 2019; Li et al. 2021). The process is recently being employed to recover heavy metals including precious metals from different wastewaters and leachates (Istiroyah et al. 2021; Chen et al. 2021a, b; Kunthakudee et al. 2022).

It is reported to be an easy and low in cost process having high efficiency employed for recovery of metals. The catalyst used are not toxic and produce less secondary harmful pollutants. Metal recovery and removal of organic pollutants occur simultaneously. Drawbacks include long duration of time, high capital cost and limited applications (Avid 2019; Zhang et al. 2019; Li et al. 2021).

4.4.8 Hybrid Techniques for Metal Recovery

Efforts are made continuously to modify the available techniques to recover metallic resource from wastewater so as to make them more efficient, economic and eco-friendly. Recent efforts are also made to use the chemical and/or physical and biological methods in conjunction with each other, as chemical/physical processes are reported to have better efficiency and biological processes are environment friendly. The hybrid techniques have advantages of both chemical/physical and biological methods. Few hybrid techniques which are used are.

4.4.8.1 Microbial Fuel Cell and Microbial Electrolysis Cell

This technique involves biodegradation of organic matter by microbes. This generates electrons, which are utilized for reducing the metals at cathode and an electric current is produced. While in microbial electrolysis cell external source of electric potential is required to produce hydrogen or methane from organic chemicals and removal of metals. Recently these techniques is being used in hybrid for removal and then recovery of metals from water. It is affected by operating conditions like pH, temperature, initial metal concentration and voltage applied (Park et al. 2018; Li and Zhou 2019).

4.4.8.2 Electrocoagulation and Microfiltration

Clogging and fouling of membrane decreases its efficiency to separate the metal contaminants and hence, pre-treatment of the inlet wastewater is required. Amongst the many available techniques electrocoagulation is reported to be very effective. Its application reduces the changes in membrane caused by clogging and fouling by minimizing the dissolved organic substances, improving rejection efficiency. Electrocoagulation can be combined with other metal recovery techniques like microfiltration and excellent performance has been reported. Iron base electrocoagulation combined with microfiltration has been found to increase the recovery efficiency by 98%, while combination of aluminium-based electrocoagulation with microfiltration reduced the membrane fouling by forming a cake of particles larger than those present in inlet wastewater (Mavrov et al. 2006; Chellam and Sari 2016; Garcia-Segura et al. 2017).

4.4.8.3 Adsorption and Microfiltration

Adsorption using activated carbon is utilized in conjunction with microfiltration to enhance the metal recovery efficiency. Efforts are made to enhance the size of smaller particles, which are not properly retained by microfiltration membrane, by adsorbing the particle on activated carbon. The particle thus becomes larger in size and thus retained and separated by membrane. For the purpose of adsorption both granular and powdered activated carbon can be used. Powdered activated carbon is having better adsorption efficiency than granular because of larger surface area (Guo et al. 2005; Ezugbe and Rathilal 2020).

4.5 Conclusion

Rapidly growing global population, urbanization and industrialization has resulted in generation of wastewater, leachates consisting of various water pollutants including heavy metals. Wastewaters contaminated with metal have short-and long-term human and environmental hazards even at lower concentrations. It thus becomes necessary to remove and then recover heavy metals in order to not only eliminate the environmental damages and health effects it may cause but also because of their economic potential value. The present chapter aimed at outlining the various aspects of the techniques, state-of-art knowledge and emerging trends and developments in recovering metal resources present in wastewater. The various conventional and advanced methods are categorized broadly into three categories as physical, chemical, and biological. There are many trending hybrid techniques as well. The factors which should be given importance in order to select the most appropriate and efficient metal recovery technique are operational simplicity, technical applicability, recovery efficiency, cost effectiveness and environment friendliness.

Literature review shows that the recovering metals from wastewater as well as leachates with the help of biological means and methods like biosorption and bioleaching are economic, effective and eco-friendly methods in recovering metals efficiently. It has also been reported that chemical modification and immobilization of these biological materials enhanced the efficiency of metal recovery. Thus, there is need to focus on novel economic methods of modification to enhance the efficiencies of microbes and other biological materials for removal and recovery of metals. Further, more research needs to be focused on finding novel eluant solvents for desorption and recovery of adsorbed metal ions on adsorbents.

Membrane filtration is also a promising technique of metal recovery from wastewaters. Amongst them, membrane distillation is advantageous over other membrane separation techniques like forward osmosis, reverse osmosis, that it shows high metal recovery efficiency, highly purified water for reuse, almost negligible operational pressure, and smaller footprints. However, it is reported to be energy intensive which has lowered its popularity for industrial application. Liquid membranes are an emerging membrane filtration technique which shows higher metal recovery efficiency, however, there are few challenges which needs the attention of researchers to enhance the practical applicability of liquid membranes. The challenges include leakage or damage of emulsion liquid membranes and stability of supporting porous material liquid.

In order to attain all the possible targets related to metal recovery from wastewater, like cost effectiveness, higher recovery efficiency, smaller footprints, much focus has been given in recent years to employ hybrid techniques i.e., using chemical or physical techniques in combination with biological techniques to gain the advantage of both methods. Thus, giving proper attention and understanding to all the aspects related to the practical applicability, understanding the advantages, drawbacks and challenges of metal recovery techniques can help in selecting the most appropriate technique for metal recovery and thus leading to achieve sustainability and other goals of circular economy including resource recovery from wastewater.

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Chapter 5
Heavy Metal Removal and Recovery: Sustainable and Efficient Approaches

Nalini Singh Chauhan and Abhay Punia

Abstract The production of municipal and industrial wastewaters and leachates, together with an increase in metal emissions, is one of the effects of the world's population growth. Metal-rich wastewaters have been shown to be harmful even at low concentrations, and they can harm the environment both abruptly and over time. Because of the potential economic worth of metal recovery from wastewaters as well as the environmental harm and health effects it might cause, this topic is becoming more and more important. Metals (such as Ag, Au, Pa etc.) are very important because of their numerous industrial uses and high market value and are also found in industrial wastes, effluents and water resources. This chapter will comprehensively and critically discuss various recovery methods used in terms of removal performance, operational circumstances, and advantages and disadvantages. This article will also discuss various biological materials that might be created and used, as well as other eco-friendly and sustainable methods, to remove and recover metals from wastewater.

Keywords Bioremediation · Green technologies · Wastewater management · Nanomaterials · Pollution control

5.1 Introduction

Industrialization has accelerated over the past century, increasing the need for reckless use of the world's resources and the global environmental crisis (Briffa et al. 2020). Unlike other pollutants visible in the environment, such as petroleum hydrocarbons and municipal solid waste, trace metals can accumulate to dangerous levels unnoticed. Metals with a density greater than water are referred to as heavy metals (Tchounwou et al. 2012). The most common forms of heavy metals in nature are sulphides, oxides, carbonates, and silicates. These organic materials are often water

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insoluble and only very gradually deteriorate through weathering, precipitation, and groundwater. Because of their non-biodegradable, poisonous nature and biomagnifications in food chains, metals represent a significant danger to marine ecosystems and services (Kaushik et al. 2009; Li et al. 2019). To stop these potentially harmful health effects, environmental regulations that restrict the amount of heavy metal ions in water are becoming more stringent (Fu and Wang 2011). Hazardous ions of heavy metals should be removed from wastewater to safeguard local communities and the environment. According to reports, heavy metals can have major negative consequences on a person's health, including kidney damage, bone abnormalities, neurological damage, skin cancer, skin blemishes, and lung cancer (Jaishankar et al. 2014; Liu and Corma 2018). It is crucial to eliminate these utilizing a variety of methods from sewage and water. Adsorption, ion exchange, chemical precipitation, and electrolytic recovery are a few methods for removal and recovery (Esmaeili et al. 2005). Among these, adsorption is seen as a promising alternative to conventional methods for the recovery of rare earth ions in low concentrations from secondary sources such as industrial effluents due to its convenience, low cost, high reliability and easy accessibility. However, for wastewater with very low REE concentrations, the utility of NM as adsorbents presents a viable technology due to their potentially high adsorption effectiveness (Kegl et al. 2020). Due to their technological limitations in reducing these oxidised metal ions, conventional methods like adsorption, chemical precipitation, and ion exchange are unable to accomplish substantial metal recovery despite the prevalence of metal-laden effluents. The use of biological methods to remove heavy metals from wastewater has increased significantly in recent years as they are considered to be more environmentally friendly, less expensive and less energy intensive (Das 2010). In recent years, the biological removal and recovery of metals from contaminated water utilising micro- or macro-organisms has gained significance. It has been demonstrated that a number of micro- and macroalgae can remove heavy metals from aquatic environments effectively, mostly because the extra electronegative charge on the algal cell wall enables significant interaction with metal ions (Kiran and Kaushik 2012). Today, a number of microbes have developed as replacements that can be genetically modified, grow more quickly, require less expensive handling, and are tolerant to various metals (García-García et al. 2016). Metal removal in microorganisms such as microalgae, cyanobacteria, bacteria, and fungi is mostly accomplished through biosorption on the cell wall, bioaccumulation in living tissue, adsorption to metalloproteins, or binding to the organic compounds of exopolysaccharides formed by microbes (Mona and Kaushik 2015). More work is being put into creating novel metals recovery techniques to make the procedure affordable and long-lasting (Wang and Ren 2014). In order to promote systems that are both economically viable and sustainable, the emphasis has recently switched increasingly toward energy-assisted wastewater treatment methods (Kaushik et al. 2011; Kaushik and Mona 2017; Reddy et al. 2019; Sharma et al. 2020).

5.1.1 Heavy Metal Pollution

Heavy metals are frequently released in wastewater by numerous industries. Surface treatment practices, leather tanning, textiles, paints, dyes and pigments, oil refining and processing industry, film manufacturing and also metal finishing pollute water with heavy metals like lead, zinc, chromium, copper, platinum, titanium, cadmium, nickel, silver and vanadium (Renu et al. 2017). This metal's toxicity has a significant impact on living organisms, resulting in permanent damage, life-threatening diseases, and chronic conditions in the pivotal body systems (Zhao et al. 2018). Heavy metal inputs into wastewater come from two different sources. The first category comprises man-made pathways such as urban runoff, sewage and industrial waste, while the second category includes natural pathways such as rainfall, excess sodium and soil erosion. The increase in various industries and urban populations, however, is the leading cause of all these pollutants. Heavy metals are currently classified as 35 elements, 23 of which are known to be the most toxic metals. The physiological function of heavy metals and the nature of the metal in the life history are among the factors that influence their toxicity (Hasanpour and Hatami 2020). Contrarily, the human body requires a limited quantity of chromium, zinc, and copper, but excessive amounts can cause poisoning. The widely known metals mercury, lead, arsenic, cadmium and arsenic all play a role in human poisoning. Sources, harmful effects, and standard human health concentrations of various heavy metals are summarized in Table 5.1.

5.1.2 Need for Recovery

Metals have long been linked to industrial development and higher living standards in contemporary society (Wernick and Themelis 1998). In recent decades, heavy metal pollution has increased dramatically (Naaz and Pandey 2010). Several industries, including mining, metallurgy, electronics, electroplating, and metal refining, release heavy metals into the ecosystem and because of their higher toxicity and tendency to accumulate in organisms, their removal and recovery is of crucial importance (Singh et al. 2023). Thus, it becomes absolutely essential to recover harmful and useful elements from industrial waste. The issue has two crucial components: protecting the environment against scattered harmful substances, in particular heavy metal compounds, and economics. Therefore, research is being done to create new or updated methods for separating metals, primarily from industrial waste byproducts (Chmielewski et al. 1997; Bosecker 2001; Verstraete 2002). Contrary to polymer plastics, metal's qualities can always be fully, if not always easily, recovered, independent of their chemical or physical structure. Nonetheless, the capability to economically recover metals after use depends greatly on how they are originally used in the economy and on their chemical reactivity. The success of secondary metals markets depends on the costs of recovering and processing metals embedded in

Table 5.1 Typical heavy metals existing in wastewater and their sources, in addition to the health issues caused by improper quantities and the permitted amounts in drinking water based on the world health organization (WHO) recommendations

Common heavy metal	Sources	Main organs and systems affected	Standard concentration (μg/dL)
Lead	Lead-based batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes, and plastic stabilizers	Bones, liver, kidneys, brain, lungs, spleen, immunological system, hematological system, cardiovascular system, and reproductive system	10
Arsenic	Electronics and glass production	Skin, lungs, brain, kidneys, metabolic and cardiovascular system, immunological system, and endocrine	10
Copper	Corroded plumbing systems, electronic and cables industry	Liver, brain, kidneys, cornea, gastrointestinal system, lungs, immunological system, and hematological system	2000
Zinc	Brass coating, rubber products, some cosmetics, and aerosol deodorants	Stomach cramps, skin irritations, vomiting, nausea and anemia	3000
Chromimum	Steel and pulp mills and tanneries	Skin, lungs, kidneys, liver, brain, pancreas, tastes, gastrointestinal system, and reproductive system	50
Cadmium	Batteries, paints, steel industry, plastic industries, metal refineries, and corroded galvanized pipes	Bones, liver, kidneys, lungs, testes, brain, immunological system, and cardiovascular system	3
Mercury	Electrolytic production of chlorine and caustic soda, runoff from landfills and agriculture, electrical appliances, Industrial and controlinstruments, laboratory apparatus, and refineries	Brain, lungs, kidneys, liver, immunologicalsystem, cardiovascular system, endocrine, and reproductive system	6
Nickel	Stainless steel and nickel alloy production	Lung, kidney, gastrointestinal distress, pulmonary fibrosis, and skin	70

Source Qasem et al. (2021)

abandoned buildings, discarded products and other waste streams and their relationship to primary metal prices. The various methods involved are discussed in the following sections.

5.2 Adsorption Based Separation

The adsorption mechanism is determined by the physico-chemical characteristics of the heavy metals and the adsorbent as well as the operating circumstances (i.e. temperature, amount of adsorbent, pH, adsorption time and initial concentration of metal ions). The usage of adsorption for precious metal separation as well as recovery has been discussed in a number of publications. For the separation, removal and recovery of precious metals, selective adsorption is an appealing technology. Low operating costs, high removal capacity, easy implementation, and easy treatment by regenerating the adsorbed heavy metal ions have all been reported for this method (Bolisetty et al. 2019). Various types of adsorbents such as carbon-based, mineral-based, magnetic-based and biosorbents have been developed for wastewater remediation, as discussed in the following sections.

5.2.1 Carbon-Based Adsorbents

Carbon-based nanoporous adsorbents, in particular activated carbons, carbon nanotubes, and graphene, are employed extensively in the removal of heavy metals due to their enormous surface area (500–1500 m^2/g) (Karnib et al. 2014). To improve heavy metal uptake, surface functional groups (such as carboxyl, phenyl, and lactone groups) can increase the charges on the surface of the carbon (Demiral et al. 2021). Nitrogenation, oxidation, and sulfurization are the most commonly used techniques to improve specific surface area, pore structure, adsorption capacity, thermal stability, and mechanical strength among the various modification methods as shown in Fig. 5.1 (Kumar et al. 2015). Surface modification decreases their surface area, increasing the amount of surface functional groups. The number of metal ions that can be retrieved and adsorbed is increased as a result (Marciniak et al. 2019).

Although multi-walled carbon nanotubes (MWCNTs) have sparked interest for their potential to remove heavy metals (Owalude and Tella 2016), they are extremely hydrophobic and prone to fast aggregation in aqueous environment because of strong van-der Waals interactions which reduces their adsorption ability. Furthermore, present surface modification techniques necessitate high temperatures/pressures, strong acids/bases, or intense oxidation/reduction reactions. Carbon-based adsorbents are expensive due to their complicated manufacturing process, making it challenging for them to be widely used in industries. As a result, researchers should propose new surface modification techniques that are low-cost and environmentally

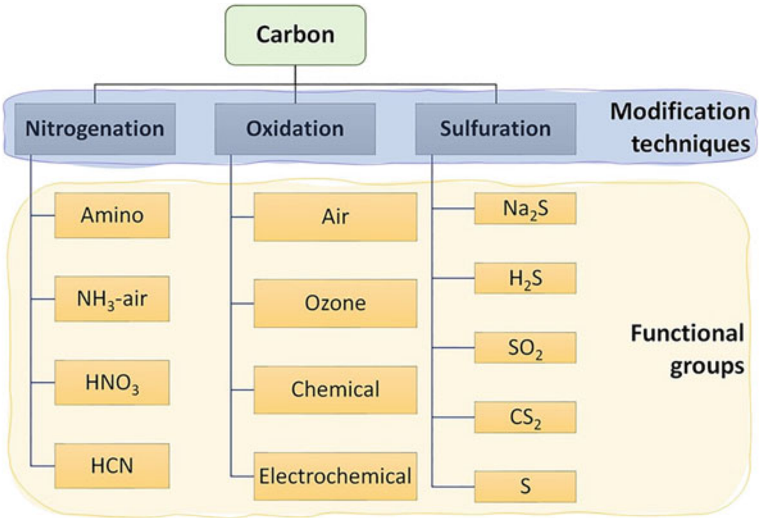

Fig. 5.1 Different modification strategies used to functionalize carbon with different functional groups for enhancing adsorption capacity and stability

friendly. Adsorption uptake is influenced by changes in adsorbent surface area, adsorbent dose, starting metal ion concentration, and contact time. But they mostly rely on adsorbent materials, which can occasionally be too costly (Duan et al. 2020). The cost of the adsorbent should then be taken into consideration while selecting the ones that are truly necessary.

5.2.2 Chitosan-Based Adsorbents

Because of its amino (NH_2) and hydroxyl (OH) groups, chitosan (CS) is a natural adsorption polymer that has an affinity for pollutants in wastewater (Ngah and Fatinathan 2008). Because of its poor mechanical stability and strength, regeneration is ineffective. CS is challenging to employ in powder or flake form due to its poor porosity, small surface area, resistance to mass transfer, and high crystallinity (Upadhyay et al. 2021). As a result, suggestions for structural and chemical alterations to get around these limitations have been made. By forming bridges between polymer chains and functional groups, the cross-linking chemical modification strengthens the CS. However, this strategy reduces adoption (Vakili et al. 2018). Grafting is a chemical alteration method in which functional groups are covalently attached to the backbone of CS, resulting in a significant expansion of adsorption process (Mohammadzadeh Pakdel and Peighambardoust 2018). It has also been suggested that the adsorption rate, mechanical properties and thermal properties of CS can be increased by integrating it with other adsorption materials (Refaat Alawady et al.

2020). Adsorbents with high selectivity for target metal ions have been created using the ion imprinting technique (Kazemi et al. 2017). The main factor influencing CS absorption is protonation or non-protonation of amine and phosphorus groups, which alter the pH of the effluent. Chitosan based adsorbents has limited reusability without the modifications. Strong binding, low chemical stability, low mechanical capability, insufficient desorption, decrease in absence of adsorption sites and efficient adsorbate-adsorbent association could all be factors contributing to this behaviour (Liu et al. 2012). To improve the reusability of CS, modifications and alternative regeneration techniques should be suggested.

5.2.3 *Mineral Adsorbents*

Mineral adsorbents such as zeolite, silica, and clay are thought to be suitable options for affordable purification of water (Li et al. 2017). Clay has a high capacity for cation exchange, selectivity for cation exchange, surface hydrophilicity, expansion capacity and surface electronegativity (Zhang et al. 2020). Additionally, acid washing, thermal processing, and column storage may improve pore size, volume, and particular surface area, which would significantly boost adsorption ability (Zhang et al. 2020). The pH level, temperature, adsorption time, and adsorbent dose are all significant elements in the adsorption mechanism in addition to the previously mentioned parameters. The effectiveness of adsorption removal increases as the pH increases and the starting concentration decreases (Alshameri et al. 2019). However, the removal efficiency may decline after a few cycles (Hao et al. 2016). Numerous modification techniques, including calcination and impregnation, have been suggested to improve the removing effectiveness of these adsorbents (Hao et al. 2016). But these modifications also add new chemical agents to the surroundings and raise the expense of the procedure. By grafting functional groups, it is possible to create ecologically responsible and multipurpose adsorbents that are ideal for treating different kinds of wastewater. New low-cost, increased adsorbents based on one-dimensional clay and two-dimensional nanosheets of nanotubes may be created.

5.2.4 *Magnetic Adsorbents*

Magnetic adsorbents are a type of material that contains iron particles (Li et al. 2019). Carbon, CS, polymers, starch, or biomass could be used as the starting ingredient. The magnetic field, the surface charge, and the characteristics of the redox activity all influence the adsorption process. They showed reusability, relatively high charge, cheap cost, and ease of synthesis. Numerous magnetic adsorbents have been proposed, including magnetite (Fe_3O_4), zero-valent iron nanoparticles (ZVI-NPs), iron oxides (hematite, maghemite, and spinel ferrites), and zero-valent iron nanoparticles (ZVI-NPs). The surface form and magnetic properties of the adsorbent have an impact on the sorption mechanism and dynamics. The starting pollutant dosage, effluent temperature, adsorbent concentration, irradiation time, and pH levels all have an impact on an adsorbent's capacity (Hua et al. 2012). Iron particles in the adsorbent are extremely effective at removing metal ions from wastewater (Behbahani et al. 2020). Coating Fe_3O_4 particles to remove heavy metal ions has been the subject of some research. The most often employed methods for coating include co-precipitation, high-gravity technology, and grafting (Liu et al. 2020a, b, c). The transplantation procedure has been deemed the best option because it is both versatile and simple. However, it is highly dependent on the quantity of active functional groups and the active hydroxyl on the outside of magnetite particles. The insufficient cycle stability of the produced adsorbents is a hindrance to their commercialization.

5.2.5 Biosorbents

The use of biosorbents in precious metal recovery was also studied for economic reasons and in pursuit of more ecologically friendly sorbents. The biosorption process is accelerated by the presence of several functional groups such as carboxyl, amino, hydroxyl, phosphate, thiol, etc. on the surface (Costa et al. 2021). Electrostatic interaction, aggregation, complexation/coordination, microprecipitation, ion exchange, reduction, and oxidation are some of the ways contaminants interact with the surface of the biosorbent (Abdel Maksoud et al. 2020). The surface charge density of the biosorbent and the ionization of functional groups on the biosorbent surface are affected by the pH of the solution (Ali et al. 2019). When the pH is low, cations seem to be almost persistent and can adhere to the surface of the biosorbent. However, as the pH rises, the solubility of metal cations decreases, increasing the likelihood of precipitation. Due to reduced solution viscosity, Gibbs free energy reduction, and bond cleavage, biosorbent capacity may rise at higher temperatures. These factors increase the frequency of collisions between biosorbent and metal ions and strengthen the biosorbent's active sites, resulting in increased affinity (Abdel Maksoud et al. 2020). Rising temperatures, on the other hand, may reduce the binding force between the biosorbent and contaminants, lowering the biosorbent's sorption capability. It has been discovered that as the mixing agitation speed is increased, the removal efficiency improves (Gupta et al. 2013).

5.2.5.1 Common Biosorbents

Biomasses can be split into two categories: dead and alive. Long-term biosorption-desorption cycles can be used with the dead biomasses. They use simpler mechanisms in the process, and their growth is unrestricted by the environment. Most dead biomass, on the other hand, has a poor mechanical strength and is in the form of a powder with a very tiny particle size. As a result of this phenomenon, significant biosorbent is lost during recovery, and the spent biosorbent is difficult to separate from the treated solution (Baysal et al. 2009; Michalak et al. 2013). Despite these drawbacks, dead biomass has been shown to be more effective than live biomass in terms of metal recovery (Park et al. 2010). Numerous factors, such as the availability and affordability of biosorbents, influence biosorption's industrial usefulness (Won et al. 2014). Although biosorbents are often thought to be low-cost solid sorbents, the expenses of their manufacturing and pre-treatment cannot be overlooked. All biosorbents can be split into two categories in theory: inexpensive and expensive (Fig. 5.2 Source; Ghomi 2020). Fungi, bacteria, and waste biomass are examples of living biomaterials that are considered low-cost. On the other hand, the use of specific culture media and treatment methods increases the overall cost of adsorbent material products. Typically, biosorbent manufacturing method involves three low-cost steps: (i) providing raw biosorbent (for example, algae should just be obtained from offshore and coastal regions, chitosan should be extracted from shells of crustaceans, etc.); (ii) pretreatment of biosorbents (washing, classification, purification, and modification of biosorbents); and (iii) analysing the biosorbent manufactured on fungi and yeasts, two different kinds of microorganisms (Senthil Kumar et al. 2018).

Fungi and Algae

For precious metal extraction, a variety of fungal structures can be utilized, ranging from unicellular yeasts to developed complexes (such as mycelial and polymorphic fungi). The most significant advantages of fungi are their apathogenic nature, excellent binding ability, great selectivity (Kotrba 2011; Bindschedler et al. 2017). For the

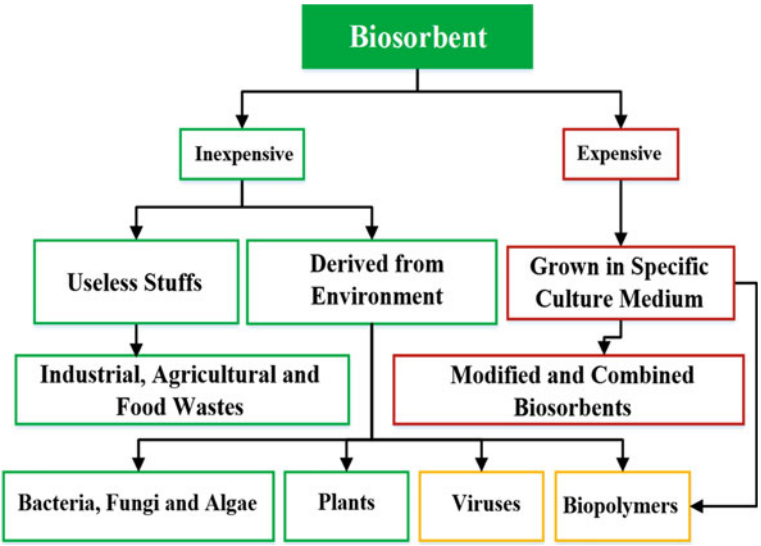

Fig. 5.2 Classification of biosorbents on the base of cost

majority of the recognized fungal sorbents, such biomasses also have the advantage of being a quick-growing, affordable, and straightforward growing medium in dim environments. Numerous fungi (such as *Aspergillus niger*, *Saccharomyces cerevisiae*, and others) are widely available in industrial, food and fermentation effluents, making them reasonably inexpensive. In recent years, such unique characteristics of macro (such *Pleurotus platypus* and *Clonostachys rosea*) and micro (like *Saccharomyces cerevisiae* and *Aspergillus niger*) fungi have piqued attention for usage in metal biosorption from wastewater (Das 2010; Nora and Mahmoud 2015; Cecchi et al. 2017). Algae, unlike bacteria and fungus, have a wide range of shapes and sizes. They require certain circumstances, like enough light, for proper growth and reproduction. Green algae (Bakatula et al. 2014), brown algae (Vijayaraghavan et al. 2011), and red algae (Ju et al. 2016) have all been utilized as biosorbents, as have diatoms (*Bacillariophyceae*) (Janani and Kumar 2018) and Dinoflagellates (Lage et al. 2018). Algae biosorbents have a high capacity for sorption, do not produce toxins during photosynthesis, and do not require large quantities of nutrients (Schwartz and Fritsch 1965). Another essential characteristic of algae is their biocompatibility, which allows them to produce ecologically friendly chemicals and by-products during biosorption (De La Noue and Pauw 1988; Ebrahimi et al. 2016). However, low selectivity and the difficulty of separating sorbed metals from metal-loaded cells are some of the drawbacks (Shen et al. 2017). Despite their superior qualities to bacteria, the number of published studies on noble metal biosorption by fungi and algae appears to be limited. The varying sorption capacities of fungal, bacterial, and algal species toward various metal ions are related to their various features, such as functional groups, cell walls, metabolites, and so on.

Bacteria

Milanowski et al. (2017) investigated the silver biosorption capacity of numerous*Lactococcus* bacteria species (including *L. casei* and *L. lactis*). The primary process underlying gold ion biosorption was discovered to be reduction in *Shewanella haliotis* (Zhu et al. 2016). Hydrogen and Sulphur containing molecules in *S. putrefaciens* and *S. oneidensi* species, and –H_2 and sodium lactate-containing molecules in *S. haliotis* species, are capable of donating to reduce Au(III) to Au(0) for each sorbent. Depending on the type of the electron donors, different sorption capacities will be produced when reduction is the primary mechanism of metal ion biosorption. Another key issue connected to sorbent type that affects overall performance is the capability of metallic ions to permeate into the cell. The outer layers of *L. lactis* were discovered to be thicker in comparison to*L. casei* before they were employed for biosorption in TEM pictures. The cell walls of *L. casei* bacteria thickened after exposure to silver solution, but the walls of *L. lactis* bacteria deteriorated. One of the reasons for *L. casei's* increased silver biosorption capacity has been hypothesized to be its resilience to cellular breakdown. Additionally, *L. casei* and *L. lactis'* respective amide (II) and amide (III) concentrations were crucial for the biosorption of Ag (Milanowski et al. 2017). Other research examining the gold ion biosorption capacities of three bacterial species, *Shewanella putrefaciens* CN32 (Varia et al. 2014), *Shewanella oneidensi* (Corte et al. 2011) and *Shewanella haliotis* (De Corte et al. 2011) reported, reduction to be the main mechanism of biosorption. When reduction is the primary method of metal ion biosorption, variable sorption capacities would be obtained depending on the type of electron donors. Another crucial element connected to sorbent type that has an impact on effectiveness is the capacity of metal ions to permeate into the cell. Studies on the sorption of palladium by *Bacillus benzeovorans* and *Bacillus wiedmannii* MSM (Omajali et al. 2015) revealed that only *Bacillus benzeovorans* offers favourable conditions for subcellular sorption, amidst both bacteria's capacity to form palladium nanoparticles on the exterior of biosorbent. Due to its ability to bioaccumulate Pd and two different types of electron donor groups (hydrogen and formate) that can reduce metal ions to nanoparticles, *Bacillus benzeovorans* demonstrated improved overall performance in the removal of palladium.

Viruses

Viruses are regarded potent weapons in nanotechnology, and they are used in a variety of industries ranging from agriculture to medical due to their widespread availability and small particle size (Chaudhary et al. 2023). Virus particles typically contain nucleic acid and capsid (envelope) proteins in different proportions. Each monomer of a coat protein is made up of amino acids, the majority of which have a positive surface charge, making them ideal for the sorption of complexes made up of negatively charged metal ions. One of the remarkable qualities of viruses like bacteriophage is their ability to produce enormous amounts of food quickly and safely amid calm circumstances in the presence of essential nutrients. Moreover, phages are particularly stable in acidic and alkaline environments, as well as in organic solvents, demonstrating their strong resistance to these conditions (Jończyk et al. 2011). It's worth noting that viruses could be employed to make battery electrodes, nanowires, nanocircuits and semiconducting materials because of their nanoparticle size and metal ion biosorption capacity. Tobacco mosaic virus (TMV), for example, is a well-known plant virus that may spread to a variety of plant hosts. TMV has a high physical stability because to the strong interactions between nucleic acids and envelope proteins (Farzadfar et al. 2002). The biosorption ability of TMV towards various metals, such as *B. palladium*, was investigated, and it was discovered that adding cysteine to the coat protein of the wild-type isolate considerably boosted the Pd sorption capacity. This could be because the addition of cysteine causes the creation of sulfhydryl groups, which leads to the development of strong interactions with metal ions (Lim et al. 2010). Another example is filamentous phage M13 particles (fp). According to studies, this phage has a maximum gold sorption capacity of 571 mg/g (2.8990 mmol/g). This larger capacity can be due to the phage's nanosized particles, which give it a large surface area to interact with the gold ions. Corresponding to eggshell in terms of gold adsorption efficiency and much superior to

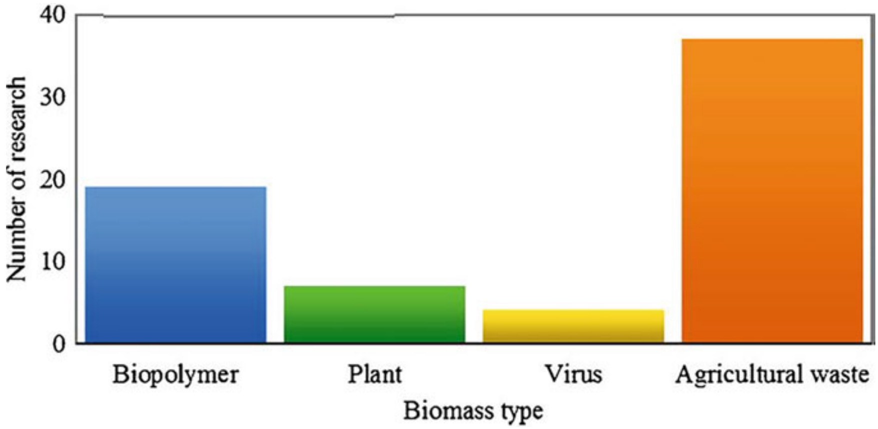

Fig. 5.3 Accumulation and formation of protruding and nail-shaped nanoparticles around modified and spherical particles of the phage (*Source* Ober 2018)

commercial activated carbon (Norit GF-40) and Amberlite XAD-7HP (Setyawati et al. 2014). According to studies, rearranging the virus's structure from filamentous to spherical particles and using some physical and chemical modification techniques to the virus can affect the final structure of the nano-gold products (Fig. 5.3) (Lim et al. 2010).

Biowastes

Potential sources for biosorbents in their native environments include biowaste from various industrial and agricultural processes. Agricultural and industrial wastes have previously been used as biosorbents, including sunflower seed hulls, rice and wheat wastes (husk and straw), tea waste, orange peel, fermentation wastes, and anaerobic and activated sludge (Das 2010; Crini and Badot 2010; Niazi et al. 2020). Due to their limited porosity, these materials have a very high capacity for sorption, which is strongly related to their chemical structure and surface functional groups that can chemically bind and exchange metal ions from aqueous solutions. A popular method for recovering biowaste in addition to wastes utilized in their natural form is the pyrolysis of commercial and agricultural wastes into carbonaceous adsorbents (such as bone char, charcoal, coke, and activated carbon) (Sud et al. 2008; Nora and Mahmoud 2015). In recent years, a variety of cellulose and lignin biowastes, such as husk, hay, and various fruit shells and stones, have been utilized in the synthesis of non-traditional activated carbons and biochar (Sud et al. 2008). The use of carbonized biomass resources for biosorption is not the focus of the current research. Two common biosorbents that are categorized as biopolymers in the classification of biowaste and byproducts are chitin and chitosan (a chitin derivative). The most prevalent sources of these elements are insect cuticle, fungal cell walls, and crustacean (shrimp and crab) shells. The essential characteristics of such biomaterials are multifunctionality and hydrophilicity (Crini et al. 2007). Chitin and chitosan's alkaline nature allows them to chelate metals, resulting in greater metal binding (Weltrowski et al. 1996; Aranaz et al. 2009; Pillai et al. 2009). In particular, it is demonstrated that, despite chitosan's low surface area (3 m^2/g), the amine surface groups act as boosters to achieve high selectivity and large sorption capacity towards precious metals (Chen et al. 2011). Furthermore, some evidence suggests that chitin and chitosan have a high rate of gold uptake, with more than 80% of gold recovered in less than two hours (Zazycki et al. 2017). Apart from chitin, chitosan, and their derivatives (Yamashita et al. 2015), biopolymers such as calcium alginate (Cataldo et al. 2015), modified cellulose (Zhu et al. 2015) and keratin (Khosa and Ullah 2013) have demonstrated adequate results in the biosorption of precious metals from aqueous solutions.

Living Plants

Phytoremediation is one of the most recent techniques for recovering metals from diverse living plant parts. Phytoremediation is categorized into six major types ((phytoextraction, phytostabilization, phytorhizofiltration, phytotransformation, phytostimulation and phytovolatilization) according to the mechanisms involved in metal removal (Kotrba 2011; Mahmoud and Hamza 2017). Among them, phytorhizofiltration has a direct connection to biosorption, in which substance is absorbed through the root cell walls of plants. The review of the literature reveals that heavy metal removal has been the primary focus of recent research on phytorhizofiltration, but plants like *Pistia stratiotes*, wheatgrass, *Sinapis alba*, and *Lepidium sativum* have been successfully used for the biosorption of silver and platinum ions from aqueous solutions (Hanks et al. 2015; Asztemborska et al. 2015; Shah et al. 2016). *P. stratioids*, for instance, performed well in the adsorption of Ag(I) from solutions with an initial concentration of less than 0.02 mg/L. Additionally, it has been determined that its efficacy in eliminating heavy metals is satisfactory (Hanks et al. 2015). Studies on industrial-scale applications demonstrated that employing the plant roots (*Sinapis alba* and *Lepidium sativum*) for Pt biosorption resulted in a simpler recovery step and less money than using the plant stems (Asztemborska et al. 2015). There have been further reports of successful gold and silver extraction from the roots and leaves of plants like *Cercis siliquastrum*, *Eichornia*, and *Lagerstroemia speciosa* (Zolgharnein et al. 2013; Patil et al. 2015).

Modified Biosorbents

Biosorbents are frequently modified to create materials with improved sorption qualities (e.g., increased capacity and selectivity) (Viswanathan and Meenakshi 2010). By altering the availability, variabilityand type of active sites, as well as their chemical states, modification approaches have an impact on sorption performance (Hima et al.

2007). Additionally, a number of techniques can help to address the structural issues with crude biosorbents, including their poor density, mechanical strength, particle size, and recovery (Vijayaraghavan and Yun 2008; Gadd 2009; Viswanathan and Meenakshi 2010). Any simple preparation can have a considerable impact on the highest sorption capacity and selection of biosorbents. Many modification strategies such as chemical procedures, such as treating *Saccharomyces cerevisiae* biomass with sodium hydroxide and ethanol, cellulose with taurine, persimmon peel with diethylamine, and chitosan with side branch grafting are also proposed (Oke et al. 2014; Dwivedi et al. 2014; Xiong et al. 2009; Sharma and Rajesh 2017). Table 5.2 provides a classification of the transition from straightforward to complex procedures. Colica et al. (2012) gave *Rhodo pseudomonas* bacterial strains an acidic pretreatment and the treated biomass had a greater ruthenium sorption capacity in the presence of copper, zinc and nickel. *Nitzschia obtuse*, a diatom species, was discovered to be a moderately favourable sorbent for gold uptake at extremely low concentrations and its physical alteration resulted in a substantially better sorption capacity by Chakraborty et al. (2006). Living cell immobilization is another key approach that has received a lot of attention in recent years. Liu et al. (2014) used chitosan to immobilize tannin (produced from persimmons). At pH 3 and an initial gold concentration of 350 mg/l, it was discovered that the modified tannin had a very large capacity for gold sorption (1500 mg Au/g or 7.61 mmol/g) (Liu et al. 2013). A good biosorbent for gold (917.43 mg Au/g or 4.66 mmol/g) and palladium (196.43 mg Pd/g or 1.85 mmol/g) was discovered by immobilizing tannin with Fe_3O_4@SiO_2 microbeads in another study (Fan et al. 2019). Huang et al. (2010) have demonstrated that immobilizing tannin with porous silica transforms it into an unique and potent Au(III) biosorbent with a sorption capacity of 642 mg/g (3.26 mmol/g) at 50 °C (Huang and colleagues 2010). Woińska and Godlewska-Żyłkiewicz (2011) developed a biosorbent from *Aspergillus* sp. Cellex-T cellulose resin immobilized fungus for the recovery of platinum and palladium from acidic environments (pH = 1) with a recovery efficiency of over 99 percent for both metals. Capacity of 0.47 (2.4103) and 1.24 (0.0116) mg/g (mmol/) were found at starting concentrations of 0.020 ng Pt/mL and 0.012 ng Pd/mL, respectively. *Pseudo choricystisellipsoidea* microalgae residues extracted during the biodiesel production process were used to make gel biosorbents by Khunathai et al. (2017). This sample was subjected to two types of modification treatments: dithiooxamide immobilization and chemical modification with polyethyleneamine. The sorption capacity for silver was improved by both approaches to 2.4 mmol/g and 2.7 mmol/g, respectively (Khunathai et al. 2010). Furthermore, cell modification is a strategy for improving biosorbent structure that uses two approaches: (i) improving the culture medium and (ii) using genetic engineering technologies. Techniques for altering cells, including the recently created protein design approach, enhance metal-biosorbent binding and increase the cell's selectivity for metals (Pazirandeh et al. 1995; Valls and Lorenzo 2002). Severe-condition resistance (Ziagova et al. 2014), for example, employed TMV on *Nicotiana tabacum* cv Xanthi as a host and purified it for gold and palladium sorption (Lim et al. 2010). Increased selectivity for palladium was achieved by using a genetic alteration technique on viral proteins. It was discovered that when the modified sorbent was used in consecutive

Table 5.2 Different modification methods to prepare modified/hybrid biosorbents

Method	Category	Detailed methodology	Case studies
Physical modification	–	Autoclaving, steam treatment, lyophilization, thermal drying, cutting, grinding, etc.	Rubcumintara (2015)
Chemical modification	Pretreatment Enhancement of binding groups Elimination of inhibiting groups Graft polymerization	Acids washing, alkalis washing, washing with organic solvents, washing with other chemicals Amination, carboxylation, phosphorylation, carboxylation, saponification, sulfonation, xanthanation, thiolation, halogenation, oxidation, etc. Decarboxylation, deamination, etc. High energy radiation grafting, photochemical grafting, chemical initiation grafting	Gong et al. (2016), Kondo et al. (2015), Garole et al. (2018), Hong et al. (2020)
Immobilization	–	Living cell immobilization on inert support materials	Huang et al. (2010), Khunathai et al. (2017)
Magnetic modification	–	Introducing ferro-, ferri- or superparamagnetic materials into biopolymers, plant derivatives and microbial and algal cells to improve biosorbent separation/ recovery	Mahamadi (2019), Tang and Fu (2020)
Cell modification (during growth)	Culture optimization Genetic engineering	Optimization of culture conditions for enhancing biosorptive capacity of cells Over-expression of cysteine-rich peptides, Expression of hybrid proteins on the surface of cells	Milanowski et al. (2017)

Source Veglio' and Beolchini (1997), Mallampati (2013)

cycles, the palladium sorption capacity was larger in each cycle than when the crude sorbent was used (Freer et al. 2013). Elahian et al. (2017) found that a recombinant biomass from *Pichia pastoris* produced a maximum of 31 IU/mL of enzyme and had a silver sorption capacity of 163.9 mg/g (1.519 mmol/g). Furthermore, as compared to the original biomass, the changed biomass can create smaller metallic nanoparticles (Elahian et al. 2017). The researchers modified the *Escherichia coli* gene sequence from RP437fliC to RP437CysFliC to boost the amount of cysteine in each subunit, knowing that it is a significant contributor in gold sorption due to its sulphur and nitrogen activities. Despite having smaller flagella, the modified bacterium's gold sorption capability increased due to higher cysteine levels (Deplanche et al. 2008).

Metal–Organic Frameworks Adsorbents

Metal–organic frameworks (MOFs) are often made via. a reticular synthesis method, which involves tightly binding metal ions to organic linkers. Thousands of MOFs were proposed by the researchers. The majority of the organic ligands utilized to make numerous MOFs have been discovered to be both expensive and toxic (Xu et al. 2021). Because of the ease of inclusion of functional groups and hydrolytic-thermal stability, such as amine, carboxyl, hydroxyl and oxygen (Jamshidifard et al. 2019) or by employing the cross-linking method (Zhang et al. 2021) the zirconium MOF family are attractive nanostructured materials for sorption applications. MOF adsorption capability could be improved further with composite-based MOF adsorbents. Despite their fascinating features and excellent capacity to remove heavy metal ions, MOFs have micropores that some target metals cannot penetrate. Furthermore, the majority of them have poor water stability. MOFs have been made out of Mn, Fe and Cu, however the majority of them have poor chemical stability (Rad et al. 2014; Alizadeh et al. 2016; Malik et al. 2017; Hayati et al. 2018; Yi et al. 2018a, b; Zeng et al. 2019; Wang et al. 2020; Liu et al. 2020a, b, c). As a result, more study is required to fine-tune the structure of MOFs and scale them up for industrial wastewater applications. To increase the stability and sorption kinetics of MOFs, various fictionalization strategies should be devised and implemented.

5.3 Membrane-Based Filtration and Separation

Membranes have become more widely used for wastewater filtering and heavy metal ion extraction as technology has progressed. Figure 5.4a–c show simplified schematics for several membrane-based filtering procedures, whereas Fig. 5.4d shows numerous contaminants that can be separated using various membrane techniques (Rahmati et al. 2019).

5.3.1 Ultrafiltration

At low transmembrane operating pressures, ultrafiltration (UF) is used. Because the UF membrane pores are larger than the heavy metal ions, additives can bond to the metal ions and increase their size. Micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) are two methods that have been proposed. MEUF is made up of UF and surfactant bound together. MEUF has a high flux and selectivity, which means it uses less energy, has higher removal efficiency, and has a smaller footprint (Rahmati et al. 2017). MEUF works well in effluents with low heavy metal concentrations (Huang et al. 2017). A surfactant is applied to the wastewater at a concentration that is higher than the Critical Micellar Concentration at MEUF (CMC). Surfactant monomers, in addition to CMC, assemble in the

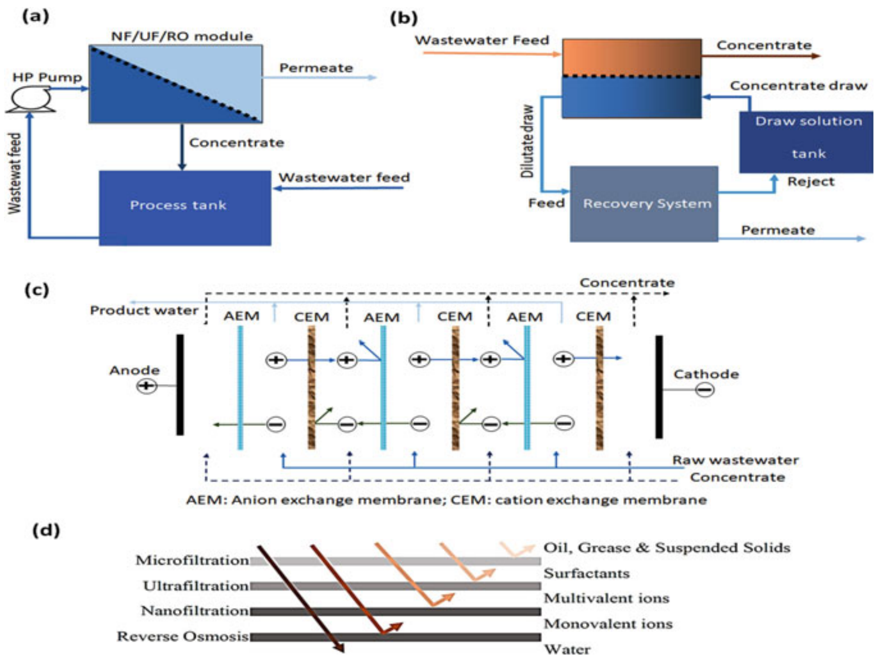

Fig. 5.4 **a** nanofiltration, ultrafiltration, or reverse osmosis method **b** forward osmosis process **c** electrodialysis method in which alternative charged positive and negative membranes take place, and **d** the separation capabilities of different membranes against different pollutants

solution and enhance the production of certain micelles. A hydrophobic tail and a hydrophilic head make up the surfactant. Due to electrostatic interactions, the micelles' inner hydrophobic core might solubilize organics (low molecular weight) as solubilisate, while the surface adsorbs countermetal ions on its surface (Tanhaei et al. 2014). Surfactants with the opposite electrical charge to the metal ions usually have the best retention (Paulino et al. 2006; Oyaro et al. 2007; Fu and Wang 2011). Polyelectrolytes (PE), cationic surfactants [e.g. sodium dodecyl sulphate (SDS)], and anionic surfactants [cyl sulphate (SDS)] are utilized in this context for successful heavy metal extraction (Fu and Wang 2011). MEUF's performance is influenced by a variety of parameters, including the solutes employed, the type of surfactant used, the operating circumstances, and the membrane type used. PEUF is created by combining UF and binding polymers. The binding polymers' functional groups can be sulfonate, phosphonic, carboxyl, or amine groups, and they're connected by chelating or ionic bonds (Rivas Bernabe and Eduardo Pereira 2009). PEUFs are also known as complexation-assisted, polymer-assisted, size-enhanced and complexation-enhanced ultrafiltrations. The PEUF method prevents and removes polymer-bound metal ions (Huda et al. 2015) while water and uncomplexed components can pass through the membrane pores. The identification of acceptable water-soluble polymer macroligands, however, remains the most difficult aspect of this technology's development.

5.3.2 Nanofiltration

Nanofiltration (NF) is a technique for concentrating constituents with molecular weights greater than 1000 Da and removing solutes with molecular weights greater than 200 Da (Wang et al. 2011). As a result, the operating range of NF lies somewhere between ultrafiltration (UF) and reverse osmosis (RO) processes55. Polymercomposites of multiple-layer thin-films of negatively charged chemical groups make up the NF membranes. Through phase inversion, anti-fouling NF membranes containing CeO_2/Ce_7O_{12} and PES were produced and used to extract Fe^{3+}, Al^{3+}, Co^{2+}, Cd^{2+}, $Cu^{2+}$and humic acid from wastewater, with extraction efficiencies ranging from 94 to 98% (He et al. 2020).

5.3.3 Microfiltration

Microfiltration (MF) removes micron-sized particles, bacteria, viruses, protozoa, contaminants, pollutants and other contaminants from a solvent/liquid/solution using a microporous membrane (Wang et al. 2011). Low-pressure membrane processes like the MF process have membrane pores with a minimum diameter of 0.110 m. Some MF membranes contain silica, ceramic, zirconia, alumina, PVC, polysulfone, PTFE, polypropylene, PVDF, polyamides, polycarbonate, cellulose acetate, cellulose esters, or composite materials. Commercial applications of MF are common in the biological and pharmaceutical industries. However, the MF system is used in the semiconductor industry for particle removal in rinse water, sterilization of beer and wine, clarity of various juices and cider and wastewater treatment (Wang et al. 2011). Because of its limited removing ability, the use of MF in the recovery of heavy metals has received little consideration. However, by altering the membrane or chemically pretreating the feed solution, it has been employed. The MF method is accessible in two primary configurations, depending on the type of application: crossflow and dead-end.

5.3.4 Reverse Osmosis

Only smaller molecules can pass through a semi-permeable membrane (0.51.5 nm pore size) during the pressure-driven separation procedure known as reverse osmosis (RO). By supplying pressure (20–70 bar) > equivalent to the osmotic pressure of the feed solution, the RO process turns the typical osmotic process on its head. The inhibited solutes typically have molecules between 0.00025 and 0.003 m in size. 95–99% of inorganic salts and charged organics may be extracted using the RO technique. The RO process has a high rejection efficiency and is small. However, the primary drawback of RO systems is membrane fouling and degradation (Wang et al. 2011). With a removal efficiency of > 98.7562, the RO separation process was employed to remove heavy metal ions from the electroplating effluent, including Ni^{2+}, Cr^{6+}, and Cu^{2+}.Commercial effluent from Coster field mines in Victoria, Australia, has recently been purified using RO with mean extraction efficiencies of 10%, 48%, 82%, 66%, and 95% for Fe^{3+}, Zn^{2+}, Ni^{2+}, As^{3+} or Nb^{3+} (Samaei et al. 2020).

5.3.5 *Forward Osmosis*

Forward osmosis (FO) is an osmosis procedure that uses a membrane to balance the infiltrating water's selectivity and flux (Rahmati et al. 2019). As shown in Fig. 5.2b, a semi-permeable membrane separates the feed and draw solutions at FO. In comparison to the feed solution, the draw solution normally has a higher osmotic pressure. Water is carried from the feed solution to the bleed solution due to the osmotic pressure difference between the feed and bleed solutions, retaining the rejected solutes on the feed side and the treated water on the bleed solution (He et al. 2020). Because FO does not require hydraulic pressure, it saves energy. Because the FO process is environmentally favourable, simple to clean, and pollutes little, it is commonly employed in wastewater treatment (He et al. 2020). However, FO has drawbacks such as draw solution reconcentration, membrane selection problems, and internal and external concentration polarization (Cui et al. 2014).

5.3.6 *Electrodialysis*

Electrodialysis (ED) is a technique that uses an electric potential difference to separate ions. To separate ionic solutes, ED employs a collection of cation exchange membranes (CEM) and anion exchange membranes (AEM), which are alternately placed in parallel (Rahmati et al. 2019). Anions flow through AEM in the ED process, while cations move through CEM. In this situation, half of the ED stack channels create the treated stream, while the other half expels the concentrated stream, as shown in Fig. 5.2c. Electrodialysis has a high recovery rate, requires no phase shift, reaction, or chemical involvement (Al-Amshawee et al. 2020) and may function at a wide pH range. Membrane fouling, high membrane costs, and a necessity for electric potential are all present in ED. ED has been used in a variety of situations. Membrane fouling, high membrane cost, and a necessity for electric potential are all present in ED. Through an unique ED heterogeneous CEM (composed of 2-acrylamido-2-methyl propane sulfonic acid-based hydrogel and PVC), ED has been used to separate $Ni2^{2+}$, Pb^{2+}, and K^+ from synthetic solution, with extraction efficiency of 96.9%, 99.9%, and 99.9% for Ni^{2+}, Pb^{2+}, and K^+, respectively (Nemati et al. 2017). To recover Pb^{2+}, a batch ED method was used, which achieved a maximum separation efficiency of 100% (Gherasim et al. 2014). Cu^{2+}, Ni^{2+}, and traces of Cd^{2+}, Fe^{3+}, Cr^{6+}, and Zn^{2+} were also extracted using a pilot-scale ED system, which achieved a 90 percent removal rate (Min et al. 2021). ED removed As^{3+} and As^{5+} from metallurgical effluent with a removal efficiency of 91.38% (Basha et al. 2008).

5.4 Chemical-Based Separation

Chemical processes for the removal of heavy metals from waste water are mature and are being used at an early stage. In this section the chemical based methods are discussed including precipitation, coagulation flocculation and flotation.

5.4.1 Precipitation

Chemical precipitation is one of the most extensively utilized and well-established processes in industry. It converts dissolved metal ions into solid particles, allowing them to settle more easily. By altering pH, electro-oxidation potential, or co-precipitation, reagent coagulation (coagulant) precipitates metal ions (Ojovan et al. 2019). Sediment removal is usually the next step. Hydroxide precipitation is commonly utilized due to its low cost, ease of usage, and ability to change pH (Yadav et al. 2019). It is carried out by adding a hydroxide to the agitated effluent, resulting in the formation of insoluble metal hydroxide precipitates. A metal ion, for example, could combine with calcium hydroxide (lime) to form metal hydroxide precipitates and calcium ions and pH when maintained in the range 9–11 provides better efficiency of precipitation (Park et al. 2014).

$$\mathrm{Metal}^{n} + \mathrm{Ca(OH)_2} \leftrightarrow \mathrm{Metal(OH)}_n \downarrow + \mathrm{Ca}^{2+} \tag{5.1}$$

However, because this method necessitates a significant dosage of precipitates, the method's high pH is considered a disadvantage. One of the best hydroxide precipitates for treating inorganic wastewater with a heavy metal concentration of 1000 mg/l is lime (CaO or $Ca(OH)^2$) (Kurniawan et al. 2006). This approach mostly eliminates Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cr^{3+} metals. Aside from the need for a high dosage to maintain an ideal pH, there are certain drawbacks, such as a relatively big dosage. In comparison to the hydroxide process, the sulphide participation procedure has a better removal efficiency and lower dissolved solids gain. This approach has been used to treat heavy metal ions that are hazardous (Al-Hemaidi 2012). Lower sulphide levels result in increased zinc concentrations in the effluent, whereas higher sulphide levels result in a malodour problem due to residual sulphide. It may also produce hydrogen sulphide gas, which has a bad odour and is poisonous. As a result, it is recommended that the sulphide precipitation be carried out at a neutral pH (Anoti et al. 2007). Equation (5.2) reaction shows the metal sulphide precipitation.

$$\mathrm{Metal}^{n+} + \mathrm{S}^{2-} \leftrightarrow \mathrm{Metal\,n\,S} \downarrow \tag{5.2}$$

Carbonate precipitation showed good efficiency and optimal precipitation at lower pH values as an alternative to hydroxide precipitation (Patterson et al. 1977). Sodium carbonate or calcium carbonate could be used for this purpose Eqs. (5.3 and 5.4) (Zueva 2018).

$$\mathrm{metal}^{n+} + n\,\mathrm{NaCo_3} \leftrightarrow n\,\mathrm{Metal\,(CO_3)} + n\,\mathrm{Na}^{+} \tag{5.3}$$

$$n\,\mathrm{Metal(Co_3)} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} \uparrow + \mathrm{(MeOH)}_n\mathrm{CO_3} \downarrow \tag{5.4}$$

It may have a smaller sludge volume, but it may produce CO_2 bubbles and require more chemicals for effective precipitation (Zueva 2018). The primary metals extracted by this method are copper and manganese, as can be observed. Zinc and lead might be removed with ease as well. In chemical precipitation procedures, the Fenton reaction is commonly utilized to improve removal as well as recovery efficiency. Heavy metal complexes are decomplexed using the Fenton or Fenton-like oxidation method. The chemical precipitation mechanism, on the other hand, adjusts the pH. (e.g. NaOH). Fenton chemistry is complex and involves a number of processes that rely on active intermediates like $(Fe^{IV}O)^{2+}$ and hydroxyl radicals (Bossmann et al. 1998; Kremer 2003). Fu et al. (2010) describes the conventional Fenton reaction as follows:

$$\mathrm{Fe}^{2+}\ \mathrm{H_2O_2} \leftrightarrow \mathrm{Fe}^{3+} + \mathrm{HO} + \mathrm{OH}^{-} \tag{5.5}$$

$$\mathrm{HO} + \mathrm{dye} \leftrightarrow \mathrm{oxidized\,dye} + \mathrm{H_2O} \tag{5.6}$$

5.4.2 *Coagulation and Flocculation*

By neutralizing the forces that keep colloids apart, coagulation destabilizes them, whereas flocculation is the aggregation of destabilized particles (Ibarra-Rodríguez et al. 2017). Aluminum, ferrous sulphate, and ferric chloride are common coagulants. Using a flocculant such as polyaluminum chloride (PAC), polyferrous sulphate (PFS), polyacrylamide (PAM), and other macromolecular flocculants, flocculation binds the particles together into huge agglomerates (Chang et al. 2009). Although the PE has been described as one of the most useful flocs, the sludge produced may be harmful (Ibarra-Rodríguez et al. 2017). In most cases, the flocculants are synthetic and non-biodegradable (Nourani et al. 2016). Inorganic coagulant toxicity and health concerns, huge sludge volume, selective for particular metals and inefficient at emerging contaminants, growing effluent colour, inefficiency at employing natural coagulants, and difficult scaling are some of the flaws (Teh et al. 2016). Cu^{2+}, Pb^{2+} and Ni^{2+} are examples of heavy metals that can be eliminated using this method. Other metals such As^{2+}, Se^{2+}, Cr^{2+}, Sb^{3+}, Sb^{5+} and Ag^{2+} could be effectively removed as well.

5.4.3 Flotation

Various metal ions can be removed via flotation. Numerous studies have been conducted on dissolved air flotation, ion flotation, and precipitation flotation. In dissolved air flotation, air (or gas) is introduced to the effluent to form microbubbles that may bind the metal ions, resulting in lower-density agglomerates, leading the floc to rise through the effluent. The accumulated slags on the surface can be easily removed (Edzwald 2010). The ion flotation procedure depends on making metal species more hydrophobic by adding surfactants; as a result, the hydrophobic species are eliminated by air bubbles. The additional surfactants serve as scavengers, and the indices of ion flotation are controlled by the frothers (Peng et al. 2019). Ion flotation appears ineffective when the amount of metal ions present in a big volume of wastewater is minimal (Hoseinian et al. 2020). Ion flotation has shown to have low energy usage, a small volume footprint, less sludge volume, and selective processing. This precipitation flotation takes a short time to be efficiently completed (Mahne and Pinfold 2007). In general, the flotation methods have advantages such as fast operation, compact process, and moderate cost. Among all flotation processes, considerable attention has recently been paid to ion flotation. Effective and non-toxic surfactants are needed since ion flotation rely on them for their scavenger functions. Surfactants made of chemicals were first introduced because of their potent collecting power, superior selectivity, and straightforward design. Cost and toxicity concerns, however, put a cap on them. Biosurfactants, on the other hand, appear more environmentally benign, but they process (Peng et al. 2019). Nanoparticles have been proposed as novel collectors in this context, demonstrating the benefits of both synthetic and biological surfactants (Peng et al. 2019).

5.5 Electric-Based Separation

This section discusses a variety of electrochemical processes, including ion exchange processes and electrochemical processes including electrochemical reduction (ER), electrochemical flotation (EF), and electrooxidation (EO). Electrochemical therapy in an electrochemical system, the reduction process occurs at the cathode (negative side), whereas oxidation occurs at the anode (positive side), where electrons are exchanged. By removing metals, these two chemical processes, collectively referred to as redox (reduction–oxidation), purify water. For example:

$$\text{Metal}^{n+} + n\,\text{H}_2\text{O} \leftrightarrow \text{Metal}^{m+}(\text{H}_2\text{O})_n\ \text{solution} \downarrow + me^{-}\text{metal} \quad (5.7)$$

The type of electrochemical technique and the efficiency with which particular metal ions are removed are largely determined by the anode and cathode used. Monopolar electrodes in series (MP-S) and monopolar electrodes in parallel (MP-P) are the most cost-effective options, and they also produce high-quality results. ER, EC, EF, and EO processes are the most common electrochemical processes. The ER process selectively deposits atoms or molecules on the surface of the cathode, also known as electrodeposition and electroplating. This treatment does not result in sludge that needs to be treated further. It's worth mentioning that cathodes having a high overpotential for hydrogen evolution are better at removing or reducing pollutants (Yang et al. 2018). Under acidic conditions, carbon-based or sulphur mixture cathodes with varied ratios are suitable for removing Hg^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+} from wastewater (Jin et al. 2020). Regardless of the starting concentration of Cd^{2+}, a titanium anode covered with iridium oxide found to be the ideal material for 100% efficiency. To improve wastewater treatment performance, more attention should be paid to reactor design and operating conditions (Baghban et al. 2014).

Steel (iron) or aluminium electrodes, which are non-toxic and dependable, are commonly employed in the EC method (Moussa et al. 2017). The EC method works by dissolving anodic metal cations (Eq. 5.8), forming hydroxo complexes (coagulants, Eq. 5.9), aggregation stability and phase separation, and finally precipitation and flotation. The colloidal particles are destabilized by the cations from anode forming coagulants that react with wastewater pollutants (−vely charged) (Eq. 5.10)

$$\text{Metal} \rightarrow \text{metal}^{n+} + ne^{-} \quad (5.8)$$

$$2\text{H}_2\text{O} + 2e^{-} \rightarrow \text{H}_2(g) + 2\,\text{HO}^{-} \quad (5.9)$$

$$\text{Metal}^{n+}(\text{aq}) + \text{OH}^{-} \rightarrow \text{Metal}(\text{OH})_n(\text{S}) \downarrow \quad (5.10)$$

As a result, flakes (fine particles) float whereas metal hydroxide (bigger particles) that have a density greater than that of water precipitates (settles). Another advantage of EC procedures over other technologies is that the coagulants are produced on-site by anode oxidation. In general, it has been found that less power usage and better removal efficiency are obtained when AC power is used instead of DC power. The time of the test is also shortened by an increase in the temperature, power, and pH. Electrode passivation and comparatively high consumption of electricity are drawbacks of EC, along with the difficulty of finding large-scale applications with lower energy consumption (Zaied et al. 2020). Numerous effective methods, including aggressive ion addition, AC operation, polarity reversal operation, ultrasonic treatment, mechanical cleaning of electrodes, chemical cleaning of electrodes, and hydrodynamic cleaning, have been suggested to reduce the passivation of the electrode. However, each route has disadvantages, such as the generation of hazardous by-products, costly additional treatment and infrastructure, and increasing sludge production (Tarpani and Azapagic 2018). Accordingly, the EC procedure is not yet fully operational. The mechanism of EF is mainly based on performing water electrolysis on insoluble electrodes while introducing the flotation effect to facilitate the treatment process (Sillanpaa and Shestakova 2017). Therefore, homogeneous, small (0.15 mm) bubbles are necessary for the technique to be effective. The ideal pollutant concentration was found to be between 10 and 100 mg/L, with 200 mg/L being the upper limit (Shammas et al. 2010). The heavy metal removal efficiency of the EF process is limited due to low O_2 evolution overpotentials (Chen et al. 2002). Therefore, a viable strategy to enhance system performance in general for heavy metal removal was the hybridization of EF, membrane, and EC (Mazumder et al. 2020).

This method uses both direct (simpler) and indirect mechanisms to remove chemicals from wastewater. It is independent of the current and relies on the NaCl content for indirect chlorine oxidation to function (Ammar et al. 2016). Electrode deactivation and decreased efficiency occur as a result of the contaminants directly exchanging electrons with the anode surface and forming a polymer layer there. When organic pollutants interact with oxidants, oxidized contaminants are produced in solution. The following equations describe the EO process:

$$\text{Metal} + H_2O \rightarrow \text{Metal}(:\ OH) + H^+ + e^- \tag{5.11}$$

$$\text{Metal}(:\ OH) \rightarrow \text{Metal}\,O + H^+ + e^- \tag{5.12}$$

$$\text{Metal}\,O + R \rightarrow M + RO \text{ and } \text{Metal}\,O \rightarrow M + 1/2\,O_2 \tag{5.13}$$

Anodes made of platinum, gold, nickel, boron-doped diamond (PbO_2), and mixed metal oxides (MMO) (such as SnO_2, PbO_2, Ti/TiO_2, IrO_2, Sb_2O_5, RuO_2) are commonly utilized (Martínez-Huitle and Ferro 2006). Anode materials that are very efficient are costly. As a result, alternative materials should be offered in order to influence efficiency and cost. Furthermore, the presence of various types of metal ions in wastewater has an impact on treatment efficiency. As a result, finding effective anode materials with high efficiency in dilute solutions is critical. Future developments should look into the efficacy of combining EO with other water technologies to tackle problems.

5.5.1 Ion Exchange Treatment

The ion exchange process is a reversible chemical reaction that replaces unwanted metal ions with harmless and environmentally friendly ones (Dąbrowski et al. 2004).

In place of the solid particle cation, a heavy metal ion is removed from a waste water solution by being bonded to an immobile solid particle. Solid ion exchange particles can be made of organic resins or inorganic zeolites, which are both naturally occurring materials. Target heavy metal ions including Pb^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, V^{4+}, V^{5+}, Cr^{3+}, Cr^{4+}, Cu^{2+} and Zn^{2+} can be removed (partially or completely) from the wastewater using the ion exchange method (Dąbrowski et al. 2004).The ion exchange mechanism for metal removal can be explained in the following reaction, since the ion exchange particle uses an ion exchanger of MEC^+ (M is the fixed anion and EC^+ is the exchange cation; Na^+ and H^+ are often used as exchange cations) to exchange its cation (EC^+) with the wastewater cation (WC^+) (Tenorio and Espinosa 2001).

$$M^-EC^+ + WC^+ \leftrightarrow M^-WC^+ + EC^+ \tag{5.14}$$

Different types such as Amberlite (Kang et al. 2004) and Diaion CR11 (Cavaco et al. 2007) have been studied for cation removal. Zeolite are found to have an excellent ion exchange ability due to its negative charge resulting from Si^{4+} located at the center of the tetrahedron undergoing isomorphous exchange with Al^{3+} cations. MOFs have recently been suggested as good candidates for the ion exchange removal process (Kobielska et al. 2018). Some reported MOFs used for ion exchange reactions are AMOF-1 for Cd^{2+}, Pb^{2+} and Hg^{2+} (Fang et al. 2010), ZIF-8 [for Cu^{2+} removal (Zhang et al. 2016)] and ZIF-67 for Cr^{6+} removal (Li et al. 2015). The process of ion exchange needs more investigation into stability and reusability, similar to adsorption.

5.6 Photocatalytic-Based Separation

The photocatalytic based process has been described as a simple wastewater treatment method using light and semiconductors such as titanium dioxide (TiO_2) (Barakat 2011). Three main steps are performed in this method: photogeneration of charged carriers, separation of charged carriers and diffusion to the surface of the photocatalyst, and redox reaction on the surface of the photocatalyst (Nasir et al. 2020). The effluents from real soil wash effluent were treated with an outdoor dual solar photocatalytic process with a flat plate collector to remove 93.5% Cu^{2+}, 99.6% Fe^{3+} and 99.4% Zn^{2+} (Onotri et al. 2017). Simulated ultraviolet (UV) solar TiO_2 photocatalysis was used to remove ethylenediamine-N,N-disuccinic acid (EDDS) and Cu^{2+} from wastewater (0.2 mM EDDS and 0.2–1.4 mM $CuSO_4$) to achieve a conversion efficiency of 100% to be reached at 24% grade of mineralization (Satyro et al. 2014a). A significant removal efficiency of 41% Cu^{2+}, 100% Fe^{3+}, 100% Zn^{2+} and 100% EDDS were observed from synthetic soil wash solution (Satyro et al. 2014b). Under visible light irradiation, a synthesized rhodium/antimony co-doped TiO_2 nanorod and titanate nanotube (RS-TONR/TNT) were used to remove Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and organic pollutants with 70 and 80% degradation efficiency for dye or bisphenol A to extract from the wastewater (Dhandole et al. 2020). The photocatalytic activity employing $CeO_2/BiOIO_3$ composites with Ce^{4+}/Ce^{3+} redox centers was utilized to achieve Hg^{2+} removal efficiency of 86.53% (Xiao et al. 2020). In an aqueous solution containing As^{5+} and Cr^{6+} (concentration of 0.10 mg/L), a synthesized 3D Fe_2O_3 was used to achieve nearly 100% removal rates using sunlight exposure and photocatalytic activity (Lee et al. 2018). A prepared CH-GEL/ZSPNC hybrid nanocomposite ion exchanger achieved extraction efficiencies of 90% Ni^{2+}, 94.9% Zn^{2+}, 95% Mg^{2+}, 100% Pb^{2+}, 90.3% Cd^{2+}, 88.9% Cu^{2+} and 84% Rhodamine B (dye) (Kaur and Jindal 2018). A fabricated CS/Silver bio-nanocomposite (CS/PVDC/Ag) was used in a photocatalytic oxidation process for 97% Cu^{2+}, 88% Pb^{2+}, 89% Cd^{2+} and 77% dye removal (Al-Sherbini et al. 2019). This approach has some drawbacks despite its on-site creation of reactive radicals, lack of chemical use, and lack of sludge production. When several metals are present, it is still a laboratory-scale, low productivity, pH-dependent process that is ineffective (Crini and Lichtfouse 2019).

5.7 Removal and Recovery of Heavy Metals Using Microbial Fuel Cell (MFC)

In order to promote systems that are both economically feasible and sustainable, the emphasis has recently switched increasingly toward energy-assisted wastewater treatment techniques (Kaushik et al. 2011; Kaushik and Mona 2017; Reddy et al. 2019; Sharma et al. 2020). It has been demonstrated that photoelectrocatalytic technologies are particularly effective in treating wastewater while producing power with increased efficiency (Rao et al. 2019; Reddy et al. 2020a, b). Microbial fuel cell technology offers opportunities for metal recovery rather than simply removing the metals from the effluent (Roy et al. 2023). Microbial fuel cell technology offers opportunities for metal recovery rather than simply removing the metals from the effluent. In addition to treating biologically rich wastewater and removing or recovering heavy metals, harnessing the bioelectrochemical characteristics of microbial fuel cells (MFCs) is a new and innovative strategy that also produces electricity (Mathuriya and Yakhmi 2014). Intriguingly, MFC technology is now developing for its potential applications in a number of other fields, including the recovery of pure materials, the treatment of specific pollutants, bioremediation, the recovery of heavy metals, the decolorization of dyes, the use of biosensors, denitrification, and many others (Mathuriya and Yakhmi 2014; Singh and Kaushik 2019). The final electron acceptor in the cathode, which normally would be oxygen, is replaced by the metal present in the effluent in accordance with the electrochemical principle for metal removal using MFC, which also results in the reduction of the metal to a less hazardous form. From a biological perspective, the MFC can integrate the biotransformation, biosorption, and bioaccumulation procedures (Nancharaiah et al. 2015). Current researches on the use of MFCs for power production, metal elimination, water treatment, and groundwater rehabilitation, as well as other purposes have been reviewed and addressed, along with the MFC's basic workings (Cecconet et al. 2018;

Chakraborty et al. 2020). These metals can be utilised by bacteria as nutrients and changed into a less harmful form. Additionally, the metals are capable of adhering to microorganisms' surfaces. By digesting or changing a heavy metal's chemical form, these bacteria assist in reducing its toxicity. The redox potential of the metal, initial metal concentration, single or mixed metals, biotic or abiotic cathode, type of microbes, type of gaseous environment at the cathode, type of electrode, type of substrate, pH value, external resistance, and the anode–cathode volume ratio studied by various researchers all appear to have an impact on the metal removal potential of MFC. The ability to guide the organic waste to the anode compartment, where the anodic biofilms mediate electricity generation, and the metal-bearing waste water to the cathode compartment is another significant advantage of using MFC for removal of metal ions. The biofilm may experience a rapid shock, though, if catholyte seeps to the anode. The type of substrate present in the anode is likely to have an important impact on the tolerance of biofilm microbes to toxic shock. While there are limited studies, the presence of glucose appears to help the microbes survive the shock (Tao et al. 2011). Another element that has been demonstrated to be essential for high MFC performance is biofilm maturation. This element, along with adequate biofilm stabilisation and acclimation, must therefore be the main emphasis of long-term application of MFC for metal removal as well as recovery. The introduction of metal-tolerant microorganisms in the inoculum is necessary since most metals above a threshold limit are harmful to living cells and therefore function as one of the limits limiting the metal removal capability in MFCs. According to certain research, aeration in the cathode improves metal removal by MFCs because it reduces hydrogen peroxide, a potent oxidant. In order to make ventilation less expensive, microbes that could produce such conditions in the cathode must be sought for. It is crucial to take into account the key factors covered in this study when applying MFCs in metal removal/recovery to the real market. Even though there have only been a few field experiments on MFCs (Dong et al. 2015; Ge and He 2016; Ieropoulos et al. 2016), upscaling to larger sizes with certain adjustments to lower costs and increase energy sustainability appears to be feasible. For the large-scale applications of MFC technology, which are currently absent, more consideration needs to be given to the development of in situ treatments and the deployment of models to simulate data.

5.8 Conclusion

Agrochemicals, household products, pharmaceuticals, and other industries all employ heavy metals. Their inevitable discharge into wastewater makes it crucial to remove and recover them in order to stop them from building up to dangerous quantities that are known to harm aquatic ecosystems and negatively impact human health. The issue has two crucial components: protecting the environment against scattered harmful substances, in particular heavy metal compounds, and economics. Various conventional industrial and municipal wastewater treatment techniques are not only expensive and energy-intensive, but they also create poisonous sludge.

Therefore, in recent years, the focus has shifted more to energy-assisted as well as ecofriendly wastewater treatment processes to promote economically viable and sustainable systems. As an alternatives, a number of microbes have recently come to light that can withstand a variety of metals, grow more quickly, require less expensive handling, and can be genetically modified. The advantages of MFC technology, which treats wastewater while also producing electricity from it, have been discussed in this article. Future study should take into account the best method for achieving effective metal recovery with minimal negative effects on the environment and low costs.

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Viruses are regarded potent weapons in nanotechnology, and they are used in a variety of industries ranging from agriculture to medical due to their widespread availability and small particle size

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Chapter 6
Recovery of Various Metals from Industrial Wastewater by Biological Methods

Ankita Ojha, Ankitendran Mishra, Dhanesh Tiwary, and Avinash Singh

Abstract Industrial wastewater contains a variety of hazardous chemicals as well as high metal concentrations. Metal-contaminated wastewater is hazardous to the environment and can have serious health consequences if it enters biological systems. However, the recovery of metals from wastewater can increase the sustainability of treatment processes and enhance cost-effectiveness. There are numerous conventional treatment methods for recovering metals from wastewater, including physical, chemical, and even biological methods. Physical and chemical processes are primarily energy and chemical-intensive. New-age research uses novel bio-recovery methods to extract and remove metals from wastewater. Various methods like sorption, biomembranes, bioelectrochemical techniques, etc., have been discussed in this chapter in a summarized form. Further, insights into energy-efficient recovery methods and their applications have been elaborated.

Keywords Bio-recovery · Bioleaching · Bioelectrochemical · Sorption · Biochemical

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6.1 Introduction

Water, which has always been an essential constituent of the living system, has been depleted to a great extent, and hence, the present time demands recycle and reuse of water from wastewater. Not only this many naturally occurring minerals and resources are also decreasing rapidly and, therefore, need serious attention. Resource recovery has gained momentum in recent times due to the limited availability of natural resources. Even though this is not a new process and has been in the application at many wastewater treatment facilities in European countries (Meena et al. 2019). Metals have been an important part of society for ages and hold historical significance. Heavy industrialization has increased a tremendous demand for heavy metals, and with ever-increasing demands, there is an anti-parallel depletion in the availability of these metals. The increasing need for important metals drawn tremendous attention because of their severe scarcity, least substitutability, and high degree of unequal distribution. The present time is looking for alternate sources of these metals. Recovery of metals from the wastes is one such alternative that serves the dual role in metal extraction and environmental cleansing (Jadhav and Hocheng 2012; Moss et al. 2011). Wastewater discharged from various industries like mining and metallurgy, tanneries, semiconductor and alloys manufacturing units, plastic manufacturing units, anticorrosive agents, dyes and pigments, batteries, and electroplating contains a heavy dose of metals, especially transition metals. Hence, they also serve as a great source of metal recovery from wastewater. Low pH, reduced COD, and higher dosages of heavy and toxic metals tend to be some of the important properties of such wastewater. Most of these metals are toxic and are present in high concentrations. However, suitable methods may be applied to recover these metals by reducing their toxicity and converting them into insoluble forms (Kumar et al. 2021). Heavy metals, unlike organic pollutants, are redundant and non-biodegradable, highly toxic, and bioaccumulate in living tissues, allowing them to pass through generations. Nearly 60% of the world's population affected by pollution is because of heavy metal toxicity. Most of these heavy metal pollutants include Hg, Cd, Cu, Ag, Pb, Zn, and Co. Electroplating industries in China generate more than 4 billion tons of heavy metal-loaded wastewater (Sahinkaya et al. 2017). These metals if not removed can tend to leach into groundwater or move across biological systems which highlight a serious need for their removal from wastewater. Metal pollutants are highly carcinogenic and quite damaging to living systems. Not only this, their free discharge into the living system led to serious loss the natural resources too. Various kinds of metals that are present in wastewater are—Cu (electronic and metal finishing wastes), Zn (electronic and metallurgical wastes), Ni (petrochemical refineries), Pb (automobile industries), Ag and Au (electronic wastes), etc. (Chmielewski et al. 1997).

Several available technologies such as adsorption, chemical precipitation, ion-exchange, reverse-osmosis, electrofiltration, electrosorption, electrodialysis, coagulation and membrane filtration have been applied with success in the removal of toxic and heavy metals from wastewater. However, these methods, though highly effective, had certain drawbacks such as high economic investments, larger chemical and reagent wastage, non-specific removal of metal ions, high energy requirements and sludge as well as secondary contaminant generations (Amanze et al. 2022; Khulbe and Matsuura 2018). Metal bio-recovery is not a new concept and it has also been part of biomining activities in the past as well as the bioremediation of heavy metals and their ions from industrial wastewater. The combined knowledge of biomining and bioremediation has been successfully used up in the bio-recovery processes. While biomining involves processes such as bioleaching through chelation, bioaccumulation (use of living microbes to take up metals intracellularly), acidification and oxidation (microbe-assisted oxidation–reduction reactions of metals used for metal detoxification) which is mainly a process of metal mobilization; methods like bioreduction, bioprecipitation and biosorption form an integral part of bioremediation technology (Puyol et al. 2017).

Extraction of metals from wastewater is a tedious task as the metal concentration is quite low. Especially, the physicochemical techniques pose serious challenges in case of low or very low concentrations. Bio-recovery processes play a heroic role in such situations. Even if numerous techniques are available for removal and recovery of metals from industrial wastewater, biological and biotechnical methods are one of the most promising and highly efficient techniques. Microbial techniques are not only energy-efficient but also environmentally friendly. They show high specificity while targeting metal ions as they are mostly enzyme-dependent in action. They do not require highly acidic or alkaline conditions for their operations which reduces chemical wastage. In a way, they are mostly part of healthy, robust and sustainable environmental remediation methods. This chapter explores various critical aspects of conventional techniques for the removal and recovery of metals from wastewater and spans over various bio-recovery processes that can be applied. Attention has also been drawn towards the limitations of these methods and plausible solutions for overcoming problems.

6.2 Metal Recovery from Wastewater Using Conventional Methods

Recovery of heavy metals from industrial wastewater is not a very recent technology but a very old and established practice in treatment technology. They have been classified into physical (membrane filtration, ion-exchange, solvent extraction) and chemical methodologies (precipitation, electrodeposition, coagulation, photocatalysis and complexation) and sometimes even physicochemical (adsorption). Techniques such as micro-, nano- and ultrafiltration as well as Reverse osmosis depends on the application of pressure and membrane to retain elemental metals or metal ions from their aqueous solutions. Chemically-modified membranes are also used as sorbents for the selective removal of heavy metals from wastewater. Polycysteine-functionalized microfiltration membranes have been found to be effective in the removal of Hg and Cd (Ritchie et al. 2001). Physical separation techniques are mainly applicable to metals present in particulate form. These processes are mainly involving hydrodynamic application, mechanical screening techniques, scrubbing, gravity separation, magnetic separation etc. However, these processes are limited to certain optimum conditions and are mainly dependent on the particle size of metals. Moreover, physical processes cannot be applied in cases of low concentrations of metals present in aqeuous solutions (Fu and Wang 2011). Because of its ease of operation and simple handling, the precipitation method is the most commonly used chemical technique in the removal of heavy metals from industrial wastewater. It mainly targets the conversion of heavy metals into their oxides, hydroxides, carbonates, sulphides, sulphates, phosphates etc. It is followed by coagulation and flocculation for the separation of metal salts from wastewater. Removal efficiency can easily be enhanced by changing and tuning the pH and hence separating different metals at different pH (Ku and Jung 2001). The coagulation and flocculation of metal precipitates mainly depend on their zeta potential (ζ; electrostatic interaction between metals and flocculating agents). The electrochemical treatment method is the process where metals are deposited on the surface of electrodes by applying an electric current between them. These electrodes are dipped in a metal-containing solution and the anode used is insoluble. Various types of electrochemical methods that are used in the recovery of heavy metals from wastewater are electrodeposition, electrooxidation and electrocoagulation (Shim et al. 2014). Factors such as temperature, pH, metal concentration, and the presence of interfering radicals in wastewater all have a significant impact on chemical processes. Ion-exchange process is mainly a process of ion-uptake from their aqueous solution into a solid substrate and is one the most significant methodology used in water treatment industries. It is a cost-effective, easily operative and highly effective method applied in the separation of heavy metals even at minute concentration. Ion-exchanger resins are used for the exchange of cations and anions which are water-insoluble solid substrates capable of absorbing positive or negative ions from their electrolytic solutions (Hamdaoui 2009).

Membrane filtration and ultrafiltration remove heavy metals from their solution through a size-dependent separation technique. The ultrafiltration method uses a permeable membrane of pore size 5–20 nm and has 90% removal efficiency. Polymer-supported ultrafiltration is the addition of water-soluble polymer-based ligands that produce macromolecular complexes in interaction with metal ions. They are well-known for their high selectivity, low-energy consumption and faster kinetics (Trivunac and Stevanovic 2006). Another membrane-based separation technique is Reverse-Osmosis (RO) where pressure is applied to force metal-containing solution. The membrane retains metal on one-side and solvent passes through the membrane through a diffusion-mechanism. The process of separation depends on the concentration of solute, pressure applied on the membrane and flux-rate (Sarai Atab et al. 2016). Electrodialysis is a highly effective membrane technology that involves passing ionised species in an aqueous solution through an ion-exchange membrane using an electric potential. On passing through cell compartments the anion migrates towards the anode and cations migrate towards the cathode by passing through the ion-exchange membranes (Robeson 2012). The major disadvantage of this technique is the corrosion of the membrane. Other factors that affect electrodialysis are flow rate, temperature and electrode potential applied at different concentrations. All these methods have their own advantages and disadvantages. The major drawback of these techniques lies in their high-energy application. Membrane-based techniques are quite viable and are highly effective in the removal of metal ions but they still it hold some serious drawbacks. The problem of membrane fouling is one of the most serious and needs proper consideration while application. They have a high cost of application due to high energy consumption. Similarly, ion-exchange resins though highly effective are limited in their applications are limited in solutions with higher metal concentrations. Because of its high surface area and ease of availability, activated carbon is one of the most affordable heavy metal adsorption alternatives. It has a tendency to adsorb various metals such as Ni, Cu, Hg, Zn, Fe, etc. Now adays even wastes such as rice husk ash and fly ash as used as sorbents in the removal of metals from wastewater (Wang and Ren 2014). To overcome the shortcomings of various treatment methods it was necessary to devise some technique which is highly selective, cost-effective and uses natural sources for their operation. Hence, bio-recovery is a new method which is discussed here. It primarily employs plants, their biomasses, and microbial systems for heavy metal removal and recovery from wastewater.

6.3 Biological Methods of Recovery

6.3.1 Bioelectrochemical

Bioelectrochemical system (BES) stands as one of the cleanest and most novel water treatment methods for biorecovery of metals from wastewater. It is a new-age bioengineering technique that generates electrical energy from the chemical energy of biomass by the application of biocatalysts which are mainly exoelectrogenic microorganisms (Syed et al. 2021). BES is a fundamental technology that uses microorganisms to convert chemical energy stored in biomass into electrical energy and chemicals. Because of its ability to provide a common platform for oxidation and reduction-oriented processes, it serves the dual purpose of waste treatment and electricity generation at the same time, as well as resource recovery (Wang and Ren 2014). It is mainly known for its high efficiency, reduced energy consumption and environmentally friendly applications. Furthermore, they function under anaerobic conditions by degrading organic matter via exoelectrogens. These release electrons which move towards the anode by an external circuit and hence electricity is generated (Li et al. 2008; Nancharaiah et al., 2015). A classical BES reactor system constitutes a pair of anode and cathode and an optical separator. The BES system configurations vary as per their target pollutants. Wastewater is oxidized in the anodic chamber by the microbes and generates a current at the cathode. These electrons in the cathode chamber are either used for the direct generation of electricity as common in MFC or oxidize chemicals such as metal ions or organic compounds (Wang and Ren 2014; Wang and Ren 2013).

There are four mechanisms which have been reported for the bioelectrochemical recovery of metals from wastewater as shown in Fig. 6.1. Out of this first method is the direct recovery of metals from wastewater through an abiotic cathode (Fig. 6.1a) using a Normal hydrogen electrode using electron donors and target metals are mostly Cd(II), Cu(II), Fe(III) and Zn(II); the second method is the recovery of metal using abiotic cathodes provided with external sources of energy (Fig. 6.1b) and targets metals with lower redox potentials mainly Ni(II), Cu(II), Pb(II), Cd(II) and Zn(II); the third one is the conversion of metal by bio-cathodes (Fig. 6.1c) and targets Cr(VI), Au(III), As(V), Ag(I), Se(VI) and Se(IV) using a dissimilatory metal reducing bacteria (DMRB) such as *Trichococcus pasteurii, Pseudomonas aeruginosa, Aspergillus niger, Geobacter sulfurreducens, Clostridium,* etc.; and the fourth mechanism is the conversion of metal by bio-cathode with external energy supply (Fig. 6.1d) and targets metals with lower redox potentials and external power sources promotes reduction for metals such as U(VI) and Cr(IV) by bacteria *Geobacter sulfurreducens*. From a microbial fuel cell, exoelectrogenic strains of Castellaniella sp. A5, B3, and A3 were isolated (MFC) and used as bioelectrochemical systems for the generation of bioelectricity and hence can be used in the treatment of industrial wastewater in pure as well as mixed form. They were discovered to be extremely effective at removing Cu, Cd, and Cr metals, with removal efficiencies of 99.8, 99.91, and 99.59, respectively. A microbial-assisted electrochemical system was used to reduce the Cr and Cu in industrial wastewater [which were present in the form of Cr(VI) and Cu(II)]. In the case of Cd(II), precipitation was either in the form of hydroxide or carbonate (Amanze et al. 2022).

6.3.2 Bioprecipitation/Biomineralization

Biomineralization/Bioprecipitation is mainly a process of immobilization of soluble metals into solid forms. Bioprecipitation of metals in wastewater is mainly done using microorganisms through detoxification methods. This technique promotes the removal of metals from their aqueous solutions through solid precipitate and then filtering out by simple solid–liquid extraction (Ike et al. 2017). Fungal metal biorecovery is a novel, cost-effective and highly efficient technology for metal processing, especially for the extraction of cobalt and nickel. *Aspergillus niger has been studied for its ability to biorecover Co and Ni from their phosphates and oxalates.* The use of extracellular polymeric substances promoted the precipitation of these metal ions. Extracellular polymeric substances (proteins or polysaccharides) play a critical role in bioprecipitation processes. They control and regulate nucleation and crystal growth (Yang et al. 2020; Ferrier et al. 2021). A typical bioprecipitation involves the reduction of metals to their lower oxidation states and hence slowing down their mobility. Sometimes, they are even transformed into their elemental forms. The reductive degradation of Se(VI) and Se(IV) to Se(0) using the bacterium Thauera

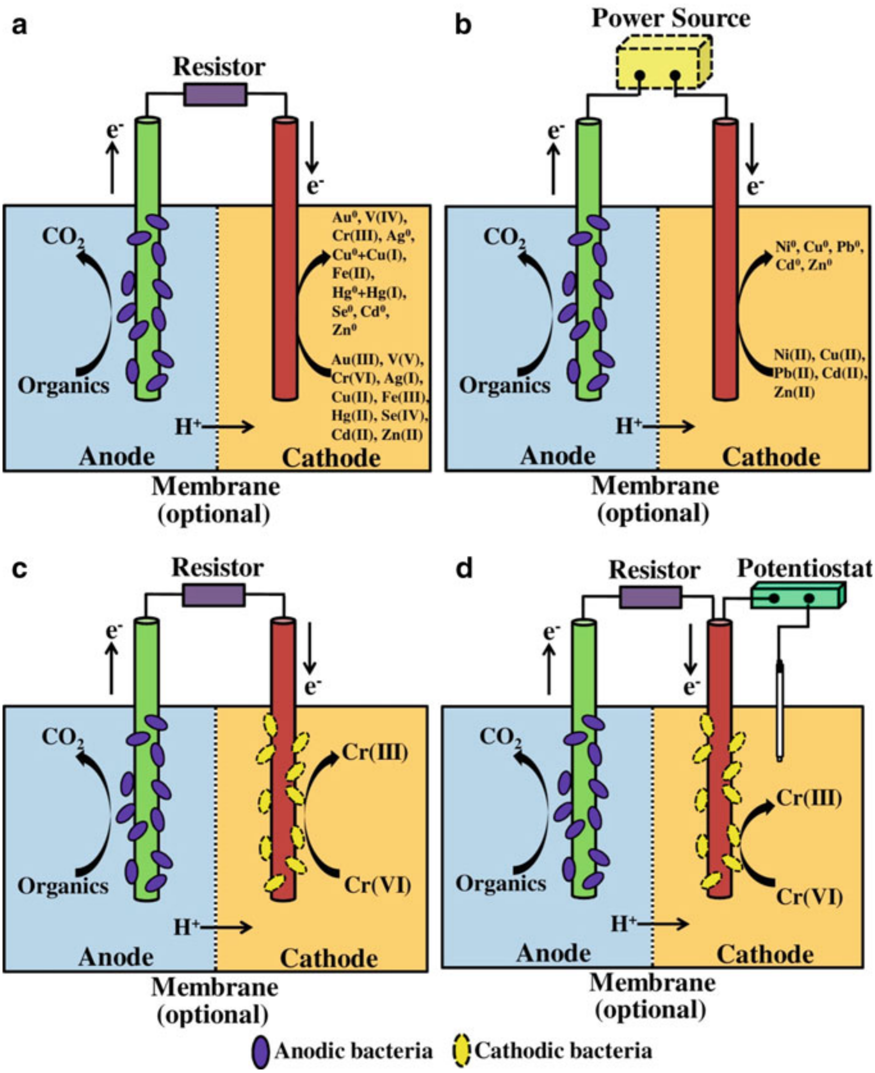

Fig. 6.1 Types of bioelectrochemical systems for biorecovery of metals and their mechanisms [Reprint permissions received]

selanatis has been successfully applied in cleaning drainage water (Cantafio et al. 1996). *Lysinibacillus* has been found to immobilize Pb(II) at a pH of 2 and the best part of using this bacteria is achieving reusability of bacteria (Zhang et al. 2022). *Lysinibacillus fusiformis* DB1-3 bacteria has been applied in the biomineralization of calcium carbonate and magnesium carbonate and leading to the precipitation of these metal ions (Yan et al. 2020). *Bacillus cercus* has an unusual speciality of precipitating Pb(II). In this process of biomineralization, cysteine is degraded intracellularly to

Fig. 6.2 Synthesis of TATS@AC [Reprint with Permission; Naushad et al. 2020]

H_2S which travels to the cell surface and reacts with Pb(II) leading to the formation of PbS (Staicu et al. 2020).

Biological sulphide precipitation is an efficient method for heavy metal biorecovery from wastewater. It mainly employs sulphate-reducing bacteria and the major advantages of this technique are low cost of application, formation of insoluble salts as precipitates and effectiveness at even very low concentrations. Sulphate reduction even under anaerobic conditions is one of the major benefits provided by this method. One such application of SRB is the generation of CdS nanocomposites through biomineralization using biomolecules as precipitating agents and then its further application in the photocatalysis of tetracycline which is an organic pollutant pharmaceutical waste (Ren et al. 2020). *Alcaligenes faecalis* K2 has been found effective in the biomineralization of Cd(II) with an efficiency of 85.5%. The microbe produces Secretory Organo-Biominerals (SOBs) which act as highly effective adsorbent (Ye et al. 2021). The metal sulphides that are extracted in the Nanoscale can be applied in solar cells, photocatalytic dye degradation and electroplating. The removal of metal and its recovery is done either in a single step or multistep. Here are some of the salient features that prove the efficacy of SRB over other conventional techniques of recovery of metals (Kumar et al. 2021):

- Insoluble salts formation even at very low pH (2–3.5)
- Different solubility products of metals with Sulphide lead to high selectivity
- Precipitate settles easily, densely and easily dewatered
- Cost-effective method.

6.3.3 Biosorption

Biosorption is defined as the binding of metals or other chemical ions to the surface of biomolecules from their aqueous solutions (Gautam et al. 2012). It is mainly done using dead biomass as compared to other processes such as bioaccumulation.

This is one of the most well-known non-destructive biological treatment methods for removing recalcitrant compounds. This method mainly depends upon the affinity of sorbate (chemical) and the sorbent (biomass). Metals in wastewater are adsorbed on external polysaccharides, lipids and proteins that are present in the biomass. The biomolecules that are primarily involved in this process include lipopolysaccharides, proteins, peptidoglycans and phospholipids (Kikuchi and Tanaka 2012; Vijayaraghavan and Yun 2008). Temperature, pH, biomass loading, time of equilibrium, biological systems, and metal ion concentration in wastewater all are the factors that affect the sorption potential. Metal ions are adsorbed on the biomass materials through various interactions (Van der Waal, electrostatic, surface precipitation, complex formations or sometimes a combination of two or more forces may be involved). Biomass materials used in this process include a diverse range of biological systems such as bacteria, fungi, algae, plant tissues and wastes, shells of crabs, shrimps, or other sea animals, lichens, and seaweeds. These have been found to be excellent binding materials for metals and have been used as sorbents widely (Kikuchi and Tanaka 2012). Microbial and algal cell walls bind to the metal ions through complexation, electrostatic interactions or ion-exchange mechanisms. The surface of cell walls contains many active functional groups such as hydroxyl, amines, phosphates, carbonyls and carboxyl (Ahluwalia and Goyal 2007).

Some of the bacteria that are capable of biosorption of metals from the wastewater are: *Bacillus licheniformis* (Cr, Cd, Pb, Zn), *Bacillus firmus* (Pb, Cu, Zn), *B. coagulans* (Cr), *B. megaterium* (Cr), *Enterobacter* (Cd, Pb), *Alcaligenes* (Pb), *Ochrobactrum intermedium* (Cu, Cr) etc. (Jacob et al. 2018). Damodar river water was assessed for the presence of heavy metals and it was found to contain Cr(III), Fe(III), Co(II), Cu(II), Ag(I), Pb(II) etc. due to discharge from nearby industrial sources. This water was studied for metal uptake via biosorption using the bacterium Geobacillus thermodenitrificans (st. MTCC 8341), and metal sorption was highly affected by the initial concentration of metals as well as the pH of the sample solution (Chatterjee et al. 2010). Not only microorganisms have been used in biomass but plant materials hold importance too. Sunflower stalk wastes have been used in the adsorption of Cu(II), Zn(II), Cd(II), and Cr(III); coir pith was used in the adsorption of Co(II), Cr(III), and Ni(II); and chitosan was used in the removal of Cd(II) and Cr(III); all of these are examples of non-microbial biomass applications (Gautam et al. 2012). Some of the advantages that are offered by biosorption are a metabolically-mediated fast process with higher cost-effectiveness; easier recovery of metals from the loaded biomass with the use of simple chelating agents such as EDTA; higher performance due to easier physical and chemical treatment; wide range of applications and so on. Hence, biosorption is a great treatment process (Golnaraghi Ghomi et al. 2020).

6.3.4 Biomembranes

Membrane technology has been widely accepted as a treatment technique for wastewater. Many membrane-based remediation methods have been developed for the removal of organic and inorganic pollutants, and have been known for their application for a wide range of pollutants. Silica and zeolites-based biomembranes are very well-known for their diverse range of separation behaviour. Biomembranes are organically derived membranes for the separation of metals from wastewater. They are mainly plant- or animal-based biomasses such as cellulose, gelatin, hemicellulose, chitosan and lignin. The OH^- groups present on the surface of cellulose act as a perfect metal binder. The surface of cellulose is well modified for the adsorption of heavy metals. Polymer-Biomass nanocomposites are also a newly developed technique where polymers are grafted on the surface of biomass as per desired metal to be treated (Kaur et al. 2022). Polyethyleneimine-Grafted Gelatin Sponge has been used to remove lead and Cadmium from wastewater with 90% and 80% efficiency, respectively (Li et al. 2016). An activated nylon-membrane with Chitosan modification has been applied in the removal of Cu(II) ions with a high metal affinity (He et al. 2008). This involved three steps:

- Functionalization of nylon membrane through the deposition of a layer of chitosan.
- Polymer stabilization through cross-linked epichlorohydrin and promoting grafting.
- Grafting using iminodiacetic acid.

Fabrication of Chitosan-Nylon-6 was done using the Solution Blow Method with Nylon to chitosan in 6:4 ratios. This has been done through the replacement of nylon-6 with chitosan. This nanofiber membrane was found to be effective in removing Cu(II) ions from wastewater, with a removal efficiency of around 90% and an 8-times recyclability (Kakoria et al. 2021). Triaminotriethoxysilane is grafted on oxidized activated carbon (TATS@AC) through silanization using an ultrasonicated synthesis approach (as shown in Fig. 6.2). This material has been used for the removal of Cd(II) from wastewater (Naushad et al. 2020).

Chitosan-based Schiff bases (CSBs) form an interesting range of biomembranes. As Schiff bases are well-known for their metal-binding properties, these CSBs biomembranes provide an excellent binding and removal medium for heavy metals from wastewater. These CSBs can easily be tuned as per the need for the target metal ions, and metals can be recovered through acid treatment. For example, Fe_3O_4-coated CSBs are magnetically active and can be applied to the recovery of magnetically active ions (Antony et al. 2019). In Indonesia, a group of researchers studied the membrane biofilter made of banana stem for the separation of lead ions. *Acetobacter xylinum* was used for microbial cellulose preparation from the banana stem. Cellulose acetate was extracted to prepare biomembrane (pore size = 5 microns) using dichloromethane, and it was applied to the removal of lead from wastewater. Efficiency has been found to be around 94% for this biomembrane (Sulastri and Rahmidar 2016). Tomato peels were found to be effective biofilters for a wide range of metal pollutants in another set of experiments, including Cr, Ni, As, and Pb. Propanol was used to remove anthocyanins from the peel, and the peels were washed, dried, and used in the separation of metal ions from their mixed aqueous solutions. This holds a better perspective on the application of plant-based biomembranes (Mallampati and Valiyaveettil 2012).

6.3.5 Bioleaching

It is one of the oldest methods for the biological extraction of metals and has been a part of biohydrometallurgy. It has been applied in the mining of copper at the commercial level. Bioleaching emphasizes the application of chemolithotrophic microorganisms, which produce acid. It holds high potential in recovering precious metals in bioremediation (Gu et al. 2018). This is one of the most effective techniques of metal recovery, and metal-loaded bioleachates is suitable for the extraction of metals. Metal leaching in mineral ores by acidophilic iron- and sulfur-oxidizing bacteria is already a research topic in the biomining industry. *Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans are two such major bacteria that have been widely used in bioindustry to remove toxic metals from polluted water and sludge. Acidithiobacillus ferrooxidans* mainly targets metal sulphides and causes indirect oxidation and *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* both together directly can directly lead to the direct oxidation of sulphides (Gadd 2000). *Acidithiobacillus thiooxidans* was also used for the recovery of Ni from the electroplating wastewater sludge. One kind of Sulphur-reducing bacterium (SRB) plays a major role in the efficient removal of Ni from wastewater and the metal is extracted in the form of precipitates of NiS and Ni (Yang et al. 2015). Ni removal from wastewater with the application of ZVI (Zero-valent Iron)-SRB was done and it was found that ZVI-SRB had very high efficiency (> 98%) as compared to simple SRB systems (Zhang et al. 2016a). In a similar but novel approach, SRB was applied in the biorecovery of MnS. The application of Mn is very high in semiconductors and optoelectronics. Eriochrome Black-T was used as a complexing agent here (Zhang et al. 2016b).

Various classes and sub-classes of microbes that are used in bioleaching are (Gu et al. 2018):

- **Mesophilic bacteria**: Bacteria that grow best at temperatures ranging from 25 to 35 °C.
- **Acidithiobacillus**: Rod-shaped, Gram-negative, Non-spore producing, Aerobic. They oxidize sulphur compounds like sulphides, sulphur and thiosulphates and the final oxidation products are sulphates. *Acidithiobacillus* are most important in this.
- **Leptospirillum**: Use Fe(II) as an energy source. Can work at lower pH (~ 1.2). Targets metals like U, Mo, Ag and high affinity for Cu. Cannot oxidize sulphur compounds.
- **Thermophilic bacteria and Archae**: They are spore-forming bacteria. Can withstand higher temperatures. Thermophiles at extremely high temperatures are called archaea and they can grow above 60 °C. *Sulpholobus* sp. Can utilize Fe(II), elemental S and Sulphides as a source of energy.
- **Heterotrophic bacteria and fungi**: They primarily rely on organic compounds for energy in metabolism. *Bacillus* (bacteria) and *Aspergillus*, *Pencillium* (fungi) are used in bioleaching.

Printed circuit boards from the chip manufacturing industries are heavily loaded with metals such as Ni, Cu, Zn and Pb. In this sequence, *A. thiooxidans* and *A. ferrooxidans* were used as mixed cultures for bioleaching and the result for extraction was reported to be around 94, 89, 86 and 90, respectively, for each metal. The increased redox potential and lower pH of the filtrate indicated that mixed culture was equally involved in the bioleaching processes (Liang et al. 2010).

6.3.6 Bioremediation

Bioremediation is the in-situ application of plants and related microbes or microorganisms to remove harmful contaminants from the environment. It is useful not only for removing polyaromatic hydrocarbons or organic compounds, but it is also very effective for removing heavy metals. The plants or microbes accumulate heavy metals in their vascular or cellular system through metabolic uptake in their vegetative as well as reproductive parts (Rezania et al. 2016). It is an eco-friendly and cost-effective environmental cleaning technique that serves a dual purpose of water as well as soil cleaning together. The uptake of contaminants follows different mechanisms such as phytoextraction (contaminant uptake through root and accumulation in shoot), rhizodegradation (reduction of heavy metal ions into the rhizosphere via rhizospheric microbes), phytovolatilization (conversion of heavy metals to less toxic forms and release into the environment), and phytostabilization are all processes that occur in plants (reduction and assimilation of heavy metals in the roots of the plants). *Eichhornia crassipes*, an aquatic weed, is well known to uptake Cadmium at even very high contamination (Borker et al. 2013). *Brassica juncea, Sedum alfredii* and *Helianthus annuus* are plants that are well known for the phytoextraction of many heavy metals very efficiently (Milner and Kochian 2008). Phytofiltration is yet another method in which free-floating or submerged plants tend to absorb heavy metals from the water. *Some of the plants that have been extensively studied for their role in the phytostabilization of heavy metals from wastewater include Agratis capillaris, Fetuca rubra, and Lupinus albus* (Kidd et al. 2009).

Hg and Se are two very hazardous metals that need special treatment for their biorecovery. In this regard, phytovolatilization methods are among the safest, as these metals are converted to their volatile form and released into the environment via plant leaves or foliage. *Pteris vittata* is one such plant that can easily take up Arsenic and convert it to a volatile form. The best part about phytovolatilization lies in the fact that the plants are not needed to be harvested and disposed of at regular intervals (Sakakibara et al. 2010). The rhizosphere of plants contains sugar, amino acids, flavonoids and many other components much higher than the rest of the plants. The microbes present here produce many organic chelating compounds such as oxalic acid, citric acid, gluconic acids and different types of surfactants. Siderophore-producing rhizobacteria can increase the bio-uptake of Cr and Pb in plants (Braud et al. 2009); *Gluconacetobacter diazotrophicus* can uptake Zn compounds (Saravanan et al. 2007); some rhizobacteria can increase the uptake of Fe(III) and Mn(IV) through redox-mediated uptake processes (Gadd 2010). Microalgae *Scenedesmus incrassatulus* can easily remove Cr(VI), Cd(II) and Cu(II) from wastewater up-to 78%. Similarly *S. obliqus* and *S. quadricauda* also showed good removal efficiency of Zn(II) (Soeprobowati and Hariyati 2012). Some of the other microalgae which are found effective in heavy metals bioremediation from wastewater have been listed below (Goswami et al. 2021):

- *Chlorella* sp. (Pb, Cd, Cu)
- *Chaetoceros* sp. (Pb)
- *Porphyeridium* sp. (Cd and Cu)
- *Spirulina* (Cd)
- *Chlorella vulgaris* (Ni, Zn, Cd, Cu).

6.3.7 Radionuclides Biorecovery

Radioactive metals are rarely a part of industrial wastewater. But, their presence or their impact can never be ignored as they hold some relevance because of their discharge in wastewater from mining and metallurgical industries. Uranium mining is one of the biggest concerns because of its high radioactivity (Gadd and Pan 2016). The major part of Uranium pollution in industrial wastewater is as U(VI) salts and has easily leaching properties, thereby contaminating the groundwater. The hexavalent state of Uranium is soluble, while its tetravalent state is highly insoluble. Most of the chemical-based techniques for Uranium removal are not much effective, and bioremediation has been found to be the most effective of all the available methods (Williams et al. 2013). One of the most widely used methods for removing Uranium from wastewater is bioconversion of U(VI) to U(IV). However, the presence of oxidizing agents in the atmosphere may interfere with the process and make the bioreduction process a completely useless method. Biomineralization of U(VI) can be therefore counted as a more promising method where the phosphate precipitats U(VI) in the form of Uranyl phosphate complex which is completely immobile. Phosphate is released by bacterial phosphatase activity, and Citrobacter is commonly used for this (Macaskie 2007). Since U(VI) has a high reduction potential, it acts as a suitable electron acceptor at the cathode, and hence MFCs can be one of the techniques for biorecovery of Uranium.

The low concentration of U(VI) and sluggish electrode kinetics of Uranium make a need for nitrate ions at the cathode, and the recovery of U(VI) is activated using denitrifying bacteria that flourish at the cathode and generate phosphatase enzyme. The phosphatase enzyme catalyses the formation of phosphate ions, which then form a complex with U. (VI), and recovery is possible. An MFC has been designed in this regard using *Pseudomonas* sp. at the cathode with glycerol 3 phosphate (Genders et al. 1996; Vijay et al. 2020). *Landoltia punctata* was found effective for the elimination of U(VI) by forming insoluble nano uranium (in IV and VI oxidation state) phosphate in both healthy fronds as well as dead biomass. This remediation process is entirely pH dependent of the wastewater and the initial Uranium concentration, and it has been established that the accumulation capacity of biomass is four times that of living fronds. The process follows the sequence of biosorption followed by bioreduction of Uranium and ultimately biomineralization of Uranium as uranium phosphate (Nie et al. 2017).

6.4 Limitations

Despite the fact that biorecovery processes provide excellent opportunities for heavy metal removal and replenishment from wastewater, their limitations cannot be neglected at all. Some of the important points that are quite important have been discussed below:

- The biosorption process is highly dependent on various factors such as ionic strength, and pH of surrounding ions and suspended impurities in wastewater. The pH needed for the metal ions sorption is majorly neutral; however, the pH of wastewater is generally lower. *Sphaerotilus natans* is a Gram-negative bacterium that has been used in Cu biosorption. High ionic strength negatively impacts the biosorption process (Beolchini et al. 2006). Besides this hardness of water also plays a key role in the biosorption processes. Ca and Mg-induced water hardness has been found to have a significant impact on the biosorption of Fe and Al in industrial wastewater (Lee et al. 2004).
- Biological sulphate reaction, even though it holds multiple advantages over conventional systems, has some serious limitations as well. As it is very well established that this process leads to the formation of metal sulphate, the toxicity of metal sulphates cannot be undermined. If anyhow, these metal sulphates leach into the environment, they can cause serious troubles, especially if the leachates are in the Nanoscale range. The toxicity of nanosized metal sulphates is already well-established for living beings (Kumar and Pakshirajan 2019).
- Bioelectrochemical cells, even though highly clean and viable technology, hold certain limitations. The purity of H_2 generated by microbial electrolytic cells is much higher than in other hydrogen production methods. The H_2 gas produced is accompanied by CO_2. The rate of H_2 generated reduced as the process went on. Most of the BES from the suggested literature showed lower hydrogen generation and decreased current density when applied at the pilot level. Some of the factors that highly affect this phenomenon of the electrochemical system are the geometry of the reactors, material of the electrode, glass fibre-based separators, general electrical resistances and microbial factors that slow down the starting of the reactor (Wilberforce et al. 2020).
- Biomembranes are a promising candidate for separating metal ions from wastewater. There are varieties of pure and composite as well as polymer-grafted biomembranes that are applied for metal ions removal. They are cost-effective, low energy consuming and the cleanest method available. However, the application of biomembranes is limited as the pore diameter of biomembranes ranges around that

of the size of hydrated metal ions. Due to this, sometimes the pores are clogged. Biomembranes need to be cleaned and replenished from time to time to prevent biofouling and membrane protection. Self-cleaning biomembranes and composite biomembranes that prevent bacterial growth will surely be a help in this.

6.5 Conclusions

Metal ions and their biorecovery have been discussed in quite a detail in this chapter. As we have seen, water and metal both hold an essential position in modern times and their demand will keep on increasing with the increasing population. Also, heavy metals are well known for their toxicity and thus, their removal from wastewater is an important thing needed to be taken care of. Several physical and chemical methods for recovering heavy metals from wastewater have already been proposed. These included coagulation, filtration, electrodialysis etc., which were less effective and highly expensive with the production of secondary pollutants/contaminants and sludge. Most of the physical and chemical techniques of biorecovery were not that effective and needed combination of two or more technologies for their success. Biorecovery, which is not an old-school method, played a great role in the metal recovery from wastewater. As we passed through different biorecovery processes, we have come across many methods. BES system has been found to be the most novel and cleanest recovery treatment for metals in wastewater. It depends on the generation of electric current with separation application, hence, serving the dual purpose of cleaning and energy production. It has been proved to be effective for a variety of heavy metals including Fe, Cu, Cd, Zn, As, and Ni. Biomineralization or Bioprecipitation involves the immobilization of metals from their aqueous solutions into solid surfaces or as precipitates. This is primarily used as microbe applications and has been used for metal removal such as Se, Pb, Cd, and others. This process also promotes nanoscale sulphides and oxides formation from the metals and their further applications in environmental cleaning. Biosorption of metals on the surface of biomass is an adsorption-based process where biomass serves as sorbent and metals in wastewater act as sorbate. The interaction may be physical or chemical, or both, depending on the outermost layer of biomass. Biomembranes, as already been discussed, are an old but reliable technique for wastewater treatment and are applied to a variety of metals. Bioleaching is the oldest method for extraction of metals and has been part of the biometallurgy and biomining industries. It uses acidophile and thermophile bacteria for the extraction of metals from their sources. It mainly relies on sulphur-reducing bacteria and Fe, Ni, Zn target metals and radionuclides. Bioremediation applies plants or microbial systems for the removal of harmful metal ions from wastewater. They take up metal ions within their cellular or tissue structure and store them. Metals can be extracted from them after a certain time frame. Radionuclides can also be recovered from their wastewater by the different methods discussed above. All of the methods discussed in this chapter are clean, energy-efficient, and highly specific techniques for heavy metal biorecovery from wastewater. In contrast, each of them comes with one or the other limitations which need to be taken into account before their pilot-level application.

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Chapter 7
Book—Resource Recovery from Wastewater Through Biological Methods Publisher—Springer Nature

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Abstract Environmental contamination caused by various toxins has become a global problem. The discharge of various metals from factories, agriculture, and other facilities into water is the cause of water pollution. Due to industrialization and urbanisation, the treatment of wastewater is regarded as the greatest challenge in both emerging and industrialised nations. Approximately 80% of wastewater is dumped straight into water streams without treatment, causing climate, environmental, and health problems. Treatment of wastewater prior to its discharge is crucial for minimising the negative effects of wastewater. There are various methods for treating wastewater, including conventional and modern technologies. This review focuses on the utilisation of microorganisms such as bacteria, algae, and fungi, as well as contemporary developments in wastewater treatment, to recover heavy metals and reuse water.

Keywords Heavy metals · Wastewater · Advancements · Sources · Methods · Treatment

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Abbreviations

Hg	Mercury
Ni	Nickel
Cr	Chromium
Zn	Zinc
Pb	Lead
Cd	Cadmium
Cu	Copper
Co	Cobalt
Al	Aluminium
Fe	Iron
As	Arsenic
Ag	Silver
Bi	Bismuth
Mn	Manganese
Sn	Tin
Th	Thorium
Sb	Antimony

7.1 Introduction

About 71% of the planet's surface is covered by water. It serves multiple applications, including gardening, washing, cooking, bathing, and as a coolant in industries. The used water is released as wastewater. This effluent lacks aesthetic and commercial value, threatening the health and sustainability of water bodies and the marine species dependent on these water bodies (Sonune and Ghate 2004). Approximately 70–80% of all provided water is discharged as effluent. Microorganisms, bacteria, nutrients, suspended particles, minerals, and hazardous metals are present in this effluent, posing a severe threat to human health (Metcalf et al. 1991). Heavy metals are regarded as extremely hazardous pollutants. Cadmium, arsenic, copper, chromium, mercury, lead, zinc, and nickel are carcinogenic, persistent, and dangerous elements that can accumulate in the environment and in humans (Yusuf 2019; Lellis et al. 2019). As a result, extensive research has been conducted on the treatment of wastewater to discover novel methods for cleaning wastewater containing heavy metals. Physical, chemical, and biological approaches are included. Traditional physical and chemical wastewater treatment techniques include screening, sedimentation tank, skimming, flotation, aeration, adsorption, membrane technology, grit chamber, granular filtration, ion exchange, UV light, ozone, chemical precipitation, advanced chemical oxidation, and chlorine disinfection (Bhargava 2016; Esfahani et al. 2018; Mintening et al. 2017; Iskurt et al. 2020, Dhangar and Kumar 2020, Ahmed et al. 2021; Choi et al. 2020). Due to limited finances, a lack of expertise, and design problems, these treatment processes do not improve treatment efficacy. In contrast, biological technologies such as bacteria, algae, and fungi are viable alternatives to conventional methods for treating wastewater effluents (Zhu et al. 2019a, b). In biological approaches, microorganisms aid in the treatment of effluents by immobilising the molecular structure of heavy metals, which results in a partial breakdown, mineralization, and transformation of pollutants (Varjani et al. 2020). For the treatment and recovery of heavy metals, biological methods have made great advances in recent years. To increase the recovery of pollutants from wastewater, a number of innovative technologies are being developed. These technologies or procedures are chosen based on the quality of the wastewater to be treated and other parameters, such as the presence of volatile solids, chemical oxygen demand, and heavy metal concentration. These technologies can be utilised in both combined and independent fashions (Armah et al. 2020). Modern technologies employing microbes have also been examined in depth in this chapter.

7.2 Sources of Heavy Metals in Wastewater

A vast array of activities occurring naturally as well as carried out by living organisms lead to contamination of basic components of the environment i.e., air, water and soil. Among the various contaminants being added to the environment, Heavy metals (HMs) are one of the toxic elements which are found in enormous quantities in different water bodies may it be rivers, ponds, lakes etc. The different sources which lead to the introduction of HMs in these water bodies may be natural, agricultural, industrial or domestic in addition to some other anthropogenic activities. These are discussed in detail in Table 7.1.

7.3 Methods of Recovery of Heavy Metals from Wastewater

Water contaminated with different concentrations of different HMs is unsuitable for use in any kind of agricultural or industrial activity. Also, if such kind of water is discharged into the environment directly, it may make entry into the plant system and pose a serious threat to the normal growth and development of plants. Some harmful effects of the intake of metallic water by humans include respiratory problems, arthritis, diarrhoea, paralysis, vomiting and pneumonia (Kumar et al. 2021). Therefore, to make it fit for sustainable application, it is subjected to treatments by different methods. These methods may be physical, chemical or biological. These methods are employed for the removal of HMs from wastewater so that both HMs and water treatment can be used separately for different purposes. Each of these different methods is based on different principles for extraction of HMs from metallic wastewater and is discussed in detail in the following subsections.

Table 7.1 Sources of heavy metals in wastewater

S. No.	Name of source	Activities leading to HM pollution	Reference
1	Natural	• Weathering of geologic igneous rocks	
2	Agricultural	• Application of organic and inorganic fertilizers • Pesticide spray leading to the introduction of Cd • Continuous application of fungicides, insecticides and herbicides • Animal manures, liming and sewage sludge application to crop plants	Mohod (2015), Zhou et al. (2016), Kalali et al. (2011)
3	Industrial	• Coal mining leads to the production of effluents rich in As, Cd, Fe, etc. • Gold mining is a major source of Hg pollution in water bodies • Smelting occurring at high temperatures leads to the vaporization of HMs which combine with atmospheric water to form aerosols that are then introduced into water by rain or wind • Surface run-off of dust and waste produced from mining industries and leaching of HMs into water • Textile and paper industries processing operations • Electronic mining activities along with wood preserving industries	Wang et al. (2022), Kumar et al. (2021), Verma and Dwivedi (2013)
4	Domestic	• Water remnants left after biological treatment • Sewage sludge discharged into water bodies • Ionic detergents used for household activities	Kaushik and Singh (2020), Wang et al. (2020), Wang and Ren (2014)
5	Other sources	• Burning of solid wastes in closed sites at very higher temperatures • Landfill sites • Production of fumes from automobiles, aircraft and other vehicles • Burning of fossil fuels mainly coal	Bhatia et al. (2017), Vikrant et al. (2018)

7.3.1 Physical and Chemical Method

Heavy metal pollutant elimination from wastewater may be accomplished using chemical, physical and biological methods. The physical and chemical methods are well-established and well-known way from ancient times (Singh et al. 2022). Some of the frequently used physical wastewater treatment methods are screening, sedimentation, skimming, aeration, adsorption, comminution, flow equalization, flotation, thermal treatment, granular-medium filtration, membrane-based technology and so on. And some of the frequently used chemical methods are Ion exchange, Disinfection with chlorine, ultraviolet (UV) light, Ozone, Neutralisation, Precipitation, Conventional Chemical oxidation (Photolysis, Ozonation, Fenton process) and Advanced chemical oxidation (Photocatalysis, Photo-Fenton) etc. (also shown in Fig. 7.1).

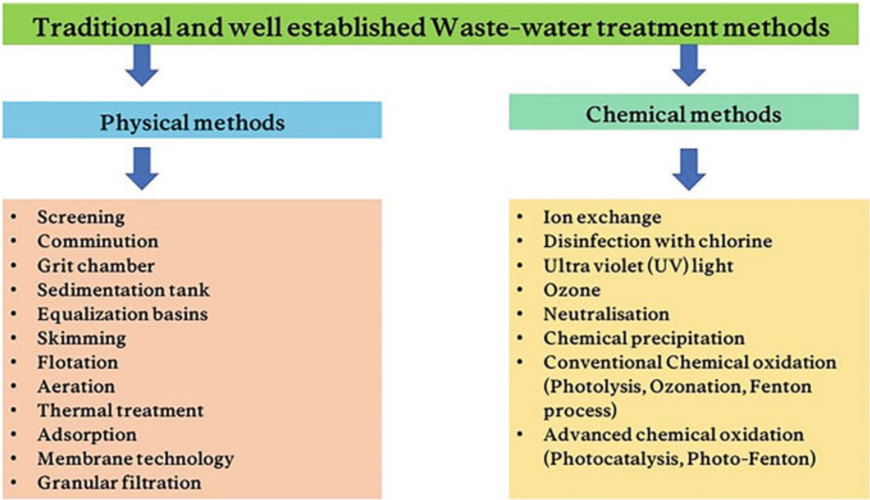

Fig. 7.1 Detail illustration of types of physical and chemical wastewater treatment methods

The physical process is contingent upon mass transfer (Samsami et al. 2020). Physical treatments are technologically easy, versatile, and adaptable to a variety of treatment designs since they utilise simple equipment (Ahmed et al. 2021; Crini and Lichtfouse 2019). Screening, sedimentation, and skimming are the physical pre-treatment processes for wastewater treatment (Ahmed et al. 2021). Following is an overview of all physical techniques in Table 7.2.

Chemical treatment involves a sequence of chemical reactions that aid in the disinfection of wastewater (Diamond et al. 2018). Chemical wastewater treatment procedures are used when mechanical and biological approaches aren't enough to enable treated water to enter aquatic bodies. Some agricultural and industrial wastes need chemical treatment because of hazardous pollutants (Moharir et al. 2019). Some chemical methods for treating wastewater are ion exchange, disinfection with chlorine, ultraviolet (UV) light, ozone, neutralisation, and precipitation (Ahmed et al. 2021; Collivignarelli et al. 2017). The chemical oxidation method is one of the chemical treatment strategies that has recently developed as new technology (Ahmed et al. 2021). In this approach, chemical oxidants are used to convert pollutants into a form that can be controlled and is not harmful to humans. Wastewater with low levels of chemical oxygen demand (COD) is often treated via the chemical oxidation method for the removal of contaminants. Chemical oxidation uses oxidants to remove impurities and convert pollutants to harmless by-products (e.g., water, carbon dioxide) (Kao et al. 2020). However, wastewater with a greater COD must be treated with additional, costly chemicals using an Advanced Oxidation Process (AOP). Some of the advanced oxidation methods used to clean up wastewater are the photo-Fenton, photocatalysis, and solar-driven processes (Gutierrez-Mata et al. 2017). Therefore,

Table 7.2 Detail illustration of physical methods used for wastewater treatments for the recovery of contaminants

S. No.	Type of physical method	Principle characteristics for wastewater treatment system and recovery of contaminants	References
1	Screening	Eliminate big, floating solid debris that can obstruct subsequent treatments	Naidoo and Olaniran (2014)
		Screening may be of two forms: fine screening and coarse screening, depending on the types of pollutants that are removed Coarse screening eliminates particles, dirt, and rags larger than 6 mm, whereas fine screening removes 0.001–6 mm solids	Bhargava (2016)
2	Comminution	When the screening method is unsuitable, comminution is used. During this process, different types of cutters are used to break up the solid materials. Cutters are usually inserted between the grit chamber and the sedimentation tank. Crushed debris is separated from wastewater	Chauhan and Kumar (2020)
3	Grit chamber	Isolating of the materials that are floating independently. A grit chamber sediments big solid particles to prevent system clogging. There are different kinds of grit chambers based on their size, characteristics, and purpose i.e. Horizontal flow, vortex flow, and aeration grit chambers	Esfahani et al. (2018)
4	Sedimentation tank	In the sedimentation tank, heavier solids are separated from liquid sludge	Esfahani et al. (2018), Naidoo and Olaniran (2014)
		Additionally, biologically contaminated sludge is separated from water in sedimentation tanks	Pickering and Hiscott (2015)

(continued)

Table 7.2 (continued)

S. No.	Type of physical method	Principle characteristics for wastewater treatment system and recovery of contaminants	References
5	Equalization basins	Improve the efficacy of secondary and tertiary wastewater treatment levels by reducing flow and pollutant levels and by regulating system temperature	Verlicchi et al. (2015), Khatri et al. (2020)
6	Skimming	Skimming removes oil, grease, and fat-like particles. Depending on the quantity and kind of oil-like impurities, skimmer types (wire, brush, disc, etc.) vary. The process of skimming can only be used to get rid of particles that are less dense than water	Mintenig et al. (2017)
7	Flotation	Physical method that may be utilised in place of skimming. Flotation uses fine gas particles to separate solid or liquid pollutants from wastewater. There are different kinds of flotation methods based on the type of mechanism used. For example, in air flotation, the gas compounds are introduced through a rotating impeller. In vacuum flotation, air is introduced in an aeration tank or through the suction side of the pumps. More pollutants (e.g., solids, liquid, oil, gaseous contaminant) may be separated from wastewater using this method	Bhargava (2016)

(continued)

Table 7.2 (continued)

S. No.	Type of physical method	Principle characteristics for wastewater treatment system and recovery of contaminants	References
8	Aeration	Aeration is another gas-based physical treatment method used in hybrid processes. This approach uses air to collect gaseous, dissolved, and volatile organic pollutants. In most large-scale wastewater treatment plants (WWTPs), this is one of the first procedures that is implemented. This physical technique aids chemical and biological treatments. Before chemical treatment, aeration removes nutrients from household water or electrochemically oxidises it. Even biological wastewater treatment needs pure oxygen aeration	Iskurt et al. (2020), Jehawi et al. (2020), Skouteris et al. (2020)
9	Thermal treatment	Along with aeration method, thermal treatment, which may remove pollutants under specific circumstances, is another significant physical pre-treatment	Bhargava (2016), Yaqoob et al. (2020)
10	Adsorption	Adsorption is the term used to describe the physical process of removing soluble molecules by the attachment of adsorbent (solid substrates). Adsorbents must be activated before use by removing adsorbates. Activated carbon is used to activate adsorbents smoothly and effectively. Adsorption removes organic, inorganic, and hazardous heavy metals pollutants	Samer (2015), Dhangar and Kumar (2020)

(continued)

Table 7.2 (continued)

S. No.	Type of physical method	Principle characteristics for wastewater treatment system and recovery of contaminants	References
11	Membrane technology	Membrane technology filters pollutants based on their size and characteristics over a membrane. Hydrostatic pressure drives membrane filtration. The pore size of a membrane might affect membrane technology or filtration	Ahmed et al. (2021)
12	Granular filtration	In addition to membrane-based filtration, granular filtration can be employed to remove pollutants on a smaller scale. Water flows through layers of granular filter beds, isolating contaminants in the process	Ahmed et al. (2021)

two general approaches to chemical oxidation treatment exist, conventional oxidation and advanced oxidation (Buthiyappan et al. 2016). A detail of all the chemical methods i.e. conventional and advanced oxidation approaches was given in the following Table 7.3.

7.3.2 Biological Methods

Biological methods of recovery of heavy metals from wastewater are an efficient, cheap, and eco-friendly adsorption approach. These methods have a fast operative time and are most appropriate for the spontaneous adsorption of heavy metal ions. There are two phases of biological methods which include biological adsorptive (solid phase) and a solvent (liquid phase). The mechanism of adsorption of heavy metal ions includes adsorption, and evacuation (using organic acids, mineral acids, or electro- or thermochemical methods) (Patel 2021). Various factors like biological material, adsorbate type, pH of dyes, and initial level of heavy metal ions all stimulate the biological adsorption method i.e., independent of metabolic activities within the cell wall. Moreover, the process was little affected by temperature but sturdily influenced by the concentration of adsorbate, and pH (affected the chemistry of metal ions, and the activity of the functional group of adsorbates). Therefore, due to this effective performance, and cheapness, a wide variety of biological materials like algae, fungus, yeasts, and bacteria have gathered more consideration for heavy metal ions removal from wastewater (Singh et al. 2022).

Table 7.3 Illustration of some chemical methods used for wastewater treatments for the recovery of contaminants

S. No.	Type of chemical method	Principle characteristics for wastewater treatment system and recovery of contaminants	References
1	Chemical precipitation	In the precipitation procedure, a dissolved substance is transformed into a non-soluble substance, which can then be filtered out	Ahmed et al. (2021)
2	Photolysis (solar and UV rays photolysis)	Photolysis is the process by which hydroxyl radicals are created when energy is transmitted from electromagnetic radiation to water molecules, causing them to break apart. Solar and UV rays may cause photolysis. Photolysis is a cost-effective technique since it doesn't need catalysts or oxidising agents	Cuerda-Correa et al. (2019), Choi et al. (2020)
3	Ozonation	Ozone is a powerful oxidizer that may react with organic and inorganic compounds. Since no toxic by-products are created in ozone reactions, this chemical has been used extensively in wastewater treatment. Ozonation increases wastewater biodegradability by oxidising it with ozone. In recent years, the process of catalytic ozonation has been widely acknowledged as a potentially fruitful method for the treatment of wastewater	Coca et al. (2016)
4	Fenton oxidation	Hydrogen peroxide and ferrous ions are utilised in the Fenton oxidation process to generate hydroxyl radicals. This technique eliminates harmful organic compounds in wastewater. In addition, the Fenton method has been recognised an environmentally friendly method for flotation, dehydration, and wastewater treatment. In addition to the Fenton method's effectiveness in reducing heavy metal concentrations such as copper, chromium, and aluminium, etc.	Ahmed et al. (2021), Borah et al. (2020), Chen et al. (2020)

(continued)

Table 7.3 (continued)

S. No.	Type of chemical method	Principle characteristics for wastewater treatment system and recovery of contaminants	References
5	Photocatalysis	Method uses catalysts to aid the transmission of energy from a light molecule to a water molecular. UV photocatalysis reduces total carbon content (TOC) three times more efficiently than colour reduction	Johnson et al. (2019)
6	Photo-Fenton process	The photo-Fenton process is the result of the combination of the Fenton reaction and exposure to UV light. As a result of the creation of hydroxyl radicals, the synthesis of secondary chlorinated compounds is restricted in this process, which is one of the reasons why it is considered to be an effective approach for the purification of wastewater. This technique of cleaning wastewater is easy, cost-effective, and very effective at removing pollutants, especially antibiotics	Barrera-Salgado et al. (2016)

7.3.2.1 Remediation by Algae

The adsorption process of heavy metal ions by algae includes metal ion absorption and selectivity of the substrate. Among all algal species, the brown algal species are more effective and commonly used due to their genetic makeup like cell wall characteristics which is more important for the absorption of metal ions. This adsorption of metal ions is an external process in which the groups (sulfhydryl, carboxyl, amino, and sulfonate) that are engaged in the adsorption process (Geng et al. 2022). However, peptidoglycans, proteins, and polysaccharides (sulfated polysaccharides, alginic acid) are structural compounds that institute the cell wall of algae. The mechanisms of adsorption of metal ions by algae includes exchange of ions. There is a new purifying technology using biological-based algal species to treat metal contaminated water and soil.

This technique gained attention in the resource recovery of metal ions from wastewater using various methods. Biological method using algal species is more eco-friendly, efficient, and precised because the converted organic metal product is harmless and stable (Bhatia et al. 2017). Sarkar and Dey (2021), reported the following advantages of utilizing algae for wastewater treatment. It maximise the population of cell in a short period of time, has capability of minimizing the negative impact of metal adsorption mechanism and sequestration of CO_2, has the ability to grow in any kind of water (fresh, sea, waste or saline), is unaffected by harsh weather changes, improves alleviating property and also produces stable and valuable end products.

7.3.2.2 Remediation by Fungi

Mycoremediation can be an eco-friendly and cost-effective approach to degrade and capture the contaminants from the soil. Fungi are regarded as biosorption agents for the remediation of heavy metals from wastewater. The toxic metal species directly come in contact with fungal cell wall; therefore the components present in their cell wall have a high binding affinity for metal ions. The cell wall is composed of polysaccharides like chitin (N-acetyl glucosamine units), chitosan, glucronic acid, glucan, mannon and small traces of glycoproteins (Zhu et al. 2019a, b). *Saccharomyces cerevisiae Aspergillus niger*, *A. fumigatus, Penicillium simplicissimum, P. brevicompactum, Trichoderma* and *Termitomyces clypeatus*, etc. are some fungal species aid for elimination of heavy metals from wastewater (Rana et al. 2019a, b; Yadav et al. 2019a, b). The cell components containing different functional groups such as carboxyl (–COOH), hydroxyl (–OH), phosphate (PO_4^-, PO_3^-), amine (–NH_2) and sulfhydryl (–SH) perform an important role in the absorption of heavy metal ions (Yin et al. 2018). Metal ions interacted with fungal cell wall through various mechanisms such as complexation, ion exchange, precipitation and adsorption. In the fungal cell, biotransformation of metal ions occurs by oxidation, reduction dealkylation and methylation which lessen their toxicity effects through volatilization. The fungal hyphae are easy to grow due to their short life cycle and are cheaper than other conventional techniques, therefore a large amount of fungal biomass is used in industries for fermentation and the removal of toxic metals from polluted water (Siddiquee et al. 2015). The factors that affect the growth of filamentous fungi are medium/solute concentration (Potato dextrose medium), biomass nature and concentration, and physicochemical characteristics such as pH, temperature, oxygen and moisture contents. The lignocellulolytic enzymes of fungi are good adsorptive agents for oxidizing aqueous pollutants. *Funneliformis geosporum, a* mycorrhizal fungus, accumulates Zn from the soil and enhanced the growth and yield of *Triticum aestivum.* Table 7.4 summarizes the biosorption and bioaccumulation of heavy metals by non-pathogenic fungal strains.

7.3.2.3 Remediation by Bacteria

Earthly biomass shares a plethora of microbial populations that have a large fraction of diverse bacterial populations. (Singh et al. 2022). These bacterial populations reside in the soil, as well as free-living populations, or can act as symbionts in the vicinity of roots of different plant species. However, these bacteria are also found as by-products of multiple fermentation processes. Among these bacterial populations, certain bacterial strains like *Micrococcus, Bacillus, Streptomyces, Pseudomonas,* and *Escherichia* etc. have their ameliorative roles in the removal of different Heavy

Table 7.4 Bio-recovery of heavy metals by different fungal strains

S. No.	Fungal strains	Heavy metals	Source of contamination	References
1	*Cladosporium* sp., *Didymella glomerata, Fusarium oxysporum, Phoma costaricensis,* and *Sarocladium kiliense*	Hg	Chloralkali plant in Turda, Cluj County, Romania	Văcar et al. (2021)
2	*Kalmusia italica*	Ni. Cr, Zn, Pb	Soil samples from untouched soil from the Andaman Islands	Sumathi et al. (2021)
3	*Aspergillus niger, Penicillium chrysogenum* and *Rhizomucor* sp.	Cd, Pb, Zn	Refuse dumpsite soil samples from Tudun Fulani, Nigeria	Bala et al. (2020)
4	*Trichoderma, Penicillium,* and *Aspergillus*	Cu, Co	–	Dusengemungu et al. (2020)
5	*Rhizopus arrhizus*	Cu	Soil samples from agriculture field in Meerut, Uttar Pradesh, India	Chauhan et al. (2020)
6	*Aspergillus niger* and *Penicillium simplicissimu*	Al	Low-grade bauxite, from Alcoa, SP, Brazil	Shah et al. (2020)
7	*Paecilomyces* sp., *Penicillium* sp., and *Aspergillus niger*	Co(II)	Wastewater dumps from Tanque Tenorio, México	Cárdenas González et al. (2019)
8	*Aspergillus tamarii* NRC 3	Pb^{2+}, Co^{+2}, Ni^{2+}, Fe^{+3}, and Cr^{3+} in addition to Cu^{2+}	Industrial effluent from the Egyptian Company for leather tanning (El-Basateen, Cairo)	Saad et al. (2019)
9	*Penicillium chrysogenum* and *Aspergillus ustus*	Cd (II), Cu (II), and Pb (II)	Wastewater samples collected from Western, Eastern, and Northern region of Saudi Arabia	Alothman et al. (2020)
10	*Aspergillus flavus*	Pb, Cd, and Zn	Contaminated soil sample from a smelting industry site, located in Zhuzhou City, Hunan Province, China	Qayyum et al. (2019)
11	*Aspergillus niger* (M1DGR), *Aspergillus fumigatus* (M3Ai), *and Penicillium rubens* (M2Aii)	Cd and Cr	Samples from contaminated soil at Hattar Industrial Estate, Pakistan	Khan et al. (2019)

(continued)

Table 7.4 (continued)

S. No.	Fungal strains	Heavy metals	Source of contamination	References
12	*Fomitopsis meliae, Trichoderma ghanense and Rhizopus microsporus*	Cd, Cu, Pb, As, Fe	Soils from gemstone and gold mining sites in South western, Nigeria	Oladipo et al. (2018)
13	*Penicillium chrysogenum*	Cu^{2+} and Cr^{6+}	–	Xu et al. (2018)
14	*Pleurotus eryngii*	Pb, Zn, Cr, Co, Cu and Zn	Coal washery effluent	Vaseem et al. (2017)
15	*Funneliformis geosporum* (Mycorrhizal fungi)	Zn	Contaminated soils from rhizosphere of *Hibiscus sabdariffa* L., *Zea mays* L., *Lycopersicum esculentus* L., *Cicer arietinum* L. and *Triticum aestivum* L. from Assiut Governorate, Upper Egypt	Abu-Elsaoud et al. (2017)
16	Aspergillus alliaceus, *Trichoderma harzianum, Clonostachys rosea*	Ag	Samples from waste-rock dumps (Libiola Mine, Italy)	Cecchi et al. (2017)
17	*Acremonium persicinum, Penicillium simplicissimum, Seimatosporium pistaciae, Trichoderma harzianum, Alternaria chlamydosporigena and Fusarium verticillioides*	Cd, Pb, Zn and Cu	Samples from lead–zinc mining in Zanjan Province, Iran	Mohammadian et al. (2017)
18	*Aspergillus flavus* and *Aspergillus niger*	Cu, Pb	Wastewater-treated soil samples of Hudiara drain, Lahore	Iram et al. (2015)

metals (Kapahi and Sachdeva 2019; Iravani and Verma 2020). Bacterial cell walls are potential HMs chelating mediators as well as secrete certain polysaccharide slime layers with unique affinities to bind with the HMs. These bacteria involve a two-step process to adhere the HMs ions to the reactive groups present on the bacterial cell surfaces. Whereas the 2nd step involves the deposition of HMs ions on the peptidoglycan chain of glutamic acid through its carboxyl ends. However, bacteria also lead in metabolism-independent methods to absorb HMs (Singh et al. 2022).

Bacterial populations are highly effective in removing the dyes or discolouration of dyes through consortia as well as pure cultures. However, the bacterium consortium is much more effective in comparison to the pure isolates in removing the dyes. Roy et al. (2018) found that the application of *Enterobacter* sp. CV-S1 inoculates to Crystal Violet dye shows its discolouration effects within 72 h of this bacterium application at pH 6.5 and at a temperature of 35 °C. RNA sequencing of the 16 s ribosomal entities of *Enterobacter* sp. CV-S1 has concluded the effective roles of these biodegradable catalysts in removing the CV dyes. On the other hand, Kalaimurugan et al. (2020) found that the inoculations of two bacterial species *Bacillus safensis* and *Pseudomonas fluorescens* have potential roles in the removal of Cr with 72 and 84% after its effective application. Further different studies have been done on the role of bacterial species in the removal of metals which are tabulated in Table 7.5.

7.4 Reactions by Microbes for Metal Recovery

Microbes have an impact on the geochemical cycles of metals as they play a vital role in catalyzing metabolic reactions of various metal elements (Gadd 2010). These reactions involve oxidation, reduction, methylation, hydrogenation, and alkylation that modify the redox state of metal. The microbes have developed an ability to the influx and efflux metal ions; concurrently they utilize metals as minor nutrients. Relatively, as metal reacts with metal-binding proteins, and acids inside microbial cells or in the environment, the behaviour of the metal is changed. Hence, these microbe–metal interactions lead to the conversion of metals into a soluble form or gaseous form resulting in easy recovery of metals from wastewater as shown in Fig. 7.2. Microbial processes available for metal recovery can be classified into bio volatilization, biosorption, bioleaching and bioprecipitation/biomineralization.

7.4.1 Biomineralization/Bioprecipitation

Biomineralization/Bioprecipitation is a process that leads to restricting the motion of soluble metals by binding them to the solid phase (Gadd 2000). Removal of metal from the water phase is based on solid–liquid separation methods. The microbial metabolic reactions cause bioprecipitation, most commonly by the process of reduction. It changes metal into a lower redox state resulting in reduced metal mobility. Also, microbial reduction transforms metal into a less soluble form facilitating its precipitation (Oremland 1994). Se was successfully removed from wastewater by reductive microbial reactions. Cantafio et al. (1996) used Se (VI)-reducing bacterium *Thauera selanatis* to treat drainage water. Similarly, microbial reduction processes transmute extremely soluble Cr(VI) into less soluble Cr(III). This reaction aids in the reclamation of wastewater (Shen et al. 1996). Also, metals like antimony (Sb), vanadium (V), gold (Au), Ag, palladium (Pd), molybdenum (Mo), technetium

Table 7.5 Role of different bacterial species in the removal of metals and dyes

S. No.	Bacteria species	Heavy metal/ Dye removed	Effectiveness in removing dyes and HMs (%) and effective pH	References
1	*Micrococcus luteus*, *Bacillus megaterium*, and *Bacillus pumilus*	Azo dye, namely Remazol Blue	23.7–69.9% at 7 pH	Karatay et al. (2015)
2	*Bacillus aryabhattai* DC100	Dyes Coomassie Brilliant Blue G-250 (CBB), Indigo Carmine (IC) and Remazol Brilliant Blue R (RBBR)	14–50%	Paz et al. (2017)
3	*Bacillus* sp. VITAKB20 and *Lysinibacillus* sp. KPB6	Azo dyes Reactive Orange 16 (RO-16) and Reactive Blue 250 (RB-250)	*Bacillus*. sp. VITAKB20 degrade 92.38% of RO-16 and *Lysinibacillus* sp. KPB6 degraded 95.36% of RB-250 under static conditions	Pandey et al. (2020)
4	*Stenotrophomonas rhizophila* (A323) and *Variovorax boronicumulans* (C113)	Zn, Pb, and Cd	*S. rhizophila* removed 96.25% (Pb), 71.3% (Cd), and 63.91% (Zn) whereas *V. boronicumulans* removed 95.93% of (Pb), 73.45% of (Cd), and 73.81% of (Zn)	Jalilvand et al. (2020)
5	*Aeromonas hydrophila*	Reactive Black 5 (RB5)	76% at 7 pH	El Bouraie and El Din (2016)
6	*Lysinibacillus* sp. KMK-A	Orange M2R dye/ Cr VI	–	Chaudhari et al. (2013)
7	*Pseudomonas extremorientalis* BU118	Congo red dye	–	Neifar et al. (2016)
8	*Streptomyces ipomoeae CECT 3341*	Acid Orange 63	Neutral pH	Blánquez et al. (2019)
9	Mesophilic *lactobacilli* and *lactococci*, and Thermophilic *lactobacilli* and *lactococci*	Dorasyn Red azo dye	3–6.8 pH	Sofu (2019)
10	*Sporosarcina* kp-4 and kp-22	Cu, Zn, Ni and Cd	Cu (75.10%), Zn (98.03%), Ni (59.46%), and Cd (96.18%)	Qiao et al. (2021)

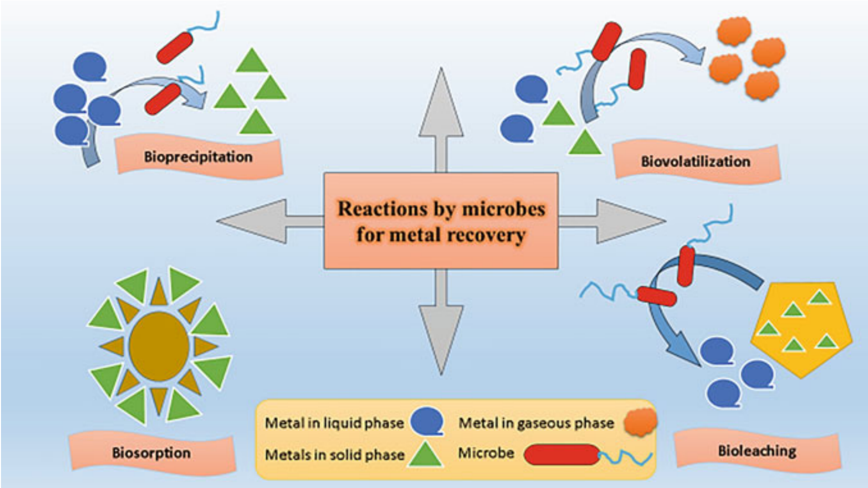

Fig. 7.2 Microbial mediated metal recovery from wastewaters by processes of bioprecipitation/biomineralization, biovolatilization, biosorption, bioleaching

(Tc) and uranium (U) can be reductively precipitated post microbial interactions. Metals like Cr, Au, Ag, Pd, U, and Tc can bioprecipitated reductively by utilizing sulfate-reducing and iron-reducing bacteria (Lovley and Coates 1997). Apart from oxidation, microbial oxidation also results in metal immobilization. It is well documented that Fe (II) is converted into Fe (III) by iron-oxidising bacteria. Likewise, Mn (II) movement is restrained by oxidising into Mn(III/IV) by Mn-oxidizing bacteria (Hennebel et al. 2009). Hence, Fe/Mn bioprecipitation reactions aid in the removal of Fe/Mn and other metals from wastewater (Suzuki and Sahabi 2012). Another process is microbial sulfide precipitation, which involves the formation of precipitates of Cu, Cd, Pb, Bi, Hg, Sb, Sn under acidic conditions and with Zn, Co, Ni under alkaline conditions (Gadd 2010). Sulfate or sulfur-reducing bacteria are anaerobic heterotrophs, that utilize elemental sulphur as the terminal electron acceptor, ultimately forming sulphide. The sulfate-reducing bacteria can be efficiently used for the effective removal of various metals from sulfur-containing wastewater (White et al. 1998). On a parallel basis, microbial reactions also generate phosphates that can support the precipitation of some metals as insoluble salts. It is facilitated by polyphosphate-accumulating microorganisms that bring about phosphate formation by polyphosphate hydrolysis. Microbial phosphate precipitation of U, La and Zr has been documented (Boswell et al. 2001).

7.4.2 Biovolatilization

Biovolatilization is a microbe-mediated process involving the conversion of metals into their volatile forms. It offers a feasible approach to converting metals present in the liquid phase into a gaseous phase. Hence, this technique can be applied for the removal of metal from wastewater and also from solid waste produced by wastewater treatment. Also, if the volatilized metals can be trapped by employing a gas scrubber, they can be consequently recovered. Microbe-mediated biovolatilization of metals is linked to methylation or alkylation of metals while mercury's volatilization is mediated by its reduction (Barkay and Wagner-Dobler 2005). The process of methylation or alkylation of metals contributes majorly to geochemical cycling (Gadd 1993). Lovley (1995) documented the use of bioreactors for the effective removal of Hg from contaminated water using biovolatilization (Lovley 1995). Amongst all metals, Se volatilization has received a lot of attention due to its potential bioremediation applications. Se present in soil and water is mobilized into the atmosphere by microbial volatilization. Se is methylated to generate dimethyl selenide ($(CH_3)2Se$; DMSe) and small amounts of dimethyl diselenide ($(CH_3)2Se_2$; DMDSe). Biovolatilization via methylation has been better reported for metals like Hg, As, and Te. Methylation of Hg (II) yields methyl mercury ($(CH_3)Hg^+$) that is further converted into dimethyl mercury ($(CH_3)2Hg^+$). Similarly, methylation of As results in mono-, di-, and tri-methyl arsines ($(CH_3)nAsH_3{-}n$, n = 1, 2, 3). The main volatile compound of Te produced microbially is dimethyl telluride ($(CH_3)2Te$; DMTe). It was reported by Dias-Bone and Van DeWiele (2009) that apart from methylation/alkylation, biovolatilization can also be brought by the hydrogenation of metals. The only drawback of biovolatilization of metal removal from wastewater is its slow reaction rate.

7.4.3 Biosorption

Biosorption is a physicochemical process rather than a biological process. It refers to the elimination of substances from the water phase or solution by sorption to biological materials (Vijayaraghavan and Yun 2008). Metals are removed from water phase by biosorption with microbial biomass or using microbial products as biosorbents (Gadd 2010). However, bioaccumulation is another microbial metal removal process which is very similar to biosorption. Both processes have very less variability, where bioaccumulation refers to the uptake of metals by living cells, and biosorption is a passive association of metals onto biomass, which may be inactive or even dead (Wang and Chen 2009). Biosorption is better than bioaccumulation as it does not require cell activity maintenance and promises a rapid recovery rate. The studies done so far suggest that there is a specificity of biosorbents for certain types of metals. Table 7.6 enlists some of the biosorbents for metal removal.

Table 7.6 List of biosorbents reported for specific metal removal

S. No.	Microbe	Target metal removal	References
1	*Penicillium canescens*	As (III), Cd, Pb	Say et al. (2003)
2	*Aspergillus niger*	Cd, Cu, Ni	Kapoor et al. (1999)
3	*Penicillium chrysogenum*	Cd, Cu, Pb, Th, U, Zn	Deng and Ting (2005)
4	*Saccharomyces cerevisiae*	Au, Co, Cr (VI), Cu, Fe, Hg, Ni, Th, U, Zn	Deng and Ting (2005)
5	*Chlorella vulgaris*	Cd, Cu, Fe(III), Ni, Zn	Klimmek and Stan (2001)
6	*Pseudomonas aeruginosa*	Cd, Pb, Cu	Chang et al. (1997)
7	*Bacillus subtilis*	La, Ag, Cd, Cu	Mullen et al. (1989)
8	*Pseudomonas putida*	Cd, Pb, Zn	Pardo et al. (2003)

The mechanism of metal biosorption is not completely decoded but is associated with the combination of ion exchange, chelation and micro-precipitation (Wang and Chen 2009). The specificity and selectivity of bio sorbents depend upon the surface of microbial cells. Also, the functional groups of the cell wall (carboxyl, carbonyl, amine, amide, thiol, imine, imidazole, sulfonate, phosphonate) play a critical role in metal biosorption. Hence, artificial amendments are used for enhancing metal uptake competency. For example, alkali treatment of fungal cell considerably improved their metal uptake rate (Wang 2002). While altering genes for metal-binding peptides, such as metallothionein and phytochelatin, on the microbial surface, it will enhance its metal binding capacity. Likewise, a recombinant yeast S. cerevisiae was created to exhibit metal-binding histidine hexapeptide for effective Cu binding (Kuroda et al. 2002).

7.4.4 Bioleaching

Bioleaching is a process that involves the dissolution of metals from the solid phase by certain microbial activities (Babel and Mundo 2006). Although, when bioleaching is concerned with the extraction and recovery of metals from mineral ores, the process is termed biomining (Rawlings 2002). Microbe-mediated bioleaching occurs primarily via the formation of inorganic or organic acids, chelators and oxidation and reduction reactions of metals. The process of bioleaching was well established in industries for removing Cu, Au, and U using acidophilic autotrophic bacteria (Bosecker 1997). Supply of S, oxygen, Fe (II) and acidic conditions are required for chemolithotrophic leaching. Lab-scale studies were reported for the bioleaching of toxic metals from sewage sludge samples (Tyagi et al. 1990). Chemoorganotrophic leaching is brought about by heterotrophic microbes that have the capacity for organic acid production. Also, they produce lactic, oxalic, and succinic acids that assist in metal solubilisation. Both *Aspergillus* and *Penicillium* species are applied for metal recovery from various solid wastes (Santhiya and Ting 2005). The process of bioleaching is mainly a two-step process. Firstly, microbes are cultivated in a reactor to achieve cell-free solutions high in metal-solubilizing agents. Successively, this solution is placed in contact with solid waste for metal extraction. From electronic scrapes, cyanogenic heterotrophic bacteria *Bacillus megaterium, Pseudomonas fluorescens* can recover Au, Ag and Pt (Brandl et al. 2008). Acidophilic chemolithoautotrophs, acid-producing heterotrophs and cyanide-forming bacteria are major categories of microbes that play key roles in bioleaching from solid waste.

7.5 Recent Advances in Heavy Metal Recovery from Wastewater

Mankind uses clean water to perform agriculture, gardening, washing, cooking, and also in industrialization which ends up as wastewater. This contaminated wastewater loses its economic value and reaches into the rivers and oceans and further poses harmful impacts on the marine ecosystem (Manea et al. 2019). Also, the disposal of wastewater into fresh surface water and other water streams significantly degrades the quality of freshwater resources which leads to health issues and other devastating effects on man. Thus, primarily requires to be treated to minimize the hazardous impacts of the wastewater on human health and other ecosystems. In this direction, for years the primary goal was to remove harmful bacteria, dissolved organic materials, oxygen-demanding materials, and other suspended solids. In recent years more emphasis was given to improving the municipal waste treatment units to minimize solid waste. Conventional methods include physiochemical and biological methods to treat wastewaters which undergo preliminary treatments, primary treatment, and secondary and tertiary treatments to manage the solid wastes. Nowadays modern wastewater treatment techniques have been developed and introduced to process wastewater. However, to implement these modern technologies it is important to first study the nature of the waste and the wastewater and, to identify and characterize such wastes as total solids, salt contents, chemical oxygen demand, volatile solids, etc. (Crini and Lichtfouse 2019).

7.5.1 Nanofiltration

The nanofiltration method is a type of membrane filtration process which is effectively applied to treat supply water which is used for drinking as well as non-drinking purposes (Maryam et al. 2020). This method involves the pre-treatment of water following the elimination of undissolved and suspended organic and inorganic pollutants to ensure the longevity of the nanofiltration membranes. In addition to this, heavy metals and salt treatments were provided to increase the molecular size of the pollutants so that a particular membrane with a pore size smaller than the suspended pollutants could be implied for separation (Abdel-Fatah 2018). Membrane filtration has multiple aspects which have an edge over conventional methods. The first aspect includes the asymmetrical formation of the membrane in which the pollutants first come in contact with the small pore size, which however lowers the chances of plugging tendency of the membrane by reducing the cross-membrane pressure. On the other hand, strong cross-flow mechanisms over the membranes eliminate the chances of filter cake formation. Also, there are some advantages over the conventional filtration techniques which involve processes that are highly selective, have very fast reaction kinetics and require low energy (Vigneswaran et al. 2005). NF is highly applicable and can be distinguished when applied under Ca and Mg ions lead in soft water whereas the addition of Na^{2+} ions during the filtration process is applicable in ion exchange units. Thus, NF does not require extra cooling and heating of feed when compared to distillation processes (Nageswara 2014).

7.5.2 Application of Algae in Wastewater Treatment

Microalgae are found to have successfully been used to eliminate the pollutants from the wastewater and are thus used as conventional methods to remove various toxic effluents. This low-cost and effective method has overshadowed the expensive high-energy required systems for municipal wastewater treatments. These algal materials can further be used as phosphorous and nitrogen supplements in agriculture and can also be fermented to generate energy from methane. These microalgal species can eliminate toxic materials like arsenic, zinc, and selenium from aquatic environments (Essa et al. 2018). Also, some of the algal species can accumulate radioactive materials in their tissues e.g. *Spirogyra* incorporates radio-phosphorus. However emerging pollutants (Eps) like pharmaceuticals, pesticides, and cosmetics require technologies to neutralize and eliminate the toxic pollutants which mainly utilize physio-chemical and certain biological tools. However, these EPs can be eliminated from the water bodies by purely applying microalgal populations. In these aquatic environments, algae come in symbiotic associations with certain bacterial species. These algal counterparts supply oxygen to their bacterial counterpart and further consume the CO_2 and minerals generated through the oxidation mechanism by these aerobic bacterial species (Armah et al. 2020).

7.5.3 Microbial Fuel Cells

These fuel cells are efficiently used in the generation of electricity from organic wastes by employing certain microbial populations as catalysts. These microbial fuel cells are comprised of electrodes that are finely separated by certain cation or anion exchange membranes (Prakash et al. 2021). These electrodes should be biocompatible in nature. However, the anionic part of the electrodes faces the wastewater in the chambers whereas the cationic part faces the air-containing chambers. These cells are typically composed of materials like platinum, carbon cloth, graphite granules, etc. This advanced method requires a high amount of suspended waste in wastewater to get vital results. This process involves the application of anaerobic bacteria which shows their activity in the absence of oxygen and is further required to initiate the transfer of electrons to the anodes externally as a byproduct of its metabolic processes. Thus, the anode acts as an electron acceptor and further supplements the cathode counterparts with these electrons, and thus the generation of electric currents takes place. Finally in the cathode region exposed to air commences a reaction mechanism that comes into action to utilize oxygen, protons, and the available electrons and resulting in the generation of water. Thus, the microbial fuel cells technique is 50–90% efficient in disposing of solid wastes (Armah et al. 2020).

7.6 Conclusion

It is impossible to stop the production of wastewater, but wastewater can be treated to mitigate the effects of toxins found in wastewater. Even though 75% of the earth's surface is covered with water, less than 1% of it is drinkable. Therefore, it becomes crucial to treat wastewater prior to its disposal. Traditional technologies exist for the treatment of wastewater, but due to their cost, administrative expenses, and design, the emphasis has turned towards the utilisation of microbes, bacteria, fungi, and algae. However, there is an enormous information gap that must be filled by future research. To deploy these living systems for therapeutic purposes, fundamental research must be conducted. Before using living organisms, it is necessary to do in-depth research on a variety of variables, including the identification of a suitable strain for particular contamination, the nutrient requirements of these species, and the interaction between species.

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Chapter 8
Physico-Chemical Pathways for Wastewater Effluents

Anuradha, Darshan Singh, Divya Mathur, and Surendra Kumar

Abstract With the rapid developments in science and technology, the demand for critical materials, comprising gold, platinum-group metals, and rare earth elements, is rising rapidly. The harmful impact on the life cycle of living beings has prompted an increase in interest in studies focusing on the removal of metals from industrial effluents. Metals are divided into four categories depending on their properties. The first category includes harmful heavy metals like Ti, Ag, Si, Sr, As, Pb, Cr, and Hg. The second category includes radioactive metals like Am, Ra, Th, Rn, U, and Tc. The third category includes metals necessary for metabolisms, such as Zn, Cu, Ni, Fe, Ca, K, and Mo. The last category includes metals used to identify the efficiency of biological systems, such as B, Po, Te, Sb, and Ge. The primary sources of these metals are several industries, including those that produce coating, paper, metallurgy, tanning, mining, batteries, agricultural chemicals, and other industries. Currently, the emphasis of the study is on the removal of metals and their subsequent reuse for numerous productive purposes. Here in this chapter, we will be discussing the recovery of resources from wastewater using commonly practised Physico-chemical pathways.

Keywords Wastewater · Radioactive metals · Metabolism · Physico-chemical

8.1 Introduction

A growing worldwide population increases not just the quantity of municipal solid waste but also the need for a variety of raw materials utilized in the production of products. The presence of different metals in wastewater and leachates is greatly

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influenced by the deposition of these raw materials and several subsequent production processes. Wastewater production is unavoidable since it is a crucial link in the value chain of every area of life. All wastewaters are pure water containing pollutants. Freshwater supplies may be augmented and safe drinking water may be made available to everyone via effective wastewater treatment. This seems to be the most obvious way of dealing with water scarcity. Metal-rich wastewaters not only cause environmental problems and related health issues, but they may also be economically valuable if the metals can be recovered. Around the world, more than 80% of wastewater that is released into the environment has not been treated, with industry making up 28% of the total (https://swachhindia.ndtv.com/80-percent-worlds-wastewater-discharged-untreated-un-5738/). The worldwide generation of vast volumes of wastewater has accelerated due to industrialization. Heavy metals included in industrial effluent may contaminate water sources and harm people's health.

Cadmium (Cd), Chromium (Cr), and Copper (Cu) are the most often found heavy metals in effluent from the petroleum, tannery, distillery, and chemical sectors. Elements having a specific gravity larger than 5 and an atomic weight ranging from 63.5 to 200.6 make up heavy metals. Typically, these heavy metals are employed in manufacturing. Nickel–cadmium batteries are produced with Cd owing to their superior temperature adaptability, multiple rechargeability, and simplicity of maintenance. Cadmium is used as a pigment in paints, glasses, ceramics, and plastics owing to its capacity to endure high temperatures. Cr is used in many processes such as refractory materials, catalysis, tanning, pigments, and wood preservatives applications. In the meantime, Cu is utilized extensively in plumbing, roofing, electrical wires, as well as industrial system. Cardiovascular disorders, cancer, diabetes, kidney damage, high blood pressure, and other associated health problems are brought on by exposure to increased quantities of these metals. Thus, industrial wastewater comprising heavy metals should be treated anterior to its discharge. These metals may be extracted from wastewater to produce valuable industrial goods that have positive economic and financial effects (Amanze et al. 2021).

Toxic metals like Ni, Zn, Cd, Cu, and Cr, build up in the food chain. These metals may be taken up by living things due to their solubility in marine conditions. They may accumulate in the human body after moving through the food chain. When metals are consumed in excess of the recommended concentration, they may result in major health issues. Hence, metal-contaminated wastewater must be treated before being released into the environment (Kurniawan et al. 2006). Latterly, many strategies were investigated for the creation of more affordable and efficient technologies, both to reduce the production of wastewater and to enhance the quality of the treated effluent.

In this chapter, we will discuss the various Physicochemical wastewater treatment techniques such as coagulation, flocculation, Flotation, Membrane filtration, neutralization, Membrane filtration, and ammonia stripping.

8.2 Coagulation

Coagulationis one of the most significant physicochemical processes employed in water and wastewater treatment and may be performed using chemical or electrical methods (Edzwald 2006). Small particles are blended into bigger aggregates (flocs) during coagulation and dissolved organic matter is adsorbed into particulate aggregate so that these contaminants may be separated during the following liquid/solid separation procedures (Jiang 2015). There are three primary prospects for the chemical method of removing organics by coagulation (Teh et al. 2016). (1) Metal ions and molecules of soluble organic matter combine to generate precipitates and insoluble complexes (2) Electrical neutralization, destabilization, and aggregation occurs between negatively charged organic colloids and positively charged metal ions; and (3) Organics are physically and chemically adsorb on the alum's surface.

Stricter, traditional coagulation technique has failed to satisfy individuals 'needs for the safety of water quality because environmental contamination issues grow severe and water quality criteria become more demanding. Optimized and enhanced coagulation is strengthened based on the current process of water treatment facilities and taking into account the operating circumstances of earlier and later processes (Cui et al. 2020).

The colloid particles, which range in size from 10 to 7 to 10 to 14 cm, are marked by coagulation. The colloid particles move in water with Brownian motion; their negatively charged surfaces cause them to push against one another, resulting in a stably dispersed suspension. The electric negative charge is neutralized by the addition of colloid ions or particles with a positive electric charge (Sahu and Chaudhari 2013).

Common coagulants for water treatment are ferric sulfate (a kind of iron coagulant that performs best then aluminium sulfate. This chemical mixture may produce a denser floc than aluminium sulfate and is commonly utilized in conjunction with chlorine. Aluminium sulfate (Aluminium sulfate comes in a variety of forms, such as kibble, block, or ground, but it does result in a noticeably heavier hydroxide sludge). Aluminium sulfate produces an aluminium hydroxide floc when applied to naturally alkaline water (which normally includes calcium bicarbonate). Other options include ferric chloride (a less popular alternative to ferric sulfate due to chloride's potential to make water more corrosive), and sodium aluminate (a compound made of aluminium and sodium oxide). This substance is categorized as aluminium or iron salt and typically has a sodium aluminate content of 70 to 80% in solid forms and 30% in liquid forms. Typically, coagulation treatment is performed before sedimentation and filtration. In this procedure, water is treated with a coagulant, whose positive charge neutralizes the negative charge of any pollutants suspended in the solution. Suspended particles join together (hence the term) as a result of neutralization. These particles gather in "flocs" at the bottom of the treatment tank, where filtration may be used to efficiently remove them from the water.

The coagulant is rapidly mixed with the water during this procedure, enabling it to be disseminated throughout the whole water sample. After being coagulated, the water may be filtered to remove the settling particles using ultrafiltration, microfiltration, or medium filter membrane. The big particles may also be eliminated by moving the water into a settling tank where they will settle to the bottom.

Coagulation eliminates suspended particles and organic natural matter such as bacteria, protozoa, iron, clay, algae, sand, and even gravel. When present in high concentrations, several of these pollutants may give water a scorching favour and a brown or orange appearance.

Nonetheless, this treatment procedure is used in conjunction with other water-cleaning techniques since not all pollutants may coagulate within the same time range. Within 2 min of neutralization, gravel, sand, and fine sand may all coagulate. Protozoa, clay, and algae take up to two hours equivalently.

Bacteria and algae with a one-micron diameter require around eight days to coagulate as well as settle to the bottom of the water supply, whereas viruses with a 0.1micron diameter take two years to coagulate and settle. To destroy microbiological pollutants considerably more quickly and ineffectively, medical intervention is required. Numerous contagions adhere to coagulated particles, which are then eliminated during filtering.

Coagulation is still a crucial step in the water treatment process even if it does not ensure the safety of the water. A disinfectant may be more effective if it eliminates contaminants that make the water more difficult to disinfect, and this process reduces the amount of chlorine needed.

8.2.1 How to Select a Coagulant for Water Treatment

One's local water treatment facility's choice of coagulant will often be based on availability and convenience. The favoured option for public water treatment across the globe is aluminium sulfate since it is readily accessible, inexpensive, and very effective.

The most commonly utilized coagulants for treating water are usually made of metal. However, there are also biopolymer and synthetic coagulants, such as natural biopolymers derived from fungi, animals, and plants. These provide the benefit of creating less sludge and posing fewer toxicity or safety concerns (https://www.wwdmag.com/editorial-topical/what-is-articles/).

1. Coagulation is a crucial step in the water treatment process, but it could not function by itself. To guarantee that water is free of dangerous impurities and suitable for disinfection, sedimentation, filtration, and drinking are also necessary.

8.3 Flocculation

The term "flocculation" comes from the word "floc," which refers to material flakes. When a solution flocculates, the sediment aggregates into bigger flakes, making it simpler to identify and eliminate the sediment. The detachment of a solution, often the sediment removal from a liquid, is referred to as flocculation. This procedure happens naturally, but it may also be influenced by flocculants, or/and physical processes. Physical agents known as flocculants stimulate the aggregation of small molecules in the sample to form flocs that either float to the surface (flotation) or settles to the bottom (sedimentation). This might then be taken out of the liquid more quickly.

Flocculants may be inorganic or organic and come in versatile charges, molecular weights, forms, and charge densities.

Nowadays, the most widely used flocculants are organic polymers, owing to their ability to generate flocculation with a comparatively low dosage. The emphasis is now shifting to biopolymers, which are more ecologically friendly, due to their absence of biodegradability and the resulting dispersion of potentially hazardous monomers into water systems. The problem with them is that they need a larger dose than organic polymeric flocculants and have a shorter shelf life. Hybrid approaches are being explored to overcome this, where polymers are grafted into natural polymers to provide customized flocculants for water treatment that give the greatest advantages of both. A wide range of sectors, from civil engineering firms, and biotechnology, along with earth sciences to cheese and breweries use flocculants (https://www.netsolwater.com/dewatering-flocculants-for-wastewater-treatment.php?blog=1948).

Nevertheless, flocculants are mostly utilized in the wastewater treatment sector for water clarification, solids dehydration, sludge thickening, lime softening, and solids removal. Water may comprise colloidal materials such as plankton, clay particles, bacteria, decomposing plant matter, or other organic material. Flocculation was used to filter water as early as 2000 BC when the ancient Egyptians employed almond smears applied to vessels to clean river water (John 2016). In addition to managing sewage, stormwater, and industrial wastewater, flocculation is utilized to clean drinking water.

Flocculantsmay be used alone or in conjunction with coagulants, based on the charge and chemical configuration of the solution to be separated. Coagulants function by changing the particles already existing in a stable solution to aggregate and enabling flocculants to bind them. Particles are combined with flocculants to form flocs, which are then removed from the solution as sediment or by floatation to the surface.

The proper mixture of inorganic or organic flocculants and coagulants will be depending on the kind of materials being extracted from the water and the technique of separation being employed in the water treatment facility (such as floating, sedimentation, and so on).

Despite the fact that flocculation and coagulation are both often employed procedures in water treatment and refining, they are not the same. In coagulation, chemical properties are altered to promote coagulation. Coagulants started the natural process that happens in milk when the pH of the fluid alters and the milk solids cluster jointly. Because they are often salting, coagulants decompose to release negative or positive charges. A cloud is initially produced by the physical process of flocculation, which causes particles to gather together, and the precipitate is then produced. Polymers called flocculants are frequently used to cause particles to aggregate into bigger flocs or flakes (Rubio et al. 2002).

8.4 Flotation

Flotation originated in mineral (ore) processing and was utilized for decades in solid/solid separation uses employing stable froths to selectively separate distinct minerals from one another. The primary uses were for the removal of ions, fibers, macromolecules, and solids from water. DAF ("Dissolved air flotation") has been employed by civil and chemical engineers for a number of years in wastewater and household sewage treatment applications.

It is also utilized for the treatment of effluents from pharmaceutical sectors, metal finishing, cold-rolling, and tanneries. In standard sedimentation tanks, particles having a density similar to water have a hard time settling and take a long time to separate. In these instances, aeration of the effluent, which attaches air bubbles to the suspended material, may speed up the separation process. This has the impact of raising the particles' buoyancy, causing them to float to the surface, where they may be simply eliminated.

Chemical coagulants, like aluminium and ferric salts or "polymer coagulant-aids", are frequently employed to assist in the flotation process. These compounds enhance the flocculent nature of the floating particles, allowing them to catch air bubbles more readily.

8.4.1 Two Main Methods of Flotation Are

1. DAF (Dissolved air flotation)
2. Dispersed-air flotation.

Under very high pressure, DAF generates bubbles by dissolving air into water. Typically, the diameter of bubbles varies between 10 and 100 μm. In this method, pH, hydraulic retention duration, bubble size, recycling flow, and saturator pressure are among the factors that determine the effectiveness of this approach (Fuad et al. 2018). It is possible to utilize collectors to enhance the aggregate formation and a rise in the size of microalgal particles to enhance the effectiveness. DAF is superior to dispersed air flotation because it produces smaller bubbles. However, this approach is more costly since it needs pressurized air.

Add-on to the conventional DAF process, there is a revised form of this procedure known as PosiDAF. Due to the saturator's injection of chemicals, this process results in positively charged bubbles. Polymers, coagulants, or surfactants with a hydrophobic and hydrophilic portion may be added to the saturator to improve the bonding between cells and bubbles.

The DAF process takes advantage. Pretreated wastewater is given a dosage of a chemical coagulant (for example metal salt), as indicated in Fig. 8.1, and then is sent to a coagulation-flocculation tank. The blend is transported to the flotation tank after the target compounds have coagulated, where it is discharged in the existence of recycled effluent that was recently concentrated with air under a few atmospheres of pressure inside the pressurization system. Just before entering the flotation tank, the coagulated wastewater is given a coagulant assist injection. An appropriate centrifugal pump drives some of the treated effluents into a pressure holding tank, where it is then saturated with air under pressure to create the recycled effluent. A valve at the pressure holding tank's outlet controls all three aspects of the tank's operation simultaneously: pressure, flow rate, and retention time. An air compressor keeps the pressure-holding tank's air supply flowing at the proper rate. A concentration of air from the compressor that is higher than the saturation value at standard atmospheric pressure diffuses into the water under pressure in the tank. In other terms, at standard atmospheric pressure (14.7 psig), around 24 ppm of "air" (oxygen plus nitrogen) may be "dissolved" in water. The actual concentration is computed using a "correction factor" (f), which ranges between 0.5 and 0.8 since air dissolving into the water in the pressurized holding tank is below 100% points effective.

After being kept in the pressure holding tank with compressed air, the recycled wastewater is discharged at the bottom of the flotation tank, adjacent to where the

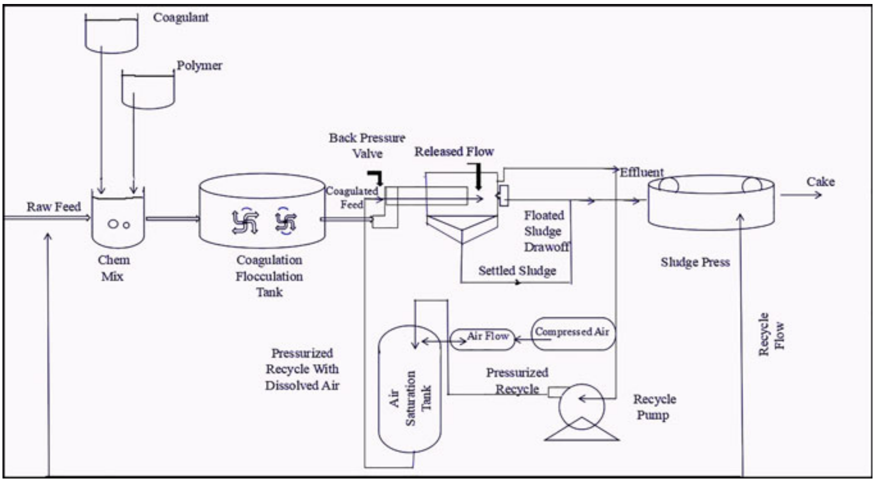

Fig. 8.1 Dissolved air flotation process. *Source* Methods for Treating Wastewaters from Industry**,** Woodard & Curran, Inc., in Industrial Waste Treatment Handbook (Second Edition), 2006

coagulated wastewater is being discharged. The pressure that was delivered to the recycled wastewater was decreased to one atmosphere plus the pressure that the flotation tank's depth created. There, the air's "solubility" is slightly lower than the number of atmospheric pressures in the pressurization system, but there is more water available for the air to diffuse into thanks to the volume of the recycling stream.

In practice, effluent will already be oxygen-free due to biological activity and already be nitrogen-saturated. Therefore, the surplus air in the pressure, recycled waste will precipitate from the "solution" and the "solubility" of air at the bottom of the flotation tank would be around 25 ppm. This air condenses into small, practically microscopic bubbles that adhere to the coagulated materials as they precipitate. The coagulant continues to work while the anionic polymer is present, causing the accumulation of bigger solids that trap several of the adsorbed air bubbles. The result is that the solids float to the top of the flotation tank, where they may be removed from the wastewater by some kind of collection.

In certain DAF systems, the whole forward flow that travels to the flotation tank is pressured rather than the recycling system, which is not always pressurized. This sort of DAF, also known as "direct pressurization", is not often employed for the treatment of industrial wastewater owing to the pump and valve unintentionally shear chemical flocs.

When air is dissolved in dissolved-air flotation, it comes into close contact with the wastewater at a pressure of several atmospheres. A back-pressure valve is used to raise the liquid's pressure to atmospheric pressure, which releases tiny bubbles with a diameter of just a few microns (https://www.yourarticlelibrary.com/essay/flotation-as-primary-treatment-of-waste-water-explained).

These tiny air bubbles in the flotation tank are responsible for lifting oil and suspended particles to the surface. Following chemical treatment, flocculent suspensions or oil emulsions often deteriorate due to the pressurization system's vigorous mixing of air and wastewater. To stop these degradations, a part of the clean effluent is recycled for pressurization.

The retention tank comes into close contact with compressed air after it is added to the recycling pump's outflow. A back-pressure valve is used to return the recycled flow after the compressed air is released and combined with the influent for flotation. About 30 min are spent in the flotation tank.

Air is directly injected into the liquid during dispersed-air flotation using a rotating diffuser or impeller. The air bubbles produced by dispersed air flotation devices are approximately 1 mm in diameter, and they often induce turbulence that breaks up the delicate floe particles.

Because of this, dispersed air flotation is not a preferred method for treating municipal wastewater, despite having a small number of applications for handling industrial wastes that include oil, grease, and fine particles (http://www.tectrapro.com/wp-content/uploads/waste.pdf).

8.5 Neutralization

It comprises the use of an acid (pH < 7) to reduce the pH of an alkaline (or basic tank) liquid (pH > 7), or the usage of an alkali (or base) to increase the pH of an acidic liquid tank. This technique maintains a liquid's "neutral" pH of 7.0 (neither acidic nor base). The renewal of the resins applied during cation, anion, as well as "mixed bed ion exchange" systems often produces wastewater in the water treatment sector. Extreme pH values are present in the chemicals employed to regenerate the resins. For instance, Sodium hydroxide, which has a pH between 13 and 14, is used to renew the anion resin, whereas sulfuric acid, which has a pH between 1 and 2, is used to regenerate the cation resin. The water that contains these compounds should be discarded after the regeneration procedure. The effluent cannot be immediately discharged because of its excessive pH since doing so would usually be against municipal laws governing the pH of wastewater disposal. For instance, the pH standard for stream discharge under the NPDES ("National Pollutant Discharge Elimination System") is 6 to 9. Location and discharge destination affect the permissible pH of the discharge (like a well, a sewer, or a stream that leads to a municipal waste treatment plant). A supply of alkaline liquid is required to counteract the very acidic effluent from the regeneration of cation resin. The effluent from the regeneration of anion resin, which is often carried out concurrently, is alkaline. The pH is "neutralized" and becomes closer to 7 when these 2 wastewater streams are blended. The pH of the mixed liquids must be shifted into the permitted range by adding more acid or base if the final pH is outside of it. In most cases, the chemicals that are utilized to modify the wastewater are also those that renew the resins in ion exchange systems. In a mixed bed ion exchange system, wastewater produced during the resin regeneration may be both extremely acidic and highly basic. The mixed wastewater streams from two anion and cation ion exchange systems are often larger than the total volume of wastewater produced. The 2 wastewater streams that come from the mixed bed system's regeneration may be blended, regardless of volume, to almost neutralize one another.

8.5.1 The Following Four Steps Are Involved in the Neutralization Process

8.5.1.1 Collection of Wastewater

The wastewater that is still present after an "ion exchange resin" regeneration cycle often has an excessive pH and could not just be sent into the drain. The effluent is instead sent to a tank for "batch neutralization". The tank's function is to collect all of the wastewater streams in one place. Once gathered, the objective is to utilize the streams' broad pH variances to make them balance each other out.

8.5.1.2 Combining and Mixing Wastewater Streams

The alkaline and acidic waste volumes within the batch tank need to be well-mixed for full "neutralization" to take place in an acceptable length of time. Numerous mixing strategies might be taken into account. The tank's contents may be blended using a motor-driven mixer on a shaft. Long shafts must be carefully balanced with submerged bearings to keep them in position since tall tanks are often utilized in this application. By mounting the mixer unit to the tank side, these needs are eliminated, but an underwater seal is added. Both of these techniques may be challenging to maintain. By pumping air into the bottom of the neutralization tank, mixing may also be accomplished. This approach eliminates the need for moving components and the accompanying maintenance difficulties, although a sufficient air supply is necessary. This approach often requires a substantial number of blowers to deliver the pressure and volume of air needed to mix a full tank of water.

The wastewater in the tank may be recycled by centrifugal pumps using a different mixing technique. With a piece of equipment that requires very little maintenance, this method offers a quick and effective mix. Any extra pumps are for redundancy as there is only one operating pump. In a recycling mixing arrangement, water travels from the neutralization tank's bottom to the recycle pump's operational suction. The water is then redirected into the batch tank after being discharged from the pump. The "turnover rate" is the amount of time needed to pump the tank's whole contents out once. Turns per hour may be used to quantify this, with one turn representing one passage of the batch tank's volume via the pump.

An "educator" who mixes water from the pump (the motive fluid) with water from another area of the tank is used to mix the water as it enters the tank (the entrained fluid). To evenly mix the contents of the tank, the batch tank has many eductors on the laterals. Water from the recycling pump is forced via an eductor, creating a suction that draws in around four times as much water as is being pumped. The turnover rate is dramatically reduced since five gallons are released for each gallon pumped into a single tank mixing eductor. When utilizing many educators distributed throughout the batch tank, the discharge stream's agitation also promotes the mixing of the contents of the tank.

8.5.1.3 Measuring the pH

pH Evaluation an inline sensor constantly monitors the pH of the recycled wastewater. The pH is measured when the effluent is mixed in the tank to ensure that it is within allowable limits for disposal. The water is sent to the drain if the batch's pH is within acceptable limits. Before the batch is released, more chemicals are added to the batch if the pH is beyond the permissible range.

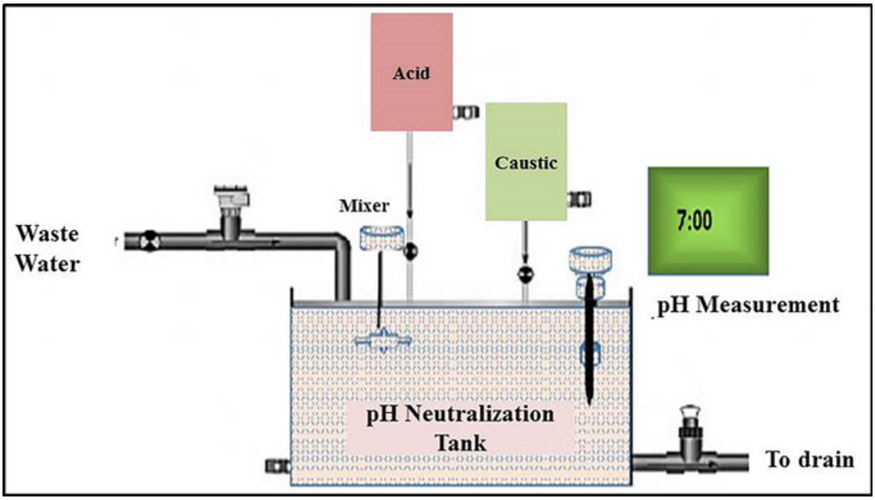

Fig. 8.2 pH neutralization process. *Source* https://www.yokogawa.com/library/resources/application-notes/batch-neutralization

8.5.1.4 Adjusting the pH of the Wastewater

The batch has to be changed if the mixed wastewater from a cation and anion resin regeneration does not provide an appropriate pH for release. The quantity of acid or caustic that has to be added to the batch tank is calculated by a control system algorithm using the pH sensor. Where the chemicals are applied is shown in Fig. 8.2. Acid is added to a batch if the pH is too high. Caustic is added to a batch if the pH level is too low. The quantity supplied ought to be enough to put the pH of the batch tank's contents within the desired range. Commonly, the chemicals are the same ones that are used to regenerate cation or anion resin. The pH of the wastewater batch is once again tested to check that it is within the permissible range after the adjustment chemical has been applied and the tank's contents have been properly mixed. The batch neutralization tank's contents are sent to drain if the pH is within acceptable limits. If the pH is not acceptable, another cycle of adjustment is carried out until the batch's pH is acceptable (Takht Ravanchi et al. 2009).

8.6 Membrane Technology for Wastewater Treatment

A membrane, in its simplest form, is a barrier that distinguishes 2 phases by limiting the flow of certain components across it (Fane et al. 2011). The invention of membranes dates back to the eighteenth century. Since then, several advancements have been made to increase the suitability of membranes for a variety of applications (Sagle and Freema 2004). Membranes may be categorized as **isotropic** or **anisotropic** based on their characteristics.

The composition and physical composition of isotropic membranes remain constant. They are capable of becoming microporous, which would result in quite large penetration fluxes compared to nonporous materials (Baker 2012). On the other hand, dense anisotropic membranes have distinct layers with various structures and compositions that are not uniformly distributed across the membrane area. A larger, more permeable layer supports a thin selective layer that is present in these membranes. They are specifically used in operations involving RO (Reverse Osmosis).

Membranes are categorized as either organic or inorganic based on the composition of their constituent materials. Organic membranes are produced using artificial organic polymers. Membranes using pressure-driven separation techniques including reverse osmosis, nanofiltration, ultrafiltration, and microfiltration are often composed of synthetic organic polymers. These comprise cellulose acetate, polypropylene, PTFE (“Polytetrafluorethylene”), and PE (“Polyethylene”), among others. Inorganic membranes, are made from such materials as silica, zeolites, metals, or ceramics. They are often employed in industrial applications such as microfiltration, ultrafiltration, and hydrogen separation because they are chemically and thermally stable (Yang et al. 2016).

Numerous driving forces are used to propel various media across the membranes. Reverse osmosis, ion exchange, gravity, and adsorption are a few of the techniques that have been developed to treat wastewater. Due to its cheap cost, diversity of accessible adsorbents, and ease of application, adsorption has been extensively utilized to remove pollutants from water. Activated carbon, magnetic nanoparticles, nanotubes, and polymer nanocomposites are some of the several adsorbents that were used (Beita-Sandí and Karanfil 2017; Carr et al. 2016; Hatton et al. 2017; Saleh et al. 2017; Saleh 2016; Ma and Hsiao 2019).

8.6.1 MF (Microfiltration)

The 1st and earliest process class in membrane manufacture are MF. It is a membrane unit, as opposed to traditional filtering systems, that allows for the retention of small size particles in the wastewater. Bacteria, silt water, clay, and big colloidal materials may all be distinguished from particles between 0.05 and 1.5 μm in size. HF or tubular membrane configurations are used in the design of MF. In the treatment of drinking water, MF techniques are used in a variety of ways. MF units are employed in these applications after the usage of fine grids. Additionally, it may be used as a pretreatment step before NF or RO or as the primary treatment technique. In MF, the concentrated portion of the flow that cannot pass through the membrane is employed parallel to the surface membrane, and this concentrated portion accumulates on the membrane. On the membrane surface, resistance rises with time. The membrane has to be cleaned or replaced when membrane filtration becomes uneconomical, which happens when filtration effectiveness falls. Utilizing horizontal flow in these types of membranes may help to prevent the development of a solid cake layer on the membrane surface. In addition to other techniques like vortex currents, vibrations, and electrical fields, approaches like chemical cleaning that don't harm the membrane may also be employed to lessen the effects of concentration polarization and occlusion during MF operation. It is recognized as the initial pre-treatment for RO and NF membrane processes. When pre-treatment is used, the amount of organic material that may be removed might increase. MF eliminates little to no organic matter. A virus cannot completely pass through MF. However, MF seems to suppress these microbes in water when used in conjunction with disinfection.

8.6.2 UF (Ultrafiltration)

UF membrane techniques may separate chemicals between 0.005 $\approx$ 10 μm which is between RO and MF. UF membranes are very effective water filters that use little energy to get rid of suspended particles, macromolecules, and harmful microbes, among other things. However, the inability to eliminate any dissolved inorganic contaminants from water and the need for regular cleaning to sustain high water flow are only two of the disadvantages of UF. A synthetic method for a hybrid UF membrane for water treatment was created by Mocanu et al. To create their membranes, they employed the wet-phase inversion approach using graphene and polysulfonenanoplatelets altered with poly ("styrene"). ZnO was applied on one membrane surface using water-soluble polymers. According to the research by Igbinigun et al., the improved GO-membrane recovered flux 2.6 times better than the unmodified membrane, proving that it is advisable to change the membrane with GO to improve flux recovery. They utilized a basic technique called UV-induced amination, which has been discovered to produce a high flux UF membrane that is resistant to organic fouling and may be utilized in applications of wastewater treatment. The more hydrophilic surface membrane will result from adding hydrophilic elements to the surface of these polymers.

A super-fine filter known as the UF membrane filters particles to sizes 5000 times lower than a human hair. Using ultrafiltration, these pollutants are reduced by 90–100%. A 0.05-micron carbon block prefilter may be added to a system to minimize chlorine taste and odour, cysts, lead, MTE ("Metallic Trace Elements"), and VOCs ("Volatile Organic Compounds"), even if UF can't eliminate certain organics. A UF membrane has a two-year lifespan.

8.6.3 NF (Nanofiltration)

The pressure-driven membrane technology for liquid-phase separations that was most recently developed is called NF. Owing to its high flux rates and reduced energy usage, NF has largely supplanted RO in applications. The NF membrane's characteristics are in between those of nonporous RO membranes (when transport is driven via a solution-diffusion process) as well as porous UF membranes (when separation is often believed to be owing to size exclusion and, in certain cases, charge influences). Commercial NF membranes contain a fixed charge as a consequence of the dissociation of surface groups like carboxyl or sulphonated acids. As a result, the characteristics of NF membranes enable the separation of ions using a mix of the size and electrical impacts of UF and the ion contact processes of RO. The technology used in wastewater treatment systems that is relatively recent is called the NF membrane. Even tiny uncharged solutes are strongly rejected by NF membranes due to the size of the pores, which is typically 1 nm, but monovalent ions and multivalent ions are primarily retained due to the surface electrostatic characteristics. Due to these characteristics, NF membranes are very effective for fractionating and removing specific solutes from complicated process streams. Advancement of NF technology in recent years has increased its use in a wide range of industries, including pulp-bleaching wastewaters from the textile sector, metal recovery from wastewater, demineralization inside the dairy industry, pharmaceuticals separation from fermentation broths, and virus removal from wastewater.

One of the potential methods for treating inorganic and organic contaminants in surface water is NF. Because the osmotic pressure of the surface water is minimal, NF may operate at low pressures. The NF method rejects organic materials at a high rate, including precursors of disinfection byproducts. Natural organic chemicals in surface waters that have relatively big molecules contrasted to the size of membrane pores might be removed by a sieving process, while inorganic salts might be eliminated by the charge influence of the membranes as well as ions. Charge and particle size both play significant roles in the NF rejection process because the NF membrane has characteristics that lie in between those of UF and RO. NF has been characterized as a charged UF system by Simpson, while a low-pressure RO system by Rohe. Nevertheless, NF has a benefit over RO in that it operates at a lower operating pressure and has a greater organic rejection rate. Physical sieving might be the primary method of rejection for colloids and big molecules, while solution diffusion and the charge effect of membranes would be the primary methods of rejection for ions and smaller molecular weight compounds (Shon et al. 2013).

8.6.4 FO (Forward Osmosis)

It is an alternate desalination method that removes freshwater from seawater/brackish with an even more concentrated draw solution, primarily employing the osmosis pressure gradient as the major driving mechanism. The drawing solution side of the FO membrane, which has a greater osmosis pressure, is where pure water will essentially flow through from the seawater/brackish side. The process is depicted in Fig. 8.3 that uses a sugar solution at a high concentration as the draw solution. However, it would need the energy to separate water and recover the draw solution, thus the energy usage could be higher than with RO membrane-based processes. Energy-efficient draw solutions have made considerable strides in recent years. One example is ammonia-carbon dioxide, which rapidly separates into gases when heated and may be recovered and utilized again in a closed-loop system.

The usual membranes employed in the FO process also have a TFC structure, which is identical to that of the RO process. The barrier (selective) layer is an aromatic polyamide that has been cross-linked. Nevertheless, the support layer for the FO operation must be a highly porous substrate in order to reduce the problem of concentration polarization, decrease the barrier to mass transfer, and maximize the water flow.

In 1977, the first FO system was shown. Since then, a wide variety of systems have been created, and their potential for energy savings is becoming close to that of RO operations. The Yale group achieved the FO operation's breakthrough in 2007 when they showed how to desalinate saltwater using real energy-efficient drawing solutions and recovery processes. For instance, after the FO procedure, the ammonium chloride- or sugar-based draw solutions might be further concentrated for use in various applications.

The possibility of reduced overall energy usage and improved fouling resistance to the various contaminants are FO's main advantages over RO. In particular, the FO process only needs a low-pressure circulation system to move water to the draw solution side from the feed side, using little energy (i.e., high pressure). The low-pressure feature of the FO process is advantageous for lowering the requirement of mechanical strength for the membranes and reducing the likelihood of fouling. FO,

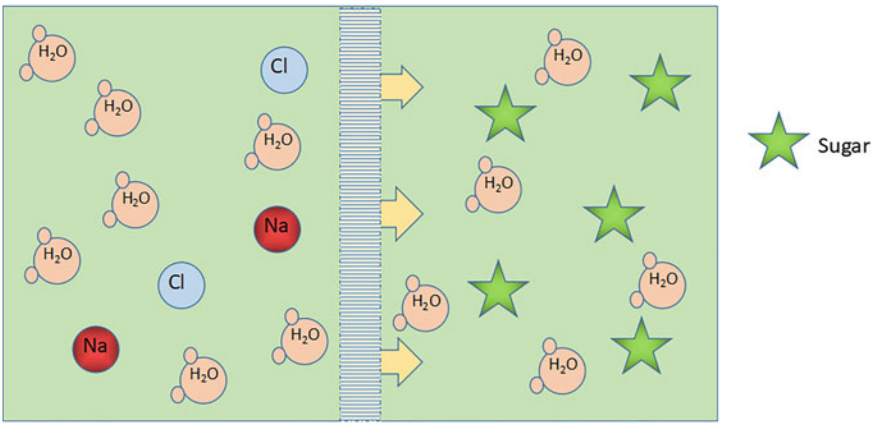

Fig. 8.3 Forward osmosis

however, has an even bigger problem in terms of concentration polarization across a membrane (both internal and external) as compared to RO, owing to a higher concentration of draw solution, which should be addressed. The creation of a dense salt layer on the FO membrane's surface causes external polarization, whilst the air in the voids of the membrane causes internal polarization, which may significantly reduce the permeation flow. High hydrophilic substrate and High porosity, such electro spun nano-fibrous scaffold, seem to be best suited for the FO operation to solve these issues (Lofrano et al. 2016). FO occurs naturally when a solvent travels through a porous barrier from an area of lower concentration to an area of greater concentration. Since drawing solution regeneration for desalination procedures is quite costly, so instead nano-filtration or reverse osmosis is used. This approach is discovered to be very effective with low-rate brine production and is widely explored since it will help to alleviate water shortages globally.

8.6.5 RO (Reverse Osmosis)

Membranes of RO were shown to reduce significantly the presence of heavy metals, bacteria, viruses, organic pollutants, heavy metals, total dissolved solids, along with other contaminants dissolved. Commercial membrane wastewater treatment facilities' experience has shown that certain design requirements should be addressed to avoid fast membrane fouling and, therefore, lower high system maintenance costs and substantial downtime. Using microfiltration or ultrafiltration membranes to eliminate colloidal debris, maintaining a chloramine residual for preventing bio-growth, choosing the right antiscalant chemicals, reducing the recovery rates for RO to avoid membrane scaling, and using membranes that reduce organic fouling are all examples of current best practices. In the West Basin Wastewater treatment facility in California, and others, certain traditional polyamide, and low fouling membranes were employed effectively in plants like the Bedok and Kranji plants in Singapore. These large-scale plants serve as the foundation for even bigger plants, which will increase their contribution to the water supply in underdeveloped areas. Such wastewater has been successfully treated using RO membranes, which also provide water that meets or exceeds the standards for reuse. Municipal wastewater is currently being recycled in a significant number of commercial membrane facilities. These plants include the 50,000 m^3 per day capacity of many West Basin, California, plants, the 40,000 m^3 per day Kranji plant in Singapore, and the 32,000 m^3 per day Bedok facility. The use of membrane technology has been used by some of these facilities for more than ten years. Furthermore, even bigger plants have recently started operation (380,000 m^3 per day plants for Sulabaiya, Kuwait) or will soon start operation (170,000 m^3 per day "UluPandan" plant in Singapore), and the (270,000 m^3 per day plant in Orange County, California, United States). The size of these RO-based reclamation facilities illustrates the recent increase in acceptability of this technology.

Only water molecules may flow via RO, which uses pressure to remove dissolved solids and tiny particles. The pressure provided to RO should be adequate for water to overcome the osmotic pressure. Since RO membranes' pores are significantly smaller than those of UF membranes and can effectively remove all particles, germs, and organic matter, they are less maintenance-intensive and can turn hard water into soft water. Some drawbacks include the utilization of high pressure, the cost of RO membranes in comparison to other membrane processes, and the fact that they are prone to fouling. Sometimes a significant amount of pre-treatment is necessary. RO has very tiny pores and can filter out particles as little as 0.1 nm. The removal of Escherichia coli and reduction in BSA fouling was reported by Huang et al., using RO membranes coated with functionalized "graphene oxide" in addition to a smooth, antibacterial, and hydrophilic membrane (Nqombolo et al. 2018).

8.7 Ammonia Stripping

Some wastewaters have high levels of sodium and/or chemicals containing nitrogen that could easily turn into ammonia. Ammonium (NH_4^+) nitrogen may enter the aquatic environment directly (for example, via municipal wastewater discharges) or indirectly (for example, through agricultural operations). According to European Law and WHO rules, the maximum permitted ammonia content in the surface water is less than 1.5–0.2 mg/L. NH_4^+ is harmful and toxic to human health only if its consumption exceeds the body's detoxifying capability and the permissible limitations.

The elimination of NH_4^+ from wastewater is required to safeguard the environment and public health. Different techniques, including physicochemical and biological, are employed to remove nitrogen from wastewater. Alternative techniques based on Physico-chemical mechanisms have been advocated due to the negative impact that high ammonium levels have on microorganisms (during the biological treatment process).

The mass transfer concept serves as the foundation for the ammonia stripping procedure. It is a procedure where wastewater is exposed to air to remove any ammonia gas that may be present. Ammonium ions, as well as ammonia gas, are the two types of ammonia that may be detected in wastewater. The temperature and pH of wastewater affect the relative levels of ammonium ions and ammonia gas. By raising the pH, which causes the chemical balance to shift to the right and encourages the creation of ammonia gas, ammonia gas generation is encouraged. Because efficient ammonia stripping requires a high pH, lime is applied to raise the pH of wastewater before ammonia stripping (Wang et al. 2006). In fact, a number of designs for ammonia stripping processes were used to treat different kinds of wastewater that including ammonia nitrogen. For example, research on nitrogen removal via stripping on a secondary effluent of a municipal wastewater treatment facility was carried out by O'Farell et al. Before stripping, lime is added to the influent to raise the pH, and then a re-carbonation process is used to neutralize the result. Along with increasing the pH of the wastewater, calcium oxide (lime) produces calcium carbonate inside the wastewater and acts as a coagulant for particles and hard substances. Furthermore, O'Farell et al. found that the ammonia stripping technique can eliminate up to 90%

of the ammonia from the secondary effluent (O’Farell et al. 2018). The effectiveness of the ammonia stripping procedure for cleaning up groundwater contaminated by leachate was also studied by Raboni et al. In the research, iron, sodium hydroxide, and polyelectrolyte (iii) chloride was introduced for the processes of coagulation and sedimentation at pH levels greater than 11 (Raboni et al. 2013). The system also included a heater that heated the wastewater to 38 °C and an ammonia extraction process that used sulphuric acid as an absorption medium. Finally, sulphuric acid was added to the efluent to neutralize it. They discovered that, with an initial ammonia level of 199.0 mg/l, the ammonia stripping system for groundwater contaminated by leachate demonstrated removal effectiveness of 95.4%. The effectiveness of an air-stripping device to remove ammonia nitrogen from industrial effluent was then explored by Genon and Saracco. They claimed that this technique was only practical if the industrial effluent had a high ammonia content and reasonably high temperature. The absorption and crystallization processes came after the stripping procedure. Genon and Saracco determined that the recovery system and ammonia stripping were technically viable and simple to manage (Sarraco and Genon 1994).

A straightforward desorption method called “ammonia stripping” is employed to minimize the ammonia levels in wastewater streams. Ammonia removal from wastewater is often simpler and less costly than first converting nitrogen to nitrate-nitrogen and then removing it. Ammonium hydroxide is created when water, a weak acid, combines with ammonia, a weak base. Lime or caustic is added to the wastewater throughout the ammonia stripping process until the pH level hits 11.

In a cross-flow tower, the alkaline wastewater flows downhill while the solvent gas (air) enters throughout the whole depth of fill and passes through the packing. Water is pushed to the top of a crowded tower, which has apertures at the bottom through which air is drawn. Droplets of water that are falling into the air are stripped of their free ammonia (NH_3), which is subsequently released into the atmosphere. When wastewater contains between 10 and 100 mg/l of ammonia, ammonia stripping is effective (Wastewater Technology Fact Sheet Ammonia Stripping 2000). Alternative ammonia removal technologies, including steam stripping or biological processes, may be more cost-effective for greater ammonia concentration (more than 100 mg/l) situations. Another method to get rid of a lot of hydrophobic organic compounds is air stripping (Arezoo Zangeneh et al. 2021).

8.8 Conclusion

The result of a fast-expanding world population is a growth in the production of industrial and municipal wastewaters, leachates, and related rises in metal emissions. With toxicity often shown at low levels, metal-rich wastewater may cause both short- and long-term environmental harm. As a result, metal recovery from wastewater is becoming an increasingly important problem, not only because of the environmental harm and health consequences it may have but also due to its potential economic value.

In this chapter, we discuss the powerfulness of various physicochemical wastewater treatment techniques such as coagulation, flocculation, flotation, neutralization, membrane filtration, and ammonia stripping to remove metals from wastewater.

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Chapter 9
Biofertilizers from Wastewater: Strategy to Check Water Pollution and Chemical Fertilizers in Agriculture

Archna Kumar, Deepika, Kashika Kapoor, Tarkeshwar, and Kapinder

Abstract Human population explosion resulted in accelerated urbanization and industrialization that caused rapid environmental degradation leading to serious threats in developing societies. Wastewater generated from various industries, households and other human activities consists of various pollutants as well as an enormous amount of several nutrients such as starch, fats, proteins, phosphates, sulfate, nitrate and many more which could damage the aquatic environment if released untreated. The effluent released from different sites exhibits different compositions and properties that change with time and operational conditions and hence need to be considered during nutrient recovery. There are several strategies available to treat wastewater and recover nutrients as biofertilizers. Wastewater released from the sweet potato starch industry, olive mill, and dairy effluent could work as biofertilizers and increase crop productivity. Hydrophytes and Macrophytes can absorb large amounts of nutrients as well as produce high biomass. The microalgae provide a consistent way to glean nutrients from wastewater especially ammonia and phosphorus. Therefore, they could be used to treat wastewater and produce rich biofertilizers. The recovery of nutrients from wastewater directly influences the bio-economy sector as it helps to recycle nutrients and make human activity more sustainable in terms of crop productivity and to check water pollution. Therefore, it is a present need to build up a hybrid method to develop biofertilizers with the management of intractable wastewater. This chapter aims at describing various techniques utilized in valuable nutrient-recapturing processes from wastewater treatment plants at the commercial level. Their merits and demerits also have been discussed.

Keywords Biofertilizers · Wastewater · Microalgae · Nutrients

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9.1 Introduction

The ever-increasing population has resulted in the continuous use of resources, rapid urbanization, and industrial development. The use of resources has increased resulting in a huge amount of waste. The treatment of waste is a difficult task in today's world. Solid and liquid waste should be treated for a definite period for a healthy environment. For the survival of all living organisms, water is crucial. For environmental balance water is necessary. As fresh water is utilized by the human population it becomes contaminated with several impurities and turned into wastewater. Depending on the utilization and management, wastewater generated through various activities may be a severe environmental problem or a potential source for mankind. In urban areas, population pressure is increasing day by day, especially in developing countries. This increase accelerates the consumption of freshwater in various domestic, commercial, and industrial activities, resulting in the generation of greater large volumes of wastewater (Lazarova and Bahri 2004; Qadir et al. 2007; Asano et al. 2007). Maintenance of this large volume of wastewater is a great challenge for every municipal corporation. Long-term storage is the main cause of the depletion of nutrients like starch, fats, proteins, phosphates, sulfate, nitrate etc., and the elevation of highly toxic substances. To fulfil the demand for agricultural activities, farmers of urban and peri-urban areas, utilized nearly in all developing countries who need wastewater for irrigation purposes have often no other choice than to use wastewater. They even deliberately use undiluted wastewater as it provides nutrients or is more reliable or cheaper than other water sources (Keraita and Drechsel 2004; Scott et al. 2004). It indicates wastewater released from various sources has a great potential for recovery of several nutrients such as starch, fats, proteins, phosphates, sulfate, nitrate and many more along with some harmful substances which can be hazardous to the environment and mankind thus the treatment of wastewater is a necessity of the hour. Wastewater is of great potential and also an asset to us if used and treated wisely. Thus researcher's main focus is to develop strategies for the separation of nutrient elements quickly from wastewater. Nutrients recovered from wastewater can be further used as biofertilizers.

At today's time in modern agriculture, fertilizers based on chemicals degraded the fertility of soil leading to severe health and environmental hazard like pesticide poisoning, contamination of soil and water table, erosion of the top layer of soil etc. Biofertilizers naturally enrich the soil with nutrients and have a major edge over chemical fertilizers as they are a low-cost renewable source of nutrients to the crops and emerged as a boon to agriculture in recent years as they are affordable and help us in establishing a sustainable system.

This book chapter describes in detail about latest technologies used to recover nutrients in wastewater treatment and their mechanism (Fig. 9.1). This includes chemical methods, biological technologies, membrane systems and advanced membrane systems. To mention a few, wastewater recovery from Micro-Algae, water treatment using electrocoagulation, sewage wastewater treatment (electro-oxidation) using

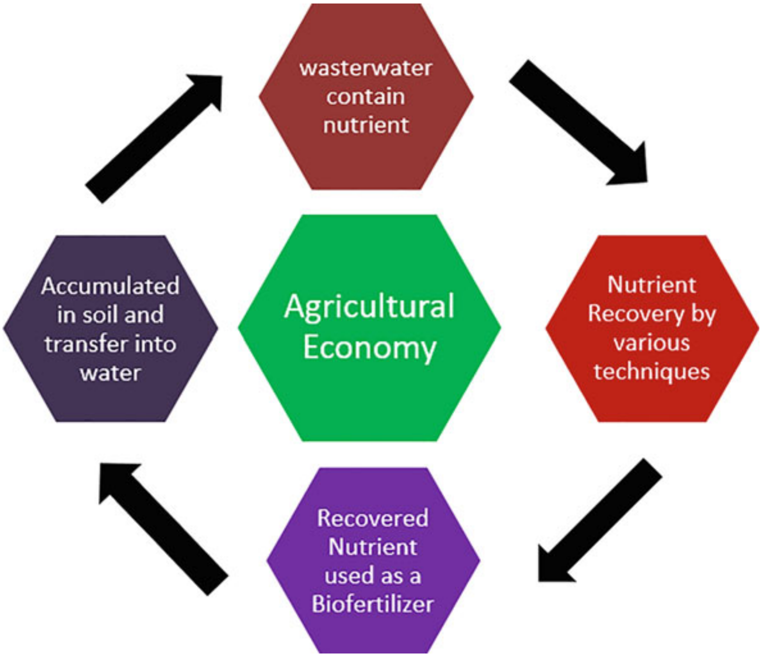

Fig. 9.1 Nutrient recovery in agricultural wastewater

microbial decontamination and many more such methods will be explained in this chapter.

The wastewater coming from various sources like sewage, households and industries like food, dairy, textile etc. has toxic and harmful substances which have a major impact on human health. However, wastewater also consists of useful nutrients such as nitrogen, phosphorous and potassium, which when extracted properly can be used as biofertilizers to supplement the demand in the field of agriculture. According to a study done in 2020 by Qadir et al (2020), the estimated requirement for nitrogen is 115.5 Tg while the requirement of potassium as well as for phosphorous is 33.6 Tg and 43.8 Tg respectively. As a result, these nutrients present in wastewater can wash off their demand by 14.4% of nitrogen, 6.8% phosphorous and 18.6% potassium as a nutrient fertilizer globally.

There is a constant need to implement resource recovery to meet the ever-growing demand for freshwater and scarce water resources under stress due to population increase and urbanization. The ultimate goal of wastewater management is the protection of the environment and the recovery of useful nutrients which is beneficial for mankind. Thus, for harnessing the potential nutrients from wastewater and for use of these recycled nutrients there are some methods involved which will be explained in the next section.

9.2 Wastewater from Agriculture

Excess utilization of chemical fertilizers and animal manure by farmers increases unutilized concentrations of nitrogen and phosphorus. As a result, these excess amounts of unwanted chemical fertilizers create a negative impact on downstream water quality. This superfluous nitrogen and phosphorus can be washed from farm fields and into water bodies and phosphorus can cause eutrophication of water bodies. Eutrophication can lead to hypoxia ("dead zones"), causing death of fishes and decline in aquatic life. It also can cause harmful algal blooms (HABs) in freshwater systems, which not only disrupt wildlife but can also produce toxins harmful to humans.

The traditional technologies used for removing various nutrients from agricultural wastewater include active sludge process, chemical precipitation, nitrification–denitrification and others (Iorhemen et al. 2019) However, removal of nutrients is not achievable in sustainable waste-water management strategies with low-carbon and energy intake conditions and re-source recovering (Sun et al. 2016). As it is well-evident that nitrogen and phosphorus are essential for all living organisms because they are integral components of all vital biological pathways. Recent studies emphasized the huge demand for phosphate and ammonium which are the essential raw material for the production of various fertilizers at the industrial scale for the increasing world's population. It has been perceived that great amounts of nutrients are present not only in the agriculture wastewater but also in the wastewater retrieved from sludge, which is now considered to be a valuable source of nutrients. Resources of these nutrients are limited and could be exhausted in the coming few decades. Thus, its retrieval gains the attention of researchers. Wastewater from agriculture and some other sources like municipalities and some industries consists of high concentrations of such nutrients and if not treated, can cause eutrophication. In recent years, the treatment and reuse of such nutrients from wastewater especially from phosphate mining have achieved significant attention. Various treatment methods like chemical precipitation, biological, combined chemical and biological treatment are suggested by various researchers to treat phosphorus-rich wastewater (Mukherjee et al. 2020). Therefore, it is reflected, nutrient retrieval from wastewater could make the wastewater treatment process sustainable, reduce the costs associated with nutrient removal (e.g., less production of surplus sludge), and provide supplementary fertilizers for food production. In recent years, various procedures are being probed for their efficiency in the nutrients recovery process, including traditional methods such as chemical precipitation and adsorption, and recent advanced approaches like bio-electrochemical systems (BESs), osmotic membrane bioreactors (OMBRs) and many more. Besides these, the nutrient recovery may be executed from the sludge phase (dry surplus sludge and sewage sludge ash) and from the liquid phase (anaerobic digestion supernatant, reject water and sludge dewatering filtrate) in the wastewater treatment process. Most technologies used for recovering nutrients are executed in the liquid phase while wet-chemical and thermo-chemical treatments may extract phosphate from the sludge (Fig. 9.2).

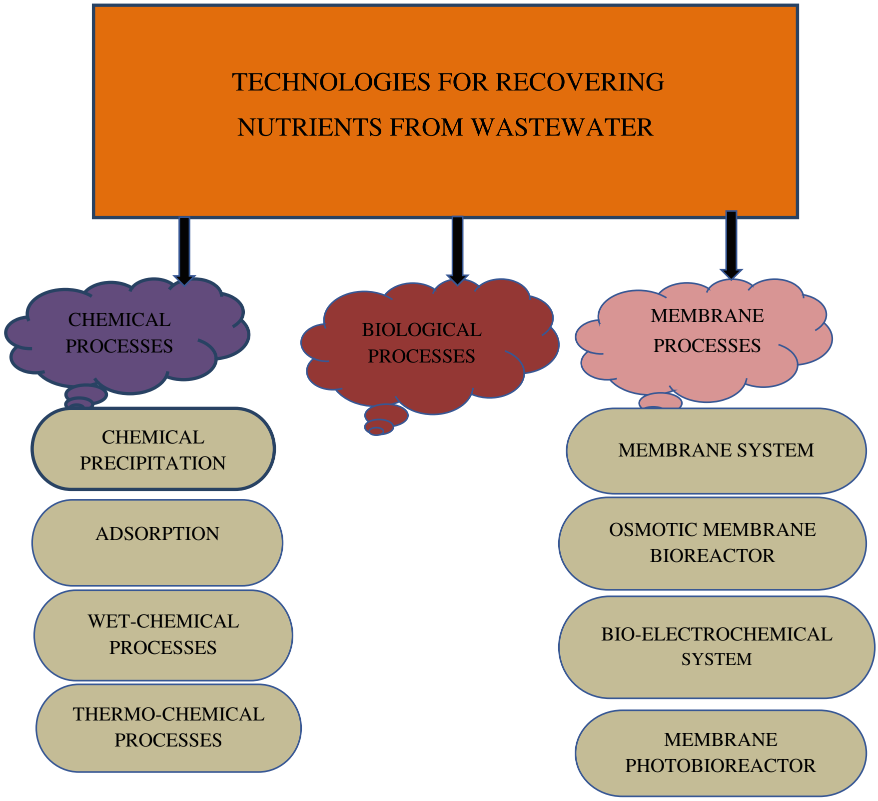

Fig. 9.2 Technologies for recovering nutrients from wastewater

9.3 Traditional Technologies for Nutrient Recovery

9.3.1 Chemical Process

Chemical absorption and precipitation are the main approaches to the nutrient recovery process during wastewater treatment. Calcium and magnesium-based materials are reacted with nutrients present in wastewater to form the hydroxyapatite ($Ca_5(OH)(PO_4)_3$) and struvite ($MgNH_4PO_4{\cdot}6H_2O$) in the chemical precipitation process. These reactions are shown below

$$Mg^{2+} + PO_4^{3-} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4.6H_2O$$
$$5Ca^{2+} + 3PO_4^{2-+}OH^- \rightarrow Ca_5(OH)(PO_4)_3$$

Generally, hydroxyapatite is utilized as a raw material in the phosphate industry while in the agriculture sector, struvite served as a successful fertilizer. Wastewater composition is responsible for the standard pH and ratio of Ca:P and Mg:P:N. Overall, the improvement in the effectiveness of nutrient recovery by chemical precipitation requires a more thorough understanding of the effect of pH as well as the selections of Mg/Ca materials for acting as precipitators.

Rather than the chemical precipitation phenomenon, adsorption is exploited as an effectual method for nutrient retrieval because of its simple procedure, lower price and higher consistency. In this regard, desorption is an essential step and it is performed just after the adsorption. For the adsorption process to recover the phosphate, frequently metal-based adsorbents are utilized due to their high effectiveness and easy availability. In phosphate adsorption, three main approaches are electrostatic attraction, ion exchange and surface precipitation.

As well as while treating wastewater a sufficient quantity of phosphate may be deposited in the sludge (Kahiluoto et al. 2015; Qin et al. 2015). To overcome from the phosphate accumulation problem, thermo-chemical and wet-chemical treatments are applied to remove phosphate from the sludge (Appels et al. 2010), this make it easier in handling and manageable for the phosphate recovery process. Thus, plants and crops can absorb it easily. Acid and alkaline solutions are often utilized to transfer the phosphate ions from the sludge phase to the liquid phase. The choice of alkaline and acidic solutions must be completed by observing the characteristics of the sludge, including its treatment technology and contents. For the phosphate-containing sludge, thermo-chemical treatment can be performed with chloride as an additive material (e.g., magnesium chloride, calcium chloride). It should be added at high temperatures, i.e., 800–1000 °C (Adam et al. 2009). This process is capable to remove heavy metals as well (Herzel et al. 2016) which enhance the quality of the recovered phosphate. This also facilitates the supply of phosphate to the plants from the treated sludge (Donatello and Cheeseman 2013).

9.3.2 Biological Process

Biological phosphorus (P) is a key nutritive element present in wastewater. Its recovery is possible by integrating the phosphates into the activated sludge, in this process polyphosphoric-accumulating organisms (PAOs) also play a significant role. When there is an addition of microbes like (PAOs)/or denitrifying PAOs (DPAOs) it is considered as enhanced biological phosphorus removal (EBPR) which is a well-known approach for removing phosphorus (Wong et al. 2013).

Under alternating anaerobic and aerobic (PAOs)/or anoxic (DPAOs) circumstances, DPAOs and PAOs are capable to help in P retrieval from wastewater. In anaerobic conditions, the PAOs/DPAOs receive short-chain volatile fatty acids (VFAs) and store them intracellularly as poly-β-hydroxy-alkanoates (PHAs). The required energy for this process is obtained through the hydrolysis of stored polyphosphate (Poly-P). As a result, the phosphate (PO_4^{3-} –P) complex is liberated from the microbes, and biological phosphorus concentration in the wastewater is enhanced. Along with these few metal ions such as K^+ and Mg^{2+} also may be released from wastewater. This practice can produce energy that is mainly used to take up carbon sources (mainly the volatile fatty acids-VFAs) and then deposited in the form of poly-β-hydroxyalkanoates (PHAs).In a subsequent phase, the biological phosphorus-augmented biofilm is exposed to a smaller recovery stream augmented with an external carbon source to facilitate P release under anaerobic conditions. Biological phosphorus is attained as a highly concentrated liquid phase.

In an aerobic environment, phosphate also can be taken up and deposited in the microbial mass through PAOs. The energy utilized during this process is derived from the PHAs. At the same time, the ions of the metal can be adsorbed to the biomass (Yuan et al. 2012). Finally happens in the form of surplus sludge.

These all observations evidenced that phosphate recovery in the biological process is an accumulation of two steps–

(1) Release of phosphate and its accumulation in wastewater in an anaerobic condition
(2) Phosphate accumulation in the activated sludge under aerobic conditions.

Although enhanced biological phosphorus removal or biological phosphorus removal has great potential though this is banned in a few European countries due to the presence of heavy metals and pathogens (Schoumans et al. 2015).

9.4 Advanced Technologies for Nutrient Recovery

As conversed above, the biological and chemical processes definitely comprehend the aim of nutrient recovery from wastewater treatment process. Though, several coexisting substances like heavy metal ions and other toxic substances could seriously affect the quality of recovered products. Due to this reason, membrane technology is required. This technology provides actual enhancement and separation of pure nutrients.

9.4.1 Membrane System

The membrane technologies utilized for valuable nutrient retrieval include three major processes—

(i) The forward osmosis (FO)
(ii) Membrane distillation (MD)
(iii) Electrodialysis (ED).

Schematic diagrams for nutrient augmentation and recovery are represented in Fig. 9.1. The forward osmosis exercise uses a semi permeable membrane that is positioned between the feed i.e. input solution and output solution, and the osmotic pressure gradient between the two sides forces the water to transfer from the input to the output.

In the forward osmosis process, the nutrients may be rejected by the forward osmosis membrane and complemented in the input (Xue et al. 2015; Zhang et al. 2014), which is then applied for recuperating the nutrients. Furthermore, due to its greater hydrated radius, a larger volume of phosphate may be supplemented at the input as compared to the ammonium (Kiriukhin and Collins 2002; Zhang et al. 2014). In an alkaline environment, the forward osmosis membrane surface is negatively charged (Cartinella et al. 2006).

Subsequently, the electrostatic repulsions between the phosphate ions and membrane may enable phosphate retention in the feed side (input); in contrast, the ammonium concentration is withdrawn in this case. A neutral pH may be useful for both the enhancement of phosphate and ammonium. High pH leads to the alteration of ammonium into volatile ammonia.

In the Membrane distillation-MD process, the feed solution is heated moderately to produce volatile material which transfers to the output solution through the Membrane distillation membrane. So, the ammonium ion present in the input solution of the Membrane distillation procedure is transformed into the volatile ammonia and then received by the output solution (Ahn et al. 2011; Qu et al. 2013). Acidic solutions like H_2SO_4, are regularly employed as the key solutions. Later, they can react with the ammonia to produce the salts of ammonium. The solution pH and temperature of the input solution significantly affect the ammonium transformation and further transport. In the Electrodialysis procedure, the anion-exchange membrane (AEM) and cation-exchange membrane (CEM) are applied to separate phosphate and ammonium from the nourish solution in the recent field and enhance the nutrients in various chambers. Specifically, the ammonium and phosphate ions are determined in the anode and cathode chambers for their absorption and further retrieval (Tran et al. 2014).

9.4.2 Osmotic Membrane Bioreactor

On the base of the forward osmosis membrane technology, Qiu and Ting (2014) established an osmotic membrane bioreactor—OMBR for the retrieval of nutrients, in which the forward osmosis method is united with aerobically biological processes. In this condition, direct nutrient recapturing could be accomplished, in which more than95% of phosphate and ammonium can be supplemented at the feed side and then recuperated/removed in the form of calcium phosphate/struvite precipitates. More prominently, no chemicals were supplemented to identify the objective of the nutrient recovery process, but supplementary alkaline chemicals were essential for pH advancement. On the other way, using $MgCl_2$ as the major solute could complement the Mg^{2+} ions for nutrient retrieval through chemical process, which is accredited to the reverse draw flux, a specific property of the forward osmosis procedure.

9.4.3 Bio-electrochemical System

Bio-electrochemical system-BESs involves electrochemical reactions and microbial metabolism to generate electricity. Microbial fuel cells (MFCs) establish an original type of BES, which has been reconnoitred for nutrient retrieval in the past decade. This also may be elaborated to microbial recovery cells (MRC) and microbial electrolysis cells (MEC) (Catal et al. 2019a, b; Li and Chen 2018; Yadav et al. 2020). A standard MFC comprises two chambers (i.e., anode chamber and cathode chamber) that are segregated by a CEM. The anode chamber is accountable for the formation of protons and electrons, and the electrons respond with the electron acceptor (e.g., air) in the cathode chamber to accomplish the electrical loop. The Microbial fuel cells activity reactions are illustrated as follows-

$$C_6H_{12}O_6 + 6H_2O \rightarrow CO_2 + 24H^+ + 24e^-$$
$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

In this case glucose act as the carbon source.

The ammonium ions can transfer from the anode chamber to the cathode chamber across the CEM due to the concentration-gradient-caused diffusion and current-driven migration. Ions of ammonium might be concentrated in the cathode chamber (Kelly and He 2014; Kuntke et al. 2012). The pH confined in the cathode upsurges due to the cathode activities, this may cause for the conversion of ammonium to volatile ammonia (Ye et al. 2019a, b). Air stripping may be used to drive out the volatile ammonium present in the cathode chamber. This volatile ammonium is then absorbed by the acid solution to produce ammonium salts. Alternatively, the phosphate in ionic form could be recuperated by chemical precipitation since the cathode chamber can provide a great pH zone for precipitation (Chen et al. 2015, 2017; Ye et al. 2020). The precipitates frequently occur on the exterior of the cathode electrode.

9.4.4 Membrane Photobioreactor

In the past few years, microalgae-based processes have been popularized for recuperating nutrients from wastewater in a photobioreactor (PBR) (Ye et al. 2020). To complement the growth and accretion of biomass in the PBR, the membrane technology is joined with the PBR (MPBR) to decouple the Hydraulic retention time (HRT) and Solid retention time (SRT), which has greater nutrient retrieval effectiveness and a minor footprint than PBR. The procedure costs of traditional PBRs (US $0.65–0.96/m^3) are greater than that of MPBRs (US $0.113/m^3) (Xue Sheng et al. 2017). In the membrane photobioreactor, energy obtained from the sun or other light sources is compulsory and photo digestion could convert the organics into hydrogen (González et al. 2017). The nutrients and carbon dioxide may be integrated into the microalgae with the solar energy being deposited. The microalgae may be transformed into valuable goods such as input for animals and fertilizer biogas (Jankowska et al. 2017). As formerly conversed, this indicates physical separation involved in the membrane system which does not necessitate biological processes. Some additional advantages to utilizing these membrane systems for valuable nutrient recapturing are—

(1) Some countries with deficient energy sources
(2) Decentralized wastewater treatment schemes
(3) Some regions fail to conduct biological processes due to extreme climate
(4) Some countries do not have centralized wastewater treatment systems (Hube et al. 2020).

Economic perspective, the retrieval of nutrients by forwarding osmosis processes utilized in wastewater treatment units positioned close to the sea is extremely commended since readily accessible seawater may be exploited as the draw solution to reduce the overall costs using Mg^{2+} ions. Besides, the MD filtration method may be employed to recuperate ammonium from complex industrial wastewater, in which the FO procedures are unsuccessful (Li et al. 2019). Significantly, it is commercial for the ammonium repossession by membrane distillation procedure (MD) from wastewater including high temperature as there is no need of extra energy sources and wastewater with accessible low-grade thermal energy (like solar energy) (Hube et al. 2020). To enhance the application and improve nutrients recovery process membrane systems may be integrated with biological processes in consolidated wastewater treatment systems. Specifically, the OMBR scheme utilized to improve nutrients can decrease the membrane fouling probability, which turns to the enhancement of the commercial feasibility of the recovery system. Besides this, the BES containing anaerobic treatment may be used to delight more complex wastewater e.g., industrial wastewater. In this nitrogen and phosphorus may liberate in the form of ammonium ions (NH_4^+) and phosphate ions (PO_4^{3-}), respectively. These may be consumed for recovery of nutritive substances by succeeding chemical precipitation. The BES can also yield electrical energy for being an energy-efficient wastewater treatment. It is noticeable that the BES needs biodegradable organic matter for energy recovery. It may take a little longer time for MPBR to accomplish the nutrient retrieval with additional light sources despite its lesser environmental footprint (Table 9.1).

9.4.5 Hydrophytes and Macrophytes Are Used for Treating Wastewater

Currently, conventional systems used to treat wastewater are not very effective in the complete elimination of water pollutants and modern approaches are not easily manageable and their high cost creates difficulty in handling wastewater. Such there is a requirement for eco-friendly highly sustainable control processes for this problem. In this, several aquatic plants play a major role to absorb additional pollutants such as

Table 9.1 Technologies for recovering nutrients from wastewater

S. No.	Methods	Nutrient recovered	Requirements	References
1	Chemical precipitation	Phosphate	Calcium based product	Ye et al. (2020)
2	Chemical adsorption	Phosphate, ammonia	Mg^{+2} and Ca^{+2} based adsorbents	Barampouti et al. (2020)
3	Wet chemical and Thermochemical procedure	Phosphate	Acid and alkaline solution, additives like $MgCl^2$ and $CaCl^2$	Liu et al. (2021)
4	Biological process	Phosphate	Mg^{+2} and K^+ ions	Yan et al. (2018)
5	Membrane system	Ammonia and phosphate	Ammonia and phosphate ions	Tran et al. (2014)
	Forward osmosis	Magnesium, ammonia and phosphate	Magnesium flux	Singh et al. (2019)
	Membrane distillation	Ammonia	Low concentration H_2SO_4	Zarebska-Mølgaard et al. (2022)
	Electrodialysis	Phosphate	Alkaline PH	Wang et al. (2022)
6	Osmotic membrane bioreactor	Ammonia and phosphate	Mg^{+2} ions	Viet and Jang (2022)
7	Bio-electrochemical system	Ammonia and phosphate	Ammonium biocarbonate	Kashima (2020)

organic and inorganic pollutants present in wastewater. Aquatic plants may be used for phytoremediation by phytoextraction, phytodegradation, etc., but the elimination of pollutants may be depended on the pH, temperature, and exposure of pollutants. (Anand et al. 2017). Continuously, various types of aquatic plants species may exploit for the handling of wastewater such as free-floating plants Azollapinnata, Eichhorniacrassipes, Salviniamolesta etc., submerged plants Hydrillaverticillate, Vallisneriaamericana, Najas marina etc., and other aquatic plants like *Cyperus* spp., *Justicia americana*, *Iris virginica*, have been used for treating wastewater.

9.4.6 Microalgae Used for the Treatment of Wastewater

Treating of wastewater and nutrient recovery cannot be managed by a single technology due to their variable sources and types of contaminants etc. Thus the progress of effective wastewater treatment methods and their economic value is a great concern.

Since the 1960s microalgae have been used for treating wastewater and depend on the composition of wastewater (Acién et al. 2016). Due to their capability to achieve photoautotrophic, heterotrophic or mixotrophic microalgae can be opt as a promising source for the treatment of wastewater (Hu et al. 2018; Subashchandrabose et al. 2013).

9.4.7 Conventionally Microalgae Are Used for the Treatment of Wastewater

Chlorella vulgaris has been used as treating wastewater due to its ability to produce biomass from food waste compost like tofu wastewater, corn steep liquor and industrial dairy effluent etc., (Wollmann et al. 2019). Arthrospiraplatensis removed high P (80.52%) and N (81.51%) from synthetic wastewater. This study has been conducted by Zhai et al. 2017.

Another study was also evaluated by Hena et al 2018 in which the accumulation of lipids was formed by *A. platensis* while developing on dairy farm wastewater which was total biomass of 4.98 g L^{-1} and 30.23 wt% of lipid content. Hence, it can be used for biofuel production.

9.4.8 Microalgae Used for Harsh Wastewater

The composition of industrial wastewater ranging from high organic loads, extreme temperature and highly acidic ($2.0 < pH < 8.0$) makes it difficult to treat wastewater by conventional technology. So these are achieved by some special microlalgae. *Galdieria sulphuraria*, also denoted as *Cyanidium caldarium* is such microalgae that are adapted with extremophilic growth properties (Varshney et al. 2015). *Galdieria sulphuraria* was reported to be grown on 27 different sugars and sugar alcohols (Schmidt et al. 2005). *Galdieria sulphuraria* has adapted to grow in neutral environment as well as in highly acidic environments and it also acidify the environment by active proton efflux, thus decreasing the contamination level (Delanka-Pedige et al. 2019). Not only the acidophilic nature, they can also grow in thermophilic conditions up to 56 °C (Selvaratnam et al. 2014).

Chlamydomonas acidophila is another microalgae that can grow in extreme environments such as pH values ranging from 1.7 and 3.1 (Cuaresma et al. 2011). It has some special properties that can grow mixotrophically in the absence of CO_2 by utilizing other carbon sources, especially glucose, starch, glycerol having pH 2.5 and it can also remove NH_4 (Escudero et al. 2014). Antioxidant carotenoid lutein can be accumulated by *C. acidophila* from wastewater is the most promising feature for biomass production (Garbayo et al 2008).

9.4.9 (Photo-) Bioreactor Systems

Photobioreactor (PBR) systems is the advance technology used by microalgae for the treatment of wastewater. In PBR sufficient amount of $CO_2$and light energy is needed because it is a totally photoautotrophic process. There are mainly two approaches for treating wastewater i.e., suspended and immobilized methods for treating wastewater.

9.4.10 Suspended WWT Systems

For bacterial wastewater treatment, Pond systems are most commonly used (Young et al. 2017). They are also the most frequently used variety of large-scale reactors for microalgae development, due to their easy creation and low asset costs. Still, due to a greater light path of > 30 cm, causing in a restricted light source, changing outdoor temperatures, and inadequate combination, as a result, the biomass revenue of pond systems is at a low levelcontrast to tubular techniques or extra specific PBRs like flat-panel PBRs (Park et al. 2011). The inadequate amount of CO_2 reduces algal biomass yield due to the adverse C: N: P ratio in wastewater (Kesaano and Sims 2014). However, it has been shown that specific aeration and the addition of CO_2 can enhance biomass productivity and removal rates of undesired water constituents. The addition of N or P is sometimes used to ensure molar ratios of nutrients for optimal algal growth (Christenson and Sims 2012) and co-cultivation with bacteria can be favourable about to heterotrophic oxidation of organic compounds in wastewater by microorganisms that benefit from increased oxygen levels, induced by photoautotrophic algal growth. The removal efficiency of total N and P by microalgae from wastewater has been determined to be between 10 and 97% and is highly dependent on culture mode, tank size, type of wastewater, and the microalgae strain (Park et al. 2011) indicating that there is no single technology/species combination that is able to fulfil every WWT goal.

9.4.11 Immobilized Approach

Microalgae immobilization presents a hopeful method for acquiring both metabolic transformation of wastewater pollutants and simple and low-cost collection of the generated biomass (Lam and Lee 2012). Immobilized approach can be accomplished in different methods. For pond ecosystems, Algal Turf Scrubber (ATS) is a process that is used for the removal of N and P from municipal and agricultural wastewater and it utilizes immobilized community of algae, bacteria and *Cyanobacteria.*

9.5 Merits and Demerits of Technologies for Recovering/Enriching Nutrients from Waste Water

In recent decades, various procedures at the laboratory or pilot scale came to light. These all contributed a lot to the wastewater management system. The merits and demerits of a few procedures are described (Table 9.2).

Table 9.2 Merits and demerits of technologies

Method	Merits	Demerits
Chemical precipitation	This input is in the Liquid phase and it has very high efficiency	It requires a high amount of chemicals
Chemical adsorption	The liquid phase is the input phase and very high stability is observable	Specific adsorbents are required to accomplish the procedure Also added practice such as desorption desired
Wet chemical and thermochemical procedure	It is an efficient method. This Sludge phase is the input phase	The downstream procedure is desirable. Energy and chemical requirement is more
Biological process	In this, input is in the liquid phase and this procedure is eco-friendly	Stability seems little. Low applicability of recuperated harvests comprising foreign matters
Membrane system: forward osmosis membrane distillation electrodialysis	Input is in the liquid phase. In forwarding the osmosis process Low energy input. Low fouling potential. Easy fouling clean. During membrane distillation, operation pressure is less and Renewable energy is available for being used. In the Electrodialysis procedure, high nutrient enrichment is there	In forwarding osmosis reconcentration procedure of draw solute is required. In the membrane distillation procedure, organic accumulation and Membrane wetting are common issues. In electrodialysis low current efficiency and high energy, input is required
Osmotic membrane bioreactor	Low membrane fouling potential. Removal of organic is possible. It requires low energy input and low salinity level	Reconcentration of draw solute needed
Bio-electrochemical system	Low chemical input	Formation of recovered products on the cathode surface
Microalgae	Ecofriendly	Need more expertise

These all descriptions indicated that in the future integration of techniques for recovering/enriching nutrients from wastewater may be applied.

9.6 Conclusion

Valuable Nutrient retrieval from wastewater helps in environmental protection and fulfilment of the demand for useful nutrients for mankind. Thus, for harnessing the potential nutrients from wastewater and for use of these recycled nutrients there are some methods involved which will be explained in the next section.

Available Conventional technologies are not sufficient for obtaining high quantity and quality of nutrients. Thus there is a need of integrating conventional technologies with recent technology. In brief, the chemical precipitation, chemical adsorption, Wet chemical, and Thermochemical procedure, Biological Processes, membrane system-forward osmosis, membrane distillation and electrodialysis, osmotic membrane bioreactor, bio-electrochemical system and use of Microalgae based systems have been discussed for their implementation in nutrient recovery. It seems that efforts are needed to reduce operating costs and improve their technical feasibility, which would make the recovery system more eco-friendly, accessible and efficient.

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Chapter 10
Wastewater into a Resource: Biofertilizers

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Abstract Rapid urbanization, over-population, and industrialization induce rise in freshwater scarcity considerably and are responsible for the generation of wastewater in larger amounts. Disposal of untreated wastewater causes eutrophication, and water pollution, disturbing the aquatic ecosystem beyond repair. On the other hand, growing global food demand increases the usage of chemical fertilizers. Although chemical fertilizer enhances plant growth, development, and productivity efficiently, it degrades the soil quality and nutritional food value, destroys soilbiota thus becomes a life-threatening factor. The adverse effects of these have lead to the search for cost-efficient, eco-friendly alternative options. The generation of biofertilizer from wastewater is a promising approach that can be used as a replacement for "chemical fertilizer" for wastewater disposal and also helps to mitigate eutrophication, improve soil quality and give a future roadmap for better possibilities for environmental sustainability. Proper treatments, can turn wastewater into a resource to alleviate water scarcity and for the betterment of the environment.

Keywords Wastewater · Biofertilizer · Chemical fertilizer · Wastewater to resource · Environment sustainability

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10.1 Introduction

Freshwater scarcity has become the greatest concern in the last decades due to the rapidly increasing population, changing climatic conditions, increasing water demand, consumption and decreasing water availability (Gosling and Arnell 2013; Falkenmark et al. 2009; Schewe et al. 2014). As, the population-size of the world continuously increases, more strain will be applied to the available environmental resources (Vaish et al. 2016). According to a recent study, an almost 600% increase has been noticed in global water demand in the last 100 years and by the end of 2050, it will be increased by 20–30% more (Boretti and Rosa 2019).

On one side demand for clean and safe water is increasing gradually and on the contrary, overpopulation, rapid urbanization, and increasing industrial and anthropogenic activities are responsible for the generation of wastewater in larger amounts (Qin et al. 2014; Singh et al. 2015; Singh and Sarkar 2015). Previous studies also reported that rapid urbanization was one of the major causes that were responsible for the generation of wastewater and not only that, it deteriorates the water-quality (Kannel et al. 2007; Zhao et al. 2006; Ren et al. 2003; Sarkar et al. 2018). Furthermore, wastewater disposal without proper treatment not only causes water pollution but also disbalances the aquatic ecosystem.

Most of the time the wastewater was enriched in nutrients like nitrogen and phosphorus and continuous discarding of such nutrient-dense effluent into water-resources, accelerates the eutrophication. Formation of algal bloom, decrease in oxygen level and species biodiversity, deterioration of quality of water-resources, even exterminating the aquatic ecosystem are the outcome of the eutrophication (Goncalves et al. 2017). Several biological and chemical methods have been used to minimize the concentration of nitrogen plus phosphorus (Lewis et al. 2011; Boelee et al. 2011; Goncalves et al. 2017). Besides nitrogen, phosphorus, wastewater also contains lots of micro and macro elements, heavy metals, magnesium and different organic material which make it a potent environmental pollutant (Ali 2005; Suzuki et al. 2007; Liu et al. 2011). Pathogens and several disease-causing organisms may also be present in the untreated wastewater which can reside in the intestinal tract of humans thus making it a risk factor for human health (Seow et al. 2016).

As reported by Umami et al. (2019) and Khalofah et al. (2022), plants require essential nutrients like nitrogen along with phosphorus to grow and survive as well as agricultural yield. ‘Chemical fertilizers’ contain these primary nutrients which help plants to grow rapidly. However, using these chemical fertilizers continuously accelerates degradation of the soil quality, decreases the nutritional value of food, destroys soil biota and negatively affects the life of the plant, and animals and humans, thus becoming a life-threatening factor (Sneha et al. 2018; Boraste et al. 2009). On the contrary, phosphorus-based fertilizers have become more costly day by day because it is a non-renewable resource which cannot be replaced by any other substance (Fraunhofer-Gesellschaft 2012). So biofertilizers could be a substitute for chemical fertilizers that increases plant growth, maintains soil condition as well as enhances the capacity of the soil to produce crops (Sneha et al. 2018).

Biofertilizers are mainly organic materials that help plant to grow by improving available nutrient amounts, increasing soil's capability, plant productivity and ensuring environmental sustainability (Ghany et al. 2013; Sneha et al. 2018). Biofertilizers are renewable sources with a lower cost which become a promising, eco-friendly, future-based approach for sustainable agriculture thus it also provides food safety and security (Boraste et al. 2009; Srivastava et al. 2020). According to a recent study, the global population tends to shoot upto 9.5 billion by the end of 2050 which results in increasing food demand day by day (Kumar et al. 2022). Besides over-population, urbanization, deforestation, climatic changes and different abiotic and biotic stressor can affect growing-rate and yield of plants negatively (Glaser and Lehr 2019).

Dasgupta et al. (2021) disclose that several approaches have been opted for generating biofertilizers from different sources as they can effectively replace chemical fertilizers and increase plant productivity thus maintaining sustainable agriculture (Dasgupta et al. 2021). Biofertilizers, directly and indirectly, help plants to grow, by increasing nutrient-availability and stress tolerating-ability and phytostimulation (Liu et al. 2020; Riaz et al. 2020; Shirmohammadi et al. 2020). However, their responses are inconsistent due to different soil quality, lower shelf-life and proper application procedures making their uses limited even today (Debnath et al. 2019).

Therefore this chapter aimed to bring light on global statistics, different sources and compositions of wastewater and the importance of proper treatments of wastewater before disposal. The importance of biofertilizer usage and its implication for sustainable agriculture are also discussed. Furthermore, this chapter aimed to bring up different ways of biofertilizer formation from wastewater and its importance for a sustainable environment as a back up for hazardous chemical fertilizers. Generation of biofertilizer from wastewater is a practical, promising, cost-effective yet environment-friendly approach for wastewater disposal and also helps to mitigate eutrophication, improve soil quality and give a future roadmap for better possibilities for environment sustainability.

10.2 Wastewater

Wastewater can also be interpreted as used water as, it has been adulterated by human, industrial and other anthropogenic deeds (Mateo-Sagasta et al. 2015).

10.2.1 Global Statistics of Wastewater

According to a report by UN WWDR (2017), globally 80% of the total wastewater remains in the environment, in the form as it is, without proper treatment which is responsible for water pollution. But according to the latest report, the untreated wastewater percentage has decreased; almost 56% of the domestic wastewater has been treated safely before disposal (UN WATER 2021). Due to the disposal of this untreated wastewater into the environment several diseases such as cholera, dysentery etc. spreads rapidly in developing countries (UN WWDR 2017). Almost 1.8 billion people are drinking contaminated water even today which leads to the spread of several waterborne diseases like dysentery, polio, typhoid and cholera (WHO 2015).

Due to rapid urbanization, it is expected that almost ‘2.1 billion people’ may be settled in metropolitan-areas by the end of 2030 which results in large amounts of wastewater generation (Mateo-Sagasta et al. 2015). Jones et al. (2021), reported that almost 359 billion cubic metres of wastewater has been generated every year which is almost equal to the amount of water contained in 144 swimming pools of Olympic-sized.

However, with proper application, wastewater with nutrients, organic matter and water content can be reused in multiple ways; thus making it a ‘resource’, not a ‘waste’ (WWAP 2017; Qadir et al. 2020).

10.2.2 Sources of Wastewater

Based on different sources, wastewater can be categorized into the following categories (Agrawal et al. 2014) (Fig. 10.1).

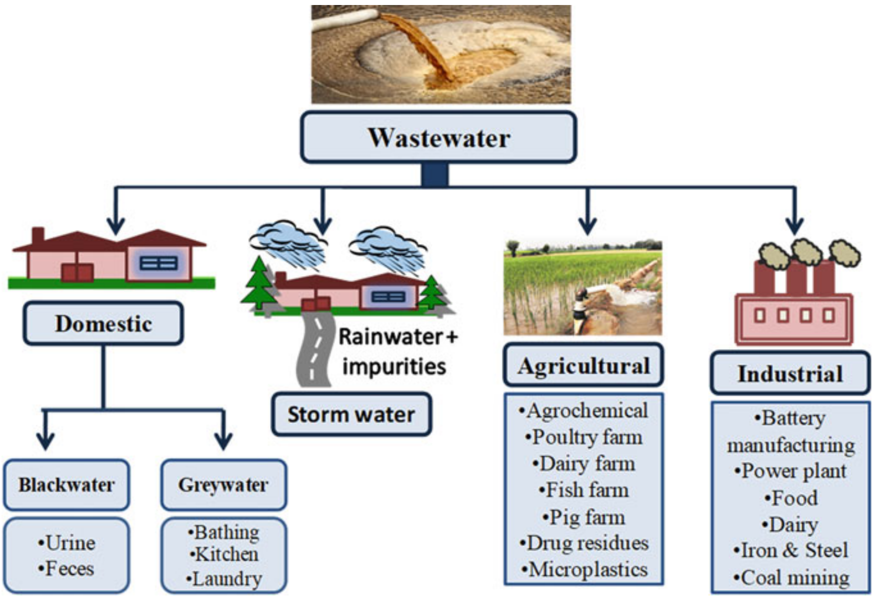

Fig. 10.1 Sources of wastewater

10.2.2.1 Domestic Wastewater

Domestic wastewater is used water from houses and apartments due to human activities which mainly contains 99.9% of water, organic matter in small concentrations, pathogenic bacteria and some toxic elements like lead, zinc along with cadmium (Joshi et al. 2020). Domestic wastewater can be further divided into two categories: blackwater and greywater; water from toilets including both urine and faeces has been placed under 'blackwater' whereas, kitchen, laundry and bathing water has been placed under 'greywater' (Asano et al. 2007) (Fig. 10.1).

10.2.2.2 Industrial Wastewater

Rapid urbanization also influences the expansion of industrialization mainly near urban areas. Mainly used water from different industries such as battery manufacturing, power plant, mining, food, dairy, iron, steel, oil and gas industry is categorized as industrial wastewater (Sathya et al. 2022; EPA 1976, 1982, 2002, 2015, 2017, 2018) (Fig. 10.1). Rapid industrialization also increases the generation of industrial waste; the quality and quantity of wastewater depend on the type of industry (Ahmed et al. 2021a, b).

10.2.2.3 Agricultural Wastewater

Agricultural sources are one of the major sources of wastewater generation. Excess amount of water running through the field along with different agrochemicals such as pesticides, herbicides, fungicides, fertilizer and animal waste from different farm industries like poultry, dairy and pig farms, drug residues and microplastics are the main pollutants (Fig. 10.1). It becomes a major life-threatening factor which gives rise to severe health-consequences (Evans et al. 2019; Pedrero et al. 2010).

10.2.2.4 Stormwater

Stormwater is mainly rainfall with high impurities due to flowing through streets or open areas. It contains many toxic pollutants like plastics, heavy metals, chemicals, and even pathogenic microorganisms. With proper treatments and storage systems, stormwater can become the most useful source of freshwater in nearby future (Sewnet 2011; Bani 2011).

10.2.3 Composition of Wastewater

The major component of wastewater is water which is almost 99.9% and the rest are some dissolved and suspended organic, inorganic matter and pathogenic microbes (Hassan et al. 2017). Organic components that are generally biodegradable include both macro compounds which range from 10^3 to 10^6 dalton and micro compounds which range from 0.001 to 100 μm (Templeton and Butler 2011; Pempkowiak and Obarska-Pempkowiak 2002; Painter 1973). Carbohydrates, chlorophyll, amino acids, proteins, lipids and nucleic acids are major organic compounds. Besides that, wastewater often contains several toxic chemical compounds like polychlorinated biphenyl (PCB), polyaromatic hydrocarbon (PAH) and dichloro-diphenyl-trichloroethane (DDT). Human pathogenic organisms such as viruses, coliform bacteria, streptococci, and protozoa as well as non-pathogenic microbes are also very common in wastewater due to the presence of faeces from both human and animal and industrial waste in it (Shon et al. 2007; Huang et al. 2010; Abdel-Raouf et al. 2012; Symonds and Breitbart 2014). Inorganic components such as cadmium, copper, chromium, zinc and lead are also identified in it (Li et al. 2012; Fuentes et al. 2008). Besides that, nitrogen and phosphorus are also identified in excess amounts in wastewater which is responsible for eutrophication in water bodies and also causes a threat to human-health (Yamashita and Yamamoto-Ikemoto 2014) (Fig. 10.2).

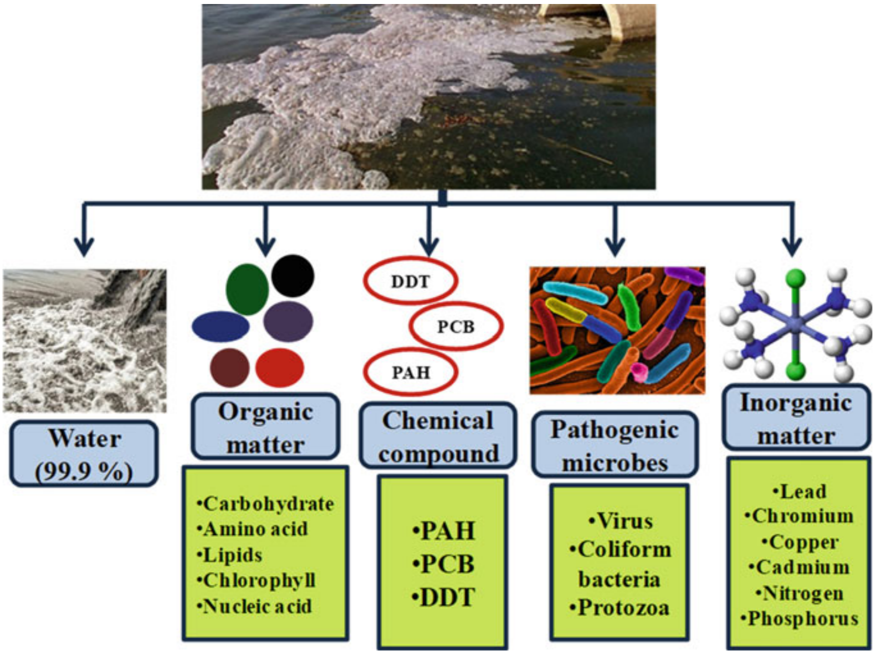

Fig. 10.2 Components of wastewater

10.3 Biofertilizer and Its Implication for Sustainable Agriculture

Biofertilizer can be any organic substances such as waste, animal manure or other substances that contain different types of microorganisms, including bacteria, algae and fungi which stimulates plant health effectively yet efficiently by producing hormones, increasing nutrient and mineral availability and has the potential to replace chemical fertilizer, increase soil fertility, help in environment restoration (Yasin et al. 2012; Sneha et al. 2018).

10.3.1 Types of Biofertilizer

Based on their physical nature, biofertilizers can be classified as 'solid carrier-based' and 'liquid-based' biofertilizers. Mostly, liquid-based fertilizers are more beneficial as compared to solid carrier-based biofertilizers and their availability is also increasing day by day (Dey 2021). Liquid biofertilizers are organic substances containing dormant microorganisms in a liquid medium that can enhance plant growth, development, soil fertility, capacity of the soil to hold water, and also withstand high temperature and UV radiation; Solid biofertilizers are organic substances that contain microorganisms in a solid medium which can be both organic and inorganic depending on the price and availability such as soil, animal manure, compost, biochar, peat, plant materials, charcoal, perlite, zeolite, corn cob. Most importantly liquid biofertilizers have a longer shelf life and their application is very easy too (Singh and Kumar 2020; Verma et al. 2018, 2011; Uparivong 2012; Tripti et al. 2022; Sohaib et al. 2020; Pacheco-Aguirre et al. 2017). On the other hand, solid biofertilizers are highly temperature sensible, having a lower shelf life, and more possibilities for contamination, and it also has a high transportation cost thus it becomes more costly (Verma et al. 2011; Hindersah et al. 2021).

10.3.2 Components of Biofertilizer

'Biofertilizers' are the modern form of organic fertilizer that contains different beneficial microorganism which stimulates plant growth and soil productivity. The nature and character of biofertilizers are depending on the source and procedure of biofertilizer formation (Hanapi et al. 2012). The main component of biofertilizer is different microorganisms like nitrogen-fixers, phosphorus-solubilizers, potassium-solubilizers, and phosphorus mobilizers. These microorganisms are incorporated in different carrier-based medium (both solid and liquid) with or without the addition of fungi. Generally, this microorganism is closely associated with plant roots (Srinivasan et al. 2020; Khosro and Yousef 2012; Daniel and Tariku 2019). Different types of microorganisms present in biofertilizers are discussed in Table 10.1.

10.3.3 The Mechanism of Biofertilizer for 'Plant Growth, Development and Productivity'

Biofertilizer contains microorganisms which enhance plant health either 'directly' or 'indirectly' (Santoyo et al. 2021).

10.3.3.1 Direct Mechanism

Direct mechanisms include producing phytohormones, and increment of several nutrient-availability like nitrogen, phosphorus, potassium, zinc etc. (Mahumud et al. 2021).

Phytohormones Production

Biofertilizer enhances plant growth by producing or altering the concentration of different phytohormones, including 'gibberellins' (GA), 'indole acetic acid' (IAA), 'cytokinins' (CK), 'ethylene' (Chi et al. 2010; Abd El-Fattah et al. 2013). These phytohormones trigger root and shoot growth, flowering, fruiting, germination and senescence and activate cell division, cell elongation, differentiation, and enhance stress tolerances. It increases root hair length through that plants can easily absorb 'water and nutrients' from deep soil (Khan et al. 2020; Tsegaye et al. 2017; Kumar et al. 2022; Mahumud et al. 2021).

Nitrogen Fixation

Nitrogen, one of the most abundant elements, is an essential component of nucleic acid, amino acid along with chlorophyll. It also enhances vegetative and reproductive growth, and increases productivity and biomass (Werner and Newton 2005; Banik and Dangar 2019; Avila et al. 2020; Verma and Agrawal 2018). Though 80% nitrogen is present in the atmosphere, yet plants cannot use atmospheric nitrogen directly. However, biofertilizers containing nitrogen-fixers microorganisms are capable of reducing 'atmospheric nitrogen' into 'ammonia' (NH_3) which is an 'easily accessible form' for directly used by plants (Moniish Kumaar et al. 2020). Nitrogen fixation by microorganisms is a cost-efficient, eco-friendly way to fix atmospheric nitrogen

Table 10.1 Microorganisms and their mode of action, association, and benefits

Sl.No.	Microorganisms	Association	Mechanism	Benefits	Reference
1	1. *Azotobacter* sp. 2. *Anabaena* sp. 3. *Nostoc* sp.	Free-living	Nitrogen fixation	Enhance chlorophyll formation thus enhancing photosynthesis, crucial for nucleic acid and protein synthesis, enhancing plant-productivity	Srinivasan et al. (2020) Bano and Iqbal (2016) Xu et al. (2012) Avila-Ospina et al. (2014)
2	1. *Rhizobium* sp. 2. *Frankia* sp.	Symbiotic			
3	1. *Azospirillum* sp.	Associative symbiotic			
4	1. *Boletus* sp. 2. *Amanita* sp.	Ectomycorrhiza	Phosphorus mobilizing	Promote plant growth, enhance phosphorus availability by mobilizing it, influence agriculture production	Srinivasan et al. (2020) Fox et al. (2014) Nannipieri et al. (2011) George et al. (2018)
5	1. *Glomus* sp. 2. *Sclerocystis* sp. 3. *Acaulospora* sp. 4. *Scutellospora* sp.	Arbuscular mycorrhiza			
6	1. *Pezizella ericae*	Ericoid mycorrhiza			
7	1. *Rhizoctonia solani*	Orchid mycorrhiza			
8	1. *Bacillus* sp. 2. *Acidothiobacillus* sp. 3. *Paenibacillus* sp.	–	Potassium solubilizing	Enhance plant growth and development, increase crop productivity, enhance starch synthesis, carbohydrate metabolism, photosynthesis	Ahmad et al. (2016) Etesami et al. (2017)
10	1. Fungi	–	Phosphorus solubilizing	Increase availability of phosphorus, enhance soil fertility, enhance hormone production, increase plant growth and productivity	Srinivasan et al. (2020) Baliah (2018) Kannapiran and Vijayan (2011)
11	1. Bacteria	–			

(continued)

Table 10.1 (continued)

Sl.No.	Microorganisms	Association	Mechanism	Benefits	Reference
12	1. *Bacillus* sp.	–	Zinc solubilizing	Stimulate plant growth and development, essential for tryptophan synthetase which helps in hormone synthesis, help in photosynthesis, membrane function, carbohydrate metabolism	Srinivasan et al. (2020) Hafeez et al. (2013) Tavallali et al. (2010) Bhatt and Maheshwari (2020)

into readily available form and it has the potentiality to cut out 'chemical fertilizers' (Mahumud et al. 2021).

Solubilization of Nutrients

Biofertilizer enhances the soil quality by making it nutrient-rich; these nutrients including both micro and macro nutrients carry out a leading role in plant health and lack of them leads to various malfunctioning like yellowing of leaves, plant growth reduction (Sneha et al. 2018).

Potassium, key macronutrient, is crucial for plants as it increases stress tolerance and disease resistance, improves water and nutrient uptake ability, and triggers enzymes related to photosynthesis, translation, sugar transport and other physiological processes (Xu et al. 2020). Potassium-solubilizing microorganisms can efficiently convert potassium from 'insoluble form' to 'soluble form' (Ahmed et al. 2021b).

Phosphorus, the most vital macronutrient, is needed for growing plants. But phosphorus is existed in the 'insoluble form' that is inaccessible to plants (Raghothama 2015). Phosphorus-solubilizing microorganisms can solubilize phosphorus by generating several organic acids of 'low-molecular-weight' including oxalic, formic, along with maleic acid (Mahumud et al. 2021).

Zinc, a vital micronutrient, is required for growing crops, but only a small percentage of zinc is available in the 'soluble form' which has led to zinc deficiency which further results reduction in plant growth and development, chlorosis, root necrosis, dwarf leaves (Yadav et al. 2022; Kabata-Pendias and Pendias 2001; Rudani et al. 2018). Biofertilizer containing zinc-solubilizing microorganisms can solubilize zinc by several mechanisms thus increasing the availability of zinc in the rhizospheric region which further enhance plant growth (Kushwaha et al. 2020).

10.3.3.2 Indirect Mechanism

Siderophore Production

Iron is existed in ‘Fe^{3+} form’ that is not available for plant usage as they absorb iron in Fe^{+2} form (Ghazy and El-Nahrawy 2021). According to Rroco et al. (2003) biofertilizer increases iron availability by iron sequestration through siderophore. These siderophores are minute, low-weight, chelating elements that can attach with Fe^{3+}form and can convert it into readily available Fe^{+2} form (Kashyap et al. 2017).

Ammonia and Hydrogen Cyanide (HCN) Production

HCN has antifungal properties that can effectively prevent fungal phytopathogens such as *Fusarium oxysporum*, *Sclerotinia sclerotiorum*, *Rhizoctonia sclerotinia* thus stimulating plant growth and productivity. Besides that HCN can also chelate ions, produce cell wall degrading enzymes that can regulate plant pathogens, and increase the availability of phosphorus (Zain et al. 2019; Rijavec and Lapanje 2016; Ramette et al. 2006). Ammonia helps to fulfil the nitrogen requirement of plants and promotes plant growth (Rodrigues et al. 2016).

Chitinase Production

Chitinase production is another mechanism of biofertilizer that enhance plant growth. Basically, chitinase is a cell wall degrading enzyme that degrades chitin, a vital component of insects and cell wall of fungi and it alters the cell-wall structure, provides the ability to resist these pathogens (Esteban et al. 2017; Sadfi et al. 2001).

10.4 Generation of Biofertilizer from Wastewater

Generally, wastewater contains nutrients in high concentration, especially nitrogen and phosphorus and if this nutrient-rich wastewater isn’t treated properly, it will lead to eutrophication (Goncalves et al. 2017). There are several technologies to recover nutrients from wastewater, but most of them are costly and have some limitations so a search for alternative options has been started (Zhang et al. 2016).

10.4.1 Struvite Crystallization

Struvite crystallization is the best cost-efficient and effective way of recovering nutrients from wastewater and it is being used as a biofertilizer directly or indirectly.

Struvite is basically a crystal containing magnesium, ammonium, and phosphate in the ratio of 1:1:1 ($MgNH_4PO_4.6H_2O$) that is generated from wastewater. As a low concentration of magnesium presents in the wastewater, an external source must be added during struvite formation (Decrey et al. 2011; Egle et al. 2016; Ramaswamy et al. 2022). pH, temperature and concentration of calcium, magnesium, ammonium and phosphate affect struvite crystallization (Hao et al. 2008). Struvite releases nutrient slowly, contains nutrients in high amount and control phosphorus loss (Nguyen et al. 2018; Talboys et al. 2016). Therefore, struvite has been used as a fertilizer as it increases soil fertility, especially for magnesium requiring crops (Gaterell et al. 2000).

10.4.2 Biofertilizer Production Using Microalgae

Several technologies have been developed for wastewater treatment but they are not sustainable due to high cost and maintenance. Wastewater treatment using microalgae is an effective and cost-efficient way to clean and disposal of wastewater, recover nutrients from wastewater and produce algal biomass that can recover nutrients from wastewater and use as a back up for available 'chemical fertilizers' (Mounika et al. 2022; Das et al. 2018). This nutrient-rich wastewater provides optimal conditions for microalgal growth (Renuka et al. 2015). Photoautotrophic microalgae are efficient in the reduction of inorganic matter into organic matter in presence of solar radiation and produce algal biomass which is biodegradable and non-toxic (Fernandez et al. 2018; Mandal et al. 2022). Das et al. (2019) reported that the algal biomass is a slow-release biofertilizer that emphasizes the nutrient-absorbing-ability of plants. According to Ronga et al. (2019) and Sampathkumar et al. (2019), algal biomass increases nutrient availability, enhances soil fertility and produces different stimulating products for plant growth.

10.5 Challenges of the Biofertilizer Production from Wastewater

- Field performance is the major limiting factor for biofertilizer production. Beneficial microorganisms of biofertilizers may perform excellently under lab conditions but not in the field (Keswani et al. 2019).
- Variations in the environment including different biotic and abiotic stress bring changes in the performance of biofertilizers (Mitter et al. 2021).
- External supply of carbon dioxide is needed for microalgal growth and efficiencies (Posadas et al. 2015).
- Storage condition affects the shelf life of biofertilizers. So proper storage conditions must be maintained to increase shelf life (Brar et al. 2012).

- Finding a suitable carrier for culturing microorganisms is also a limiting factor (Win et al. 2018).
- Though microalgae can remove contaminants effectively yet high concentrations of contaminants suppress the efficacy of microalgal culture (Hena et al. 2021).
- Presence of higher concentrations of ammonia has led to toxicity and a negative impact on some microalgal cultures (Das et al. 2018).

10.6 Conclusion

In this twenty-first century, due to overpopulation and increasing global food demand, chemical fertilizers are used excessively. Though these chemical fertilizers help plants to grow more rapidly, yet they destroy soil biota and make it unsuitable for the next batch of crops, degrade food values and productivity, contaminate nearby water bodies due to rainfall, cause health risks and deteriorate the overall environment. Observing these scenarios, the search for a sustainable alternative option has increased. 'Biofertilizers' are supposed to be an effective measure for 'chemical fertilizers'. The application of biofertilizer was found as an interesting option for the reason that, it enhances plant health and quality efficiently yet effectively, and intensified soil productivity by making it nutrient-rich. Furthermore, biofertilizer production from wastewater is a low-cost and environment-friendly, beneficial mechanism which helps in reducing eutrophication and utilizes wastewater as a resource. This is a practical wastewater application for agriculture sustainability and the betterment of the environment. Further, extensive studies should emphasize making biofertilizers more cost-effectively, and more attention have to be paid for increasing their shelf-life.

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Chapter 11
Microalgae-Mediated Wastewater Treatment for Biofertilizer Production

Indu Sharma, Sandeep, Raj Bala, Nakul Kundra, Tejinder Kaur, and Ashutosh Sharma

Abstract Water obtained after the utilization of fresh water in various human activities or rainwater runoff, which generally cannot be utilized for any useful purpose, is referred to as wastewater. Different phytonutrients may accumulate in wastewater during the conversion of fresh water into wastewater, making it an excellent medium for the growth of microalgae. Microalgae grown in such wastewater can be utilized as an effective biofertilizer to promote plant growth. The utilization of the biofertilizer prepared from wastewater microalgae not only recycles nutrients in the agricultural ecosystem but also reduces dependence on chemical fertilizers. Microalgae generally have a high growth rate, a brief life span and a high carbon dioxide fixation rate; therefore, their cultivation is environmentally sustainable. However, there are some challenges in the large-scale adoption of the technique for preparing biofertilizers from microalgae in wastewater. The present chapter highlights the up-to-date efforts made in the area of the cultivation of microalgae in wastewater and its utilization as a biofertilizer. It also touches on the effects of the procured biofertilizer on plant growth. Besides, it also explores various challenges in the large-scale adoption of the technique under study.

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11.1 Introduction

Fresh water is one of the basic requirements for human survival, and the initial human settlements used to be on the river banks (Cascalheira et al. 2022). Water obtained after the consumption of fresh water in different unavoidable human activities is commonly called wastewater, as it cannot generally be further utilized. According to an estimate, wastewater generation worldwide is around 380 trillion litres (380 billion m^3) and is anticipated to increase by 24% by the year 2030 (Qadir et al. 2020). Wastewater is variously classified based on its source and the nature of contaminants present in it (Henze and Comeau 2008). Wastewater from different sources has different compositions; however, the most common source of wastewater is domestic sewage water, especially in urban setups. Domestic sewage wastewater is a complex matrix made up of suspended solids (both inorganic and organic), micro-organisms, phytonutrients and heavy metals (Jain et al. 2021). Further, rainwater also gathers in sewage systems and increases the volume of wastewater. With the development of science and technology, the perspective of looking at wastewater has gradually changed. Now, it is also being looked at as a useful resource in terms of biofuel, biomass or as a nutrient-rich medium for microbial biomass growth.

Microalgae, out of the various microbes present in wastewater, are of particular interest, as they are capable of carbon fixation using sunlight and phytonutrients available in wastewater. Microalgae are efficient in nutrient recovery, and one kilogram of dry biomass may be produced from each m^3 of sewage (Acién Fernández et al. 2018). The microalgal biomass contains the valuable organic bio-molecules. The most significant advantage of microalgae lies in its shorter generation time, which enables it to grow rapidly if adequate nutrients are available (Morais et al. 2021). Its shorter lifespan, high rate of biomass production and CO_2 utilization efficiency make it a preferable candidate for resource recovery from wastewater by producing biofertilizers (Hussain et al. 2021). The most effective resource that microalgae can recover from wastewater is phytonutrients (particularly N and P), which leach out from agricultural soils supplemented with inorganic fertilizers and reach wastewater streams in addition to domestic wastewater. The uptake of phosphorous (P) from nutrient-rich wastewater streams by microalgal cells to produce algal biomass capable of fertilizing crop plants has been extensively reviewed by another group (Solovchenko et al. 2016). Many microalgal species can multiply in wastewater, and their nutrient removal efficiencies are more than 70%, sometimes up to 100% (Díaz et al. 2022; Marín et al. 2022).

In an experiment involving *Chlorella vulgaris*, it was suggested that microalgal production in municipal wastewater treatment systems seems to be a promising approach for the removal of nutrients (Cabanelas et al. 2013). Several nutrients and other resources can be recovered from wastewater using the microalgal biomass to prepare valuable end-products. This microalgae grown in wastewater may be used to prepare more than one valuable product like biogas, biodiesel, biofertilizer, biopolymers, etc. (Ali et al. 2021; Goswami et al. 2021; Rashid et al. 2020). The advantage of using microalgae looks more beneficial if more than one valuable product is prepared simultaneously (i.e., biodiesel and biofertilizer). Entire oil extracted from microalgal biomass can be used in the production of biodiesel. The de-oiled microalgal biomass may later be used as a biofertilizer to enhance crop productivity (Silambarasan et al. 2021; Nayak et al. 2019). Further, the biofertilizer application increases plant growth (Braun and Colla, 2022) and improves soil health by enhancing its microbial diversity (Lv et al. 2020).

The safe and eco-friendly management of wastewater could be a solution to water-related sustainable development goals. Wastewater (especially municipal and agricultural wastewater) is now considered as a valuable source of nutrients, water and energy. Microalgae can be effectively cultured in wastewater, and phytonutrients may be recovered to generate biofertilizers. At the same time, treated wastewater can be used for irrigation in agricultural fields. A schematic diagram explaining the utilization of microalgae for biofertilizer production for the agricultural sector has been presented in a simplified manner as Fig. 11.1. Although microalgae are an important group of photosynthetic microbes capable of biofertilizer production from wastewater, other types of microbes, like bacterial consortia, are also capable of generating enough biomass to be processed as a biofertilizer, capable of promoting plant growth. The efficient conversion of dairy wastewater into a biofertilizer using such a bacterial consortium has also been reported by Gogoi et al. (2021).

Wastewater management includes the recovery of some valuable resources from wastewater (in terms of biomass/bioenergy) and also the reuse of treated wastewater.

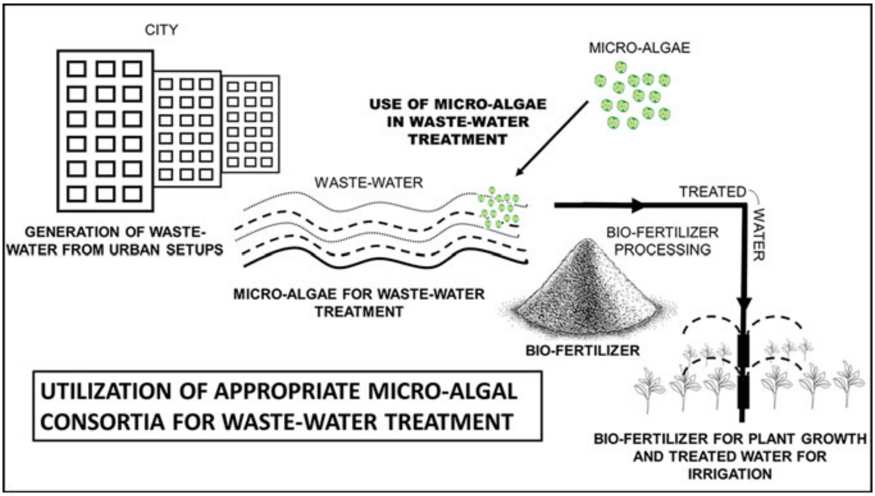

Fig. 11.1 A flow chart explaining the utilization of microalgae for biofertilizer production for the agricultural sector

However, only a small proportion of wastewater is treated at present. Notably, there has been a gradual shift towards the research and practices supporting the collection, treatment and utilization of treated municipal wastewater (Qadir 2018; Qadir et al. 2020). Therefore, the present chapter focuses on the potential of microalgae to treat wastewater and recover the nutrients present in it; it also studies how microalgal biomass containing recycled nutrients is used as a biofertilizer based on recent research in this area. The utilization of biofertilizers prepared from wastewater is not only a boon for economy but also an environment-friendly step towards sustainable agriculture. Towards the end of this chapter, some recent studies on using microalgal biofertilizers to enhance agricultural productivity in different crops have also been referred to. Therefore, this chapter attempts to present up-to-date knowledge in the field of microalgal biofertilizers from wastewater and their utilization in enhancing agricultural productivity and minimizing the use of chemical fertilizers for achieving sustainable wastewater management.

11.2 Microalgae in Wastewater

Microalgae are photo-autotrophic in nature and utilize solar energy to reduce inorganic nutrients present in wastewater to produce its biomass (Acién Fernández et al. 2018). Recently, microalgae-based wastewater treatments are gaining attention due to economic gains (in the form of biofuels, biofertilizers, bio-stimulants and some other high-value compounds) from the process (Morais et al. 2021). The use of biofertilizers is preferred due to their ecological benefits in agricultural ecosystems. The increased use of chemical fertilizers has an environmental bearing, as it can lead to the eutrophication of our water bodies (Youssef and Eissa 2014). On the other hand, using these biofertilizers from wastewater is a sort of ‘cash from trash’ situation.

However, unlike laboratory bio-reactors, in commercial microalgae-based treatments, multiple microbes exist in the same medium (not a pure culture). Such a consortium of microalgae and other bacteria, which actually exist in nature, is also desirable. These bacteria may oxidize the organic matter into inorganic compounds, and the microalgae may subsequently uptake these inorganic nutrients (in the presence of light) to build their biomass, releasing O_2, which is required by the bacteria (Muñoz and Guieysse 2006). In a study involving the integration of anaerobic degradation of food waste using photosynthetic microalgae to obtain nutrient-laden algal biomass (with *Chlorella vulgaris* and *Pseudoanabaena* sp. as main species), the maximum removal efficiencies of 100% were achieved for total phosphorus and total nitrogen, on a pilot scale (Marín et al. 2022). Further, the identification of the microalgal strains with more bio-mass generation potential is also an important task to upscale the microalgal biomass production. In a study aimed at finding the best desirable interaction between bacteria and microalgae, municipal wastewater was treated using microalgae activated sludge consortium.

It is generally better to isolate the local strains of microalgae, which can better adapt to resource recovery from the wastewater under the local environment. A local strain of *Chlorella* sp. CW2 was found to be better than *Chlorella* sp. Pozzillo strain, previously isolated. In this study, the most promising treatment was when the microalga *Chlorella* sp. CW2 was introduced along with the activated sludge in a ratio of 1:5 (Lima et al. 2022). Therefore, more effort should be made to isolate native micro-algal strains, which are likely to perform better than exotic strains. Further, it is always beneficial to have a microbial consortium in place rather than using a single microalgal strain after their careful evaluation and optimization. In an experiment involving three different consortia (viz., containing native filamentous micro-algae, containing native single celled micro-algal strains, and selected microalgal strains from germplasm) in relation to nutrient removal, the production of bio-mass using primary treated sewage water and water quality improvement; it was recorded that the consortia of filamentous strains from the native environment was more effective in nutrient removal as well as in biomass production (Renuka et al. 2013).

Further, there are seasonal changes in the nature of microalgae in wastewater. However, some genera are consistently found throughout the year. In a study by Renuka et al. (2014), *Phormidium* sp. was the dominant genus in the wastewater in New Delhi (India) region throughout the year. Several species of microalgae and cyno-bacteria (blue green algae) like *Chlorella*, *Phormidium*, *Pseudoanabaena*, *Spirulina*, *Scenedesmus* and *Anabaena*, etc., have been now well known to be capable of resource recovery from wastewater and to produce sufficient biomass, capable of acting as a biofertilizer. The foliar applications of microalgal extracts have also been used as a plant growth biostimulant. *Spirulina platensis* extracts were found to increase the total chlorophyll, photosynthetic rate, photosynthetic capacity, growth and production of *Lupinus luteus*, thereby ensuring their role as promising biofertilizers for sustainable organic agriculture (Shedeed et al. 2022).

Besides the use of microalgae as biofertilizers, burgeoning studies have revealed their potential role in bio-remediation due to their capacity to remove contaminants from wastewater. As per a recent study by Meril et al. (2022), aquaculture wastewater was considered a good substitute for algal biomass, and the significance of microalgal-based wastewater treatment was also analyzed for bioremediation. Out of 18 immobilized microalgae evaluated in the study, *Chlorella marina, Picochlorum maculatum* and *Tetraselmis suecica* were effective in the removal of inorganic NH_3-N, and NO_2-N; *Picochlorum maculatum* was effective in reducing PO_4^{3-}, whereas *Navicula* sp. and *Nitzchia microcephala* were capable of reducing silicates. Further, *Chlorella marina* was found to be the most efficient microalga for the maximum removal of total nitrogen and total phosphorus. Their study emphasized the potential role and feasibility of utilizing immobilized microalgae as a replacement for aquaculture wastewater's nutrient remediation. The co-cultures of microalgae and bacteria have been found to play a critical role in the sustainable production of biomass and biodiesel by assisting interactions among species leading to change in the indigenous bacteria's population in wastewaters and thus augmenting the bio-remediation of wastewater effluents (Perera et al. 2022). The co-culture of *Tetradesmus obliquus* and *Variovorax paradoxus* was found effective in lowering the total N, PO_4^{3-}-P and COD (chemical oxygen demand). It also effectively increased the growth of microalgae and native bacterial cells in wastewater.

Moreover, the microalgal-mediated bio-remediation of water pollutants-rich landfill leachate was studied, and landfill leachates were used as a nutrient rich medium for growing microalgae (Martínez-Ruiz et al. 2022). Microalgae were found to be an effective option for the bio-remediation of leachates. Besides this, various high-value products formed by microalgae may be utilized as biofuels and bioplastics. The algal biomass can be used as a substrate for culturing other microbial species (fungi or bacteria) at an industrial scale. The residual biomass of *Lyngbya limnetica* can also be used as a substratum for the production of fungal cellulase, and its production is further increased by Nickel ferrite nanoparticles ($NiFe_2O_4$ NPs) by stimulating the activity of crude cellulase enzyme (Srivastava et al. 2021). This crude cellulase enzyme can further be utilized for the hydrolysis of rice straw, resulting into the production of sugar hydrolysate. Therefore, residual algal biomass can enhance cellulase production and the consequent production of hydrogen through dark fermentation.

11.3 Steps in Microalgae Based Biomass Production

The major driving force in microalgae-based biomass production is the solar energy harvested by these photoautotrophs. Depending on the local environment, various microalgae species can be used for wastewater. Different microalgae species used for wastewater treatment, their nutrient removal rates from wastewater and their advantages have been reviewed in detail elsewhere (Díaz et al. 2022). For microalgal treatment, wastewater collection and the allocation of space for microalgal growth and harvesting are essential prerequisites.

Acién Fernández et al. (2018) have suggested five major steps in the process (Fig. 11.2). The first step is generally the pre-treatment of the effluent, which may involve filtration to reduce total solids and increase the transparency of wastewater. It is followed by nutrient recovery and biomass production. The third step is harvesting biomass, followed by the treatment of this wastewater for its recirculation or usage. The final step is the transformation of the generated biomass into more valuable products like biofertilizers. However, one or other steps can be added or removed depending on the nature of the setup. Although each of these steps is important, the harvesting step of biomass, which requires a major input in terms of money and effort, is the basic requirement to form a biofertilizer.

11.4 Harvesting of Micro-Algal Biomass

The harvesting of microalgae means the removal of valuable biomass from microalgal cultures, which can involve up to 30% of the entire biomass production expenses (Grima et al. 2013). The basic harvesting technology involves centrifugation, but several other technologies like sedimentation and flotation, which may involve the

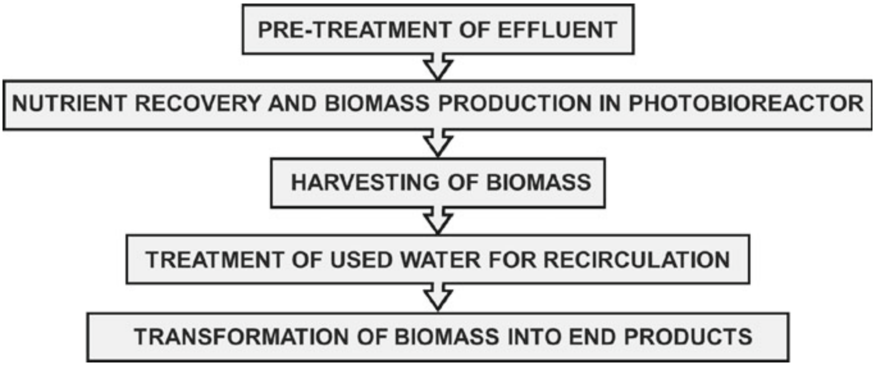

Fig. 11.2 A flow chart explaining the major steps for a microalgae-dependent process for nutrient recovery from wastewater, as suggested by Acién Fernández et al. (2018)

use of coagulants/flocculants (chemical or natural), gravity sedimentation, tangential filtration and dissolved air-flotation may also be employed, depending on the need of downstream processing of the harvested biomass of microalgae (Udom et al. 2013; Gutiérrez et al. 2015; Acién Fernández et al. 2018; Christenson and Sims 2011). In an experiment to study chemical flocculation using aluminium sulphate and ferric chloride for harvesting the biomass of micro-alga *Chlorella* sp., it was found that ferric chloride was better for the micro-algal flocculation (Hashmi et al. 2014). Further, two natural bio-flocculants (viz., Ecotan and Tanfloc) were found appropriate for microalgae biomass harvesting from wastewater treatment systems (Gutiérrez et al. 2015). In another experiment, an auto-flocculating microalga (*Ankistrodesmus* sp.) was successfully utilized as a bio-flocculant for harvesting micro-algal biomass of *Chlorella* sp. (Lananan et al. 2016). At present, this step is considered the most expensive step in microalgal biomass production from wastewater. Any effort to cut down the cost of this step will lead to the overall economy of the process and may lead to the large-scale adoption of the technology worldwide. Christenson and Sims have extensively reviewed the challenges and prospects of microalgae harvesting methods, harvester designs and harvesting processes (Christenson and Sims 2011).

11.5 Enhanced Production of Microalgal Biomass

Generally, in microalgae-based wastewater treatment, it is considered that the lesser culture depth is related to higher irradiance and higher nutrient (mainly N and P). However, the lesser culture depth also leads to lowering of the volume of wastewater, which is being treated (Acién Fernández et al. 2018). One of the major factors that lead to higher microalgal biomass production is the utilization of appropriate consortia, as the biomass yields of consortia are generally higher than mono-cultures (Nath et al. 2017). Further, a 20% increase in microalgal biomass was recorded under the co-cultivation of the siderophore-forming bacteria *Idiomarina loihiensis* along with *Chlorella variabilis* (Rajapitamahuni et al. 2019). The acid-tolerant microalgae strains can be effectively used to treat acidic wastewater. The acid-tolerant microalage, viz., *Heterochlorella* sp. MAS3 and Desmodesmus sp. MAS1 were found to tolerate cadmium (Cd) stress also at 3.5 pH (Abinandan et al. 2019). The produced microalgal biomass was found to possess higher amounts of bio-diesel with more fatty acid esters at this acidic pH. Such acid-tolerant microalgal strains can grow and produce higher algal biomass even at pH 3.5 in an environmentally sustainable manner.

Microalgal biomass production is affected by different micro-environments such as pH, type of nutrient media and sodium nitrate ($NaNO_3$) treatment (Sharma et al. 2018). For the production of biodiesel, consortium of microalgae viz. S16 and S1 were used, and pH was observed to play a critical role in amending the biomass production of these microalgal consortia. The pH 7 and 8 were recorded to be the most suitable for increasing the lipid and total chlorophyll contents and for maximum algal biomass production. In contrast, pH 5 and 6 were more appropriate for increasing the levels of proteins. BG-11 medium and Bold Basal Medium were reported to be favourable for increasing the biomass, total chlorophyll, protein, and accumulation of lipids, respectively, in microalgae. Besides Bold Basal Medium, medium with deprived nitrogen (i.e., N-stressed medium) also enhanced the contents of lipids in algal consortia. Algal biomass production and total chlorophyll contents were also increased by the treatment of $NaNO_3$ at 1.0 g/L. However, 0.1 g/L application of $NaNO_3$ was the most favourable for increasing the contents of both lipids and proteins.

11.6 Microalgae as Biofertilizer: Use in Sustainable Agriculture

Different species of microalgae or cyanobacteria can grow in wastewater. However, it is not easy to grow a particular species in a preferred manner. However, by modifying the conditions like nutrient composition or pH etc., it can be achieved (Acién Fernández et al. 2018). Some of these microalgae and cyanobacteria are capable of producing plant growth regulators (PGRs) (Tarakhovskaya et al. 2007; Lu and Xu 2015). Moreover, the species of growing microalgae is less important than the microalgae production rate. The use of microalgae as biofertilizers or bio-stimulants is extensively reviewed elsewhere (Braun and Colla 2022) for sustainable agriculture. The effects of microalgae in providing plant nutrition to enhance the growth and yield-related attributes in some important crop plants have been listed in Table 11.1.

Different methods of microalgae-based biofertilizers have been suggested; they include soil drenching, soil application of dried microalgal biomass with or without other chemical or biofertilizers, soil application of microalgal cell suspension, soil application of de-oiled biomass alone or with other chemical or biofertilizers, and

Table 11.1 Impact of microalgae-based biofertilizers on plant growth and yield related parameters

S. No.	Crop	Micro-algal treatment	Effect	References
	Triticum aestivum	Micro-algal consortia made with unicellular and filamentous microalgae	• Savings of 25% N • Improved yields	Renuka et al. (2016)
	Lactuca sativa	*Chlorella vulgaris*	• Reduced the use of minerals in hydroponic production • Enhanced vitamin C and total soluble solids	Ergun et al. (2018)
	Oryza sativa	De-oiled micro-algal biomass of *Scenedesmus* sp.	• Enhanced growth and yield	Nayak et al. (2019)
	Zea mays	*C. vulgaris* and *Spirulina platensis* along with cow-dung manure	• Enhanced growth and yield	Dineshkumar et al. (2019)
	Abelmoschus esculentus	Blue green algae (*Spirulina* and *Oscillatoria*)	• Enhanced plant height, number of leaves, branches and pods per plant • Decreased the number of days to flower • Increased crop yield and productivity	Uddin et al. (2019)
	Allium cepa	*S. platensis* and *C. vulgaris* (alone or with cow-dung)	• Improved growth and enhanced yield	Dineshkumar et al. (2020a)
	Vicia faba	Seed pre-soaking seed treatment with *C. vulgaris* and *Nostoc muscorum*	• Improved growth parameters • Enhanced production of metabolites • Enhanced yield • Modulated activity of antioxidant enzymes viz., peroxidase and catalase • Lowered lipid-peroxidation	Osman et al. (2020)

(continued)

Table 11.1 (continued)

S. No.	Crop	Micro-algal treatment	Effect	References
	Vigna radiata	Foliar sprays of *Spirulina platensis* and *Chlorella vulgaris* extracts	• Improved growth parameters • Higher mineral composition of flour	Dineshkumar et al. (2020b)
	Vigna radiata	Treatment of sulphur coated urea and algae (*S. platensis*)	• Increased seed yield • Enhanced oil and nitrogen percentage of the seeds	Essa et al., (2021)
	Cucumis sativus	Application of micro-algal cell suspension (*Anabeana circinalis* and *Scenedesmus quadricauda*) in soil	• Improved growth	Lv et al. (2020)
	Brassica oleracea var. *italica*	Microalgae treatment (*C. vulgaris*)	• Mitigated drought stress by enhancing the nutrient uptake • Enhanced production of secondary metabolites • Improved anti-oxidant defense system	Kusvuran (2021)
	Solanum lycopersicum	De-oiled micro-algal biomass of algal consortium (*Chlorella* sp. + *Scenedesmus* sp.)	• Improved growth and enhanced yield	Silambarasan et al. (2021)
	Lycopersicon esculentus	*C. vulgaris*	• Enhanced the fruit quality, growth and yield of tomato was enhanced under soilless conditions • Increased levels of Vitamin C, average weight and volume of tomato fruit • Increased contents of P, Na and Mg in tomato fruit • Reduced the electric conductivity (EC) at the root zone of tomato	Aydoner Coban et al. (2018)

(continued)

Table 11.1 (continued)

S. No.	Crop	Micro-algal treatment	Effect	References
	Lycopersicon esculentus	*C. vulgaris* grown on *treated* sewage wastewater and the plant growth regulators produced by *A. oryzae*, *C. vulgaris* and *N. muscorum*	• Enhanced growth parameters	Elakbawy et al. (2022)
	Glycine max	Treatment of Sulphur coated urea and algae (*S. platensis*)	• Enhanced growth and productivity • Enhanced contents of proteins and carbohydrates • Increase in oil-percentage	Essa et al., (2021)
	Lupinus luteus	Spray of methanolic extracts of *S. platensis*	• Enhanced photosynthesis • Improved growth and yield • Increased protein profile • Enhanced accumulation of carbohydrate • Enhanced production of bio-active molecules	Shedeed et al. (2022)

liquid micro-algal extracts as a foliar spray (Nayak et al., 2019; Dineshkumar et al. 2018, 2020a, b, 2022). In an experiment to explore the effectiveness of wastewater based microalgal biofertilizer to increase wheat production, it was found that the micro-algal consortia led to 25% N savings and improved yields (Renuka et al. 2016). The maize plants displayed better growth and yield when grown using microalgae (*Spirulina platensis* and *Chlorella vulgaris*) together with cow-dung manure under polyhouse conditions (Dineshkumar et al. 2019). Further, the microalgal dry biomass of *S. platensis* and *C. vulgaris* mixed with cow-dung improved the growth and yield attributes in onion than cow-dung and microalgae alone (Dineshkumar et al. 2020a, b).

Further, the microalgae biomass left after oil extraction for biodiesel production may also be used as a fertilizer. In rice, the de-oiled microalgal biomass waste of microalga *Scenedesmus* sp., cultivated in wastewater, was found effective in highly improving growth and yield of the crop when used in combination with chemical fertilizer (50% N from each) than all other treatment combinations (Nayak et al. 2019). Besides using de-oiled algal biomass as a biofertilizer, it is also recommended as an additional renewable energy source or feedstock for the sustainable bio-ethanol and bio-polymer production (Kumar et al. 2020). The hybrid pre-treatment approach was the most suitable for enhancing the sugar solubilization. Saccharomyces *cerevisiae* at pH 5.5 favoured the highest bioethanol production from the de-oiled algal biomass. Thus, the hydrolysis of de-oiled algal biomass through the integrated method was most suitable for the highest resource recovery and was observed as the most suitable sustainable microalgae-mediated bio-process in the bio-refinery. In a study conducted on cucumbers, it was recorded that the application of cell suspension of microalgal biomass (*Anabeana circinalis* and *Scenedesmus quadricauda*) not only improved growth but also increased the microbial diversity of soil in terms of microbial abundance in cucumber rhizosphere, capable of improving plant growth (Lv et al. 2020).

Foliar applications of *C. vulgaris* was effective in alleviating drought stress in broccoli plants grown under water deficit conditions (Kusvuran 2021). The microalgal treatments significantly enhanced the levels of photosynthetic pigments and nutrition uptake, lessened the membrane damage, enhanced the contents of total flavonoids and phenolics, and stimulated the activities of antioxidant enzymes in broccoli. In another study, the effects of microalgae (*Chlorella vulgaris*) grown on *treated* sewage wastewater and the PGRs (plant growth regulators) produced by *Anabaena oryzae*, *Chlorella vulgaris* and *Nostoc muscorum* were analyzed on tomato plantlets and soybean callus (Elakbawy et al. 2022). The application of treated sewage wastewater and *C. vulgaris* increased the number of leaves and enhanced branching, shoot length and root initiation in soybean callus and tomato plantlets. Cyanobacteria (*A. oryzae* and *N. muscorum*) and micro-algal extracts (*C. vulgaris*) also resulted in an increase of fresh biomass in soybean callus. Therefore, it was revealed that microalgae and cyanobacteria, due to the presence of vitamins, hormones, enzymes, and various nutrients, might be utilized as bio-stimulants for the growth and development of plants. Another study on okra revealed that foliar applications of blue-green microalgae viz., *Spirulina* and *Oscillatoria* enhanced the chlorophyll percentage, plant height, single pod weight, pod length, and pod breadth and enhanced the number of pods per plant, leaves, and branches (Uddin et al. 2019). Consequently, the okra yield per plant and hectare was enhanced. This study emphasized the possible use of blue-green algae as a biofertilizer for enhancing the crop productivity using microalgae-based organic amendments.

Chlorella vulgaris has been reported to be effective in saving mineral nutrients in tomatoes grown in the greenhouse under soil-less conditions (Aydoner Coban et al. 2018). The fruit growth, yield and quality were enhanced under soilless conditions by the treatment of *C. vulgaris*. The microalgal treatment enhanced the levels of Vitamin C, average weight, and volume of tomato fruit. Besides this, the levels of minerals such as phosphorus (P), sodium (Na) and magnesium (Mg) in tomato fruit also increased by the treatment with microalgae. *C. vulgaris* was not reported to affect the pH, but it reduced the electric conductivity (EC) at the root zone of tomatoes. In sandy soils, the treatment of Sulphur coated urea and algae (*Spirulina platens*) stimulated the growth and production of leguminous crops (soybean and mung-bean) in sandy soils (Essa et al. 2021). The fertilization with coated urea and algae was found to enhance protein, carbohydrates and percentage oil, yield and its components in the seeds of soybean and mung bean.

The foliar spray of methanolic extracts of *Spirulina platensis* enhanced seed attributes, photosynthetic rate, overall growth and the yield of *Lupinus luteus* (Shedeed et al. 2022). The pre-soaking seed treatment with priming solutions of *C. vulgaris* and *Nostoc muscorum* of broad bean resulted in enhanced shoot length, root length, root dry weight, photosynthetic pigments, levels of carbohydrates and proteins, seed weight, and the stimulation of the activity of some important antioxidant enzymes like catalase and peroxidase (Osman et al. 2020). The algal treatment was found effective in reducing the rate of lipid peroxidation (degradation of lipids) in the broad bean plant.

11.7 Future Prospects

With the urbanization and migration of more and more people to cities, the magnitude of wastewater generation in urban areas has gone up drastically. The need an eco-friendly, economical, and sustainable method for wastewater treatment is much fill. The microalgae-mediated wastewater treatment technology has gained a fairly sufficient attention as an eco-friendly method for generating a valuable resource (micro-algal biomass) that may be utilized as a biofertilizer to enhance agricultural productivity by reducing our dependence on chemical fertilizers. At present, the biggest hurdle in the large-scale adoption and commercialization of microalgal biomass production is financial resources, especially in the harvesting of microalgae. More research is required to explore more economical alternatives for harvesting microalgae. Moreover, we mainly rely on inorganic fertilizers for several phytonutrients from the agricultural perspective. Chemical fertilizers supply major phytonutrients (N and P). In particular, the rock phosphate required for making P fertilizers is a non-renewable resource. Excessive use of such chemical fertilizers is also leading to an excess of such nutrients in our wastewater. The efficient recovery of these phytonutrients by microalgae-based from wastewater to produce biofertilizers is an efficient method for nutrient recycling leading to a sustainable agricultural practice. Further, being a photo-autotroph, microalgae can assimilate CO_2, produce O_2 and reduce the production of greenhouse gases. The biofertilizers hence prepared, may improve the soil characteristics and enhance organic carbon in soil.

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Chapter 12
Book: "Resource Recovery from Wastewater Through Biological Methods" Biofertilizers from Wastewater

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Abstract Overuse of water has led to degradation and scarcity of water resources. This has paved path for adaption of sustainable measures to save water by reusing and recycling it. Wastewater treatment using these potent microbes has now become a growing trend due to its economic and environment benefits. Bacterial and microalga mediated wastewater (WW) treatment are used to treat municipal, agricultural and industrial wastewater. As these microbes grow, they utilize carbon dioxide, nitrogen, phosphorous which are potential pollutants from wastewater. This makes them a replacement to energetically expensive treatment steps in conventional wastewater treatment. Apart from their cleansing role, they also serve as a source of value added product such as biofertilizers. Biofertilizers comprises of living microorganisms that provide all nutrients for plant growth. Biofertilizers production includes cultivation, harvesting, drying and finally using biomass as biofertilizer. Biofertilizers serve as substitute to chemical fertilizers. They aid in improving soil fertility, makes nitrogen

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and phosphorous bioavailable, reclamation of saline soil and plant growth prompters. Hence, Biofertilizer production is a green-clean technology that serves as a cheap and renewable source of nutrients and aids in wastewater recycling.

Keywords Biofertilizers · Microbes · Wastewater treatment

12.1 Introduction

Water is the most treasured resource on the face of Earth as it helps to sustain many lifeforms. It was reported by Shahat et al. (2015) that only 71% of earth's surface is covered with water of which only 2.5% is available as freshwater. It has been documented that the world's population will increase by double in following 30 years, resulting in high demands for portable water. Furthermore, the rapid urbanization and industrialization have led to filthy discharge of wastewaters from municipal, agricultural, medical and industrial sources (Goswami et al. 2021c). The untreated wastewater so released leads to precarious impacts on human health and environment (Qu et al. 2016). The traditional wastewater treatment (WWT) technologies are based on physical, chemical and biological methods. They included adsorption method to eliminate heavy metals or utilizing activated sludge to remove organic matter and nutrients from wastewaters (Dutta et al. 2018). Conversely, these methods have drawbacks since they have high energy demands, setup needs large land area and leads to heavy discharge of activated sludge (Montwedi et al. 2021). Moreover, the nutrients in wastewater are not efficiently recycled (Jin et al. 2014). Hence, new promising technologies are emerging for competently cleaning the wastewaters than the conventional methods (Li et al. 2019a, 2019b). These upcoming green technologies include use of microorganisms that can degrade recalcitrant wastes and obtain energy in exchange for their growth and multiplication. Hence, Bacterial and Microalga mediated wastewater treatment approaches are becoming very popular these days. Bacteria are most commonly used microorganisms for WWT owing to their diverse abundance and enzymatic potential in sewage water (Nascimento et al. 2018). Bacterial genus including *Flavobacterium, Archromobacter, Pseudomonas* are commonly used for WWT. Both autotrophic (requires inorganic substances as energy sources) and heterotrophic (requires organic substances as energy sources) bacterial strains are employed under Bacterial mediated WWT. Whereas, Microalga mediated WWT employs eukaryotic algae and cyanobacteria as promising proxies for bioremediation of wastewaters. The term "phycoremediation" is used for bioremediation projects that includes algal species (Poo et al. 2018). Most frequently used algal taxa are *Tetraselmis* sp., *Chlorella* sp., *Chlorella vulgaris*, *Scenedesmus* sp. and *Picochlorum* sp. (Goswami et al., 2021c). Various cyanobacterial strains comprises of *Spirulina* sp., *Hapalosiphon* sp., *Scytonema* sp., *Dolichospermum* sp., *Leptolyngbya* sp., *Gloeocapsa* sp., *Pseudospongiococcus* sp., *Chroococcus* sp., *Lyngbya* sp., *Oscillatoria* sp. and *Synechocystis* sp. (Dutta et al. 2019). For production of biofertilizers, the biomass needs proper separation from the medium. The general process includes harvesting followed by drying of biomass, making the product available as biofertilizer. Harvesting of biomass is done through sedimentation, centrifugation and filtration (Grima et al. 2004). However, selection criteria for harvesting method depends upon the quality of the product. The process of sedimentation is used for sewage-based work and centrifugation is preferred for alga that is processed for food and aquaculture applications. After harvesting the biomass efficiently, the algal slurry needs to be processed quickly in order to protect it from being spoiled. Dehydration is done by methods such as spray-drying, freeze-drying, drum-drying and sun drying. Hence, microalga can be used to produce value added products rich in carbohydrates, lipids, proteins, vitamins and antioxidants (Chew et al. 2017). Biofertilizers so obtained by following the stated procedure aids in increasing N, P bioavailability to promote plant development and improves soil fertility. Researchers across the globe are working in order to develop valuable bioproducts consecutively solving the problems that arise with the use of harmful chemicals in the environment (Sartori et al. 2021).

12.2 Types of Wastewater

Wastewater has been usually divided into two main types: sewage wastewater and non-sewage wastewater (Schoen and Ashbolt 2010). Sewage wastewater comprised of discharge from household activities whereas the effluent released due to commercial activities like from industrial plants, mills and factories is categorised into non-sewage wastewater. Stormwater and rainwater produced after heavy rainfall are also a type of non-sewage wastewater. Majorities of human activities are reliant on water so for effective management and depending upon target treatment, wastewater has been further classified into three types i.e. municipal, agricultural, and industrial. Many nutrients (C, N, S, P etc.) are present in these types of wastewater for the growth of microalgae. It has been studied that wastewater management by using biofertlizers not only clean or treat the water but the generated biomass can also be used to obtain biofuels especially from microalgae and also for other applications (Hernández-García et al. 2019; Katam and Bhattacharyya 2018; Zhou et al. 2011, 2018).

12.2.1 Municipal Wastewater

Municipal wastewater is a type of low strength waste streams and one of the most studied wastewaters for the farming of microalgae. Municipal wastewater can be categorised into four kinds i.e. unprocessed sewage waste before primary sedimentation, wastewater after primary sedimentation, wastewater (secondary effluent) generated after activated sludge treatment and centrate generated after the dehydration of sludge (Zhou et al. 2014; Wang et al. 2010a, 2010b). The growth status of microalgae depend on the nutrient distribution of these four kinds of wastewater. It has been observed that *Chlorella* sp. can survive under all these kinds of municipal wastewater and showed maximum growth in fourth (centrate) type (Wang et al. 2010a, 2010b). The rate of elimination of N, P and COD (Chemical Oxygen Demand) was directly related to the amount of nutrient in the wastewater. It has been investigated that the thiocynate in wastewater is degraded into ammonium (NH_4^+) and other nitrogen forms by algal–bacterial cultures containing *Chlorella protothecoides* and *Ettlia* sp. (Ryu et al. 2014). Autochthonous microalgae is used to treat the municipal wastewater and reduced the total nirates and phosphates (Lima et al. 2020). *Desmodesmus communis*, *Tetradesmus obliquus* and *Chlorella protothecoides* were studied and reported for the removal of phosphorus from the municipal wastewater (Lavrinovičs et al. 2020).

12.2.2 Agricultural Wastewater

The letting off agricultural wastewater in the management of animal breeding, cultivation of crops, and production of agricultural products. Some reports showed the usage of agro-product processed wastewater (Palm Oil run-off, starch, and potato processed wastewater) in the cultivation of microalgae (Tan et al. 2019; Khalid et al. 2019; Li et al. 2019a, 2019b). Animal compost was the foremost source of agricultural wastewater as it contained high level of nutrients. Moreover, this process of using wastewater for microalgae growth accomplished the purpose of resource consumption of wastewater and also slashed the cultivation cost of microalgae (Wang et al. 2010a, 2010b; Zhou et al. 2012; Li et al. 2020). Animal compost processed wastewater has high chromaticity and murkiness which was not favourable for penetration of light and also a high content of Nitrogen: Ammonia will affect the PS II (Photosystem II) hindering the microalgal growth (Gutierrez et al. 2016). To maintain nutrient levels in wastewater treatment, the dilution of animal compost processed wastewater was used for microalgal cultivation (Pittman et al. 2011). It was studied that the culturing of *Phormidium* sp. and *Spirulina maxima* in animal wastewater was used as feedstock (50% diluted with distilled water) for animals (Canizares-Villanueva et al. 1995).

Zhu et al. (2013a, 2013b) found that the cultivation of microalgae by using a photobioreactor having a tube-shaped bubble column in pig farm wastewater (with altered diluted fractions) for 10 days resulted in a 90% reduction of the total nitrogen (TN), total phosphorous (TP), and chemical oxygen demand (COD). Further studies were made to make the wastewater technology less expensive and more effective in improving the removal percentage of nutrients. It was documented that the removal efficiency of total nitrogen and phosphates was enhanced while diluting the pig farm wastewater with the brewery effluent by using *Chlorella* sp. MM3 whereas the *Chlorella vulgaris* had been used to remove the wastewater pollutants from cow's farm effluent (Lv et al. 2018).

12.2.3 Industrial Wastewater

Industrial wastewater included paper-making, pesticide, tanning, metallurgical, dyeing, printing textile and chemical manure wastewater contained pollutants (antibiotics, grease, toxic chemicals, heavy metals, etc.) that have less biodegradability and high level of organic matter (Udaiyappan et al. 2017). Industrial wastewater treatment has constrictions in using the type of microalgae. It has been studied that the researchers mainly emphasized the degradation and amputation of toxic compounds of algal biomass (de Bashan and Bashan 2010). Industrial wastewater was not suitable for all species of microalgae but it had been reported that some specific strains of microalgae were used for industrial wastewater treatment (El-Kassas and Mohamed 2014; Rajkumar and Sobri 2016). *Chlorella vulgaris* has the ability to treat the effluent of textile resulting in removing the P (phosphorous), N (nitrogen), colour and COD (chemical oxygen demand) from textile effluent.

Chinnasamy et al. (2010) has reported that the purification of carpet wastewater was obtained by a grouping of 15 algal species resulting in the removal of nutrients by 96%, and also attained high biomass and lipid yield after three days of algal consortium cultivation. Moreover, another algal consortium (*Tetraselmis* sp.) was studied to remediate the tannery effluent by reducing the TP, COD, and TN showed effective biosorption of toxic heavy metals from wastewater (Pena et al. 2020). It was reported by Moreno-García et al. (2021) that the group of algal strains (isolated from secondary colonies) adsorbed 99% of chromium ions (Cr (III)) from the tannery effluent. The nutrients and essential elements present in wastewater were a necessary medium for the cultivation of microalgae. There was still more exploration in the field of wastewater treatment and also selected the suitable algal strains that can be acclimatized to various effluents resulting in developing the effective method to execute at a large-scale.

12.3 Nutrients in Wastewater

Different types of wastewaters are specific in their properties (both chemical and physical). There are different factors that are very important and needs consideration concerning productivity of biomass, growth of algae and nutrient recovery from wastewater (Barreiro et al. 2015). Varying amounts of pollutants and nutrient contents are present in waste water. During profiling of waste water, strength and content of nutrient is very important for characterization of the waste water. Moreover, microalgae needs specific conditions to grow in waste water. Therefore in case of artificial medium, the amount of nutrients both macro and micro are formulated in order to provide favourable conditions for the growth of algae in waste water. But as this scenario cannot be achieved in natural conditions, so conditions are made conducive for the growth of algae or trained micro algae are used so that they can adjust in unfavourable conditions in waste water. For better outcome, both these strategies are used simultaneously in order to improve the growth of algae (Li et al. 2019a, 2019b). There are many factors which are very important for maintaining the nutrient amount in waste water such as photoperiod and light intensity, N/P and C/N ratios and additional carbon sources. These factors play very critical role in maintaining the nutrient level in waste water and thus growth and development of micro-algae (Li et al. 2019a, 2019b). In this section, various nutrients available in water and their impacts on the growth and development of micro algae have been discussed.

12.3.1 Nitrogen

Nitrogen is considered as an important nutrient required for algal growth. It is also involved in the synthesis of chlorophyll, proteins, enzymes, peptides, deoxyribonucleic acid, ribonucleic acid, adenosine triphosphate and adenosine diphosphate in the algae (Ghosh et al. 2017). When the amount of nitrogen is less in water and is not properly available to algae, it results in inhibition of protein synthesis and also leads to the accumulation of carbohydrates and proteins in microalgae. Whereas, when the concentration of nitrogen is present in excess in water, protein synthesis is promoted (Obeid et al. 2019). Microalgae can also accumulate nitrogen in other forms as well such as ammonia, simple nitrogen (organic in form of urea and amino acids), nitrite and nitrate. Accumulation of nitrogen in these forms is responsible for synthesizing phospholipids, proteins and nucleic acids (Zhu et al. 2013a, 2013b). It has been observed that an ideal algae has the ability to assimilate nitrogen for their growth. As nitrogen in the form of ammonia is used by algae (due to less energy required for assimilation) rather than other forms, so nitrogen is first converted to ammonia by algae (Nagarajan et al. 2020). Actively or passively transported nitrate in algae is first converted to nitrite with the help of nitrate reductase. This nitrite is then transported to chloroplast where it is reduced to ammonia with the help of ferredoxin. Finally with the help of glutamine oxoglutarate amidotranferase and glutamine synthetase the ammonia formed from nitrite is assimilated to amino acids (Wang et al. 2014; Sanz-Luque et al. 2015).

Waste water mainly from agriculture are rich source of ammonia. Due to excessive use of nitrogen fertilizers, agricultural waste acts as main source of ammonia in these bodies of water (Castro et al. 2017). As ammonia in excess can limit the algal growth so its concentration in water must be always sufficient (Lu et al. 2016). Experiments conducted by Kang and Wen (2015) found that when *Scenedesmus dimorphus* can assimilate up to 90% of ammonia. Similarly *Chlorella* was used by He et al. (2013) to check its efficiency for ammonia assimilation and maximum limit of ammonia in water which is required for the growth of microalgae. It has been observed that ammonia do not require any reduction–oxidation when assimilation occurs so it is mostly used by the algae (Lin et al. 2007). Before the exploitation of any other form of nitrogen, algae assimilates and utilize all the ammonia present in the waste water (Collos and Harrison 2014).

12.3.2 Phosphorous

Phosphorous is the one of the most important nutrient of the earth's biogeochemical cycle's (Blake et al. 2005). Phosphorus has been called the "staff of life" involve in the synthesis of nucleic acids, ATP, phospholipids, and proteins (Juneja et al. 2013). Due to phosphorous deficiency various type of affects in biological process such as reduction of cell division, declining of protein synthesis etc. are observed (Su 2021). Phosphorus discharged in different wastewater can lead to water pollution (Peng et al. 2018). Excess phosphorous in wastewater is a global concern causing eutrophication, which involves decline in oxygen concentration and in turn effect the aquatic organism (Torit et al. 2012), but low amount of phosphorous enhance the productivity of aquatic life (Correll 1998). Three different forms of phosphorus in wastewater are: orthophosphate, polyphosphate and organic phosphorus (Wang and Li 2016).

a. **Orthophosphate** in wastewater involve in "eutrophication" (Hussain et al. 2011). Orthophosphate is the most readily form of phosphorous in wastewater which involve in algae and plant growth (Feng et al. 2020). Orthophosphate is present at the bottom water and induces depletion of dissolved oxygen (Mallick 2002).
b. **Polyphosphate** in wastewater accumulate in microalgae involve in removal of phosphorous (Kosma et al. 2010).
c. **Organic phosphorus** also accumulates in algae and is converted into orthophosphate via phosphatise (Larsdotter 2006).

12.3.3 Heavy Metal

Heavy metals are major environmental pollutants and are non-biologically degradable (El-Sherif et al. 2013). Heavy metals in wastewater have been increasing due to rapid industrialization and anthropogenic activity (Tchounwou et al. 2012). Industrial toxic flows into sewage and reservoirs (Salem and El-Fouly 2000). There are different types of heavy metals in wastewater and their phytotoxicity, effect on human health and permissible limit in water (Demiral et al. 2021) are shown in Table 12.1.

12.4 Role of Micro-Organisms in Wastewaters Treatments

Numerous microbes play a vital role in the treatment as well as remediation or reclamation of wastewaters. This processes is called bioremediation and it is eco-friendly, efficient and less-hazardous towards environment. These microbes are commercially used as a novel and effective tools for promoting green technology for waste water treatment (Fig. 12.1). Due to their ability to undergo degradation of the recalcitrant pollutants, which are normally left non-treated by conventional processes they

Table 12.1 Types of heavy metals existing in wastewater and their sources, in addition to phytotoxicity, effect on human health and permissible limit in water

S.no.	Heavy metal	Permissible levels in wastewater (ppm)	Source of heavy metal in wastewater	Phototoxic	Effect on human health	References
1	Cadmium (Cd)	0.003	Pesticide, fertilizer, welding and plastic	Itai-itai disease and carcinogenic	Lung cancer, kidney damage	Singh et al. (2006) Nandi and Chowdhuri (2021)
2	Lead (Pb)	0.01	Cement industry, Electroplating, pigments, mining, paint, burning of coal and manufacturing of batteries	Pb poisoning	Kidney, liver, anemia, brain damage etc.	Cho et al. (2005) Barakat (2011) Cho et al. (2020)
3	Zinc (Zn)	3	Brass manufacturing	Reduced efficiency of photosynthetic	Neurological disorder and causes depression,	Bhattacharya et al. (2006) Bonnet et al. (2000)
4	Copper (Cu)	2	Juice and Jam industry Polishing and paints	Narrow tolerance for plants	Insomnia, diarrhea and dissiness	Kobya et al., 2005 Zalloum et al. (2008) Costa et al. (2020)
5	Nickel (Ni)	0.07	Electroplating and porcelain enameling	Affected Calvin cycle and CO_2 fixation	Loss lung function	Singh and Rattan (2011) Sheoran et al. (1990)
6	Arsenic (As)	0.01	Smelting, mining, rock sedimentation and pesticides	Blackfoot disease	Skin disease, cancer	Babel and Kurniawan (2005) Cui et al. (2021)
7	Mercury (Hg)	0.006	Paper mill industries, paint and batteries	Biomagnifications	Kidney, eye skin and nervous damage	Babel and Kurniawan (2005) Frachini et al. (2020)
8	Chromium (Cr)	0.05	Fertilizers, Mine and minerals	Carcinogenic	Headache, diarrhea, nausea, vomiting	Al-Qodah et al. (2017) Kobielska et al. (2018)

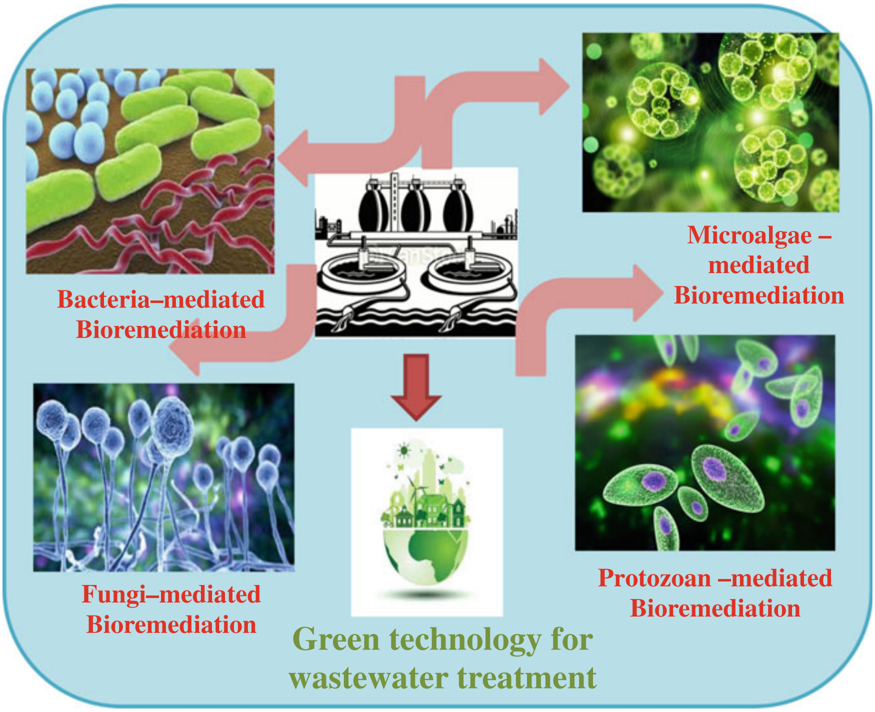

Fig. 12.1 Schematic representation of Microbe-mediated remediation of wastewaters and promoting green technology for wastewater treatment

are considered as best alternative strategy for treating waste waters. In return, the microbes get the energy for their survival as well as for sustenance. Below mentioned are some of the processes adopted by microbes in wastewater treatments.

12.4.1 Bacterial Mediated Wastewater Treatment

Bacteria has been considered as most common and effective method for the treatment of wastewaters owing to its range of enzymatic activities and presence within sewage water (Nascimento et al. 2018). Bacterial cells within the size range of approximately 0.5–5 μm and different shapes such as rod, straight rods, cocci, spiral, spherical and curved are usually present. Moreover, they are found either as single or in pairs and also in chains based on their cell morphology (Young 2007). In general, bacteria are sub-divided into two categories, heterotrophs and autotrophs. The heterotrophs such as *Pseudomonas, Flavobacterium, Alcaligenes* and *Archromobacter* etc. depends purely on organic substances for their carbon and energy requirement. And on the basis of oxygen requirement, heterotrophs are further divided into, aerobic (require oxygen to decompose organic matter), anaerobic (do not have any oxygen requirement for decomposition of organic matter) and facultative with the ability to undergo organic matter decomposition in the presence as well as absence of oxygen (oxic and anoxic situations) respectively (Hellingwerf et al. 1994).

12.4.1.1 Aerobic-Bacteria in Wastewater Treatment

Aerobic bacteria are primarily used in wastewater treatment process like in the form of activated sludge treatment process and trickling filter process. They are involved in the catalysing decomposition of organic material/wastes as per following equation:

$$\text{Organic material} + O_2 \xrightarrow{\text{aerobic bacteria}} CO_2 + H_2O + \text{Energy}$$

The aerobic degradation of different organic substances is beneficial and autocatalytic in nature where the bacteria acts as biocatalysts. The different concentration levels of aerobic bacteria is entirely dependent on the pH, moisture, temperature and process involved. For instance, activated sludge comprises of largest bacterial concentration. Besides, this process is also inexpensive in nature, simple to operate and highly practiced method for converting large amount of substrate under aerobic wastewater treatment (USEPA 1997). Moreover, the aerobic bacterial metabolism is much more rapid than that of anaerobic. Although, the main drawback of aerobic method is the excessive production of biomass, called as clarification sludge (Milieu Ltd W. RPA 2008). The management as well as disposal of this abundant sludge seems to be the most challenging that arises numerous serious environmental hazards like emission of greenhouse gases. Further, an agricultural sector utilization of sludge as fertilizer is also not feasible due to the presence of huge contaminants, toxic heavy metals and many other hazardous substances. Therefore, it entails the treatment as well as processing of sludge before disposing it onto land (Singh and Agrawal 2008). Additionally, the dispose of sludge by land filling may also cause leaching of toxic metal ions and other organic pollutants within the soil as well as ground water reservoirs, thereby causing the secondary pollution (Pathak et al. 2009).

12.4.1.2 Anaerobic-Bacteria in Wastewater Treatment

In order to overcome the negative effects of aerobic treatment in terms of elevated energy costs and sludge disposal, anaerobic treatment have attracted immense popularity due to its stringent environmental laws, regulations and policies (Pant and Adholeya 2007). Anaerobic bacteria also catalyse the degradation of organic pollutants within wastewaters in oxygen deficient conditions and it gains energy from certain compounds such as sulfates and nitrates etc. (Ji et al. 2019). The equations pertaining to same have been mentioned below:

$$\text{Organic material} + NO_3 \xrightarrow{\text{anaerobic bacteria}} CO_2 + N_2 + \text{Energy (nitrate bounded)}$$

$$\text{Organic material} + SO_2^{4-} \xrightarrow{\text{anaerobic bacteria}} CO_2 + H_2S + \text{Energy (sulfate bounded)}$$

However, the anaerobic degradation process is quite slower with restricted metabolism and needs massive quantities of microbes with prolonged habitat for effective reduction of organic matter (Wilkie et al. 2000). On the other hand, it has numerous advantages in terms of cost effectiveness due to its zero or very minimal requirement of any mechanical equipment for aeration. They also show high yield performance in comparison to activated sludge process which comprise of the restriction of oxygen transfer. In addition, it is also energy efficient as there is no use of oxygen and subsequently, it also do not produces any aerosols. Heavy metal reduction can also be done by precipitation in contrast to oxidative precipitation and the energy generated is utilized as biogas respectively. Apart from this, there is very limited production of sludge. Therefore, it reflects a realistic example of waste disposal as approximately 96% of the organic material is converted into an inflammable gas.

In the forging arguments, we have presented the different pros and cons of aerobic and anaerobic processes. Henceforth, there is a great prominence on prudent blending of both aerobic as well as anaerobic processes in order to take benefits of both the processes and maximizing their influence on the final process. Along with this, many variations have also been formulated through combining the operations of both these treatment processes for achieving the desirable results (Ranade and Bhandari 2014). To elucidate, the concatenation of these two protocols where one side does aerobic degradation, whilst the other side does anaerobic degradation. And this combined setup lowers the sludge formation along with reduction of odour and phosphorous levels in the effluent. The distillery wastewater is the typical example of this combined process where the anaerobic treatment results in biogas formation subsequently followed by the aerobic decomposition in order to achieve wastewater standard (Pant and Adholeya 2007). Apart from this, an important aspect that is to be kept in mind is the utilization of bacteria for wastewater treatment for bioelectricity generation through microbial fuel cells. This technology is the novel technology that produces the electricity via various metabolic processes mediated by different microbes (Chaturvedi and Verma 2016). This strategy mainly involves the use of microbes, specifically bacteria for transforming chemical energy generated during oxidation of organic material present in effluents into electrical energy. Several microbial species such as *Shewanella oneidensis, Streptomyces enissocaesilis, Klebsiella pneumonia, Escherichia coli* and *Nocardiopsis* spp. etc. have been found to be involved for the generation of electricity from wastewaters released from different industries of paper and pulp, agricultural sector, dye and textile industries (Palanisamy et al. 2019). The microbial fuel cells like any ordinary fuel cells comprises of two main segments of anode and cathode that is further sub-divided by a proton-exchange membrane respectively (Palanisamy et al. 2019). At anode portion, the oxidation of wastewater comprising of organic material occurs that generate few protons and electrons. And these protons and electrons move from anode towards cathode through the membrane and circuit, generating the electric current. Thus, the microbial fuel cells are most reliable for generating electricity due to its economical nature where organic matter is used as substrate and it seems to be the most clean, eco-friendly, economical, renewable and reliable process without any release of toxic by-product (Chaturvedi and Verma 2016).

12.4.2 Microalga Mediated Wastewater Treatment

Micro-algae comprises of eukaryotic algae as well as many species of cyanobacteria, the photosynthetic microbes that serve to be most prominent elements for bioremediation or wastewater treatment using biological methods (Goswami et al. 2021a). This is also one of the eco-friendly and sustainable technique that involves the elimination of heavy metals, pollutants, organic contaminants and nutrients from the industrial effluent as well as municipal wastewater (Oyetibo et al. 2017). The general term that has been given to the technique using algae for remediation purposes is known as 'phycoremediation' (Poo et al. 2018). Several algal species used for phycoremediation include *Tetraselmis* sp., *Scenedesmus* sp., *Chlorella vulgaris, Picochlorum* sp. etc. (Goswami et al. 2021b). And different cyanobacteria that are utilized for this purpose are *Oscillitoria* sp., *Spirullina* sp., *Anabaena* sp., *Scytonema* sp., *Dolichospermum* sp., *Leptolyngbya* sp., *Hapalosiphon* sp., *Gloeocapsa* sp., *Chroococcus* sp., *Lyngbya* sp., *Synechocystis* sp. and *Pseudospongiococcus* sp. respectively (Dutta et al. 2019). The most common reason behind the enhanced interest towards phycoremediation is due to the fact that they possess the potential to grow rapidly by the use of organic carbon and inorganic carbon, nitrogen and phosphorous within wastewaters leading to lower the eutrophication levels. Additionally, its photosynthetic potential of algae also allows the conversion of solar energy into algal biomass for CO_2 fixation (Almomani et al. 2019). Moreover, they possess rapidly growing characteristics due to short cell cycle with the least requirement of nutrients in contrast to other organisms (Salama et al. 2017). They enable heterotrophic bacteria to stimulate biodegradation by making them oxygen available for the process that has been released during photosynthesis (Manzoor et al. 2016). The biomass generated by the utilization of raw material makes it most cost-effective and also make the harvest of algal biomass easy and this biomass is very easily renewable and reusable through adsorption as well as desorption methods (Mehariya et al. 2021; Goswami et al. 2021a). The advantages of this algal biomass includes that it can be used in both continuous as well as discontinuous systems and is suitable in both aerobic as well as anaerobic treatment plants (Salama et al. 2017). It is most competent than other membrane processes for removing heavy metals and there is no or minimal generation of sludge or any other hazardous chemical (Ajayan et al. 2011). The immobilization process is not crucial and the algal biomass production takes place any time during the year and is not affected by any environmental cues (Darda et al. 2019). The biomass is further utilized as a target source for production of energy due to the fact that the treatment plants generate greenhouse gasses at limited rates because maximum nitrogen assimilation via microalgae takes place than that of being converted into nitrogen oxides (Guieysse et al. 2013). The wastewater treatment with the aid of microalgae in combination of bacteria can also be employed as single-step process. And in this process there is no need to switch among the operating systems for expediting inorganic nitrogen and phosphorous removal. Therefore, the complexity and energy required for the process can also be lowered (Gouveia et al. 2016). All these above-mentioned aspects depict that microalgae system forms a perfect remediating tool in various treatment systems.

12.5 Biofertilizers Production Technology

The microalgae-based technology is being effectively utilised for treatment of wastewater and production of biofuels. However, in order to obtain more benefits from this pleiotropic technology, it has been employed for the production of biofertilizers which act as eco-friendly and economically feasible source of enhancing soil fertility and crop productivity (Kim et al. 2017). The production of biofertilizers from algal biomass and its utilisation in agricultural sector is sequential process of different steps beginning from cultivation, harvesting, drying and finally applying the dried biomass as a biofertilizer (Fig. 12.2). Each of this step is discussed in following sections in detail.

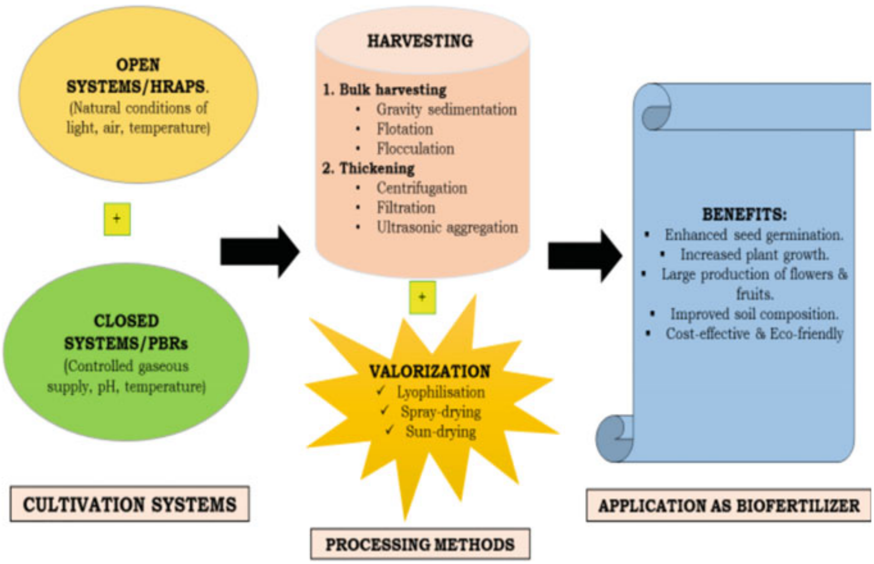

Fig. 12.2 Biofertilizer production technology using Micro-algae

12.5.1 Cultivation

Production of microalgae on large scale can be done using suspended as well as immobilised cultures by three different systems i.e., open, closed and hybrid. However, high cell densities and cost limit the use of immobilised cultures for cultivation of microalgae.

- **Open Systems:** These may be natural (open lakes and ponds) or artificial (High-Rate Algal Ponds (HRAP). Usually, blue green algae are cultivated using these systems. HRAPs are employed rather than natural lakes and ponds as they need less surface area for three-fold production of microalgae as compared to latter. These are shallow raceway type ponds 0.2–0.4 m deep with one or more than one loop whereby paddlewheel moves water at optimum velocity thereby preventing sedimentation (Kumar and Singh 2020). Though these are easy to construct and operate but their large dependency on external sources of light as well as nutrients and exposure to harsh climatic conditions such as rainfall, high temperature and variety of contaminants make them less efficient than closed systems for microalgal cultivation (Santos and Pires 2020).
- **Closed Systems:** These systems are also called as Photo-Bioreactors (PBRs) and such systems work under controlled conditions of light, temperature, gaseous supply and pH thereby lessening the risk of contamination and evaporation which results in increased yield of algal cultures. There are 3 types of closed PBRs including tubular, flat and column systems (Kim et al. 2013). All of these systems provide high density production of microalgae; column system being more efficient than other two. Despite of their great efficiency these systems are used in limited areas due to their high cost of construction and operation (Dragone et al. 2011). Also, control of penetrating light is difficult with increase in cell density of algae within such kind of systems.
- **Hybrid Systems:** Such systems combine the mechanisms of open & closed systems via two step sequential process.

12.5.2 Harvesting and Drying

This step includes the separation of algal biomass from suspension culture cultivation system by using different techniques of solid–liquid separation such as centrifugation, sedimentation, flotation, flocculation and filtration in systematic and sequential process. The process of harvesting is usually done in two succeeding phases: Bulk harvesting followed by thickening. The former step includes separation of microalgal biomass collected from HRAPs or PBRs through sedimentation, flocculation or floatation techniques. Sedimentation employs the input of long pre-treatment, lamella separators, high temperature and sedimentation tanks and is used for harvesting cyanobacteria (Santos and Pires 2020). The technique of flocculation is based on using chemical flocculants (ferric chloride, ferric sulphate, aluminium sulphate) to enhance the aggregation of microalgae leading to flocs formation. Similarly, floatation technique includes application of gaseous bubbles to the suspension leading to separation of solid algal biomass with air and is used for separation of smaller microalgae as they have greater chances to get floated with air or gases.

The latter step of thickening leads to further concentration of algal biomass through techniques of filtration, centrifugation and ultrasonic aggregation. Filtration is done through membrane filters and mainly used for large microalgae it is only suitable for harvesting of small quantities of microalgae. The technique of ultrasonic aggregation employs usage of acoustic forces for harvesting of microalgae whereas centrifugation is based on principle of separation of biomass due to rotation at high speeds with effect of centrifugal forces (Kumar and Singh 2020). Though the method used for harvesting varies from species to species, still centrifugation is most reliable, cost-effective and hygienic method for harvesting large quantities of microalgal biomass.

Harvesting is followed by drying of algal slurry to prevent it from getting waste. Different methods that can be adopted for drying are freeze drying, sun drying, drum drying, and spray drying (Uduman et al. 2010). Lyophilisation is another term for freeze drying in which the biomass is frozen and ice crystals are directly sublimed to vapours at pressure below the triple point of water. This method is a fine method of preserving algal biomass but requires high energy and cost investment. The rapid and comparatively economical method that can be used is spray drying whereby hot water droplets of small size are projected on algal slurry at high pressure using atomizers or gas–liquid jets (Kim et al. 2013). Similarly, sun drying is also economical and easy to operate but owing to the large water content of algal biomass it takes a lot of time to complete the process and is therefore not used frequently for this purpose.

12.5.3 Using Biomass as Biofertilizers

The obtained microalgal biomass can be utilised for availing different benefits for production of cosmetics, food supplements, biofuels as well as biofertilizers. Owing to their rich nutrient composition and tendency to enhance crop productivity and soil fertility, microalgae act as potent eco-friendly biofertilizers (Hussain et al. 2021). Microalgae *Acutodesmus dimorphus* has been extensively used a biofertilizer to enhance seed germination, plant growth, flower and fruit production in tomato (Garcia-Gonzalez and Sommerfeld 2016). Similar effects of application of *Chlorella sorokiniana* have also been observed in wheat where the nutrient composition of crop was found to enhance by 51% (Coppens et al. 2016). Hence, utilisation of microalgal technology for treatment of wastewater and then using the algal biomass as biofertilizer boost up nutrient recycling thereby locking the healthy nutrients within the soil ultimately leading to crop improvement (Singh et al. 2022).

12.6 Application of Biofertilizers

Modern agriculture relies heavily on synthetic fertilizers to sustain the world's ever-increasing population. Mineral fertilizers are indispensable for ensuring food security as today nearly half of the world's productivity is dependent upon them (Singh and Ryan 2015). For the year 2022, the forecasted global demand for N, P and K for agricultural use is about 111.6, 49.1 and 40.2 million tonnes. However, the synthesis and consumption of these inorganic chemicals contribute to environmental deterioration. The overexploitation of chemical fertilizers causes soil acidification, eutrophication and global warming. The biggest challenge for achieving agrarian progress in contemporary times is a reliable nutrient source for crops that does not compromise the country's resources or economy (Khan et al. 2019). Consequently, biofertilizers being economical and eco-friendly are gaining prominence nowadays. Microalgae are a group of organisms comprising both prokaryotic phototrophs (cyanobacteria) and eukaryotic phototrophs (green algae etc.) holding huge potential in addressing contemporary agricultural challenges (Alvarez et al. 2021). Wastewater treatment via microalgae is a solar-driven technology of nutrient recycling from wastewater (Solovchenko et al. 2016). This technology offers twin benefits of recovering various nutrients from wastewater and concomitant synthesis of microbial biomass which can be used as a sustainable slow-release biofertilizer or other value-added products (Renuka et al. 2017). Depending on the species, as well as the environmental and operational circumstances, microalgae uptake nutrients in different ratios. Usually, N:P assimilation ratios of 10–30 have been recorded for microalgae and cyanobacteria (Suleiman et al. 2020). Microalgae based biofertilizers mainly work on the soil to boost crop productivity, they tend to build and maintain soil fertility by supplying essential plant nutrients and secretion of various secondary metabolites such as polysaccharides, antimicrobial compounds, hormones, etc. (Renuka et al. 2018; Gonçalves 2021).

Microalgae can be used as biofertilizers since they contain significant quantities of plant nutrients (Garcia-Gonzalez and Sommerfeld 2016). Several studies have indicated that using microalgae biomass produced in wastewater as a biofertilizer improves crop yields and can successfully replace inorganic fertilisers. For example, Khan et al. (2019) analysed the potential of the algal biorefinery approach and suggested that synthetic fertilizers worth about 5584 USD ha^{-1} $year^{-1}$ could be saved by exploiting microalgae for phycoremdiation followed by biofuel and biofertilizer production. Another study demonstrated that soil supplementation of live algal biomass containing *Chlorella pyrenoidosa* species improved the growth characteristics of *Abelmoschus angulosus* by about 30% relative to synthetic fertilizer treatment (Umamaheswari and Shanthakumar 2021). Spirulina based fertilizer produced from aquaculture treatment enhanced the growth and seed germination of various leafy vegetables (Wuang et al. 2016). Similarly, an increase in the yield of paddy was observed by the inoculation of *C. vulgaris* and *Spirulina platensis* dry algal biomass (Dineshkumar et al. 2018). Hence, the utilization of algae biomass produced from microalgae-based wastewater treatment as a biofertilizer makes this technology more economical and sustainable and helps in achieving a zero-waste policy and a circular economy (Morais et al. 2021; Hussain et al. 2021).

12.6.1 Improving Soil Fertility

Crop productivity is directly proportional to soil health which is often analysed by evaluating its physical, chemical and biological properties. Typical characteristics of the fertile soil comprise the presence of a high amount of organic matter, biological activity, and aggregate stability (Yilmaz and Sönmez 2017). The main suggested mode of action of living microalgae-based fertilizers is biostimulation. These fertilizers augment and modify soil microbial community while dead algal biomass requires microbial decomposition to release nutrients (Marks et al. 2019). Cyanobacteria and microalgae form self-sustainable microbial communities known as biocrust or biofilms which aid in the restoration of soil microbiota and vegetation cover (Abinandan et al. 2019). These biocrusts work as ecosystem engineers especially, in soils of arid and semi-arid environments by protecting soil sediments against various soil degradation drivers thereby sustaining soil fertility and stability (Kheirfam et al. 2017). However, the magnitude of the positive influence of cyanobacteria inoculation on soil fertility is dependent on the selected species and soil conditions. In comparison to fine texture soils, where cyanobacteria develop more consistent and resilient biocrust, sandy soils form sleeker and more delicate biocrust. Similarly, soil restoration works better in low fertility soil (Chamizo et al. 2018).

These microorganisms secret several extracellular polymeric substances (EPSs), chiefly, polysaccharides, lipids, nucleic acids and proteins. EPSs, in particular, retain their stable matrix structure and form a 3-D polymer matrix that facilitates cells to communicate with one another and adhere to surfaces, allows soil particles to aggregate, and entrapment of nutrients and moisture in the soil (Xiao and Zheng 2016; Costa et al. 2018). Soil aggregates are the fundamental unit of soil structure which regulates numerous soil processes, including soil compaction, water infiltration, root penetration, soil nutrient cycling, soil erosion and crop production. Hence, higher aggregate stability promotes better soil structure which is vital for soil fertility and sustainability (Zhou et al. 2020).

Microalgae alone or being a part of biocrust improve various physicochemical soil properties as they execute a crucial role in fixing C and N, regulating soil water retention, soil pH and electrical conductivity (Marks et al. 2017). Microalgae supplementation also augments soil’s organic matter which in turn improves soil cation exchange capacity (CEC) which is a significant soil chemical quality factor and indicator of soil’s ability to provide certain essential nutrients (de Siqueira Castro et al. 2017). The increase in organic content of the soil following the application of biomass to the soil as a bio-fertilizer may be due to the locking of the portion of the microalgal carbon in the soil (Das et al. 2019).

12.6.2 Nitrogen Bioavailability

Although inorganic nitrogen fertilizers are applied to meet the nutritional requirements of crops, much of N is lost to the environment through ammonium volatilization, denitrification, nitrification, surface runoff, leaching or due to microbial immobilization (Alvarez et al. 2021). Certain cyanobacteria, for example, *Nostoc* and *Anabena* contain specialized nitrogen-fixing cells called heterocycts which can fix atmospheric nitrogen to plant usable forms such as ammonia. This nitrogen-fixing tendency of cyanobacteria is responsible for its significance as a sustainable substitute of the N source for crops. Pereira et al. (2009) demonstrated the significant potential of cyanobacteria based biofertilizer in increasing nitrogen use efficiency in rice, resulting in a 50% reduction in synthetic fertiliser consumption for the same yield. Similarly, a study evaluating the potential of dried consortia of both unicellular and filamentous microalgae biomass isolated from sewage as a biofertilizer for wheat crops has ascertained a reduction of about 25% in usage of N fertilizers for similar crop yield by enhancing microbial activity and bioavailability of nutrients in the soil (Renuka et al. 2017).

Once these bacteria fix atmospheric nitrogen it is transferred to plants mainly by bacterial mineralization after their death (Alvarez et al. 2021). The soil microbial degradation allows gradual release of organic N which benefits in achieving lower N losses to the environment than the mineral fertilizers. For instance, de Siqueira Castro et al. (2017) analysed the efficacy of microfilms against commercial urea for the cultivation of *Pennisetum glaucum* and observed that urea exhibited a higher loss of N (18.9%) through ammonia volatilization than microfilms where the loss was merely 4.6%. The main benefit of this relatively slow release of nutrients is that the plants have access to nutrients throughout their growth, allowing for synchronisation between nutrient availability and plant requirements (Suleiman et al. 2020). Biofilms formed by the addition of viable algal cells can stabilize nitrogen within the soil profile both spatially and temporally. In addition to locking N into organic biomass as proteins, algae also regulate nitrogen availability by absorbing inorganic nitrogen ions, for example, NO^{3-} (Marks et al. 2019).

12.6.3 Phosphorous Bioavailability

The commercial phosphoric acid is produced through a chemical reaction of sulfuric acid with phosphorus as it is extracted from phosphate rock called apatite. The by-product of this process is phosphogypsum that contains highly toxic impurities like uranium and thorium. Cadmium (Cd) is also present in phosphorus fertilizers that poses health risks to humans (Roberts 2014). The increased agricultural demand requires increased phosphate mining thus posing an acute environmental hazard. However, finding sustainable alternatives to chemical fertilizers, minimizing the nutrient loss through leaching/runoff and increasing their bioavailability to the plants represents a probable solution. It has been observed that crops can only uptake approximately 45% of the added phosphorus. Formation of insoluble compounds and precipitates due to elevated pH/chemical reaction with soil minerals results in decreased availability of phosphorus to plants (Santos and Pires 2020). Cyanobacteria have been found to play a major role in enhancing the bioavailability of phosphorus to the plants. Phosphatase enzyme produced in their cells solubilizes the insoluble forms of phosphorus like $Ca_3(PO_4)_2$, $FePO_4$, $AlPO_4$, and hydroxyapatite ($Ca_5(PO_4)_3OH$) as well as the organic phosphorus in soil. The mechanism of solubilization of phosphorus by cyanobacteria operates either through synthesizing a chelator for Ca^{2+} that help in dissolution of the compound without altering the pH of soil (Roychoudhury and Kaushik 1989) or through secreting the organic acids that solubilize the phosphorus (Bose et al. 1971). It has also been hypothesized that cyanobacteria first solubilize inorganic phosphate, scavenge it for their own nutrition and incorporate it into their cell biomass. It is later on released into the soil slowly through secretion or after the death of the cyanobacterial cells. The plants and other organisms take up this phosphorus after mineralization (Kumar and Singh 2020). Further, compared to inorganic phosphate the uptake has been observed to be much higher in case of microalgal inoculation. The domestic and agro-industrial wastewaters containing large amounts of nutrients can be used as a culture medium for algae like *Chlorella vulgaris, Scenedesmus obliquus* and *Scenedesmus dimorphus* etc. that on one side can be used to treat wastewaters and on the other hand can be used as biofertilizers (Morais et al. 2021). Microalgae along with assimilating inorganic phosphate can also mineralize organic phosphate into orthophosphate with the help of phosphatase enzyme and then further assimilate it. Some marine diatoms have also been reported to convert the phosphate into polyphosphate granules through polyphosphate kinase that are acid insoluble and are stored within the cells (Liu and Hong 2021). The microalgal fertilizers also show a higher release of phosphorus in soils when mixed with soil phosphorus solubilizing organisms (Hussain et al. 2021).

12.6.4 Reclamation of Saline Soil

The excessive amount of salts in the saline soils make them less productive. Their top layer is firm and impermeable to water. The plant roots face difficulty in water and nutrient absorption due to the high osmotic tension caused by high salt concentration in the soil. The cyanobacteria are capable of surviving in extreme conditions like saline soils thus making them an ideal agent to be used to reclaim such soils. Cyanobacteria restrict the influx of sodium ions and accumulate inorganic/organic osmoregulators in the cell interior in order to survive under saline stress. Microalgal species like *Anabaena oscillarioides*, *Anabaena aphanizomenoides*, and *Microcystis aeruginosa* have been found to tolerate salt concentrations ranging from 7 to 15 g/L (Moisander et al. 2002). These cyanobacterial strains produce exo-polysaccharides which result in better soil particle binding thus improving the water-holding capacity of these soils. Cyanobacteria have also been reported to produce oxalic acids that solubilize nutrients from insoluble carbonates. These acids also lower down the pH, electric conductivity and hydraulic conductivity of saline soil, leading to improvement in soil aggregation (Kumar and Singh 2020). Another contributing factor in improving the soil quality is the formation of soil aggregates by microalgae and cyanobacteria through release of various compounds such as polysaccharides, peptides, and lipids that bind the soil particles together. The increased polysaccharide content of soils also enhances the soil aggregate stability ultimately improving the water holding capacity of the soil. The soil macro aggregates are further strengthened and resist soil erosion due to wind and water through the mucilaginous filaments network of cyanobacteria. Also, the cyanobacterial growth improves soil aeration, hence reducing the compaction in soils.

12.6.5 Plant Growth Prompters

The microalgal biomass finds its application as a biofertilizer due to its documented potential in enhancing nutrient efficiency and consequently increasing crop yields. Various studies have shown the efficacy of microalgal species like *Acutodesmus dimorphus* (Garcia-Gonzalez and Sommerfeld 2016), *Chlorella sorokiniana* (Kholssi et al. 2018), and *Nannochloropsis* (Coppens et al. 2016) as biofertilizers triggering faster germination and enhanced plant growth in terms of higher number of branches and flowers, increased plant height, increased dry biomass, increased sugar, chlorophyll and carotenoid contents etc. (Santos and Pires 2020). Cyanobacteria have been reported to produce plant growth promoting hormones like gibberellins, cytokinins, auxins and vitamins (vitamin B or amino acids). Microalgal strains like *Anabaena*, *Anabaenopsis*, *Calothrix*, *Chlorogleopsis*, *Cylindrospermum*, *Glactothece*, *Nostoc*, *Plactonema*, *Synechocystis* have been reported to produce auxins (Sergeeva et al. 2002; Mohan and Mukherji 1978; Selykh and Semenova 2000); *Anabaenopsis*, *Cylindromum* to produce Gibberellins (Mohan and Mukherji 1978); *Anabaena*, *Chalrogleopsis*, and *Calothrix* to produce Cytokinins (Selykh and Semenova 2000) in different plants. Many species are symbiotic and colonize epidermal cells, intercellular spaces, cortex and sub-stomatal chambers of plants (Sartori et al. 2021). Further, the high content of amino acids in microalgal biomass and/or extracts lessens the effects of abiotic stress and exhibits a positive effect on the growth and yield of the plants (Gemin et al. 2019). The amino acids like tryptophan and arginine are actually the metabolic precursors of phytohormones such as auxins, salicylic acid and polyamines, and hence the microalgal extracts are being included in the commercially available biostimulant formultions (Morais et al. 2021).

12.7 Conclusion

The use of microalga and bacteria have proven to be very beneficial for both wastewater treatment and biofertilizers production. By uniting it with WWT, the production of microbe based biofertilizers can overcome many modern day challenges in agricultural sectors. The use of biofertilzers at commercial scale can reduce dependency on chemical based fertilizers. However, there is a dire need to identify most suitable microbial strains that can efficiently adjusts themselves to existing wastewater treatment plants, ultimately making the process environmentally sustainable and budget friendly. Hence, the green technology can pave way to new era of biofertilzers application across the globe.

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Chapter 13
Advancements in Microbial Fuel Cells Technology

Neha Singh and Pallavi Agarwal

Abstract Microbial fuel cells (MFCs) technology has shown tremendous potential to produce clean electricity and clean up wastewater. MFCs use electrochemically active microorganisms known as biocatalysts to generate electricity which relies heavily on refined chemicals for energy production. Extensive research on MFCs' design and performance has led to rapid advancements in these fields. However, reducing operational costs and reliance on refined chemicals are major challenges to improving MFC technology power output. In this chapter, we focus on topics of future study that will help us better understand MFC performance for water treatment and renewable energy harvesting simultaneously.

Keywords Microbial fuel cells · Operational cost · Water treatment · Renewable energy

13.1 Introduction

Water sanitation is not just a problem in developing nations; it is a fundamental human and environmental necessity everywhere. The ever-growing population, urbanization, industrial and agricultural production, and chemical consumption contribute to the pollution of surface and ground water (Raji and Mirbagheri 2021). Currently present wastewater treatment methods require high energy and cost; therefore, new technology is needed to increase energy and resource recovery (Munoz-Cupa et al. 2021).

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The wastewater released from domestic, agricultural and industrial facilities contaminates drinking water sources by causing eutrophication, hypoxia, and algal bloom in surface water. However, this wastewater cannot be used directly to generate electricity. Therefore, the wastewater is first converted into an activated sludge by adding microorganisms (bacteria, protozoa, and fungus) as clumped fine particles and held in suspension by stirring, and then organic debris is removed from it. The activated sludge process produces excellent results with rapid processing times, but aeration costs up to 55–70% of the plant energy, whereas sludge treatment and disposal could account for up to 30% of overall operating expenses (Gandiglio et al. 2017). Presently, most of the world's wastewater treatment systems rely on the time-tested activated sludge technique; however, this procedure requires a lot of energy and chemicals (Sustarsic 2009).

The high energy demand of present wastewater treatment processes needs to be improved to reduce its cost (Gude 2016). Additionally, along with sludge hazardous gases such as carbon dioxide (CO_2), nitrous oxide (N_2O), and other chemicals release into the environment during the wastewater treatment, which needs to be disposed. The United States Environmental Protection Agency (USEPA) estimates that approximately 3–4% of all energy used in the US is consumed for treating water, which results in the annual release of nearly 45 million tons of greenhouse gases (Otondo et al. 2018). This shows that the current wastewater treatment systems need to be advanced further for a more sustainable wastewater treatment system (Khandaker et al. 2021).

Because of its remarkable potential for environment friendly wastewater treatment and contamination removal, microbial fuel cells (MFC) have been receiving more attention. MFCs are environmentally sustainable technique to address the water sanitation needs of the present and future generations (Venkata Mohan et al. 2013). In the present chapter, we will concentrate on the current advancements and hurdles in implementing the MFCs to treat wastewater, keeping in focus the various factors which influence its performance.

13.2 Microbial Fuel Cells (MFCs)

MFCs, a new bio electrochemical process, utilize microorganisms as biocatalysts to oxidize organic and inorganic compounds to generate electricity while also desalinating water, treating wastewater, producing bio-hydrogen and volatile fatty acid, and removing heavy metal.

In general, MFC comprises an anode and a cathode separated by a proton exchange membrane (PEM) (Ucar et al. 2017). Based upon presence or absence of PEM, MFCs are divided into two types: MFC with mediator or without mediator. One chamber MFCs are mediator less and are developed in the 1970s (Naseer et al. 2021). The redox proteins such as cytochromes on the outer membrane of one chambered MFCs transfer electrons directly to the anode, hence no mediator is required. In the twentieth century, the two-chamber type MFC was introduced in which a mediator such as a chemical transfers electrons generated in the cell from the bacteria to the anode (Tsekouras et al. 2022). In wastewater treatment two-chamber type MFCs are more common.

13.3 Functioning of the MFC

MFCs use microorganisms as catalysts to convert chemical energy stored in organic substrates into useful electrical energy (Vishwanathan 2021). A basic schematic configuration presented in Fig. 13.1 illustrates the functioning of an MFC. In an MFC, at the anodic surface, exoelectrogenic or electroactive microorganisms' breakdown the organic matter to generate electrons. These electrons travel through the PEM and mix with protons at the cathode and oxygen, to produce water. It is convenient to use bio-electrocatalysts to carry out the reduction reactions at the cathode. Any organic material that can degrade, including clean fuels (ethanol and glucose), complex organic mixtures of human and animal waste, and wastewater from food processing, can generate electrons.

A single chamber MFC does not contain a separate cathode compartment and PEM as depicted in Fig. 13.1a. Therefore, the design is simple, and cost is lower than two chamber MFC (Liu et al. 2004). The cathode in a single chamber MFC is exposed to water on one side (the inner side) and air on the outer side (Wang and Han 2008). Due to its high oxidation potential and easy accessibility, the oxygen in the air reacts immediately with the anode and used as an electron acceptor in single chamber MFC similar to a two chamber MFC. However, to improve cathode reaction efficiency and broaden the usage of MFC, research has recently concentrated on the use of different electron acceptors.

Whereas a two-chamber MFC has a PEM separating the anaerobic anode chamber from the aerobic cathode chamber (Parkash 2015). The microorganisms in the anode chamber oxidizes the substrate as fuel, and release protons and electrons (Venkata

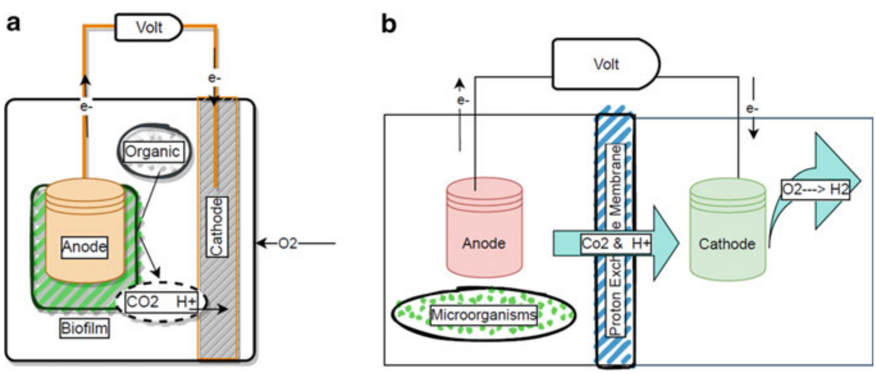

Fig. 13.1 **a** One chambered MFC; **b** Two chambered MFC. MFC, Microbial fuel cell

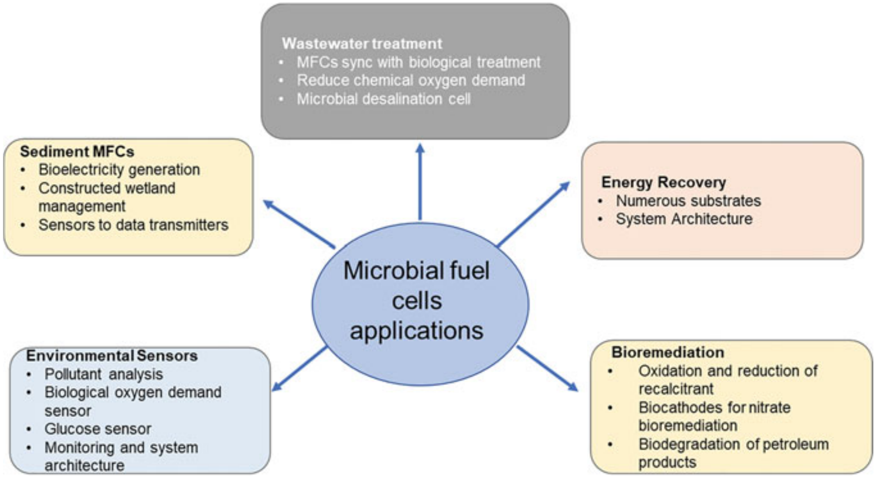

Fig. 13.2 Microbial fuel cells in different applications

Mohan et al. 2008), which are transported to the cathode chamber via PEM, where protons and oxygen combines to form water (Rabaey et al. 2008). A general oxidation (acetate)–reduction (oxygen) in two chambered MFC (Scott and Eileen 2015):

$$CH_3COO^- + 2H_2O \leftrightarrow CO_2 + 7H^+ + 8e^-$$
$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

MFCs' distinctive qualities sets MFCs apart from other competing technologies and make it the superior choice. Firstly, MFCs' ability to yield productive outcomes at varied temperature (from 20 to 40 °C); secondly, the cathode can operate with passive aeration, therefore, during operation the aeration process used by MFCs to produce oxygen does not require external electric current (as electron acceptor).

Although the most important characteristic of MFC, which sets MFC technology apart from other current bioenergy approaches is that they can generate energy from various sources, including natural organic matter and complex organic waste. As MFC utilizes organic waste to generate electricity it helps to reduce carbon footprint and environmental pollution. Many industries have adopted MFC technology for various applications as shown in Fig. 13.2.

13.4 Waste Treatment Principles Using MFCs

MFC transforms the chemical energy into electrical energy. In a two chambered MFC, at the anode compartment, organic compounds such as acetate, ethanol, glucose, and lactate undergo anaerobic oxidation, which generates electrons and protons (along with carbon dioxide) and passes through PEM to the cathode compartment to generate electric current and water. Oxygen or ferricyanide are commonly used as cathode electron acceptors. In summary, during wastewater treatment organic material is oxidized at anode as fuel and used as a source of energy. The MFC reaction can be represented in an equation as follows:

Anode reaction	PEM	Cathode reaction
$CH_3COO^- + 7H^+ + 8e^- + 2H_2O + 2CO_2$	|	$O_2 + 2H_2O + 4e^- + 4H^+$

MFC reaction have a negative Gibbs free energy; therefore, there is a potential for a spontaneous generation of electricity. The MFC redox reaction can be summarized as follows (Yasri et al. 2019):

Anode reaction	Cathode reaction
$CH_3COO^- + 4H_2O \rightarrow 2HCO_3 + 9H^+ + 8e^-$	$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$
$(E^\circ = -0.289\ V)$	$(E^\circ = 0.805\ V)$

Total: $2O_2 + CH_3COO^- \rightarrow 2HCO^-{}_3 + H^+$ (Gibbs free energy $[\Delta G] = -847.60$ kJ/mol; Electromotive force [EMF] = 1.094 V)

13.5 Construction of MFC

The microorganisms, anode, cathode, and PEM (Fig. 13.3) significantly influence the MFC performance, which in turn affects the applications where MFCs are used, such as bioelectricity generation, wastewater treatment, bioremediation of dangerous substances, biohydrogen production, and biosensors (Kumar et al. 2018).

13.5.1 Identifying Microbial Communities

Microbes in microbial biofilms can have different performances. Therefore, microbial biofilms were analyzed under different operational conditions to obtain best results (Dolch et al. 2016). To date, Gram-negative bacteria make up the majority of electroactive microorganisms in MFCs (Greenman et al. 2021), and they have been shown to generate more power at higher flow rate than the Gram-positive bacteria (Juang et al. 2011).

Gram-negative and Gram-positive bacteria have different cell wall composition, which in turn impacts the electrogenic activity of the bacteria, which influence the substrate degradation potential of the bacteria. Generally, greater number of electroactive species degrades the substrate more rapidly thus producing more electrons and protons. Due to the presence of teichoic acid in their peptidoglycan layer, Gram-positive bacteria have a high zeta potential than Gram-negative bacteria who have

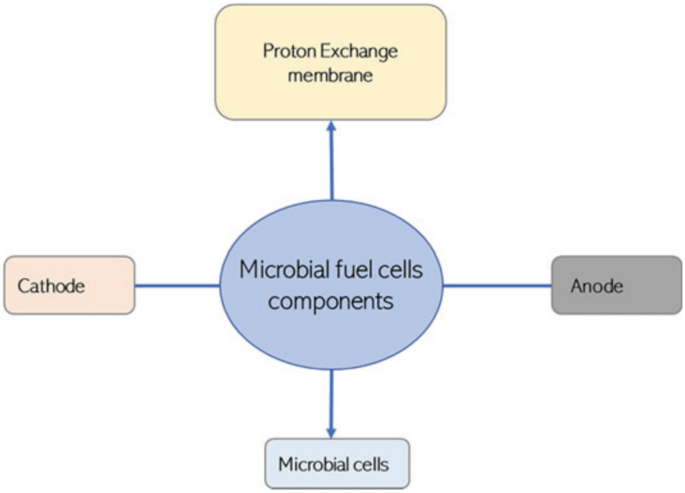

Fig. 13.3 Components of microbial fuel cells

lipopolysaccharides in their call wall. Therefore, the interaction between the material used in the MFCs and the bacterial surface charge is critical in optimizing MFCs output. Hypothetically, if all the electrons generated upon substrate breakdown can be directed for producing energy, it will greatly boost the MFCs output.

Inoculum, which is commonly obtained from wastewater or anaerobic sludge greatly impact the biofilm formation (Salar-Garcia et al. 2020) because it determines the dominant bacterial population in an MFC. When the primary purpose is the treatment of wastewater, these mixed cultures are typically preferred (Read et al. 2010). More electron flow generates in biofilms created from a combination of different microbial population rather than just one; however, as the bacterial community is made up of a variety of bacterial species, it is questionable whether such a biofilm can be replicated. On the contrary, for specific uses, such as to detect biological oxygen demand single species (pure cultures of *Clostridium butyricum, P. aeruginosa*) are used to ensure consistent signal from batch to batch.

During wastewater treatment, these microbial biofilms react in different ways to different operational conditions, such as: (a) set-potential operation with the anode electrode potentiostatically controlled to + 100 mV; (b) open circuit operation (zero current generation); and (c) MFC operation using a 750 Ω external resistor (0.3 mA current production) (Ishii et al. 2013). When bacteria present in municipal wastewater are used to digest complete organic matter in an MFCs it usually takes 8–12 days; however, at set-potential condition it takes 4–6 days, and at open circuit operation approximately 15–20 days. This shows that during MFC wastewater treatment, higher current generation reduces the organic matter breakdown time.

The 16S rRNA gene sequencing of the microbial community in set-potential condition reactor, open circuit reactor, and reactions carried out using a 750 Ω external resistor showed that family *Deltaproteobacteria* and *Bacteroidetes* were the most common families in microbial biofilms (Ishii et al. 2013). Within *Deltaproteobacteria*, *Desulfobulbaceae* and *Geobacteraceae* phylotypes were significantly increased when the set-potential condition was higher. However, in the open circuit condition reactor, no such specificity was found. This shows that *Desulfobulbaceae* and *Geobacteraceae* family in MFC systems can help improving the wastewater treatment turnover, thus resulting in improved energy recovery in the biofilm.

13.5.2 Anode

The material used in an anode should be conductive, cheap, safe for the environment, nonreactive to the anolyte (the electrolyte in the anode chamber), and exhibit large surface area (Caizán-Juanarena et al. 2020). Most commonly used anode material in a MFC are carbon-based electrodes, which includes graphite plates, graphite rods, graphite felt electrodes, graphite granules, carbon cloth, carbon brush, and stainless steel (Yaqoob et al. 2020). To improve MFC performance, bare electrodes with limited surface area can be simply changed with conductive nanomaterial such as graphene with a greater surface area (Caizán-Juanarena et al. 2020). There are various ways to cover the bare electrodes with nanomaterial. As of yet, the MFC have shown positive results from anodic alterations with nanoparticles. Biofilm growth on the anode is encouraged by nanomodification so as to reduce the time to start MFC, improve electron transfer, and reduce internal systemic resistance (Godain et al. 2022).

13.5.3 Cathode

Three elements—a cathode, a catalyst, and an electron acceptor—make up the cathode compartment (Liu et al. 2022). An anode can be used as a cathode material, and platinum is used as a catalyst to remove oxygen from the cathodes by reducing electrons. Whereas low cost, wide availability, and high redox potential make oxygen a good electron acceptor (Bajracharya et al. 2016).

Presently, in laboratory size MFC experiments, using costly and potentially dangerous chemical agents like ferricyanide as cathodes (electron acceptors) or platinum catalyst as air cathodes is not in consideration with environment sustainability. Therefore, understanding the fundamental bio-electro-chemical principles behind the mechanisms that control electron uptake in the cathode chamber can aid in the development of low-cost cathodes (Gude 2016).

13.5.4 Membrane

In MFC, PEM mediates the transfer of protons from the anode to the cathode chamber and vice versa. Commonly used PEM are Nafion and Ultrex CMI-7000, among which Ultrex CMI-7000 is significantly less expensive (Borja-Maldonado and López Zavala 2022). In addition to electrons and protons, the PEM can leak oxygen, anolyte or bacteria, which can transfer to the cathode, and catholytes can diffuse to the anode. This undesired transfer of anolytes and catholytes to cathode and anode reduces the MFC performance. Therefore, studies are going on to minimize this PEM mediated leaky transfer and measure PEM's long-term influence on MFCs efficiency (Ghosh et al. 2018).

13.6 Functional Parameters Affecting MFCs' Efficiency

As different components influence MFC performance, similarly different functional parameters are critical in improving its efficiency and lowering operating cost, which can increase its commercialization. These functional parameters are reactor design and configuration; external resistance; feed rate; ionic strength; microbial diversity; pH; sheer stress; temperature; time; and wastewater type (Malekmohammadi and Mirbagheri 2021). Different MFC applications require optimum settings of these parameters for best performance.

Operational conditions affecting the efficiency of an MFC:

(a) *pH*

Microorganisms are sensitive to their environment, therefore, electrolyte's pH effects their growth and viability. Even a little pH variation can disrupt cellular metabolism, yet microorganisms can adapt to altering pH in order to carry out metabolic functions (Jin and Kirk 2018).

Various studies report that MFCs work best around pH 7 (Mahmoud et al. 2022; Raghavulu et al. 2009; Puig et al. 2010). The use of wastewater as a substrate exposes bacteria to changing pH levels (Patil et al. 2011). Changing wastewater pH changes microbial community composition, which inhibits anode-formed biofilm activity, reducing MFCs' power output efficiency (Zhang et al. 2011). Therefore, maintaining pH is critical for MFCs functioning, which can be achieved by using appropriate catalysts, new PEM, and inclusion of buffering agents.

However, adding acid or alkali to maintain pH raises the operating costs. Therefore, most investigations focused on maintaining pH with buffer or PEM. To regulate and maintain system's pH in order to obtain high power and biodegradation.

(b) *Temperature*

Based on temperature, bacteria are classified into three groups, psychrophile (< 15 °C), mesophile (15–40 °C), or thermophilic (> 40 °C). This reflects the importance of temperature in optimum functioning of MFCs (Gadkari et al. 2020). As microbes are the main player in MFCs, therefore, temperature affects biofilm development and electrolytic activity (Liu et al. 2011). Most microbes used in MFCs are the electroactive bacteria, which are mesophilic. However, few electroactive microbes are also thermophiles and psychrophiles. Generally, MFCs are fed with mixed cultures, therefore, they have variable optimal temperatures, which determines microbial growth. Thus, temperature affects the kinetics and thermodynamics of anodic processes, which affects biofilm formation.

(c) *Feed rate*

MFCs are fed with organic substrates such as simple sugars, complex carbohydrates, lignocellulose biomass, and inorganic substrates such as sulfide. The substrate used as a growth medium in an MFC determines the microbial species, which will dominate the microbial community. Studies have shown that the dominant microbial species determine the MFC power output. Interestingly change in the substrate concentration also changes the dominant species, and a greater concentration of substrate is found to be harmful to biofilms. For high coulombic efficiency, it is necessary to put every free electron from the substrate's oxidation to good use in the form of energy production. However, some of these electrons are lost by MFC, reducing its efficiency. Thus, growth of biofilms and loss of electrons affect the electric current generation.

13.7 Different Waste Material Segregation from the Wastewater

A variety of substrates such as pure compounds (acetate, glucose, butyrate) and complex mixtures (such as municipal wastewater, brewery effluent, starch production) have been studies in MFCs (Obileke et al. 2021). In order to learn more about the practicality of the MFCs working principle and to enhance energy recovery, organic removal efficiencies, and MFC performance artificial wastewaters have been tested. However, more recent research has concentrated on using real wastewater from the below mentioned resources. The studies have shown that treating the whole wastewater does not maximize the nutrient recovery and recycling. Therefore, separating the different waste components can help in targeted treatment, which reduces the wastewater treatment cost (Kujawa-Roeleveld and Zeeman 2006). Therefore, selecting a resource-efficient method can maximize the resource recovery and make it economically viable process.

13.7.1 Urine as Energy Source

In urine, excluding uric acid and urea, which cannot be utilized by the bacteria, the mean calorific value of 1 g of the organic components (carbohydrates, peptides, proteins or amino acids) has been estimated as 2.08 kcal (Ieropoulos et al. 2012).

In the wastewater, urine is a major component. The primary urine component, that is, ammonia, is separated by absorption. Additionally, to reduce the wastewater volume, evaporation, partial freezing or reverse osmosis techniques are employed (Maurer et al. 2006). In this way, the leftover wastewater mixture contains much fewer nutrients that can be treated at the wastewater treatment plants.

However, using urea as a substrate raises the pH at the anode, which reduces the anodic performance. Whereas Ca^{2+} and Mg^{2+} ions precipitate at the cathode in form of struvite, potassium struvite, and hydroxyapatite on the cathode surface. A recent study showed that adding sea salt additives increases struvite recovery (up to 21–94%) and MFC power output (up to 10%) (Merino-Jimenez et al. 2017). Further research is required to overcome cathode precipitation upon using urine as a starting substrate (Santoro et al. 2020).

13.7.2 Human Feces and Other Wastes as Energy Source

MFCs are tested to generate electricity from wastewater that contain human feces (Fangzhou et al. 2011). Two-chamber MFC's removal efficiencies for total chemical oxygen demand, soluble oxygen demand, and ammonia is 71%, 88%, and 44%, respectively, after operating for 190 h. The highest power density measured was 70.8 mW/m^2, which suggests that MFC is viable and suitable for treating human feces wastewater. To further improve the power density from human excreta wastewater, first it is fermented, which led to a 47% increase in power density (22 mW/m^2 compared to control unit with no fermentation). Research has been done to test other animal waste, such as cow dung and chicken droppings to generate bioelectricity (Gazali et al. 2017).

Similarly, manure fed MFC performance were evaluated with the aim of maximizing power production (Zhang et al. 2015) (Lee and Nirmalakhandan 2011). Study done by Wang et al. (2014) showed that even low-moisture dairy manure (< 80%) could be used as MFC substrate (Wang et al. 2014). These studies show that human and animal waste have significant potential for usage as feedstock or substrates in MFCs, which would allow for effective and environment friendly onsite waste management as well as energy generation.

Agricultural, dairy, residential, food, industrial and landfill leachates are some of the many biodegradables organic compounds that can be used in MFCs.

13.7.3 Metal Removal in MFCs

To remove metal ions, present in wastewater necessitates the use of specific treatment technologies to remove it and to lessen the risk posed on health and environment. The high redox potentials of some of these heavy metal-containing groups make them a good electron acceptor, which can help in the reduction and precipitation processes (Wang and Ren 2014). Wang et al. discussed four methods to recover metals from wastewater, that is, (1) direct metal recovery using abiotic cathodes; (2) metal recovery using abiotic cathodes supplemented by external power sources; (3) metal conversion using bio-cathodes; and (4) metal conversion using bio-cathodes supplemented by external power sources (Wang and Ren 2014). However, further research is going on to develop improve methods to remove heavy metals from the wastewater and to recover these metals for other purposes.

13.8 Challenges of Working with MFCs

MFCs can be a better replacement for conventional wastewater treatment plants that also generates electricity. However, MFCs have never been viewed as a major contender in the wastewater treatment or renewable energy domain despite being the only technology that can produce energy rather than use it. Nonetheless, MFC are receiving more interest from researchers studying wastewater treatment to overcome operational costs due to costly electrode materials, current collector, catalyst, and separator and low power production.

The primary obstacle limiting the use of MFCs in wastewater treatment, is fouling at the membrane, which diminishes MFCs' performance by interfering with proton migration and substrate breakdown (Choi et al. 2011; Xu et al. 2012). The membranes make up the majority of an MFC's overall cost due to their high cost. Therefore, a membrane-less MFC can lessen the cost while processing wastewater, which makes them the subject of extensive research (Zhang et al. 2016). However, the absence of the ionic membrane in the membrane less MFC restricts the substrate in the anodic chamber with no cross-over, which reduces the power density and Columbic efficiency of MFCs, hence affecting MFC's performance (Tartakovsky and Guiot 2006). Whereas using a dual anode in membrane-less MFC enhanced the reaction surface and prevented the organic matter cross-over, thus enhancing its performance (Kim et al. 2016).

Additionally, Lee et al. suggested that multiple electrodes in separate chambers may also be an innovative design for a large-scale MFC to lessen the inhomogeneity of the flow and concentration fields (Lee et al. 2015). However, when using MFCs technology on a big scale, using multiple electrodes (graphite rods and plates, carbon cloth and paper) will further add up to the cost to build MFCs. Additionally, materials such as carbon paper or graphite rods cannot be used for scaling up because they lack intrinsic durability and structural strength. Since the use of electrodes made up of standard carbon-based materials by high costs; therefore, research is going on to develop cheap carbon-rich electrodes with high-current-output from materials such as used tires. The carbonized waste tires are used in MFCs as anode materials. This provides a fresh source of anode material for MFC engineering applications and lessens the secondary pollution brought on by old tires (Chen et al. 2018).

Additionally, enhancing electron transport through the use of nanoengineering methods can help MFCs' work better (Scott et al. 2007). Different techniques and modification procedures employing nanomaterials have been tried to increase the MFCs' energy output (Zhou et al. 2011). When used as an anode, carbon nanotubes (CNTs) and polyaniline nanostructure composite can increase electrode surface area and electron transfer capacity (Qiao et al. 2007).

Any new technology ought to perform well to the status quo and ideally outperform it. MFCs have the potential to offer superior benefits beyond just energy savings. It is important to assess the efficacy of current methods for disposing of radioactive material, pharmaceuticals, and personal care products that include hazardous and micro contaminants. Therefore, system-specific removal techniques should be used. More research is required in this area to accurately define the capability of MFCs in removing these pollutants.

13.9 Conclusion and Future Perspectives

MFC is a new technology with many unexplored possibilities. Despite major research efforts to enhance their performance through the development of innovative structural designs, electrode materials, catalysts, and microorganism MFCs are not yet suitable for use in commercial applications. The major obstacle is the insufficient energy output for an operation to be energy-neutral at a realistic scale, in addition to their significant operational and capital expenses. Recent literature shows that the energy output for larger scale MFC are five times less in magnitude (100 mW/m^2) in comparison to the chemical fuel cells (104–105 W/m^2). Therefore, using MFC as a substitute for chemical fuel cells is not a realistic option. Furthermore, when using full-scale MFCs, the power density is lower compared to their mini-size due to scale-up variables such as inhomogeneous biofilm structures formed on electrodes, poor mixing, external mass transfer resistances, and other scaling-up factors. All these factors show that the MFCs' start-up and operation characteristics have a significant impact on productivity and efficiency, therefore taking these factors into account can assist create the ideal MFC. In conclusion, commercializing MFC is not impossible given improvements and optimization that can be made in the near future.

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Chapter 14
Microbial Fuel Cell and Wastewater Treatment

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Abstract Microbial fuel cell (MFC) systems oxidize organic and inorganic substrates using the bio-electrochemical catalytic activity of microbial biofilms. This chapter is about the current wastewater treatment methods and the energy required. MFCs work on the principle of chemical oxygen demand removal, which can be affected by various operating conditions. There are many different types of MFCs (e.g., single circuit, double circuit, mediator MFCs, mediator free MFCs), biocatalysts (e.g., Axenic bacterial culture, mixed bacterial fuel culture), feedstocks (e.g., simple sugars, chemical compounds, urban sewage, wastewaters from various industries like agricultural, brewery, food and dairy farms) that can be managed to recover and recycle different resources (e.g., organics, nutrients, and metals). This also summarize the literature on recent pilot studies, the benefits and drawbacks of current MFC technologies, the technical challenges MFC operations face, and the cost-effectiveness of using MFCs in wastewater treatment.

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14.1 Introduction to Microbial Fuel Cell

Scientists are constantly finding new ways to maintain life in the best possible manner and make this planet a better place. One such attempt is to generate electric current or energy from trash by exploiting minute microscopic entities that could ultimately lower the waste pressure globally. A microbial fuel cell is a type of structure in which bacteria utilize organic or inorganic waste and make energy from it. Any type of life, whether microscopic or macroscopic, uses metabolism to carry out its daily tasks. Cellular respiration is a critical component of metabolism during which electrons from food are sequestered and utilized to produce energy in the cell. The similar thing happens with microbial fuel cells. In layman's terms, microorganisms and their food (substrate) are housed in a glass container, and the microbes execute their daily regular activities while the electrons generated by cellular respiration are employed to generate electricity by connecting electrodes to the container.

Bacterial metabolism is divided into nutritional categories based on three criteria: first, the kind of energy utilized for growth, second, the carbon source, and third, the electron donors used for growth. Anaerobic bacteria oxidize organic substrates and create power in a complicated process in microbial fuel cells. Anaerobic bacteria have developed over time by reducing substances to sustain their metabolism. A bacterial cell obtains energy from organic substances and uses it to develop and sustain essential biological activities. Bacteria frequently select the metabolic route with the maximum energy gain.

According to Fuhrmann (2021), bacteria can select between a respiratory and a fermentative route based on the terminal electron acceptor (TEA). The respiratory route reduces the oxygen available as TEA and oxidize the organic substrate. The electrons during this process are being delivered to the TEA through the electron transport chain. Aerobic respiration is the most energy-efficient mechanism, whereas anaerobic respiration happens when there is no oxygen in the system (Radlinski and Bäumler 2022). On the other hand, photo microbial fuel cells are the fuel cells that use sunlight to create electricity (Gouveia et al. 2014) while photosynthetic algal microbial fuel cells use energy from algal photosynthetic machinery. Therefore, MFCs based on type of photon use as energy source classified into two types: photosynthetic fuel cells and photo microbial fuel cells (He et al. 2014).

14.2 Microbial Fuel Cell Working Principle

Bacterial respiration is a fundamental large-scale redox activity and microbial fuel cells take benefit from it. During respiration, movement of electrons initiates an electromotive force that could be exploited to achieve beneficial work. A membrane selective for cations is used to separates the anodic and cathodic chambers. Microbes present in anodic side oxidize the organic fuel which generates protons (cations) that flow across the membrane to the cathodic side. The electrons generated at anodic side flow through an external circuit and generates current. Electrons upon reaching to the cathode, react with oxygen and proton and produce water (Obileke et al. 2021). The optimum temperature for a microbial reaction range from 15 to 60 °C. The substrate for microbial fuel cells can be different types of alcohol, carbohydrates, organic substances, protein, volatile acids (Tariq et al. 2021) and recalcitrant compounds like cellulose (Shrivastava and Sharma 2022). Flagella, mediator, or cytochrome can be an intermediate in MFCs (Mathuriya and Yakhmi 2016).

When organic substrate is acetate at the anode side in an MFC, one molecule of acetate is oxidized to produce eight electrons and seven protons. Both electrons and protons move to the cathodic chamber, where one molecule of oxygen produces two molecules of water. At the anode, two molecules of carbon dioxide are generated. MFC are constructed in a way to avoid this carbon dioxide generation. Microorganisms are kept away from oxygen or any other TEA, such as nitrate, sulphate, and iron, which may easily infiltrate into the cell and make other products (Ganesh 2012).

14.3 History and Invention

Luigi Galvani (1791) was the first who inspected the bioelectric phenomena (Galvani 1791), while Michael Cresse Potter (1911) was the first who demonstrated the voltage generational and current deliver by microorganisms. However, the first microbial fuel cell was designed by Rohrback group and they used *Clostridium butyricum* to generate hydrogen by glucose fermentation (Rohrback et al. 1962). Still, it did not gain much popularity and remained futile and doubtful because most of the MFCs before 1999 required an intermediate chemical e.g., thionine, humic acid, toluylene red, methylene Blue, and methyl viologen for electron transmission from bacteria to electrodes. Since this method was complex, harmful and expensive it remained unsuccessful. However, in 1999, Kim and his group invented mediator-less MFCs by using Fe(III)-reducer *Shewanella putrefaciens* which was able to utilize anode naturally as TEA (Flimban et al. 2019).

14.4 Microbial Fuel Cell Operating Conditions

Traditional MFCs consist of a cathode, anode, proton exchange membrane (PEM) also known as salt bridge, and resistor to transfer electrons as shown in Fig. 14.1. Most instances, bacterial consortium immobilizes the anode while the microbial source remains stick to the cathode chamber (Gouveia et al. 2014). The organic material (He et al. 2014) or fuel source is loaded into the anode chamber to be oxidized. Protons travel across the proton exchange membrane (PEM) after oxidation and are reduced to water at the cathode (Angelaalincy et al. 2016).

An ideal MFC have separate anodic and cathodic chambers made up of glass, Plexiglass and polycarbonate. A proton exchange membrane (Ultrex or Nafion) separates the two segments (Prathiba et al. 2022). Electrode material should be a conductive material and mostly used electrodes in MFCs are made up of carbon and graphite as paper, fiber or cloth, rods, granules, plates and reticulated vitreous carbon (RVC). Both electrodes can be made up of same material or can be customized for example platinum cathode is used when oxygen is present as an electron acceptor (Wang et al. 2019).

Microorganisms digest organic substrates for growth and energy production and generate protons and electrons in the anodic chamber. Effective electron acceptor is required to increase the power density. It should be long-lasting without toxic effects or interference with other system components or microbial communities. Because of non-toxic nature of oxygen, it has been regarded as best oxidizing agent in MFC operation (Flimban et al. 2019).

To perform the needed redox reaction, a bio-film is utilized as a biocatalyst rather than a precious metal catalyst like platinum (Allen and Bennetto 1993). The bio-film requires a large surface and the structure that must support the weight of bio-film and water (Zhao et al. 2006).

14.4.1 Anodic Compartment

Materials that are conductive and chemically stable in the reactor solution are favored for anode production. Non-corrosive stainless steel is the preferred metal anode; however, it is not suitable for use as an electrode due to the poisonous effects of copper ions. Carbon is the most suitable material for electrode construction (Mier et al. 2021).

14.4.2 Microbial Culture

Bacteria in MFCs must have membrane-bound electron transport relays, such as c-type cytochromes, in order to transmit electrons directly. A variety of microorganisms

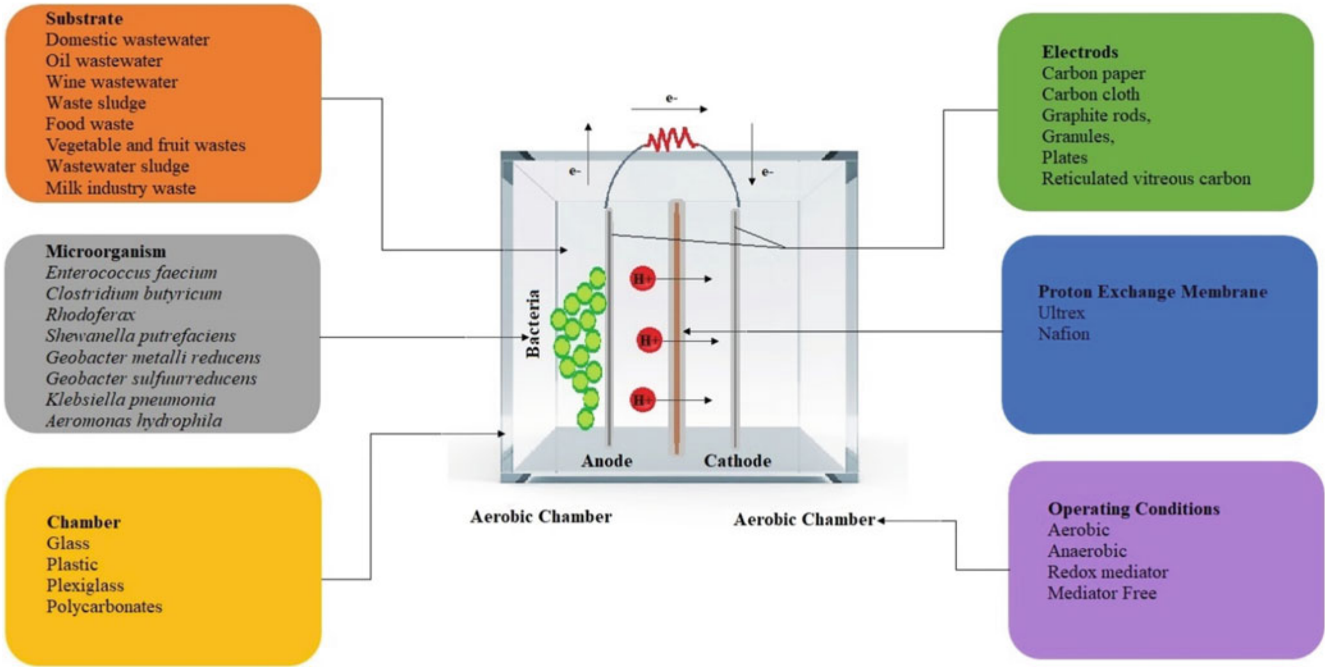

Fig. 14.1 Single circuit microbial fuel cell and available choices for each component

can generate electricity. Many new bacterial strains have been discovered for their adaptability to generate current in MFCs such as *Enterococcus faecium*, *Clostridium butyricum*, *Stenotrophomonas maltophilia* MK2, and others, as well as fungi such as *Saccharomyces cerevisiae*. Photosynthesis, combined with electricity generation, eliminates carbon dioxide from the atmosphere, which is a unique benefit of utilizing photosynthetic bacteria in microbial fuel cells (Kannan and Donnellan 2021). Mixed cultures of microbial populations, such as natural microbial communities, domestic wastewater (Raghav et al. 2022), brewery effluent, and sediments from lakes and oceans (Yang and Chen 2021) have also been utilized in microbial fuel cells.

14.4.3 Substrates

Substrate could be a chemical source or simple carbohydrate source like glucose, sucrose (Chen et al. 2001), alcohols, acetate (Catal et al. 2008), grape juice (Liu and Dong 2007); or some complex carbon sources like wastewaters from various sources (Velasquez-Orta et al. 2011). Organic wastes could be used for bacterial anaerobic digestion, such as domestic-wastewater (Choi and Ahn 2013), oil-wastewater (Choi and Liu 2014), waste-sludge (Choi and Liu 2014), food-waste, vegetable and fruit wastes (Choi and Ahn 2015; Logroño et al. 2015), volatile fatty-acids (Choi and Ahn 2015), milk industry waste (Pant et al. 2016). Because of the number of choices available, the microbial fuel cell is globally considered a suitable method for generating bioelectricity from various renewable biomass.

14.4.4 Redox Mediators

These are the chemical that are added in the growth media to improve the internal electron conduction from microbes to anode. Mediators need to have the proper redox potentials and usually chemicals with low redox potential are exploited as mediators (Sevda and Sreekrishnan 2012). Their potentials should fall between the anode and cathode's thermodynamic potentials. Most mediated biofuel cell systems that have been reported so far have open circuit volts (OCV) that ranged between 0.2 and 1 V. Recently, it was discovered that a mediated H_2/O_2 biofuel cell has an OCV of 1.17 V (Mazurenko et al. 2017), which is extremely near to the fuel cell's typical thermodynamic potential (1.22 V). *Desulfovibrio vulgaris* was utilized to catalyze the oxidation of hydrogen using methyl viologen, whereas bilirubin oxidase was employed to catalyze the reduction of oxygen using 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) (Shiraiwa et al. 2018). Ferricyanide is the most often utilized soluble mediator for cathodic responses in microbial fuel cells. Compared with oxygen, it has faster reduction kinetics, a higher redox potential on the cathode and higher solubility (Uddin et al. 2021).

14.4.5 Cathodic Compartment

Both traditional carbon-based and novel electrodes (graphite fiber and paper) are used in forming cathode (Mashkour and Rahimnejad 2015). An electron acceptor, such as ferricyanide or oxygen in cathode chamber used for the reduction of the electron and produces water molecules (Hamelers et al. 2010).

14.4.6 Exchange Membrane

Ultrax and Teflon are primarily utilized as proton exchange membranes because they have the lowest resistance. According to researchers, they could eliminate the membrane by using pressed carbon-paper as a separator (Kumar et al. 2019a, b).

14.5 Different Types of MFCs

14.5.1 Single Circuit MFCs

Single circuit microbial fuel cells have no cathode and anode membrane, allowing for a more straightforward design and lower manufacturing costs as shown in Fig. 14.2b.

It consists of single compartment with an air cathode that is exposed to the atmosphere and made a single circuit of microbial fuel cell. Protons diffuse through the electrolyte from anode to porous air cathode in single circuit microbial fuel cells. The first single circuit was consisted of cylindrical plastic vessel with an anode inside and a cathode outside (Okamoto et al. 2011). Another model was created in which a

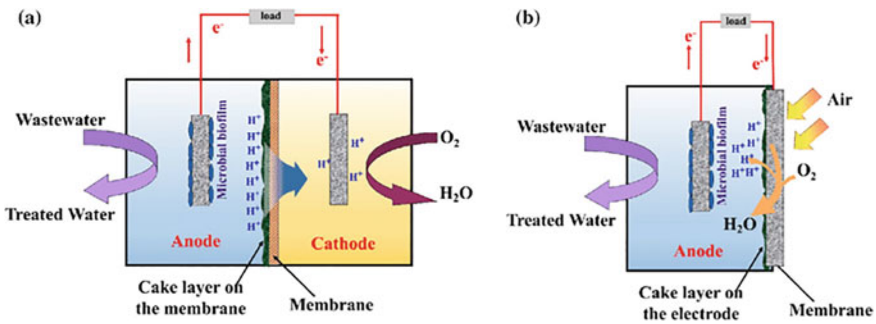

Fig. 14.2 Diagrammatic representation of **a** Double versus **b** single circuit MFCs. Diagram adapted from Chang et al. (2020)

cylindrical reactor was wrapped in an air cathode composed of platinum-coated (Pt/C) and carbon cloth (Gorby et al. 2006).

This configuration is more adaptive and attractive to the researchers due to the limited necessity for regular oxidative medium, aeration changes, lower internal resistance, enhanced proton diffusion and decreased electrode spacing. Single chamber cube microbial fuel cell also produces more power than bottle type microbial fuel cell (Logan et al. 2007). Single circuit microbial fuel cells lack a proton exchange membrane, which lowers their proton transfer resistance. It also has a higher oxygen diffusion rate from cathode to the anode than double circuit microbial fuel cell, resulting in more aerobic substrate degradation. Rather than producing energy, bacterial growth on the anode consumes a significant amount of the substrate (Gorby et al. 2006). However, liquid leakage, rapid oxygen diffusion, and evaporation are significant disadvantages of such fuel cells (Flimban et al. 2019).

14.5.2 Double Circuit MFCs

It has a proton exchange membrane for proton transmission from anode to the cathode while preventing oxygen diffusion into anode as shown in Fig. 14.2a. This membrane completes the circuit. Such designs are more commonly utilized for wastewater treatment and power generation simultaneously. Higher energy output is provided by a batch system with chemically specified medium such as acetate or glucose solution (Asensio et al. 2017).

However, the distance between electrodes in such fuel cell reduces the microbial fuel cell performance by increasing the internal resistance (Sun et al. 2009). For the double circuit microbial fuel cell cathode, a variety of immersed cathodes with higher redox potentials, like permanganate, persulfate, hydrogen peroxide, and triiodide have been suggested. Such electron acceptors, on the other hand, are usually not regenerative and must be replaced once they have been depleted (Jafary et al. 2015).

14.5.3 Mediator MFCs

Mediators are also called electroactive metabolites. Some microorganisms lack electrochemically active surface proteins for transmission of electrons. Such microorganisms when sued in MFCs require agents that help them to improve the availability of transferred electrons in higher concentration. Mediators can be synthetic, such as neutral red (Kumar et al. 2019a, b); or natural mediators, such as sulfate/sulfide (Dai et al. 2020), depending upon the involved species of microorganism.

The fuel cells are intended to infiltrate the microbial cell's naturally occurring electron transport chain (ETC) and receive electrons generated by inorganic mediators under anaerobic circumstances. Mediators pass the plasma wall and the lipid membrane of the outer cell; electrons from the ETC are released and carried by other intermediates. The reduced mediators then exit and oxidized as they deposit the carrying electrons to anode making it negatively charged. On the other hand, when oxygen is present, all of the electrons will be received by oxygen due to electronegativity difference with mediator. Mostly used mediators in MFCs include methylene blue, resorufin, natural red, and thionine (Flimban et al. 2019).

These electrons move through an external circuit and subsequently to oxidizing agent to complete the process. It is important to note that those electrons are first utilized as electrical current to power the electronic devices prior reaching the cathode, where they are converted to oxygen, which is necessary for the bacterial optimum growth (Ieropoulos et al. 2005).

However, mediators are usually costly and toxic thus, mediator-free MFCs should be developed to enhance power output and lower capital costs for the treatment of wastewater. Exogenous mediators also have a number of disadvantages, including an inflated cost, limited lifetime, and toxicity for natural ecosystems. Moreover, this system can work at high sustained activity level when bacteria produce mediator or transfer the electrons directly to electrode (Flimban et al. 2018).

14.5.4 Mediator Free MFCs

Direct transfer of electron is another name for mediator free electron transfer in microbial fuel cell (MFC). It has been observed in microorganisms called “electricigen” or “electrogen” or “anode-respiring bacteria” or “electrochemically active bacteria” or “anodophiles” that they can transport final electrons from oxidized organic-matter directly to electrode of microbial fuel cell. The main point in microbial fuel cell technology is electron transport to electrode. Final electrons are then transferred to a solid extracellular substrate. This transport can occur when the solid substrate and the cell surface are in contact directly (Roy et al. 2017).

However, some microbes can be used to generate electricity without the use of mediators. Microbial fuel cells without mediators have an advantage over microbial fuel cells with mediators, as it has low-cost and non-toxicity. They are based on metal reducing bacteria such as *Rhodoferax* (Konovalova et al. 2018); *Shewanella* (Baniasadi and Vahabzadeh 2021) include *Shewanella putrefaciens* (Rewatkar and Goel 2022); *Geobacteraceae* (Kim et al. 2021) include *Geobacter metalli reducens* (Liu et al. 2021), *Geobacter sulfuurreducens* (Kondaveeti et al. 2020); *Klebsiella pneumonia* (Zhang et al. 2008); and *Aeromonas hydrophila* (Pham et al. 2003), to function without the exogenous electron carriers. However, when a mediator free microbial fuel cell is used, some factors must be taken into consideration, for example the presence of redox enzymes, external circuit resistance, reduction of oxygen, oxidation of fuel, and proton transfer through membrane. These factors limit the electricity generation (Flimban et al. 2018).

When permeability of proton membrane is inadequate proton transfer to cathode chamber could be a major limitation. As a result of these limitations, activity of microbes and transportation of electron could be reduced because of pH change and delayed cathodic reactions due to the limited supply of proton. Redox enzymes present in the outermost membrane allow *Geobacteraceae* spp. to transfer electrons straight to anode. However, these mediator free microbial fuel cells convert methanol and monosaccharides from leftover food to hydrogen for bacteria (Pandit et al. 2021).

14.6 Bio-electrochemical Catalytic Activity of Biofilms

MFCs are used to collect energy from various environmental processes by employing biofilms made up of microorganisms that are effective at transporting electrons to and from solid electron acceptors (Sharma and Kundu 2010). Any syntrophic consortia of microorganisms in which cells attach to one other and, in many cases, to a surface is referred to as a biofilm. Electrochemically active biofilms (EABs) are biofilms that form on the electrodes of MFCs. Electricigens, electrochemically active microorganisms, exoelectrogenic bacteria, and anode-respiring or anodophilic species are all terms used in the MFC literature to describe EABs (Marsili et al. 2010).

When electrons move via outer membrane proteins (Gorby et al. 2006), they make physical contact with the anode or other bacteria nearby, resulting in direct extracellular electron transport. In general, Gram-positive bacteria produce less current on their own than Gram-negative bacteria (Marshall and May 2009). In most circumstances, the bacteria in the microbial fuel cell grow onto the electrode and create a biofilm.

14.7 Current Wastewater Treatments in Use

Wastewater is currently being explored as a source of water, energy, and nutrients for plant fertilization (Tauseef et al. 2013). Physical, chemical, and biological approaches are all available for treating wastewater. Current wastewater treatment systems have a number of drawbacks as a result of their inability to meet these conversion goals. Traditional aerobic sludge treatment systems, for example, are known for being energy demanding, producing huge amounts of residuals, and being unable to extract the potential resources present in wastewater. Table 14.1 compares and contrasts the benefits and drawbacks of each wastewater treatment process and type of wastewater for which the process used. Based on this analysis, it can be stated that the approaches available now are beneficial in certain circumstances but harmful in others. Some of the processes, such as reverse osmosis, nano-filtration, and ultra-filtration, are quite costly, while other are source of producing methane that is a strong greenhouse gas with a global warming potential 25 times that of CO_2, and its release into the atmosphere must be rigorously managed (Chen et al. 2016).

Table 14.1 Current Wastewater treatments and their advantages and disadvantages

Processes	Advantages	Disadvantages	Wastewater type
Activated carbon adsorption	Suspended solids and organic compounds are significantly decreased	Cost of activated carbon	Water, municipal wastewater, and organic industrial wastewaters
Biodegradation	Elimination rates by oxidizable compounds are approximately 90%	Dye biodegradability is low	Sewage wastewater
Coagulation-flocculation	Insoluble dyes are removed	Sludge-blocking filter producing	Surface water
Electrochemical processes	Adaptive capabilities for different volumes and pollution loads	Iron hydroxide sludge	Sewage
Nano-filtration	Separation of low-molecular-weight organic molecules and divalent ions from monovalent salts. High-concentration treatment	Cost	Tertiary wastewater
Ozone treatment	Good de-colorization	No reduction of the Chemical oxygen demand	Industrial effluent wastewater
Reverse phase osmosis	Exclusion of mineral salts, hydrolyzes reactive dyes and chemical auxiliaries	High pressure	Wastewater from manufacturing industries
Ultrafiltration–microfiltration	Low pressure	The treated wastewater is of inadequate quality	Biologically contaminated wastewater

Sources Monika (2012), Dos Santos et al. (2007), Forgacs et al. (2004)

14.8 Wastewater Treatment Using Microbial Fuel Cells

Wastewater may be converted into potable water for humans. Wastewater contain human waste, spoiled food, oils and fats, soaps and detergents, chemicals used in toilets, and used water from washing machines, and dishwashers etc. Industries also contribute to the volume of wastewater that must be disposed off. However, wastewater also have biodegradable organic elements of diverse types that can be utilized as source of energy. Economic sustainability, operational feasibility and ease of maintenance are considerable factors for making a wastewater treatment successful. MFC is an efficient method of wastewater treatment due to pollution reduction, cost effectiveness, electricity production, sustainability and less production of solid sludge (Li et al. 2014). The optimal supply of oxygen to the cathode compartment and supply of wastewater to the anode compartment is required for MFC operation to be productive.

The MFC system's internal resistance, as well as the surface area of the electrodes, shape its efficacy (Logan 2010).

Domestic wastewater has been identified with several hazardous chemicals that pose a health concern (Mara 2013). Recent studies have estimated that globally 359.4 $\times 10^9$ m^3 yr^{-1} wastewater is being produced (Jones et al. 2021), if properly treated, this hazardous wastewater may be reused, nutrients may be recovered, and bioenergy can be generated. Furthermore, the amount of activated sludge produced by typical aerobic treatment is enormous (Scherson and Criddle 2014). Sludge operating expenses at sewage treatment facilities typically account for more than half of overall management investments (Xiao et al. 2011). By lowering sludge treatment expenses, overall wastewater treatment costs can be decreased.

The majority of water pollution in the world is caused by effluent discharges from water-intensive industrial sectors. For example, one kilogram of finished leather generates 30–35 l of effluent in the tanning business. This tannery effluent is rich in chromium, salt, calcium, ammonium, and magnesium, as well as organics such as lipids, colors, and acids (Saranya and Shanthakumar 2020). The traditional technique of industrial wastewater treatment consumes more energy, but a contemporary wastewater treatment system may provide high-quality treated water while also producing electricity. The cattle business produces a large volume of animal excrement effluent, which is recognized as the primary component of crop agricultural wastes (Zornoza et al. 2016). Table 14.2 depicts many MFC-based wastewater treatment applications.

14.9 Benefits and Drawbacks of Current MFC Technologies

14.9.1 Benefits/Applications

MFCs have emerged as a viable option for energy generation, wastewater treatment, and biomass cultivation. Microbial fuel cell (MFC) technology is a potential method for removing pollutants while recovering energy (He 2017). These devices have lately received some attention in the literature for a variety of reasons. Researchers have identified their potential application as alternative energy sources in particular. MFCs deserve all of the attention they get, even if some of the expectations for their potential to supply enormous volumes of energy and high power at the same time appear excessively optimistic. MFCs have been shown to be an effective source of energy for continually powering electronic equipment that demand minimal (Donovan et al. 2008, 2011). The concept of collecting energy from wastewater treatment operations, which are currently inefficient processes in which energy-rich streams are recovered without generating useful energy, has sparked a lot of interest in MFCs.

Table 14.2 Use of MFCs in variety of wastewater treatment processes

Type of MFC	Type of wastewater	Performance (COD removal in %)	Power output	References
MFC with air cathode	Domestic wastewater	71%	173 mW/m^2	You et al. (2006)
Single-chambered with air–cathode MFC	Municipal wastewater	40–50%	464 mW/m	Cheng et al. (2006)
Double-chambered MFC	Urban wastewater	30%	25 mW/m^2	Rodrigo et al. (2007)
MFC reactors of four combination and an anaerobic fluidized bed membrane bioreactor	Domestic wastewater	92.5%	0.0186 kWh/m^3	Puig et al. (2011)
MFC with air cathode	Domestic wastewater	80.0%	1.14 W/m^3	Puig et al. (2011)
Single-chambered with air–cathode MFC	Domestic wastewater	60.0%	404 mW/m	Sciarria et al (2013)
Single-chambered with air–cathode MFC	Domestic wastewater	44%	420 mW/m^2	Choi and Ahn (2013)
Separator electrode assembly MFC and spaced electrodes assembly MFC	Domestic wastewater	62–94%	328 mW/m^2	Ren et al. (2014)
Stackable horizontal MFC (SHMFC)	Domestic wastewater	79%	116 mW/m^2	Feng et al. (2014)
Dual-compartment microbial fuel cell	Municipal wastewater	85.0%	598.9 mV	Ye et al. (2019)
Up-flow MFC with activated carbon air–cathode made of PVDF	Domestic wastewater	5.11 ± 0.94 kg/t	3.96 ± 3.01 W/m^2	Okabe (2020)
Microbial fuel cell with algal biofilm assistance	Domestic wastewater	80.2%	62.93 mW/m^2	Yang et al. (2018)
Flat-panel air–cathode MFC	Domestic wastewater	85%	6.3 W/m^2	Park et al. (2017)
Up-flow anaerobic sludge blanket reactor-MFC	Beet-sugar wastewater	53.2%	1410.2 mW/m^2	Cheng et al. (2016)

(continued)

Table 14.2 (continued)

Type of MFC	Type of wastewater	Performance (COD removal in %)	Power output	References
Anaerobic baffled stacking microbial fuel cell	Beet-sugar wastewater	50.0–70.0%	115.5 ± 2.7 mW/m^2	Zhao et al. (2013)
A fuel cell-type electrochemical cell	Starch processing wastewater	50 mg/L	0.2 mA	Liu et al. (2014)
Air–cathode MFC	Starch processing wastewater	98%	239.4 mW/m^2	Zhang et al. (2011)
Single-chamber membrane-free MFC	Starch processing wastewater	87%	209.4 mW/m^2	Wilson and Richards (2000)
Floating-type FT-MFC	Starch processing wastewater	380 ppm	8 mW/m^2	Carty et al. (2008)
Single chambered microbial fuel cell	Starch processing wastewater	90.2%	30 mW/m^2	Ge and He (2012)
Single-chamber non-catalyzed MFC	Dairy industry wastewater	78.07%	–	Wang et al. (2011)
Two-chamber MFC	Dairy industry wastewater	90.2%	–	Wang et al. (2013)
Up-flow MFCs	Dairy wastewater	94%	3.5 W/m^3	Marassi et al. (2019)
Single-chamber	Dairy wastewater	96%	1.1 W/m^3	Mohan et al. (2010)
Dual-chamber	Dairy wastewater	92%	644 mV	Sanjay and Udayashankara, (2021)
Single-chamber	Vegetable wastes	70%	70 mW/m^3	Clauwaert et al. (2008)
Single-chamber	Slaughterhouse	72%	32 mW/m^3	Niessen et al. (2004)
Up-flow tubular	Animal carcass wastewater	51%	2.19 mW/m^3	Li et al. (2013)
Serpentine-type	Brewery wastewater	80%	4.1 W/m^3	Zhuang et al. (2012)
Tubular MFCs	Winery wastewater	85%	890 W/m^3	Ge and He (2016)
Dual-chambered	Chicken feathers	10%	1206.8 mW/m^2	Zhuang et al. (2012)

(continued)

Table 14.2 (continued)

Type of MFC	Type of wastewater	Performance (COD removal in %)	Power output	References
Dual-chambered	Slaughterhouse wastewater	68%	700 mW/m^2	Prabowo et al. (2016)
Dual-chambered	Cow waste	84%	0.34 mW/m^2	Yokoyama et al. (2006)
Dual-chambered	Human feces	71%	22 mW/m^2	Fangzhou et al. (2011)
Single chamber	Swine wastewater	84%	228 mW/m^2	Kim et al. (2008)

14.9.1.1 Bioelectricity Generation

Although microbial fuel cells have existed since the late 1800s (Piccolino 1998) but only recently MFCs have been designed to obtain electricity, opening up new possibilities for practical use (Liu and Logan 2004). The direct transfer of fuel molecules into electricity without generating heat is another benefit of microbial fuel cells. The technology of microbial fuel cells has the potential to be a long-term energy source. Microbial fuel cell technology may be used to create bio-batteries. Microbial fuel cells' fundamental and core architecture may be adjusted in a variety of ways to serve as a platform for generating new concepts and applications (Du et al. 2007).

Microbial fuel cells are more efficient at converting energy than traditional internal combustion engines and can achieve energy efficiency levels well beyond 50%. The primary goal of microbial fuel cells is to achieve an appropriate power and current for use in small electronic devices (Rahimnejad et al. 2012). Microbial fuel cells can also operate on a smaller scale e.g., in some situations, only 7um thick by 2 cm long electrodes are required, allowing a microbial fuel cell to replace a battery (Chen et al. 2001). It is a renewable source of energy that does not require recharging and perform well at temperatures ranging from 20 to 40 °C and a pH of 7. Aquatic plants, such as algae, can be used in power stations and can share its electrical lines with an existing power grid (Bullen et al. 2006). Microbial fuel cells produce little power, but a larger voltage may be obtained by connecting many microbial fuel cells in series or parallel (Wilkinson 2000).

14.9.1.2 Wastewater Treatment

It is the most practical application of MFCs. Traditional wastewater treatment facilities are made up of several treatment units that are arranged in various ways, but the most critical factor in any setup is achieving maximum efficiency. Several wastewater treatment techniques have been developed; however, most of these techniques

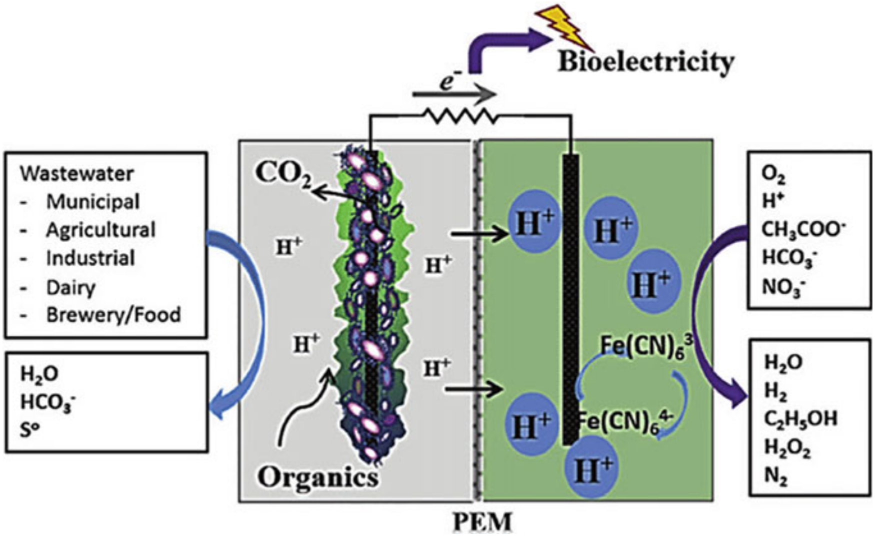

Fig. 14.3 Wastewater treatment using MFCs. Diagram adapted from (Bhadra et al. 2018)

are limited by the lack of time or a high cost. In addition, most treatment approaches require a high level of operational systems (Du et al. 2007).

A human right to safe drinking water is undeniable. Each year, a significant amount of industrial and agricultural wastewater is generated. To prevent water contamination and odor control, animal feces must be processed before being disposed of in the environment. It should also be noted that high phosphate and nitrate levels cause water pollution (Fig. 14.3).

Municipal, industrial, and other wastewater effluents act as major source for harvesting energy. It is an effective bioremediation substrate. Microbial fuel cell technology is proving to be an outstanding wastewater management solution and potential alternative to traditional treatments. Traditional wastewater treatments for the removal of organic pollutants are expensive and energy consuming due to the necessity for aeration and the disposal of residual sludge created during the process (Du et al. 2007). They are constructed with low-cost components including graphite anodes and activated carbon cathodes (Zhang et al. 2009; Dong et al. 2012). Microbial fuel cells are used in wastewater treatment to generate electricity from anaerobic digestion. Pathogens can also be reduced with this method. However, microbial fuel cells require temperature rise (more than 30 °C), and supplementary steps for biogas transformation to electricity (He et al. 2013).

14.9.1.3 Biological Hydrogen Production

Microbial fuel cells may simply be modified to gather biohydrogen instead of generating energy. Hydrogen may be stored and used later. These cells could be used as renewable hydrogen carrier to fulfil total hydrogen demand in a hydrogen economy (Medisetty et al. 2020). The bio-catalyzed electrolysis method can be used to modify microbial fuel cells to generate hydrogen gas where oxygen is eliminated at cathode and moderate voltage is added (Prathiba et al. 2022). Anode operating potential of bacteria is – 0.3 V with only a 0.11 V increase in total cell potential, the electrons and protons generated at anode can interact at the cathode to produce hydrogen gas. Practically, however, due to over potential at cathode, 0.25 V or more should be supplied into the circuit to create hydrogen gas (Mohan et al. 2008).

14.9.1.4 Biosensors

Microbial fuel cells can be used in biological oxygen demand measurement sensors because of incorporation of bacteria as biological sensing components to provide a signal proportional to the analyte concentration (Parkhey and Mohan 2019). Efficiency of biosensing system is directly related to biological oxygen demand in fluid current. *Shewanella* spp. has been found to be useful for measuring biological oxygen demand in wastewater as bio-based catalytic systems. It also helps in the measurement of other materials (Yi et al. 2020).

In diabetic patients, chemical sensors are required to monitor oxygen and blood glucose levels. Blood pressure, pulse, and other basic signs have also been measured using the sensors (Hart et al. 2003). *Shewanella putrefaciens* has also been reported to use microbial fuel cells to measure the lactate. This biosensor could detect lactate concentrations of up to 50 mM (Kim et al. 1999). Another application is biosensing for process monitoring and pollution measurement (Jadhav et al. 2021).

Data from the natural environment could help in the study and modelling of ecosystem response, but sensors dispersed across the environment require energy to operate. Complex sensor networks in remote areas require low-cost power sources to operate, and maintenance operations must be kept to a minimum (Roy et al. 2017). MFC Biosensors could be utilized to recharge such devices, especially in deep-water and river situations where accessing the system to change batteries is challenging. Environmental systems like as rivers, streams, and oceans are being monitored using sediment microbial fuel cells. Microbial fuel cells can be used as chargers of electrochemical sensors and small telemetry systems where conventional batteries have a finite lifetime and must therefore be recharged or changed. While MFC batteries are sustainable for up to 5 years.

14.9.1.5 Bioremediation

Sustainable soil bioremediation and water management aims to recover and reuse nutrients as well as degrade organic pollutants. MFCs are being utilized as self-powered bio-electrochemical devices in natural environments for the bioremediation of inorganic-contaminated water (Wang and Ren 2014). Here, MFCs are not utilized for electricity generation; instead, they are utilized to generate desired reactions for degradation or chemical removal (Agrawal et al. 2019). As bacteria receive electrons from cathode and donate them to an electrode, during biodegradation, uranium could be deposited directly onto the cathode. When electrodes are utilized as electron donors, nitrate could also be turned to nitrite (Joicy et al. 2019).

14.9.1.6 Biorecovery

The recovery of essential metals by MFC has made significant progress in recent years. These methods simultaneously remove organic contaminants, recover vital metals, and produce energy. Critical metal biorecovery rates, however, are unstable and can vary widely. The primary determinants of MFC performance are the initial metal concentration, temperature, and pH value, which are crucial to the metabolic process of the microorganisms in MFC. Therefore, investigating the ideal settings for real-world MFC applications on key metals recovery from wastewater can increase biorecovery rates and offer fresh perspectives on how industrial wastewater is actually treated (Yu et al. 2020).

14.9.1.7 Microorganisms Employed in Microbial Fuel Cells

In the current situation, microbial fuel cells have caught the interest of numerous researchers all over the world. Various types of studies are being conducted to determine the efficacy of these cells. Microbial fuel cells have been reported to use bacteria such as *L. discophora*, *C. vulgaris*, *T. ferrooxidance*, *K. pneumonia*, *R. rubrum*, *P. fluroscens*, *G. metallireducens*, *D. desulfuricans*, and other anaerobic and aerobic bacteria. Other microorganisms, such as some microalgae and cyanobacteria, are thought to play important roles in microbial fuel cells. The field's expected future will be to improve the functioning of microbial fuel cells to produce exponential yields. Microbial fuel cells contribute to biohydrogen generation via biohydrolysis (Rozendal et al. 2007), biosensors (Chang et al. 2007), bioremediation (Lovley 2006), and in-situ power source for remote locations in addition to wastewater treatment, biomass, and bioelectricity production (Logan and Regan 2006).

14.9.2 Drawbacks

The electrons transfer to electrode by the microorganisms, rate of fuel oxidation, circuit resistance, transfer of proton to cathode via the membrane, reduction at cathode and oxygen supply are all factors that affects the performance of the MCF. Short life spans, low output rates, high costs, membrane fouling, restricted efficiency, instability, and the inconvenient nature of maintaining microbe-based systems are the prominent disadvantages of MFCs (Flimban et al. 2019). The sustainability of cathode catalysts and, in most cases, membrane deterioration has always been a source of concern for microbial fuel cells life span (Breheny et al. 2019).

The excessive cost of materials is a limiting issue for microbial fuel cells utilization in general. The first biggest drawback of microbial fuel cell technology is insufficient power production. Second, the expensive cost of electrode materials, cathode catalyst, and membranes is a barrier to the technology's advancement (Pham et al. 2006). The microbial fuel cells power might be insufficient to operate a transmitter or sensor constantly. However, the problem can be resolved by electrodes' surface area extension. Another solution is utilization of ultra-capacitors as a proper power management system (Rahimnejad et al. 2014).

14.10 The Technical Challenges Faced by MFC Operations

MFCs have showed a significant increase in overall power output during the last few years, yet they cannot be termed as the energy supplying sources. To solve the challenges that still exist, identification and optimization of alternative membranes and enough sturdy materials for conventional technologies are necessary (Angelaalincy et al. 2016).

When it comes to field applications, microbial fuel cells have both benefits and limitations. High operating expenses and limited power production are two operational challenges that must be addressed before the microbial fuel cell technology can be commercialized (He et al. 2017). MFCs capital cost is much higher (at least thirty times) than the conventional sludge treatment system for household wastewater. Significant attempts have been made over the last twenty years to improve the performance of microbial fuel cells by developing and modifying electrode materials. However, several challenges with present microbial fuel cell technology must be addressed before industrial applications may be successful. First, the costs of electrode materials remain a major challenge to their widespread adoption. Despite the fact that carbon paper and carbon cloth may provide reasonably higher output power, its prices are still expensive. Second, long-term electrode material sustainability is a major concern in wastewater treatment procedures and majority of research have concentrated on output power rather than electrode material stability which leads to failure in industrial applications (Do et al. 2018).

The high initial cost of traditional carbon-based composites is another major problem in MFCs implementation. Some researcher have manufactured the low-cost, high-current-output, carbon-rich anode material from scrap tyres to offer a sustainable source of anode material for MFCs as well as to minimize secondary pollution from waste tyres (Chen et al. 2018). Multiple electrodes within individual chamber may be an innovative concept for reducing concentration fields and inhomogeneity of flows in large-scale microbial fuel cell operation (Lee et al. 2015).

To sustain biofilm, a large surface area is necessary but weight of bio-film and water is a major concern in constructing such surfaces. The most often used electrode materials are carbon cloth, graphite rods, carbon paper, and plates. Carbon paper and graphite rods are examples of materials that are difficult to scale up owing to inherent durability, cost, or structural strength restrictions. Future researches should concentrate on conductive coating for material structural support. Carbon fibers connected to noncorrosive elements like titanium and nickel could also be used as cathode materials (Hasvold et al. 1997). The use of nanoengineering technologies to facilitate the electron transfer more easily could be effective in improving the performance of microbial fuel cell technology by modifying the anode electrode (Scott et al. 2007).

Another issue is cost of membranes, and they comprise the majority of the expense of creating a microbial fuel cell. Biofouling of membranes, decreases the MFC performance due to the disruption of proton migration completion (Choi et al. 2011; Xu et al. 2012). The solution to this problem is membrane-less microbial fuel cell that could have potential to minimize the cost of wastewater treatment. However, membrane-less microbial fuel cells are currently being studied extensively (Zhang et al. 2016).

Microbial fuel cells are still being investigated and experimented in laboratories; however some innovative designs have now been developed to combine microbial fuel cells into some other treatment processes of wastewater (Liu et al. 2017). But still they are far away from commercial usage, despite significant efforts by researchers to increase their performance by inventing novel structural designs, catalysts, electrode materials, and microorganisms. Long-term stability, as well as finding a solution for power production and cost, is a major problem for researchers (Rahimnejad et al. 2015).

Despite major scientific achievements, bio-energy production faces a variety of technical challenges that must be addressed before it could compete with the fossil fuels (Hallenbeck et al. 2016). Pretreatment procedures are also required (Zheng et al. 2014). Apart from technological challenges, there are problems such as a high cost of production and a lack of current infrastructure for production process, when compared to first generation biofuels (Rai et al. 2016). To obtain high yield and quality of bioenergy, these drawbacks need the development of optimization and production solutions (Patumsawad 2011).

Recently, MFC has made significant progress toward scale up and practical implementation. However, there are numerous challenges to be addressed. First and important, a successful pilot scale research demonstrating microbial fuel cell technology's feasibility for practical implementation is essential. A stronger focus on scaling up the flat-plate designs in near future will almost definitely lead to substantial advancements in transferring this MFC technology from laboratory to pilot-scale and beyond. To make microbial fuel cell technology comparable with alternative waste to energy technologies, materials being used in microbial fuel cells, particularly separators and electrodes must have long life span and be inexpensive (Janicek et al. 2014). As a result, the engineering features of microbial fuel cells should be considered as well. Microbial fuel cells (MFCs) have evolved as a long-term energy source (Moon et al. 2005). There is reason to believe that this technology will be implemented successfully in future (Kumar et al. 2019a, b).

14.11 Economic Feasibility of MFCs

The most major impediment to MFC adoption may be a lack of economic sustainability (Hoang et al. 2022). For wastewater with various compositions, different MFCs will produce varying quantities of power, at varying processing costs, and with varying material replacement cycles. For instance, pure acetic acid (Tariq et al. 2021) and glucose (Asensio et al. 2017) treated by MFCs would generate energy more efficiently in the initial phases of processing than will water treated by MFCs containing complicated combinations of contaminants. The costs and advantages of MFCs are significantly influenced by water quality. The advantages are also impacted by MFC size. Future research will need to provide information in order to address all of the issues raised above.

14.11.1 Operational Cost of MFCs

When compared to many alternative treatment methods, the operation of MFCs might save energy as this treatment doesn't need electricity (Fan et al. 2012). MFC may potentially create a net normalized energy recovery of roughly 0.004 kWh kg^{-1} of chemical oxygen demand (Zhang et al. 2013), equating to an additional economic income of about \$0.0005 kg^{-1} of chemical oxygen demand at a \$0.12 kW h^{-1} average electricity price. While the cost for sludge-based wastewater treatment plants is around \$0.12 kg^{-1} of chemical oxygen demand, assuming an energy consumption of 0.6 kWh kg^{-1} of chemical oxygen demand (McCarty et al. 2011) and that energy consumption accounts for 60% of the operation cost. By products and expensive metals recovery from wastewater may strengthen the economic case for MFCs (Van Eerten-Jansen et al. 2013) but the profitability of such procedures is debatable due to the often poor yield and the high cost of downstream processing for product.

14.11.2 Capital Cost of MFC's

There is no doubt that MFC's components are not very cost effective. Cost of electrodes based on type of material used, type of current collecting device, catalyst used for completing, enhancing the reaction and material used for separating membranes all together makes the capital cost of MFC's high and researcher still devising cost effective alternates for the successful MFC's employment (Li et al. 2011; Koroglu et al. 2019).

Ultrex membranes are most favored separators used larger-scale MFCs and cost of this membrane is approximately 110 USD/m^2, whereas Nafion® 117 costs more than 1500 USD/m^2 (Ramirez-Nava et al. 2021). Several studies have shown that even with relatively affordable electrodes and separator, the capital expenses of an air based cathode MFC for household or municipal wastewater treatment are roughly 3 USD/kg-COD (or around 1.5 USD/m^3 of household wastewater). However recently, biocompatible graphene quantum dots have been discovered as electrodes. Microorganisms have the ability to stick to and grow on graphene quantum dots, where they can act as an excellent source of electrons and provide a strong current via an MFC (Zheng et al. 2015). This could increase the output efficiency of an MFC. Large directional channel conductors made of plant fibers coated with poly (3,4-ethylenedioxythiophene) may be less expensive than traditional metal electrodes.

The minimum estimated cost for an MFC setup comprises a cathode of 1500 USD/m^2, anode of 100 USD/m^2, a separator of 1 USD/m^2, a reactor of 5000 USD/m^3, a ten-year lifetime and treatment capacity of 25 kg-COD m^3/d^1, but still this capital cost is thirty times higher than that of a standard sludge system (Okabe 2020). As a result, before MFC technology can be commercialized, its capital cost must be significantly decreased.

14.12 Conclusion

MFCs are considered to be a promising means of disposing of organic waste and transforming it into electrical energy. However, the energy production of MFCs is still insufficient to meet the population's needs. The environmental benefit is not obvious, process effectiveness deteriorates with time, and MFC ingredients are sometimes prohibitively costly. While current research is anticipated to improve such features relatively high capital cost still may persist which makes this technology less competitive. Other than updating MFC technology, other acceptable ways for meeting the sustainability standards should be studied. Integrating MFCs with other processes, in our opinion, is a more practical solution. Additionally, to increase the effectiveness with which MFCs are used to produce power and filter wastewater, cost–benefit analysis models for the lifecycle costs and advantages of MFCs should be developed.'

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Chapter 15
Advancement in Biodiesel Production Methodologies Using Different Feedstock

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Abstract The overuse of fossil fuels due to industrialization is directly linked to the increase in greenhouse gases and global warming. These issues are affecting the stability/life of living organisms globally at alarming rates. This urges the demand for an alternative energy source that can replace natural fossil fuels. In a way, various biofuels have been explored like biomethane, biohydrogen, Biodiesels, bioethanol, etc. Out of these, biodiesel has gained the attention of scientists and researchers, who are continuously working to enhance its efficiency in terms of energy production and cost. Biomass containing high lipid content, its cultivation, harvesting, and lipid extraction are the primary and most important factors for biodiesel generation. In this chapter, we'll study the advancement in three generations of biodiesel production utilizing (a) Seeds, grain, or sugars, (b) lignocellulosic biomass, and (c) algae and seaweeds as substrate (biomass). We'll also discuss the different factors required for biodiesel production from different lipid-containing biomass.

Keywords Biofuel · Biodiesel · Lipid · Lipid harvesting · Lignocellulosic biomass · Algae and seaweed

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15.1 Introduction

The increased industrialization and urbanization have enhanced the demand for energy leading to the overuse of fossil fuels. This over-exploitation has resulted in a decrease in the natural reserves that are predicted to be over by this decayed. Another problem associated with using these fossil fuels is the green house gas emission forwarding the world towards global warming and pollution. It has been reported that in 2017 an increase in carbon dioxide emission by 1.6% has been seen from fossil fuel combustion (Jackson et al. 2018). These problems are affecting the homeostasis of living beings world wide at an alarming rate. Seeing these circumstances there is an urge to find alternatives to fossil fuels. One such alternative is biofuels. Biofuels are developed by either transesterification or fermentation of the biological feedstocks. These feedstocks are rich in lipid, carbohydrate, and fermentable sugar. These feedstocks are converted into different energy forms like electricity, heat, biodiesel, bioethanol, biogas, etc. According to Dwivedi and his team the production of biofuel is needed to be improved from 9.7×106 GJ d^{-1} to 4.6×107 GJ d^{-1} in the year 2016–2040 (Dwivedi et al. 2022).

Biofuels are classified into different types depending upon their generations and categories that is First, second, and third. The first generation of biofuel utilizes edible feedstock such as rice, wheat, potato, barley, and sugarcane. These feedstocks have been recognized worldwide. The lipid or oil are extracted from these feedstocks and converted into biodiesel through the transesterification process. The feasibility of first-generation feedstock is debatable as these feedstocks compete with food crops as it requires land area, water supply, and fertilizers. This results in inefficient utilization of the already available energy resources and high production costs. To overcome this limitation the second generation feedstock was proposed including nonedible feedstock like woody biomass and forest residues. This feedstock requires no specific land area, fertilizer, or water supply. It releases fewer greenhouse gases than other generations (Goh et al. 2022). The main advantage of the second-generation feedstock is that it utilizes waste as a source thus requiring no cultivation. The only limitation with it is the complicated and expensive process equipment that increases the capital cost of the production. It requires a series of pretreatment processes to recover the lipid and sugar for biofuel production (Thanigaivel et al. 2022). Considering the limitation of first and second generations, exploration of an advanced feedstock attained algal utilization in form of the third generation feedstock. Algal biomass includes a series of advantages over any other biomass used in different biofuel generations. Algae don't require arable land to grow and thus don't compete with biomass used in the first generation of biofuels like sugarcane, maize, and corn. They have a high biomass growth rate with high oil content which counts around 15–20 times higher than any other land-based oleaginous crop (Nagappan et al. 2021). Owing to these advantages algal biomass over any other source of feedstock has recently gained a lot of acceptance from scientists and researchers worldwide for the production of biofuel at a large scale.

A lot of studies have reported the biotechnological application of microalgae. It is a rich source of vitamins, proteins, lipids, carbohydrates, etc. (Ansari et al. 2021). It has also been reported that microalgae globally reduce around 40% of the CO_2 in the atmosphere (Mat Aron et al. 2020). However, the only drawback associated with it is the high economic cost due to the high harvesting cost and low lipid content yield in microalgae. To overcome these challenges scientists have tried to find alternative techniques like bio-flocculation, insitu transesterification, utilization of wastewater as a growth medium, etc. (Peter et al. 2021). This has significantly decreased the overall cost of biodiesel production. Thus more research is required to develop methods for enhancing the algal growth and lipid content. This will help in the development of low-cost biofuel production sustainably. Past few years many scientists have reported different strategies and methods to enhance high lipid accumulation in the microalgal biomass.

This chapter will study the advancement in different generations of biodiesel production in terms of feedstock, biomass harvesting, lipid extraction, and lipid-to-biodiesel conversion methods.

15.2 Biodiesel

Fossil feedstocks are not regarded as a sustainable approach to fulfilling the increasing demand of the population (Demirbas 2006; Kamm et al. 2006). Feedstock derived from renewable biomass such as agricultural residues, crops, aquatic plants, and lipid-containing microorganisms is some of the versatile feedstock sources for the generation of biofuel. The development of new biomass systems from the enhanced utilization of waste biomass needs tremendous effort. In this system production, conversion, and utilization of biobased products are carried out efficiently in near harmony with nature (Naik et al. 2010). Renewable and carbon-neutral biodiesel is a promising alternative source of fuel due to its eco-friendly nature. According to the International energy agency (IEA) the world biodiesel production in the year 2020 was 37 billion liters elevated to 43 and 45 billion liters in the year 2021 and 2022 respectively. The forecast for 2023–25 was expected to be 46 billion liters which shows an elevating demand for biodiesel for production. However, the success rate depends on the ease of availability of sustainable renewable feedstock to change biological raw materials to fossil. In India, IS 15607 specifies the standard for biodiesel such as density, acid number, flash point, etc., and has been shown in Table 15.1 (Singh et al. 2019). As per the definition given by the American society for testing and material (ASTM), biodiesel a monoalkyl ester of long-chained fatty acids derived from various renewable sources of oil. European Academies Science Advisory Council (EASAC) says that, Raw material used for the biodiesel production can be distiguished into three different generations of feedstocks. Production of biodiesel from edible biomass rich in oil content such as oil seeds are termed as first-generation, non-edible biomass as oil source by second generation, and microorganism-derived

Table 15.1 Standards of biodiesel as per the specification of IS 15607

S. No.	Parameter	Units	Limitations
1	Acid number	Mg KOH/g	0.5 maximum
2	Carbon residue	% m/m	–
3	Cetane number	–	–
4	Copper corrosion	–	Class 1
5	Density @ 15 °C	kg/m^3	860–900
6	Flash point	°C	120 minimum
7	Free glycerin	% Mass	0.02 maximum
8	Kinematic viscosity at 40 °C	mm^2/s	2.5–6.0
9	Oxidation stability	–	06 h minimum
10	Sulfated (S 50 grade)	ppm	50 maximum
11	Water and sediments	vol%	0.05 maximum

oil as third-generation. For the biodiesel production, Utilization of all these biomass as feedstocks are naturally renewal and sustainable approaches (Singh et al. 2020).

The demands for petroleum increased rapidly because of the incrementing industrialization and up-gradation of the world. Such economic development has resulted in higher energy demands, in which the main part of the energy was obtained from the fossil sources like natural gas, petroleum, and coal. Hence, a limited reserve of fossil fuels had drawn the focus of several scientists to focus on alternative fuels that were formed from renewable feedstock. Biodiesel is getting many focuses due to its environmental advantages. There was about 4 primary process to form biodiesel: pyrolysis, blending, transesterification, and microemulsion. One of the most commonly applied processes is termed to be the transesterification of the triglycerides (vegetable oil and animal fats) with alcohol and a catalyst. At a time there was an attentiveness for *Jatropha curcas* oil as a feedstock for the productivity of biodiesel. This attentiveness was because of the non edible nature due to the presence of toxins which lead to its noncompetency with the edible oil and will not create the food crises. The seeds of *J. curcas* has higher oil contents and biodiesel produced carries the same properties to such of petroleum-based diesel. The key factors affecting the yield of biodiesel are a molar ratio of a reaction temperature, catalyst concentration, alcohol oil, and reaction time. Along with that economical and environmental aspects of biodisel had also been taken to consideration. The biodiesel developed from rapeseed, soybeans and, several other feedstocks was the least resistant to oxidation as compared to petroleum diesel (unadditives). The companies which store and transport the biodiesel were concerned that the biodiesel must also form the sediment at the time of storage. Vehicle, and equipment operators, require assurance it may sediment, and thus gum will't be formed during use. It was also reported that at the highest levels of oxidation the blends of biodiesel were separated into two phases which are the reasons for injector operational and fuel pump problems (McCormick et al. 2007). It has been observed that to fulfilling the increased requirement of energy, increased demand for alternative fuels such as biodiesel provides the preferred biodiesel oil that substitutes the conventional diesel for internal combustion (IC) engines. Biodiesels may offer some major alternatives to fossil based diesel oil since they were renewable with the same properties. Biodiesel was found to be a promising substitute because of the predicted shortage of conventional fuels and environmental concerns. Biodiesel derived from waste cooking oil by the chemical coversion process (transesterification) represent one of the promising utilization of waste cooking oil. Hence, the current focus may rely on the applicability of waste cooking oil as substantial feedstock for biodiesel production (Ewunie et al. 2021). Biodiesel is found to be a diesel with low-emissions substitute fuel that were produced from waste lipids and renewable resources (Leung et al. 2010).

15.3 The First Generation of Biodiesel

The production of Biodiesel from the first-generation feedstock includes edible biomass that is rich in fatty acid content. First-generation biomass was a quite popular source during the start of the biodiesel era. The popularity of first-generation-driven biodiesel was due to the ease raw materials availability (Singh et al. 2020). Biodiesel driven from first-generation feedstock can be achieved by transesterification. Which is a process that includes combining oil extracted from oilseeds along with alcohol. The oil-bearing seed and nuts such as Soybean oil, Coconut oil, Rapeseed oil, Palm oil, Rice oil, etc. are some of the most extensively utilized resources for biodiesel production.

15.3.1 Feedstock

The feedstock selection aiming toward the production of biodiesel relies on the chemical composition and physicochemical properties of the fatty acid content. The Fatty acid content and its chemical composition in the oil varies with its driven source from (Yasin et al. 2015). For the biodiesel production around 350 oil-bearing seeds and grains have been found as potential source, globally. The extensive availability of first-generation biomass is the reason behind the elevation growth of biodiesel production (Atabani et al. 2012; Shahid and Jamal 2011). To ensure the cost effectiveness, selection of feasible biomass as raw material governs a vital part in the overall process. So that it can provide a competitive edge to conventional fuels. The largest production of biodiesel is associated with the European Union (EU) which is about 65% of world production. In Eurpian Union rapeseed, soybean in the United States, coconut oil in Latin America and palm oil in tropical Asian countries (like, Indonesia and Malaysia) are the most preferred crops for biodiesel production.

Rapeseed oil is a highly recommended oilseed for biodiesel production in European countries and comprises of good fatty acid profile. Which includes arachidic (7–10%), Erucic (45–60%) linoleic acid (12–15%), oleic acid (10–15%), palmitic acid (1–3%) and linolenic acid (8–12%) (Li and Khanal 2016). On the other hand, soybean is a popular choice in the US and Latin American countries for biodiesel production. It can be grown in both tropical as well as temperate conditions due to its nitrogen-fixing ability. Soybean requires less fertilizer for their growth which leads to a positive fossil energy balance. Coconut (Cocos nucifera), is one of the feedstock sources from the first generation that is widely used in the Philippines for biodiesel production. Coconut oil is a triglyceride in nature with high saturated fatty acids about 86% with monounsaturated fatty acids in less amount, and polyunsaturated fatty acids 6% and 2% respectively. Reports have suggested that coconut oil yields a high amount of biodiesel (Li and Khanal 2016). This has been observed that automobiles operated on coconut oil-based biodiesel enhanced the mileage by 1–2 kilometers. The enhanced mileage is due to the enhancement of oxygenation. Even with the minimum blend (1%), the emission level has been reduced by 60% (Ahmed et al. 2014). Similarly, In European countries, Palm oil-based biodiesel production increases rapidly due to high oil yield per hectare and economical nature as compared to other edible oils-based feedstocks. Brazil and Nigeria have a high potential for Palm oil production. Palm oil contains monounsaturated fatty acids and medium-chain saturated acids in large amounts (Li and Khanal 2016). The density, viscosity, and heating values of Palm oil are 897 kg/m^3 (at 15 °C), 40.65 mm^2/s (at 40 °C), and 39.867 MJ/kg respectively (Singh et al. 2020). A Flowchart for the large-scale production of Biodiesel from vegetable oil has been shown in Fig. 15.1.

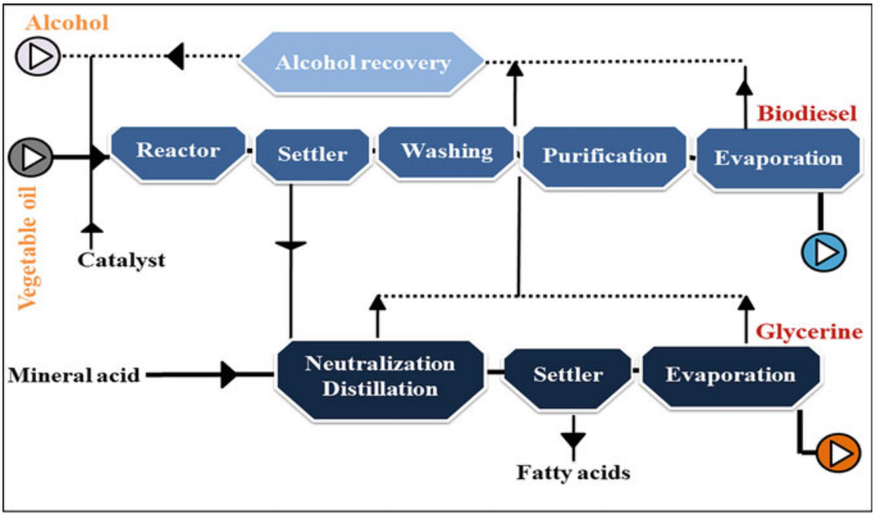

Fig. 15.1 Flow diagram for the production of biodiesel from vegetable oil

Although biodiesel is the greener and more sustainable alternative to fossil fuels. Production of biodiesel origination from first-generation feedstock is somehow simple when it comes to the availability of crops and the conversion process. It still has several disadvantages over its generation through first-generation feedstock which need to be overcome. Production of biodiesel by first-generation feedstock (edible oilseed crops) is still not considered economically feasible due to the current crises of food versus fuel. Using these crops as feedstock limits the food supply. This is the biggest disadvantage as it increase the cost of the other food products (Ojumu et al. 2013). Cost ineffectiveness and limitation of cultivation area due to increased urbanization is also the major obstacle to biodiesel production by the First generation feedstock. Such limitations constrained researchers to shift to more feasible alternate feedstocks for biodiesel production (Duan et al. 2012).

15.4 Second Generation of Biodiesel

In various regions, the limiting factors of first-generation biomass such as short rotation crops, inadequate supplies, and, direct competition with the food chain tend to find new improved sources for biodiesel production. The feedstocks used in second-generation consist of non-edible lignocellulosic masses and can be distinguished majorly into three groups. The groups are homogeneous groups such as, agroforestry residues group, wood chips and non-homogeneous group which includes low-valued industrial and municipal solid wastes. The second-generation feedstock is the most redily available renewable feedstock on the earth offering the promising perspectives (Somerville et al. 2010). This has been estimated that around 3700×10^6 tonnes of agricultural waste are produced worldwide as agro-forestry by-products every year (Zuccaro et al. 2020). Instead of all efforts, there are very few companies like Verenium, Mascoma, and lignol who have been focusing on scaling up the biorefining technologies aiming toward the advanced biodiesel production from non-edible lignocellulosic biomass feedstocks (Isikgor and Becer 2015).

15.4.1 Lignocellulosic Biomass as Feedstock

The second-generation feedstock is the most abundant and renewable resource available for human exploitation. The term 'Second generation refers to lignocellulosic material derived from the non-edible agro-forestry residue as it makes up the majority of it (Gomez et al. 2008; Zabaniotou et al. 2008). The fraction of Cellulose, hemicellulose, and lignin vary by species, age, and growing conditions of the source (Hirani et al. 2018). Lignocellulosic biomass generation mainly involves hard fibrous plant materials generated by municipal or lumber waste derived from sawdust, hybrid poplar, wood pellets, and chips. The lignocellulosic composition comprises macrofibril and microfibril arranged in crystalline structures. Which needs to be pretreated to promote access to each of the lignocellulosic compositions (cellulose, hemicellulose, and lignin) in the sub-sequential steps for hydrolysis (Galbe and Zacchi 2002). Its variability in composition and recalcitrance contents represent some economic and technical challenges as well. The general pathway for lipid production from lignocellulosic biomass includes two major routes that are biochemical and thermochemical. The biochemical route consists of four major steps. Pre-treatment of biomass to remove recalcitrance (lignin) increases the accessibility of cellulose and hemicellulose for hydrolysis (Galbe and Zacchi 2002). Afterward, saccharification of cellulosic and hemicellulosic components is carried out which is a process of hydrolysis. This process is aimed at polymeric carbohydrates releasing monomeric sugars and is subsequently fermented to ethanol. Saccharification is achieved either chemically with the help of acid hydrolysis or biologically by the use of enzyme systems of Fungi and bacteria. Carrying this process under mild conditions such as temperatures of 40–50 °C and pH 4.5–5.0 will ensure reducing corrosion problems, reduced generation of toxic by-products, and low energy consumption (Singh et al. 2020). Finally, it proceeded with fermentation and lipid production. Carbon to nitrogen is a crucial parameter when it comes to biodiesel production to prevent citric acid production instead of lipid accumulation. Nowadays a combination of lipid extraction and its conversion to biodiesel is done in a single step called in situ transesterification. Direct transesterification could be an alternative to reduce the amount of necessary equipment making biodiesel production cost-effective.

Second-generation feedstocks have several advantages such asno competition with agricultural food sources, low environmental stress, stability over a wide range of climatic conditions, less land allocation and the ability to grow in a mixture with different plants, potential rehabilitation of degraded lands, possibility to produce useful by-products, resistance to pests and diseases, biodegradability, the broad range of availability, low aromatic hydrocarbons and sulfur (Sitepu et al. 2020; Anwar et al. 2019; Pikula et al. 2020). Despite various existing advantages of second-generation feedstock, its lower oil yielding capacity and consumption of high alcohol during the production process as compared to first-generation feedstock are some of the concerns that need to be fulfilled (Singh et al. 2019).

15.5 Third Generation of Biodiesel

In the current years, microalgae had achieved a lot of attention because of their significant carbohydrate and lipid production and the capability to grow with the help of non-potable water sources. Themicroalgae were scrutinized as a potential feedstock having higher yielding for the productivity of biofuel. The production of biodiesel mainly relies on the selection of microalgae strains. The strain selection is dependent upon several factors, like CO_2 tolerance, lipids content, the productivity of biomass, and the requirements of nutrients (Singh and Mishra 2021). In both engineered and natural systems, the microalgae were been exposed to a lot of environmental conditions which affected the cellular compositions and the growth rate. Therefore, the amount of carbon fixed in the carbohydrates, and lipids, were influenced highly by the availability of nutrient (e.g., carbon, trace metals, phosphorus, and nitrogen) and by environmental factors (like temperature, pH, and light) (Farooqui et al. 2021; Chavan et al. 2014).

15.6 Factors Affecting Microalgal Lipid Production

At the time of photosynthesis, the algae produce lipids, carbohydrates, and proteins. A relative amount of such types of metabolic products have been linked tightly with nutrient and environmental conditions consisting of the intensity and amount of sunlight, pH, CO_2 levels, available nutrients, and temperature. Oxygen, hydrogen, and carbon are needed as non-mineral nutrients for the growth of algae and the macronutrients consist of sulfur, potassium, phosphorus, nitrogen, and magnesium. The micronutrients (mangnaease and iron) are also needed in smaller amounts. Although elements such as molybdenum, zinc, cobalt, boron, and copper were found to be essential trace elements (Ghafari et al. 2018). In a way, the biochemical composition of the algae is highly influenced by environmental conditions (mainly light and temperature) and the nutrients availability. Other factors like as pH range and existence of heavy metals were also responsible for affecting the metabolism and growth of the algae. Generally, all these factors may affect photosynthesis, hence altering the carbon fixation and allocation of the carbon into several macromolecule types. In turn, the composition of a cell's macromolecular may determine its efficiencies in the productivity of biofuels (Kumar and Olaniran 2022).

15.6.1 Temperature

Temperature is a main environmental factors which influence various parameters of algae. Such as growth rate, size of the cell, nutrient requirements, and biochemical compositions. In the US, biomasses of algae grow up under a broader range of 15–40 °C temperatures, depending upon the region, strain, and season. Temperature below the optimal growth temperatures results in the lower size of cells, and the nitrogen and carbon fixing capacity decreases (Li et al. 2021). Also, the temperature must play an important part in the photoinhibition, that had known to affect the growth rate of algae. A lot of methods of temperature-dependent photoinhibition were postulated.

(i) Low temperature leads to the reduction of electron transport at the specific flux rate of a photon because of the decremented rate of fixation of carbon dioxide.
(ii) Low temperature might inhibit an active oxygen species which can increase the reduction of photoinhibition by protecting PSII.

(ii) Low temperature might inhibit the D1 protein synthesis which was degraded at the time of photoinhibition, consequently impeding a PSII repair cycle (Vonshak and Torzillo 2004; Che et al. 2022).

15.6.2 Light

As we know that light is an energy source at the time of the photoautotrophic growth phase and an organism applies the light energies to convert the carbon dioxide into an organic compound—mainly, sugars. The intensity of light range in the United State of America varies from about 1500–8500 Wph/m^2/day depending upon the season (Juneja 2015). The intensities of light may also affect the algal growth by their impacts on photosynthesis. The algal growth rate is higher at the saturation light intensity and decreases beyond the saturation intensity. Hence the photoacclimation or photoadaptation method of an alga may result in variations in the cell constituents according to light availabilities. The adaptation takes place through multiple phenomenon-like, like changes in types and quantities of pigments, dark respiration rate, growth rate, and presence of essential fatty acids. The morphological photo acclimation has been followed by variations in the cell number along with the volume and density of the thylakoid membranes. The algae may get rid of the limitation of light by the desaturation of chloroplast membranes. The intensity of the light may enhance the saturation limit leading to photoinhibition due to the break down of chloroplast lamellae resulted by the higher intensities of light and enzyme inactivation involved in the fixation of CO_2. For example in *Dunaliella viridis*, an increase in the light intensity from 700 to 1500 μmolm^{-2}s^{-1} results in the decline of the growth rate by 63%. This means that the light intensity can also affect the chemical composition of algae. The *Dunaliela tertiolecta* may exhibit a decrement in contents of protein and an increment in a fraction of lipid with incrementing the intensities of light up to the saturation (Gordillo et al. 1998).

15.6.3 pH

During the cultivation of algae pH plays a key role in the determination of solubility, availability of CO_2, essential nutrients. Hence may affect the metabolism of algae as the inorganic carbon uptake by an alga, significantly the pH may increase in an algal culture. The maximum growth of algal may take place at neutral pH, and the optimum pH is the initial pH of the culture where the algae were adapted to grow. The change in the pH of media limits algal growth with the help of metabolic inhibition. It was also reported that the *Thalassiosira pseudonana* cells were adjusted to the lower pH (upto 6.5) and had a higher growth rate when pH was adjusted upto 8.8 (sub-optimal). The normal growth rates were reestablished after pH was decremented by the addition of the HCl. Similarly, the outcomes were also announced, where the rate of photosynthesis and the growth of algae was found to be minimal at a pH of 9.0, but the rates of uptake of carbon had incremented when the pH was decremented upto 8.3 (Juneja et al. 2013; Chen and Durbin 1994).

15.6.4 Salinity

Salinity is another vital parameter that can affect the biochemical composition of algae. Exposure to a higher concentration of salinity to the algae than its natural/ adapted varies its growth rate and alters the chemical composition. In a study, it has been observed that *Dunaliella*, a type of marine alga has shown an inclination in the saturated fatty acids along with an increase in the concentration of Sodium chloride (0.4–4 M) (Zhang et al. 2018). In *Dunaliella tertiolecta*, a significant increase of 60–67 and 40–56% has been observed in its intracellular lipid and triglyceride content, when its NaCl concentration has been increased from 0.5 to 1.0 M (Patel et al. 2017). In another study increase in the NaCl concentration of the cultures of the *Botryococcus braunii*, which is a fresh water alga, offers lipid and carbohydrate content enhancement. A significant increase in the growth rate has also been observed. In another study an enhanced lipid content of *Botryococcus braunii* was observed when grown at 0.5 M NaCl as compared to the media without the addition of NaCl but the protein, carbohydrate, and pigments contents have declined. With the same alga, it also has been found to there was a decrement in the protein content while the lipid and carbohydrate content remains unchanged with increased salinity concentration. Contrary to the above results, in a study *Tetraselmis suecica* showed a reduction in the content of protein per cell at 20%,and with increase in salinity concentration (Fabregas et al. 1984).

15.6.5 Nutrients

The variations in biochemical compositions in the algae under the state of nutrient limitations had been observed. Generally, the Algae growth rate and rate of the limiting nutrients under optimal temperature and pH are proportional to each other and is given by the Michaelis-Menten equation (Titman 1976). Phosphate and Nitrogen are the two key macronutrients vital for the algal cell's metabolism and growth. Nitrogen is fundamental element to form nucleic acids and proteins and phosphate is an essential part of the RNA and DNA backbone. As it is not unusual for the algae for becoming nutrient-limited (phosphorus, nitrogen) in the natural environment. The limitations of these important nutrients may move the metabolic pathways of an organism. As an example, phosphorus and nitrogen starvation may shift the metabolism of lipids from the synthesis of membrane lipids to the neutral storage of lipids. Ultimately incline the total content of lipids of the green algae (Harris 2012). An abundance of oxygen and hydrogen in a media for the cultures of algae means that its availabilities were not termed as major challenge for metabolism and cellular growth. Carbon is another vital nutrient that is important for the photosynthesis and hence, reproduction and growth of algae. Carbon fixation either be applied for respiration as an energy source or as raw material in additional cell formation. The decrease in the rate of carbon fixation may imply decrement in the growth rate of algal. An alga needs inorganic carbon sources for performing photosynthesis. The carbon is utilized in a form of carbonate, CO_2, and bicarbonates for autotrophic growth and the form of glucose and acetate for heterotrophic growth. Trace metals are found to be metals that were available in algal cells in extremely smaller quantities (<4 ppm), but that was termed to be a key component of the phycophysiology. The metals like Manganese (Mn), nickel (Ni), cobalt (Co), iron (Fe), copper (Cu), and zinc (Zn) are major key trace metals that are needed by algae for several metabolic functions. The inadequacy of trace metals may affect the growth of algae, and excessive concentrations of metal (above the toxicity threshold) must impair photosynthesis, inhibit growth, damage the cell membrane, and deplete antioxidants (Bruland et al. 1991). Phosphorus is reported to be primary limiting nutrient than that of nitrogen responsible for the algal growth environment. Hence is the key nutrient of growth and development of algal cell (Larned 1998).

15.7 Conversion of Lipids to Biodiesel

Biodiesel is found to be one of the promising biofuels having sustainable outcomes in the management of greenhouse gas emissions. Conventionally, Pyrolysis, blending, microemulsions, transesterification (TE), and esterification (E) are the methods that are employed for biodiesel production. Among all these methods Transesterification and esterification are the most preferred method for biodiesel production on large scale. It is a phenomenon of chemical conversion which includes a reaction between lipids and Alcohol to produce FAAE (fatty acid alkyl esters). Preference for these methods is due to their several advantages over other methods such as cost-effectiveness, high conversion efficiency, reduction in the fuel viscosity to enhance fuel characteristics, employment of the variety of feedstocks, and miscibility of the biodiesel with any proportion of fossil fuel (Talebian-Kiakalaieh and Aishah Saidina 2020). The process of esterification is carried out before transesterification. The major insight of the following process aiming toward the production of biodiesel is given below.

15.7.1 Esterification and Transesterification

Esterification and Transesterification are chemical conversion phenomena. Which includes a reaction between lipids and Alcohol to produce fatty acid alkyl esters (FAAE) or Biodiesel. In this conversion process when the free fatty acid (FFA) reacts

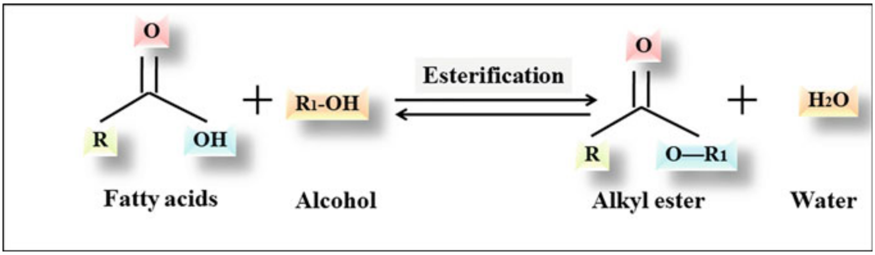

Fig. 15.2 Esterification reaction for the production of biodiesel

with alcohol to form FAAE and water as the product which is known as esterification shown in Fig. 15.2.

When these conversion processes are assisted by various chemical and biological catalysts it is known as catalytic transesterification/esterification and is widely adopted by the industries due to its higher yield capacity. The general mechanism of esterification for biodiesel production in presence of strong acid (e.g. H_2SO_4) as a chemical catalyst involves five sequential steps. The first step is the protonation of free fatty acid which give an oxonium ion. The oxonium ion further undergoes an exchange reaction with alcohol which in turn loses a proton to become an ester. Once the mixture was stirred and heated, free fatty acids were finally converted to biodiesel (Haigh et al. 2014). The biggest pros of the esterification process are that it enables the utilization of industrial by-products and residues rich in free fatty acids like crude oil, frying oil, acid sludge, suet, or lard (Haghighi et al. 2022). The key factor that can affect the method of esterification is the impurity of feedstocks. Hence, it's crucial to ensure that the feedstock is filtered adequately and is free from contaminants as well as water. Because in the presence of water, which is a stronger electron donor than aliphatic alcohols, the exchange reaction is not favored and esterification will not fully proceed (Haigh et al. 2014).

On the other hand, during transesterification, triglycerides react with alcohol to produce Fatty AcidAlkyl Esters and glycerol as the main products shown in Fig. 15.3.

Generally, the transesterification process is preferred where there is the presence of a high concentration of triglycerides. It comprises sequential steps, in the very first

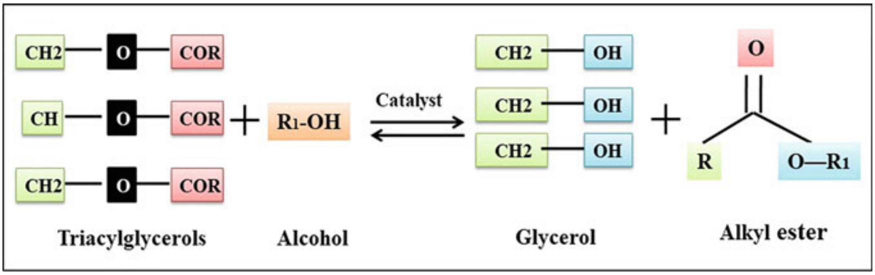

Fig. 15.3 The diagrammatic representation of transesterification reaction

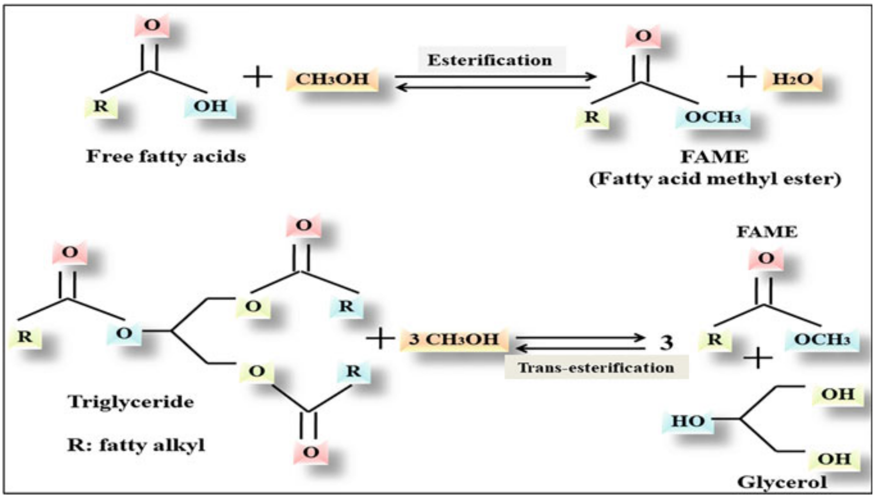

Fig. 15.4 Schematic representation of esterification and transesterification reaction producing fatty acid methyl ester (FAME)

step a reaction is carried out between triglycerides and alcohol to convert them into diglycerides. In the second step, diglycerides are converted into monoglycerides and glycerol to yield Methyl/alkyl ester at each stage (Roy et al. 2021). Since transesterification is a reversible process, it requires excess alcohol to accelerate the equilibrium reaction towards the product formation. Generally, ethanol and methanol are used as alcohol to carry out the reaction due to their low cost, polarity, and, superior reactivity (Avhad and Marchetti 2015). The process of esterification/transesterification with methanol produces Fatty acid methyl esters (FAME) along with the water/glycerol as a by-product as shown in Fig. 15.4 (Narwal and Gupta 2013).

The production of biodiesel by transesterification and esterification is highly affected by the use of enzymes (Chemical/Biological). The reason behind this is that usually feedstock oils are immiscible with alcohol. Hence, are incapable of forming a single-phase reaction mixture. This leads to the reduced surface area for the reaction to carry out efficiently ultimately having a slow reaction rate. With the addition of a suitable catalyst, the contact area between the reactants will increase and ultimately improves the rate of reaction. Another important factor is the source of feedstock oil because around 60–80% of the biodiesel production cost is accompanied by raw materials that have been used for biodiesel production (Binhayeeding et al. 2020). In a way, biodiesel costs can be minimized significantly by opting the raw material that is feasible and sustainable. Such as Algal oil, waste cooking oils, and non-edible oil. Other than that temperature, pressure, reaction time, alcohol-oil molar ratio, and mixing are some other factors that may affect the biodiesel yield.

15.8 Future Prospective

Biodiesel is a promising alternative of fossil fuels because of its environmental friendliness, renewability, biodegradability, and sustainability, mainly with comparable properties of fuel to diesel. Plant oil based chemo-catalytic biodiesel is widely utilizedin the large scaleproduction because of its cost-effectiveness and higher conversion rate. Enzyme-catalyzed biodiesel has earned extensive focus becaus of its environmental friendliness and sustainability in the past few decades. The major obstacles in the production of microbial biodiesel at the industrial level are cost uneffectiveness, lack of enzyme stability and reusability. Firstly, this chapter shows a state-of-the-art production of microbial biodiesel, consisting of (1) the accumulation of lipid of the oleaginous microorganisms from pretreated lignocellulosic biomasses and (2) biodiesel production from the microbial oils by the process of transesterification by immobilized lipase. Therefore, next-generation developmental trends and technological challenges were reported to give a possibility of much economical large-scale industrial productivity. This chapter discusses the opportunities for sustainable and eco-friendly productivities of enzymatic biodiesel in the next generation (Wang et al. 2021).

The modern world faces many challenges like oil price, energy security, climate changes, and resource depletion, which directly and indirectly affect the environment. Hence, these challenges have stricken noteworthy advancements in the research and production of fuels and energy that are biomass driven. In this regard, biofuel was expected to be essential to lighten such issues in a more sustainable way that can generate a circular bioeconomy. In the transport sector, biofuel usage is the most feasible way to decrease carbon dioxide emissions. Therefore, biofuels were easily obtained from indigenous resources that were locally available. Currently, algal biofuels are attractive and have been termed the most promising alternative to eliminate the global energy crisis. A major advantage of the utilization of algae is that it gives a higher yield of oil along with null competition with the food crops when it comes to land as well as fresh water resources. Several types of research are going on all over the world for the improvement of biofuel production. As we know, biofuel is a fast-moving industry and a fast-growing research field; therefore, key research progresses in the technologies for biofuel production have to be made. A major understanding of the methods for producing biofuel has also been attained. However, fossil fuels are not completely replaced by biofuels, along with a lot of integrated approaches to biology and engineering are still needed for the optimizing production of biofuels at a commercial scale. So, combining more, an understanding of how these biofuel formations are going to be affected by the changes in climatic is much required so that a sustainable biofuel economy is attained. So, biofuels as the alternative to fossil fuels in an upcoming generation were going to be a principal supplier of energy in a sustainable manner along with capabilities in incrementing security of the supply; and also this will mainly decrement the amounts of the emissions by vehicles (Kour et al. 2019).

15.9 Conclusion

The enhanced concern regarding the natural nonrenewable sources of energy and the environment has urged us to find an alternative energy source. In a way, a lot of focus has been shifted towards the areas of alternative fuels such as biodiesel for providing a suitable substitute for diesel oil for internal combustion engines. The feedstock that is currently utilized for biodiesel production still has a lot of limitations. The most advanced generation utilizing microalgae as feedstock is not able to compete economically with the first and second generations. Thus, it still lacks to meet the sustainability goals and world population demand. However, the continued research in harvesting, extraction, conversion techniques, and genetically modified microalgae has given hope. The biofuel produced by all generations emits less amount of greenhouse gases in comparison to the natural non-renewable fuels. Microalgae are well known to trap the CO_2 resulting inmanaging carbon from the environment. Therefore, algae play a dual function serving as a feedstock for biofuel production and remediates carbon from the environment. Thus the third generation of biofuel using microalgae as feedstock has a lot of potential for generating biodiesel that can reach the commercial level.

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Chapter 16
Lipid Biomass to Biofuel

Darshan Singh, Anuradha Bhardwaj, Divya Mathur, and Amar Kumar

Abstract Fossil fuels are the main energy sources worldwide even today. But with the alarming pace at which fossil fuels are exhausting, there would be a need for sustainable and economically viable alternatives in the near future. Fossil fuels pose severe environmental threats like air pollution, soil pollution, global warming etc. It is reported that the utilization of algal biomass to produce bioenergy could be one of the solutions. Microalgae offer many unique features with the potential to store lipids in their cells just like plant oils, CO_2 sequestering capability, low space requirement, rapid growth, ability to grow in wastewater and rich in lipid and carbohydrate content. Although an array of nutrients is required for an algal bloom that could be fulfilled by nutrients from wastewater. In a way, it is the biological wastewater treatment technology producing green energy (WtE). Methods like supercritical fluid extraction, microwave and ultrasonic-assisted extraction, and Soxhlet extraction could be used for the microalgal lipid extraction. So, this chapter explores the possible methods to isolate lipids from biomass and their energy utilization.

Keywords Fossil fuels · Algae · Extraction methods · Environmental problems · Green energy etc.

16.1 Introduction

Coal, natural gas and crude oil are called fossil fuels because they are formed by the natural decomposition of animal bodies and plants buried beneath the earth at very high temperatures and pressure after several thousand years. It is said that lives did exist on earth but due to some natural calamities, the earth underwent disaster due to which living beings and plants were buried under the earth for several years

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which led to the formation of fossil fuels. They are mainly made up of carbon (high content), hydrogen and oxygen. These fossil fuels have been the major energy sources in the world since the industrial revolution whether it is to drive a car, or machine or generate electricity. Burning fossil fuels have a great impact not only on the environment but also on our future. Population explosion has further increased the pace of their consumption and environmental pollution (Singh et al. 2011). To accommodate a large population, we have to cut our green cover. Loss of flora and fauna means going towards the next disaster. The future of coming generations will be at stake as fossil fuels might be critically depleted by then. These anthropogenic activities have made the globe not to fit to live (Shafiee and Topal 2009). It has become a global problem. Exploitation of various renewable energy sources like wind energy, solar energy, water energy etc. as future sources of energy is the need of the hour. But the technologies involved are quite expensive and also their limited availability has made the situation worst. Among the various renewable sources of energy, biofuel has gained much importance due to its versatility. Biofuel means energy is generated from natural biomass. It is a sustainable and green alternative to the existing fossil fuels. Biodiesel is a feasible diesel fuel replacement as the operation of biodiesel does not require any specialized technology and alteration in the present engine structure (Liew et al. 2014). Biodiesel is a mixture of variety of ester-based oxygenated fuels. They are non-toxic, environment-friendly, free of sulphur and aromatic compounds. Many countries are now producing biofuels from natural sources. For example, Brazil uses sugarcane, Asian countries and Europe are using palm oil and Japan, USA, China etc. are producing biofuels from microalgae (Georgianna and Mayfield 2012).

16.2 Generation of Biofuels

Different types of raw organic materials can used to produce biofuels and these are grouped into the following three generations of biofuels.

16.2.1 First-Generation Biofuels

First-generation biofuels are based on edible feedstocks i.e., used for human consumption (Dragone et al. 2010). These include major commercial crops like wheat, maize, sugarcane, sugar beet, palm oil etc. These crops are rich in carbohydrates and oil. For example

- **Sugars**: Bioethanol is commercially more matured and is mainly produced from corn, sugarcane and in small amounts from wheat and sugar beet. The process is simple as sugars are fermented into ethanol using a *saccharomyces cerevisiae* yeast. Conversion of biomass to bioethanol is a tedious process that requires the pretreatment of feedstock followed by the addition of a mixture of enzymes. These enzymes hydrolyze polymeric carbohydrates into simple sugars that can undergo fermentation. Its commercialization is still at the back due to few commercial ethanol facilities.

- **Vegetable oil**: Biodiesel can be formed by a transesterification process where animal fats or vegetable oils are treated with alcohol particularly methanol in presence of the alkali catalyst (sodium hydroxide or potassium hydroxide). Methyl esters (FAME) and glycerol are separated from each other and purified. Mainly palm oil is used in Asia for the generation of bioenergy. Much of biodiesel comes from soybean due to their bumper production and low cost. The soybean-based biodiesel, called methyl soyate or soydiesel is the main form of biodiesel in the USA. Cottonseed, peanuts, sunflower seeds and canola are some of the potential feedstocks for biodiesel. Biodiesel from these oils can successfully be used as automotive fuel, although they differ in physical properties, cetane number, energy content etc.

16.2.2 Second-Generation Biofuels

These are lignocellulosic based fuels (Balat et al. 2008). It is a non-edible part of the food crops i.e., discarded parts like leaves, husks and stems. In general, they are called "nonfood biomass," which is recognized as a low-cost viable source of renewable energy. It is produced in enormous amounts, moreover residual impurities such as N, S or metals are present in trace amounts. These biomasses do not undergo pretreatment and are disposed of, which can pollute the atmosphere. There are two kinds of agricultural wastes one is obtained from the field which mainly includes husk, stalks and leaves; another one is obtained from food processing industries including seeds, peels, pulp etc. These biomasses are rich in cellulose, hemicellulose and lignin. Conversion of lignocellulosic material takes place in two phases: Pretreatment processes and Pyrolysis. The pretreatment step involves the breakdown of biomass into cellulose, hemicellose and lignin (a form of simple sugars) by chemicals or enzymes. The pyrolysis step involves the heating of pretreated biomass at a high temperature to produce biofuels (Wang et al. 2018). Microwave heating is simple, efficient and produces fewer oxides of nitrogen and sulphur. The biochemical conversion process is a frequently used technique for bioethanol production using enzymes. Some biomasses show recalcitrance to enzymatic degradation hence limiting their efficiency. In the pyrolysis phase, agricultural waste is converted into biochar, bio-oil and syngas. Biochar is a black colored solid that has been used as soil conditioner or cooking fuel. Bio-oil is used as combustion fuel in boilers and furnaces. During pyrolysis, cellulose is transformed into biochar, bio-oil and syngas; hemicellulose is transformed into bio-oil and syn gas whereas lignin is primarily to biochar (Wu et al. 2014). Biofuel production from commercial crops (edible) or their left-over parts (non-edible) is not a viable solution as their manufacturing depends upon the availability of land for their cultivation. Land space is limited and moreover, their production competes with food crops.

16.2.3 Third-Generation Biofuels

Third-generation biofuels are the solutions to overcome these drawbacks i.e., manufacturing biofuels from a microorganism such as microalgae, bacteria and fungi (mold and yeast) (Fig. 16.1). They have capability of producing and storing a large amount of their dry mass as lipids (Knothe et al. 2005). Microorganisms having more than 20% lipid content are called oleaginous. Oleaginous microorganisms include microalgae, Bacteria, yeast and molds. They have lipid content in the range of 20–75, thus finding potential in biofuel production (Chisti et al. 2007; Ramalingam et al. 2010).

16.2.3.1 Microalgae

Microalgae are minuscule plants invisible to the naked eye. They are called phytoplankton, found in freshwater water as well as seawater (Williams and Laurens 2010). They are sensitive to environmental changes hence, best indicators for monitoring the quality of water. If the number and diversity of phytoplankton are declining that means water quality in water bodies is deteriorating. Microalgae can be eukaryotic or prokaryotic (also called cyanobacteria). They can be grown photoautotrophically in closed photobioreactors or open water bodies using natural sunlight, carbon dioxide and inorganic nutrients for their growth releasing oxygen in an atmosphere. Commercial production of phototrophic microalgae has a limitation of low biomass production due to constricted light. Alternatively, microalgae can be cultivated in

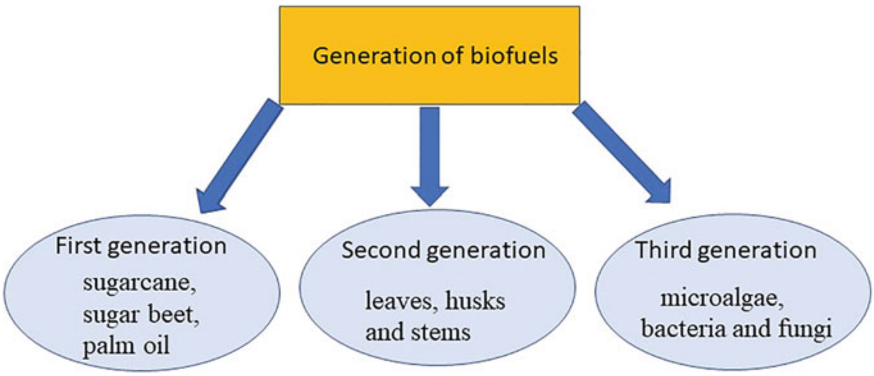

Fig. 16.1 Generation of biofuels

a heterotrophic or mixotrophic conditions in the absence or presence of light and using organic carbon for their growth. It is a common practice that increases the algal biomass production (Mata et al. 2010). Since some of them can carry out the process of photosynthesis, hence play important role in reducing CO_2 gas responsible for global warming. Among the available renewable energy sources, microalgae have been receiving much attention due to many unique features like rapid growth, high oil content, less land requirement, capable of growing even in wastewater (Morais et al. 2020). Moreover, microalgae lack sulphur, so non-toxic, biocompatible and biodegradable. Algal oil becomes a part of livestock feed and residue can be used to produce bioethanol. Countries like the USA, China, Japan etc. produce energy from microalgae. Various species of microalgae e.g., *Botryococcus braunii*, *Chlorella* sp., *Cylindrotheca* sp., *Crypthecodinium cohnii*, *Isochrysis* sp., *Dunaliella primolecta*, *Monallanthus salina*, *Schizochytrium* sp., *Nannochloris* sp., *Neochloris oleoabundans*, *Nannochloropsis* sp., *Nitzschia* sp., *Phaeodactylum tricornutum*, *Tetraselmis sueica* etc. have high oil content hence biodiesel production from microalgae is many more times higher than other feedstock such as palm oil, jatropha, sunflower, soybean etc. (Chisti 2007; Ramalingam et al. 2010). The high cost involved in the production is the major limiting factors for the commercialization of microalgal-based biofuels as a fossil fuel substitute. Microalgae produce a variety of lipids; polar, non-polar, sterols and isoprenoid like carotenoids, terpenes, quinine etc. Polar lipids are mainly comprised of polyunsaturated fatty acids (PUFAs). Sterols and phospholipids are structural constituents of the cell membrane. Triacylglycerols or triglycerides (TAGs) are the main storage lipids containing saturated and unsaturated fatty acids. Microalgae can store a very small amount of TAGs during exponential growth and a maximum amount during the stationary phase. TAGs are mainly synthesized under natural light and stored in cytosolic lipid bodies. These accumulated TAGs are then used for polar lipids synthesis when the light is not available. These triacylglycerols are converted into fatty acid methyl ester (FAME) during the transesterification process. However, wild microalgae are not capable of producing a large quantity of these lipids under natural environmental conditions. Therefore, different techniques and approaches have been explored to increase microalgal lipid production.

16.2.3.2 Molds/Yeasts

Oleaginous molds also called filamentous fungi, can accumulate high quantity of biomass as lipids (Murphy 1991). There are several species of yeast (*Rhodotorula glutinis*, *Candida curvata*, *Cryptococcus albidus*, *Lipomyces starkeyi*) and molds (*Mortierella isabelline*, *Aspergillus oryzae*, *Humicola lanuginose*, *Mortierella vinacea*) which produce a high amount of γ-linolenic acid (GLA) and arachidonic acid (AA) (Ramalingam et al. 2010). The amount of these fatty acids varies with environmental factors like C/N ratio. Lipid content gets increased on increasing C/N ratio (Patil 2010). There seems to be no effect on the concentration of neutral, phospholipid and glycolipid. Fungi can be grown on waste molasses, wastewater, sewage sludge and agricultural residues. Yeasts (single-celled fungi) are made up of at least 20% of lipids. Yeasts have a faster growth rate and oil content is high (Li et al. 2008). They can be cultivated on several organic carbon sources and can store lipids depending upon the levels of their growth and nutrient-limiting conditions.

16.2.3.3 Bacteria

Bacteria have a high growth rate under normal physiological conditions (Meng et al. 2009). Few species e.g., *Acinetobacter calcoaceticus*, *Arthrobacter* sp., *Bacillus alcalophilus*, *Rhodococcus opacus* (Ramalingam et al. 2010) can store a high amount of triacylglycerols (TAG) but its chemical composition varies with species to species and source of carbon. Actinomyces group of bacteria have the ability to accumulate higher amounts of intercellular TAGs grown on a glucose-rich medium. Accumulation of TAGs mostly takes place in the stationary growth phase (Olukoshi and Packter 1994). Their use is limited in biofuel production as compared to microalgae and yeast.

16.3 Factors Affecting the Lipid Content in Microalgae

The chemical constitution of microalgae is not the same in all but it varies depending on the species and climate conditions. Cell growth and lipid content in microalgae depend upon several factors like light intensity, pH, CO_2, dissolved oxygen (DO), the concentration of nutrients such as N, P, Si and Fe and sources of organic carbon. These parameters are to be varied to enhance algal oil production. However, this is not always true. Sometimes the condition that enhances cellular growth rate might result in low lipid content and vice versa. High lipid content in microalgae can be attained under environmental stress conditions (Li et al. 2008). Accumulation of lipids in microalgal cells tends to depend upon the growth phase of microalgae (Roessler et al. 1994).

16.3.1 Effect of Nutrients Availability

Nitrogen and phosphorus are important for the synthesis of protein and thus affect microalgae growth. These elements are abundant in the waste water. Therefore, one must have observed plenty of microalgae in wastewater as it is rich in these two elements. Some microalgae adapt as per the environment by varying their chemical composition. Few species have the ability to replace phospholipids with non-phosphorus lipids in the membrane due to a lack of phosphorus. It has also been observed that nitrogen and phosphorus strive conditions increase lipid production in the algal cell. Nitrogen stress condition leads to a decrease in saturated fatty acids content and an increase in unsaturated fatty acids (Dean et al. 2010). The lipid-storing ability of microalgal cells is not correlated with their growth. It is reported that a lack of nitrogen in a medium almost stops the cell division but carbon metabolism continues to take place which leads to the diversion of carbon to lipid production (Beopoulos et al. 2009). Neutral lipids, in particular, are increased in some strains and although few species showed decreased lipid accumulation. The nature of the source of nitrogen also has an impact on algal growth and lipid productivity (Illman et al. 2000). Algal growth was found to be higher for ammonium ions and least for nitrate ions, whereas it is intermediate for urea. It is believed that H^+ released from the consumption of ammonium ions reduces the media pH which inhibits cell growth.

16.3.2 Effect of CO_2

Carbon dioxide has a great impact on algal growth and lipid content. It not only decreases the media pH but also provides the source of carbon (as bicarbonate). *Nannochloropsis oculata* cells grow faster as the CO_2 fraction is enhanced from 0.003 to 2%. But a further rise in carbon dioxide fraction decreases cell production and cell growth is completely inhibited at 5% CO_2 (Hsueh et al. 2009). As per several research papers, the optimum range of CO_2 could be 0.03–15% (Lakshmikandan et al. 2020). The fatty acids composition is an important criterion for biodiesel production. A low CO_2 concentration (0.3–2%) favours the saturated fatty acids synthesis whereas a high concentration of CO_2 favours the unsaturated fatty acids (PUFA) (Tang et al. 2011). It is noted that tolerance of microalgae to a high concentration of CO_2 may be related to the activity of the Rubisco enzyme. In a few species, this enzyme gets inactivated due to acidity caused by an excess of CO_2. On the other hand, high CO_2 level under nitrogen starvation condition enhances lipid content.

16.3.3 Effect of Carbon Sources

Carbon sources influence the synthesis and fatty acid composition in microalgae due to metabolism differences. Hexose is the common source of organic carbon related to the release of energy and lipid synthesis. Glucose metabolism takes place through various pathways like the TCA cycle or EMP pathway or Entner-Doudoroff (ED) pathway or PPP pathway. Glucose is found to enhance the lipid concentration in microalgae and approximately 85% of it is stored as starch (Tang et al. 2018). Fructose is said to modulate microbial lipid accumulation; however, it is less as compared to glucose due to a rise in pH during heterotrophic cultivation. In recent years, the use of acetate in the medium tend to increase the lipid concentration (De Swaaf et al. 2003). Crude glycerol produced during FAME synthesis can also be used as a source of organic carbon. It has been observed that microalgae cultured in a glycerol-rich medium showed higher lipid content (Pyle et al. 2008). It is further noted that the presence of an organic carbon source could lead to bacterial contamination in the culture medium. Microalgae and bacteria grow at a different rate which disturbs the symbiosis balance and leads to low biomass accumulation.

16.3.4 Effect of Light

Light plays important role in the bloom of microalgae and accumulation of lipid in phototrophic conditions. The rate of growth of microalgae becomes high on increasing the photo irradiation flux till the optimum value (photosynthetically active range (PAR) is 400–700 nm) is reached. After that, it reaches the saturation point and beyond that that no further growth is observed (Gordon and Polle 2007). For example, the growth of marine *Chlorella* sp. and *Nannochloropsis* sp. increases with increasing the light intensity from 2000 to 10,000 lux but lipid content is decreased (Feng et al. 2011). Low light intensity is good for lipid accumulation. This might be due to the fact that microalgae may use that energy to divide themselves rather than accumulate. When light energy is more than 10,000 lux, it causes photonic energy to be dissipated as heat that impairs cellular functions (Luo and Al-Dahlan 2004).

16.3.5 Effect of Sodium Chloride (NaCl)

The concentration of NaCl and N in the cultivating medium may have a remarkable effect on total lipids and the composition of fatty acids in a few algal species. High salinity affects the fluidity and permeability of the membrane. Very high concentrations of NaCl can destroy microbial cells but optimal stress can enhance lipid production. A higher yield of monounsaturated fatty acids (FAs) (16:1 and 18:1) which make up the neutral lipids has been achieved by increasing the concentration of NaCl from 8 to 16% (El-Baky et al. 2004). While amounts of polyunsaturated FAs (PUFA) particularly linolenic acid (18:3) decrease substantially. This trend is consistent till the optimum concentration of salt is reached and after that, it gets changed.

16.3.6 Effect of Temperature

Temperature can significantly affect the fatty acid composition in microalgae. In general, an optimum temperature range of 20–35 °C is needed for the growth of microalgae. But there is no fixed trend, it varies with species and other stress conditions also. For example, in a few species like *N. oculata* lipid content has been found to increase on raising the temperature from 20 to 25 °C. While species like *C. vulgaris* lipid content decreases with increasing temperature from 25 to 30 °C (Converti et al. 2009). It has also been observed that the content of saturated fatty acid decreases on increasing the temperature and unsaturated fatty is increased. Lipids containing a high amount of PUFA tend to have poor cetane number and oxidative stability (Ramos et al. 2009).

16.3.7 Effect of pH

The growth media pH is another essential factor for the cultivation of microalgae. Just like temperature, the optimal pH conditions for the cultivation of microalgae depend on the strain and it lies in the pH range of 4.4–7.9. For example, a pH range of 7.2–9.0 is needed for *Cyclotella cryptica* (Jiang and Chen 2000), 6.5 for *Trichosporon fermentans* (Zhu et al. 2008), whereas a pH of 8.3 is required for *Rhodomonas* sp., *Cryptomonas* sp. and *Chaetoceros* sp. (Renaud et al. 2002). The pH of the medium not only influences microalgae growth, but also the solubility of CO_2 which is required for cultivation.

16.3.8 Mode of nutrition

Nutritional mode is another important factor that affects the lipid formation and growth rate. Generally, microalgae can be cultivated autotrophically, heterotrophically and mixotrophically. Heterotrophically grown algae possess higher lipid content as compared to autotrophic microalgae. High biomass, as well as high lipid content, have been observed in heterotrophically grown algae in presence of low light and organic carbon (Xu et al. 2006). For example, Autotrophically cultivated *C. protothecoides* possess a 14.57% lipid content, whereas those cultivated heterotrophically have 55.2% lipid content. The highest growth rate has been observed under the mixotrophic condition with the rapid cellular lipid production, it might be due to minimum cell mass loss during the dark cycle (Chojnacka and Noworyta 2004).

16.4 Stages for Biofuel Production from Microalgae

16.4.1 Cultivation of Microalgae

This is the first and very important step in microbial biofuel production. The suitable microalgal strain should be cultivated outside in bioreactors providing suitable conditions responsible for its high growth over a period of time.

16.4.2 Dewatering

After a specified period of time, harvest the microalgal culture and dewater it using a disk stack centrifugation to prepare the concentrate. Disk stack centrifuges are the most widely used method to separate the microalgal strain and have the capability of maintaining a force between 4000 and 14,000 times gravitational force, thus reducing the separation time. The microalgal paste so obtained is rinsed with distilled water to remove the impurities.

16.4.3 Cell Disruption Methods/Pretreatment Methods

Microalgae-based biofuel production depends upon how easily the content of a microbial cell can be extracted. This is done by various pretreatment methods wherein cell disruption is essential to destroy the cell wall of the microorganism so that intracellular matter leaks into the solvent. Cell disruption can be done mechanically and non-mechanically (Fig. 16.2).

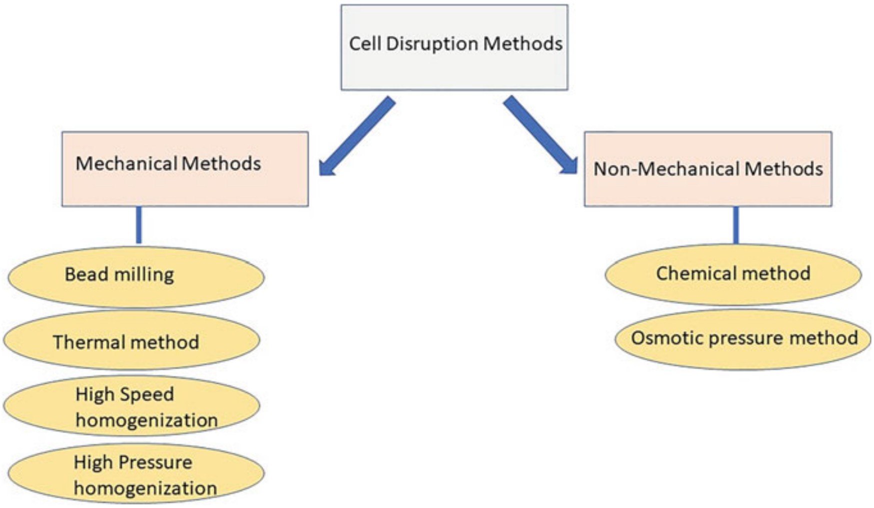

Fig. 16.2 Cell disruption methods

16.4.3.1 Mechanical Methods

Bead Milling

It is based on the principle of mechanical disruption of the cell wall by smashing the cells with the beads in bead mill machines. It is done by grinding biomass against some solid surface. The efficiency of cell disruption depends upon the dimension and load of the beads. Zirconium and glass are mostly used in making beads (Anton 1995). This process produces more lipids as compared to Soxhlet extraction and can be applied on large scale. However, it requires energy and cooling of the biomass throughout the process.

Thermal Treatments

These are physical methods involving heat such as thermolysis (Mcmillan et al. 2013), autoclaving (Larrosa et al. 2018) and steam explosion (Lorente et al. 2015). These are simple and low-cost technologies but have poor efficiency, a high energy requirement, production of unwanted cell debris and thermal resistance in some cases. Steam explosion offers many advantages like low maintenance cost, low energy requirement, economical etc. In addition, it needs a low temperature (150–300 °C) to avoid thermal degradation of biomolecules and vapour pressure in the range of 1.03–3.45 MPa. Disruption is caused by the depressurization of the system.

High-Speed Homogenization (HSH) and High-Pressure Homogenization (HPH)

High-speed homogenization is based on hydrodynamic cavitation as a result of high speed (10,000–20,000 rpm) and shear forces at the interphase (Gunerken et al. 2015). Although, it has the limitation of denaturation of proteins and needs high energy. Still, it is the most widely used method for commercial purposes as it consumes less time. Whereas in high-pressure homogenization method, high pressure of 20–120 MPa causes a turbulence and liquid shear stress. The process efficiency can be improved by optimization of operating pressure and the number of homogenization passes (Gomes et al. 2020).

16.4.3.2 Non-mechanical Methods

Chemical Method

It is a simple method in which chemicals like acids, alkali, detergents, solvents etc. are used to promote cell disruption. Many interactions take place between chemicals and cell wall constituents that rupture the cell membrane. Detergent is a surfactant that interacts with phospholipids in cell membranes thus causing cell disruption (Singh et al. 2019; Castro et al. 2015; Juárez et al. 2016). This process has the disadvantage of environmental pollution and is not economical too.

Osmotic Pressure Method

It is an ecological, innovative and cost-effective approach. The algal cell wall can be disturbed by a rapid change in the concentration of salt in the aqueous medium. This leads to a change in osmotic pressure balance inside and outside the cell wall. An algal cell can be damaged by employing two types of osmotic stresses: hyper and hypo-osmotic stresses. When concentration of salt is higher outside the cell then it suffers hyperosmotic stress and shrinks as the fluids inside the cell diffuse out. When salt concentration is low outside then it suffers hypo-osmotic stress and fluids move into the cell. As a result, the cell bursts and releases the cell content into the medium (Adam et al. 2012). A hypo-osmotic method is generally employed.

16.4.4 Lipids Extraction Methods

The composition of the microbial cell differs from one species to another. There are many types of compounds present in microalgal cells but only a few are of interest that need to be separated or isolated (Fig. 16.3). This is done by various methods which are as follows.

16.4.4.1 Solvent Extraction Methods

It is a well-known method for microbial lipid extraction which involves the disruption of the cell to promote the solvent access to inner cell compounds. Therefore, enhances the yield of the extraction compounds. It includes several methods.

Soxhlet Extraction Method

It is a classical method performed in a specialized apparatus known as the Soxhlet apparatus. In this, a sample is brought in contact with the extracting solvent, commonly hexane or petroleum ether repeatedly during the entire process. Though, it is a simple and cost-effective process but has the disadvantages of longer extraction time and large consumption of solvent (Soxhlet 1879). In the last decade, this method has been modified like high-pressure Soxhlet extraction, microwave-integrated Soxhlet extraction etc. to enhance the process efficiency (Luque de Castro and García-Ayuso 1998).

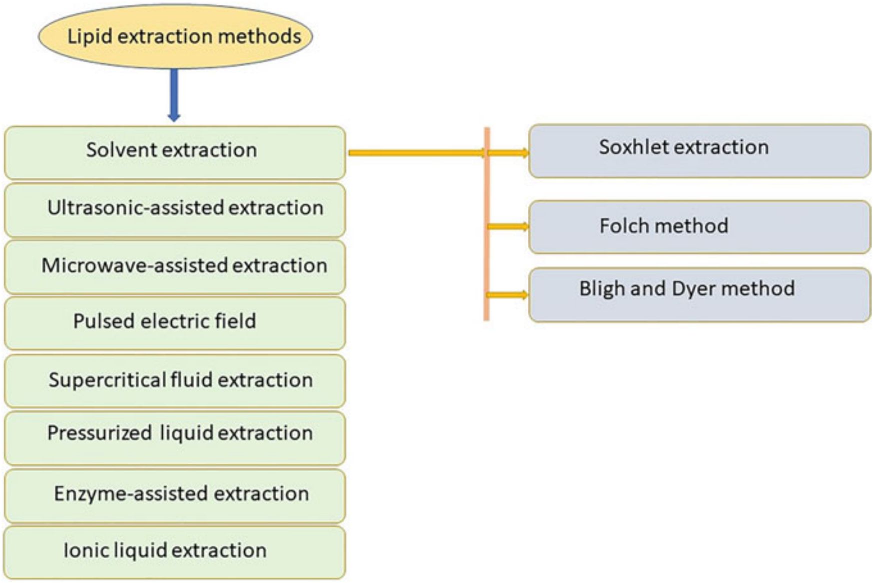

Fig. 16.3 Lipids extraction methods

Folch Method

It is the most reliable method (Jordi et al. 1957). In this method, chloroform and methanol mixture (2:1 v/v) is added to the microalgal biomass to extract the lipids followed by the addition of water to achieve phase separation. Lastly, the lipid is extracted by rotary evaporation of the chloroform layer. This method does not require drastic conditions like high pressure and high temperature. To get a better result, it has been modified by using a different combination of solvents comprising typically one polar and one non-polar solvent (Kumari and Singh 2019). It is less widely used nowadays as it poses threat to the human health and environment due to the use of toxic reagents.

Bligh and Dyer Method

It is the most extensively used method nowadays. It is based on two-phase solvent extraction. Although it is very much same as that of Folch method but differs in solvent/solvent and solvent/tissue ratios. It involves the overnight soaking of crushed cell biomass in a 1:2 (v/v) mixture of chloroform and methanol. After removing the solid residue, it is treated with 0.9% NaCl (separating funnel) and left overnight. Lipids can be extracted from the chloroform layer by evaporating the solvent (Bligh and Dyer 1959). Later on, many combinations like chloroform: methanol, dichloromethane: methanol, and ethanol: KOH have also been used to enhance the extraction of lipids. There is a safety concerns and hassle involved with the use of chloroform. Dichloromethane or hexane could be used as its substitute.

16.4.4.2 Ultrasonic-Assisted Extraction

Ultrasound-assisted extraction (UAE) is a highly efficient technique that is used for cell disruption, thus extraction of microbial lipids. It is a clean technology that uses less solvent, has a smaller extraction time, economical and environment friendly (Dang et al. 2017). This method uses ultrasonic waves having frequencies in the range of 20 kHz–10 MHz, found between audible waves and microwave ranges. There are 2 regions in the ultrasound range, first is the power ultrasound region (20–100 kHz) with high intensity mainly used in extraction, and the second is the diagnostic ultrasound region (100 kHz–10 MHz), used for clinical diagnostic purposes and quality assessment (Tiwari 2015). It works on the mechanism of acoustic cavitation (AC). It is a physicochemical phenomenon involving the evolution, growth and burst of bubbles in a solvent by ultrasonic waves. Passing of ultrasonic waves through the medium creates intermittent regions of low and high pressure depending upon applied power and produces gas bubbles. These bubbles then grow in size as per pressure applied, thus leading to compression and rarefaction after reaching a critical size collapse. The explosion of cavitation bubble near the solid surface creates a series of surface physical phenomena like erosion, fragmentation, sheer stress etc. resulting in the disruption of the cell membrane and releasing the constituents into the solvent (Saini and Keum 2018). Basically, six types of mechanisms take place in ultrasound-assisted extraction. Fragmentation occurs by the collision between particles and shockwaves produced as a result of the collapse of the bubble in solution. It reduces the particle size means a larger surface area for better mass transfer and hence becomes a driving force for better extraction yield. In erosion, solid particles are released in the solvent when bubbles collapse near the biomass (Chemat et al. 2017). The application of ultrasonic waves in a liquid generates shear force onto the biomass surface rupturing the cell and extracting constituents into the solvent (local shear stress). Sonoporation is another mechanism where cell permeability is increased that helps in the release of cell components into the solvent (Meullemiestre et al. 2016). Sono capillary is the penetration of solvent into the pores or canal of solid biomass, thereby better extraction rate whereas detexturation is the destruction of a solid matrix by ultrasounds (Pingret et al. 2012).

16.4.4.3 Microwave-Assisted Extraction (MAE)

It is a simple, cost-effective and scalable technique for microalgal cell disruption as well as the extraction of microbial lipids. It requires heating of 2500 MHz and the cell membrane is ruptured by the application of electromagnetic radiation (Piasecka et al. 2014). In microwave heating, heat is passed from inner side to outer side throughout the medium to provide the heat to the whole sample. After electromagnetic irradiation, cells absorb energy that rises the pressure and the cell wall is destroyed. Biomolecules can be extracted into a suitable solvent. Microwave absorption capabilities vary with the solvent (Virot et al. 2008). More polar solvents have better microwave absorption. Thus, the use of polar lipids can enhance lipid yield by a significant amount. But it is not suitable for volatile components of the cell.

16.4.4.4 Pulsed Electric Field (PEF)

Cell disruption from wet biomass by the application of an electric field has been a promising technique. It is more useful in the release of small molecules and water-soluble enzymes, non-polar compounds etc. from the cell (Ganeva et al. 2003). PEF induced disruption is electroporation phenomenon which is a due to the transient microbial membrane permeabilization and electrophoretic movement into the cell brought by charged species (Lafarga 2020). However, it is noted that lipid does not release into the medium after PEF due to a greater amount of lipid content. In such cases, amphiphilic emulsifiers like proteins and polysaccharides must be removed before lipid extraction. It may also require other disruption methods like an ultrasound for further rupturing the cell wall for better lipid extraction (Grimi et al. 2014). It is an energy-efficient method but not a practical method to extract microalgal lipids. It is affected by soluble ions hence, must be removed for a non-conductive medium before PEF treatment. So, this technique cannot be employed to saltwater algae.

16.4.4.5 Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction is the most effective technique for the extraction of lipids. A supercritical fluid is defined as a compound in a critical state having temperature and pressure above the critical point (Nagappan et al. 2019). It has the advantage of the use of green solvents. Among all supercritical fluids, carbon dioxide (CO_2) is mostly used because of its low cost, less toxicity, low critical temperature and pressure, and low operational cost. It prevents thermally sensitive biomolecules from degradation (Bhargavi et al. 2018). Under normal conditions, CO_2 is escaped as gas from extract, thus no need for solvent separation. It has the highest extraction rate as compared to other techniques.

16.4.4.6 Pressurized Liquid Extraction (PLE)

Like SCF, it is also a clean and green technology that uses a combination of temperature and pressure. In this, water is used in the supercritical state. When water is heated above 100 °C (boiling point) but less than the critical point keeping controlled pressure to keep the water in a liquid state. When the water reaches its supercritical state, its properties like polarity and dielectric constant change for better extraction results.

This technique is also called supercritical water extraction (Wani 2021). In the last few decades, it has been combined with microwave and ultrasonic techniques to enhance the efficiency of the process. Microwave-assisted subcritical water or dimethyl ether, propane, n-butane etc. have also been used by many researchers (Reddy et al. 2014).

16.4.4.7 Enzyme-Assisted Extraction

Disruption of the microbial cell wall is crucial in the extraction of biomolecules. To improve the results, scientists have explored a number of methods to destroy the cell wall (PEF, UAF etc.), but these techniques usually require costly instruments. Therefore, biochemical processes have been used to overcome these difficulties. Enzyme-catalyzed cell disruption is a highly selective method with low energy requirement and works under mild conditions (Zheng et al. 2016). It can prevent the degradation of thermally sensitive components. The commercially used enzymes are *cellulases*, *proteases*, *lysozyme*, *glucanases* etc. and they are used in the immobilized form (Gomes et al. 2020). These enzymes enable the extraction of intracellular lipids from microalgae after degrading the polymers responsible for the cell wall structure. It has several limitations such as low production capacity, the long process time and possible product inhibition. High cost and pretreatment prior to enzymatic hydrolysis further limit their applications. Lipid recovery can be increased many folds by pretreating the biomass with microwaves prior to enzyme-catalyzed reaction.

16.4.4.8 Ionic Liquids (ILs) Extraction

Ionic liquids are organic salts having melting points up to 100 °C. They are considered to be environmentally safe. They can be customized as per the requirement so a large number of ILs can be made. Commonly used cations are alkylammonium, alkylnitride. These cations are asymmetrical thus preventing the formation of ionic liquid crystals (Skoronski et al. 2020). They are inflammable and have high solvating power and thermal stability. Lignocellulose, the main constituent of the cell wall is soluble in ILs and thus has the capability in extracting lipids from microalgae (Kilpelainen et al. 2007). Lipid extraction by microwave/ultrasound-assisted techniques using ILs shows promising results as compared to conventional techniques. However, all ionic liquids (ILs) are not safe, ecofriendly and non-toxic. While some lead to the generation of toxic substances during the process.

16.5 Conversion of Microalgal Lipid to Biofuel

Microbial lipid is converted to biofuel by several processes such as transesterification, pyrolysis, gasification, photobiological etc.

16.5.1 Transesterification

Biodiesel is synthesized by transesterification of triacylglycerols (TAGs) or triglycerides found in the microalgae. Conventionally, reaction is carried out between microalgal lipid and alcohol in presence of a catalyst. Fatty acid alkyl esters (FAAE) or Fatty acid methyl esters (FAME) in the case of methanol used as alcohol and glycerol are the products of this reaction. Biodiesel produced by this process has the same properties as that diesel. Transesterification of microbial lipids can be carried out by homogenous catalysts as well as the heterogenous catalyst. A homogeneous catalyst such as KOH or NaOH has been used more frequently having advantages like faster reaction rate under normal temperature and pressure conditions. These catalysts have the limitation of formation of soap if free fatty acids are present in microbial lipids which creates a hurdle in biodiesel separation and purification. An acidic catalyst such as sulphuric acid, or hydrochloric acid is considered to be better to overcome this limitation. However, they usually require high temperatures and more time for completion. Conventionally, algal biomass undergoes several pretreatment steps before transesterification. This includes cultivation of microalgae, harvesting followed by drying, cell disruption and oil extraction then treatment with suitable alcohol (transesterification) under different reaction conditions to produce biodiesel. In another method where microalgal biomass is treated directly with solvent in presence of a suitable catalyst. It is a single-step process. In this process, extraction and transesterification take place simultaneously in one pot (in situ) (Patil et al. 2018). Such type of arrangements will reduce the cost of apparatus installation and energy requirements. However, there is a limitation of catalyst efficiency in a wet sample. Different straight-chain alcohols have been used such as CH_3OH, C_2H_5OH and C_3H_7OH and C_4H_9OH, but methanol is the preferred one due to its low cost and good chemical and physical properties. In several cases, both the acidic and basic catalysts have been used together. First of all, the acidic catalyst is added to reduce the free fatty acid followed by heating with an alkali for transesterification. Enzyme-catalyzed transesterification has several advantages of catalyzing a mixture of fatty acids, biocompatible and by-product removal are easy (Muller et al. 2014). Generally, lipase enzyme is used. Enzymes catalyzed reactions have some limitations like high cost, longer time and denaturation of enzymes under drastic conditions which make them unsuitable for commercial purposes. A heterogeneous catalyst such as potassium-exchanged aluminum and alkali-exchanged zeolite was found to be more promising due to ease of recovery and removal of unwanted free fatty acid, thus leading to the formation of cleaner biodiesel. These catalysts also suffer from a few limitations like high temperature and pressure and extended reaction time due to the formation of different phases.

16.5.1.1 Supercritical Transesterification

Conventional method of transesterification generally results in the formation of soap if free fatty acid is more than 0.5% and less yield in case of water present in the microalgae. Microalgae can be converted to biodiesel using supercritical methanol or supercritical ethanol and ethyl acetate transesterification (SCMT or SCET). The cost of use of anhydrous alcohol and moisture removal from microalgae are reduced. Hence, economically feasible and also eliminates the need of alcohol loading. However, it produces poor-quality biodiesel as it contains negligible C–C bonds (Wahidin et al. 2018).

16.5.1.2 Microwave-Assisted Transesterification (MAT)

The use of microwave technology in the production of biodiesel reduces the reaction time, enhanced biodiesel yield and makes the recovery of the catalyst easy. The reaction conditions like concentration of catalyst and microwave power can be optimized for better results. Though, it has the advantage of being an environment-friendly method because of the use of green solvents but has the limitation of low biodiesel production (Han et al. 2020).

16.5.1.3 Factors Affecting the Transesterification Process

- **Moisture content**: It is an important parameter that affects the process efficiency hence, the cost of biodiesel production. High moisture may make the reaction reversible, shield the oil and deactivate the catalyst. In a nutshell, high moisture content decreases the conversion efficiency of lipids to FAME.
- **Nature and concentration of alcohol**: Ideally, fat to alcohol ratio should be 1:3 as three ester bonds are to be esterified. A high concentration of alcohol promotes transesterification in a shorter time. However, it leads to higher alcohol recovery costs (Leung and Guo 2006).
- **Reaction time**: The formation of biodiesel via the transesterification process is slow in the beginning due to the dispersion of alcohol and lipid. After that, it becomes faster. A longer reaction time makes the reaction reversible and reduces the yield of the end product (Eevera et al. 2009).
- **Free fatty acid (FFA)**: The presence of FFA in microbial lipids leads to soap formation if the transesterification process is carried out with alkali as the catalyst. This enhances the viscosity of biodiesel. The formation of foams further makes the purification of biodiesel difficult (Demirbas 2005).
- **Role of catalyst**: Most commonly used catalysts in the transesterification process is NaOH and KOH. It is reported that the use of sodium methoxide in place of a mixture of methanol and sodium hydroxide is better as water produced in the latter causes hydrolysis of the end product. Also, the rate of formation of biodiesel increases with an increase in catalyst concentration (Guo 2005).

16.5.2 Biochemical Conversion

Microbial lipids can be converted to biodiesel by the use of microorganisms/yeast. It includes anaerobic digestion, alcoholic fermentation and photobiological techniques that produce different biofuels.

16.5.2.1 Anaerobic Digestion

Microalgae is rich in nutrients like proteins, lipids and carbohydrates. Complete utilization of algae biomass is an economic, environment-friendly and sustainable approach (Sialve et al. 2009). Wet algal biomass with a moisture content of up to 90% can also be used in anaerobic digestion (Brennan and Owende 2010). In anaerobic digestion, leftover microalgal biomass is transformed into biogas by microorganisms. Biogas consists of CH_4 and CO_2. Anaerobic digestion takes place in three phases. Hydrolysis is the first phase in which the complex molecules break down into simple molecules. These simple molecules then undergo fermentation (second phase) into fatty acids, acetic acid, volatile alcohols and a mixture of H_2 and CO_2 gases. In the final phase called methanogenesis, this gas mixture produces biogas which consists of methane and carbon dioxide (Cantrell et al. 2008). Besides main nutrients, microalgae also contain traces of elements like Zn, Fe, Co etc. which promote methanogenesis. The presence of more lipids in microalgae generates more methane although the hydrolysis reaction is slow. The recalcitrant nature of microbial cell wall is a challenging task as it further slows down the process. Cell disruption techniques can be employed to rupture microbial cell wall to tackle this issue.

16.5.2.2 Alcoholic Fermentation

Algal biomass of a few strains like *Botryococcus braunii*, *Chlorella*, *Chlamydomonas*, *Scenedesmus*, *Dunaliella* is rich in various types of carbohydrates and proteins that are used for the biofuels production such as biohydrogen, biodiesel and bioethanol (Song et al. 2018). Algal-based bioethanol has the advantage of high-octane number and high heat of vaporization as compared to conventional fuels (Formighieri 2015). Carbohydrates are found in the cell wall and cytoplasm of microalgae. Bioethanol is produced using chemical and biochemical approaches (Fan et al. 2012). Although, microbes have difficulty in metabolizing the polysaccharides so they are first hydrolyzed by chemicals (acid or alkali) method or enzymes. In the biochemical process, biomass is fermented using ethanologenic microbes under aerobic or semi-anaerobic conditions. The production of bioethanol is an extensive process that involves the collection and handling of microalgae to preserve its extract and prevent the algae from gelling (Nguyen and Vu 2012). After that, it is subjected to pretreatment methods like washing, drying and milling followed by hydrolysis of complex polysaccharides like cellulose and hemicellulose to monomeric fermentable sugars. Finally, these simple sugars are fermented by microorganisms like *Cerevisiae*, *E. coli*, *P. stipites*, *Kluyveromyces fragilis*, *Z. mobilis* etc. to bioethanol. Fermentation is a metabolic conversion of monosaccharide to bioethanol and other byproducts under suitable temperature and pH conditions. Yeast or bacteria releases enzyme that act on sugar moiety to form organic acids, gases or alcohol in anaerobic conditions (Mussato et al. 2012). *S. cerevisiae* is regarded as safe to use by FDA and non-pathogenic in nature. It is the most widely used yeast.

16.5.2.3 Photobiological Hydrogen Production

Few algal biomasses are capable of producing hydrogen gas in the presence of light. Water is converted into oxygen and hydrogen ions by microalgae during photosynthesis stage. Hydrogenase enzymes then reduce hydrogen ions into hydrogen gas. However, oxygen released during the process of photosynthesis impedes the hydrogenase enzyme and interferes with H_2 gas production. Therefore, an anaerobic condition is to be maintained for growing microalgae for H_2 gas production (Cantrell et al. 2008). There are two approaches that are involved in the photosynthetic generation of H_2 gas. In the first approach, oxygen and hydrogen are produced simultaneously in plenty of light. Oxidation of water produces electrons that are consumed by hydrogenase enzymes to produce hydrogen gas. The second approach consists of two steps where the first step involves the culturing of microalgae under normal conditions and the second step is the production of hydrogen gas under anaerobic and lack of sulphur conditions. The deficiency of sulphur put the microalgae in the survival stage and the energy requirement by the cell is fulfilled by the release of hydrogen (Ghirardi 2000). Although the first method has a higher yield as compared to the second method but hydrogen production is limited by the production of oxygen (Melis and Happe 2001).

16.5.3 Thermochemical Conversion Technologies

In thermochemical conversion technologies, organic matter in biomass is decomposed to produce biofuels. It has the advantage of a shorter time as compared to biological conversion. Moreover, it has the potential to be integrated into existing petroleum processing structures. These technologies include pyrolysis, liquefaction and gasification that produce liquid/ gaseous biofuels that can be upgraded to drop-in biofuels (Karatzos et al. 2014).

16.5.3.1 Pyrolysis

Pyrolysis is made up of two words pyro means high temperature and lysis means to break down. It involves the breaking of large molecules of biomass at high temperature (~500 °C) in oxygen-deprived conditions and produces a mixture of gases, biochar and H_2O soluble and insoluble organics, also called bio-oil (bioliquids). The yield and properties of fraction obtained during pyrolysis depend upon temperature, residence time, heating rate and catalyst. This process produces large amounts of syngas due to the existence of high amount of volatile matter and no moisture. In pyrolysis, high amount of CO_2 is produced when the temperature is up to 300 °C but on increasing the temperature to 600 °C, it is converted to CO. Pyrolysis is categorized as slow pyrolysis and fast pyrolysis according to vapour residence time. In slow pyrolysis, vapour residence time is from several minutes to hours and it has been used for the production of charcoal for many centuries. Residence time is decreased to a few seconds during fast pyrolysis to maximize liquid yields. Emphasis has been out on the production of bio-oil as it can easily be stored and transported for its upgradation to high-quality drop-in fuels. It can be a suitable substitute for light and heavy fuel oils in the industrial boiler (Mohan et al. 2006).

Microwave-Assisted Pyrolysis (MAP)

Traditional pyrolysis uses heated sand or surface whereas MAP is a modern technique in which electromagnetic waves are passed through material to cause oscillation and generate heat. MAP has an advantage over traditional pyrolysis because of the following reasons:

- Uniform heating thus, can be applied on large particles.
- Syngas produced in MAP has higher heating value as there is no dilution by carrier gas like the traditional method.
- Products are clean because of no agitation and fluidization in the process.
- It is easy to scale up.

Algal biomass is a poor absorber of microwave radiation. The addition of microwave absorber material improves its heating. The biochar obtained from the pyrolysis of biomass is an excellent absorber of microwave radiation. In MAP, algal biomass is mixed with biochar in a variable proportion. After that, the sample is placed in a commercial microwave under an inert atmosphere of nitrogen gas. The condensable volatiles are to be collected by cooling them with water. The nature of feedstock and reaction conditions determines bio-oil and biogas composition.

16.5.3.2 Liquefaction

It is similar to pyrolysis and is used to convert biomass to bio-oil or biocrude with hydrogen at low temperatures (250–380 °C) and elevated pressure (40–220 bar) in the presence or absence of a catalyst. Hydrothermal liquefaction (HTL), also called hydrous pyrolysis uses subcritical water (SCW) (Dimitriadis and Bezergianni 2016). This method uses wet algal biomass to minimize the cost of the drying or dewatering phase. Woody biomass is suitable feedstock as it contains a high amount of cellulose, hemicellulose and lignin. The yield of bio-oil is influenced by operation conditions, catalyst and solvent (Langholtz et al. 2016). Deep eutectic solvents (DESs) can be used in place of ionic liquids owing to their simple preparations, low toxicity, economical and stable nature (Alhassan et al. 2016). Sewage sludge can be a promising feedstock for hydrothermal liquefaction. But wet sludge has a high moisture content that affects the quality of bio-oil.

16.5.3.3 Gasification

In gasification, microalgal biomass is partially oxidized into fuel gas at very high temperatures. During the process, the biomass is subjected to pressure (of 1–40 bar) at a temperature of more than 800 °C in the presence of limited supply of oxygen. This process usually carried out with air or steam, converts carbonaceous material into a mixture of CO, H_2, CO_2 and low M.wt. hydrocarbons (Demirbas 2001). A mixture of H_2 and CO is called synthesis gas or syngas. It is an efficient technique in H_2 gas production in terms of its recovery and higher heat capacity (Ahmad et al. 2016). It involves a simple conversion of CO and CO_2 of syn gas to synthetic natural gas by catalytic methanation. The composition of gas produced in the gasification process depends upon the type of catalyst, gasifier, gasifying agent and size of particles.

Limitation of Biofuels

1. Oxygen content in bioethanol and FAME biodiesel is nearly in the range of 35–11% by weight of these biofuels. The energy density of bioethanol/FAME is reduced due to the presence of oxygen, which in turn decides the size of the fuel tank and transportation mode. Fuel density significantly influences the volume and mass of a fuel which has a greater impact on take-off weight for aviation, thus affecting economics.
2. These biofuels are more reactive because of the presence of oxygenated functional groups in biodiesel (FAME or bioethanol). This accelerates the formation of gums, acidic compounds and other impurities that affects the stability, hence storability of biofuels (Pearlson 2011).
3. The biofuels are hygroscopic in nature further contaminating the fuel. Adsorption of water from atmosphere encourages the bacterial growth (acetobactor) which produces CH_3COOH that damages the metal pipes in engines. This is the main problem associated with them thus make unfit to be used in aged vehicles and marine engines.

4. Biofuels and bioethanol are not compatible with the present engine system and thus need modification. Also, change of existing infrastructure like vehicle engines, fueling stations etc. involves a high cost.

16.6 Drop-in-Biofuels

Drop-in-biofuels could be the potential alternative. "Drop in biofuels has been defined as liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels but their chemical composition is different" (Sergios et al. 2017). For example, hydrotreated vegetable oil (HVO). This technology is relatively mature and commercialized. Other techniques to develop drop-in-biofuels are at the development stage. Functional properties of biofuels are measured against standard specifications such as ASTM standards like carbon number, freezing point, boiling point, flash point, aromatic content etc. Petroleum fuels are characterized on the basis of carbon number and boiling point. Gasoline is composed of hydrocarbons (C_4–C_{12}) with aromatic constituents of 20–40%. Diesel contains C_{10}–C_{22} hydrocarbon with 25% of aromatic compounds. Aviation fuel contains C_8–C_{16} with aromatic components up to 25%. Jet fuel has a very low freezing point of −40 °C, low viscosity at low temperatures and is thermally stable. But biodiesel freezes at 0 °C in spite of having similar energy density, thus unsuitable for aviation applications.

16.6.1 Upgradation of Pyrolysis Oil

Pyrolysis oil also called py-oil or bio-oil needs to be upgraded due to above-mentioned reasons. Listed below the methods involved in its upgradation.

16.6.1.1 Hydrodeoxygenation Upgradation (HDO)

HDO also called hydrotreatment that imparts additional benefits like high yield and quality of oil with higher carbon content. In this process, oxygen is eliminated from oxygenated hydrocarbons by catalytic reaction at high pressure of around 2000 bar at a temperature of 400 °C in presence of hydrogen (Bridgewater 2012). It does it by hydrogenation of functional groups like carbonyl group, double bonds in alkenes, dehydration of C–OH groups, hydrogenolysis of C–O–C bonds and condensation and decarbonylation reaction (Huber et al. 2006). It improves oil stability, storability and increases density (Zhang et al. 2013).

16.6.1.2 Catalytic Upgradation

In this, the catalyst is used in bio-oil upgradation. This is done in two ways. The first method involves the use of a metallic catalyst and the second one is integrated catalytic pyrolysis (Dhyani and Bhaskar 2018). In the catalytic method, vapours produced during pyrolysis are cracked further within the catalyst pore. These catalysts convert compounds like –COOH, –CO, responsible for acidity and viscosity to alcohol. Mostly zeolites are used in oil refineries. Zeolites being capable in breaking down the long hydrocarbon chains and promote the formation of aromatic hydrocarbons, are mostly used in oil refineries. The size of mesopores in zeolite catalysts is an important consideration. Large-size mesopores ensure the entry of large-size biomass into zeolite (Perkins et al. 2018). In integrated catalytic pyrolysis, unique temperature condition and a catalyst that can withstand high temperature and mechanical conditions are required. It has less scope in working conditions as the catalyst used are quite complex.

16.7 Analysis and Characteristics of Biodiesel

The percentage yield of biofuel can be calculated by the following formula

$$\text{Percentage of bio-oil (yield)} = \frac{\text{mass of bio-oil}}{\text{mass of microalgae}} \times 100$$

16.7.1 FT-IR

The FT-IR analysis is done to know the functional groups present in the biodiesel. Three types of peaks are generally observed in biodiesel i.e., FAME is characteristic of alkanes, esters and alkyls. The stretching bands due to symmetric and asymmetric modes of vibrations of C–H bonds tend to appear around 2800–2950 cm^{-1}. Peaks observed in the range of 1700–1750 cm^{-1} and 1320–1100 cm^{-1} are due to C=O bond and C–O bond stretching that confirms the presence of the ester bond in biodiesel.

16.7.2 Gas Chromatography (GC) Analysis

GC is carried out to know the fatty acid composition of each fuel by comparative analysis with the standard test method. It is an important tool to know the quality of biodiesel on the basis of the composition of biodiesel.

Table 16.1 Properties of microalgae-based biodiesel and petroleum diesel (Amin 2009; Xu et al. 2006; Haik et al. 2011; Azad et al. 2014)

Properties	Microalgal based biodiesel	Petroleum diesel	ASTM biodiesel standard
Density	0.864 kg/L	0.838 kg/L	0.86–0.90 kg/L
viscosity (40 °C)	5.2 mm^2/s	1.9–4.1 mm^2/s	3.5–5.0 mm^2/s
Calorific value	41.0 MJ/kg	43.8 MJ/kg	–
Cloud point	7 °C	− 15 to 5 °C	− 3 to – 12 °C
Pour point	− 6 °C	− 35 to – 15 °C	− 15 to – 16 °C
Flash point	115 °C	75 °C	100 °C (min.)
Solidification point	− 12 °C	− 50 to 10 °C	–
Cold filter plugging point	− 11 °C	− 3.0 °C (max − 6.7)	0 °C (summer) and <− 15 °C (winter)
H/C ratio	1.81	1.81	–

16.7.3 Properties of Biodiesel

Green biodiesel or microalgal diesel is a liquid fuel that can be employed for internal combustion (IC) engines. After synthesizing biodiesel from microalgae, it is essential to know its fuel properties for its application as engine oil. The biodiesel can be characterized by its higher heating value, density and viscosity. The heating value of biodiesel differs from species to species of microalgae. A comparison of the properties of biodiesel and petroleum diesel has been summarized in Table 16.1.

16.8 Conclusion and Future Directions

Microalgae are unicellular microorganisms which are capable in production of large amounts of triacylglycerols (TAGs) that can be converted into biofuel. The microalgae-based biofuels are the potential alternative to fossil fuels for an internal combustion engine. It is a green and renewable source of energy. Microalgae cultivation on a large scale is feasible, hence biodiesel production. Microalgae can be cultivated easily, have a high growth rate and lipid content can be enhanced by employing various stress conditions. They are also considered an indication of a healthy environment as they can use greenhouse CO_2 gas for their growth. Green solvent and less energy requirement-based extraction processes such as supercritical fluid extraction (SCF) and microwave/ultrasound-assisted extraction (UAE) seem to be better. However further options can be explored. Due to the high cost involved in harvesting, dewatering and oil extraction from microalgae their commercialization is limited. Manipulation of cell biology of microalgae that allows easy secretion of lipids directly into the growth medium will greatly reduce the cost of biofuel production. Hence, some work needs to be done in this direction.

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Chapter 17
Future Research on the Sustainable Utilization of Wastewater as Resources with Emphasis on Plastics

Gustavo Emilio Santos-Medrano, Daniel Robles-Vargas, Ignacio Alejandro Pérez-Legaspi, and Roberto Rico-Martínez

Abstract The depletion of macronutrients, the increasing costs of producing nutrients and fertilizers, metal components, concerns about environmental effects, recycling trends in big companies, are among others significant factors boosting the need for obtaining resources from wastewater. New biological, chemical, and physical technologies allow the recycling of metals, nutrients, plastics, gases, and other materials from wastewater with affordable prices and friendly environmental conditions. The goal of sustainable wastewater management is to recover, recycle and transform hazardous materials into useful products. A critical review of the most recent publications in this field is needed together with recommendations and suggestions for future research.

Keywords Wastewater management · Wastewater treatment plants · Environmental toxicology · Metal toxicity · Eutrophication · Recycling

17.1 Introduction

In the last years many authors have proposed drastic changes in the traditional water management. Water recycling is now seen as a key feature in the future of water management (Chanan et al. 2013). The strategy proposed by several authors include an integrated system, multidisciplinary cooperation, small scale options to solve specific problems that would allow water recycling (Chanan et al. 2013). Water recycling is considered an important strategy for urban water management (Marks

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P. Singh et al. (eds.), *Wastewater Resource Recovery and Biological Methods*, Springer Water, https://doi.org/10.1007/978-3-031-40198-5_17

2006). In this strategy wastewater is seen as a valuable resource rather than as a nuisance and can be treated to obtain differential qualities for different uses (Hakim 2002). Wang et al. (2018) has suggested that water infrastructure which is evolving towards resource recovery should go in hand with ecological natural processes to enhance harmony with nature.

As the population grows, the demand for water increases and the availability of the vital liquid decreases. There are alternatives to resolve this problem as an example: Increase and improve programs for their efficient use, generate new and better monitoring, recovery, and control projects. Reinforce participation between society, politicians, water administrators, technicians and scientists; develop and transfer new technologies for supply and treatment; in addition to making existing technologies more efficient, and promoting and giving priority to water reuse projects, which would contribute considerably to reducing its demand, contamination and overexploitation, generating a reduction in the costs that these aspects require, in addition to obtaining a cleaner environment and the sustainable use of water.

It is important to point out that there is a very close relationship between collection, conduction and treatment of water. However, there are differences between these processes, since each one has its own objectives. For example, treatment requires the above steps to achieve its objectives, and these in turn pursue different purposes: protection of aquatic life, reduction of eutrophication in water bodies by removing nutrients and solids, prevention of pollution of groundwater, protection of public health, and reuse of treated wastewater (Fig. 17.1).

In this chapter we would summarize the state-of-the-art research and ideas on reutilization of wastewater.

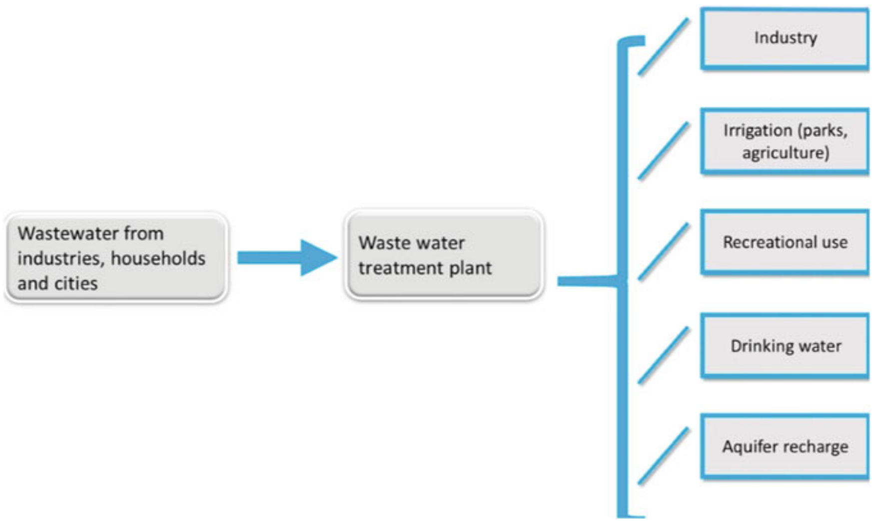

Fig. 17.1 Scheme indicating the possible uses of treated water from different sources

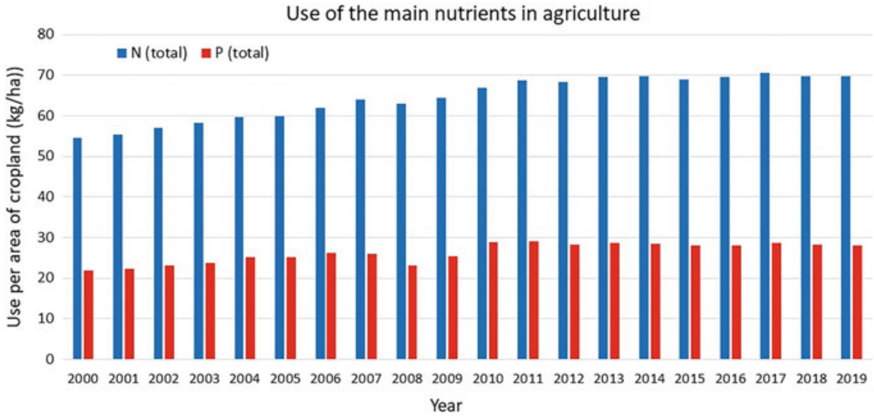

Fig. 17.2 Increased use of the main nutrients used in agriculture

17.2 Fertilizers (Mainly Phosphates and Nitrogen and Their Salts)

Fertilizer consumption is one of the main indicators of agricultural intensification and agricultural development, where the most used nutrient is nitrogen, since it directly affects yields and product quality. The effect of nitrogen on the environment should be noted with concern, as it can source eutrophication of waters, excessive growth of algae, acidification of the soil and the destruction of natural habitats with low nutrient content (Tassara and Ortega 2003). This increase in the use of P and N is observed in Fig. 17.2.

According with Winpenny et al. (2010) the agriculture area is well known for the major user of water (nearly 70% of global water usage). It is estimated that worldwide 20 million hectares are irrigated with wastewater (Ecosse 2001).

About a 20 million hectares worldwide are irrigated with wastewater suggests a major source for irrigation. However, most of the wastewater used for irrigation is not treated (Scott et al. 2009). Untreated water includes risks due to the presence of toxic compounds such as heavy metals, pesticides, fertilizers, drugs, etc.

17.3 Wastewater Treatment

Primary treatment: This initial step is intended to remove solids from the raw sewage. The wastewater treatment process includes screening to trap solid objects and gravity sedimentation to remove suspended solids. This stage of treatment reduces the BOD of the incoming wastewater by 20–30% and the total suspended solids are approximately 50–60% (Kesari et al. 2021).

Secondary Treatment: This stage removes the dissolved organic matter remaining from the primary treatment. The microbes consume organic matter to create carbon dioxide, water and energy. Additional sedimentation removes more suspended solids and reduces the amount of Biological Oxygen Demand (BOD) by approximately 85%. After the water is processed through a sedimentation pond, it is chlorinated. At this point, the water may still contain several types of contaminants (chemical and biological). Therefore, in order for the water to be reused for irrigation, it must pass through filtration and then be disinfected. Sodium hypochlorite is used to disinfect wastewater. Following this process, the treated water is considered safe to use for irrigation purposes (Kesari et al. 2021).

The tertiary treatment process ensures that nearly 99% of all impurities are removed from the wastewater. To make the treated water for drink, the water is treated individually or in combination with advanced methods such as ozone, ultrasound and ultraviolet light. This process helps remove bacteria and heavy metal contaminants left in the treated water; at this point and after making sure that appropriate purification standards are accomplished, the treated water can be available for drinking, agriculture or recreation (Kesari et al. 2021).

17.4 Other Technologies for Tertiary Treatment

At the end of the 1980s, nanofiltration (NF) membranes were developed, with intermediate properties between ultrafiltration (UF) and reverse osmosis (RO). The main characteristic of these NF membranes is that they have a size of 1 nm, which corresponds to a molecular weight limit of 300–500 Da, a property of these NF is that when in contact with an aqueous solution they are also slightly charged. Due to dissociation of surface functional groups or adsorption of charged solute (Mohammad et al. 2015). NFs have been shown to remove pharmaceutical and personal care products (PPCPs) that are generally barely removed in most conventional wastewater treatment plants (Lin et al. 2014; Mohammad et al. 2015). Lin et al. (2014) investigated two NF membranes (NF90 and NF270) for removal of six PPCPs, including carbamazepine, ibuprofen, sulfadiazine, sulfamethoxazole, sulfamethazine, and triclosan, with a 90–100% removal rate. Röhricht et al. (2010) used nanofiltration membrane at a relatively low pressure of only 0.7 bar; at such a low pressure, the membrane does not retain a large part of the salts. This is advantageous in wastewater treatment because no salt concentrate is produced, however carbamazepine was only slightly retained by the nanofiltration membranes, while diclofenac was retained by approximately 65%.

To date, there is knowledge for the treatment of residual water and its reuse, however, the economic conditions of each country affect the development of these technologies, as well as political interests. It is disappointing that worldwide only 43% of water is treated and only 15% is reused, it is necessary to raise awareness among citizens, governments and private companies to have a sustainable use of water (Fig. 17.3).

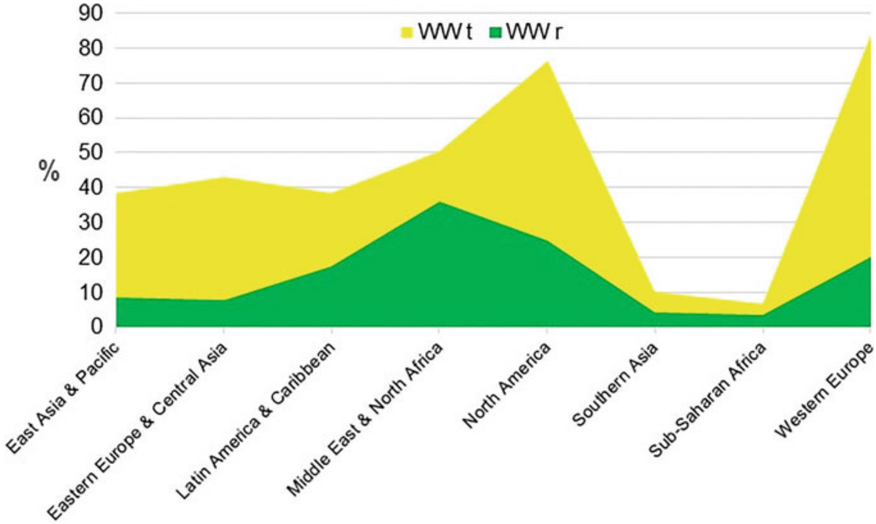

Fig. 17.3 Percentages of water treatment (WWt) and reuse (WWr) in the different regions of the world (Jones et al. 2021)

17.5 Plastics

Plastics have become a practical solution not just for companies but for the whole society as they cover important needs specially in packaging, consumer products and construction (Plastic Soup Foundation 2022). Worldwide plastic production has increased considerably in last decades which doubled from 2000 to 2019 and reached 460 million tonnes in 2019 (OECD 2022). Due that most plastics are single-use no policies (if available) for a proper management, disposal, recycle or processing have been stablished (Klemeš et al. 2021), which unfortunately has contributed to their accumulation in the environment including aquatic systems (Du et al. 2021). Among the main plastic polluter industries, soft drink producers contribute with the highest pollution rate (56%) followed by the nutrition industry with 27% (Plastic Soup Foundation 2022) (Fig. 17.4). Even though a recycling culture has raised in different countries only 9% of global plastic waste is recycled (OECD 2022) and approximately 79% ends in landfills or in natural environments (Van Emmerick and Schwarz 2019).

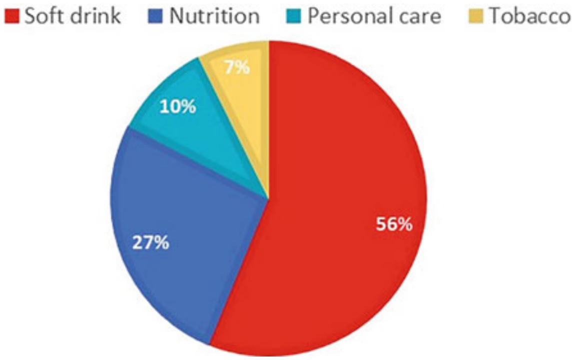

Fig. 17.4 Main plastic polluter industries

17.6 Current Scenario

Once plastics have reached water bodies they might undergo a gradual degradation due to different factors, such as ultraviolet light exposure, mechanical fragmentation, hydrolysis, and biodegradation (Eriksen et al. 2016) that lead to the formation of small pieces of plastics which according to their diameter are denominated microplastics (MP) (<5 mm) and nanoplastics (<100 nm) (Windsor et al. 2019). The former, are generally classified as primary and secondary microplastics as well depending on their origin, while the primary are originated from personal care products, the secondary are generated by the degradation of larger plastics (Liu et al. 2022). There are other categories of plastics regarding their size, nevertheless, here we review only the smallest particles that became relevant in past decade to evaluate their impact in microfauna from aquatic systems. Different studies have evaluated microplastic pollution in marine waters from all continents, however, studies are still limited to a few countries and there is an evident lack of information about the level of contamination in freshwater systems (Fig. 17.5) (Szymańska and Obolewski 2020; Chen et al. 2021).

17.7 Ecotoxicological Studies in Planktonic Organisms

Microplastics are widespread in the environment, unfortunately, their impact in aquatic biota is poorly understood, and majority of studies have been performed in marine systems (de Sá et al. 2018), however, in this section we review the effects in freshwater species. In general, microplastic and nanoplastic might affect digestive system, feeding and antipredator behavior or cause death (Gregory 2009; Barboza et al. 2019). Main findings related to microplastic and nanoplastic effects on freshwater organisms are shown in Table 17.1.

In addition, some other studies evaluated the effect of plastics combined with toxicants. Tourinho et al. (2022) found that polyethylene terephtalate microplastic

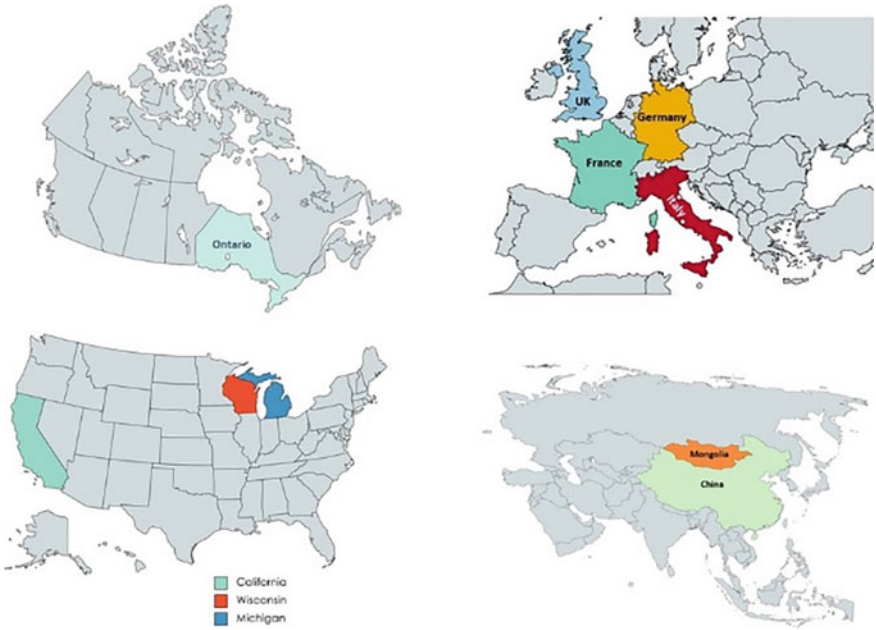

Fig. 17.5 Geographic zones where have been performed studies to evaluate microplastic pollution

fibers (360 μm average length) alone or in combination with silver reduced cellular energy allocation (biomarker for metabolic cost of contaminant exposure). Yuan et al. (2020) tested the toxicity of four metals (Pb, Cu, Cd and Ni) mixed with polystyrene microplastic (10 μm) on the cladoceran *Daphnia magna* and observed greater toxicity at a microplastic concentration between 100 and 1000 mg/L. Furthermore, Liao et al. (2020) reported cavitation in *Euglena gracilis* induced by particles of PS (5 μm) in presence or absence of cadmium. Regarding the effects of microplastic and organic pollutants, Schrank et al. (2019) assessed the toxicity of flexible PVC which contains the plasticizer diisononylphthalate on *D. magna* and noted an increase in body length and less offspring. Finally, Zhang et al. (2019) studied the combined effects of the antibiotic roxithromycin and PS (1 μm) on *D. magna* and found that the co-exposure to these pollutants can lead to a strong oxidative stress in the organisms.

17.8 Microplastics in Aquatic Media

There are different ways for MP to enter the aquatic environment, such as discharges of wastewater treatment plants (WWTP), agricultural runoff from land treated with sludge (used as fertilizer), overflow of sewage water, escapes from industrial facilities, and atmospheric deposition (Eriksen et al. 2013; Vermerein et al. 2016). Furthermore, Lebreton et al. (2017) estimated that rivers may transport between 1.15 and

Table 17.1 Effects of plastics in freshwater organisms

Microplastics		
Species	Effect/Finding	Reference
Chlorella pyrenoidosa	**PS**: GI, DPA, SD, CWT	Mao et al. (2018)
Microcystis aeruginosa	**PE**: GI	Luo et al. (2020)
Microcystis panniformis	**PS**: GI	Cunha et al. (2019)
Raphidocelis subcapitata	**PP, PS, PVC**: Leachates of microplastics induced GI	Capolupo et al. (2020)
	PE: GS	Canniff and Hoang (2018)
Scenedesmus obliquus	**PS**: DPA	Liu et al. (2019)
Scenedesmus subspicatus	**PE**: GI	Baudrimont et al. (2019)
Danio rerio	**PA, PE, PP, PVC** and **PS**: Morphological and histopathological changes	Lei et al. (2018)
Hyalella azteca	**PP** and **PE**: Mortality	Au et al. (2015)
Nanoplastics		
Organism	Effect/Finding	Reference
Chlamydomonas reinhardtii	**PS**: Transfer to higher trophic level through diet with toxicity	Chae et al. (2018)
	PS: DPA, GI, MD	Li et al. (2020)
Euglena gracilis	**PS**: GI, OD, DPA	Liao et al. (2020)
Microcystis aeruginosa	**PS**: DPA	Zhang et al. (2018)
Raphidocelis subcapitata	**PS**: SD	Bellingeri et al. (2019)
Scenedesmus obliquus	**PS**: GI, DPA	Besseling et al. (2014)
	PS: MD	Liu et al. (2019)

Abbreviations CA: cavitation; CWT: cell wall thickening; DPA: decrease photosynthetic activities; GI: growth inhibition; GS: growth stimulation; MD: membrane damage; OD: oxidative damage; PA: polyamide; PE: polyethylene; PP: polypropylene; PS: polystyrene; PVC: polyvinyl chloride; SD: structural damage

2.41 million tonnes of plastic to oceans every year. Sludge generated in WWTP have become a hotspot due their high content of MP as shown in the review of Rolsky et al. (2020). Moreover, Li et al. (2018) estimated that in average 1.56×10^{14} of sludge-based MP enter into natural environment each year in China as sludge is commonly applied in farmlands (Nizzetto et al. 2016). Besides, from the analysis of data performed by Gatidou et al. (2019), WWTP are able to remove from 72 to 99% of microplastic, nevertheless, despite these MP removal efficiencies, large amounts of plastics are released into the environment given the high volumes involved. For example, a WWTP near Vancouver, Canada, even when retain up to 99% of MP the facility releases approximately 30 billion MPs to the environment every year (Gies et al. 2018). In the US, Mason et al. (2016) tested 17 WWTP and estimated that near 4 million MP are released per facility per day.

17.9 Microplastic Removal in Wastewater

To date, there are several recycling methods for sustainable plastic waste management which are classified as primary, secondary, tertiary and quaternary recycling and are fully described by Kumar et al. (2021) and Chen et al. (2022), however, these methodologies are applied on large plastics while treatments for small plastic particles recovery from wastewater are still under study at lab level. Ordinary treatments from wastewater treatment plants exhibit high removal efficiencies as shown in Fig. 17.6, where the media percentage from different studies is plotted (Tang and Hadibarata 2021).

In addition, some researchers have tested novel alternatives. Misra et al. (2019) assessed a magnetic nanoparticle composite to remove spherical polystyrene beads (1 and 10 μm) and registered a 100% removal. Wang et al. (2020) added biochar to sand filter systems and reported an efficiency above 95%. Perren et al. (2018) were reached a 90% microbeads removal using the Al-based electrocoagulation technique. Sarkar et al. (2021) coupled pulse clarification and filtration and removed up to 85% of MP.

Each method may have its advantages and disadvantages. However, the final target must be a high MP removal or chemical modification for a later use which could include generation of syngas, chemicals or use of plastic waste in thermo-chemical processes for energy generation (Kumar et al. 2021). Further studies are needed to assess the possibility to use treated water in farmlands, industries, or even to recharge watersheds or for recreative activities.

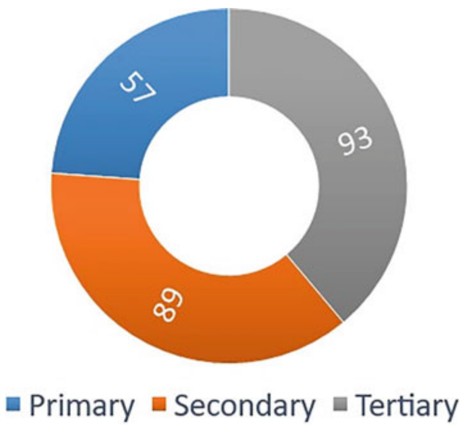

Fig. 17.6 Removal of microplastics by conventional wastewater treatments

17.10 Metals

Metal recovery is a big part of the research proposed and already taking place in urban wastewater treatment. A chapter in this book (Sect. 17.11) is dedicated to this topic. Suffice to say that many improvements are currently being designed and applying in WWTPs worldwide and many experiments are being conducted to improve many of the techniques in specific ways. Today, metals like Ag, As, Au, Cd, Cr, Cu, Fe, Mo, Pd, Se, U, and V (among others) have been recovered from wastewater (see Sect. 17.11). Research in Bioelectrochemical Systems (BES), coagulation, flocculation, precipitation, electroplating, electrochemical systems, photocatalysis and other techniques used to recover metals should continue. Especially important is to design and escalate these techniques to ensure they are introduced as part of WWTP's for agricultural and municipal discharges in a bigger scale, yet in selected locations designed for specific discharges.

17.11 Conclusions and Prospectives

Today macronutrients like nitrogen (N) and phosphorous (P) are recovered in many WWTPs worldwide and many other WWTPs are well suited to pass from removal to recovery of N and P. Calcium (Ca) and potassium (K) are also recovered from several WWTPs worldwide. Particular industries are well suited for recovery of other nutrients. Microplastics and metals can also be removed and eventually recovered from the environment in agricultural, industrial or municipal WWTPs. However, the methodologies to be implemented sometimes are costly and adequate only for selected discharges. Metal recovery is an area of great opportunities as some metals can be considered micronutrients indispensable for life. Some industries might view metal recovery from wastewater as a valuable economic enterprise for specific discharges. We have included plastics in this chapter as a remainder of the need for plastic removal in our wastewater to avoid entrance of microplastic in trophic webs. Besides, some plastics might be worth to recover from the filters of wastewater in municipal WWTPs. Today many researchers are employing different and sometimes sophisticated techniques for metal recovery and for recovery of specific nutrients for certain industries. Experimental set ups dedicated to answer specific scenarios in nutrient recovery are being implemented every day. The results of these investigations would likely result in changes in particular WWTPs that will incorporate nutrient recovery in the routinary processes. The incorporation of these technologies already developed at the experimental level would likely result in a more sustainable world.

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