Journal of Environmental Chemical Engineering 5 (2017) 2782–2799

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Review

Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review

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ARTICLE INFO

Keywords:
Heavy metals
Wastewater
Environment
Treatment technologies
Sequestration

ABSTRACT

The controversy related to the environment pollution is increasing in human life and in the eco-system. Especially, the water pollution is growing rapidly due to the wastewater discharge from the industries. The only way to find the new water resource is the reuse of treated wastewater. Several remediation technologies are available which provides a convenience to reuse the reclaimed wastewater. Heavy metals like Zn, Cu, Pb, Ni, Cd, Hg, etc. contributes various environmental problems based on their toxicity. These toxic metals are exposed to human and environment, the accumulation of ions takes place which causes serious health and environmental hazards. Hence, it is a major concern in the environment. Due to this concern, the significance of developing technology for removing heavy metals has been increased. This paper contributes the outline of new literature with two objectives. First, it provides the sketch about treatment technologies followed by their heavy metal capture capacity from industrial effluent. The treatment performance, their remediation capacity and probable environmental and health impacts were deliberated in this review article. Conclusively, this review paper furnishes the information about the important methods incorporated in lab scale studies which are required to identify the feasible and convenient wastewater treatment. Moreover, attempts have been made to confer the emphasis on sequestration of heavy metals from industrial effluent and establish the scientific background for reducing the discharge of heavy metals into the environment.

1. Introduction and scope

Today, the environmental importance of water is considered as basic necessary everywhere in the world. The primitive requirement for human livelihood is water. The serious environmental burden is rising due to the water contamination and water insufficiency and its limited availability is increasing nowadays due to the destruction of natural water supports. This makes the reduction in the development of economic status, human sustenance and environment [1]. Environmental protocols were changed in the past few years to diminish the water pollution [2]. Due to the rapid rise of urbanization, climatic change, utilization of natural resources and food requirement, around 40% of the population are facing the water scarcity issues [3]. The utilization of fresh water for agricultural and industrial purposes are growing which results in water demand. This concern can be solved using reclaimed wastewater is a recent authority for water supply [4]. But this authority is based on the updated wastewater regulations. Though, the reclaimed water plays a major in reducing the above-mentioned issues, certain health effects can occur due to the presence of pathogenic organisms, endocrine disrupting chemicals (EDC), pharmaceutical products, personal care products (PCP), organic compounds in it [5–7]. This review paper attempts to devote the summary of treatment technologies available for the sequestration of heavy metals from the industrial effluent. The main intention is to provide useful information about the most relevant features of the removal methods and to give a sketch of several studies. Based on this topic we have categorized the treatment practices into seven techniques. They are coagulation/flocculation, ion exchange, flotation, membrane filtration, chemical precipitation, electrochemical treatment, and adsorption. This paper gives the brief view on the research studies about the merits and demerits of treatment methods. The current review article also deals with the critical issues and health effects about the heavy metals. We have incorporated the recent studies in this review based on the heavy metal elimination using different techniques.

1.1. Wastewater

The disposal of highly polluted wastewater is rising during the past

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http://dx.doi.org/10.1016/j.jece.2017.05.029
Received 4 March 2017; Received in revised form 2 May 2017; Accepted 22 May 2017
Available online 25 May 2017

decades because of certain actions like urbanization, industrialization, and agricultural practices [8,9]. The major complications related to deficient wastewater management lead to human illness and environmental problems. Additionally, researchers and government have been executed and focussed on promoting feasible technologies for removing pollutants from wastewater. Generally, the wastewater is classified as domestic wastewater and industrial wastewater. The domestic wastewater includes solid and liquid discharges from a non-manufacturing process that includes sewage, bacteria, viruses, toxic and non-toxic organisms, sanitary outputs, garbage, detergents etc [4]. But the release of untreated wastewater from the industries is the major source of the water pollution. The effluent originating from the industries which contain a different concentration of pollutants are discharged into the rivers or other water resources. During the initial discharge, the wastewater may incorporate a high concentration of organic and inorganic pollutants. Wastewater generated from industries is due to the fabrication process, process dealing with paper and pulp, textile, chemicals and from different streams like cooling tower, boiler and production line, etc. and based upon the above specified, the composition and the combination of pollutant in water effluent differs [10]. The contaminants from the industrial wastewater that pursue in the environment are pesticides, dyes, aromatic hydrocarbons, oils, heavy metals etc. [11–16] and these contaminants are a major hazard to the individual's health and surroundings [17].

1.2. Heavy metals

Pollutants generated in the effluent is classified as organic and inorganic pollutants which have a different range of toxic levels in it. Biological, physical and chemical method are widely used in the treatment of organic pollutant. But these methods are not suitable for the inorganic pollutant like heavy metals. Because of their qualities like solubility, oxidation-reduction characteristics, and complex formation, the heavy metal decomposition plays a major concern [18]. The element which has the atomic weight between 63.5 and 200.6 and a specific gravity greater than 5.0 indicates that the element is heavy metal [19]. They appear as a natural element in the environment. The word heavy metal refers to the element which has a higher density and toxic even at low concentration. In recent years, heavy metals in wastewater are a major problem in the environment, because the high risk is associated with ecosystems and human health even at very low concentration. Because of its flexibility, accumulation, non-biodegradable and endurance, the heavy metal pollution is a major environmental burden [20,21]. Industries like paper industries, pesticides, tanneries, metal plating industries, mining operations, etc., discharges heavy metal effluent into the surroundings which is found to be non-biodegradable and toxic or harmful to the human physiology and other biological systems. But they can be converted into less harmful substances. The toxic metals can remain either in chemical form or mixed form, thus it is difficult to remove from the wastewater [22]. Certain heavy metals create essential components which are required by the living beings in short amounts for metabolic activities [21] at the same time these metals can cause incurable toxicity to the human health in larger amounts [23]. Heavy metals in open waters lead to the end of aquatic life, oxygen insufficiency and algal blooms. When they discharge into the rivers, the heavy metals get converted into hydrated ions which are highly toxic than the metal atoms. These hydrated ions disrupt the enzymatic process as well as the absorption is faster in it. Hence the removal of heavy metals is compulsory to lower the public risks. To limit the water pollution level, World Health Organization (WHO) and Environmental Protection Agency (EPA) have set the most admissible discharge level of heavy metal into the environment. Yet, the discharged effluent contains a high concentration of heavy metals than the permissible limits which causes the human health problems and environmental problems

1.3. Types of heavy metals and their effects

Some of the toxic heavy metals like nickel, arsenic, chromium, zinc, copper, cadmium, cobalt, antimony, etc. which induces the dangerous and toxic effects to the living environment. Ionic forms of metals like Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+} and As^{3+} reacts with bioparticles in the body to form toxic compounds which are crucial to isolate. The toxic characteristics are depending upon the elevated biomagnification and concentration to such an extent. Ligand and oxidation state plays a vital role in bioavailability of heavy metals. When the concentration of heavy metals is beyond the permissible limit, then the heavy metal is a toxic metal if the metal disrupts the metabolism of the cell [24]. The toxicity of metals results in lowering of the cerebral and nervous function, harm the blood content, lungs, kidneys and other organs, bring out weakness, memory loss, an increase of allergies, increase the blood pressure in the human body. Cell death also takes place due to the formation of free radicals and these radicals are responsible for the oxidative stress [25]. Due to these effects, health authorities are increasing worldwide and several regulatory bodies have adopted the permissible limits to the heavy metal discharge effluent. Researchers also concentrated on developing the treatment techniques because of the presence of critical effects in wastewaters [26]. The potential health effects of various heavy metals are described in Table 1

1.3.1. Cadmium

Cadmium appears in the form of natural deposits which consists of other elements. It is also most toxic heavy metal found in industrial effluent. It plays a major role in the industries like plating, cadmium −nickel battery, phosphate fertilizers, stabilizers, and alloys. Even at low concentration, the cadmium compounds are hugely harmful and gets concentrated in the ecosystem. "Itai-Itai" disease induced by the cadmium accumulation in the river and causes the softening of the bones and fractures to the human beings [30]. Additionally, they also bring out the effects like hepatic toxicity, lung cancer, and diseases and create harm to the respiratory system, kidney, liver, and reproductive organs [31,32]. Hence economically reliable and efficient treatment is required to remove cadmium from the wastewater.

Table 1
Health consequences of some toxic metals [27–29].

S.NO	Heavy metals	Toxic effects
1	Cadmium	Renal failure, human carcinogen, Osteomalacia, itai–itai disease, weakens the bone, respiratory disease, gastrointestinal diseases, birth defects, anemia, inhibits the calcium control in biological systems
2	Chromium	Genotoxic, alopecia
3	Nickel	Anaphylaxis, lung cancer, hair loss, destroys red blood cells, cause liver diseases, nephrotoxic
4	Lead	Damages the developing infant brain, kidney failure, affects the sense organs and circulatory system, loss of voluntary muscle function
5	Copper	Liver illness, cancer in respiratory tract, lack of blood, stomach and intestinal irritation
6	Mercury	Affects the joints in the human body, kidney disease, affects the muscle movements, death, unconsciousness, abortion, skin cell death in humans, inflammation of gums, painful extremities, nervousness, affects the vision, memory loss
7	Zinc	Creates dizziness

1.3.2. Chromium

The most available seventh element in the earth is chromium. Chromium exists in the form of ore, which composed of ferric chromite ($FeCr_2O_4$), crocoite ($PbCrO_4$), and chrome ochre (Cr_2O_3). The major industry source for chromium heavy metals is leather industries, tanning industries, electroplating industries, textile industry, etc. These industries develop a waste product in which hexavalent form of Cr (VI) and trivalent form of Cr (III) are available [33]. But Cr (VI) is more harmful than the Cr (III) [29,31] for plants, animals, and organisms. Cr (VI) are mostly present in the chromate salt production industry Cr (III) are useful in fat metabolism and plays a primary part in sugar [33,34]. These two forms are utilized in the industries like steel production, chrome plating, wood conservation, glass industry, pigment fabrication, plating and electroplating industries and as leather tanning agents. Chromium metal also acts as cleaning agents, titrating agents and additives in mold production and magnetic tape fabrication process etc [35]. It causes skin inflammation, liver and kidney damage, pulmonary congestion, vomiting and the creation of ulcer [35,36]. Because of these effects, the chromium must be considerably removed from the wastewater before it gets released into the environment or needs to modify the chromium metal into less toxic forms.

1.3.3. Nickel

Nickel is hard and silver metal that has the atomic number of 28. It is the type of non-biodegradable heavy metal found in wastewater. The industrial sources like printing, electroplating industries, silver refineries, battery manufacturing industries, alloy industries subject to the nickel metal [37,38]. Nickel is used in various applications like catalysis, coins, jewelry,batteries, alloys, resistance wires, machinery parts, etc. The huge utilization of nickel leads to various environmental problems. The effects of nickel are a dry cough, chest pain, creates breathing problem, nausea, diarrhea, skin eruption, pulmonary fibrosis, gastrointestinal ache, renal edema etc. [31,37–39]. To avoid the certain health and environmental risks, an attractive treatment methodology is needed to recover the nickel metal.

1.3.4. Lead

Lead is harmful metal that readily gets collected in the human body. It is heavy and soft metal exists in the form of sulfide, cerussite ($PbCl_2$) and galena [40]. The main cause of the association of lead in the industrial effluent is mainly due to Lead-acid battery wastewater. Lead often appears in wastewaters from the industries like electroplating industries, electrical industries, steel industries, explosive manufacturers, etc. It also helps in inducing the synthesis of protein and DNA and cell replication [40]. It creates illness like kidney and nervous system damage, mental retardation and cancer to the human body [41,42]. The availability of lead is riskier to the plants and animals also. So, various researchers around the world are now focussed on the treatment technology for the removal of lead.

1.3.5. Copper

Copper is generally considered as a highly harmful metal at high concentration. It is an essential element needed by humans and plays a vital role in enzyme synthesis, bone development and in tissues [43,44]. The different forms of copper are Cu^0 (metal), Cu^+ (cuprous ion), Cu^{2+} (cupric ion) in which cupric ion is found to be more toxic and appearing element in the environment [45]. The major contributors of copper are mining industries, metallurgy, chemical manufacturing, steel industries, printing circuit, electroplating industries, paints, fertilizers etc. [46–48]. The effects of copper are hair loss, anemia, kidney damage and headache [49]. Accumulation of copper takes place in liver, brain, pancreas and leads to death [50]. So, adequate treatment technology is needed to recover the copper from the wastewater.

1.3.6. Zinc

Zinc helps in controlling the biochemical mechanisms [51] and physiological operations of living tissues. This metal acts as a protective and decorative layer for other metals. For example, when the zinc is added to the steel the corrosion is avoided. The zinc is applied in industrial activities like steel processing, mining and coal combustion [52]. Though it is required by the humans in trace level, it creates some health disputes like pain, vomiting, skin inflammation, fever, vomiting, anemia [52]. The industrial sources responsible for the zinc metal are electroplating industries, paper and pulp industries, steel making industries, and brass metal works. The above-mentioned effects together with the needed for effective treatment for the removal of zinc from the wastewater.

1.3.7. Mercury

Worldwide awareness about the mercury pollution has been increased due to the mercury poisoning incident happened in Japan [53]. The highly toxic heavy metal in the wastewater is mercury. Mercury exists in different forms like elemental mercury (Hg^0), mercurous ion (Hg_2^{2+}) and mercuric ion (Hg^{2+}) [54]. The mercury metal can transport in aquatic systems and accumulate in ecosystems [55,56]. Due to its availability in the environment, it creates various environmental problems. To preserve the human health and the environment from the mercury, Minamata convention is designed in 2013 [57]. This convention has regulated the products containing mercury and bring out stricter emission standards. One of the mercury compounds like methyl mercury damages the enzyme sites and affects the protein synthesis [58]. Generally, the large amount of mercury is added in industries like paper and pulp, plastic industries, chloro-alkali industries, pharmaceutical industries oil refineries etc [59,60]. The possible consequences of mercury include damage to kidney, brain, reproductive and respiratory system. Therefore, the removal of mercury from the industrial effluent has recently gained a lot of attention by the researchers.

The above mentioned heavy metals can accumulate at any time and gathered faster than their excretion and highly toxic to humans and the environment. Even at low concentration of heavy metals, the effects are highly to aquatic environments and natural degradation does not occur. Because it reduces the activity of microorganisms which was already present in the waste streams. Henceforth, nowadays researchers are highly focussed on the heavy metal removal from the waste effluent.

2. Treatment technologies

The disposal of pollutants in wastewaters is controlled by the particular protocols. Due to the presence of inhibitory properties, a high removal enforcement method is required to remove the pollutants [61]. So, the industries face many problems in order to reduce the pollutant discharge, usage of water and consumption of energy [61]. Hence, to protect the environmental safety, several treatment methods were created which has been grown into an important research area. Each technology has certain advantages and disadvantages. Ion exchange, supercritical fluid extraction, adsorption [62], filtration, electrodialysis, precipitation [63], microbial system, the electrochemical process [64], an advanced oxidation process and membrane bioreactors [61] are better challenging and assuring techniques available for the disposal of heavy metals. The above-mentioned methods are broadly classified into three sections: physical, chemical and biological. But depending upon the nature of heavy metals the treatment techniques are applied. Each technology has certain advantages and disadvantages which are described in Table 2. For effective treatment, the sequence of several techniques is used for the removal of heavy metals.

2.1. Coagulation/flocculation

This is a current and alternative treatment available for the precipitation of heavy metals to form low soluble compounds like carbonates, sulfides, and hydroxides [71]. A colloid is a suspension

Table 2
Comparison of advantages and disadvantages of various treatment techniques accessible for the removal of heavy metals from wastewater.

S.NO	Techniques	Advantages	Disadvantages	References
1	Coagulation	Cost effective, Dewatering qualities	Generation of sludge, Utilization of chemicals is high	[64]
2	Membrane filtration	High removal of heavy metals, lower space requirement	Very expensive, membrane fouling, complex process.	[64]
3	Adsorption	Easy operation, less sludge production, utilization of low cost adsorbents	Desorption	[65]
4	Electrochemical treatment	Efficient for the removal of important metal ions, low chemical usage	Initial investment is high, need high electrical supply,	[64]
5	Electrodialysis	High segregation of metals	Clogging and energy loss	[66]
6	Ion exchange	High transformation of components	Removes only limited metal ions, operational cost is high	[67]
7	Photocatalysis	Eliminates both the metal ions and organic pollutants concurrently	It takes prolonged time to remove the metals	[68]
8	Biological treatment	This technology is beneficial in removing heavy metals	Need to be developed	[69]
9	Oxidation	No need of electricity	Rusting occurs in the system due to the usage of oxidation	[70]

molecules/atoms whose density are equal to water density. Because of this low density, these particles are unable to settle down [72]. In order to increase the density or to remove these colloidal particles, coagulation treatment strategies are carried out. The effectiveness of coagulation depends upon the types of the coagulant used, the dosage of coagulant, pH, temperature, alkalinity, mixing conditions. In this process, chemical reagents or inorganic flocculants like $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$ [73] and derivatives of these materials such as poly aluminium chloride and poly ferric chloride were used as flocculants in the wastewater treatment process. Flocculants are added which agglomerates the destabilized particles to form larger particles with the help of mixing or stirring. Straining or flotation and filtration are employed to separate these larger particles. A new type of macromolecule flocculants like mercaptoacetyl was prepared by Chang et al. [74] by reacting chitosan with mercaptoacetic acid which reports that it can remove heavy metals along with turbidity. Other flocculants like poly aluminium zinc silicate chloride are used in oil wastewater treatment, achieved the removal rate of turbidity and COD is about 98.9% and 71.8% [75]. The examples of complex coagulant and flocculant are CAX and anionic poly acrylamide increase the removal efficiency of oil in wastewater [75].

Yan et al. [76] studied the removal of arsenic (Sb) by the coagulation process with the help of aluminium and ferric salts which are found to be efficient coagulant for arsenic removal. Sb(V) removal was effective with the less dosage of ferric coagulant. The coagulants destabilize the colloidal particles by neutralizing them and brings about sludge settling. These colloidal particles get entrapped on the metal surface to form precipitation. The sludge formation occurs due to the large utilization of chemicals in this separation process which is one of the major disadvantages of the coagulation process. Sometimes water soluble polymeric flocculants like sulfonic acid and carboxylic acid polymers [76] are also used in this separation process rather than inorganic chemical reagents. The advantages of these polymers are easy to use, low sludge formation, easily available and environmental friendly [77]. Certain researchers tried to remove the heavy metal using two popular chemicals such as ferric chloride and poly-aluminium chloride (PAC) which is found to be an excellent coagulant around optimum concentrations [78]. Research also carried out in the removal of bounded heavy metals by the coagulation/flocculation process. Heavy metal complex removal was done by using polyelectrolyte flocculation method followed by centrifugation and filtration method[79]. The heavy metal like zinc and lead bound with the humic acid material and that gets coagulated with the cationic polyelectrolyte polydiallyldimethylammonium chloride, which is a polyelectrolyte flocculation technique carried out to build up the removal of heavy metals.

This treatment cannot completely eliminate the heavy metal from wastewater, hence it is necessary to include the other treatment techniques like precipitation, spontaneous reduction along with coagulation or flocculation process. For example, Bojic et al. [80] utilized combined technique, i.e. spontaneous reduction-coagulation process in order to separate the metal from wastewater based on the micro-alloyed aluminium composite, can efficiently lower the copper and zinc ions in different concentrations. According to the Smoluchowski coagulation theory, nanoparticles can precipitate the colloids immediately present in the surface water [81]. Nano coagulant like Silver nano particles deposit the heavy metals and can drop the TOC concentration in the wastewater [81]. The large amount of sediment flocks leads to the formation of sludge which takes place in the coagulation process due to the usage of coagulants like alum, iron, etc. The sludge formed after the coagulation process was found to contain heavy metals like cadmium, chromium, nickel, lead and zinc [82]. The solution for sludge management is recovery, recycling and reuse [83]. Though coagulation/flocculation is efficient for the removal of heavy metals from wastewater, it may create by-products like flocks which are termed as a secondary pollutant and the added chemical solvents are low reusable that is harmful to both the human and environment.

2.2. Ion exchange

Ion exchange is a separation process which substitutes the ions with another for the wastewater treatment with high removal efficiency of metal ions. When compared with coagulation process, the sludge production is low in the ion exchange process [84]. Ion exchange resin is a material used to recover or remove the metals. Based on the chemical property of resins, the isolation of a specific set of metal ions takes place which was investigated by Hubicki and Koodynsk [85]. Basically, they were designed in a form of strain and stress-free to prevent the natural degradation and requires substrate-ligand communication which stimulates the polymer support on that communication. The resins are made up of cross-linked polymer matrix in which the functional groups are attached through covalent bonding in the resin structures and spaces in the structures allows the ions to transfer appropriately. These resins are classified into two types such as synthetic and natural resins [84], either one of the resins have been used to replace the metal ions with cations. Among these resins, synthetic resins are widely favored than the natural resins to separate the metals infinitely [84]. The main application of synthetic resins can remove the arsenic metals from drinking water [86]. Fouling of matrix occurs in case of high concentrated metal solution which is the demerits of synthetic resins [87]

The most favored ion exchanger is cationic exchanger which consists of strongly acidic resins and weak basic resins. Sulfonic acid groups are present in the acidic resins and carboxylic acid groups are present in the basic resins [79]. Hydrogen ions can deliver the transmutable ions with the metal cations. Certain researchers used cationic exchange resins for the removal of Ce^{4+}, Fe^{3+}, and Pb^{2+} which was stimulated by the ionic charge present in the resins [88]. Natural zeolites show best cation exchange capacity for the elimination of heavy metal in wastewater which was proven by many researchers

[89]. Zeolites are crystalline in structure, consists of aluminium and silicate atoms connected through oxygen bridges. Na^+, K^+, Ca^{2+}, Mg^{2+} are alkaline charge balancing cations responsible for the ion exchange efficiency of zeolites and these cations bound electrostatically with the Al atoms [90]. Zeolites play an important role in the removal of chromium metal in indirect methodology because the zeolites are formerly altered to avoid the repulsion from the negative ions [90]. Alyuz and Veli [91] used zeolite as an ion exchange material for the removal of nickel that was shown to be very efficient. Jamil et al. [92] used two zeolites prepared by using Egyptian Kaolin for the heavy metal removal like Cu, Cd, Pb, Zn from industrial wastewater. They depicted that the removal of metals from the prepared zeolite was 98%. The removal efficiency of Barium (Ba^{2+}) was investigated by Pepe et al. [93] from the wastewater by using natural zeolite tuff namely *Campanian ignimbrite* which contains chabazite and phillipsite as an exchange phase in the structure. But zeolites are more efficient in the case of laboratory usage, more research work needed to utilize the zeolites in the large scale. The first ion exchange resin, i.e. magnetic ion exchange resin (MIEX) was used in 1995 for the removal of natural organic matter [94]. There are two types of ion exchange systems, cation, and anion exchange resins. Anionic exchange resins are most suitable to the low contaminated wastewaters. Kononova [95] et al. used cation and anion exchangers for the removal of toxic metal like chromium (VI) and manganese (II). Regeneration of ion exchange resin by using chemical reagents is one of the disadvantages of ion exchange resin which causes secondary pollutant. Additionally, it increases the operational cost as well as it cannot be utilized in large scale for the wastewater treatment [84].

2.3. Flotation

Flotation is a solid-liquid separation technology in which the tiny droplet is flowed into the wastewater and the heavy metals escape from water by sticking to the bubbles. These bubbles get suspended at the top and the concentrated hydrophobic particles get removed, used for other processing. It has a great potential towards the wastewater treatment because the formation of sludge is low and separation efficiency is high. It is most suitable for the compounds having altered physical and chemical nature [96]. Bubble size, bubble velocity, bubble formation frequency, confirms that they are the most meaningful parameters for regulating the flotation process [70]. The demerits of flotation are high cost of operation and maintenance.

2.3.1. Dissolved air flotation (DAF)

The principle of dissolved air flotation is to raise the agglomeration of suspended particles by passing the air bubbles in water solution that can be easily detachable from the surface of the water. To strengthen the performance, surfactants are added in this method to increase the agglomeration between positively charged air bubbles with negatively charged flocs. In the case of manganese removal, DAF precipitates the lower concentration of manganese by the inclusion of oxidizing agents like Cl_2, $KMnO_4$, and O_3. Reagents like collectors enhance the junction between the particles and bubbles which can physically or chemically adsorb on the surface in DAF process [97]. Organic polymers are most widely used collectors in DAF which forms a monolayer onto the surface of particles during the agglomeration process and these polymers represented by the molecular weight and polymer chain length [97]. Al-Zoubi et al. [98] used different types of polymers like polyvinyl alcohol (PVA), modified PVA, polyethylene glycol and chitosan in the DAF process for the removal of heavy metals like $CdCl_2$, $ZnCl_2$, $MnCl_2$, Pb $(NO_3)_2$, and $NiCl_2$. This research has been studied various parameters like the type and concentration of collectors, types, and concentration of heavy metals and modification PVA. Chitosan shows the better result in the removal of Cd (29%), Ni (27%), Mn (31%), and Pb (29%) when compared with used polymers. The modified PVA established the effective removal of heavy metals like Ni (30%), and Zn (28%) in this research [98]. Certain researchers like Amaral et al. [99] investigated the removal of sulphate ions from acid mine drainage by dissolved air flotation process using micro and nanobubbles. The use of this way reduces the sulphate ion concentration from 1753 mgL^{-1} to 500 mgL^{-1} [99]. So, this treatment has the potential to remove the heavy metal loaded wastewaters.

2.3.2. Ion flotation

Ion flotation is an assuring method for heavy metal elimination from wastewater. This technique was proposed by Felix Sebba in 1960 for heavy metal removal. By using surfactants into the wastewater, the ion metal species transmitted into hydrophobic. These hydrophobic ions interact with pumped air bubbles to form flocs and removal of flocs takes place consequently [85]. Less volume of sludge production, easily applied to various levels of metals, lower energy requirement is the benefits of ion flotation [100,101]. Liu and Doyle [102] conducted the ion flotation study for the removal of Ni^{2+}, Co^{2+}, and Cu^{2+} using non-ionic surfactant namely dodecyldiethylenetriamine (Ddien). This investigation reported that 93% of nickel concentration was decreased from 0.15 mM to 0.01 mM. Hoseinian et al. [100] applied Ethylhexadecyldimethylammonium bromide (EHDABr) and sodium dodecyl sulfate (SDS) as a collector in the ion flotation process for the removal of Ni(II) and Zn(II) ions. The results revealed that the recovery of these metal ions was obtained at 88% and 92%. Bio-surfactant such as tea saponin were used in the ion flotation for the removal of lead, copper, and aluminium, maximum removal was obtained at 81.81% [103].

2.3.3. Precipitate flotation

Precipitate flotation is a type of flotation process depends on the precipitate creation of metal ions by the inclusion of chemical reagents and adhering to the air droplets which was removed finally. The precipitation may progress through metal hydroxide accumulation along with peculiar anions (sulphide, carbonate) [85]. Depending upon the bubble's charge with the reagent and the surface area of the precipitate, the separation efficiency was decided. Research work was carried out in the precipitation flotation process by Salmani et al. [104] with the help of biosurfactant like Rhamnolipid (RL) as a collector for the removal of chromium. Above 95% removal efficiency was attained, which shows that this surfactant was hugely active in precipitation flotation method [104].

2.4. Membrane filtration

Membrane filtration is present pressure driven separation technique applied in wastewater treatment. Other than heavy metal removal, disinfection also takes place in this technique [105]. Membrane filtration separates the particle based on its size, solution concentration, pH and applied pressure. By the treating membrane with the chemical agents, the filtration mechanism can be stimulated [106]. The membrane is made up of specific porous material which plays a major role in the removal of metals from the contaminated water [70]. The membrane material is classified into two types namely; ceramic and polymer. Generally used material for industrial wastewater treatment is ceramic than the polymer due to its resistance to chemicals [107]. It also has the hydrophobic capacity. The main drawback of ceramic material is weak and very costly to construct [107]. Polymeric material like Polyvinylidene fluoride (PVDF), Polypropylene (PP), Polyethylene (PE) is commercially used material because of its chemical resistance. It is a porous membrane and can foul easily since its hydrophobic nature [107]. The intercommunication between the polymeric membrane and heavy metal is high. Depending upon the pore size of the membrane material, the membrane permeability is obtained [79]. The cleaned solution is removed on one side of the membrane and the solute on the other side [79]. It is a hopeful technology for the heavy metal removal because of its efficiency, easy operation and less space requirement [79] when compared with other purification technologies. Additionally, it is also efficient to remove suspended solids and organic compounds. Though it has certain advantages, the membrane filtration is limited to heavy metal removal by cause of complex process, membrane fouling, periodic replacement of membrane and high cost [79]. The major foulant present in the membrane is a fraction of dissolved organic matter (DOM) and organic matter (OM). To avoid the presence of these DOM and OM, pre-treatment of wastewater is required which increases the performance the membrane [108]. In order to find the non-polluting separating technique, pressure driven membrane filtration process like microfiltration, ultrafiltration, nanofiltration and reverse osmosis have been used for the isolation of heavy metal from wastewater depending upon the size of metals. These processes can handle a large volume of aqueous solutions for heavy metal removal.

2.4.1. Microfiltration

The microfiltration process essentially used as a pretreatment for the removal of suspended solids. It can act as either dead- end mode or cross-flow mode. It eliminates the particles in the size range from 100 to 1000 nm. The important merits about the microfiltration process are, it has high stability, the membrane can be used for a prolonged time and can handle a large volume of aqueous solution. Clogging occurs easily in the microfiltration membrane which is the main defect in their membrane. Molgora et al. [109] used combined technology, namely coagulation followed by microfiltration for arsenic removal. They found that 97% of arsenic were removed efficiently by this combined technique when compared with other filtration techniques.

2.4.2. Ultrafiltration

Ultrafiltration is a separation technique and requires only low energy for the wastewater treatment. About 10–100 nm size range particles get removed by this process. Due to the hydrophobic and electrostatic interactions, the particles get separated easily from the aqueous solutions. Usually, this methodology is used in the form of the combined technique because it has a larger pore size membrane which is greater than the size of metal ions. So, UF membrane allows the metal ions to pass through easily. To boost up the ultrafiltration process, chemical agents, and polymeric agents were used and commonly called as miceller enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) [84].

Scamehorn et al. in 1980 proposed the MEUF for the removal of metal ions from the wastewater [110]. The excessive addition of enhancing agent leads to the precipitate formation that binds with the metal ions to form the large structure of metal and surfactant complex. This complex gets hold by the UF membrane and allows only the non-retained particles to pass through [79]. When the charge of the surfactant is opposite the metal ions, a high retention of metal-surfactant complex can be attained [79]. The complex can get back and reuse for environmental applications. The drawback about the MEUF is, it can create secondary pollutant when the metal-surfactant is not disposed of properly. Micellar enhanced ultrafiltration was used by the Landaburu-Aguirre et al. [111] to eliminate the heavy metals from phosphorous rich wastewater of a fertilizer company. They utilized response surface methodology for the improvement of exclusion coefficient of heavy metals like cadmium and copper. This study brings about that the removal coefficient of cadmium and copper is about 84.3% and 75% were obtained [111]. Researchers used several types of synthetic surfactants for the removal of heavy metals in small scale applications. The synthetic surfactant namely Sodium Dodecyl Sulphate (SDS) was used by some researchers in MEUF of zinc from synthetic wastewaters. Above the critical micelle concentration of SDS, the zinc removal is increased. In this study pseudo second order describes the adsorption of the SDS into metal ions [112]. But the use of these surfactants can lead to secondary pollution. In this case, biosurfactant is preferred which is biodegradable and renewable. El Zeftawy and Mulligan [113] carried out a research which depicts that the usage of rhamnolipid as a biosurfactant in the micellar-enhanced ultrafiltration process for the removal of copper, zinc, nickel, lead and cadmium achieved greater than the 99% rejection ratio and the optimization were done by the response surface methodology.

PEUF is a type of ultrafiltration purification technology by using the water-soluble polymeric agents. The polymeric agents get attached with the metal ions to form macromolecules and these molecules cannot pass through the membrane because the size the membrane is smaller than the macromolecules which get retained. Macromolecules which contain metal ions can be recovered and polymeric agents can be utilized for other purposes [79]. The polymeric materials are classified into three types. They are natural polymers, synthesized polymers and commercial polymers [114]. Natural and synthesized polymer usage are great in case of lab scale application but in large-scale its usage is limited [114]. PEUF technique has high removal efficiency and high formation of macromolecules which is the major advantage of this filtration process. Since the polymers have a complex structure, the separation of specific metal ions is problematic and difficult to recreate those polymers [115]. On the other hand, natural polymers are low water soluble [115]. Industrial wastewaters from battery manufacturing, mining operations, chloralkali process, the PEUF method was tested. Qiu et al. [116] applied the copolymer of maleic acid and acrylic acid as a complexing agent in the complexation-ultrafiltration process for the removal of manganese from the wastewater. This study shows that the rejection rate of manganese is about 99.6% and the permeate removal is only 2% of the total process [116]. The removal of heavy metals like Co (II), Cu (II), Ni (II), Pb (II), Fe (III), Cd (II), Zn (II) and Mn (II)) was investigated by Huang et al. [77] using polyvinyl amine as a polymeric agent in PEUF process. At 0.1% of PVA dosage, 99%, 97% and 99% of Pb (II), Cu (II), and Fe (III) rejection were obtained and found to be effective at low dosage of PVA. When the dosage level of PVA increase, there may be an increase in the rejection rate of metal ions [77]. Similar research was carried out by the Huang et al. [117] in 2015 to remove the mercury from wastewater by PEUF with the help of PVA. 99% of mercury removal was achieved but this efficiency was impossible in the ultrafiltration. In this study, the concentration of flux depends upon the PVA dosage, but this dosage did not alter the mercury elimination [117].

2.4.3. Nanofiltration

Nanofiltration is most assuring pressure driven methodology used in various chemical and biotech industries. It is an intermediate technique between ultrafiltration and reverse osmosis [84]. The advantages of nanofiltration are, energy utilization is low, an effective method in heavy metal removal, ease of operation [79], requires a lower pressure than the reverse osmosis [81]. The nanofiltration efficiency depends upon pH, pressure, temperature, membrane tendency, membrane configuration and feed concentration [114]. The membranes used in the nanofiltration process usually made up of synthetic polymers which are positively or negatively charged on the surface and this aspect helps to dissociate the heavy metals [118] or enhance the membrane performance due to the electrostatic intercommunication between membrane and metal ions. The separation mechanism of nanofiltration is size exclusion and charge exclusion [119]. Zhu et al. [119] designed dual layer nanofiltration hollow membrane using polybenzimidazole (PBI), polyethersulfone (PES)/polyvinylpyrrolidone (PVP) for the removal heavy metal ions (Cd^{2+}, $Cr_2O_7{}^{2-}$ and Pb^{2+}) from wastewater. They studied the separation performance between this membrane and these metal ions and investigated the potential of dual-layer hollow nanofiltration membrane. The rejection rate of Mg^{2+} and Cd^{2+} was achieved at 98% and 95%. When altering the pH of the solution the rejection rate of $Cr_2O_7{}^{2-}$ and Pb^{2+} can reach more than 98% and 93% [119]. In 2015 Zhu et al. [120] used the thin film composite nanofiltration membrane which is propagated by the poly (amidoamine) dendrimer (PAMAM) for heavy metal removal. The rejection rate was tested against the metals like Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and As^{5+} which reach more than 99.2%. By varying the pH of the solution,

Table 3
Types of polymeric material used in nanofiltration membrane for the removal of heavy metals from the wastewater.

S.NO	Membrane	Pore size of the membrane	Heavy metals removed	References
1	Polybenzimidazole (PBI)	0.348 nm	Chromate	[123]
2	Poly(amidoamine) dendrimer (PAMAM)	0.1 and 1.4 nm	Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and As^{5+}	[120]
3	Polysuphone supported with thin film composite polyamide	0.52 nm	Copper ion	[124]
4	Thin film composite polyamide	NA	Cadmium and nickel ions	[125]
5	Polyamide membrane	NA	Arsenic and fluorine	[126]
6	Polyvinylidene fluoride (PVDF)	NA	Cu^{2+}, Cd^{2+}, and Cr^{6+}	[127]
7	Polyamide nanofiltration membrane	NA	Lead	[128]
8	Polyethyleneimine	0.34 nm	Pb^{2+}	[121]

the arsenic rejection rate gets increased. This research shows PAMAM has a better stable activity which reveals that it has good anti-fouling property [120]. In order to increase the absorbing capacity of the membrane, chelating polymers namely negatively charged functional groups such as poly (acrylic acid-co-maleic acid) (PAM), poly (acrylic acid) (PAA) and poly (dimethylamine-co-epichlorohydrin-co-ethylene-diamine) (PDMED) on the positively charged polyethyleneimine (PEI) cross-linked P84 hollow fiber substrates were chosen by Gao et al. [121] for the removal of heavy metal like $Pb(NO_3)_2$, $CuSO_4$, $NiCl_2$, $CdCl_2$, $ZnCl_2$, $Na_2Cr_2O_7$ and Na_2HASO_4 and brings out the rejection rate is about 98%. Additionally, these chelating polymers changes the pore size of the membrane and the membrane surface charge [121]. The different polymeric material used in nanofiltration process for the removal of heavy metals is published in Table 3. Al rashdi et al. [122] studied the removal of heavy metal using nanofiltration membrane NF270 which shows higher removal when the pH is lower than the isoelectric point of the membrane. At lower concentrations (1000 mg/L) of copper ions, the rejection rate is 100% but in case of higher concentration (2000 mg/ L) of copper ions, the rejection rate gets decreased to 58% which means this NF270 membrane is suitable for the removal of lower concentration of copper ions [122].

2.4.4. Reverse osmosis

Reverse osmosis works on the principle of size exclusion and charge exclusion. It uses semi-permeable membrane for the removal of dissolved species and allows only the water to pass through the membrane [84]. RO membrane pore size ranges from 0.1 to 1.0 nm. It is widely used for the desalination process. The usage of reverse osmosis is rising in wastewater applications for the removal of heavy metals. The major fault in this process is, it requires high energy to operate. Various experiments were carried out in RO membrane to recycling or to treat the electroplating wastewater. The capability of RO membrane depends upon the membrane material, pH, temperature, pressure and clogging characteristics of the membrane [114]. To avoid fouling of the membrane, the wastewater undergoes pretreatment which removes the surface and colloidal particles from the effluent [114]. This technology is almost used in the water treatment for about ten years. Petrinic et al. [129] studied the treatment of wastewater from metal finishing industry by using combined membrane techniques like ultrafiltration and reverse osmosis for the removal of suspended solids and heavy metals from wastewater. Ultrafiltration process was used as a pretreatment process to eliminate the clogging problem in the reverse osmosis membrane. They showed that this combined membrane technology removes 91.3% and 99.8% of the contaminants from the effluent, such as metal elements, organic, and inorganic compounds and also suggested that UF process decreased the fouling of the RO membrane. Chon et al. [130] conducted a pilot study to estimate the performance of municipal wastewater plant which consists of combined coagulation–disk filtration (CC–DF) process, microfiltration (MF) and reverse osmosis (RO) membranes. They tested the removal of organic materials, metals, metalloids and nutrients from the wastewater using the above-mentioned techniques. The result shows that the most of the water contaminants were removed by the RO membrane than the other techniques [130].

2.5. Chemical precipitation

This method is comparably cheap and conventional effective technique used in various industries. In order to form metal precipitation, chemicals are added to the solution that alters the pH and cannot allow the precipitate to dissolve in the solution [131]. By the sedimentation process, these precipitates are isolated and the remaining solution is used for some other purposes [79]. Chemical precipitation is most effective in the elimination of Cu (II), Cd (II), Mn (II), Zn (II) [84]. Tanong et al. [132] carried out an investigation in the elimination of nickel and manganese by adding sodium carbonate which was found to be completely precipitated at pH 9. Usually, it is applicable to the wastewater containing a heavy metal ion concentration but in the case of low metal ion concentration, this method is not suitable. It can produce an excessive amount of sludge with high water content due to the precipitates of insoluble metals which is difficult to treat and dispose of and considered as a hazardous waste [133]. Additional methods like filtration and sedimentation process is required to remove these precipitates from water. Then the treated water can be reused or discharged in the surroundings. Yet, the chemical precipitation requires a large amount of chemicals to precipitate the metals. Because of its simplicity and low cost, they are generally applied in industrial scale applications. The current chemical precipitation process is hydroxide precipitation and sulphide precipitation.

2.5.1. Hydroxide precipitation

Hydroxide precipitation is a most preferred method for the heavy metal removal because of its ease handling and its low cost. pH modification increases the metal hydroxides which are insoluble in the alkaline media. in the case of trivalent ions layered double hydroxides are formed for the heavy metal removal for heavy metal removal [134]. Different types of precipitants like lime, calcium hydroxide, sodium hydroxide is available to form hydroxide precipitate. Lime and limestone are frequently used because of their easy availability and low cost. Jadhav et al. [135] carried out the detailed study for the removal of fluoride heavy metal from the waste stream by using the precipitants like Calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH_2)$) and calcium chloride ($CaCl_2$). These chemicals showed effective results at the pH range varying from 4 to 14. Among three salts, calcium salt was proved to be more efficient in fluoride precipitation [135]. Certain researchers carried out the combined technique electro-fenton process with chemical precipitation for the reduction of COD and zinc ions from rayon industry wastewater [136]. They found that 88% of COD was reduced due to the electro-fenton process but it does not show any effect on zinc removal. Ghosh et al. [136] used lime as a precipitant for the zinc removal which shows 99-99.3% zinc removal efficiency in the pH range of about 9–10 and it was reduced from 32 mg/L to 0.20 mg/L. Ramakrishnaiah and Prathima [137] conducted a chemical precipitation study for the removal of chromium from synthetic and industrial effluents by using 100 mg/L and 400 mg/L of $Ca(OH)_2$ + NaOH and $FeCl_3$ as a precipitant. 99.7%

removal efficiency of chromium was obtained using calcium hydroxide and sodium hydroxide with the sludge production of about 7 ml/L. They concluded that calcium hydroxide and sodium hydroxide are best-fitted precipitant for chromium removal [137]. But the usage of hydroxide precipitation method is limited because the metal hydroxide precipitate can react both as a base and as an acid [79]. Zhang et al. [138] used NaOH as a precipitant for the hydroxide precipitation of synthetic laterite waste solution containing 2 g/L Mn^{2+}, 15 g/L Mg^{2+} and 0.5 g/L Ca^{2+}. They showed that hydroxide precipitation is not sufficient to remove the manganese over the magnesium and the need for higher pH above 8.5 to obtain greater than 100 mg/L Mn and pH above 9 to obtain greater than 10 mg/L Mn with substantial co-precipitation of magnesium.

2.5.2. Sulphide precipitation

Sulphide precipitation is one of the most competent process between the precipitation method for the removal of heavy metal from the wastewater. The advantage of using sulphide precipitation is that the solubility of sulphide precipitate is lower than the hydroxide precipitate in the alkaline media. The generally used sulphide precipitants are solid (FeS, CaS), aqueous (Na_2S, NaHS, NH_4S) or gaseous sulphide sources (H_2S) [79,139]. Cao et al. [140] examined the usage of mixed culture of sulphur reducing bacteria for the removal of metals from bioleaching solution by sulphide precipitation method. This SRB produced hydrogen sulphide in the first reactor and precipitation of heavy metals were carried out in the second reactor. The reactors used in this study depicted that, it allows the quick metal recovery and the possibility of chemical precipitation using hydrogen sulphide [140]. The Sulphide precipitation process has good settling capacities, selective removal of metals and rapid reaction rates [79,139]. Sometimes sulphide precipitants dosage can result in the emission of toxic fumes in acidic condition. Hence, it is required to carry out the sulphide precipitation process in basic or neutral condition.

2.6. Electrochemical treatment

Electrochemical treatment is electrically combined with other technique which made enormous development for the removal of heavy metal from wastewater. Electrodes in the reactor shift the electrons which result in eradication of pollutants [141]. Electrochemical treatment has a potential toward the treatment of wastewater because of its versatility. The efficiency of the electrochemical reactor depends upon the electrode material and cell parameters like mass transport, current density, water composition etc [142]. Due to the demanding environmental regulations, the importance of electrochemical treatment increases for the wastewater treatment. This method is suitable for various types of contaminants which cannot release the side products. Yet it needs high maintenance facility and electrical energy for the operation. And also, limited to certain applications because of the short lifespan of electrode material, low mass transfer rates, increase in temperature during the process [143]. The performance of Polyacrylic acid (PAA) coated gold electrodes was investigated by the Le et al. [144] for the release of heavy metals from wastewater. PAA is able to arrest the metal ions even at low concentration. They used this method as secondary treatment after the ion exchange or precipitation process [144]. Cui et al. [145] created a novel poly(aniline-co-o-aminophenol) (PAOA) modified carbon felt electrode reactor for the elimination of fluoride from aqueous solution in a continuous mode. About 1.2 V, the best fluoride removal was reached 10.5 mg/g at pH 7.2 and concluded that PAOA modified felt electrode reactor is a rising technique for the removal of fluoride from contaminated waters [145]. The available electrochemical treatments like electrocoagulation, electroflotation, electrodeposition were described in this review study.

2.6.1. Electrocoagulation

The electrocoagulation reactor consists of two electrodes anode and cathode in which the external energy is applied to generate the coagulants like aluminium and iron at the anode and hydrogen at the cathode in the contaminated water [146]. These coagulants are cationic monomeric species, destabilizes the suspended particles and coagulate together which gets adsorbed to the heavy metals [79]. The reactions of Fe electrode in the electrocoagulation process are [147].

Anodic reaction:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \tag{1}$$

Cathodic reaction:

$$\langle H1\rangle\langle H1\rangle\langle H1\rangle 2H_2O + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{2}$$

Overall reaction:

$$Fe^{2+} + 2OH^- \rightarrow FeOH_{2(s)} \tag{3}$$

The reactions of Al electrode in the electrocoagulation process are [87].

Anodic reaction

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \tag{4}$$

Cathodic reaction:

$$3H_2O + 3e^- \rightarrow 3OH^-_{(aq)} + 3/2H_{2(g)} \tag{5}$$

Overall reaction:

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Al(OH)_{3(s)} + 3/2H_{2(g)} \tag{6}$$

Akbal and Camcidotless [148] investigated the efficiency of electrocoagulation in removing copper, chromium, and nickel from wastewater of an electroplating plant. The result indicated that increase in current density, pH, and conductivity, the removal efficiency increases. They achieved 100% Cu, 100% Cr and 100% Ni removal at an electrocoagulation time of 20 min by using Fe-Al electrode pair and this removal efficiency occurred due to the formation of hydrogen at the cathode and formation of aluminium and iron at the anode [148]. Several researches were carried in electrochemical technologies to bring out the change in technologies as much as possible. Mansoorian et al. [149] used Fe^{3+} as a coagulating factor instead of Al $^{3+}$ because the aluminium ions create hazardous effects like Alzheimer's disease to the human beings. They evaluated the removal of lead and zinc by using alternating current and direct current in the electrocoagulation process. The result showed that the removal efficiency of lead and zinc were obtained as 96.7% and 95.2% with iron electrodes by using alternating current in the current density of about 6 mA/cm^2. In the case of steel electrode, the removal efficiency was obtained as 93.8% and 93.3%. by using direct current in the current density of about 8 mA/cm^2 [149]. The advantage of using electrocoagulation process is, compact sludge production, easy to operate, small retention time [147] and absence of chemical usage [150]. The hidden process like the generation of Al and Fe ions, Al and Fe hydroxides formation and mass transfer of ionic species triggers the electrocoagulation (EC) process [151]. Table 4 highlights the types of metals removed from the electrocoagulation process.

2.6.2. Electrodeposition

When the electricity is applied to the surface of the electrode, the ions are required to exchange to the oppositely charged electrode in the solution [158]. Grimshaw et al. [159] investigated the research in electrodeposition process for the removal of nickel from the acidic solutions using cylindrical spouted electrochemical reactor. The numerical electrodeposition model like Tafel kinetics model was carried to analyze the electrodeposition behavior of nickel. They used nitrogen sparger which increases the current efficiency and electrodeposition of nickel. In this study, the nickel electrodeposition rate increases with increase in pH and temperature [159]. Lambert [160] employed electrodeposition process in the batch treatment of mining residues

Table 4
Types of metals removed in electrocoagulation process.

S.NO	Electrodes used	Current density	pH	Duration time (min)	Metals removed	References
1	Aluminium/iron electrodes	56–222A/m^2	3–9	20–110	Chromium	[152]
2	Graphite and iron electrodes	NA	6.5	NA	Arsenic	[153]
3	Aluminium alloy	1.0 A dm $^{-2}$	7.0	90	Fluoride	[154]
4	Aluminium and iron electrodes	20 A m $^{-2}$	NA	30	Manganese and iron	[155]
5	Aluminium electrode	6.25 mA/cm ^{2}	7	60	Manganese	[156]
6	Aluminium and iron electrode	2.5 to 3.125Adm $^{-2}$	3–7	25	Mercury	[157]

leachate using Ti/RuO2 as anode and copper (or stainless steel) as the cathode. The result suggested that electrodeposition of copper was determined as 86% with the copper electrode in the current intensity of about 1.3A with 80 min treatment time. An integrated approach like ultrasound and electrodeposition process was reported by Chang et al. [161] for the reclamation of EDTA-copper wastewater. The integrated study removes 95.6 w/w copper at a pH range from 3 to 7 with the voltage range from 0.5-2.0 V/cm and this result reveals that it has the best potential in the wastewater treatment applications.

2.6.3. Electroflotation/Electrolytic flotation

By the electrolysis process, the small bubbles of hydrogen and oxygen gases are produced which raises the waste to the top of the effluent. The electrode grid arrangement in the flotation tank provides good mixing in the aqueous solution. This method allows the separation of heavy metals and organic compounds from the wastewater [162]. Electroflotation process can be effectively used in the local water purification systems because this technique cannot produce secondary pollutant [162]. Kolesnikov et al. [162] used cationic, anionic, and nonionic surfactants of 2, 10, 50, and 100 mg/L at pH of 9.5–10.5 was studied for the removal of copper, nickel and zinc hydroxides. More than 95% removal was obtained in the electroflotation process with the current density of about 0.2 A/L and the duration time is about 30 min. Some researchers revealed that electroflotation process removes up to 97% of the Pb, Ba, and Zn by using stainless steel mesh electrodes with a power consumption of 14 kWh m^{-3} [163].

2.6.4. Electrodialysis

Electrodialysis (ED) is an electro membrane method transfers the ions aided by the electricity applied across the membrane [146]. The ED stack is embedded in the anionic exchange membrane and the cationic exchange membrane which are placed between the two electrodes. It allows only the anions and cations to pass through the membrane and gets retained on the ion exchange membrane [158,164]. Thus, the aqueous solution introducing inside the membrane is partitioned into two divisions i.e. concentrate and diluent. Electrodialysis has some advantages like usage of chemicals are the low and high recovery of water. Sadyrbaeva [165] used liquid membrane incorporated with tri-*n*-octylamine with mixtures of di(2-ethylhexyl) phosphoric acid (D2EHPA) in 1,2-dichloroethane for the removal of chromium (VI) from aqueous solutions in the electrodialysis process. The complete extraction of chromium was achieved (> 99.5) in this study by altering the current, time and concentration of components. The major drawback in electrodialysis process is, clogging and scaling of the membrane so it is limited to the wastewater applications [158].

2.6.5. Electrodeionization

The electrodeionization process is an eco-friendly process which can operate in both batch and continuous mode. It is an alternative method for ion exchange process [165]. Electrodeionization process utilizes the active media which apply the electrical field to transport the ions [97]. Ion exchange resins play a major role which is installed in the dilute chamber of electro deionization stack and can enhance the ion transport [166]. The major advantage of using this process is, it can regenerate the ion exchange resins by using electrical energy [165]. Some researchers examined and reviewed the treatment of electroplating rinse wastewater using novel integrated two-stage deionization process for the recovery of Ni^{2+} [165]. At the first stage, 94% of the nickel were removed at 15 V from the electroplating rinse wastewater and in the second stage, 96.7% of the nickel were found to be removed at 25 V. Lu et al. [166] depicted that integrated two stage EDI process may be economically profitable in the treatment of wastewater. Like electrodialysis, it also faces the problem such as membrane fouling, scaling, and concentration polarization. To overcome these drawbacks, membrane-free deionization process was suggested by certain researchers. Shen et al. [167] experimentally investigated the membrane free deionization process (MFDI) for the recovery of nickel from the dilute wastewater with help of resin bed configurations along with layered bed, mixed bed and layered mixed bed. They noticed that good regeneration and purification outcome was showed in MFDI with layered mixed bed because in purification step the nickel concentration gets reduced below the detection limit and in the regeneration step, the concentrate contains the nickel concentration was about 80 mg/L [167]. Additionally, the results revealed that the nickel hydroxide precipitation formation is absent in this study.

2.7. Adsorption

Nowadays the adsorption process is perceived as an efficient and admirable method to other technologies for the heavy metal wastewater treatment. It provides treated effluent with high quality. This process is a mass conversion method in which the waste is transferred by physical or chemical interest into the active sites present onto the adsorbent used [168]. The adsorption process is an alternate and assuring method to the traditional process for the purpose of low operating cost, low fouling problems and most economic for the heavy metal removal from the effluent. In the adsorption process, adsorbents can be recreated by the desorption process because it is reversible technique and the regenerated adsorbent can be reused for several purposes. Several methods are available for the regeneration of adsorbent. Based on the regeneration, the adsorption is considered as an environmentally acceptable method. Thermal regeneration, pressure swing method and electrochemical regeneration are the available methods widely used for the regeneration process. Accordingly, the adsorption process has become one of the leading technique in the wastewater treatment. Adsorption technique is easy to use, flexibile, simple design and does not produce toxic pollutants [169]. Various types of adsorbents have been developed for the remediation of heavy metal from the wastewater. The main aspects required for the selection of adsorbents are cost effective and are most appropriate sorbent for the technology [170]. High surface area, pore size distribution, functional groups, the polarity of the adsorbent determines the efficiency of adsorption process [171].

2.7.1. Activated carbon

The efficiency of the activated carbon can be evolved by both high surface area and large pore size. Various researchers used activated carbon for the heavy metal removal from the wastewater. Due to the deficiency of the commercial activated carbon (AC), the cost of AC increases. Activated carbon has a great potential towards the wastewater treatment because it has high surface area, high porosity and adaptability [172]. Usually, the carbon adsorbents originate from the carbonaceous materials like biomass, lignite, and coal etc., but coal is mostly used for activated carbon production. A novel biomass source like *Glebionis Coronaria* L. was used by Tounsadi et al. [173] for the activated carbon production to remove cadmium and cobalt ions. In this study, the factors like carbonization temperature (500–600 °C), activation temperature (400–500 °C), activation time (1–2 h) and impregnation ratio (g H H_3PO_4/g carbon) (1.5–2) plays a major role for the production of activated carbon in which the contact between the carbonization temperature and impregnation ratio enhanced the elimination of cadmium. Accordingly, the best sorption capacity was found to be as 57.87 mg/g for cadmium and 45.75 mg/g for cobalt [173]. The rich agricultural by-products are also used by some researchers as a source for the preparation of activated carbon [113]. For example, European black pine was used as a precursor for the production of activated carbon for the removal of lead ions from aqueous solution [174]. Langmuir model best described the adsorption of activated carbon and led to the maximum adsorption capacity of 27.53 mg/g at optimum dosage 2.0 mg/L. The kinetic studies showed that pseudo-second- order model best fitted with the adsorption. Some of the researchers have made alterations such as packing of AC with nanoparticles [175], installation of functional groups [176] and nitrogen groups [177] and the inclusion of anionic surfactants [178] etc., on the surface of the AC material to increase its capability of absorbing the heavy metals. Recently, a research was carried out in surface modification AC using an oxidation process which stimulates the adsorption efficiency in heavy metal removal [179]. They investigated that lead removal from aqueous solutions using activated carbon filter oxidized by the ammonium persulfate solutions (APS). The adsorption in Pb (II) removal followed the pseudo second order model and the equilibrium data best fitted by the Langmuir model. The maximum sorption capacity was found to be 559 mg/g [179].

2.7.2. Carbon nanotubes

Carbon nanotubes (CNT) adsorbents are mostly considered in the heavy metal treatment process because of its great properties and its uses. The carbon nanotubes are made up of cylindrical graphite sheets folded into a tube-like structure. They are classified into two types (1) single-walled CNTs (SWCNTs) which consists of a single sheet of graphite and (2) multi-walled CNTs (MWCNTs) which consists of multiple layers of graphite sheets [79]. Sun et al. [180] carried out a research on two types of multi-walled carbon nanotube in the homogeneous and heterogeneous system and compared the kinetic studies of Cu(II) adsorption. The two types of MWCNTs used in this investigation are (1) Hydroxy CNTs (CNTs-OH 3.70 wt%) and (2) Carboxy CNTs (CNTs-COOH 2.56 wt%). In a heterogeneous system, nano SiO_2 was used along with the carbon nanotubes. The results suggested that these two systems were well demonstrated by pseudo-second order system [180]. The mechanism behind the interaction between the metal ions and CNTs are due to the electrostatic attraction, sorption- precipitation, ion exchange and chemical interaction that were explained in Table 5. CNT's found to be the best adsorbent in the wastewater treatment because of its excellent mechanical properties and magnetic properties, high chemical, and thermal stability [181]. However, it should be identified that the recyclability of adsorbent was not reported in the previous study. Hence, Nalini Sankararamakrishnan et al. [186] investigated the arsenic removal by using the adsorbent called Zero-valent ion (ZVI) on MWCNTS which was doped by EDTA. EDTA acts as a chelating agent for arsenic removal as well as retaining the zero-valent ion. After the desorption process, the adsorbent was used about five that influences the adsorption of As (V) was reduced by 25% whereas As(III) adsorption decreased by ~13% at the end [186].

But the usage of CNTs has been reduced because of the strong accumulation of CNTs and their functional group shortage. In order to disperse the CNTs, certain modification like acid treatment [181], propagating with functional groups [187] and saturating with metals/metalloids [188] has to be done which also increases the efficiency to remove the heavy metal from the effluent. Therefore, some researchers used PAMAM (Polyamido amine) dendrimer for enhancing the separation of CNTs and adsorption capacity [189]. This study demonstrated that Langmuir model and pseudo second order was suitable to the Ni^{2+}, Zn^{2+}, As^{3+} and Co $^{2+}$ adsorption on PAMAM/CNT nanocomposites from the R^2 value 0.999. The maximum sorption capacity was found to be as 3900, 3800, 3650 and 3350 mg/g for Ni, Co, Zn and As respectively [189]. Though raw CNTs has adsorption capacity, the modified CNTs has better adsorption potential for the removal of heavy metals. The presence of CNTs in the treatment plant can affect the metabolic activity of micro-organisms and cause human health hazard [190]. The above-mentioned studies prove that the use of carbon nanotubes towards the wastewater treatment has good efficiency in the removal of heavy metals.

2.7.3. Biosorbents

Biosorption is rising/innovating technique in the elimination of heavy metals from the effluent. This technique is considered to be an efficient and detoxification process in the elimination of heavy metals even at low concentration. Biosorption is a kind of adsorption process which consists of solid state (sorbent) and liquid state (solvent). Both viable and non- viable biological materials are desired to remove the heavy metals. The dead material does not require any growth media for their growth which is the major advantage of using dead material than the viable material. In this method, potential sorbents like bacteria, yeast, fungi, algae, sawdust [191], seed shells [192], sugarbeet pectin gels [193] and potato peels [194] etc., are used because of its high efficiency and low cost [79]. Biosorbents are considered to be a low-cost adsorbent, feasible and can be obtained from the various industries as a waste product [195]. Due to the presence of functional groups like alcohol, aldehydes, ketones, carboxylic, ether, phenolic groups enhance the adsorption activity towards the metal removal [169]. The important factors affecting the potential of biomass in adsorption process are pH, temperature, adsorbent dosage, metal concentration and contact time etc., [169]. The major phenomena in the biosorption process are adsorption, ion exchange, complexation and surface precipitation.

Table 5
Interaction mechanism in CNTs.

S.NO	Type of CNTs	Metals removed	pH	Adsorbent dosage	Interaction mechanism	Best fitted model	R^2	References
1	Raw MWCNTs	Cr (VI)	3	75 mg	Electrostatic interaction	Langmuir	0.973	[181]
2	Raw CNTs	Cd (II)	7	50 mg	Electrostatic interaction	Langmuir Freundlich	0.979 0.912	[182]
3	Alumina decorated MWCNTs	Cd (II)	7	50 mg	Electrostatic interaction, physical adsorption, surface precipitation, Van der walls interaction	Langmuir Freundlich	0.9972 0.9830	[183]
4	MnO_2 coated carbon nanotubes	Hg (II)	5–7	NA	Electrostatic interaction	Freundlich	0.997	[184]
5	C00H-MWCNTs	Hg (II)	4.3	NA	Electrostatic interaction/Complexation	Langmuir	0.990	[185]

2.7.3.1. Algal biomass. In recent years, researchers were focussed on living and non-living algal biomass for the elimination of heavy metals from wastewater [196–198]. The adsorption capacity of living biomass is limited in the heavy metal removal because the adsorption process is taking place in the growth phase and the heavy metal uptake also takes place at this phase only which is considered as an intracellular process and adsorption mechanism are more complicated in it. But in the case of non-living algal biomass, the extracellular process is carried out because the metals get adsorbed on the surface of the cell wall [198]. Certain environmental factors like pH, temperature and contact time etc., can influence the adsorption capacity of non-living algae [199]. Algal biomass contains active functional groups on the surface of the cell wall that enhances the biosorption capacities. Ibrahim et al. [200] studied the removal of Cu $^{2+}$, Cd $^{2+}$, Cr $^{3+}$ and Pb $^{2+}$ using marine algae *Ulva lactuca* powder (AP) and the prepared activated carbon from *Ulva lactuca* (AAC). The removal efficiency was obtained as 64.5 and 84.7 mg/g for copper, 62.5 and 84.6 mg/g for cadmium, 60.9 and 82 mg/g for copper, and 68.9 and 83.3 mg/g for the lead by using AP and AAC [200]. From this result, they concluded that KOH-activated carbon from *Ulva lactuca* has more potential in the removal of heavy metals than the AP. Desorption of algal biomass can be done using HNO_3, HCl and EDTA 2Na which is the major advantage of the algal biosorption process. Some researchers like Tran et al. [201] used cynobacteria gelatinous colonies isolated from rice fields in Phu Tho Province, Viet Nam (Al-VN) for the removal of Cu $^{2+}$, Cd $^{2+}$ and Pb^{2+} from the water. They investigated both biosorption and desorption process in their study. 0.1 M EDTA 2Na and 0.1 M HNO_3 acted as good desorbent for the recovery of biomass and makes the adsorbent as reusable [201]. The usage of algae in environmental applications was found to have dual use in wastewater treatment and biofuel production.

2.7.3.2. Fungal biomass. Fungal biomass has a good sorbing capacity because of its high percentage of cell wall material. It can grow in natural environmental conditions. The cell wall is made up of chitin, glucan, mannan, proteins and other polymers like carboxyl, phosphoryl, hydroxyl, imidazole functional groups which make the fungi more potential for adsorption process [202]. Fungi can absorb the heavy metals through the mechanisms like intracellular precipitation, valence transformation, ion exchange, complexation [203]. Hajahmadi et al. [204] used NaOH treated dried *Aspergillus niger* biomass for biosorption of Zn(II), CO(II) and Cd(II) from ternary mixture. To understand the adsorption mechanism competitive Lang- muir, Freundlich, Temkin and Sips isotherm models were applied. The competitive Temkin isotherm was best explained the Zn(II) and Co(II) adsorption and competitive Langmuir isotherm explained the Cd(II) adsorption [204]. In order to forecast the minimum amount of the dosage required for 95% removal of heavy metals from aqueous solution, a single batch adsorber was created using Temkin isotherm model in this study [204]. Some researchers used fungal biomass composite with clay materials like smectites [205], kaolinites [206] and bentonites [207] which have the physical and chemical stability towards the heavy metals. Rashid et al. [203] reported that Fungal dead biomass composite with bentonite (FBC) can remove Ni(II) and Zn(II) from aqueous media. The equilibrium data were best fitted with the Langmuir and pseudo second order kinetic model for the adsorption of metals. ΔG^0, ΔH^0, ΔS^0 results recommended that the adsorption process is a spontaneous and endothermic process and found to be more potent towards the adsorption process [203]. Fungi are utilized by the researchers in two forms like mobilized condition and in immobilized cells. In the last decades, they used the immobilized systems of fungal cells for the metal uptake in the adsorption process because they are easy to use and handle. Adsorption process using immobilized cells of *Aspergillus niger* was evaluated by Tsekova et al. [208] for the removal of Cu^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pb^{2+}, Cd^{2+}) from wastewater. To overcome the loss of biosorbent after regeneration process they immobilized the fungal biomass with polymer matrixes (PVA and Ca-alginate gels). The results showed that the removal efficiency of Ca-alginate immobilized biomass were found to be higher than the PVA immobilized biomass in the remediation of the fore mentioned heavy metals.

2.7.3.3. Bacterial adsorbent. Treatment of wastewater using bacteria is a good biological approach. Bacteria has certain characteristics like smaller size, availability, and flexibility which makes the researchers focus on the bacterial adsorbent for the removal of heavy metals from wastewater. The cell wall of bacteria contains certain functional groups like ketones, aldehydes and carboxyl groups [209]. Bacterial biomass are usually used in the form of binding or supporting material to the adsorbent for the removal of heavy metals from the aqueous solutions. Researchers like Gupta and Balomajumder [210] designed an SBB (Simultaneous biosorption and bioaccumulation) batch system for the removal of Cr(VI) by using an aiding material like WTB (Waste tea biomass) for the binding of bacterial biofilm namely *Escherichia coli*. The maximum uptake of chromium metal using biosorbent was found to be 6.329 mg/g. The Freundlich isotherm model was used to determine the adsorption mechanism for the reduction of chromium in the biosorption of *E. coli* [210]. The same authors carried out the same type of research by using *Bacillus sp* as an aiding material in WTB for the reduction of Cr (VI) [211]. The maximum uptake of chromium metal using biosorbent was found to be 741.389 mg/g and Pseudo second order model was best explained the reduction of Cr (VI) [153]. There is another study in which they used bacterial biomass itself in the metal removal process [212]. They used dead and living *Arthrobacter viscous* biomass for the reduction of toxic Cr(VI) to the less toxic Cr(III) at pH 1 and 2. The adsorption mechanisms were predicted by the Langmuir adsorption isotherm model and the maximum uptake was found to be as 1161.3 mg/g in the case of living biomass. This result demonstrated that the living biomass has a good potential towards the reduction of Cr(VI) [212]. Studies have also specified that *Actinomycetes* can act as good biosorbent because of the presence of functional groups in their cell wall [213]. Researchers tested the biosorption capacity of *Actinomycetes* Ni^{2+}, Cr^{6+}, and Zn^{2+} from aqueous solutions [214]. Two strains were used in this study namely *Nocardiopsis sp*. MORSY1948 and *Nocardia* sp. MORSY2014 which was separated from the contaminated area. The results indicated that these strains have the capacity to remediate the heavy metals when the adsorbent dosage increased to 0.4% [214].

2.7.3.4. Low cost adsorbents. Though the aforesaid adsorbents are inexpensive and renewable, they have disposal problem and no economic value. So, the researchers mainly focussed on the usage of low-cost adsorbents like agricultural wastes, industrial by-products and natural substances for the removal of heavy metals from wastewater. By using these low-cost adsorbents, it becomes an alternative to the activated carbon [215]. The utilization of low-cost adsorbents onto adsorption process is studied as a low neutralization technique in wastewater treatment. Chu et al. [215] prepared an elastic double network polyvinyl alcohol/polyacrylic acid double network gel (PVA/PAA) adsorbent which was synthesized through a simple two-step method for the elimination of Cd(II) and Pb(II) pollutants bearing wastewater and they also explained the regeneration of metal adsorbed PVA/PAA gel. In this study, the regeneration process was carried out using 0.1 M NaOH solution. The removal efficiency remained 100% even at the fifth cycle. It was found that the Langmuir was more representative to describe the sorption process [215]. The application of agricultural waste in the low-cost adsorbents has been increasing in the last two years. They act as a precursor in the evolution of adsorbents because of its low cost [216]. The low-cost adsorbent namely peat was used by Bartczak et al. [217] for the removal of nickel(II) and lead(II) ions from aqueous solution. The kinetic data were found to follow closely the pseudo-second-order model. Equilibrium data were analysed by the Langmuir and Freundlich isotherm model. Langmuir isotherm provided the best fit to the equilibrium data with a maximum adsorption capacity of nickel(II) and lead(II) ions were 61.27 mg/g and 82.31 mg/g [217]. To stimulate the adsorption capacity of untreated precursors, certain treatments and modification methods are used so that the reaction sites and surface area gets increased.

A few researchers concentrated on the usage of modified low-cost adsorbent for the adsorptive removal of heavy metal from aqueous solution [218,219]. They used acrylonitrile grafted banana peels (GBPs) for the elimination of hexavalent chromium Cr(VI) [218]. Through this copolymerization technique, the availability of functional groups in the cellulose was determined and removed the peptic and viscous compounds from this banana peel. Ali et al. [218] concluded that this low cost efficient grafted banana peel could be used as an effective adsorbent for the adsorption of chromium metals. Johari et al. [219] used the surface modification technique like mercerization and bleaching methods in order to convert the coconut husk as an efficient low-cost adsorbent for the elimination of mercury. In this study, the pseudo second order kinetic mechanism was best fitted which interprets the mercury adsorption [219]. Liu et al. [220] proposed the use of nano zero valent iron in the adsorption process with the support of pumice which was represented as Pumice-nanoscale zero-valent iron (P-NZVI) for the recovery of Hg (II) and Cr (VI). They carried out the thermodynamic study and kinetic study in the process. The thermodynamic parameters like enthalpy change (ΔH^0) and Gibbs free energy change (ΔG^0) indicated that the adsorption process is endothermic and spontaneous [220]. The rate at which the adsorption takes place was well specified by the pseudo-first-order kinetic model. And the results provided that the P-NZVI has the potential to recover the heavy metals from the wastewater [220].

2.7.3.5. Agricultural waste/plant material. The biosorption process using agricultural waste/plant material is an eco-friendly and easy method. They perform as a substitute for the conventional adsorbents in the adsorption process. It has good consideration in wastewater treatment for the removal of heavy metals. This agro waste becomes more efficient when they are applied to treat the waste containing the water. The agricultural waste biomass like cashew nut shells [221], palm oil fruit shells [222], orange peel [223], palm fruit fiber [224], kenaf fiber [225], barley straw [226], and garden grass [227] is used for the heavy metal recovery from wastewater. Based on the sorbent cost and its availability, the application of agricultural waste is explored and their advantages towards the wastewater treatment should be described in detail. The hydroxyl groups are present in the cellulose, hemicellulose, and lignin available in the agricultural waste biomass will have the affinity towards the metal ions. They also comprised of various functional groups like amido, amino, carboxyl, acetamido, phenolic, alcohols and esters. These functional groups play a major role in the replacement of hydrogen ions to metal ions and form complex with the metal ions [76]. Recently the application of plant material has been increasing in the adsorption process because of its inexpensive cost and efficiency towards the heavy metal reduction. Jones et al. [228] highlighted the usage of plant material like mucilage from *Dicerocaryum eriocarpum* plant as biosorption medium in the removal of selected heavy metal ions. They compared the altered and unaltered mucilage of *Dicerocaryum eriocarpum* for biosorption efficiency. Kinetic study was best explained by the pseudo-second order with the with a coefficient values of $R^2 = 1$ for Cd(II), Ni(II), Cr(III), Fe(II) and $R^2 = 0.9974$ for Zn(II) and adsorption isotherm was best fitted with the Freundlich model than the Langmuir model. But regeneration of this biosorbent is the major drawback in this study [228]. The regeneration process is not complicated in the case of used agricultural waste. Delshab et al. [229] conferred the article regarding the biosorbent from *Sargassum oligocystum* harvested from the northern coast of the Persian Gulf, Bushehr, Iran. Isotherm and the thermodynamic study were studied onto biosorbent. 60.25, 153.85, and 45.25 mg/g of Hg^{2+}, Cd^{2+}, and Cu^{2+} ions was found as a maximum adsorption capacity in this study [229]. From this data, it was determined that *Sargassum oligocystum* is most appropriate for the selective removal of heavy metals bearing wastewater. Matouq et al. [230] tested the effectiveness of *Moringa aptera gaertn* (MAG) for the removal of copper, nickel, chromium and zinc ions from synthetic aqueous effluent. Many parameters such as initial metal concentration, contact time, temperature and adsorbent dose were described in this study [230]. The adsorption isotherm for copper could be well interpreted by both Freundlich and Temkin models and Temkin and Dubinin–Radushkevich models were best defined for nickel and the Langmuir isotherm model were best labeled the adsorption isotherm for chromium. The removal efficiency was found to be 90%, 68% and 91% for copper, nickel, and chromium respectively [230]. From this result, they depicted that this biosorbent was more pertinent for the removal of heavy metal ions.

Nowadays, researchers focussed on the usage of plant roots for the biosorption process because these roots help in the recognition of the whole plant system and can be utilized in the rhizofiltration which is a type of phytoremediation process [231]. The roots of halophyte species *Kosteletzkya pentacarpos* were used as a biosorbent for the removal of Cd and Zn [232]. These roots were grown in the absence or presence of 50 Mm NaCl. The maximum adsorption was found at the optimum conditions like the temperature at 25 °C and contact time at 15 min in the biosorption process. The higher sorption efficiency was obtained in the Cd (88.8%) than the Zn (56.9%) [232]. The researchers concluded that this plant material is beneficial in the heavy metal retention. Additionally, studies also carried out in the compost material for the biosorption process. The magnetized porous flower biomass was used as a sorbent by Lingamdinne et al. [233] for the heavy metal (Pb (II), Co(II), and Cu(II)) removal from aqueous solutions. The equilibrium isotherm was analyzed and described by the Langmuir model and the adsorption rate shows that the adsorption was well specified by the pseudo-second order kinetics. This study interpreted that magnetic iron oxide intake in the *Lonicera japonica* flower biomass can be applied in the wastewater effluent for the removal of heavy metals [233]. The compost material also acts as a remedy for the increase of soil fertility [234]. Milojkovic et al. [235] used a compost of *Myriophyllum spicatum* for the selective removal of lead, copper, cadmium, nickel and zinc ions. They investigated that this material was suitable for the heavy metal biosorption from the wastewater because it has characteristic like inexpensive, feasible and naturally available [235]. Because of the presence of binding groups on the exterior of agricultural waste biomass, the sequestration of heavy metals is easy in this adsorbent when compared with the conventional adsorbents. It has the major advantage that the regeneration of agricultural biomass is applicable in an environmental friendly way. Several kinds of literature concerning the use of agricultural biomass/plant material tested in the adsorption method for the recovery of heavy metals from the effluent are listed in Table 6.

2.7.3.6. Industrial waste. Generation of industrial waste is developing the industries throughout the world. The clearance of such industrial waste also becomes a major concern. In order to lower the environmental impact, the utilization of industrial waste in some other technique is necessary. One of the technique is the utilization of industrial waste in the adsorption process but requires only a little alteration to increase its efficiency. Industrial waste is abundant, low cost and highly efficient in the sequestration of heavy metals. Hence various types of industrial wastes used for heavy metal removal have been discussed. Naiya et al. [244] had studied the removal of Pb (II) by using basic oxygen furnace sludge which was collected from the steel industry. The maximum uptake capacity of oxygen furnace sludge has reached 92.5 mg/g. The equilibrium isotherm has been analyzed by several isotherm equations and is best described by Freundlich isotherm. Additionally, desorption studies also carried out in this research using dilute HNO_3 solution [244]. The results confirm that

Table 6
List of agricultural waste biomass/plant material applied in heavy metal removal.

Adsorbent	Optimum pH	Optimum temperature (°C)	Optimum time (min)	Modified using	Metal	Adsorption capacity (mg/g)	Suited model	References
Cashew nut shell	5	–	30	–	Cu (II)	20	Langmuir and Freundlich	[221]
Peanut hull	4	25	60	–	Cu (II)	14.13	Langmuir model	[236]
Melia azedarach L. (MAL)	5–7	–	60	NaOH	Pb(II)	35.06	Langmuir model	[237]
Loquat leaves	6	–	60	NaOH	Pb(II)	34.6	Langmuir model	[238]
Wheat straw from *Triticum aestivum*	6	–	10	Urea	Cd (II)	39.22	Langmuir model	[239]
Orange peel	5.5	–	120	NaOH and $CaCl_2$	Zn (II)	56.18	Langmuir model	[240]
Moringa oleifera tree leaves	5	39.85	50	NaOH and citric acid	Pb(II)	209.54	Langmuir model	[241]
Litchi chinensis seeds	7.5	25	–	–	Ni (II)	66.62	Langmuir model	[242]
Rooibos shoot powder	6.7	25	60	–	Pb(II)	18.90	Langmuir model	[243]

this material has the potential to remove heavy metals from the wastewater. Another study also investigated in the basic oxygen furnace sludge but modified by mechanochemistry process for the removal of Cu (II) [245]. The removal efficiency was found to be 99.9% and the adsorption equilibrium isotherm shows the best fit with the Langmuir adsorption isotherm. Due to the presence of acid neutralization capacity the modified basic oxygen furnace has the ability to eliminate the heavy metals from acidic wastewater. These studies reveal that the basic oxygen furnace is good enough to act as an adsorbent for heavy metal removal because of its low cost. Recently, researchers have focussed on the adsorbent specifications like fast kinetics which makes the adsorbent suitable for commercial research. To satisfy this criterion, Bediako et al. [246] used modified waste textile cellulose fibers for the removal of Cd(II). This adsorbent was modified by carboxymethylation process in order to incorporate the carboxyl binding sites on the surface of the waste textile fibers. They also proposed the recycling of waste textile cellulose fibers and their usage in wastewater treatment.

The major type of waste material developed from the thermal plant is fly ash. Nowadays, the application of fly ash in the adsorption process is increasing because of its efficiency and existence of silica, alumina and magnetite [247,65]. Fly ash is considered to be a substitute for available adsorbents. But the efficiency of fly ash depends upon chemical treatment, fly ash source and some physical characteristics like density, the size of particle and surface area [65]. Al-Harahsheh [248] incorporated the fly ash geopolymers for copper removal. They proved that this material is highly amorphous and has high adsorption capacity towards copper removal. The disposal problems can be reduced because of the low build-up of fly ash material. Kuncoro and Fahmi [249] conducted an experiment in coal fly ash to specify the importance and its efficiency to eliminate Hg and Pb from aqueous solution. Some researchers investigated the waste sludge adsorbent discharged from electroplating industry which contains metal hydroxides and salts. Metal sludge was used as an adsorbent by Bhatnagar and Minocha [250] to remove cadmium. Later they immobilized the used adsorbent with the cement for eco-friendly safe disposal. By this technology, the solid waste gets reduced and showed good efficiency in the adsorption of cadmium metal ions. The waste from paper industries also promotes numerous dumping problems to the environment. Two types of pulp and paper industrial wastes like lime mud (LM) and recovery boiler ash (RB) were carried out in the research to sequestrate the heavy metals from metal finishing wastewater [251]. The result confesses that the lime mud has greater efficiency in the adsorption process than the recovery boiler ash because salts are present in the recovery boiler ash which make the metals to precipitate.

3. Future outlook

The effect of treatment for the heavy metal removal gives a big significance to study. The research based on implementing the treatment technology in lab scale will get expanded to pilot scale and industrial scale due to certain aspects like the accelerated growth of industrialization, pollution caused by heavy metals and the frequent availability of heavy metals in the environment. But there is a chance to arise some unknown issues because of the above-mentioned advancement in the treatment technology. Because most of the studies discussed herein were lab-scale study. In order to apply the treatment techniques in pilot scale and industrial scale, there is a need to analyze the studies related to these future perspectives which give the best platform in industrial applications at the commercial level also. This aspect needs to be investigated more in order to build up the treatment technologies in large scale.

4. Concluding notes

Nowadays, the heavy metal uptake from the wastewater is more essential because several threats are arising to both human health and the environment. In order to meet the proposed environmental regulations, various methods like coagulation/flocculation, ion exchange, flotation, membrane filtration, chemical precipitation, electrochemical treatment and adsorption for the elimination of heavy metals were developed. This paper reviewed the usable treatment technologies for the removal of heavy metals from the industrial wastewater. The capacity of treatment method to uptake the single and multi-component heavy metals were explained in detail. It also highlighted the advantages, disadvantages, and limitations of treatment methods to find out the assuring technique for heavy metal removal.

- The coagulation process removes the pollutants with high efficiency but there is a generation of secondary pollutant which transfers the harmful compounds into the environment. Additionally, sludge formation occurs in this treatment which must be handled finally. The most widely used methods for wastewater treatment is an ion exchange process. In this method, the maintenance cost is low and bring out the good flow rate of treated water. However, ion exchange has some prosperities, the disadvantages behind this process is fouling.
- Flotation is a most probable method for wastewater treatment because the sludge formation is low when compared with the coagulation process. In membrane separation process, the space requirement is lower than the conventional treatment for the separation of many kinds of heavy metals. Additionally, it kills the pathogenic organisms from the effluent. But backwashing of the membrane is needed which gives the poor separation performance.
- Chemical precipitation may induce the toxic sludge formation and inappropriate for low metal ion concentration. The electrochemical treatment uses the electrical energy and allowing the water to reuse by eradicating the pollutants without using any chemicals.

However, the application of electrochemical treatment in wastewater is limited due to the short lifetime of electrode material.

- From the recent literature survey, it was found that the adsorption process has become the promising alternative to replace the conventional techniques in removing the heavy metals. This review paper has a great potential towards the adsorption process but it can be applied only on a laboratory scale. Overall the availability and cost effectiveness are the two main parameters needed in finding of the most probable adsorbent for treating heavy metals in wastewater.
- The available treatment technologies described in this paper can be used for the expel of heavy metals from wastewater. But it is essential to choose most applicable method based on heavy metal concentration, operational cost, wastewater characteristics etc.

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