Removal of heavy metal ions from wastewater: a comprehensive and critical review

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Removal of heavy metal ions from wastewater is of prime importance for a clean environment and human health. Different reported methods were devoted to heavy metal ions removal from various wastewater sources. These methods could be classified into adsorption-, membrane-, chemical-, electric-, and photocatalytic-based treatments. This paper comprehensively and critically reviews and discusses these methods in terms of used agents/adsorbents, removal efficiency, operating conditions, and the pros and cons of each method. Besides, the key findings of the previous studies reported in the literature are summarized. Generally, it is noticed that most of the recent studies have focused on adsorption techniques. The major obstacles of the adsorption methods are the ability to remove different ion types concurrently, high retention time, and cycling stability of adsorbents. Even though the chemical and membrane methods are practical, the large-volume sludge formation and post-treatment requirements are vital issues that need to be solved for chemical techniques. Fouling and scaling inhibition could lead to further improvement in membrane separation. However, pre-treatment and periodic cleaning of membranes incur additional costs. Electrical-based methods were also reported to be efficient; however, industrial-scale separation is needed in addition to tackling the issue of large-volume sludge formation. Electric- and photocatalytic-based methods are still less mature. More attention should be drawn to using real wastewaters rather than synthetic ones when investigating heavy metals removal. Future research studies should focus on eco-friendly, cost-effective, and sustainable materials and methods.

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INTRODUCTION

The presence of heavy metals in wastewater has been increasing with the growth of industry and human activities, e.g., plating and electroplating industry, batteries, pesticides, mining industry, rayon industry, metal rinse processes, tanning industry, fluidized bed bioreactors, textile industry, metal smelting, petrochemicals, paper manufacturing, and electrolysis applications. The heavy metal contaminated wastewater finds its way into the environment, threatening human health and the ecosystem. The heavy metals are non-biodegradable1 and could be carcinogenic2; thus, the presence of these metals in water by improper amounts could result in critical health issues to living organisms.

The most popular heavy metals are lead (Pb), zinc (Zn), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr), and arsenic (As). Although these heavy metals can be detected in traces; however, they are still hazardous. Table 1 summarizes some heavy metals, focusing on their major sources, health effects, and the permitted quantity in drinking water. The aforementioned metals and others such as silver (Ag), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), calcium (Ca), antimony (Sb), cobalt (Co), etc. are commonly available in wastewater and need to be removed.

Recent studies have focused on a particular method for heavy metal ions removal, such as electrocoagulation (EC), adsorption using synthetic and natural adsorbents, magnetic field implementation, advanced oxidation processes, membranes, etc. These studies stood on the advantages and disadvantages of a specific method for wastewater treatment, including heavy metal removal. A complete picture of the heavy metals removal methods from wastewater resources has not been drawn yet. Therefore, the present review comprehensively and critically discusses the available technologies to expel heavy metal ions from wastewater efficiently. Moreover, it is essential to choose the most applicable method based on the removal efficiency, chemicals added/adsorbents, initial concentration, optimal treated pH value, and other operating conditions.

The methods discussed in this review are classified into adsorption-, membrane-, chemical-, electric-, and photocatalytic-based treatments. An assessment for each method is conducted. Additional details about the operating conditions, removal efficiency, and important remarks of each method are listed for the reported studies in the literature in the accompanying Supplementary Information file. The literature research is selected based on the availability of the operating and performance parameters for each method.

ADSORPTION-BASED SEPARATION

The adsorption mechanism is defined by the physicochemical properties of adsorbent and heavy metals and operating conditions (i.e., temperature, adsorbent amount, pH value, adsorption time, and initial concentration of metal ions). Generally, heavy metal ions can be adsorbed onto the adsorbent’s surface, as shown in Fig. 1a. This method was reported to have low operating costs, high removal capacity, easy implementation, and simple treatment by regenerating the adsorbed heavy metal ions2. Different types were developed for wastewater remediation, as discussed in the following sections.
Carbon-based adsorbents

Carbon-based nanoporous adsorbents, especially activated carbons (ACs), carbon nanotubes (CNTs), and graphene (GN), are extensively used in the applications of heavy metal removal owing to their tremendous surface area (500–1500 m²/g)⁸. The carbon surface charges can be enhanced by surface functional groups (such as carboxyl, phenyl, and lactone groups, as shown in Fig. 1b) to improve the heavy metal uptake⁹. Among various modification methods, nitrogenation, oxidation, and sulfuration are the most commonly employed techniques to enhance the specific surface area, pore structure, adsorption capacity, thermal stability, and mechanical strength¹⁰. However, they depend mainly on the adsorbent materials, which sometimes are very expensive¹¹. Subsequently, adsorbent’s cost should be considered in choosing the most suitable adsorbents.

Surface modification often reduces its surface area and, in turn, increases the content of surface functional groups. Consequently, more metal ions can be adsorbed¹². Supplementary Tables 1 and 2 summarize the removal capacity and characteristics of carbon-based adsorbents and composite adsorbents. The adsorption uptake increases by increasing the adsorbent surface area, adsorbent dose, initial concentration of metal ions, and contact time. Although the multi-wall carbon nanotubes (MWCNTs) have received particular interest for heavy metal removal¹³, they are highly hydrophobic and suffer from rapid aggregation in aqueous solution due to large Van der Waals forces, decreasing the adsorption potential.

There is a lack of literature in quantitative assessment of functional groups’ role in heavy metal ions sorption. Moreover, the current surface modification techniques demand high heat/pressure, strong acid/base, or intensive oxidation/reduction reactions. This complex preparation process makes the carbon-based adsorbents expensive, burdening their widespread use in industrial applications. Thus, researchers should propose innovative, low-cost, and environmentally friendly surface modification techniques.

Chitosan-based adsorbents

Chitosan (CS) is a natural adsorptive polymer that has an affinity toward pollutants in wastewaters because it has amino (–NH₂) and hydroxyl (–OH) groups¹⁴. Despite its unique features, it suffers from low mechanical strength and poor stability¹⁵, making the regeneration inefficient. Also, it is challenging to use CS in its

Table 1. Typical heavy metals existing in wastewater and their sources, in addition to the health issues caused by improper quantities and the permitted amounts in drinking water based on the world health organization (WHO) recommendations⁹.

| Common heavy metal | Main sources⁹,¹⁰,¹³¹² | Main organ and system affected¹¹–¹⁵ | Permitted amounts (μg)⁹ |
|--------------------|------------------------|-----------------------------------|-------------------------|
| Lead (Pb)          | Lead-based batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes, and plastic stabilizers. | Bones, liver, kidneys, brain, lungs, spleen, immunological system, hematological system, cardiovascular system, and reproductive system. | 10          |
| Arsenic (As)       | Electronics and glass production. | Skin, lungs, brain, kidneys, metabolic system, cardiovascular system, immunological system, and endocrine. | 10          |
| Copper (Cu)        | Corroded plumbing systems, electronic and cables industry. | Liver, brain, kidneys, cornea, gastrointestinal system, lungs, immunological system, and hematological system. | 2000        |
| Zinc (Zn)          | Brass coating, rubber products, some cosmetics, and aerosol deodorants. | Stomach cramps, skin irritations, vomiting, nausea, and anemia, and convulsions. | 3000        |
| Chromium (Cr)      | Steel and pulp mills and tanneries. | Skin, lungs, kidneys, liver, brain, pancreas, tastes, gastrointestinal system, and reproductive system. | 50          |
| Cadmium (Cd)       | Batteries, paints, steel industry, plastic industries, metal refineries, and corroded galvanized pipes. | Bones, liver, kidneys, lungs, testes, brain, immunological system, and cardiovascular system. | 3           |
| Mercury (Hg)       | Electrolytic production of chlorine and caustic soda, runoff from landfills and agriculture, electrical appliances, Industrial and control instruments, laboratory apparatus, and refineries. | Brain, lungs, kidneys, liver, immunological system, cardiovascular system, endocrine, and reproductive system. | 6           |
| Nickel (Ni)        | Stainless steel and nickel alloy production. | Lung, kidney, gastrointestinal distress, pulmonary fibrosis, and skin. | 70          |

Fig. 1 Adsorption process used for water treatment. a Heavy metal ions adsorption process; the metal ions of wastewater adhere to the surface of nanoporous adsorbents, which has a high surface area due to its porosity. The adsorption process could be selective for one or more metals than others. The regeneration process could be achieved using a desorbing agent. b Various modification techniques (i.e., nitrogenation, oxidation, and sulfuration) are used to functionalize carbon with different functional groups. Functionalization enhances adsorption capacity and stability.

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powder or flake form because of its low porosity, low surface area, resistance to mass transfer, and high crystallinity\textsuperscript{15}. Consequently, structural and chemical modifications have been proposed to overcome these drawbacks. Cross-linking chemical modification imparts strength to CS by bridging between polymer chains and the functional groups. However, this approach reduces the uptake\textsuperscript{16}.

Grafting is another chemical modification method that involves the covalent bonding of functional groups (like amine and hydroxyl) on the backbone of CS, leading to a remarkable increase in the adsorption capacity\textsuperscript{17}. Combining CS with other adsorbent materials has also been proposed to enhance CS’s adsorption capacity, mechanical strength, and thermal stability\textsuperscript{18}. The ion-imprinting technique was followed to prepare adsorbents which high selectivity for target metal ions\textsuperscript{19}.

Supplementary Table 3 lists the uptake of different CSs for heavy metal ions removal from wastewater. Generally, the uptake of CS depends mainly on the presence of protonation or non-protonation of amine (\(-\text{NH}_2\)) and phosphoric (\(\text{H}_3\text{PO}_4\)) groups, which affect the pH value of the wastewater. In the absence of the modifications, CS-based shows low reusability. This behavior might be attributed to the strong bond (between the metal ions and adsorbent surface), low thermal/chemical stability, low mechanical strength, incomplete desorption, declination in the effective adsorbate-adsorbent interaction, and unavailability of adsorption sites\textsuperscript{20}. So, alternative regeneration methods and modifications should be proposed to enhance the reusability of CSs.

**Mineral adsorbents**

Mineral adsorbents such as zeolite, silica, and clay are considered good candidates for water purification with low operating costs\textsuperscript{21}. Clay has extraordinary cation exchange capacity (CEC), cation exchange selectivity, surface hydrophobicity, high swelling/expandability, and surface electronegativity\textsuperscript{22}. In addition, acid washing, thermal treatment, and pillaring could enlarge the pore size, pore volume, and specific surface area, leading to a remarkable increase in the adsorption efficiency\textsuperscript{22}. Research studies (listed in Supplementary Table 4) showed that physical adsorption, chemical adsorption, and ion exchange are the most common mechanisms controlling wastewater treatment using mineral adsorbents. Besides the mentioned parameters, the pH, temperature, adsorption time, and adsorbent dosage are also considered vital parameters controlling the adsorption process. The adsorption removal efficiency increases when the pH increases and the initial concentration decreases\textsuperscript{23}.

Using natural minerals could be cost-effective. However, the removal efficiency might decrease after a few cycles\textsuperscript{24}. Therefore, different modification methods, such as calcination and impregnation, have been proposed to enhance the removal efficiency of such adsorbents\textsuperscript{25}. However, these modifications incur additional costs to the process and release new chemical agents into the environment. Grafting functional groups could synthesize eco-friendly and multifunctional adsorbents suitable for treating various types of wastewaters. The preparation of two-dimensional nanosheets and one-dimensional nanotubes-based clay adsorbents might lead to innovative low-cost and high-performance adsorbents.

**Magnetic adsorbents**

Magnetic adsorbents are a specific material matrix that hosts iron particles (usually magnetic nanoparticles, such as Fe\(_3\)O\(_4\))\textsuperscript{26}. The base material could be carbon, CS, polymers, starch, or biomass. As illustrated in Fig. 2, the adsorption process is affected by the magnetic field, surface charge, and redox activity characteristics. They showed low-cost, easy-synthesis, extraordinary surface charge, and reusability. Many magnetic adsorbents were proposed in the literature, such as zero-valent iron nanoparticles (ZVI NPs), iron oxides (hematite (\(\alpha\)-Fe\(_2\)O\(_3\)), maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)), magnetite (Fe\(_3\)O\(_4\))), and spinel ferrites. The mechanism and kinetics of the sorption process rely on several parameters, such as surface morphology and adsorbent magnetic behavior. They are also affected by experimental conditions such as pH, irradiation time, adsorbent concentration, wastewater temperature, and the initial dosage of pollutants\textsuperscript{27}. The presence of iron particles in adsorbent is very efficient in metal ions removal from effluent\textsuperscript{28}.

Some studies have focused on coating Fe\(_3\)O\(_4\) particles for removing heavy metal ions. Co-precipitation, high-gravity technology, and grafting are the most commonly used methods\textsuperscript{29}. The grafting method was considered a preferable choice because it is flexible and straightforward. However, it strongly depends on the active hydroxyl on the surface of Fe\(_3\)O\(_4\) particles and the number of active functional groups. The produced adsorbents were not adequately cyclic stable, which is a barrier facing the commercialization of this method. Additional details about different magnetic adsorbents can be found in Supplementary Table 5.

### Biosorbents

The most recent research studies in using biosorption for wastewater treatment are listed in Supplementary Table 6. The presence of numerous functional groups (i.e., carboxyl, amino, hydroxyl, phosphate, thiol, etc.) on the surface expedite the biosorption process\textsuperscript{30}. Generally, the interaction between pollutants and the surface of biosorbent can occur through electrostatic interaction, aggregation, complexation/coordination, microprecipitation, ion exchange, reduction, or oxidation\textsuperscript{31}. The solution pH affects the biosorbent surface charge density and ionization of functional groups located on the biosorbent surface\textsuperscript{12}. When pH is low, cations are almost stable and can be bonded to the biosorbent surface. On the other hand, at higher pH values, the solubility of metal cations decreases with the possibility of a precipitation phenomenon.

The biosorbent amount is a vital factor affecting the removal efficiency due to offering more vacant biosorption sites. The biosorbent capacity could increase at higher temperatures due to decreased solution viscosity, reduction in Gibb’s free energy, and bond rupturing. These reasons increase the collision frequency (mobility and kinetic energy) between biosorbent and metal ions and enhance the biosorbent active sites, leading to a higher affinity\textsuperscript{31}. In turn, the bonding force between biosorbent and pollutants could decline at higher temperatures, and thus the biosorbent sorption uptake reduces. It was elucidated that the removal efficiency increases as the mixing agitation rate increases\textsuperscript{32}.

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Metal-organic frameworks adsorbents

Metal-organic frameworks (MOFs) are generally synthesized via reticular synthesis in which metal ions are strongly bonded to organic linkers. Researchers proposed thousands of MOFs. It was noticed that most of the organic ligands used to form many MOFs are very expensive and toxic. Zincium-MOFs family (such as UiO-66) is promising nanostructure materials for sorption applications due to the easy incorporation of functional groups and hydrolytic-thermal stability such as amine, carboxylic, hydroxyl, and oxygen or by using the cross-linking method. Composite-based MOF adsorbents could obtain further enhancement in the adsorption capacity of MOFs. Supplementary Table 7 lists the uptake of different MOFs towards several heavy metal ions in wastewater.

Despite the exciting features of MOFs and their good capability to remove heavy metal ions, they have micropores (i.e., tiny pores) inaccessible for some target metals. Also, most of them have low stability in water. Mn, Fe, and Cu have been used to form MOFs, but most of them resulted in poor chemical stability. Therefore, further research is still needed to tune the MOFs’ structure and scale up these materials to implement them into industrial wastewater applications. Moreover, different functionalization methods should be proposed and applied to enhance MOFs’ stability and sorption kinetics.

The reported maximum uptakes of heavy metal ions for a proper adsorbent are listed in Table 2.

MEMBRANE-BASED FILTRATION AND SEPARATION

Over the years, technological advancement in membrane development has led to an increase in the use of membranes for filtration and extraction of heavy metal ions from wastewater. A simplified schematics for different membrane-based filtration processes is illustrated in Fig. 3a–c, while Fig. 3d demonstrates various pollutants that can be separated by different membrane techniques.

| Heavy metal Adsorbent | Adsorption capacity (mg/g) | Ref. |
|----------------------|---------------------------|-----|
| Pb^{2+} | Polyrhodanine/ MWCNTs | 8118.0 | 38 |
| Cu^{2+} | Polyvinylpyrrolidone-reduced GO (PVP-rGO) | 1689.0 | 39 |
| Cd^{2+} | Polyvinyl alcohol/zeolite nanofibrous | 838.7 | 40 |
| Cr^{3+} | N-MCNP | 638.0 | 41 |
| Co^{6+} | GSC | 2859.0 | 42 |
| Co^{2+} | PAMAM/CNT | 494.0 | 43 |
| Fe^{2+} | MNR | 127.0 | 44 |
| Zn^{2+} | PAMAM/CNT | 470.0 | 43 |
| Ni^{2+} | Coconut husk | 404.5 | 45 |
| Hg^{2+} | MSWCNT–CoS | 1666.0 | 46 |
| As^{3+} | PAMAM/CNT | 432.0 | 43 |
| Mn^{2+} | MCS | 200.9 | 47 |
| Au^{3+} | CSGOS | 1076.7 | 20 |
| UO_{2}^{2+} | SPG | 403.8 | 48 |
| U^{6+} | CCM | 392.7 | 49 |
| Sb^{3+} | Chitosan functionalized iron nanosheet | 138.8 | 50 |

Ultrafiltration

Ultrafiltration (UF) is used at low transmembrane operating pressure (TMP). Because UF membrane pores may be larger than the heavy metal ions, additives may be bonded to metal ions to enlarge the size of the metal ions. Therefore, micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) are proposed.

MEUF is formed by bonding UF and surfactant. MEUF has high flux and high selectivity, leading to low-energy consumption, high removal efficiency, and less space demand. MEUF is most suitable for wastewater whose heavy metals are in low concentrations. In MEUF, a surfactant is mixed with wastewater in a concentration above the critical micellar concentration (CMC). Beyond CMC, surfactant monomers assemble and increase the creation of some micelles in the solution. The surfactant contains a hydrophobic tail and a hydrophilic head. The inner hydrophobic core of the micelles could solubilize organic matters (having low molecular weight) as a solubilizate, while the surface adsorbs counter metal ions on their surface due to electrostatic interactions. Surfactants, whose electric charge is the opposite of the metal ions, usually attain the highest retentions. In this regard, polyelectrolytes (PE), cationic surfactants, and anionic surfactants (e.g., sodium dodecyl sulfate (SDS)) are used for effective heavy metals extraction.

A summary of different studies on the MEUF process is given in Supplementary Table 8. The performance of MEUF depends on several factors, including the added solutes, type of surfactant, operating conditions, and kind of membrane used.

PEUF is formed through the integration of UF and binding polymers. The functional groups of the bonding polymers could be sulfonate, phosphonic, carboxylated, or amine, and they are bonded via chelating or ionic bonds. PEUF are also known as polymer-supported, complexation, polymer-assisted, size enhanced, and complexation enhanced ultra-filtrations. While permitting water and un-complexed components to permeate the membrane pores, the PEUF process blocks and extracts polymer-bonded metal ions.

A summary of studies conducted on PEUF is presented in Supplementary Table 9. PEUF shows effective polymer bonding, effective extraction, ability to recover and reuse complexation polymer of retentate, low-energy demands, and low-cost operation. However, the choice of appropriate water-soluble polymer macro-ligands remains the main challenge of developing this technology.

Microfiltration

Microfiltration (MF) employs a microporous membrane to remove micron-sized particles, bacteria, viruses, protozoa, contaminants, pollutants, etc., from a solvent/solution. MF process is also a low pressure-driven membrane process, whose membrane pores are in the range of 0.1–10 µm. Some of the MF membranes are made of silica, ceramics, zirconia, alumina, PVC, polysulfone, PTFE, polypropylene, PVDF, polyamides, polycarbonate, cellulose acetate, cellulose esters, or composite materials. The commercial application
of MF is widely found in pharmaceutical and biological industries. However, the application of the MF system may be found in particle removal of the rinse water in the semiconductor industry, sterilization of beer and wine, other juices and cider clarification, and wastewater treatment. The application of MF in heavy metal removal has not drawn enough attention because of its low removal ability. However, it has been used by modifying membrane or chemical pre-treatment of the feed solution. Depending on the mode of application, the MF process is available in two main configurations: crossflow and dead-end. Some studies on MF are summarized in Supplementary Table 11.

**Reverse osmosis**
RO is a pressure-driven separation process that employs a semi-permeable membrane (pore size 0.5–1.5 nm) to allow only smaller molecules to pass. RO process reverses the normal osmosis process by applying pressure (20–70 bar) >the osmotic pressure of the feed solution. The molecular size of the solutes blocked is usually in the range of 0.00025–0.003 μm. RO process could extract 95–99% of inorganic salts and charged organics. RO process is compact and attained high rejection efficiency. However, membrane fouling and degrading are the major drawback of RO systems. The RO separation process was used to extract heavy metal ions, including Ni²⁺, Cr⁶⁺, and Cu²⁺ from electroplating wastewater, with a removal efficiency of >98.75%. Recently, RO has been used to purify industrial wastewaters from coster-field mining operations located in Victoria-Australia with mean extraction efficiency of 10%, 48%, 82%, 66%, and 95% for Fe³⁺, Zn²⁺, Ni²⁺, As³⁺, and Sb⁵⁺ respectively. Other studies on RO heavy metals removal are summarized in Supplementary Table 12.

**Forward osmosis**
Forward osmosis (FO) is an osmosis process that requires a membrane to balance selectivity and permeated water flux.
In FO, a semi-permeable membrane separates a feed solution from the draw solution, as shown in Fig. 3b. The draw solution is usually at a higher osmotic pressure compared to the feed solution. Due to the osmotic pressure difference between the feed and draw solutions, water transports from the feed solution to the draw solution, thereby keeping the rejected solutes on the feed side and treated water on the draw solution. FO does not require hydraulic pressure; thus, it is energy-saving. FO process is also environmentally friendly, easy cleaning, and low fouling; therefore, it is widely used in wastewater treatment. Nevertheless, FO has limitations, such as draw solution re-concentration, membrane selection challenges, internal and external concentration polarization. Supplementary Table 13 summarizes the use of FO, including thin-film membranes.

**Electrodialysis**

Electrodialysis (ED) is used to separates ions at the expense of electric potential difference. ED uses a series of cation exchange membranes (CEM) and anion exchange membranes (AEM), alternatively arranged in parallel, to separate ionic solutes. In the ED process, the anions pass through AEM, while cations pass through CEM. In such a case, the treated stream (diluate) is produced from half of the ED stack channels, while the concentrated stream is expelled from the other half, as shown in Fig. 3c. ED offers high water recovery, no phase change, no reaction, or chemical involvement, and can operate over a wide range of pH values. However, ED also exhibits membrane fouling, high cost of membranes, and demand for electric potential.

ED has been used to separate Ni²⁺, Pb²⁺, and K⁺ from synthetic solution through a novel ED heterogeneous CEM (consisting of 2-acrylamido-2-methyl propane sulfonic acid-based hydrogel and PVC) to attain extraction efficiency of 96.9%, 99.9%, and 99.9% for Ni²⁺, Pb²⁺, and K⁺, respectively. A bath ED process was employed to recover Pb²⁺ and reached a maximum separation efficiency of ~99.6%. A pilot-scale ED system has also been used to extract Cu²⁺, Ni²⁺, and traces of Cd²⁺, Fe³⁺, Cr⁶⁺, and Zn²⁺, and exceeded 90% removal rate. As³⁻ and As⁵⁻ were removed from metallurgical effluent by ED and attained a removal efficiency of 91.38%.

**Other membrane-based methods**

Membrane distillation (MD) and liquid membrane (LM) are also used for wastewater treatment. MD is a hybrid thermally driven membrane separation process that consists of cold and hot compartments separated by a microporous hydrophobic membrane. MD allows only vapor to permeate its pores while blocking other molecules. MD exists in four configurations: direct contact MD, air gap MD, sweeping gas MD, and vacuum MD. MD process has been reported to achieve over 96% removal of Ca²⁺, Mg²⁺, Fe³⁺, and Fe⁷⁺, and more than 99% for As³⁻ and As⁵⁻.

On the other side, LM is made of a liquid phase or thin-layer organic phase, which acts as a barrier between two aqueous phases. LM is immiscible to the feed solution and retentate solution, and combined stripping and extraction processes in a single stage. LM is highly selective, relatively efficient, and can achieve specific molecular recognition. However, the membrane’s long-term stability is poor. LM process exists as a supported liquid membrane (SLM), emulsion liquid membrane (ELM), bulk liquid membrane (BLM), and polymer inclusion membrane (PIM). Among these types, the SLM process is an attractive alternative to traditional solvent extraction for heavy metal removal. SLM achieved a removal efficiency of 89% for Zn²⁺, Cd²⁺, Cu²⁺, and Fe³⁺.

**Chemical-based separation**

Chemical methods for removing heavy metals from wastewater are mature and used early. In this section, the chemical-based methods will be discussed, including precipitation, coagulation, flocculation, and flotation.

**Precipitation**

Chemical precipitation (the so-called coagulation precipitation) is broadly used in industries and is considered one of the most effective and mature methods. It changes the form of dissolved metal ions into solid particles to facilitate their sedimentation. The reagent coagulation (coagulant) precipitates metal ions by changing pH, electro-oxidizing potential, or co-precipitation. It is usually followed by the removal of sediments. A simple schematic of the chemical precipitation process is depicted in Fig. 4.

Hydroxide precipitation is broadly used due to its relatively inexpensive, simple, and tunable pH. It is implemented by adding a hydroxide to the stirred wastewater to form insoluble metal hydroxide precipitates. For example, a metal ion could react with calcium hydroxide (lime) to produce metal hydroxide precipitates and calcium ions as:

\[
\text{Metal}^{n+} + \text{Ca(OH)}_2 \leftrightarrow \text{Metal(OH)}_n \downarrow + \text{Ca}^{2+}
\]  

(1)

It was found that pH values of 9–11 improved this process efficiency. However, a high pH value is considered a disadvantage of this method since it requires a large dosage of precipitants. One of the most effective hydroxide precipitates for treating inorganic effluents of heavy metal concentration of 1000 mg/L is lime (CaO or Ca(OH)₂). A summary of some hydroxide precipitation studies is presented in Supplementary Table 14. It can be seen that the majority of metals removed by this method are Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, and Cr³⁺. In addition to the need for the high dosage to get optimal pH, there are some drawbacks, such as relatively large volumes of sludge leading to dewatering, disposal issues, amphoteric, and the inhabitation of metal hydroxide precipitation with the presence of complexing agents. The sulfide precipitation method distinguishes itself by higher removal efficiency and lesser dissolved solids increment than the hydroxide method. This method was reported to treat toxic heavy metal ions. Lower sulfide results in a higher zinc concentration in the effluent, while higher sulfide leads to a malodor problem due to high residual sulfide. Also, it could produce hydrogen sulfide gas which is malodorous and toxic. For these reasons, the sulfide precipitation is recommended to be executed at a neutral pH.

The metal sulfide precipitations could follow Eq. (2) reaction.

\[
\text{Metal}^{n+} + S^{2-} \leftrightarrow \text{Metal}_n S \downarrow
\]  

(2)

Supplementary Table 15 summarizes the metal ions removal using sulfite precipitations. The toxicity of sulfide and its high cost are the most shortcomings.
As an alternative method to hydroxide precipitation, carbonate precipitation shows good effectiveness and optimum precipitation at lower pH values. It could be achieved using sodium carbonate or calcium carbonate. The classical carbonates can be formed based on Eq. (3 and 4) 

$$\text{Metal}^{n+} + n\text{Na}_2\text{CO}_3 \Leftrightarrow n\text{Metal(CO}_3^2\text{)} + n\text{Na}^+$$  

Eq. 3

$$n\text{Metal(CO}_3^2\text{)} + H_2O \Leftrightarrow CO_2 \uparrow + (\text{MeOH})_n\text{CO}_3 \downarrow$$  

Eq. 4

It could have less sludge volume, but it could release CO$_2$ bubbles and needs higher reagents for efficient precipitation. Supplementary Table 16 lists some studies concerning carbonate precipitation. It can be seen that copper and manganese are the major metals removed by this technology. Zinc and lead could also be removed efficiently.

Fenton reaction is usually used to improve the removal efficiency of the chemical precipitation methods. The Fenton or Fenton-like oxidation is used for the de-complexation of heavy metal complexes. However, the pH is adjusted by the chemical precipitation mechanism (e.g., NaOH). Fenton chemistry is not straightforward, and it is performed through numerous reactions, depending upon various active intermediates, such as $[\text{Fe}^{IV} \text{O}^+ \cdot]^+$ and hydroxyl radicals. The classical Fenton reaction is:

$$\text{Fe}^{2+} + H_2O_2 \Leftrightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^-$$  

Eq. 5

$$\text{HO}^- + \text{dye} \Leftrightarrow \text{oxidized dye} + H_2O$$  

Eq. 6

$\text{Fe}^{3+} + H_2O_2$ (Fenton-like) and $\text{Fe}^0 + H_2O_2$ (advanced Fenton) are also represented as an alternative for $\text{Fe}^{3+} + H_2O_2$. Additional detailed examples of using the Fenton-integrated chemical precipitation method are summarized in Supplementary Table 17.

Some metals are represented in small volumes in bulk wastewater, such as radionuclides. The removal of radioactive metals is listed in Supplementary Table 18.

Coagulation and flocculation

Coagulation is the destabilization of colloids by neutralizing the forces that keep them parted, while flocculation is the agglomeration of destabilized particles. Traditional coagulants are aluminum, ferrous sulfate, and ferric chloride, using to neutralization of ion charges. Flocculation bonds the particles forming large agglomerates with the help of a flocculant, such as polyaluminum chloride (PAC), polyferric sulfate (PFS), polyacrylamide (PAM), and other macromolecule flocculants. The PE were reported as one of the most practical flocculations, but the produced sludge might be toxic. The flocculants are generally not natural and non-biodegradable.

The process is illustrated in Fig. 5, including the sedimentation. Some weaknesses are toxicity and health hazard. Inorganic coagulants, a large volume of sludge, selective for some metals and inefficient in emerging contaminants, increasingly effluent color, inefficient when using natural coagulants, and complex of scaling up. Supplementary Table 19 summarizes some of the studies conducted on coagulation-flocculation for heavy metal removal from different wastewater sources. The typical heavy metals removed by this method include Cu$^{2+}$, Pb$^{2+}$, and Ni$^{2+}$. Other metals such as As$^{3+}$, Se$^{4+}$, Cr$^{3+}$, Sb$^{3+}$, Sb$^{5+}$, Ag$^{2+}$, could also be efficiently removed.

Flotation

Flotation is used to remove various metal ions. The general schematic of the flotation process is shown in Fig. 6. Dissolved air flotation, ion flotation, and precipitation flotation were extensively studied. In the dissolved air flotation, air (or gas) is fed to wastewater to generate micro-bubbles that could attach the metal ions, developing lower density agglomerates, leading to raising the flocs through the wastewater. The accumulated slug at the top surface can easily be removed.

The ion flotation process relies on the increase of hydrophobicity of metal species by using surfactants; therefore, the hydrophobic species are removed by air bubbles. The added surfactant facilities as collectors, while frothers control the indexes of ion flotation. When the concentration of metal ions is low within a large quantity of wastewater, the ion flotation appears inefficient. The ion flotation process showed low-energy consumption, limited volume demands, reduced sludge volumes, and selective treatment. The precipitation flotation process is basically a chemical precipitate process that implements micro-bubbles. That precipitation flotation takes a short time to complete efficiently. Generally, the flotation processes have advantages such as rapid operation, compact process, and a moderate cost.

Significant attention has recently been paid to ion flotation among all flotation processes, as observed from Supplementary Table 20. Since ion flotation depends on surfactants as collectors, efficient and non-toxic surfactants are required. Chemical synthetic surfactants have been introduced to have strong collection ability, good selectivity, and easy construction. However, the cost and toxicity issues limit them. On the other side, biosurfactants sound more environmentally friendly, but they...
exhibited low removal rates, large dosage quantity, and longtime process\textsuperscript{94}. In this regard, nanoparticles have been proposed as new collectors that showed both benefits of synthetic- and biosurfactants\textsuperscript{94}.

**ELECTRIC-BASED SEPARATION**

In this section, different electrochemical methods (i.e., electrochemical reduction (ER), EC, electroflotation (EF), and electrooxidation (EO)), and ion exchange method are discussed.

**Electrochemical treatment**

In an electrochemical system, oxidation is performed at the anode (positive side), where electrons transfer to the cathode (negative side), at which the reduction process occurs. These two chemical reactions are called redox (reduction-oxidation), leading to water purification through metal removal. For example:

\[
\text{Metal}^{n+} + n\text{H}_2\text{O} \rightarrow \text{Metal}^{n+} (\text{H}_2\text{O})_n \text{ solution} \downarrow + \text{metal in solution} \quad (7)
\]

Selection of the anode and cathode mainly decides the type of the electrochemical method and influences the removal efficiency towards specific metal ions. Figure 7a shows different types of electrode arrangements, namely: monopolar electrodes in series (MP-S) arrangement, monopolar electrodes in parallel (MP-P) arrangement, and bipolar electrodes in series (BP-S) arrangement\textsuperscript{96}. MP-S and MP-P are preferable from the economic point of view and also yield high products.

The electrochemical processes are primarily classified into ER, EC, EF, and EO processes. In the ER method, also known as electrodeposition and electroplating, targeted atoms or molecules are deposited on the surface of the cathode, as shown in Fig. 7b.

Fig. 7  Electrochemical methods and arrangements used for heavy metals removal. a Different arrangements of electrodes in electrolysis cell (i.e., monopolar electrodes in series (MP-S), monopolar electrodes in parallel (MP-P), and bipolar electrodes in series (BP-S)), b mechanism of the electrochemical reduction method in which positive metal ions are deposited over the cathode, c electrocoagulation process showing the flotation and precipitation of metal ions, d basic electroflotation methods—anions are released from anode to combine with cations (metal ions) and then floating over the water, e electrochemical oxidation (EO) process (I) direct EO in which the ions react with OH and precipitate or (II) indirect EO in which mediators are used to forming oxidants that interact with the ions to be removed, and d electro-Fenton process in which OH\textsuperscript{−} is released at anode and reacts with metal ions, and hence wastewater is purified due to precipitation.
treatment. It is worth noting that cathodes with high over-potential toward hydrogen evolution are more efficient in pollutant removal/reduction\(^{99}\). Supplementary Table 21 lists the most recent research studies of heavy metals removal using ER and its conditions. The cathodes made of carbon-based or sulfur mixture with different ratios in acidic conditions are suitable for removing Hg\(^{2+}\), Cd\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) from wastewater\(^{100}\). Iridium oxide-coated titanium anode was found as a perfect material for Cd\(^{2+}\) removal with an efficiency of 100% regardless of its initial concentration\(^{101}\). More attention should be paid to the reactor design and the operating conditions to enhance the performance of the wastewater treatment\(^{99}\). Energy consumption is a barrier that should be solved to commercialize this type of treatment in industrial applications.

In the EC method, steel (iron) or aluminum electrodes, which are non-toxic and reliable, are mostly used\(^{102}\). The mechanism of the EC method is sequentially as; dissolving cations of anodic metal (Eq. \((8)\)), hydroxide complex formation (coagulants, Eq. \((9)\)), aggregate stability and phase separation, and precipitation and flotation.

\[
\text{Metal} \rightarrow \text{Metal}^{n+} + \text{ne}^- \quad (8)
\]

\[
2\text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(9)
\]

Cations from anode destabilize colloidal particles and also form polymeric hydroxide complex metal ions (i.e., coagulants, Eq. \((9)\)), aggregate stability and phase separation, and precipitation and flotation.

\[
\text{Metal}^{n+} (aq) + n\text{OH}^- \rightarrow \text{Metal(OH)}_n(s) \downarrow \quad (10)
\]

Therefore, metal hydroxide (larger particles) whose density is higher than water forms and precipitates (settle down), while floc (fine particles) floats, as illustrated in Fig. 7c. The coagulants are generated in situ due to anode oxidation, which is considered a further advantage of EC methods over other technologies. Supplementary Table 22 summarizes the most recent EC studies for heavy metal removal from wastewater. Generally, it was found that lower energy consumption and higher removal efficiency are achieved when the alternating current is used rather than the direct current. Also, the rise in temperature, voltage, and pH reduces the test duration.

EC drawbacks are the electrodes passivation and relatively high energy consumption\(^{103}\) and the challenge of large-scale applications at lower energy consumption\(^{104}\). Many successful approaches were proposed to alleviate the passivation of the electrode, such as aggressive ion addition, alternating current operation, polarity reversal operation, ultrasonication, mechanical cleaning of electrodes, chemical cleaning of electrodes, hydrodynamic scouring. However, each route has drawbacks, such as generating hazardous byproducts, costly, additional treatment, and infrastructure, and increasing sludge production\(^{105}\). Accordingly, the EC process is still not fully mature applications.

The mechanism of EF is mainly based on carrying out water electrolysis on insoluble electrodes, while the electrolysis reaction is introduced to facilitate the treatment process\(^{106}\), as sketched in Fig. 7d. So, the process efficiency depends on tiny (~ 0.15 mm) and uniform bubbles. Details of EF separation are listed in Supplementary Table 23. It can be concluded that Ti-based anodes were widely used in the EF process\(^{107}\). They are insoluble, non-corrosive, and have high catalytic activity reactions with Cl\(_2\) and O\(_2\) in the electrolyte\(^{108}\). It was showed that the optimal pollutant concentration is in a range of 10–100 mg/L, while the maximum could be 200 mg/L\(^{109}\). The removal efficiency of the EF process toward heavy metal is limited due to low O\(_2\) evolution over-potentials\(^{107}\). Therefore, hybridization between EF, membrane, and EC was a promising approach to improve the overall system performance to remove heavy metals\(^{110}\).

The mechanism of removing compounds from wastewater using EO is direct and indirect, as shown in Fig. 7e. The direct mechanism is simple. The performance of the indirect oxidation by chlorine depends on the NaCl concentration and is independent of current intensity\(^{111}\). The pollutants exchange electrons directly with the anode surface, and the polymeric layer is formed on the anode surface, leading to electrode deactivation and degrading efficiency. Oxidized contaminants appear in the solution when the organic pollutants interact with oxidants, as shown in Fig. 7e. The following equations describe the EO process:

\[
\text{Metal} + \text{H}_2\text{O} \rightarrow \text{Metal(OH)} + \text{H}^+ + \text{e}^- \quad (11)
\]

\[
\text{Metal(OH)} \rightarrow \text{MetalO} + \text{H}^+ + \text{e}^- \quad (12)
\]

\[
\text{MetalO} + \text{R} \rightarrow \text{M} + \text{RO} \text{and MetalO} \rightarrow \text{M} + \frac{1}{2} \text{O}_2 \quad (13)
\]

Supplementary Table 24 lists the efficiency of the EO process at specific operating conditions using different anodes. Pt, Au, Mn, boron-doped diamond (PbO\(_2\)), and mixed metal oxide (MMO) (such as SnO\(_2\), PbO\(_2\), Ti/TiO\(_2\), IrO\(_2\), Sb\(_2\)O\(_5\), RuO\(_2\)) are widely used as anodes\(^{112}\). The main advantages and disadvantages of several anode materials are listed in Table 3. Highly efficient anode materials are expensive. So, other materials should be proposed to compromise efficiency and cost. Moreover, the presence of different types of metal ions in wastewater affects treatment efficiency. Hence, there is an urgent need to find efficient anode materials with high efficiency in diluted solutions. Future trends should investigate the effectiveness of integrating EO with other water technologies to overcome operational issues. Different electrochemical treatment processes are compared in Table 4.

| Table 3. Comparison between different types of anodes used in the EO method. |
|---------------------------------------------------------------|
| Anode material | Advantages | Disadvantages |
|----------------|------------|---------------|
| Pt, Au, Mn | - Stable and inert. | - Expensive. |
|            | - More suitable for lab testing. | - Not suitable for industrial applications. |
|            | - Outstanding repeatability properties. | - Low mineralization efficiency. |
| PbO\(_2\) | - Relatively inexpensive. | - Toxic Pb could be formed. |
|            | - Suitable for mineralizing organics | - Low efficiency in industry applications |
| MMO | - Relatively inexpensive. | - Toxic Sb could be formed. |
|      | - High stability. | - Uneven coating. |
|      | - Good conductivity properties. | |
| BDD | - High potential for mineralizing organics. | - Costly. |
|      | - Superior conduction characteristics even at low temperatures. | - Not efficient in highly diluted wastewater. |
|      | - More resistive to corrosion and high electrochemical stability. | - Overrising current density more than a limited one. |
Ion exchange treatment

The ion exchange method is a reversible chemical reaction used to replace the undesirable metal ion with harmless and environmentally friendly ones. A heavy metal ion is removed from a wastewater solution by attaching it to an immobile solid particle as a replacement with the solid particle cation, as shown in Fig. 8. The material of solid ion-exchange particles could be either natural, e.g., inorganic zeolites, or synthetically produced, e.g., organic resins. The ion-exchange method can remove target (some or all) heavy metal ions, such as Pb\(^{2+}\), Hg\(^{2+}\), Cd\(^{2+}\), Ni\(^{2+}\), V\(^{4+}\), Cr\(^{3+}\), Cr\(^{4+}\), Cu\(^{2+}\), and Zn\(^{2+}\) from wastewater.

The ion exchange mechanism for metal removals can be explained in the following reaction as the ion exchange particle having ion exchanger of M\(^{-}\)EC\(^{+}\) (M\(^{-}\)is the fixed anion and EC\(^{+}\) is the exchange cation; Na\(^{+}\) and H\(^{+}\) are frequently used as exchange cations) to exchange its cation (EC\(^{+}\)) with the wastewater cation (WC\(^{+}\))

\[
M^{−}EC^{+} + WC^{+} ⇌ M^{n+}WC^{−} + EC^{+}
\]

Different types, such as Amberlite\(^{115}\) and Diaion CR1\(^{116}\), were investigated for cations removal. Zeolite has an excellent ion exchange capability owing to its negative charge resulting from Si\(^{4+}\), which resides in the middle of the tetrahedron and undergoes isomorphous replacement with Al\(^{3+}\) cations. MOFs have recently been suggested as good candidates for the ion-exchange removal process\(^{117}\). Some reported MOFs used for ion-exchange reactions include AMOF-1 (for Cd\(^{2+}\), Pb\(^{2+}\), and Hg\(^{2+}\) removal\(^{118}\), ZIF-8 (for Cu\(^{2+}\) removal\(^{119}\), and ZIF-67 (for Cr\(^{6+}\) removal\(^{22}\)). Supplementary Table 25 lists some studies that focused on the ion exchange method. Like adsorption, the ion exchange method needs more research on stability and reusability.

PHOTOCATALYTIC-BASED SEPARATION

The photocatalytic process was reported as a simple process for wastewater treatment that uses light and semiconductors, such as...
Methods of wastewater treatment

| Cost-effective | Membrane | Chemical | Electric | Photocatalytic |
|----------------|----------|----------|----------|---------------|
| Cost-effective | High     | Low      | Medium   | High          |
| Technical maturity | High | Low | Medium | High          |
| Environment friendly | Low | High | Medium | Low           |
| Automaticity | Low     | High     | Medium   | Low           |

Index: Mature | Higher | High | Low | Lower

**Fig. 9** A general comparison between the typical methods used for heavy metals removal from wastewater. The compared methods are adsorption-, membrane-, chemical-, electric-, and photocatalytic-based in terms of cost-effective, technical maturity, environment friendly, and automaticity, based on the above discussion and the reported studies in the literature. The electric- and chemical-based methods are represented here for chemical precipitation and electrochemical processes, respectively.

Titanium dioxide (TiO$_2$). Three key steps are taken in this process: charged carrier photogeneration, charged carrier separation and diffusion to the photocatalyst surface, and redox reaction on the photocatalyst surface. The efficiencies of real soil washing wastewater were treated using an outdoor dual solar photovoltaic process of flat plate collector for the removal of 93.5% Cu$^{2+}$, 99.6% Fe$^{3+}$, and 99.4% Zn$^{2+}$123. A simulated ultraviolet (UV)-solar TiO$_2$ photocatalysis has been used for the removal of ethylenediamine-N, N'-disuccinic acid (EDDS), and Cu$^{2+}$ from wastewater (0.2 mM EDDS and 0.2–1.4 mM CuSO$_4$) to obtain 100% conversion efficiency at 24% mineralization degree124. In another study, maximum removal efficiencies of 41% Cu$^{2+}$, 100% Fe$^{3+}$, 100% Zn$^{2+}$ and 100% EDDS were obtained from synthetic soil washing solution (3.6 × 10$^{-3}$ mM EDDS, 8.0 × 10$^{-2}$ mM Cu$^{2+}$, 1.0 × 10$^{-1}$ mM Fe$^{3+}$ and 8.0 × 10$^{-2}$ mM Zn$^{2+}$)125.

Using visible light irradiation, a synthesized rhodium/antimony co-doped TiO$_2$ nano-rod and titane nanotube (RS-TONR/TNT) was used to extracts Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and organic pollutant from wastewater with 70 and 80% degradation efficiency for dye and Bisphenol A, respectively. The photocatalytic process using CeO$_2$/BiOIO$_3$ composites with Ce$^{4+}$/Ce$^{3+}$ redox centers was used to attain 86.53% Hg$^{2+}$ removal efficiency under visible light absorption and photocatalytic activity. In an aqueous solution containing As$^{5+}$ and Cr$^{6+}$ (concentration of 0.10 mg/L), a synthesized 3D-Fe$_2$O$_3$ was used to achieve nearly 100% removal rates using solar light irradiation and photocatalytic activity. A fabricated CH-GEL/ZSPNC hybrid nanocomposite ion exchanger achieved 90% Ni$^{2+}$, 94.9% Zn$^{2+}$, 95% Mg$^{2+}$, 100% Pb$^{2+}$, 90.3% Cd$^{2+}$, 88.9% Cu$^{2+}$ and 84% Rhodamine-B (dye) extraction efficiencies using solar light. A fabricated Cs/silver bio-nano-composites (Cs/PVDC/Ag) was utilized in photocatalytic oxidation process for 97% Cu$^{2+}$, 88% Pb$^{2+}$, 89% Cd$^{2+}$ and 77% dye removal. Although this technology shows the in site generation of reactive radicals, no chemicals used, no sludge production, it has some drawbacks. It is still on a laboratory scale, low throughput, dependent on pH, and inefficient when different metals are present.

**REMARKS OF THE TREATMENT METHODS AND FUTURE PERSPECTIVES**

It could be figured out from the discussion above that each method used for metal ions removal is not thoroughly preferred and has its advantages and disadvantages. A general comparison between the typical techniques in terms of economic feasibility, technical maturity, less pollution to the environment, and operation control and automaticity is summarized in Fig. 9.

Among all methods, adsorption is the most considered method in recent years. It showed easy operation, low-cost, and high-sorption capacity. Developing eco-friendly and cost-effective adsorbents from wastes is the current research trend. However, disposal of such adsorbents after the adsorption process is a big challenge to avoid environmental risks. Adsorption onto ACs was reported as a feasible method for industrial scale. Adsorption of metal ions from low traces and efficient regeneration processes need additional research. The economic feasibility of industrial applications is also essential.

Membrane methods play a significant role in wastewater treatment and have become a more promising option for wastewater treatment. They are already best-suited for some separation applications such as desalination. Membrane processes are characterized by high metal ions extraction efficiency. However, membrane fouling and biofouling, low recovery for the amount of feed wastewater, process complexity, pre-treatment, periodic membrane cleaning, and high cost are some of the shortcomings of this method. The development of novel membrane materials with enhanced thermal and chemical stability for industrial wastewater treatment is needed in the future to attain better anti-fouling properties and enhance membrane selectivity for the target metals. For both adsorption and membrane methods, the automatic operation of industrial plants needs further implementation and improvement.

Chemical-based separations have widely been used for heavy metal removal owing to their simplicity and low cost. Nevertheless, chemicals are consumed for tuning pH values and enhancing the accumulation of ions. A large-volume sludge is produced that needs further treatment. The electrochemical treatment has the merits of quick treatment, well-controlled, easier sludge removal, and fewer chemicals. However, the high cost of anodes and cathodes, low throughput, high-energy consumption are the main challenges facing this technique. Coupling between different types of electrochemical treatment methods to be driven by renewable energy sources could be promising in addressing this bottleneck. Aerated EC and electrochemical oxidation methods were the best choices to be coupled with other methods due to their ability to eliminate organic and inorganic contaminants from wastewater. The flotation process forms low sludge. So, this method is an excellent candidate to be integrated to build an efficient and cost-effective electrochemical treatment system.

The ion exchange method is similar to the adsorption techniques in which the stability and reusability issues might need more investigation. The photocatalyst method offers simple treatment with no or little chemicals used and no sludge production. However, it is still under research, has low throughput, depends on pH, and is inefficient when different metals are present.

**CONCLUSION AND RECOMMENDATIONS**

Selection of the most appropriate technique for heavy ions removal from wastewater depends on many key factors, including the operation cost, initial concentration of the metal ions, environmental impact, pH values, chemicals added, removal efficiency, and economic feasibility. These methods are classified as adsorption treatments (using different adsorbents, i.e., carbon-based, carbon-composites, minerals, CS, magnetic, biosorbents, and MOFs), membrane treatments (i.e., UF, nanofiltration, reverse osmosis, etc.), and treatment systems.
microfiltration, reverse osmosis, forward osmosis, and electrodialysis), chemical treatments (i.e., chemical precipitation, coagulation-flocculation, and flotation), electric treatments (i.e., electrochemical (reduction, EC, EF, and advanced oxidation) and ion exchange), and photocatalysis.

Adsorption is the most promising method widely investigated in removing heavy metal ions from wastewater due to simple operation, strong applicability, high removal rate, and low cost of reusability. However, this preference depends mainly on selecting low-cost materials, high uptake, and efficient regeneration processes. Comparing to adsorption, the membrane method is technically more mature as it is practical; however, minimizing the separation cost and membrane fouling is still challenging.

The chemical-based methods, especially chemical precipitation, are technically mature and practical. They are also considered cost-effective methods. They depend on the chemical consumed, unlike the electrochemical method that relies on additional factors, including electrodes, electrical energy, and other fixed costs. However, they produce large volume sludge and need sedimentation separation. The electrochemical process is a relatively expensive technology because of the passivation of electrodes and high electrical energy consumption. Furthermore, electric methods, besides the photocatalytic ones, are the least mature technologies. The merit of the photocatalytic method is that no (or less) chemical consumption and less sludge production, making it eco-friendly.

In general, chemical, adsorption, and membrane methods are the most practical method addressed in the literature. It has been noticed that there is a clear knowledge gap in the performance of treatment methods for the removal of heavy metal ions from real wastewater because most studies used synthetic wastewater in which one or few metal types are present. Accordingly, additional research should be conducted using real wastewater for treating different contaminants. More research on introducing cost-effective materials and methods for heavy metal removal from wastewater should be carried out. Future studies should also focus on the pilot-scale process. The best techniques to achieve efficient metals recovery with less environmental impact and low cost are still under development and should be considered in future research.

DATA AVAILABILITY
The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information file.

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