PHOSPORUS, SULPHUR,NITROGEN AND HEAVY METALS REMOVAL

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-biodegradable and could be carcinogenic; 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. 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.

.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 ions[7]. Different types were developed for wastewater remediation, as discussed in the following sections.

Fig. 1: Adsorption process used for water treatment.
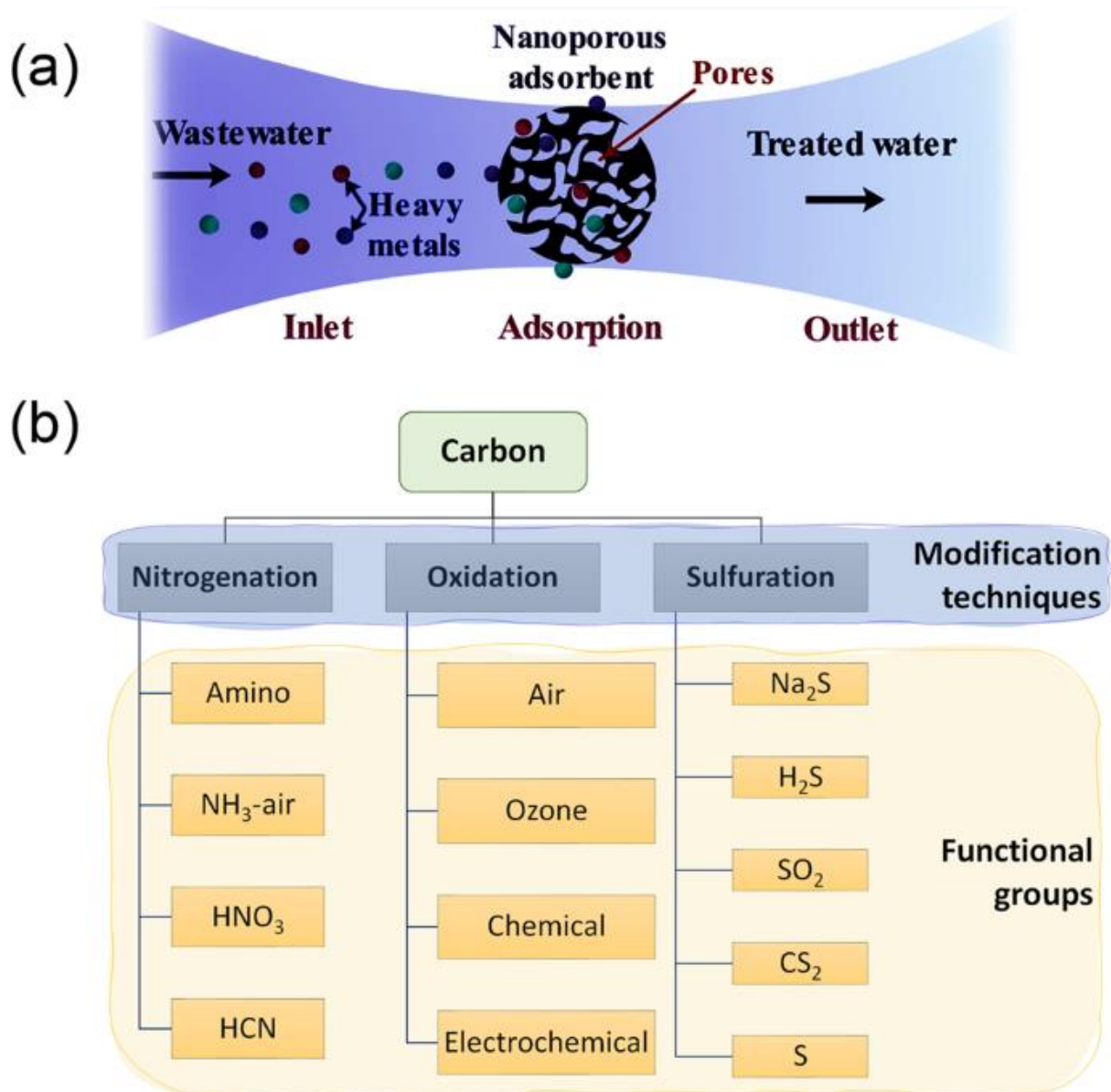
a Heavy metal ions adsorption process; the metal ions of wastewater adhere to the surface of nanoporous adsorbents, which has a high surface area due to its porosity. The adsorption process could be selective for one or more metals than others. The regeneration process could be achieved using a desorbing 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.

Full size image

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 m^2/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 uptake[9]. 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 strength[10]. However, they depend mainly on the adsorbent materials, which sometimes are very expensive[11]. 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 adsorbed[12]. 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 removal[13], 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 (–NH$_2$) and hydroxyl (–OH) groups[14]. Despite its unique features, it suffers from low mechanical strength and poor stability[15], making the regeneration inefficient. Also, it is challenging to use CS in its powder or flake form because of its low porosity, low surface area, resistance to mass transfer, and high crystallinity[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[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[17]. Combining CS with other adsorbent materials has also been proposed to enhance CS's adsorption capacity, mechanical strength, and thermal stability[18]. The ion-imprinting technique was followed to prepare adsorbents which high selectivity for target metal ions[19].

Generally, the uptake of CS depends mainly on the presence of protonation or non-protonation of amine ($-NH_2$) and phosphoric (H_3PO_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[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[21]. Clay has extraordinary cation exchange capacity (CEC), cation exchange selectivity, surface hydrophilicity, high swelling/expanding capacity, and surface electronegativity[22]. In addition, acid washing, thermal treatment, and pillar bearing could enlarge the pore size, pore volume, and specific surface area, leading to a remarkable increase in the adsorption efficiency[22].

Using natural minerals could be cost-effective. However, the removal efficiency might decrease after a few cycles[24]. Therefore, different modification methods, such as calcination and impregnation, have been proposed to enhance the removal efficiency of such adsorbents[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_3O_4)[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 (α-Fe$_2$O$_3$), maghemite (γ-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[27]. The presence of iron particles in adsorbent is very efficient in metal ions removal from effluent[28].

Fig. 2: Adsorption process via magnetic adsorption.
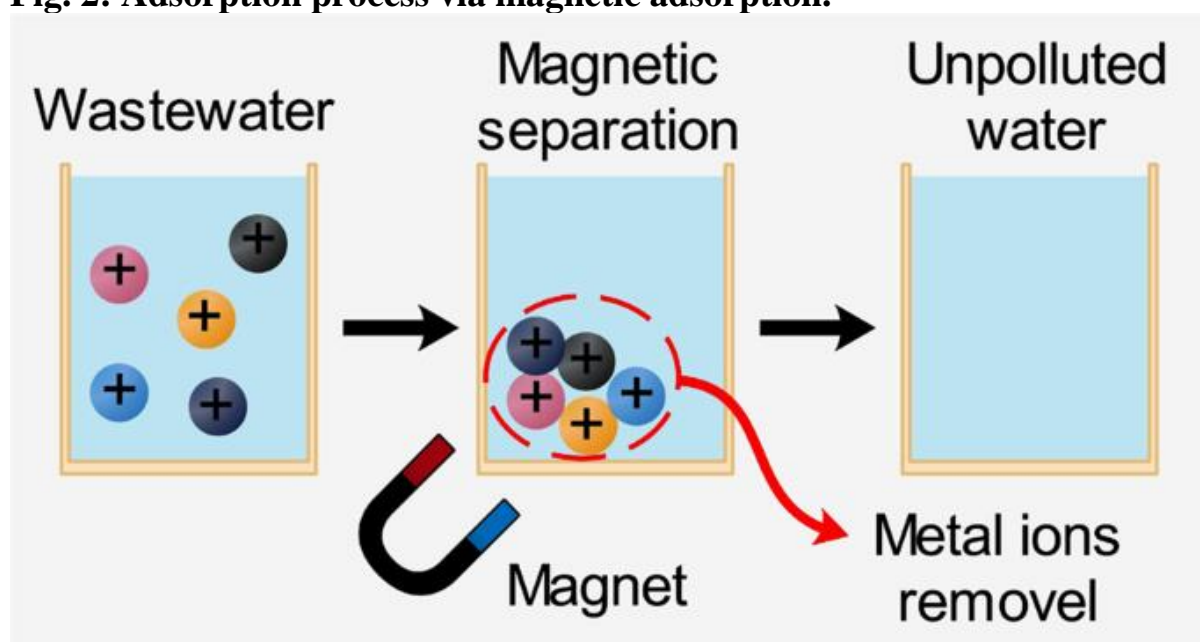
The magnetic adsorbent particles adsorb the metal ions and sequentially accumulated; thus, the wastewater is treated.

Full size image

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[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 presence of numerous functional groups (i.e., carboxyl, amino, hydroxyl, phosphate, thiol, etc.) on the surface expedite the biosorption process[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[31]. The solution pH affects the biosorbent surface charge density and ionization of functional groups located on the biosorbent surface[32]. 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[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[33].

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[34]. Zirconium-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[35] or by using the cross-linking method[36]. 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.

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[51].

Fig. 3: Different membrane-based treatments for pollutants removal from wastewater and salty water.
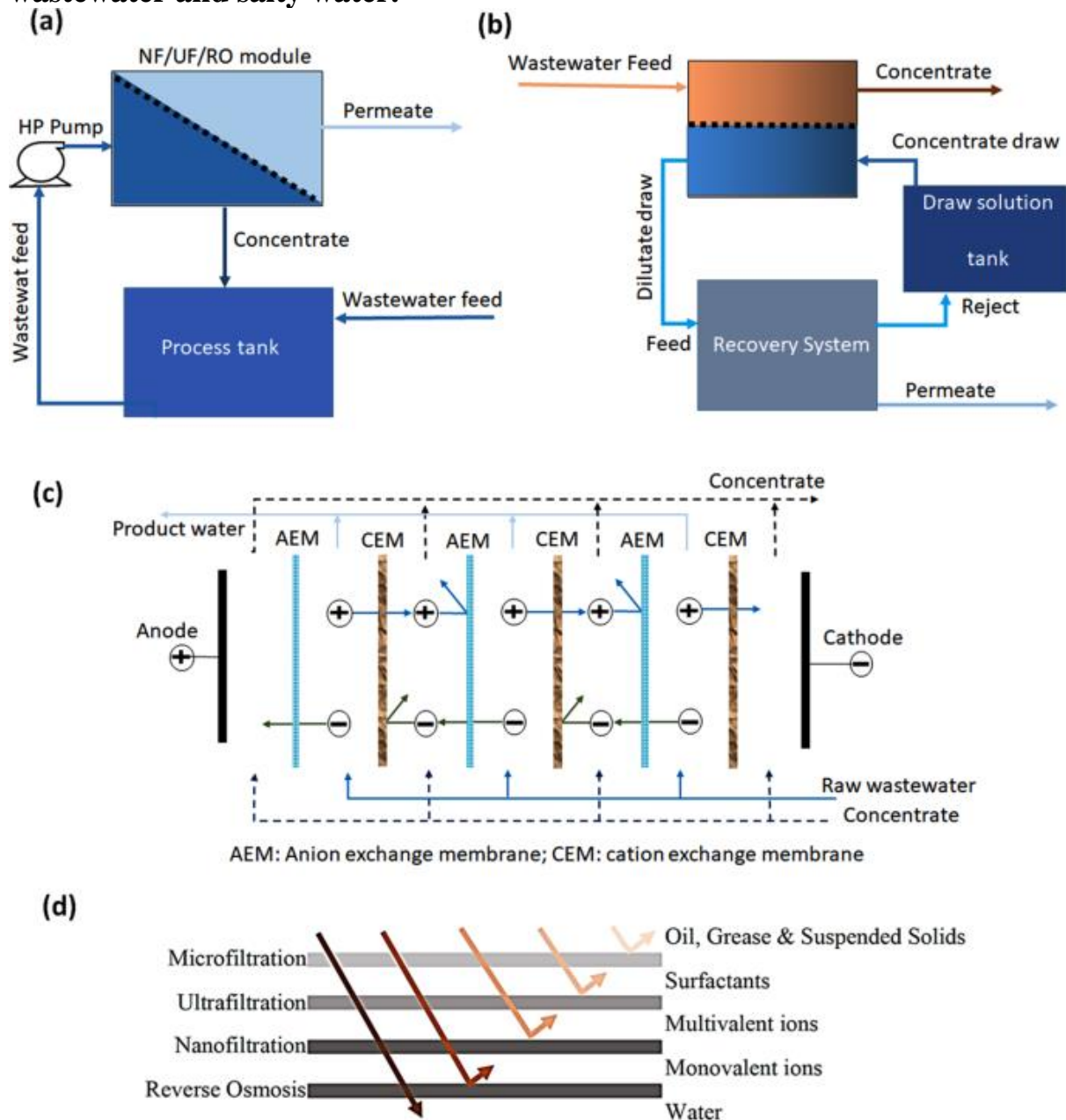
a nanofiltration, ultrafiltration, or reverse osmosis method, **b** forward osmosis process, **c** electrodialysis method in which alternative charged positive and negative membranes take place, and **d** the separation capabilities of different membranes against different pollutants.

[Full size image]

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[52]. MEUF is most suitable for wastewater whose heavy metals are in low concentrations[53]. 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[54]. Surfactants, whose electric charge is the opposite of the metal ions, usually attain the highest retentions[55,56,57]. In this regard, polyelectrolytes (PE), cationic surfactants, and anionic surfactants (e.g., sodium dodecyl sulfate (SDS)) are used for effective heavy metals extraction[55].

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[58]. 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[59].

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[51,55]. However, the choice of appropriate water-soluble polymer macro-ligands remains the main challenge of developing this technology.

Nanofiltration

Nanofiltration (NF) is used to concentrate constituents whose molecular weight is >1000 Da and remove solutes whose size of 0.0005–0.007 μm with molecular weights >200 Da[60]. Thus, the operating range of NF is between UF and reverse osmosis (RO) processes[55]. The NF membranes are composed of polymer composites of multiple-layer thin-film of negatively charged chemical groups. Anti-fouling NF membranes containing CeO_2/Ce_7O_{12} and PES were synthesized through phase inversion and used to extract Fe^{3+}, Al^{3+}, Co^{2+}, Cd^{2+}, Cu^{2+}, and

humic acid from wastewater and reached extraction efficiency between 94 and 98%[61]. Other studies are presented in Supplementary Table 10.

Microfiltration

Microfiltration (MF) employs a microporous membrane to remove micron-sized particles, bacteria, viruses, protozoa, contaminants, pollutants, etc., from a solvent/fluid/solution[60]. MF process is also a low pressure-driven membrane process, whose membrane pores are in the range of 0.1–10 μm[60]. 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[60]. 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[60]. RO process could extract 95–99% of inorganic salts and charged organics[60]. RO process is compact and attained high rejection efficiency. However, membrane fouling and degrading are the major drawback of RO systems[60]. The RO separation process was used to extract heavy metal ions, including Ni^{2+}, Cr^{6+}, and Cu^{2+} from electroplating wastewater, with a removal efficiency of >98.75[62]. 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 Fe^{3+}, Zn^{2+}, Ni^{2+}, As^{3+}, and Sb^{3+} respectively[63]. 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[51]. 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[64]. 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[64]. Nevertheless, FO has limitations, such as draw solution re-concentration, membrane selection challenges, internal and external concentration polarization[65]. 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[51]. 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[66], 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 Ni^{2+}, $Pb^{2+,}$ 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 Ni^{2+}, $Pb^{2+,}$ and K^+, respectively[67]. A batch ED process was employed to recover Pb^{2+} and reached a maximum separation efficiency of ~100%[68]. A pilot-scale ED system has also been used to extract Cu^{2+}, Ni^{2+}, and traces of Cd^{2+}, Fe^{3+}, $Cr^{6+,}$ and Zn^{2+}, and exceeded 90% removal rate[69]. As^{3+} and As^{5+} were removed from metallurgical effluent by ED and attained a removal efficiency of 91.38%[70].

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 Ca^{2+}, Mg^{2+}, Fe^{3+}, and Fe^{2+}[71], and more than 99% for As^{3+} and As^{5+}[72].

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[51], and combined stripping and extraction processes in a single stage[73]. LM is highly selective, relatively efficient, and can achieve specific molecular recognition. However, the membrane's long-term stability is poor[74]. LM process exists as a supported liquid membrane (SLM), emulsion liquid membrane (ELM), bulk liquid membrane (BLM), and polymer inclusion membrane (PIM)[51]. Among these types, the SLM process is an attractive alternative to traditional solvent extraction for heavy metal removal[73]. SLM achieved a removal efficiency of 89% for Zn^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+}[75].

Chemical-based separation

Chemical methods for removing heavy metals from wastewater are mature and used early. the chemical-based methods include 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[76]. It is usually followed by the removal of sediments. A simple schematic of the chemical precipitation process is depicted in Fig. 4.

Fig. 4: A simple schematic of the chemical precipitation process.
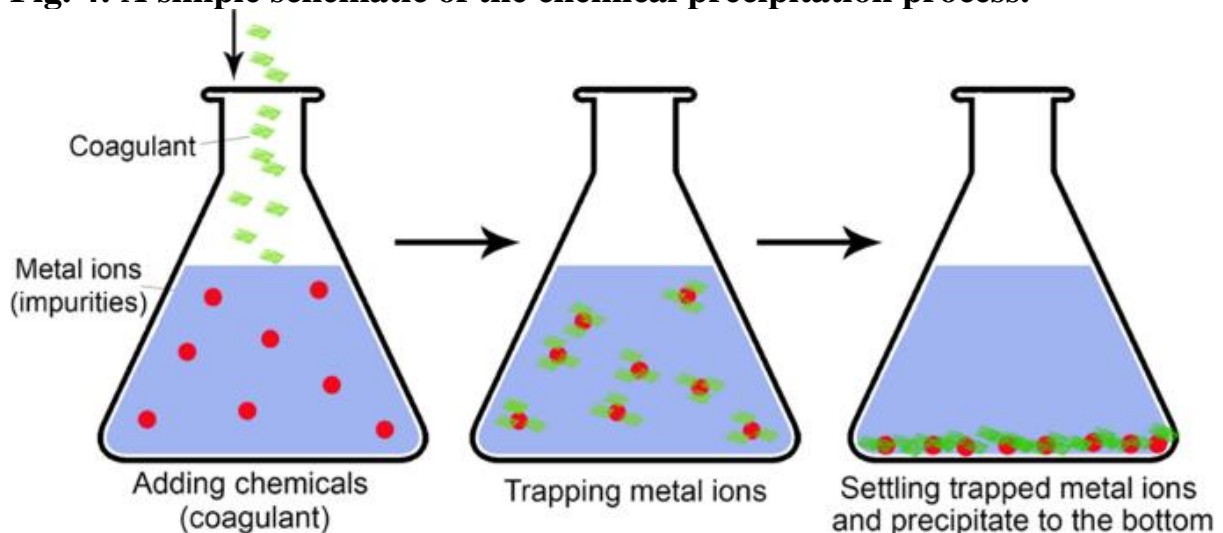
The coagulant is added to wastewater and stirred to trapping metal ions that settle and precipitate to the bottom of the container.

Hydroxide precipitation is broadly used due to its relatively inexpensive, simple, and tunable pH[77]. 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:

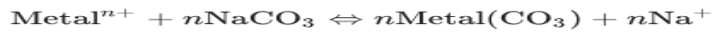$$Metal^{n+} + Ca(OH)_2 \Leftrightarrow Metal(OH)_n \downarrow + Ca^{2+}$$

(1)

It was found that pH values of 9–11 improved this process efficiency[78]. However, a high pH value is considered a disadvantage of this method since it requires a large dosage of precipitates. One of the most effective hydroxide precipitates for treating inorganic effluents of heavy metal concentration of 1000 mg/L is lime (CaO or $Ca(OH)_2$). It can be seen that the majority of metals removed by this method are Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cr^{3+}. 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 participation 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[80]. 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[81]. The metal sulfide precipitations could follow Eq. (2) reaction

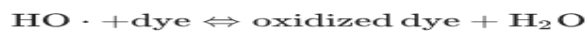$$Metal^{n+} + S^{2-} \Leftrightarrow Metal_n S \downarrow$$
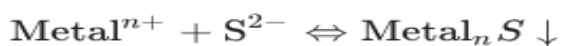
(2)

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[82]. It could be achieved using sodium carbonate or calcium carbonate. The classical carbonates can be formed based on Eq. (3 and 4)[83]:

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

$$n\text{Metal}(\text{CO}_3) + \text{H}_2\text{O} \Leftrightarrow \text{CO}_2 \uparrow + (\text{MeOH})_n\text{CO}_3 \downarrow$$

It could have less sludge volume, but it could release CO_2 bubbles and needs higher reagents for efficient precipitation[83]·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 $[\text{Fe}^{\text{IV}}\text{O}]^{2+}$ and hydroxyl radicals[84]·[85]. The classical Fenton reaction is[86]:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \Leftrightarrow \text{Fe}^{3+} + \text{HO} \cdot + \text{HO}^-$$

$$\text{HO} \cdot + \text{dye} \Leftrightarrow \text{oxidized dye} + \text{H}_2\text{O}$$

Fe^{3+}-H_2O_2 (Fenton-like[87]) and Fe^0-H_2O_2 (advanced Fenton[88]) are also represented as an alternative for Fe^{2+}-H_2O_2.