

A Review on Heavy Metal Removal Techniques in Water Treatment

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Abstract

The removal of heavy metal ions from wastewater is crucial for environmental safety and human health due to the toxic and persistent nature of these pollutants. This review comprehensively examines various water treatment methods, including adsorption, membrane filtration, chemical precipitation, electrochemical, and photocatalytic processes. Each technique is critically analyzed in terms of removal efficiency, operating conditions, and their respective advantages and limitations. Adsorption methods, particularly those using bioadsorbents, have gained significant attention for their cost-effectiveness and eco-friendliness. However, challenges like adsorbent regeneration, selectivity, and long retention times hinder their broader application. Membrane-based methods, while effective, face issues related to fouling and high operational costs. Even while chemical procedures are viable, they frequently produce enormous volumes of sludge that need to be treated further. Although less developed, electric and photocatalytic-based methods have promised advancement. Nanotechnology offers innovative solutions, with nanomaterials proving to be more efficient at heavy metal removal, although challenges remain concerning their stability, toxicity, and recovery. A key issue in many studies is the use of synthetic wastewater instead of real samples, which may not fully capture the complexities of industrial effluents. Future research should prioritize sustainable, eco-friendly materials and focus on industrial-scale implementation. Overall, a multidisciplinary approach is necessary to address the limitations of current technologies and develop more advanced, efficient, and cost-effective solutions for heavy metal removal from wastewater, ensuring the long-term protection of ecosystems and human health.

Keywords: Adsorption techniques, environmental remediation, heavy metal removal, nanotechnology in wastewater treatment, water treatment technologies.

INTRODUCTION

The increasing concentration of heavy metals in wastewater has become a growing concern due to

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rapid industrialization and various human activities, including electroplating, mining, chemical manufacturing, and the tanning industry. Hazardous heavy metals like lead (Pb), zinc (Zn), mercury (Hg), cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), and arsenic (As) are produced in large amounts by these industries and discharged into wastewater. Improper treatment of this wastewater results in the entry of these metal ions into the environment, creating severe risks to both human health and the ecosystem. Heavy metals are non-biodegradable and have carcinogenic properties, making them particularly dangerous even in trace amounts. In fact, continuous exposure to heavy metals through

drinking water, food, and air can lead to severe health issues such as cancer, organ damage, and neurotoxicity.

Heavy metals such as Pb, Hg, Cd, and As, even in small concentrations, pose significant health risks due to their accumulation in living organisms. When present in concentrations above regulated limits, these metals cause diseases and physiological disorders, affecting the digestive, respiratory, nervous, and reproductive systems. To avoid such health dangers, the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO) have established regulations that specify the allowed limits of certain heavy metals in drinking water. However, these metals continue to accumulate in water resources and ecosystems due to industrial discharges, necessitating effective and efficient removal methods [1–3].

The presence of heavy metals in wastewater is not restricted to developed regions; industrial and agricultural growth in developing countries has also contributed to increased metal pollution. In some countries, like India, the maximum allowable concentrations of heavy metals in water are strictly regulated, with limits set for metals like Cr, Cd, Cu, Ni, Zn, Pb, Hg, and As. In response to this, the need for the removal of these pollutants has led to the development and implementation of several treatment methods for wastewater remediation [4–11].

Heavy metals such as lead (Pb), arsenic (As), copper (Cu), zinc (Zn), chromium (Cr), cadmium (Cd), mercury (Hg), and nickel (Ni) are commonly found in industrial waste and have significant health impacts on humans and the environment. These metals originate from a variety of sources, including batteries, electronics, plumbing systems, and industries such as steel, glass, and chemicals (Table 1). Once released, they affect various organs and systems in the human body, with some metals being carcinogenic and toxic to vital organs like the liver, kidneys, lungs, and brain [5]. For instance, lead affects the cardiovascular and reproductive systems, while cadmium and arsenic target the bones, immune system, and cardiovascular systems. Permitted levels of these metals in drinking water and wastewater are tightly regulated due to their hazardous effects [6]. For example, permissible limits for Hg and Cd are as low as 6 µg/L and 3 µg/L, respectively, while Cu and Zn, which are essential in trace

Table 1. Common heavy metals, their main sources, affected organs, and permitted levels in drinking water.

Heavy metal	Main sources	Main organs and systems affected	Permitted amounts (µg)
Lead (Pb)	Lead-based batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes, plastic stabilizers	Bones, liver, kidneys, brain, lungs, spleen, immune system, hematological system, cardiovascular system, reproductive system	10
Arsenic (As)	Electronics, glass production	Skin, lungs, brain, kidneys, metabolic system, cardiovascular system, immune system, endocrine system	10
Copper (Cu)	Corroded plumbing systems, electronics, cables industry	Liver, brain, kidneys, cornea, gastrointestinal system, lungs, immune system, hematological system	2000
Zinc (Zn)	Brass coating, rubber products, some cosmetics, aerosol deodorants	Stomach cramps, skin irritations, vomiting, nausea, anemia, convulsions	3000
Chromium (Cr)	Steel and pulp mills, tanneries	Skin, lungs, kidneys, liver, brain, pancreas, testes, gastrointestinal system, reproductive system	50
Cadmium (Cd)	Batteries, paints, steel industry, plastic industries, metal refineries, corroded galvanized pipes	Bones, liver, kidneys, lungs, testes, brain, immune system, cardiovascular system	3
Mercury (Hg)	Electrolytic production of chlorine, caustic soda, landfills, agriculture runoff, electrical appliances, industrial instruments, refineries	Brain, lungs, kidneys, liver, immune system, cardiovascular system, endocrine system, reproductive system	6

Nickel (Ni)	Stainless steel, nickel alloy production	Lungs, kidneys, gastrointestinal system, pulmonary fibrosis, skin	70
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amounts, are allowed in higher concentrations of up to 2000 µg/L and 3000 µg/L. Given the severe health risks posed by these metals, their removal from industrial effluents is crucial to prevent long-term environmental and health damage [12–18].

LITERATURE REVIEW

Conventional Water Treatment Methods for the removal of Heavy Metals

Precipitation

Chemical precipitation, commonly referred to as coagulation precipitation, is widely employed in various industries and is recognized as a highly effective and well-established method. This process converts dissolved metal ions into solid particles, making it easier to separate them through sedimentation. Coagulants are used to precipitate metal ions by altering factors such as pH, electrochemical potential, or via co-precipitation. The resulting precipitates are typically removed through sedimentation. A basic schematic illustrating the chemical precipitation process can be seen in Figure 1.

Because of its low cost, ease of use, and easily changeable pH, hydrogen precipitation is an extensively used method. Using this technique, insoluble metal hydroxide precipitates are created by adding a hydroxide to agitated wastewater. For example, metal ions can react with calcium hydroxide (lime) to form metal hydroxide precipitates and calcium ions, as described in Eq. (1).



The process is most efficient at pH values between 9 and 11. However, a high pH is a drawback as it requires large amounts of precipitating agents. $\text{Ca}(\text{OH})_2$ is one of the most effective hydroxide precipitates for treating inorganic effluents with heavy metal concentrations of 1000 mg/L. hydroxide precipitation studies, which primarily focus on the removal of metals such as Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , and Cr^{3+} . Despite its effectiveness, the method has disadvantages, including the need for a high dosage to achieve optimal pH, large volumes of sludge, disposal issues, and interference from complexing agents [19–23].

The sulfide precipitation method offers higher removal efficiency and results in fewer dissolved solids compared to hydroxide precipitation. This technique has been used to treat toxic heavy metal ions. Lower sulfide levels can increase zinc concentration in the effluent, while higher sulfide levels can cause odor problems due to residual sulfide, as well as the formation of hydrogen sulfide gas, which is both mal-odorous and toxic. Therefore, sulfide precipitation is best conducted at neutral pH, as shown in Eq. (2).



Table 2 highlights metal ion removal via sulfide precipitation. The method's major drawbacks are sulfide toxicity and high costs [24–28].

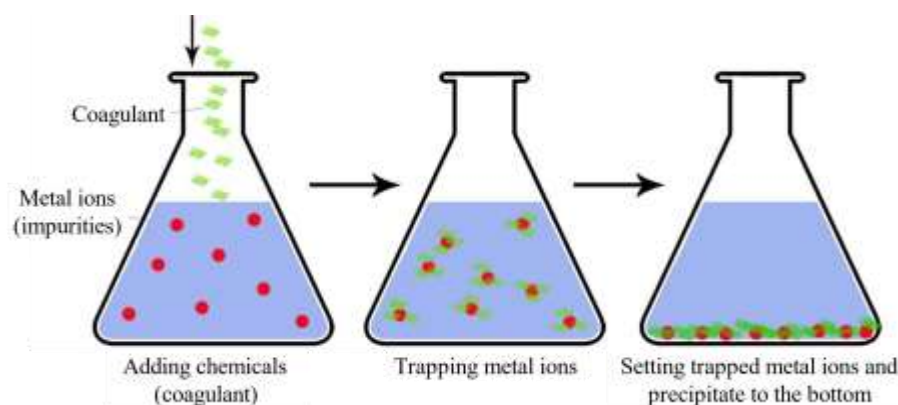


Figure 1. Chemical precipitation process.

As an alternative to hydroxide precipitation, carbonate precipitation is effective at lower pH values and can be achieved using sodium carbonate or calcium carbonate. Classical carbonate reactions are shown in Eqs. (3) and (4) [29].



While this method typically results in less sludge, it may release CO_2 bubbles and require larger amounts of reagents for efficient precipitation. carbonate precipitation studies, with copper and manganese being the primary metals removed. Zinc and lead can also be efficiently treated using this method.

The Fenton reaction is often used to enhance the removal efficiency of chemical precipitation methods. Fenton or Fenton-like oxidation helps de-complex heavy metal complexes, with pH adjustments made through chemical precipitation (e.g., using NaOH). Fenton chemistry involves multiple reactions, depending on active intermediates like hydroxyl radicals. The classical Fenton reaction is outlined in Eqs. (5) and (6), [30]



while Fenton-like ($\text{Fe}^{3+}\text{-H}_2\text{O}_2$) and advanced Fenton ($\text{Fe}^0\text{-H}_2\text{O}_2$) reactions are also viable alternatives. Certain metals, such as radionuclides, are present in small quantities in bulk wastewater.

The process, depicted in Figure 2, includes sedimentation. However, there are several limitations, such as the toxicity and health risks associated with inorganic coagulants, the generation of large volumes of sludge, selectivity for certain metals, and inefficiency in addressing emerging contaminants. A summary of research on coagulation-flocculation for the removal of heavy metals from diverse wastewater sources is provided. In addition, the process frequently causes increased effluent color, decreased efficacy when utilizing natural coagulants, and difficulties in scaling up. Cu^{2+} , Pb^{2+} , and Ni^{2+} are common heavy metals removed by this approach; additional metals such as As^{2+} , Se^{2+} , Cr^{2+} , Sb^{3+} , Sb^{7+} , and Ag^+ can also be efficiently removed [31–39].

Adsorption

Carbon-Based Adsorbents

Adsorbents typically feature heterogeneous and irregular surfaces, which enhance the adsorption of heavy metal ions (HMIs). Upon pollutant sorption, the adsorbent surface becomes smoother. When nanoparticles are used to modify these surfaces, they form macro-clusters that create a more uniform texture. Subsequent treatments, such as carbonization and calcination, restore the porosity of the

adsorbent

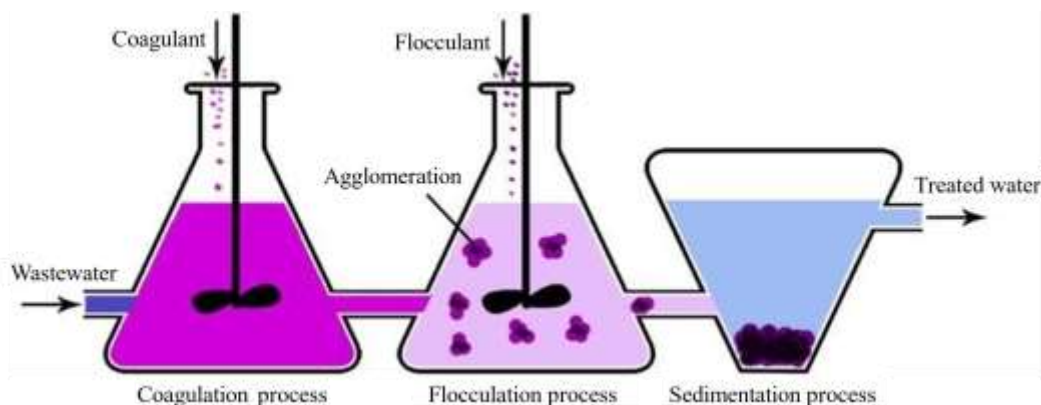


Figure 2. Coagulation-flocculation treatment process.

surfaces. While other surface modification techniques, such as chemical treatments, may decrease the overall surface area, they allow for the fine-tuning of functional groups, thereby improving the adsorption capacity. Yi x et al. [50] recently reviewed the influence of various functional groups on the adsorption of HMIs onto different carbon materials, highlighting the significance of surface modification in enhancing the physicochemical and sorptive properties of carbon adsorbents for advancing environmental remediation technologies [40–46].

Carbon Nanotube (CNT) Adsorbents

The highest adsorption capabilities of several heavy metal ions on oxidized carbon nanotubes (CNTs), multiwalled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), and activated charcoal (which includes both granular activated charcoal (GAC) and powdered activated charcoal (PAC)) are listed in Table 2 [47–52].

The study indicates the effectiveness of oxidized single-walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs), and granular activated carbon (GAC) in removing Ni^{2+} [58]. These adsorbents were evaluated under identical conditions, revealing that SWCNTs and MWCNTs exhibited superior Ni^{2+} sorption performance compared to GAC. This improvement is attributed to the greater surface area of the carbon nanotubes compared to GAC. Naghizadeh A [57] noted that the adsorption of Ni^{2+} on MWCNTs increases with higher pH levels. Additionally, the sorption affinity of Zn^{2+} for the CNT surface is stronger than that of Ni^{2+} [53].

Li Y.H et al. [52] reported significant Pb^{2+} adsorption by MWCNTs, noting that this process occurred more rapidly than with activated carbon (AC). Furthermore, Pb^{2+} can be recycled effectively using acidified MWCNTs.

In terms of Zn^{2+} removal, both purified SWCNTs and MWCNTs demonstrated greater adsorption capabilities than powdered activated carbon (PAC) under similar initial concentrations, despite PAC having a larger surface area than the carbon nanotubes [59]. The affinity of carbon nanotubes for zinc ions is greater than that for lead ions. Naghizadeh et al. [56] indicated that Cd^{2+} exhibits a lower affinity

Table 2. The maximum adsorbent capacities for various carbon-based adsorbents.

Adsorbate	Adsorbent	Max. adsorption (mg/g)	Initial concentration (mg/L)	pH	Ref.
Pb^{2+}	MWCNTs	15.6	10–80	3, 5, 7	[51]
	AC	18	10–60	5	[52]

	Oxidized MWCNTs	59		5	[52]
	SWCNTs	33.55		7	[53]
	MWCNTs	12.34		7	[54]
Cu ²⁺	Oxidized MWCNTs	28.49	5–30	5	[55]
	SWCNTs	24.29		5	[56]
Cd ²⁺	MWCNTs	4.1	4	3–12	[57]
	AC	2.9	4	3–12	[57]
	Oxidized MWCNTs	10.86	2–15	5	[58]
	SWCNTs	24.07		7	[58]
	MWCNTs	13.05	10–80	2–9	[59]
Ni ²⁺	Oxidized MWCNT	38.46	10–80	7	[57]
	Oxidized SWCNTs	47.85	10–80	7	[57]
	GAC	26.39	10–80	7	[58]
Zn ²⁺	MWCNTs	32.68	10–80		[59]
	SWCNTs	43.66	10–80		[59]
	PAC	13.04	10–80		[59]

for activated carbon compared to MWCNTs, with adsorption capacities of 2.9 mg/g and 4.1 mg/g, respectively. When comparing the adsorption of Pb²⁺, Cu²⁺, and Cd²⁺ using oxidized MWCNTs, the findings show that Pb²⁺ has a higher adsorption capacity than both Cd²⁺ and Cu²⁺. The order of adsorption capacities for various heavy metal ions on oxidized MWCNTs is as follows: Cd²⁺ < Cu²⁺ < Ni²⁺ < Pb²⁺. The maximum adsorption capacities for Zn²⁺ on SWCNTs, MWCNTs, and PAC, determined using the Langmuir model, are 43.66 mg/g, 32.68 mg/g, and 13.41 mg/g, respectively [60].

Low-Cost Bioadsorbents

The focus of research on inexpensive adsorbents has been on removing heavy metal ions from wastewater, including Pb²⁺, Zn²⁺, Ni²⁺, and Cd²⁺. The findings show that a number of variables, including adsorbent content, quantity, pH, and contact time, affect how well heavy metal ions are removed.

Eggshells and their derivatives have shown considerable potential for removing wastewater contaminated with nickel and silver ions. Comparisons between eggshells and eggshell membranes demonstrate that the latter achieves faster removal rates for Ni²⁺ and Ag [61]. Moreover, Ho J.H et al. [62] highlighted the strong adsorption potential of calcined eggshells for Cd²⁺ and Cr, while natural eggshells were more effective in adsorbing Pb²⁺. Research has indicated that the use of chicken eggshells in aqueous solutions and wastewater can effectively remove lead, zinc, chromium, and cadmium. Specifically, it has been demonstrated that the eggshells can remove 99.7% of Cu²⁺ [63], 99% of Zn²⁺ [63], 85% of Cr, 82% of Pb²⁺ [63], 86% of Cd²⁺ [64], and 96.43% of Fe [65]. The greater quantity of accessible active binding sites is the reason for these results [63, 66]. Because eggshells naturally have a pH-adjusting property and a high removal efficiency, they are also used to remediate effluent from battery production [67]. Because eggshells can effectively remove large levels of heavy metals from wastewater, they can be used as a pre-treatment option [62].

Ion Exchange Treatment

The ion exchange method is a reversible chemical process employed to substitute undesirable metal ions with harmless and environmentally friendly alternatives. In this process, a heavy metal ion is extracted from wastewater by binding it to a stationary solid particle, which then releases a cation from the solid particle as a replacement, as illustrated in Figure 3. The solid ion-exchange particles can be composed of natural materials, such as inorganic zeolites, or synthetic materials, such as

organic

resins.

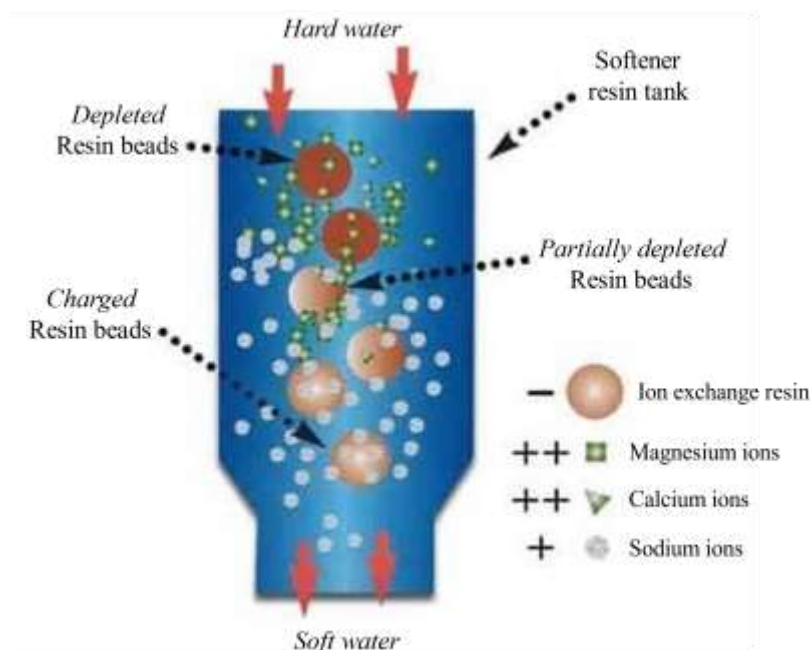


Figure 3. Ion exchange resin mechanism for water remediation.

This method is effective in removing various heavy metal ions from wastewater, including Pb^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , V^{4+} , V^{5+} , Cr^{3+} , Cr^{6+} , Cu^{2+} , and Zn^{2+} . The ion exchange mechanism for metal removal can be represented by the following reaction, where the ion exchange particle contains an ion exchanger of M-EC^+ (M- being the fixed anion and EC^+ the exchange cation, with Na^+ and H^+ commonly used as exchange cations) that exchanges its cation (EC^+) with the cation in the wastewater (WC^+) [63–68].

COAGULATION AND FLOCCULATION

Coagulation and flocculation are essential processes for the removal of heavy metals from wastewater, typically followed by sedimentation and filtration to capture the resulting foam. Common coagulants used in wastewater treatment include aluminum, ferrous sulfate, and ferric chloride, which aid in the neutralization of particle charges, facilitating the aggregation of particulates and pollutants. Chang Q et al. [69] reported using coagulation techniques that mixed sewer overflow with ferric chloride and polyaluminum chloride (PAC) to achieve exceptional results in removing heavy metal ions from water. This method effectively targets suspended particles and hydrophobic colloids, which are significant pollutants (Figure 4).

Flocculation involves the application of polymers to create bonds between flocs, leading to the formation of larger aggregates. These flocculated suspended particles can then be removed through filtration, flotation, or straining. While various flocculants, such as PAC, polyacrylamide (PAM), and polyferric sulfate (PFS), are employed in wastewater treatment, they are not suitable for heavy metal removal. However, research by Chang et al. introduced a novel flocculant, a macromolecule heavy metal flocculant created by reacting chitosan with mercaptoacetic acid, demonstrating promising results in both turbidity and heavy metal removal from water sources [70].

ADVANCED TECHNIQUES FOR HEAVY METAL REMOVAL

Membrane Filtration

The advancement of membrane technologies has revealed numerous benefits for the removal of heavy metals, including high efficiency, compact footprint, and straightforward design. Membrane

filtration processes can be classified into several categories, namely reverse osmosis, ultrafiltration, electrodialysis, and nanofiltration [71].

Ultrafiltration (UF)

Ultrafiltration is utilized in scenarios with low transmembrane pressures to effectively eliminate dissolved and colloidal substances. In this process, the pores of the membrane are larger than hydrated metal ions, which enables only low molecular weight complexes to pass through with ease. Two novel techniques, micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF), have been developed to increase the removal efficiency of heavy metals.

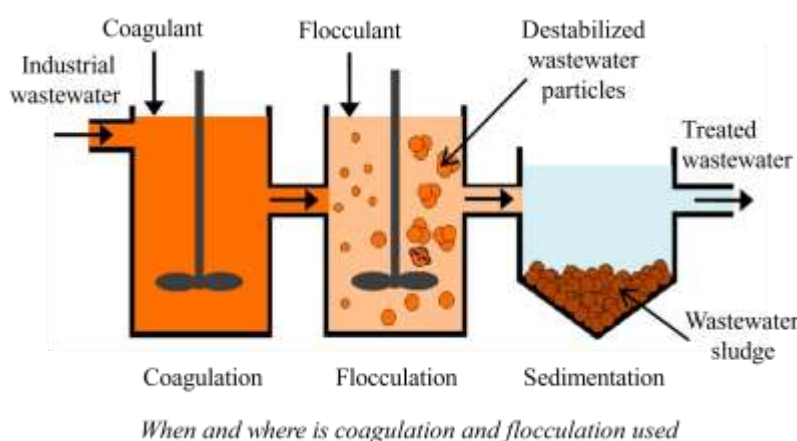


Figure 4. Application of coagulation and flocculation.

Reverse Osmosis (RO)

Reverse osmosis uses a semi-permeable membrane to filter out contaminants and only allow clean water to pass through. This technique is effective at getting rid of a variety of pollutants and is extensively used in the desalination process. Its use in environmental engineering has broadened recently to encompass many areas of wastewater treatment.

Nanofiltration (NF)

In order to remove heavy metal ions (HMIs) including nickel, chromium, copper, and arsenic from wastewater, a filtering process called nanofiltration combines the concepts of ultrafiltration and reverse osmosis. Efficiencies in heavy metal removal among RO, NF, and combined RO+NF systems. Notable benefits of nanofiltration include its simplicity, reliability, and low energy consumption, all while achieving a high removal rate [72–77] (Figure 5).

Electrochemical Technologies for Wastewater Treatment

In electrochemical processes, key factors such as potential, current, current density, and current per electrode area (i_a) play significant roles in performance. Current efficiency (CE) is another crucial parameter, reflecting the proportion of current used to produce a specific product relative to the total current consumed. For metal recovery, electrochemical reactors are evaluated based on their space-time yield (YST), which indicates the amount of product generated per unit time relative to reactor volume:

$$Y_{ST} = (i_a M / 1000 z F) \times CE.$$

The recovery of heavy metals from wastewater is very successful when electrochemical deposition is used. This method's avoidance of adding more chemicals to clean water is one of its main advantages. It also makes it possible to remove heavy metal ions selectively.

A comparison of the heavy metal removal efficiency using various techniques is shown in Figure 6. For every heavy metal tested, electroflotation consistently exhibits the highest removal efficiency among the electrochemical methods, while electrochemical removal comes in second. In contrast, electrocoagulation demonstrates lower efficiencies, particularly for chromium (Cr), nickel (Ni), and lead (Pb), with removal rates falling below 50% [78, 79].

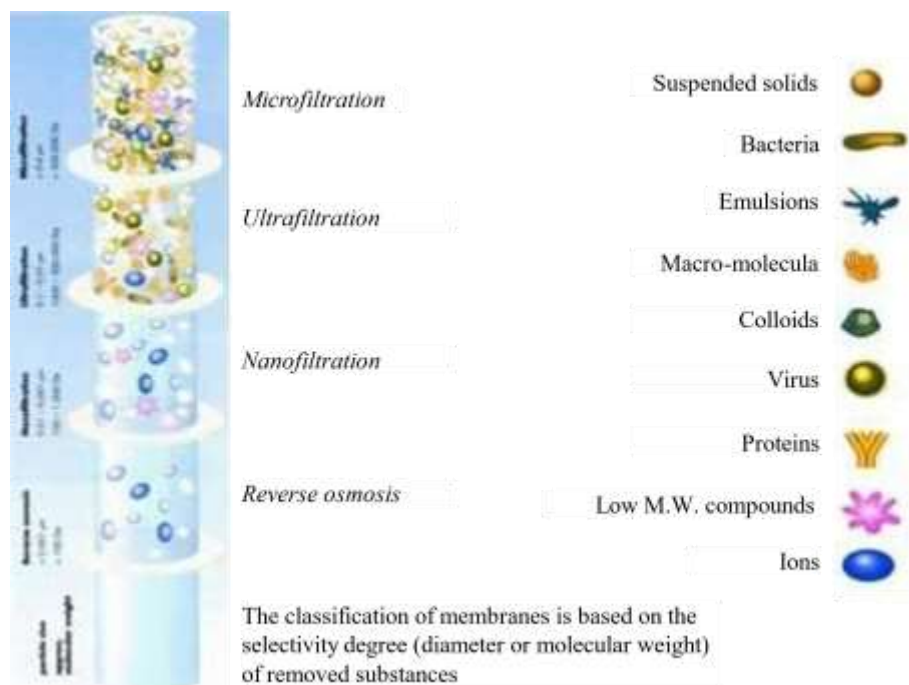


Figure 5. Membrane filtration technology.

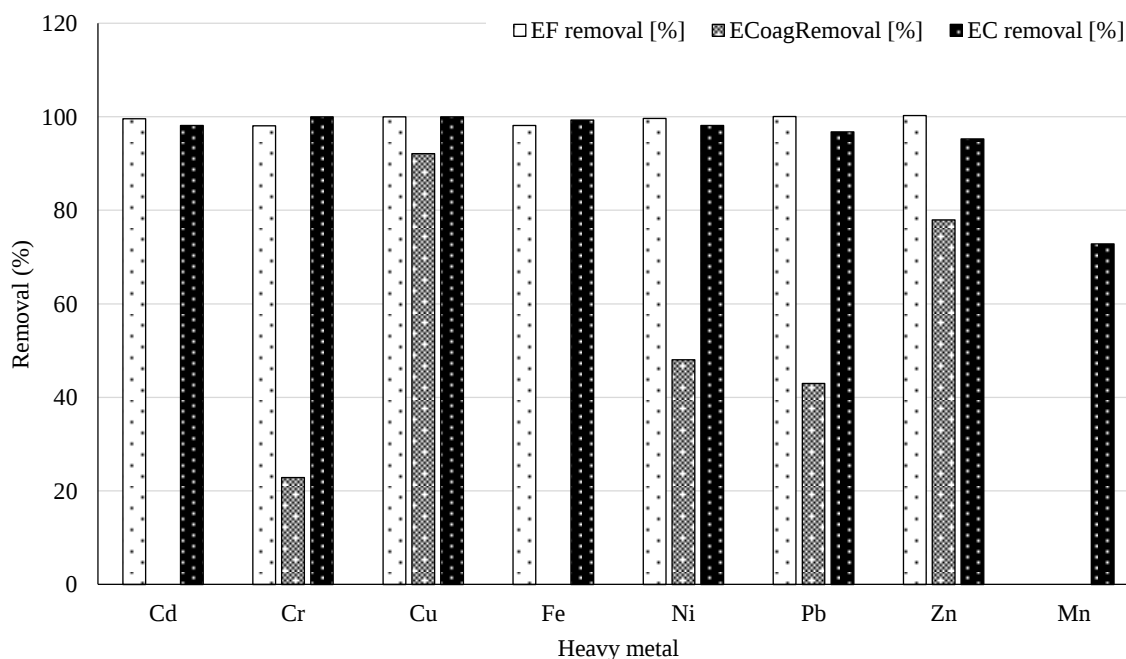


Figure 6. Comparative analysis of removal techniques.

EFFICIENCY OF DIFFERENT METHODS

When comparing different methods for removing heavy metals from wastewater, there are notable differences in how well they work. Electrochemical methods, like electroflotation and electrochemical removal, are generally more effective than traditional methods. For example, electroflotation consistently removes a high percentage of various heavy metals, while electrocoagulation tends to perform poorly, especially with metals like chromium, nickel, and lead.

Cost-Effectiveness

In terms of cost, electrochemical processes can be more economical than traditional methods. Although the initial setup costs for electrochemical systems might be higher due to the necessary equipment, their efficiency in recovering metals and lower need for extra chemicals can reduce long-term operational costs. It's important to conduct a detailed cost analysis to find the most cost-effective option based on specific treatment needs [80].

Environmental Sustainability

Environmental sustainability is a key consideration in choosing wastewater treatment methods. Electrochemical techniques have an advantage here because they avoid adding harmful chemicals to the environment. By selectively removing heavy metal ions, these methods help produce cleaner water without creating additional pollution. Overall, the combination of effectiveness, cost savings, and environmental friendliness makes electrochemical technologies a strong choice for wastewater treatment.

Challenges and Limitations in Current Techniques

Technical Barriers

Current techniques for comparing different methods for removing heavy metals from wastewater, there are notable differences in how well they work. Electrochemical methods, like electroflotation and electrochemical removal, are generally more effective than traditional methods. For example, electroflotation consistent heavy metals from wastewater face several technical challenges. These include the need for precise control of operating conditions, such as voltage and current, which can affect the efficiency of the processes. Additionally, there may be limitations in the types of heavy metals that can be effectively removed, and some methods may struggle with high concentrations of contaminants or varying water chemistry.

Scale-Up Issues

Scaling up these techniques from laboratory settings to industrial applications can be difficult. What works well in a small-scale experiment may not perform as effectively in larger systems. Factors such as equipment design, energy consumption, and overall process efficiency can change when moving to a larger scale, making it challenging to maintain the same level of performance.

Disposal of Sludge/By-products

Another significant challenge is the disposal of sludge and by-products generated during treatment. Many methods produce solid waste that must be managed properly to avoid environmental harm. Finding safe and economical ways to dispose of or recycle this waste is crucial, as improper disposal can lead to further contamination and negate the benefits of the treatment process.

CONCLUSION

This review highlights the promising potential of electrochemical methods, particularly electroflotation and electrochemical removal, for the effective treatment of wastewater containing heavy metals. These techniques not only demonstrate high removal efficiencies but also present environmental advantages by minimizing the introduction of harmful chemicals into water sources. However, the review also underscores several challenges that need to be addressed, including technical barriers related to process control, difficulties in scaling up from laboratory to industrial applications, and the management of sludge and by-products generated during treatment.

Recommendations for Future Research and Development

To further advance the field of wastewater treatment, several key areas warrant attention in future research and development efforts:

1. *Optimization of technical processes:* It is essential to focus on refining the operating comparing different methods for removing heavy metals from wastewater, there are notable differences in how well they work. Electrochemical methods, like electroflotation and electrochemical removal, are generally more effective than traditional methods. For example, electroflotation consistent of electrochemical systems to enhance their efficiency and effectiveness in removing a broader range of heavy metals. Research should also explore innovative methods to improve current efficiency and reduce energy consumption.
2. *Addressing scale-up challenges:* Future studies should prioritize the development of modular and flexible electrochemical systems that can be easily adapted for larger-scale applications. Investigating the feasibility of pilot-scale projects can provide valuable insights into the practical implementation of these technologies in real-world settings.
3. *Management of by-products and sludge:* A critical area of research involves finding sustainable strategies for the disposal or recycling of sludge and by-products produced during wastewater treatment. Investigating methods for the valorization of these materials could contribute to a more circular economy and minimize environmental impacts.

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