
| RESEARCH ARTICLE

**Advanced Treatment Technologies for Heavy Metal Removal from Water and Wastewater:
A Comprehensive Review**

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| ABSTRACT

The pollution of water bodies with heavy metals presents a significant threat to both the environment and human health because of their harmful, long-lasting, and bioaccumulating properties. As industrialization continues to grow alongside stricter environmental regulations, there is an increasing need for effective and sustainable treatment solutions. This review thoroughly investigates both traditional and advanced techniques for the removal of heavy metals from water and wastewater, including chemical precipitation, adsorption, membrane filtration, electro dialysis, ion exchange, electrochemical methods, ion flotation, and photocatalysis. Each method is carefully analyzed regarding its mechanism, effectiveness in removal, operational requirements, advantages, and drawbacks. Adsorption and membrane-based technologies are noted for their high efficiency and adaptability, particularly when employing low-cost or nano-enabled materials. Chemical precipitation and coagulation–flocculation remain effective for treating high-concentration wastewater, while ion exchange is especially appropriate for the removal of trace amounts of metals. New techniques such as photocatalysis and electrochemical solutions present promising options but encounter challenges concerning scalability and cost. The review highlights that no single approach is the best fit for every situation; instead, the choice of method should consider factors like wastewater composition, metal concentration, environmental impact, and economic viability. By summarizing current research, this paper offers a critical evaluation of existing methods and identifies potential future innovations in heavy metal remediation, stressing the importance of developing eco-friendly, cost-effective, and scalable solutions to protect water resources.

| KEYWORDS

Heavy metal removal, Wastewater treatment, Adsorption, Membrane filtration, Chemical precipitation, Ion exchange, Electrochemical treatment, Photocatalysis, Water purification, Sustainability

| ARTICLE INFORMATION

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1. Introduction

The treatment of wastewater is imperative for the reclamation of freshwater resources utilized in human endeavors and agricultural practices (Saleh et al., 2022). As the global demand for water escalates annually, various forms of pollution have adversely affected water sources (Genç-Fuhrman et al., 2016; Saleh et al., 2022). A multitude of factors contribute to the concentration of heavy metal ions in wastewater, arising from diverse industrial activities, including electrolysis, electroplating, and metal smelting, alongside environmental chemical contaminants (Chen et al., 2018; P. Li et al., 2021; Saleh et al., 2020, 2022). Metals are responsible for the modernisation and growth of

industry as well as the advancement of civilization (Lupa et al., 2023). Copper (Cu), Silver (Ag), Zinc (Zn), Cadmium (Cd), Gold (Au), Mercury (Hg), Lead (Pb), Chromium (Cr), Iron (Fe), Nickel (Ni), Tin (Sn), Arsenic (As), Selenium (Se), Molybdenum (Mo), Cobalt (Co), Manganese (Mn), and Aluminium (Al) are all examples of heavy metals (Gunatilake, 2015). In certain instances, they are vital for sustaining the body's metabolism in humans or animals, or they are crucial for the development of plants as microelements (Agarwal et al., 2018; Lupa et al., 2023; Mishra et al., 2021a). On the other hand, metals can contribute to environmental contamination and have catastrophic impacts on living things if their concentrations above specific thresholds, even if they are only trace amounts (Gunatilake, 2015; Lupa et al., 2023; Qasem et al., 2021). Furthermore, the elimination of heavy metals constitutes a significant public health issue, given their teratogenic and carcinogenic properties, as well as their association with various adverse health effects (Lee et al., 2012). Consequently, the implementation of effective treatment strategies and the permanent eradication of these contaminants is of paramount urgency (Saleh et al., 2022).

Heavy metals can be removed from industrial wastewater using a variety of treatment methods, including chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations (Gunatilake, 2015). Adsorption is one of the most extensively utilised methods because it is simple, inexpensive, and the materials are readily available (Calugaru et al., 2016; Fang et al., 2018; Zhao JianHui et al., 2016). Furthermore, with the advancement of nanotechnology, nanosorbents have demonstrated greater efficacy and faster adsorption rates for heavy metal removal than standard sorbents (Fang et al., 2018; Tahmasebi et al., 2015). Adsorption should be the best approach for removing heavy metals (Fang et al., 2018). However, industrial wastewater frequently contains numerous heavy metals, which compete for active sites on sorbents (Fang et al., 2018; Rajendran et al., 2022; Shrestha et al., 2021). Adsorption of combined heavy metals on sorbents makes it difficult to separate and recycle them (Fang et al., 2018). Thus, sequential removal and separation of several heavy metals from contaminated water remains a difficult task (Fang et al., 2018).

Many studies have explored the efficacy and mechanisms of various technologies for removing heavy metals from contaminated water sources (John, Ezechukwu, et al., 2025; Uzochukwu, Okey-Onyesolu, et al., 2025; Godspower et al., 2024; Ekwueme et al., 2023). For instance, Gunatilake, (2015) reviewed the methods of removing heavy metals from industrial wastewater. Saleh et al., (2022) reviewed and summarized the current development in recent wastewater treatment technologies to remove heavy metals. Barakat, (2011) reviewed the recent developments and technical applicability of various treatments for the removal of heavy metals from industrial wastewater. Kurniawan et al., (2023) discussed the applicability of the surface complexation (SC) model for biosorption of a target pollutant. Similarly, Aziz et al., (2023) focused on the main sources of heavy metal pollution, their biological and chemical transformation, toxicological impacts on the environment, and harmful effects on the ecosystem. It also looked at new developments in economical and effective methods of eliminating heavy metals from wastewater, like advanced oxidation processes (AOPs) for breaking down heavy metal complexes and physicochemical adsorption with biochar and natural zeolite ion exchangers. On the other hand, Singh et al., (2024) worked on recent advances in heavy metal/metalloid ion treatment from wastewater using nanocomposites and bionanocomposites. These previous studies highlight the diversity and progress of treatment techniques, but they also demonstrate persisting issues in terms of cost, sustainability, and operational complexity (Ajali, Umenwa, et al., 2023; C. Onyenanu & Emembolu, 2020a; Ajali & Onyenanu, 2023; Ajali, Victor, et al., 2023; Uzochukwu, Onu, et al., 2025). This paper discusses the various treatment strategies and methodologies used for heavy metal removal (C. Onyenanu & Nnanyelum, 2020; L. Emembolu et al., 2020; Ogbodo et al., 2023; Uzochukwu, Ezechukwu, et al., 2025; John, Onu, et al., 2025). This review adds to the discussion by providing an updated and systematic assessment of the current status of advanced treatment technologies, laying the groundwork for innovation and practical implementation in environmental water management (Uzochukwu, Kanwulia, et al., 2025; C. Onyenanu & Emembolu, 2020b; L. N. Emembolu et al., 2021; C. N. Onyenanu et al., 2023).

2. Heavy metals in water and wastewater

Heavy metals according to Srivastava & Majumder, (2008) are basically described as "elements that have atomic weights between 63.5 and 200.6 and a density greater than 5 g per cubic meter". Heavy metals such as copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), and cobalt (Co) are vital in biochemical processes in the human body (Abdullah

et al., 2019). Although there are many elements in this category, the ones in Table 1 are significant in the context of the environment (Barakat, 2011).

However, prolonged contact to these metal ions can have harmful consequences (Abdullah et al., 2019). Reduced growth and development, cancer, damage to organs, damage to the nervous system, and in severe cases, death is just a few of the serious health effects that heavy metals can cause (Barakat, 2011). Exposure to certain metals, like lead and mercury, can also lead to the development of autoimmunity (Bjørklund et al., 2024), a condition in which the immune system attacks its own cells, resulting in joint diseases like rheumatoid arthritis, as well as diseases of the kidneys, circulatory system, and nervous system, as well as damage to the foetal brain (Barakat, 2011). At higher doses, heavy metals can cause irreversible brain damage (Barakat, 2011; Marshall et al., 2019). Compared to adults, children may consume more food per unit of body weight, which could result in higher food-based metal doses (Barakat, 2011). Other heavy metals such as arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), and chromium (Cr) are dangerous (Pratush et al., 2018), even at low levels (parts per billion, ppb) since they are non-degradable and can bio-accumulate in the primary systems of human body (Abdullah et al., 2019; X. Wang et al., 2012).

Table 1 provides a summary of the Maximum Contaminant Level (MCL) criteria set by the U.S. Environmental Protection Agency (USEPA) for those heavy metals (Babel & Kurniawan, 2003).

Table 1: The MCL standards for the most hazardous heavy metals

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogen	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and nervous system	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system and nervous system	0.00003

Source: (Babel and Kurniawan, 2003)

3. Heavy metal removal technologies

Several techniques are used to recover wastewater and produce metal-free water. The suitability of a technique is determined by its ability to permanently remove heavy metal ions such as As, Cd, Cr, Cu, Pb, and Hg. Recent techniques that have been implemented are graphically represented in Figure 1.

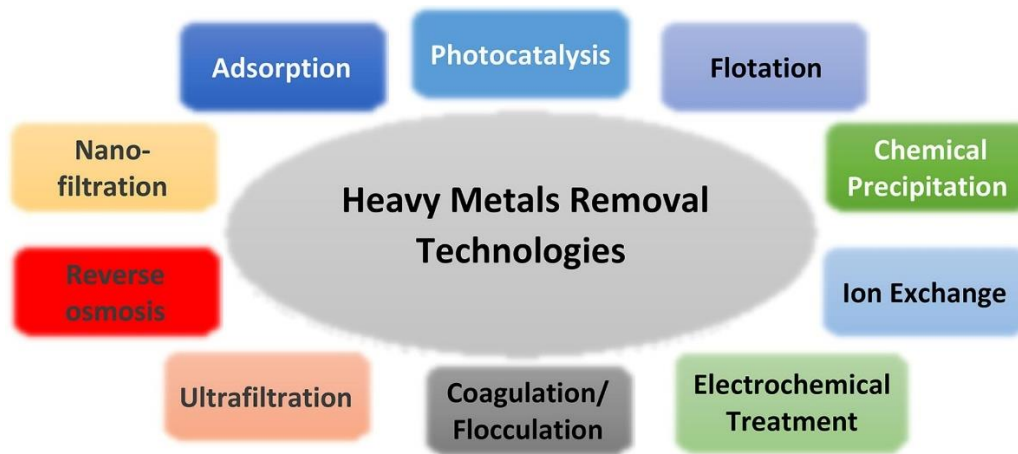


Figure 1: Graphical representation of heavy metal removal technologies (Saleh et al., 2022)

3.1 Chemical Precipitation

Chemical precipitation is the most commonly utilized method for eliminating heavy metals from inorganic wastewater (Barakat, 2011). These traditional chemical precipitation techniques lead to the formation of insoluble precipitates of heavy metals, such as hydroxides, sulfides, carbonates, and phosphates (Gunatilake, 2015). The underlying mechanism of this process involves generating insoluble metal precipitates by reacting dissolved metals in the solution with a precipitant (Gunatilake, 2015). During the precipitation process, very fine particles are produced, and chemical precipitants, coagulants, and flocculation methods are employed to enhance their particle size for removal as sludge (Fu & Wang, 2011; Gunatilake, 2015; Ku & Jung, 2001). The conceptual mechanism for removing heavy metals through chemical precipitation (Barakat, 2011) is illustrated in Eq. (1) (Wang et al., 2005):



In this context, M^{2+} and OH^{-} denote the dissolved metal ions and the precipitating agent, respectively, while $M(OH)_2$ refers to the insoluble metal hydroxide (Barakat, 2011). Adjusting the pH to basic levels (between 9 and 11) is a crucial factor that notably enhances the removal of heavy metals through chemical precipitation (Figure 2) (Barakat, 2011).

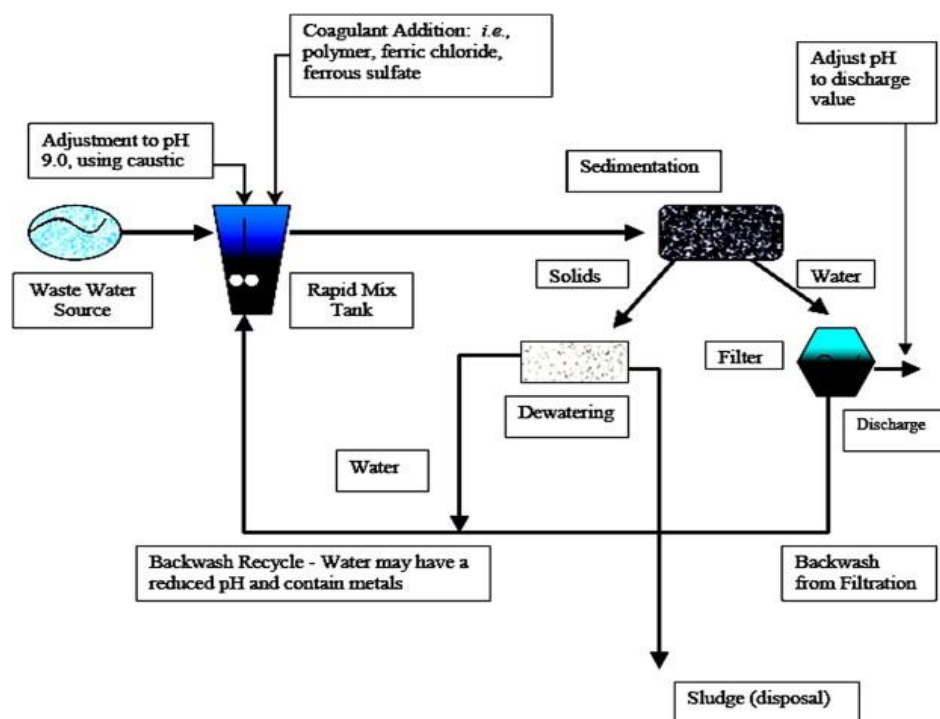


Figure 2. Processes of a conventional metal precipitation treatment plant (Wang et al., 2005)

Lime and limestone are the most frequently used precipitating agents due to their accessibility and cost-effectiveness in many regions (H. A. Aziz et al., 2008; Mirbagheri & Hosseini, 2005). Lime precipitation can be effectively utilized for treating inorganic effluents that contain metal concentrations exceeding 1000 mg/L (Barakat, 2011). Nonetheless, chemical precipitation necessitates a substantial quantity of chemicals to lower metal levels to meet acceptable discharge standards (Barakat, 2011). Other limitations include the significant production of sludge that requires additional treatment, slow rates of metal precipitation, inadequate settling, the clumping of metal precipitates, and the long-term environmental concerns associated with sludge disposal (H. A. Aziz et al., 2008). Once the metals precipitate and form solids, they can easily be removed, and low metal concentrations, can be discharged.

The advantages and disadvantages of the main precipitation agents used for the removal of metal ions from water and wastewater are summarized (Lupa et al., 2023) in Table 2.

Table 2: The advantages and disadvantages of the main precipitation agents used for the removal of metal ions from water and wastewater.

Precipitation agent	Advantages	Disadvantages
NaOH	<ul style="list-style-type: none"> • Good kinetic • Suitable for removing many parameters • The process takes place under ambient conditions • It could be automated 	<ul style="list-style-type: none"> • Expensive • Requires high pH values to obtain precipitates with lower solubility. • The pH must be strictly controlled • Could not remove complex metals. • Treatment performance is determined by the separation stage.
Ca(OH)₂	<ul style="list-style-type: none"> • Inexpensive • It is suitable for removing many parameters. • The process takes place under ambient conditions. • It could be automated. 	<ul style="list-style-type: none"> • Require a higher amount of precipitation agent dose to achieve the optimum pH. • Formation of a higher quantity of sludge. • Could not remove complex metals. • Treatment performance is determined by the separation stage.
Carbonates	<ul style="list-style-type: none"> • Operation at lower pH values. • Easy sedimentation 	<ul style="list-style-type: none"> • Slow kinetic • Foaming of the reaction mass. • Could not remove complex metals.
Sulfides	<ul style="list-style-type: none"> • Ability to directly eliminate Cr(VI) without other pretreatment steps. • Precipitates complex metals. • It does not require a final pH adjustment. 	<ul style="list-style-type: none"> • Poor sedimentation characteristics. • It requires increased attention in the handling and storage stage of the sludge due to its hazardous nature. • Excess sulfides present in the effluent can lead to the development of H₂S.

Source: (Lupa et al., 2023)

3.2 Ion Exchange

Ion exchange represents an additional technique that is effectively utilized in the industry for eliminating heavy metals from wastewater (Barakat, 2011). Ion exchange can draw soluble ions from the liquid phase into the solid phase, making it one of the most commonly used techniques in the water treatment sector (Gunatilake, 2015). As a cost-efficient approach, the ion exchange process typically utilizes inexpensive materials and offers straightforward operations; it has demonstrated considerable effectiveness in eliminating heavy metals from aqueous solutions, especially when dealing with water that has low concentrations of heavy metals (Dizge et al., 2009; Gunatilake, 2015; Hamdaoui, 2009). This method employs cations or anions with specific ion exchangers to extract metal ions from the solution (Gunatilake, 2015). An ion exchange material is a solid that can replace either cations or anions in the surrounding substances (Barakat, 2011). Typically, synthetic organic ion exchange resins are employed as matrices for the ion exchange process (Barakat, 2011). It can be used only low concentrated metal solution and this method is highly sensitive with the pH of the aqueous phase (Gunatilake, 2015). A major drawback of this approach is its inability to manage concentrated metal solutions since the matrix can easily become clogged with organics and other solids present in the wastewater (Barakat, 2011). Furthermore, ion exchange lacks selectivity and is extremely sensitive to the pH levels of the solution. Electrolytic recovery or electro-winning is one of the various methods

utilized to extract metals from process water streams (Barakat, 2011). This method employs electricity to pass a current through a metal-laden aqueous solution that includes a cathode plate and an insoluble anode (Barakat, 2011). Positively charged metal ions adhere to the negatively charged cathodes, resulting in a metal deposit that can be stripped and recovered (Z. Li et al., 2016; Syed et al., 2023). A key disadvantage noted is that corrosion can pose a considerable limitation, leading to the frequent need for replacing electrodes (Kurniawan et al., 2006). Table 3 presents a summary of the experimental conditions and outcomes for different ion exchangers used in various wastewater treatments, along with the efficiencies achieved in the removal of metal ions.

Table 3: Efficiency of various ion exchangers applied on different wastewater treatment.

Ion exchanger	Water type	Methodology	Obtained results	Ref.
Dowex M4195, and Lewatit® MonoPlus TP 220	Acidic streams with Cu ²⁺ content	Batch tests	The highest removal capacity of Cu (86.44 mg/g) was obtained using Lewatit® MonoPlus TP 220 in chloride form, at pH around 2, resin dose of 10 g/L, and treatment time of 60 min.	(Kołodziejka et al., 2014)
C107E, MTS9301 and TP214 resins	Synthetic acetic acid leachate containing Cu ²⁺ , Fe ²⁺ , Pb ²⁺ and Zn ²⁺	Batch tests	C107E developed the highest sorption capacity for the studied metal ions (q _{mCu} = 5 mmol/g; q _{mFe} = 2.1 mmol/g; q _{mPb} = 9 mmol/g; q _{mZn} = 20 mmol/g)	(Bezzina et al., 2020)
Clinoptilolite	Synthetic waters containing Pb(II), Cd(II), and Cr(VI)	Batch experiments and fixed-bed reactors	Pb and Cd were efficiently removed (>95%) from the single and binary system but were significantly affected by the presence of Cr ions or organic contaminants.	(Vaca Mier et al., 2001)
Clinoptilolite	Synthetic waters containing Cu ²⁺ , Fe ³⁺ , and Cr ³⁺	Batch tests, C _i = 0.01 N, T = 25°C, treatment time = 4 days, pH = 2–2.5.	The presence of SO ₄ ²⁻ and HPO ₄ ²⁻ anions affect the ion exchange of Cu ²⁺ and in a lower measure of Fe ³⁺ and Cr ³⁺ .	(Inglezakis et al., 2003)
Thomsonite	Synthetic waters containing Pb ²⁺ , Fe ³⁺ , and Ni ²⁺	Batch tests, C _{iMe} = 100 ppm	Extraction efficiency of ~100%, 99.9%, and 98.6%, for Pb ²⁺ , Fe ³⁺ , and Ni ²⁺ , respectively.	(Almalih & Talballa, 2016)
Zeolite	Synthetic waters containing Cu ²⁺ , Cd ²⁺ , Cr ³⁺ , Ni ²⁺ , and Pb ²⁺	Batch tests S:L ratio = 5 g: 45 mL C _{iMe} = 5, 10, 30 mg/L, T = 23°C, treatment time = 5–60 min.	Removal efficiency 99%.	(Senila et al., 2022)
Strong base anion exchange resin	Synthetic water containing heavy metal (Cu ²⁺ , Cd ²⁺ , Zn ²⁺) and cyanide ions.	Semi-fluidized and fluidized beds using a transparent acrylic resin tube, d = 20 mm h = 600 mm, m _{resin} = 20 g	The ion exchange efficiency of the studied heavy metal cyanide systems decreases as the concentration ratio of cyanide and heavy metal increases.	(Kim et al., 2002)
Dowex HCR-S synthetic resin	Synthetic water containing Cd ²⁺ , Ni ²⁺ , and Zn ²⁺	Batch experiments at different initial solution pH, stirring speeds, temperatures, initial concentrations, and resin dosages	The exchange level of 99.76%, 93.66%, and 83.1% for Cd ²⁺ , Ni ²⁺ and Zn ²⁺ , respectively, at T = 293 K, C _i = 250 mg/L, t = 60 min, pH = 2, resin dose = 2 g.	(Fil et al., 2012)
Amberlite IRC-50/IRC-86 and Amberlite IRA-67	Synthetic water containing Pb ²⁺ , Cu ²⁺ and Cd ²⁺	Column experiments, d = 17.2 mm h = 490 mm	The most efficient resin was IRC-86. The order of adsorption capacity for the metal ions tested was Pb ²⁺ > Cd ²⁺ > Cu ²⁺ . A 99% desorption of the studied metal ions was achieved using CO ₂ .	(Silva & Brunner, 2006)

Source: (Lupa et al., 2023)

3.3 Coagulation – flocculation

Coagulation-flocculation is a physical-chemical method used to eliminate metal ions from water and wastewater, consisting of three stages as shown in Figure 3. The initial stage involves the addition of a coagulation agent while stirring vigorously, which serves to destabilize colloidal substances (Lupa et al., 2023). The vigorous stirring enhances the interaction between the metal ions and the coagulant. In the second stage, a flocculant is added under gentle stirring to promote the aggregation of the destabilized particles, resulting in the formation of larger flocs that can be easily separated (Lupa et al., 2023). Gentle stirring aids in the collision of particles and the growth of flocs (Lupa et al., 2023). The final stage involves the separation of the generated sludge and clarified effluents, which can be achieved through settling, flotation, or filtration (Lupa et al., 2023; Mishra et al., 2021a; Qasem et al., 2021).

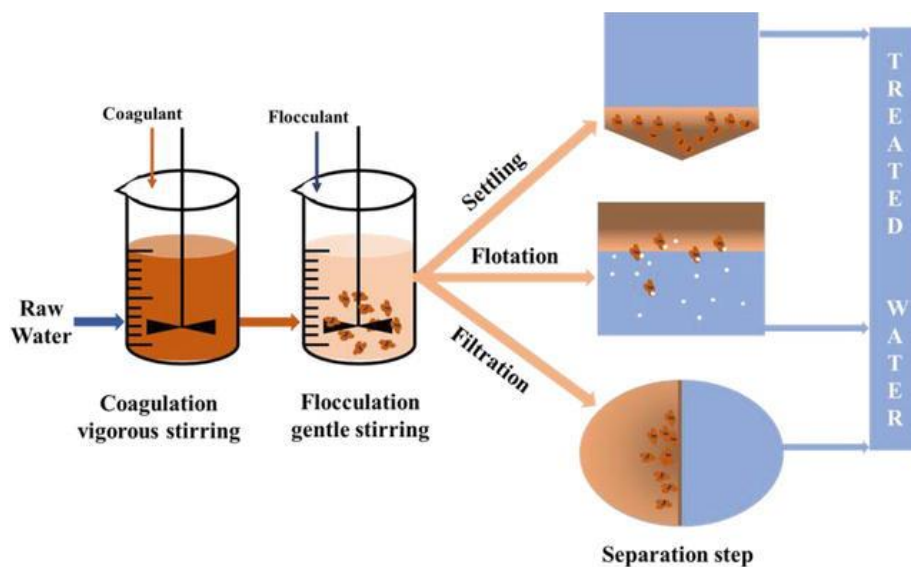


Figure 3: Scheme of the coagulation-flocculation system (Lupa et al., 2023)

After discrete particles agglomerate into larger clusters, they can be extracted or separated through means such as filtration, straining, or flotation (Gunatilake, 2015). The creation of sludge, the use of chemicals, and the movement of harmful substances into a solid form are significant disadvantages of this method (Gunatilake, 2015). Table 4 outlines the methods and findings from several studies on the effectiveness of single or combined coagulation/flocculation processes used on various wastewater types, highlighting their efficiencies in removing metal ions.

Table 4: The efficiency of various coagulation/flocculation processes applied to different wastewater treatment.

Coagulant/flocculant agent	Water type	Methodology	Obtained results	Ref.
Alum	Landfill leachate	Coagulation/flocculation process combined with continuous adsorption using eggshell waste materials (CES). Optimum dose of alum is 3.0 g/L; CES adsorbent mass 25.5 g. Hydraulic loading rate HLR = 6.37 L/m ² ·min.	Removal efficiencies of Fe, Pb, Cu, Zn, Ni, and Cr of 92%, 93%, 87%, 76%, 65%, and 60%, respectively.	(Jaradat et al., 2021)
Ferric chloride: polymer	Industrial waste waters	Ferric chloride: polymer = 200 mg/L:20 mg/L	Removal efficiencies of Cr, Fe, and Zn of 97%, 92%, and 0%, respectively. Resulted volume sludge of 120 mL/L.	(Amuda et al., 2006)
Ferric chloride	Industrial waste waters	Jar test, C _{iw} = 321 ppm, Fe/W ratio = 4, or 8, pH = 4, 6, 8 and 10.	Tungsten removal efficiency of 99%, at pH < 6. Residual concentration of tungsten was <10 ppm.	(Plattes et al., 2007)

Micro-alloyed aluminum composite (MAIC)	Wastewater containing Zn ²⁺ and Cu ²⁺	Spontaneous reduction coagulation process in a laboratory semi-flow system varying several parameters (treatment time, pH, initial metal concentration, and flow rate).	Residual concentration of Zn and Cu ions under admissible level was obtained at 20 minutes of treatment, at neutral pH, and increased initial concentration of metal ions. The presence of copper favor zinc removal efficiency and copper removal is not affected by zinc presence.	(Bojic et al., 2009)
Cationic polymers	Tannery wastewater	Jarr test methodology using cationic polymers with different weights and charge densities.	A removal efficiency of Cr > 96% was obtained using cationic polymers with molecular weight between 4 and 6 and charge density between 40 and 55% and an optimum dose of 20%.	(Haydar & Aziz, 2009)
Cactus <i>Opuntia ficus indica</i> bioflocculant	River water with Pb ²⁺ , Zn ²⁺ , Cd ²⁺ , and Cu ²⁺ content.	The coagulation-flocculation process was optimized for pH, initial concentration of Pb(II) ions, particle size, dosage, ionic strength, contact time, and temperature.	Removal efficiency of Pb, Zn, Cd, and Cu of 100%, 85.74%, 84.16%, and 93.02%, respectively, were achieved at pH 5, natural ionic strength, dosage of 8 mg/L, corresponding to zero zeta potential, with particle size < 75 µm, at 35°C for a floc settling time of 180 min.	(Nharingo et al., 2015)
Commercial tannin-based flocculant	Raw surface water with Cu ²⁺ , Zn ²⁺ and Ni ²⁺ content.	Jar-test procedure	Removal efficiency of Cu, Zn, and Ni of 90%, 85% and 70%, respectively, was achieved using pH value of 6, 7, and 8, respectively, and at a flocculant dose between 100 and 150 ppm.	(Beltrán Heredia & Sánchez Martín, 2009)

Source: (Lupa et al., 2023)

Different types of water could be treated either primary or tertiary using flocculation or coagulation techniques. The coagulant/flocculant dosage, pH, temperature, stirring speed, stirring time, settling time, and other operating parameters all have a big impact on how well metal ions are removed. The coagulation/flocculation procedure is sometimes combined with other treatment techniques to enhance the performance that is achieved (Lupa et al., 2023).

3.4 Ion-flotation

The technique that involves the use of various surfactants to destabilize metal ions found in wastewater and convert them into hydrophobic compounds, which are then removed through flotation using air bubbles, is known as ion-flotation (Chang et al., 2019; Polat & Erdogan, 2007). The ionic flotation process is based on two main concepts: one is the bonding of the metal ion to the polar end of the surfactant, and the other is the interaction between the surfactant's nonpolar end and air bubbles, resulting in the concentration and separation of metal ions at the surface of the wastewater through the formation of froth (Lupa et al., 2023). In addition to surfactants, foaming agents or frothers (such as ethanol, polypropylene glycol, and methyl isobutyl carbinol) can be utilized to achieve smaller air bubble sizes, enhancing the interaction surface area between the bubbles and the target metal ions (Polat & Erdogan, 2007). Ion-flotation can be employed for both wastewater treatment and the recovery of precious or rare metal ions. Various surfactants and collectors have been examined, including sodium dodecyl sulfate (Polat & Erdogan, 2007), polyethylenimine (Shen & Hankins, 2019), hexadecyltrimethyl ammonium bromide (Jafari et al., 2017), and 4-thiazolidinone derivatives (Kozłowski et al., 2002). This treatment method is characterized by low energy requirements and the absence of complicated, large-scale equipment, making it straightforward to operate and capable of selective separations that demonstrate high efficiency while producing minimal sludge (Lupa et al., 2023). Ion-flotation can be performed under varying operational conditions (such as pH, flow rate, treatment duration, and the molar ratio of surfactant to metal ions), depending on the specific metal ions needing removal and the surfactant or collector used (Lupa et al., 2023). Literature on this subject presents this treatment method as a simple, quick, and cost-effective approach, while also highlighting the need for the development of new, low-cost collectors that offer enhanced selectivity, environmental friendliness, and greater efficiency with reduced dosages, all of which contribute to lowering treatment costs (Lupa et al., 2023).

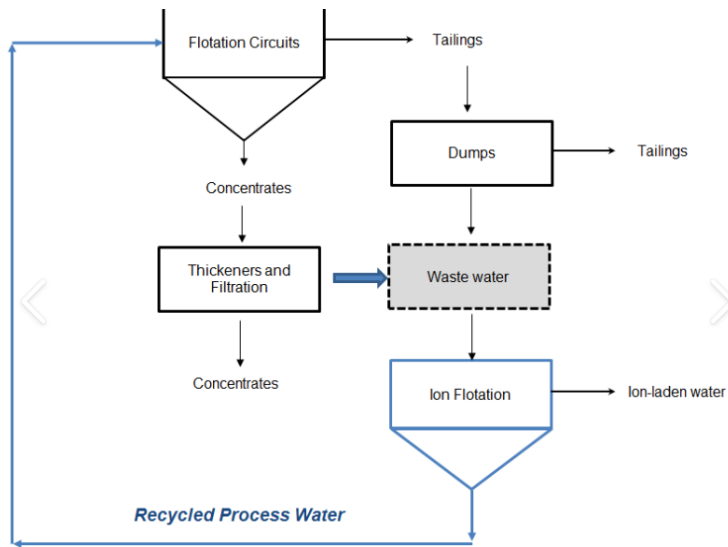


Figure 4. Water cleaning in flotation plant by ion flotation (Arslan & Bulut, 2022; Yenial & Bulut, 2017)

3.5 Adsorption

An effective advanced water treatment method for eliminating trace metal ions from water and wastewater is adsorption (Lupa et al., 2023). This separation technique involves the adhesion of metal ions found in water to the surface of a solid, known as an adsorbent (Figure 5). The mechanisms for separating metal ions from water through adsorption depend on both the properties of the ions and those of the adsorbent, determined by the interactions between them (Lupa et al., 2023). These interactions may be of a physical nature, governed by low-energy forces (such as van der Waals forces). In this scenario, the metal ions are trapped in the adsorbent's pores without electron transfer occurring (Lupa et al., 2023). Consequently, this process is reversible, allowing for the removal of the retained metal ion molecules through desorption, thereby regenerating the adsorbent (Lupa et al., 2023). When the interaction between metal ions and adsorbents involves electron transfer and the formation of chemical bonds, the process is referred to as chemical adsorption, or chemisorption. In this case, metal ions are not attracted to the entire surface of the adsorbent but to specific active sites that contain functional groups capable of reacting with the metal, which involves higher energy than that of physical adsorption, accounting for the greater selectivity of chemical adsorption (Howe et al., 2012; Mishra et al., 2021b; Renu et al., 2016).

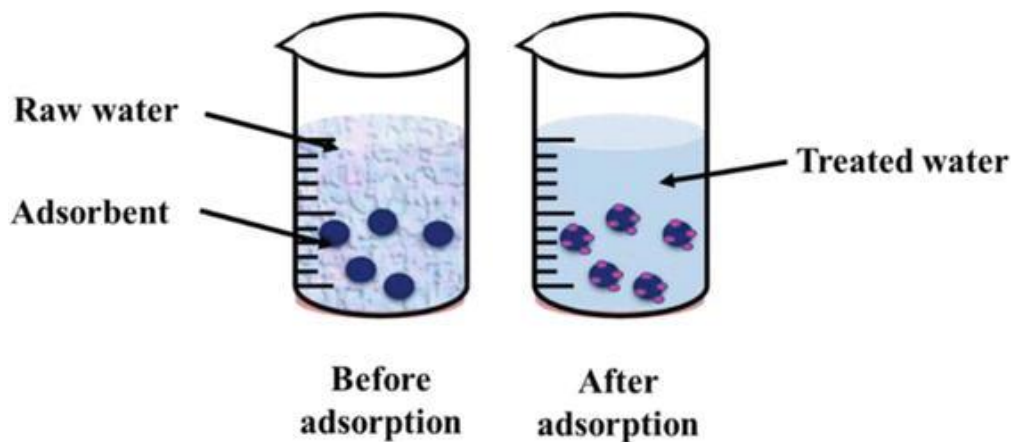


Figure 5: Scheme of the adsorption process (Lupa et al., 2023)

Table 5: Research results of various adsorbent materials used for the removal of various metal ions from different wastewater.

Adsorbent materials	Water type	Methodology	Obtained results	Ref.
Microporous (CS-1501) mesoporous activated carbon cloths	Synthetic wastewater containing Cu^{2+} and Pb^{2+}	Batch mode adsorption studies using mono or bicomponent systems ($V = 250$ ml, $m = 500$ mg, $C_i = 0.1\text{--}1.4$ mmol/L, $t = 12$ h, $\text{pH} = 3.5/5$).	The adsorption capacities of the studied metal ions are between 0.080 and 0.175 mmol/g. In binary system, a decrease of adsorption capacities is observed.	(Faur-Brasquet et al., 2002)
Activated carbon produced from the biomass recovered from the medicinal plant residue	Synthetic wastewater containing Zn^{2+} , Cd^{2+} , and Pb^{2+} and leachate waters.	Batch adsorption studies $C_i = 0.1\text{--}50$ mg/L; $\text{pH} = 4$, $T = 25^\circ\text{C}$, $t = 15$ min-5 h.	Optimum condition in synthetic waters for adsorption of Pb^{2+} , Zn^{2+} , and Cd^{2+} were $\text{pH} = 5$, $T = 25^\circ\text{C}$, adsorbent dose = 5 g/L, $t = 1.5$ h. The rate of heavy metal adsorption from landfill leachate was lower than that from artificial wastewater.	(Yan et al., 2020)
Carbon nanosheet (CNS) functionalized with amine derivatives	Seawater containing Zn^{2+} , Cd^{2+} , and Hg^{2+}	Quantum mechanics studies.	The studied adsorbent presents a negative adsorption energy (range: -75 to -93 kJ/mol). The metal ions adsorption was confirmed by the natural bond orbital and quantum theory of atoms in molecules.	(Javarani et al., 2022)
Multi-walled carbon nanotubes (MWCNTs)	Synthetic waters containing Cu^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+}	Kinetic experiments, $C_i = 0.5$ mg/L, $\text{pH} = 7$, $T = 278\text{--}333$ K, adsorbent dose = 125 mg/100 mL.	At 298 K, the binding of the metal ions by MWCNTs follows the order: $\text{Cu(II)} > \text{Pb(II)} > \text{Zn(II)} > \text{Cd(II)}$.	(Abdel Salam, 2013)
Surface-modified sawdust-based cellulose nanocrystals	Aqueous solutions containing Cu^{2+} , Fe^{2+} , and Pb^{2+}	Combination of adsorption and coagulation techniques	$q_m = 111.1$ mg Cu/g $q_m = 2.82$ mg Pb/g $q_m = 81.96$ mg Fe/g	(Oyewo et al., 2021)

Source: (Lupa et al., 2023)

Adsorption is a simple, low-cost technique for treating water that contains metal ions. It shows that scaling up to an industrial use is economically feasible (Lupa et al., 2023). This treatment method's adaptability is increased by the availability of different and affordable adsorbent materials. Unfortunately, automation is not a good fit for this approach (Lupa et al., 2023).

3.6 Electrochemical separation processes

Electrochemical treatment methods were initially applied for the electrorefining of ores in the mineral industry (Lupa et al., 2023). Researchers were hesitant to adopt these methods due to the energy requirements and the substantial initial investment in specialized equipment, which resulted in higher processing costs (Lupa et al., 2023). However, following studies that highlighted their effectiveness and the low maintenance needs of the equipment, the

implementation of these techniques for treating water with metal ion content began to show increasing promise (Lupa et al., 2023). Electrochemical methods for treating water containing metal ions can be categorized into electrocoagulation, electroflocculation, and electrodeposition (Lupa et al., 2023).

The electrocoagulation method occurs within a basic electrolysis cell that utilizes sacrificial electrodes, which can be made from the same or different materials (Figure 6). In most instances, the electrodes are composed of Fe^{3+} or Al^{3+} (Lupa et al., 2023). The electrocoagulation process involves the dissolution of the anode, generation of H^2 and HO^- at the cathode, formation of coagulant ($\text{Al}(\text{OH})_3$), destabilization and neutralization of metal ions through the application of electric current, aggregation of the destabilized metal ions, and the creation of flocks/sludge (Bazrafshan et al., 2015; Khosa et al., 2013; Mao et al., 2021; Mota et al., 2016; Shim et al., 2014). A key advantage of this method is that it does not require additional reagents, as the coagulant is produced on-site from the electrical dissolution of the sacrificial electrodes (Lupa et al., 2023). The resulting flock/sludge is stable and can be easily removed. The hydrogen produced aids in the elimination of fine particles (Lupa et al., 2023). However, the primary drawbacks include the potential for cathode passivation and the necessity for periodic replacement of the sacrificial anode.

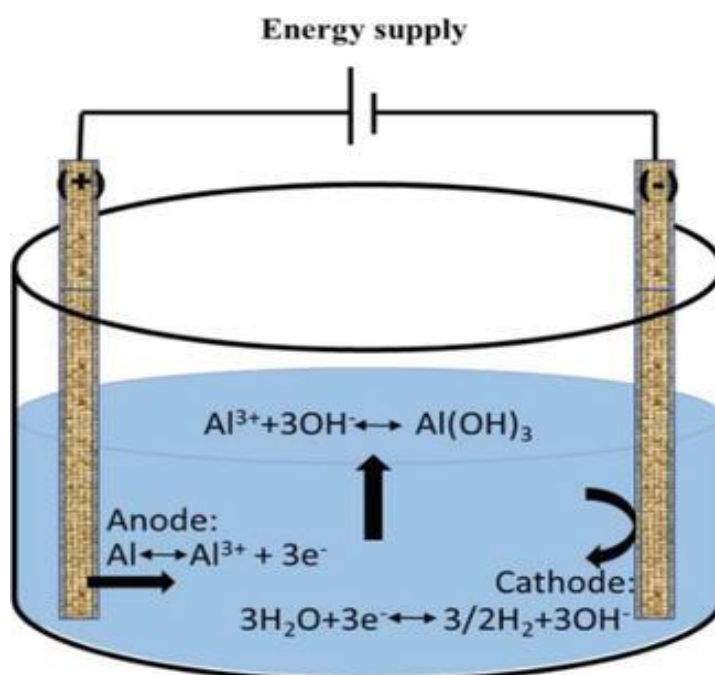


Figure 6: Scheme of electrocoagulation processes (Lupa et al., 2023)

3.7 Membrane separation processes

Membrane separation processes represent a modern method for treating water that can effectively eliminate trace amounts of metal ions from both water and wastewater (Lupa et al., 2023). These processes (illustrated in Figure 7) involve directing the water flow through semipermeable membranes that possess specific characteristics (such as pore size or electrical charge) which permit the passage of water molecules while retaining the dissolved metal ions (Al-Rashdi et al., 2011; Blöcher et al., 2003; Howe et al., 2012; Khulbe & Matsuura, 2018; Xiang et al., 2022).

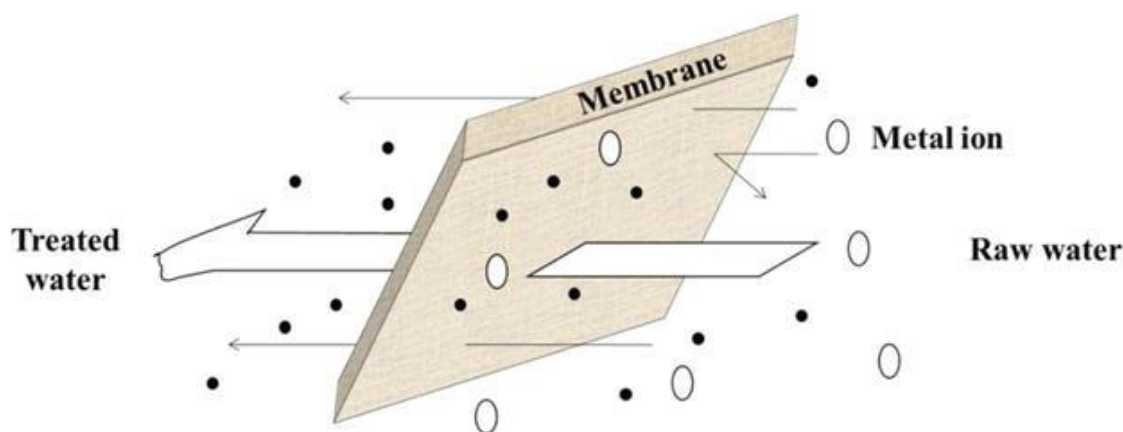


Figure 7: Scheme of the membrane separation processes (Lupa et al., 2023)

Based on the separating forces utilized and the dimensions of the particles being separated which is done by Lupa et al., (2023), membranes can be categorized into.

- Membranes that work under pressure (MF—microfiltration, UF—ultrafiltration, NF—nanofiltration, RO—reverse osmosis).
- Membranes actuated by electrical voltage (ED—electrodialysis, RED—reverse electrodialysis).

Since membrane treatment methodologies necessitate operation under elevated pressures, it is imperative that the membranes exhibit adequate compressive strength (Lupa et al., 2023). The characteristics that define membranes encompass permeability, porosity, hydrophilicity, surface charge, and thermal/mechanical stability (Lupa et al., 2023).

The majority of the membranes examined consist of composite materials constructed upon polymer substrates (Radzaminska-Lenarcik et al., 2020; Vo et al., 2020; Zahid et al., 2018). The implementation of these processes offers several advantages: they consistently ensure superior water quality, the absence of chemical reagents, compatibility with automation, and a compact design (Lupa et al., 2023). Conversely, these methods also present technical challenges: inadequate selectivity, relatively low transmembrane fluxes, operational difficulties, the potential for membrane fouling necessitating pretreatment and routine membrane cleaning, as well as economic concerns: a multitude of manufacturers utilizing diverse technologies and varying price points (Lupa et al., 2023).

3.8 Photocatalysis

In recent years, the photocatalytic process utilizing semiconductor materials in aqueous suspension has garnered significant interest for its potential in solar energy conversion (Barakat, 2011). This photocatalytic method has been effective for the swift and efficient elimination of environmental pollutants (Barakat, 2011). When the semiconductor-electrolyte interface is exposed to light energy exceeding the semiconductor's band gap, electron-hole pairs (e^-/h^+) are generated in the conduction and valence bands of the semiconductor, respectively (Herrmann, 1999). These charge carriers can migrate to the surface of the semiconductor, where they can either reduce or oxidize species in the solution that have appropriate redox potential (Barakat, 2011). A variety of semiconductors have been employed, including TiO_2 , ZnO , CeO_2 , CdS , and ZnS (Barakat, 2011). Typically, titanium dioxide demonstrates the highest photocatalytic efficiency and maximum quantum yields (Barakat, 2011). Figure 8 illustrates the conceptual reaction pathway for photocatalysis involving titanium dioxide particles.

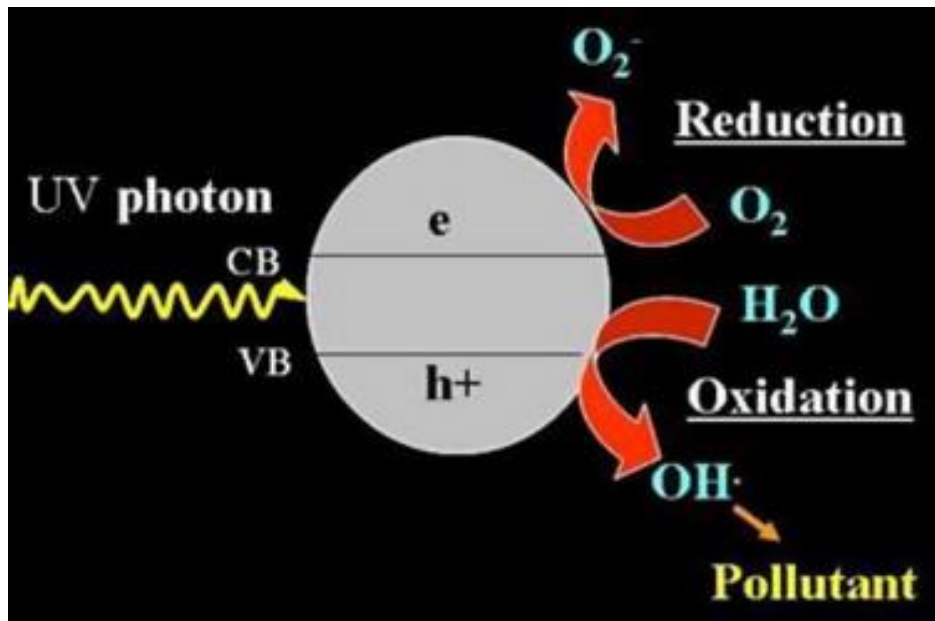
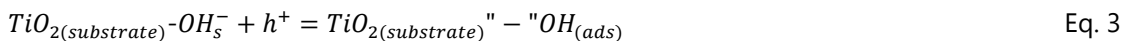


Figure 8. The conceptual reaction path of photocatalysis over TiO₂ (Herrmann, 1999).

The process of photocatalysis using titanium dioxide particles was discussed by (Zhang & Itoh, 2006). To prevent recombination, it is essential to trap the produced electron-hole pairs. Hydroxyl ions (OH⁻) are probable candidates for trapping holes, resulting in the creation of hydroxyl radicals, which serve as potent oxidizing agents. On the other hand, the traps for electrons are typically adsorbed oxygen species, leading to the generation of superoxide species (O₂⁻), which are unstable, reactive, and can undergo various transformations.



Barakat et al., (2004) investigated the photocatalytic breakdown of complex cyanide using UV-irradiated TiO₂ suspension while simultaneously eliminating copper. The findings indicated that free copper (10⁻² M) was entirely eradicated within 3 hours (Barakat et al., 2004). The presence of Cu(II) and CN⁻ increased the efficiency of removing both CN⁻ and copper; the percentage of removal improved as the Cu:CN⁻ molar ratio increased, achieving total removal of both copper and cyanide at a 10:1 ratio (Figure 9).

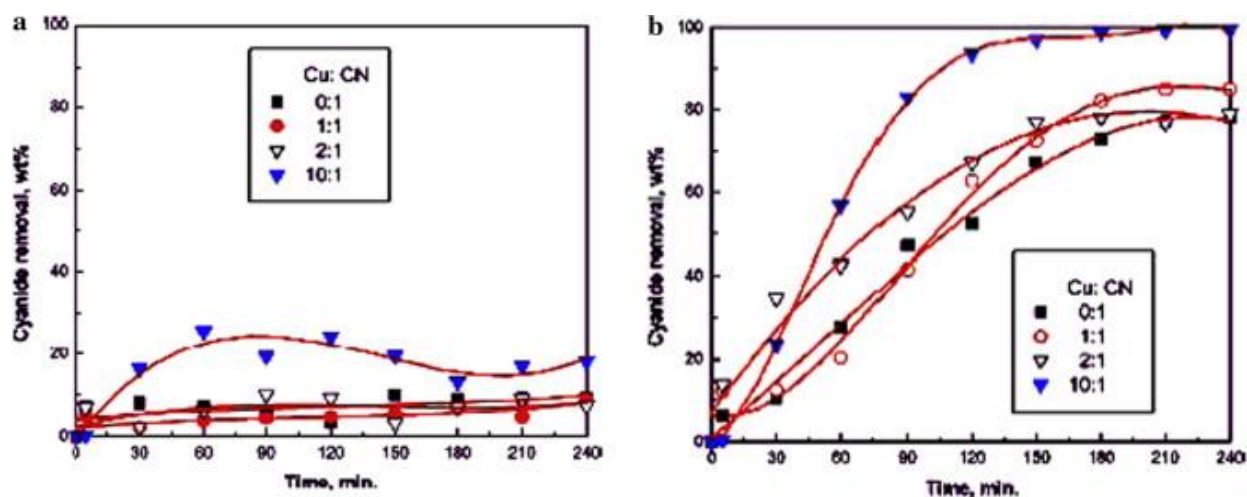


Figure 9. Cu(II) removal by UV illuminated TiO₂ at various Cu(II)/CN⁻ ratios (Barakat et al., 2004). (a) Without UV-light and (b) with UV-light.

4. Evaluation of heavy metals removal processes

Removing heavy metals from wastewater is a crucial aspect of research conducted in the environmental domain. (Gunatilake, 2015). The choice of method must align with the characteristics of the wastewater, the objectives of treatment, and the requirements for environmental compliance. Chemical precipitation is one of the oldest and most commonly utilized techniques due to its straightforward operation and cost-effectiveness, particularly for treating wastewater with high metal concentrations. Chemicals such as lime and sodium hydroxide convert metal ions into insoluble compounds for elimination. Nonetheless, this method produces a significant amount of toxic sludge and is less effective at low concentrations of metals or in cases where metals are complexed with organic compounds (Barakat, 2011; Gunatilake, 2015). Adsorption has gained attention because of its versatility, low expense, and high efficiency. This technique, utilizing materials like activated carbon, biochars, and nanomaterials, can achieve removal efficiencies surpassing 90% (Fang et al., 2018). However, challenges arise from competition among metal ions for available active sites, saturation effects, and limited recyclability of used adsorbents, particularly in systems with mixed metals (Rajendran et al., 2022). Ion exchange provides high selectivity and is especially effective for removing trace metals in the final polishing stages. Both synthetic resins and natural zeolites exhibit strong affinities for Cu²⁺, Pb²⁺, and Cd²⁺ (Bezzina et al., 2020). However, its primary drawbacks include sensitivity to pH changes, fouling caused by organic matter, and reduced efficiency at high metal concentrations (Gunatilake, 2015). Coagulation-flocculation is effective at removing suspended solids and colloidal metals. Coagulants like alum and ferric chloride facilitate the aggregation and settling of particles. While this method is efficient, particularly for Fe, Cr, and Pb, it also leads to sludge production and performs less effectively against complexed metals (Lupa et al., 2023). Membrane filtration techniques, including nanofiltration and reverse osmosis, are proficient in precisely removing both individual and mixed metal ions. Their compact nature and potential for automation are appealing; however, issues like membrane fouling, high pressure requirements, and expensive maintenance pose notable challenges (Xiang et al., 2022). Electrochemical methods, such as electrocoagulation, offer a reagent-free process with high removal rates for metals like Ni²⁺ and Pb²⁺. Despite their potential, problems like electrode wear and energy consumption can impact their feasibility over time (Bazrafshan et al., 2015). Photocatalysis, utilizing semiconductors such as TiO₂ and ZnO under UV or visible light, enables the decomposition of complexed metals and organic pollutants. Although it offers ecological benefits, its effectiveness is limited by slow reaction rates and the costs associated with catalyst recovery (Barakat et al., 2004). Table 6 outlines the key benefits and drawbacks of the different physico-chemical treatments discussed in this research.

Table 6. The main advantages and disadvantages of the various physico-chemical methods for the treatment of heavy metals in wastewater.

S/N	Treatment method	Advantages	Disadvantages	References
1	Chemical precipitation	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal	(Kurniawan et al., 2006)
2	Adsorption with new adsorbents	Low-cost, easy operating conditions, having a wide pH range, high metal-binding capacities	Low selectivity, production of waste products	(Babel and Kurniawan, 2003; Aklil et al., 2004)
3	Membrane filtration	Small space requirement, low pressure, high separation selectivity	High operational cost due to membrane fouling	(Kurniawan et al., 2006)
4	Electrodialysis	High separation selectivity	High operational cost due to membrane fouling and energy consumption	(Mohammadi et al., 2005)
5	Photocatalysis	Removal of metals and organic pollutants simultaneously, less harmful by-products	Long duration time, limited applications	(Barakat et al., 2004; Kajitvichyanukul et al., 2005)
6	Ion exchange	High selectivity at low concentrations, reusable materials	Sensitive to pH, fouling risk, ineffective for high metal concentrations	Gunatilake, 2015; Senila et al., 2022
7	Coagulation–flocculation	Effective for bulk metals, adaptable to various effluents	Chemical consumption, sludge disposal, and less effective for complexed metals	Jaradat et al., 2021; Lupa et al., 2023
8	Electrochemical methods	Reagent-free, effective for various metals, stable sludge	Electrode degradation, electrical energy needs	Bazrafshan et al., 2015; Mao et al., 2021
9	Ion-flotation	Low energy, selective separation, compact system	Limited scale-up, dependency on surfactants, and foam stability	Polat & Erdogan, 2007; Chang et al., 2019

Source: (Barakat, 2011)

5. Conclusion

In response to tighter environmental regulations and the urgent need for cleaner water systems, a variety of treatment technologies have been developed over recent years for effectively eliminating heavy metals from wastewater. This review explored many approaches, ranging from conventional procedures such as coagulation-flocculation and chemical precipitation to more sophisticated techniques like membrane filtration, adsorption, electrodialysis, electrochemical treatment, ion flotation, and photocatalysis. Among these options, chemical precipitation is still a viable method for handling high-concentration effluents due to its simplicity and affordability. Adsorption, especially through the use of low-cost or nanostructured materials, is increasingly recognized for its adaptability and effectiveness. Membrane technologies and electrochemical processes provide precise and automated alternatives, while photocatalysis is noteworthy for being a clean and innovative method that can remove both metals and organic pollutants simultaneously. However, choosing the best treatment strategy is contingent upon key factors like the composition of the wastewater, pH level, concentration of metals, environmental impact, complexity of operations, and cost. No single technique is universally the best; instead, a combined or integrated method might yield synergistic benefits. Ultimately, decisions regarding the

implementation of any treatment system aimed at reducing heavy metal pollution and ensuring long-term environmental safety should consider technical feasibility, scalability, cost-effectiveness, and sustainability.

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