Navigating Heavy Metal Removal: Insights into Advanced Treatment Technologies for Wastewater: A review.

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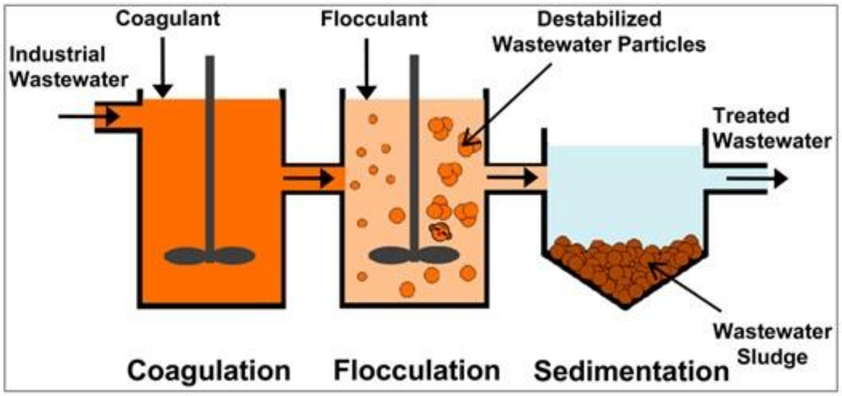
Graphical Abstract



Abstract

This paper provides an overview of heavy metal removal technologies for wastewater treatment, with a focus on adsorption, chemical oxidation, ion exchange, and various coagulation processes. The review revolves around wastewater characterization as an essential first step in creating efficient treatment systems. The study examines the uses of different treatment technologies, emphasizing both their benefits and drawbacks. Although flocculation is a rapid and economical procedure, it produces high amounts of waste and needs further filtration and sedimentation. In addition, natural coagulants are found to be more environmentally friendly than synthetic ones, their effects on water quality may make disinfectants necessary. Despite their low toxicity, stability, and environmental advantages, hybrid coagulants have certain drawbacks that are related to operational variables. Despite its broad applicability and low cost, adsorption faces challenges with regeneration and sludge creation. Although it is acknowledged to have a high metal recovery rate, ion exchange is expensive and requires special maintenance. Chemical oxidation techniques, in particular advanced oxidation processes (AOPs), are useful for eliminating heavy metals and breaking down organic materials. The limitations and difficulties of each approach are discussed in the abstract's conclusion, which highlights the necessity of future study aimed at enhancing treatment efficacy for extremely low quantities of heavy metals. The AOP shows a high efficiency in heavy metals removal with 98% of copper and 99% of cadmium. Adsorption technologies, such as activated carbon and zeolites, demonstrate high metal recovery rates of up to 95%. Ion exchange processes effectively remove heavy metals like mercury and arsenic, achieving removal efficiencies exceeding 99%

Keywords: Industrial wastewater; Removal; Heavy Metals; Treatment; Oxidation; Coagulation

1. Introduction

Due to its detrimental impacts on ecosystems and human health, sewage pollution resulting from heavy metals has grown and reached to be a significant environmental threats in recent decades. The environment can retain heavy metals for prolonged periods which may create hazards. These toxic elements enter wastewater through industrial processes, mining, agricultural runoff, and domestic sewage, endangering both aquatic organisms and human populations. Thus, one of the primary goals of contemporary environmental research and technology is the efficient removal of heavy metals from wastewater (Briffa et al., 2020). A class of metals with densities more than 4 g/cm3 is known as heavy metals. The industries that release the greatest heavy metals are electroplating, paper, fertilizer, and mining. Heavy metals are defined as elements having specific gravities more than 5.0 and atomic weights between 64 and 201 (Srivastava & Majumder, 2008). Because they are not biodegradable, heavy metals can build up in living things and lead to a different number of diseases, including cancer, organ damage, and neurological disease (S. Wang et al., 2005). Additionally, they disrupt the ecological balance of aquatic ecosystems and affect biodiversity and ecosystem services.

To mitigate these adverse effects, many methods and technologies have been developed to remove heavy metals from wastewater before they are discharged into natural water bodies or safely reused for non-drinking purposes. The kind and concentration of heavy metals, the wastewater's source, and the desired quality of the treated water are only a few of the variables that affect the difficult task of removing heavy metals from wastewater (Gupta et al., 2012). Various treatment methods have been studied and applied over the years as chemical oxidation, ion exchange, adsorption, filtration, biological methods and others (Bashir et al., 2019; F. Fu & Wang, 2011; Qasem et al., 2021; Saravanan et al., 2021). Each single approaches has benefits and drawbacks, and the best approach will rely on the particulars of the effluent as well as the relevant regulations (Barakat, 2011). In the face of increasingly rigorous regulations, toxic heavy metals have emerged as prominent environmental priority pollutants, posing a substantial risk to ecosystems and human life.

In recent years, there has been a notable shift towards exploring more sustainable and innovative approaches. Advanced treatment technologies have emerged that leverage cutting-edge materials, processes, and synergistic combinations to enhance removal efficiency and minimize environmental impact (Smith et al., 2023). These include adsorption techniques utilizing activated carbon, zeolites, and novel adsorbents tailored for specific metal ions, offering high selectivity and capacity for metal removal (Johnson et al., 2022).

Furthermore, membrane processes such as reverse osmosis and nanofiltration have gained prominence for their ability to effectively separate metal ions from aqueous solutions based on size and charge. These technologies are particularly advantageous in treating complex industrial effluents and saline wastewater where conventional methods may be less effective (Wang and Chen 2023; Zhang et al., 2023; Li et al., 2023).

Additionally, advanced oxidation processes (AOPs) like ozonation, UV irradiation, and Fenton's reagent have demonstrated efficacy in degrading organic pollutants and oxidizing metal ions to less toxic forms, thereby complementing traditional removal methods (Chen and Weng 2024; Wang et al., 2024, Sharma and Kumar 2023).

This review article comprehensively examines the present techniques utilized for heavy metal ion removal from wastewater, providing an assessment of their respective advantages and limitations in practical applications. The aim of this review is to provide a comprehensive overview of the various techniques and strategies used to remove heavy metals from wastewater. It discusses the principles, mechanisms and recent advances of these methods and their applicability to various scenarios. In addition, the environmental and economic aspects associated with each method, highlighting the need for sustainable and efficient approaches was discussed to address this pressing environmental problem.

Throughout the review, the strengths and limitations of each technology, considering factors such as cost-effectiveness, scalability, energy consumption, and environmental impact have been reviewed. In addition, recent advancements in hybrid and integrated approaches that combine multiple treatment methods to achieve synergistic effects and optimize heavy metal removal are also highlighted.

2. Industrial wastewater production and its impact on health and environment

Industrial wastewater, a byproduct of diverse industrial activities such as chemical processing, mining, manufacturing, and energy production, is categorized by contamination from various pollutants. These include suspended solids, heavy metals, toxic chemicals, organic compounds, and nutrients, rendering the water unsuitable for direct discharge into natural water bodies (Çifçi & Meriç, 2016). To safeguard the human health and environment, it is imperative to implement proper treatment and management of industrial wastewater. Metal wastes originate from multiple industrial processes, such as chromated copper-arsenate wood treatment in the wood processing industry, yielding arsenic-containing wastes. Inorganic pigment production results in cadmium sulfide and chromium compound-containing pigments. The refining of petroleum produces conversion catalysts tainted with vanadium, nickel and chromium, while photographic processes generate film with elevated ferrocyanide and silver concentrations. These processes generate significant amounts of hazardous wastes requiring thorough treatment (Barakat, 2011). Heavy metals, typically defined by a density exceeding 5 g/cubic centimeters, encompass a variety of elements. Although arsenic is considered a dangerous heavy metal, it is technically a semimetal (Barakat, 2011). Industrial wastewater, a consequence of industrial processes, is often discharged into the environment or sewage treatment plants, containing pollutants such as chemicals, heavy metals, and organic compounds, posing environmental damage and public health risks (Singh et al., 2023). The health implications of heavy metal exposure are severe, leading to stunted growth, cancer, organ damage, nervous system impairment, and, in extreme cases, death. Certain metals, like mercury and lead, can induce autoimmunity, where the immune system attacks the body's own cells, causing diseases such as rheumatoid arthritis. Moreover, heavy metal exposure has been linked to kidney, circulatory, and nervous system diseases, as well as fetal brain damage. Higher concentrations of heavy metals can harm the brain permanently (Balabanova & Gulaboski, 2015; Jomova et al., 2022). Children are particularly vulnerable as they ingest higher amounts of metals through food consumption compared to adults due to their higher food intake relative to body weight (Hussain et al., 2013; Llobet et al., 2003; Shao et al., 2017). Wastewater rules limit the kinds and amounts of heavy metals that can be present in treated wastewater in an effort to reduce the amount of dangerous substances that humans and the environment are exposed to.

2.1 Wastewater characterization and heavy metals compositions

Wastewater characterization is the process of identifying and quantifying the physical, chemical, and biological constituents of wastewater. This is an important step in the design stage, operation and optimization process of water treatment plants. Wastewater can be characterized by several parameters, including: Physical, chemical and biological parameters such as: temperature, pH, conductivity, turbidity, color, odor, chemical oxygen demand (COD), biological oxygen demand (BOD), volatile solids (VSS), Total suspended solids (TSS), nutrients (nitrogen and phosphorus), metals, organic substances, bacteria, viruses, parasites (Hiratsuka et al., 2023). The specific parameters to be analyzed depend on the nature of the wastewater and the purpose of the characterization. For example, a wastewater treatment plant designed to remove nutrients must analyze the nitrogen and phosphorus content of the wastewater (Shyue Koong Chang & Schonfeld, 1991). Characterization of wastewater can be performed using a variety of analytical methods, including conventional laboratory tests and online monitoring systems. The frequency of characterization also varies according to the needs of the water treatment plant. For example, some facilities may characterize their wastewater only once a year, while others may characterize it daily or even hourly (Mohsenpour et al., 2021). Wastewater characterization is an important tool to ensure effective and efficient operation of wastewater treatment plants. It can also help identify potential sewage problems, such as industrial waste or toxic substances (Hauduc et al., 2009).

3. Applications of wastewater treatment technology for heavy metals removal

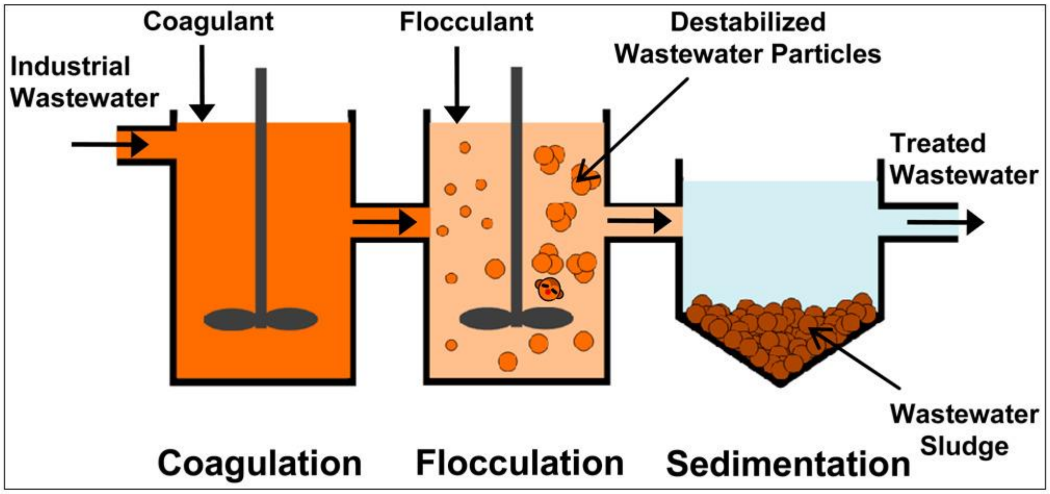
One of the most dangerous pollutants that the chemical industry releases into the environment is heavy metals. Heavy metals can be removed from inorganic effluents using conventional techniques like ion-exchange methods, which use artificial ion-exchange matrices for cation and anion, exchange-chemical precipitation, which uses precipitants like lime and limestone at basic pH conditions, and electrochemical deposition methods. (Barakat, 2011). Nevertheless, these techniques are known to demand a lot of energy and have numerous drawbacks when it comes to fully eliminating heavy metals (Azimi et al., 2017; Carolin et al., 2017). The quality of treated water can be improved more affordably and efficiently with the use of techniques including adsorption, membrane filtration, electrodialysis, and photocatalysis (Davoodbeygi et al., 2023; Manikandan et al., 2022). Many techniques can be used to successfully remove heavy metals from materials: biosorption using biological and agricultural wastes like inactive microbial biomass, orange peel, shells, hazelnut shell, pecan, maize husk or cob, etc.; modified biopolymers like chitosan, starch, chitin, and hydrogels; and industrial by-products like iron slags, hydrous titanium oxide, fly ash, and waste iron. Heavy metals can be removed from inorganic solutions using membrane filtration techniques like ultrafiltration, which use permeable membranes with pore diameters ranging from 5 to 20 nm. Reverse osmosis, which can remove 98% of copper and 99% of cadmium, polymer-supported ultrafiltration, and nanofiltration are other techniques for eliminating heavy metals (Barakat, 2011; Manna & Bhaumik, 2021). The application of ion-exchange membrane is used in the electrodialysis process to send the ionized solution through while membrane separation occurs under the influence of an electric potential (G. Chen, 2004). This separation method is effective for removing heavy metal ions such as Ni, Co, and Cd. But the photocatalysis method uses semi-conductors of titanium dioxide, which can oxidise or reduce species with the appropriate redox potential, like heavy metal ions like Cr3+, Cr4+, and Cu2+ (Barakat, 2011).

3.1 Physiochemical application

Many techniques to treat wastewater containing heavy metals have been developed recently Kurniawan et al. (2006). These techniques aim to reduce the amount of polluted water created and improve the quality of the treated effluent. While there are a number of treatment applications that may be used for the removal of heavy metals from polluted wastewater, including ion exchange, chemical precipitation, flotation, and coagulation–flocculation (Gunatilake, 2015a; Qasem et al., 2021; Renu et al., 2017), each of them has its own advantages and drawbacks in its own right. Particulate forms of metals, metal-bearing particles, or discrete particles are the main applications for physical separation techniques. Physical separation is comprised of the following processes: flotation, magnetic separation, electrostatic separation, hydrodynamic classification, gravity concentration, mechanical screening, and attrition scrubbing (Gunatilake, 2015b). Some of the soil characteristics that affect how effective physical separation is in removing metal contaminants are particle size distribution, shape, clay, humid content, moisture, heterogeneity of the soil matrix, density between the metal contaminants and soil matrix, magnetic properties, and hydrophobic qualities of the particle surface (Williford & Mark Bricka, 2000). Comprehending these soil properties is essential for formulating effective cleanup plans and choosing suitable isolation methods. The accessibility of metal pollutants to separation procedures is influenced by the particle size distribution, which is a crucial factor. Because they may have a larger surface area, smaller particles may interact with separating agents more effectively.

3.1.1 Coagulation/Flocculation

Using coagulating chemicals to clarify water has been a practice in potable water treatment since ancient times. The process of combining colloids, particles, and dissolved solids to create bigger flocs is known as coagulation. In the meantime, destabilized particles are forced to combine into bigger flocs through the process of flocculation, which will force these combined particles to settle as silt at the bottom (Alexander et al., 2012). Coagulation has been used since ancient times to cleanse wastewater, with the primary goal being the removal of colloidal contaminants and, consequently, turbidity from the water. A substance known as a coagulant is introduced to water to remove the forces stabilizing the colloidal particles and cause them to float there (Alazaiza et al., 2022). The techniques of flocculation and coagulation are frequently employed in the purification of potable water (Maćczak et al., 2022). Coagulation is a low-cost, high-efficiency technique that can be applied to wastewater pretreatment, primary treatment, and post-treatment



to eliminate organic compounds. Figure 1 shows the basic process of coagulation/flocculation treatment method.

Figure 1. Coagulation/Flocculation treatment method

Most of the suspended or solid particles in an aqueous medium are smaller and negatively charged. To accelerate the sedimentation process, the particles must thus coalesce into bigger flocs. This process is hampered by electrostatic repulsive forces, which keep negatively charged particles from adhering to the material. It takes longer to settle as a result. The particles must be destabilized with a coagulant in order to resolve this problem (Abu Amr et al., 2023). Consequently, coagulation occurs when coagulants are introduced to relatively vigorous mixing to cause natural particles and macromolecules to become unstable. Coagulation by itself is not a very helpful process; flocculation is required for successful coagulation (Mohd-Salleh et al., 2019). Water can be treated using a variety of coagulants. These coagulants may be synthetic, natural, chemical, or non-chemical (Kweinor Tetteh et al., 2017).

3.2 Chemical Coagulation

In water and wastewater treatment, chemicals are used to change the physical state of suspended and dissolved solids and make sedimentation easier. This process is known as chemical coagulation and flocculation (Alexander et al., 2012). Pretreatment of hazardous wastes, early removal of undissolved precipitating chemicals, decrease of load fluctuations, bulking activated sludge combating, phosphorus removal, and reduction of load fluctuations are all thought to be beneficial uses for chemical treatment (Shammas et al., 2021). Few research have been done to examine the use of chemical coagulation procedures, despite the fact that they may be a workable alternative for treating wastewater from many sectors (Sher et al., 2013). The two coagulants that are most frequently used are iron and alum salts. By significantly lowering the electrostatic particle surface charges in the acidic pH zone—which is the habitat of numerous hydrolyzed metal species—these coagulants encourage particle agglomeration (Santo et al., 2012). Table 1 presents a summary of different chemical coagulants for heavy metals removal from diverse wastewater sources. Alum, applied at an optimum dose of 3.0 g/L in landfill leachate, combined with continuous adsorption using eggshell waste materials, exhibited substantial removal percentages for Fe, Pb, Cu, Zn, Ni, and Cr (92%, 93%, 87%, 76%, 65%, and 60%, respectively) (Jaradat et al., 2021). Ferric chloride: polymer, at a ratio of 200 mg/L to 20 mg/L in industrial wastewater, demonstrated high removal efficiencies for Cr (97%), Fe (92%), and 0% for Zn, resulting in a sludge volume of 120 mL/L (Amuda et al., 2006). Ferric chloride, applied in industrial wastewater through Jar test methodology at various pH levels, achieved tungsten removal efficiency of 99% at pH < 6, with a residual concentration of <10 ppm (Bojic et al., 2009). Cationic polymers, employed in tannery wastewater through Jar test methodology, yielded a removal efficiency of Cr > 96% using polymers with specific molecular weight and charge density, with an optimum dose of 20% (Haydar & Aziz, 2009). A commercial tannin-based flocculant, applied in raw surface water with Cu^{2+}, Zn^{2+}, and Ni^{2+} content, achieved removal efficiencies of 90%, 75%, and 70%, respectively, at specific pH values and flocculant doses (Heredia & Martín, 2009). Chitosan/montmorillonite, used in synthetic water with CO^{2+}, Ni^{2+}, and Cu^{2+} content, in a synergic coagulation-flocculation process, demonstrated high cation removal yields at pH 6.8 and concentrations of 20–100 ppm for CO^{2+}, Ni^{2+}, and Cu 2% (Assaad et al., 2007). These studies highlight the effectiveness of chemical coagulants in heavy metals removal across various industrial wastewater scenarios, showcasing the importance of experimental conditions in optimizing removal efficiency.

Table 1. Summary of the different chemical coagulants for heavy metals removal from different wastewater.

Coagulants	Wastewater	Experimental Conditions	Removal (%)	Reference
Alum	Landfill leachate	3.0 g/L; adsorbent 25.5 g. HLR = 6.37 L/m2· min.	Fe 92%, Pb 93%, Cu, 87%, Zn 76%, Ni 65%, Cr 60%,	(Jaradat et al., 2021)
Ferric chloride	Industrial wastewater	Ferric chloride: 200 mg/L	Cr 97%, Fe 92%, Zn 0%,	(Amuda et al., 2006)
Ferric chloride	Industrial wastewater	321 ppm, Fe/W ratio 4, pH 4 - 10.	Tungsten 99%,	(Bojic et al., 2009)
Cationic polymers	Tannery wastewater	Four Cationic polymers with 20 mg/L Concentration	Cr > 96%	(Haydar & Aziz, 2009)
Modified tannin	Raw surface water.	pH 6, 7, and 8, at 150 rpm	Cu 90%, Zn 5%, Ni 70%,	(Heredia & Martín, 2009)
Chitosan/montmorillonite	Synthetic wastewater	Chitosan: weight ratio = 5%, pH 6.8, 20–100 ppm of Co$^{2+,}$ Ni^{2+}, and Cu^{2+}.	Removal capacity for Co= 76.3 mg/g, Ni= 89.3 mg/g, Cu=112.4 g/g.	(Assaad et al., 2007)

3.1.2 Natural coagulations

Interest in employing green technology for wastewater treatment has increased as health hazards and environmental issues have received more attention (Nath et al., 2019). In wastewater treatment, natural coagulants offer a competitive alternative to chemical coagulants (M. et al., 2018). Natural coagulants create ecologically benign sludge and are plentiful, readily accessible, renewable, and less sensitive to the pH of the water. Natural coagulants are composed of proteins, polysaccharides, and polyphenols based on their functional groups. Ionic or non-ionic substances can be these active ingredients (Kristianto, 2021). It is possible to extract the active ingredients in natural coagulants from bacteria, plants, and animals. Table 2 summarizes the effectiveness of different natural coagulants for heavy metals removal from various wastewater sources. Modified tannin, applied at 1% concentration in landfill leachate, demonstrated significant removal percentages: COD (42.86%), color (54.38%), NH3–N (39.39%), and TSS (60.33%) (Ayash et al., 2022). Pinecone powder, applied at 7 g/L in steel industrial wastewater, showed notable removal percentages for COD (83.3%), TSS (99%), NH3–N (83.9%), Mn (86.8%), Fe (93.7%), Zn (89.7%), Al (73.7%), and Ni (86.7%) (Abujazar et al., 2022). Rosehip seeds powder and olive seeds powder, both applied at 1 g/L in steel industrial wastewater, exhibited removal percentages for various heavy metals (Mn, Fe, Zn, Al, Ni), with Rosehip seeds achieving 100% removal for Ni (Abujazar et al., 2022; Karaağaç et al., 2022). Date stone powder, applied at 1 g/L in steel industrial wastewater, demonstrated removal percentages for Fe (61%), Mn (63%), Al (93%), Cu (51%), and Ni (86%) (Abu Amr et al., 2022). Pistacia soft shell, applied at 2.5 g/L in pulp and paper wastewater, showed removal percentages for Cu (70%) and Pb (74%) (Nazari et al., 2023). Grape seed powder, applied at 1.2 g/L in synthetic wastewater, exhibited high removal efficiency for Cr (99.7%) (El Gaayda et al., 2023). These studies highlight the potential of natural coagulants in heavy metals removal from diverse industrial wastewater streams. The experimental conditions varied, including coagulant dosage, pH levels, mixing speeds, and settling times. The results demonstrate the effectiveness of natural coagulants in reducing heavy metal concentrations in wastewater, offering a sustainable and environmentally friendly alternative for wastewater treatment.

Table 2: Summary of the different natural coagulants for heavy metals removal from different wastewater.

Coagulants	Wastewater	Experimental Conditions	Removal (%)	Reference
Modified tannin	Landfill leachate	of 6 mL modified tannin (1%), pH (9) and 100 rpm	COD 42.86%, Color 54.38%, NH_3–N 39.39% and TSS 60.33%	Ayash et al., (2022)
Pinecones powder	Steel Industrial wastewater	Coagulant Dosage 7 g/L, pH (8), 200 rpm at 15 min, 90 rpm at 30 min, settling 60 min, Sample Volume 200 mL.	COD 83.3%, TSS 99%, NH3–N 83.9%, Mn 86.8%, Fe 93.7%, Zn 89.7%, Al 73.7% and Ni, 86.7%	Abujazar et al., (2022)

Rosehip seeds powder	Steel Industrial wastewater	Coagulant Dosage 1 g/L, pH (8), 200 rpm at 15 min, 90 rpm at 30 min, settling 60 min, Sample Volume 200 mL.	Mn 86%, Fe 91.7%, Zn 90.6%, Al 73.7%, Ni 100%,	Abujazar et al., (2022)
Olive seeds powder	Steel Industrial wastewater	Coagulant Dosage 1 g/L, pH (8), 200 rpm at 15 min, 90 rpm at 30 min, settling 60 min, Sample Volume 200 mL.	Mn 80.9%, Fe 91.7%, Zn 92.6%, Al 73.7%, Ni 84.3%	Karaağaç et al., (2022)
Date stone powder	Steel Industrial wastewater	Coagulant Dosage 1 g/L, pH (8), 200 rpm at 15 min, 90 rpm at 30 min, settling 60 min, Sample Volume 200 mL.	Fe 61%, Mn 63%, Al 93%, Cu 51%, Ni 86%,	Abu Amr et al., (2022)
Pistacia soft shell	Pulp and paper wastewater	2.5g/L, 200 rpm for 5 min for flocculation mixing, 60 min settle	Cu 70%, Pb 74%	Nazari et al., (2023)
Grape seed powder	synthetic wastewater	1.2/L, pH (3-12), 200 rpm for 15 min for flocculation mixing, 3.5 H settle	Cr 99.7%	El Gaayda et al., (2023)

3.1.3 Hybrid coagulations

Recently, hybrid coagulants have drawn interest in wastewater and water treatment technologies primarily because of their outstanding performance and affordability. This procedure highlights the increasingly complex and modern presentations of hybrid coagulants in wastewater treatment. The materials used for hybrid coagulants, such as those hybridized in chemical bonds, structurally and functionally hybridized under specific combination techniques (e.g., organic/inorganic, organic/inorganic, inorganic/inorganic, organic/natural polymer, inorganic/natural polymer, organic/biopolymer, and etc.), were evaluated and compared using applications on various wastewater types, experimental conditions, and treatment efficiency. The inorganic/inorganic hybrid coagulation technique demonstrated the removal of heavy metals (99.2%), COD 73.3%; turbidity 98.5%, and colour 98% and seemed to be more successful than organic removal. The best operating circumstances for both organic and inorganic coagulants at different pH ranges (6 -12) reduced the expense of chemicals needed to regulate pH while treating industrial wastewater. Hybrid coagulation applications are successful in treating highly concentrated industrial wastewater, particularly oily wastewater, according to the evaluation results (Lee et al., 2017; Zhao et al., 2021). Hybrid materials have been utilised to enhance the coagulation–flocculation process in wastewater treatment. The use of hybrid coagulants with different property assemblages (inorganic-inorganic, organic-natural, and inorganic-organic) of hybrid material(s) for the treatment of contaminated water has been extensively researched and developed in recent years.

These methods have been successful in eliminating a number of dangerous compounds, including as turbidity, colour, and COD, in addition to lead (Pb), arsenic (As), chromium (Cr), zinc (Zn), nickel, copper (Cu), and cadmium (Cd) (Lee et al., 2017). There are different hybrid materials are used for waste water treatment where each other them Due to their biodegradability, low toxicity, renewability, flexibility, and lack of residual sludge formation, hybrid materials are environmentally beneficial. Additionally, hybrid materials require less storage space than traditional inorganic coagulants. The success of this treatment is greatly influenced by different factors, such as temperature, coagulant type and dosage, effluent pH, mixing speed, and time. Therefore, it is strongly advised to optimize these parameters in order to improve the effectiveness of coagulation therapy. Although a wide range of pH and material dosage flexibility has been shown by hybrid coagulants, suggesting that it is less expensive to adjust the two coagulation-flocculation process parameters in order to increase treatment efficiency, the effects of changing mixing times, speeds, and temperatures on the performance of hybrid materials are still not fully understood (Abujazar et al., 2022). Liu et al., (2023) utilized Versatile hybrid coagulant (VHC) for removing 9 different heavy metals from synthetic wastewater. The author reported full removal of all 9 heavy metals under the experimental conditions.

3.2 Adsorptions

The process known as adsorption refers to the molecular form of a material depositing at a greater concentration on a surface. It is dependent upon the presence of an adsorbent layer that has the ability to host a micro-substance on its surface and has a certain surface structure (L. Fu et al., 2021). The capacity of adsorption to remove even lower quantities of heavy metals, together with its cheap energy consumption and readily available raw materials, makes it a deemed effective technology. Physisorption and chemisorption are the two main forms of adsorption. During the physisorption process, Van der Waals forces hold the absorbent and absorbate together, but during the chemisorption phase, chemical bonds are established (Fiyadh et al., 2019). When it comes to influencing the effectiveness of heavy metal deposition on a particular adsorbent medium, the three most important properties are the ion exchange capacity, contact area, and functional groups on the surface. The adsorption capacity increases with surface area, particle size decreases, and the number of surface functional groups that are accessible (Maftouh et al., 2022, Xie et al., 2017). Adsorption is a productive, reversible process that works effectively even with adsorbate solutions that are diluted. When the sportive component's outermost surface has narrow pores instead of globular pores, the adsorption effectiveness is higher. Particles that have adsorbed onto the surface are specific in their structure and concentration. Temperature, the kind of adsorbent and adsorbate surface, the presence of extra pollutants, ambient and experimental circumstances (pH, pollutant concentrations, contact time, and adsorbent particle size are all important considerations) are a few variables that affect adsorption. Furthermore, pre-filtration could occasionally be necessary because the presence of suspended particles, oils, and greases reduces the efficacy of this approach (Pandey, 2021). Many traditional techniques, including as layer detachment, particle trading, ultrafiltration, filtration, sedimentation, electrodialysis, photocatalysis, flocculation/coagulation, and adsorption, are used to reduce pollution and remove heavy metals from industrial wastewater (Meepho et al., 2018). However, these techniques often involve complex operations, high costs, and increased energy consumption. Among them, adsorption emerges as the most effective strategy, noted for its significant potential in heavy metal removal (Siddeeg, 2020). Novel adsorption techniques are acknowledged for their economical viability and operational effectiveness (Tahoon et al., 2020). Adsorbents such as biomass, natural inorganic materials (clay minerals, metal phosphates, zeolites), and activated carbon are commonly utilized. Activated carbon, despite being well-recognized, poses challenges due to processing costs, leading to a search for alternative low-cost adsorbents with high adsorption capacities (S. Srivastava et al., 2015; Tahoon et al., 2020). Bio-adsorbents, derived from waste biomaterials, are considered for heavy metal removal when they exhibit strong adsorption capacity at a low preparation cost. High surface area and porosity are crucial characteristics of effective adsorbents (Abioye et al., 2018). Nanosized absorbent materials, engineered from minerals or organic matters, show promise in adsorbing pollutants from wastewater (Yong-Qian Fu, 2012). Improved nanomaterials are intended to totally scavenge heavy metal pollution. (J. Wang et al., 2018). The synthesis of optimal adsorbent nanomaterials for heavy metal adsorption requires consideration of various attributes (Yurekli, 2016). Surface modification of nanoparticles is essential to enhance their adsorption efficiency, as reflected in high adsorption capacity values (Pham et al., 2019). Additionally, the formation of M-O-M bonds involving iron, alumina, and silicon in polymeric chains contributes to their utility as adsorbents.

3.3 Chemical oxidation

Reaction mechanisms alter the structure and chemical characteristics of organic molecules during chemical oxidation processes. Smaller pieces of molecules break apart; these fragments include a larger percentage of oxygen and take the form of carboxylic acids, alcohols and etc. Oxidizing organic molecules, such ozone or OH radicals, frequently form new oxidized compounds, which are usually more biodegradable than the original ones. This general idea is the outcome of the various chemical oxidation processes. It has been found that oxidation with ozone or hydrogen peroxide is a substantial replacement for chlorination because it does not produce dangerous chlorinated organic compounds (Mota et al., 2009). Large amounts of highly mobile heavy metal complexes, which are more constant and stubborn than free heavy metal ions, can be found in wastewater from modern industry. With increased focus on their removal from wastewater, a amount of technologies have been industrialized, the most promising of which are advanced oxidation processes, or AOPs (Du et al., 2020). The degradation of organic matter is mostly caused by powerful oxidizing hydroxyl radicals, and the AOP is frequently utilized for sample preparation. By deducting inorganic mercury from the overall amount of mercury, speciation analysis of mercury may be accomplished. This procedure can also be applied to the breakdown of organomercurials (Yin et al., 2012). This hybrid system employs carbon-coated graphite paper as the cathode to remove heavy metals and a titanium plate shielded by RuO2-IrO2 as the anode for breaking down organic molecules. Cycling tests have confirmed the robust stability and effective pollutant removal of the CDI-EO system. This efficiency extended to the treatment of actual textile wastewater obtained from an industrial park. Impressively, the energy consumption of the CDI-EO system in treating textile wastewater stood at 4.66 kWh/m3, a significantly lower figure when compared to other advanced oxidation processes (Brillas & Martínez-Huitle, 2015; W. Chen et al., 2023). The electrochemical advanced oxidation process as known EAOP, used for generating potent oxidants such as hydroxyl radicals and active chlorine species in situ, emerges as a promising technique for organic material degradation. Key benefits of EAOP include high removal efficiency, user-friendliness, and consistent performance (Paździor et al., 2019). In general, EAOP uses an anode-functional arrangement to directly and indirectly degrade organic pollutants utilising metal anodes, dimensionally stable anodes (DSAs), or boron-doped diamond electrodes (BDD). Using platinum or titanium plates, the cathode functions as a counter electrode and makes minimal contribution to the elimination of pollutants (Brillas & Martínez-Huitle, 2015).

Reduced Graphene Oxide (rGO) can function as a co-catalyst with N–TiO2 to improve the photocatalytic oxidation–reduction reaction capacity under visible and UV sunlight. The creation of N-TiO2/rGO as a photocatalist to extract MB and Cr (VI) from wastewater is the main goal of this study. There has never been an application of the studied N-TiO2/rGO composite for the simultaneous removal of Cr and MB. It is anticipated that the N–TiO2/rGO will exhibit a broader spectrum of light absorption, increasing the photocatalytic activity for the removal of MB and Cr(VI) in wastewater under UV and visible light (Utami et al., 2023).

3.4 Ion exchange

A traditional technique for eliminating heavy metals from industrial wastewater involves employing an ion exchanger, a solid material capable of exchanging anions and cations. Over the past two decades, various studies have investigated the performance of different ion exchange resins. One significant advantage of this method is its capability to manage relatively large volumes while effectively removing heavy metals at parts per billion (PPB) levels. Notably, this method is efficient for eliminating both anions and cations from wastewater. For instance, Rengaraj et al. (2001) evaluated the efficacy of cation exchange resins, specifically IRN77 and SKN1, in removing chromium from synthetic coolant water. The study considered factors like initial resin dosage, agitation time, and pH. The results indicated that these resins could remove up to 98% of chromium from a solution containing 100 mg/L, with an optimal pH of 3.5 and varying agitation times for SKN1 and IRN77. Another investigation by Al-Enezi et al. (2004) demonstrated a nearly 99.9% removal efficiency for cadmium, copper, and mercury from waste sludge. This was achieved by utilizing commercially available magnetic ion exchange resin with a capacity of 4.5 meq/g and particle size ranging from 100-300 μm. In a study focused on removing Cr (III) from industrial effluents, Cavaco et al. (2007) assessed the temperature dependency of two chelating exchange resins: Diaion CR11 and Amberlite IRC86. The capacities of these resins were 1.21 and 2.77 meq Na+/g resin, respectively. Additionally, Shi et al. (2009) explored the adsorption capabilities of three fundamental anion exchange resins, namely D301, D314, and D354, for Cr(VI) ions in an aqueous solution. The study revealed that these resins removed over 99.4% of Cr6+ ions in the pH range of 1-4. Furthermore, Alyüz and Veli (2009) investigated the influence of changing experimental conditions on the adsorption capacities of D301, D314, and D354 resins, finding that at 60°C, the adsorption capacities of D301 and D314 resins surpassed those at normal temperature.

4. Limitations and challenges

The performance of several treatment methods for removing very low concentration of heavy metals need to be focused more in future work. Because chemical-based separations are easy to use and inexpensive, they have been extensively employed in the removal of heavy metals. Nevertheless, chemicals are employed to enhance ion accumulation and modify pH levels. A significant amount of sludge is produced, which needs more processing. The electrochemical method has the advantages of being rapid, well-controlled, simpler to remove sludge from, and using less chemicals. The primary drawbacks of this technology are its high energy consumption, poor throughput, and expensive anodes and cathodes. Combining several electrochemical treatment methods driven by renewable energy sources may be helpful to relieve this bottleneck. Aerated EC and electrochemical oxidation are the best technologies to combine with other methods since they have the ability to remove both organic and inorganic contaminants from wastewater. Through flotation, little sludge is produced. As such, this method is well suited for inclusion in the development of an economical and efficient electrochemical treatment system. Comparable to adsorption methods, the ion exchange approach raises questions about stability and reusability that may require more research. The photocatalyst approach provides an easy-to-use solution that produces no sludge and requires little to no chemicals. It is dependent on pH, has a limited throughput, is currently under study, and is ineffective when there are many metals present. Table 3 provides a summary of advantages and limitations for different treatment applications in heavy metal removal. For coagulation/flocculation; the method offers a quick, inexpensive, and straightforward process with easily accessible coagulating agents. However, it produces waste, exhibits low efficiency in removal, and requires additional processes like sedimentation and filtration (Segura et al., 2015). Natural coagulants are considered safer, less expensive, environmentally friendly, and more effective at treating high-turbidity water compared to chemical coagulants. Nevertheless, they may increase microbial activity, and the treated water's color, taste, and odor may change due to residual organic matter, necessitating the use of disinfectants like chlorine (Abujazar M.S.S. et al., 2022). While, hybrid materials in coagulation are environmentally beneficial due to their low toxicity, reduced sludge production, renewability, adaptability, and biodegradability. They are more unchanging in storage than conventional inorganic coagulants. However, the success of this treatment is influenced by factors such as temperature, coagulant type and dosage, effluent pH, mixing speed, and mixing duration (Abujazar et al., 2022). The adsorption method offers a wide range of adsorbents with excellent capacity at a low cost. However, it faces challenges in the difficult regeneration of adsorbents and sludge production, and different adsorbents have varying capacities for different types of contaminants (Jeevanantham et al., 2019). Ion exchange is characterized by high metal recovery, reduced sludge volume, and limited pH tolerance. However, it is a costly method with high maintenance requirements (Bhatnagar et al., 2015). In summary, each method has its benefits and limitations, and the choice of a suitable method depends on specific treatment goals and operational considerations.

Table 3: Summary of the advantages and limitations for different treatment applications

Method	Benefits	Limitations	Reference
Coagulation/ Flocculation	Offers swift processing, cost-effectiveness, and simplicity, with readily available coagulating agents.	Method has drawbacks, including the generation of waste, suboptimal contaminant removal efficiency, and the need for additional processes like sedimentation and filtration.	(Segura et al., 2015)
Natural coagulations	Compared to chemical coagulants, they are less costly, safer, greener, and more efficient in treating high-turbidity water.	May boost microbial activity and result in residual organic matter changing the treated water's colour, flavour, and scent; as a result, a disinfectant like chlorine needs to be used.	(Abujazar M.S.S. et al., 2022)
Hybrid coagulations	Because of their low toxicity, residual sludge production, renewability, adaptability, and biodegradability, hybrid materials are environmentally beneficial. Hybrid materials are more stable than traditional inorganic coagulants in terms of storage needs.	The effectiveness of the treatment is greatly influenced by operating factors like as temperature, coagulant type and dosage, effluent pH, mixing speed, and mixing time.	(Abujazar et al., 2022)
Adsorption	Offers a diverse selection of adsorbents, remarkable adsorption capacity, and a	Challenges in regenerating adsorbents and handling sludge, as well as variations in	(Jeevanantham et al., 2019)

	straightforward, cost-effective approach.	adsorption capacity among different types of adsorbents.	
Ion exchange	Offers benefits including limited pH tolerance, less sludge volume, and effective metal recovery.	High cost due to regular maintenance requirements	(Bhatnagar et al., 2015)

5. Conclusion

In conclusion, the generation of industrial wastewater poses a significant threat to both the environment and human health due to the presence of various pollutants, particularly heavy metals. These pollutants can lead to severe health issues, such as stunted growth, organ damage, and even death. Children are particularly vulnerable, as they tend to consume more food per body weight than adults. To address this environmental and public health concern, stringent wastewater regulations have been established to limit the types and concentrations of heavy metals in treated wastewater. Wastewater characterization is crucial for effective water treatment plant operation, involving the identification and quantification of physical, chemical, and biological constituents. Various treatment technologies are employed for heavy metal removal, such as adsorption, membrane filtration, electrodialysis, and photocatalysis. Adsorption, utilizing materials like zeolites, iron slags, and biosorption, has proven effective and affordable. Additionally, advanced oxidation processes and ion exchange methods are employed, each with its own set of advantages and challenges. However, these methods face limitations such as high energy consumption, the generation of sludge, and issues related to stability and reusability. . The AOP shows a high efficiency in heavy metals removal with 98% of copper and 99% of cadmium. Adsorption technologies, such as activated carbon and zeolites, demonstrate high metal recovery rates of up to 95%. Ion exchange processes effectively remove heavy metals like mercury and arsenic, achieving removal efficiencies exceeding 99%

Integration of different treatment techniques and ongoing research to improve the efficiency of these methods are essential to address these limitations. In the quest for sustainable industrial practices, the development and implementation of innovative, cost-effective, and environmentally friendly wastewater treatment technologies remain imperative.

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