



REMOVAL OF HEAVY METALS FROM WASTEWATER THROUGH ADSORPTION: A REVIEW

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1. Abstract

Heavy metal contamination in wastewater is a significant environmental concern due to its adverse effects on public health and the ecosystem. There are various methods for removing heavy metals such as adsorption, coagulation, chemical precipitation, photocatalytic-based treatments and many others. Adsorption has emerged as an effective technique for removing heavy metals from wastewater due to its simplicity, cost-effectiveness, and high efficiency. This method involves the use of various adsorbents, such as activated carbon, zeolites, and clay minerals, which selectively remove heavy metals from the wastewater by physical or chemical interactions. The adsorption process can be influenced by various factors, including temperature, initial metal concentration, pH and contact time. Optimizing these factors can improve the adsorption efficiency. Additionally, factors such as the adsorbent dose, stirring speed, and particle size also play a crucial role in the effectiveness of adsorption.

Overall, adsorption is a sustainable technique for heavy metal removal from wastewater. Further research and development of advanced adsorbents and optimization of the adsorption process are necessary to enhance the efficiency of heavy metal removal and minimize environmental and health risks associated with heavy metal pollution.

Keywords: Heavy Metals, wastewater, adsorption, contamination

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2. INTRODUCTION

Our environment is getting worse every single day, with the biggest cities approaching saturation point and unable to cope with the increasing pressure on their infrastructure. The most common environmental contaminants include sewage, agriculture wastes, and industrial effluents. The majority of industries release wastewater and harmful effluents into rivers before adequate treatment. The most significant problem in India is environmental pollution, specifically from heavy metals and minerals in wastewater.[1]

With a rise of production and human activities, such as plating and electroplating, mining, batteries, pesticides, rayon manufacturing, tanning, metal rinse processes, metal smelting, fluidized bed bioreactors, production of textiles, petroleum products, paper making, and the electrolysis process, there has been a rise in the level of heavy metals in wastewater. Wastewater that has been contaminated with heavy metals makes a way into the environment, harming both human health and

the ecosystem. Since the heavy metals are not biodegradable and can lead to cancer, their inappropriate concentration in water causes a serious risk to the health of all living things.[2]

3. HEAVY METALS

Metallic elements with a relative high density compared to water are commonly referred to as heavy metals. Assuming the weight and toxicity, heavy metals involve metalloids such as arsenic, that can cause toxicity at low exposure levels. The contamination of the environment by these metals has lately been associated with increasing ecological and worldwide public health problems. Furthermore, due to increase in their use in many industrial, agricultural, household, and technical applications, human exposure has increased greatly. According to reports, geogenic, agricultural, industrial, pharmaceutical, household effluents, and atmospheric sources include all sources of heavy metals in the environment.[3]

| HEAVY METALS | SOURCES | EFFECTS |
|----------------------|----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|
| Lead (Pb) | Lead-based paints, batteries, fossil fuels, water pipes, traditional medicines and some cosmetics. | Brain damage, anaemia, kidney damage, coma, convulsions, reproductive problems and plumbism. |
| Mercury (Hg) | Laboratory apparatus, industrial instruments, electrical appliances and refineries. | Skin rashes, respiratory problems, neurological disorders, insomnia and developmental delays in children. |
| Arsenic (As) | Glass production, some pesticides, mining, ore smelting, fish and shellfish. | Skin lesions, cancer, cardiovascular disease, peripheral neuropathy. |
| Cadmium (Cd) | Cigarette smoke, plastic industries, steel industry and corroded galvanized pipes. | Osteoporosis, lung cancer, and flu-like (chills, fever and muscle pain) |
| Chromium (Cr) | Industrial pollution, electroplating, tanneries, and alloys. | Irritation in nose, throat and lungs, damages mucous membranes of nasal passages and ulcers. |
| Copper (Cu) | Electrical equipment, corroded plumbing systems, some seafood and drinking water. | Nausea, vomiting, liver failure, Wilson's disease and Parkinson's disease. |
| Nickel (Ni) | Nickel alloy production, stainless steel, catalysts and rechargeable batteries. | Gastrointestinal distress, diarrhoea, shortness of breath and pulmonary fibrosis. |
| Zinc (Zn) | Alloys, brass coating, aerosol deodorants, paints, mining and steel processing. | Vomiting, abdominal pain, lower immunity, nausea, dizziness, lethargy and anaemia. |

4. EFFECT OF HEAVY METALS ON THE ENVIRONMENT

1. ANTIMONY: Since antimony is a metalloid, it possesses both metallic and non-metallic characteristics. Due to its special qualities, like its capacity to raise the hardness and strength of alloys, it is frequently used in a variety of industries.[4]

However, long-term exposure to high antimony levels, particularly at the workplace, can cause a number of health issues. High amounts of antimony can short-term expose people to gastrointestinal issues such as nausea, vomiting, and diarrhoea. Antimony exposure over an extended period of time may lead to lung and heart issues as well as possible human cancer.[5]

Despite these worries, the majority of antimony compounds do not bioaccumulate in aquatic life, meaning they do not gradually accumulate in the tissues of fish or other aquatic species. However, if present in sufficient proportions, antimony can still be dangerous to aquatic life.[6]

When working with antimony or compounds containing antimony, it's crucial to take the essential safety precautions, which include using the proper personal protective equipment and keeping correct handling and disposal procedures. [4,6]

2. CADMIUM: Heavy metal cadmium is hazardous and may affect people's health, especially if exposure is prolonged or occurs at high levels. Due to its chemical resemblance to

zinc, it an important micronutrient for numerous biological processes in plants, animals, and people, it is hazardous. [8]

Cadmium, once consumed by an organism, may remain for many years and gradually build up in the body. Osteocalcin and osteoporosis in both people and animals have been caused by long-term cadmium exposure. It has also been associated to renal failure, obstructive lung illness, and bone abnormalities. Although there is little evidence that it exerts these effects in people, it has also been linked to elevated blood pressure and effects on the heart in animals.[7]

Cadmium can be ingested by people from a variety of sources, including cigarette smoke, water, and air. The average daily consumption of cadmium from air and water is estimated to be 0.15µg and 1µg respectively. Although amounts may differ greatly, smoking a packet of 20 cigarettes can result in the inhalation of 2-4 g of cadmium. [9]

To reduce potential health concerns, cadmium exposure must be kept to a minimum. Avoiding smoking and limiting exposure to cadmium-containing environments, such as polluted water or air, can help with this. Additionally, it's critical to be knowledgeable about the possible dangers of cadmium exposure and to get medical help right away if any symptoms or health issues start to appear. [10]

3. CHROMIUM: Chromium is a heavy metal that is frequently utilised by variety of industries due to its advantageous qualities, including corrosion, resistance and hardness. It is also known that it causes serious health dangers to both people and the environment. [11]

Chromium exposure at low levels can irritate the skin and lead to ulceration. Long-term exposure to higher chromium concentrations can cause more serious health issues such lung cancer, kidney and liver damage, as well as harm to the circulatory and nervous systems. Additionally, because chromium may build up in aquatic life, eating fish that has been exposed to high quantities of the metal might be harmful. [12]

To avoid contaminating the environment, managing chromium safely and disposing of it properly are imperative, while working with metal, safety gear which include gloves, masks, and goggles should be worn, and the work area should have adequate ventilation. In order to stop the release of chromium into the environment, specific steps must be followed for storage, transportation, and disposal. [13]

4. COPPER: In order for numerous enzymes and biological processes in the human body to function, copper, an essential trace element, is required. However, excessive copper exposure can lead to health issues like anaemia, kidney and liver damage, as well as gastrointestinal irritation. [14]

A rare genetic disease called Wilson's disease affects the body's capacity to control copper levels. Wilson's disease patients are more likely to develop copper intoxication because their bodies are unable to adequately eliminate excessive copper. [15]

Due to corrosion of copper pipes and additives used to reduce algae development in water systems, copper can be discovered in drinking water. It is advised to use copper-free water pipes and filters that are made to remove copper from drinking water in order to reduce exposure to copper. [16]

5. LEAD: Depending on the degree and length of exposure, lead can have a variety of biological consequences on people. Infants and growing foetuses are more sensitive than adults. Lead exposure at high levels can have hazardous biochemical effects on the kidneys, gastrointestinal tract, joints, and reproductive system as well as the synthesis of haemoglobin. The nervous system may suffer short-term or long-term harm as a result. [17] Severe lead poisoning creates obvious sickness, is rare now. However, there is strong evidence that lead might have minor, subtle, subclinical effects at intermediate doses, particularly on children's cognitive development. According to some research, young children who have blood lead levels that increase from 10 to 20 g/dl may lose up to 2 IQ points. To avoid long-term negative effects, it is crucial to restrict lead exposure, particularly in youngsters. [18]

The average daily lead intake for an adult in the UK is calculated to be 1.6µg from air, 20µg from drinking water, and 28µg from food. Despite the fact that most individuals acquire the majority of their lead intake from food, some populations may also be exposed to considerable amounts of lead through sources including lead pipes and plumbosolvent water, polluted air close to emission sources, dust, dirt, and paint flaking from old houses, and contaminated land. [19]

The contamination of crops and soil by lead in the air can increase the amount of the metal in food. The World Health Organisation and the UN Food and Agriculture Organisation have set a preliminary weekly intake for lead exposure that is substantially below the levels experienced by the majority of people in the UK. [20]

6. MERCURY: Mercury is a hazardous chemical that, when inhaled or ingested in large quantities,

can result in major health issues. In addition to tremors, gingivitis, and psychological abnormalities, inorganic mercury toxicity can result in spontaneous abortion and birth defects. [21]

In aquatic environment, inorganic mercury is transformed by microorganisms to monomethylmercury, which is significantly more poisonous and can harm the brain and central nervous system. This kind of mercury exposure during pregnancy can also lead to miscarriage, congenital defects, and alterations in young children's development. [22]

Precautions must be taken to prevent mercury exposure, such as avoiding eating large quantities of fish that may contain high levels of mercury and properly disposing mercury-containing devices like batteries and fluorescent light bulbs. [23]

7. NICKEL: Nickel is a crucial trace element that the body needs in tiny amounts to produce red blood cells. However, nickel in excess can be somewhat poisonous and can result in a number of health issues, including decreased body weight, liver and heart damage, and skin irritation. [24]

Long-term exposure to nickel can be harmful to health, although short-term overexposure is not known to have any negative impacts on health. Therefore, it's important to avoid exposing yourself to too much nickel. [25]

Additionally, Nickel levels in drinking water are not currently regulated by the Environmental Protection Agency (EPA). The acceptable limits of nickel in drinking water may be governed by specific laws in some states or nations. [26]

It is essential to be aware of the potential health hazards linked to nickel exposure and to take the appropriate steps to prevent overexposure to this metal. [25,26]

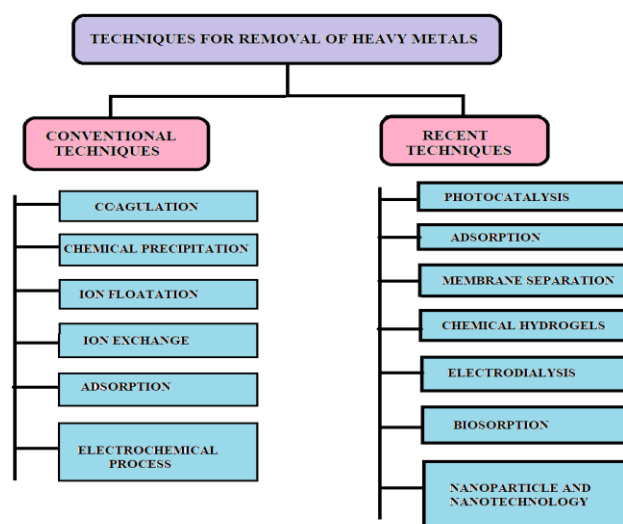
8. VANADIUM: Vanadium (V) is a transition metal that can exist in multiple oxidation states and is commonly found in the environment. Vanadium is a necessary nutrient in modest amounts, but large doses can be hazardous to both people and animals. [27]

Vanadium's toxicity is affected by a number of variables, including its form, oxidation state, route of exposure, duration, and frequency of exposure. Vanadium compounds, such as vanadium pentoxide, are considered to be the most dangerous when inhaled. [28]

High vanadium exposure can cause respiratory conditions such bronchitis, pneumonitis, and asthma. Additionally, it may result in gastrointestinal issues like nausea, vomiting, and diarrhoea. Vanadium exposure over an extended period of time may harm the kidneys and liver. [29] Additionally, exposure to vanadium has been associated to neurological effects like memory loss and reduced cognitive function, as well as reproductive and developmental damage. [30]

5. REMOVAL OF HEAVY METALS FROM WASTE WATER:

The removal of heavy metals from wastewater is an important process to prevent environmental contamination and ensure the safety of public health. Heavy metals such as lead, arsenic, cadmium, and mercury can accumulate in water sources, causing long-term damage to the ecosystem and potentially causing health problems for humans and animals. The two techniques for removing heavy metals from wastewater are conventional technique and recent techniques. It includes chemical precipitation, ion exchange, adsorption, and membrane filtration. [31]



5.1 CONVENTIONAL TECHNOLOGIES FOR HEAVY METALS REMOVAL FROM WASTEWATER

The physical and chemical conventional methods that have been used for considerable amounts of heavy metal removal involve coagulation/flocculation, chemical precipitation, ion floatation, ion exchange, adsorption and electrochemical process.

1. COAGULATION and FLOCCULATION

Coagulation as well as flocculation are important steps in the wastewater treatment process that led to the production of drinking water. When a coagulant or chemical is used in wastewater and a chemical reaction takes place, coagulation is the result. Colloidal materials combine to produce flocs or tiny aggregates in an aqueous solution. These tiny aggregates, or flocs, attract suspended substances like metals. [32]

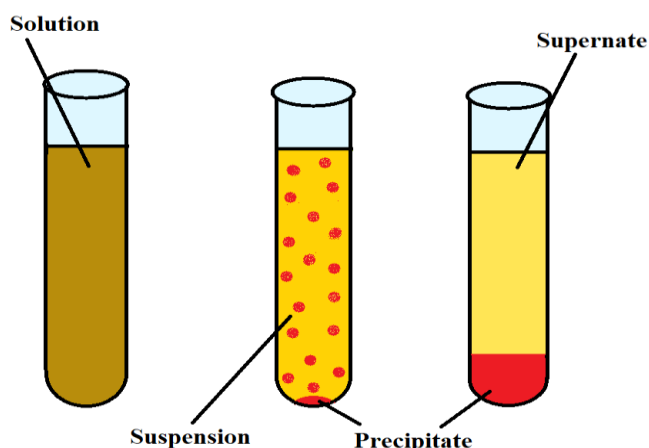
The formation of tiny flocs that grow in size and settle inside the solution may be promoted by the slow mixing of water. We call this process

flocculation. With these techniques, mostly organic pollutants are eliminated. [33]

2. CHEMICAL PRECIPITATION

The most popular technique for eliminating dissolved (ionic) metals from wastewaters containing hazardous metals, is chemical precipitation. The interaction between the soluble metal compounds and the precipitating agent transforms the ionic metals into an insoluble form (particle). By settling and/or filtration, the particles produced by this reaction are taken out of the solution. Neutralisation, precipitation, coagulation/flocculation, solids/liquid separation, and dewatering are typical unit activities needed in this technique.[34]

The type and concentration of ionic metals in solution, the precipitant used, the reaction conditions (especially the solution's pH), and the presence of other component that may block the precipitation reaction are actually all factors that affect how well a chemical precipitation process works. [35]



3. ION FLOATATION

Among the most widely used methods for removing metal from industrial effluent is ion floatation. Metal removal from wastewater has been reported on at various industrial and lab scales with varying efficiency. Biodegradable surfactant was used as a collector to remove 90% of the Fe (III) and Mn (II) from the floatation column. When compared to column floatation, the employment of bio-surfactants with dissolved air floatation systems is a more promising substitute to a synthetic surfactant. [36]

4. ION EXCHANGE

Ion exchangers are a well-known traditional technology for removing heavy metals from

industrial effluent using a solid that can exchange cations and anions. Performance analyses of various ion exchange resins have been conducted over the past 20 years.

The main benefit of employing this technology is that it can manage the relatively large volume while removing the parts per billion (PPB) levels. Another significant benefit is that this method can be used to remove either cations or anions. [37]

5. ADSORPTION

Adsorption is a surface phenomenon, is the attachment of a specific compound to the surface of a solid by chemical or physical forces. An adsorbate is a substance (pollutant) that binds to a solid surface, while an adsorbent is the solid surface itself. In heavy metals adsorption, there are

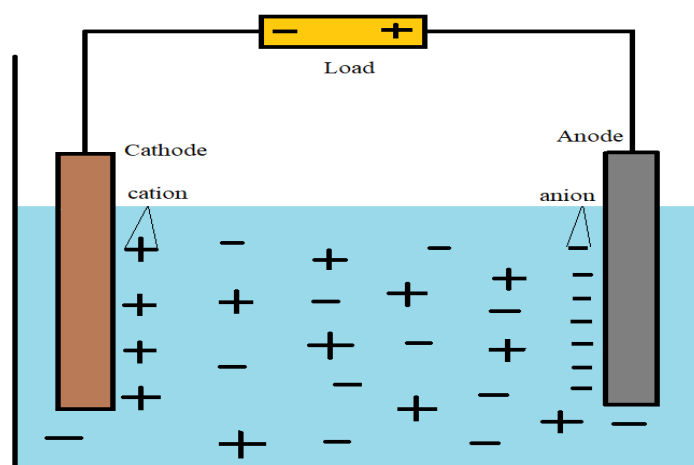
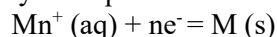
primarily three sequential steps: the movement of heavy metals from the entire solution to the absorbent surface, the adsorption of the metal to the surface of the particle, and finally the movement of the metal within the adsorbent particle. [38]

6. ELECTROCHEMICAL PROCESS

Wastewater treatment by electrochemistry involves an electron transfer reaction, which might be electroreduction or electrooxidation. Metal recovery by electrolysis has been studied for a very

long time. This method involves passing a direct current between the cathode plates and the insoluble anodes through an aqueous solution that contains metal ions. The metal ions that are positively charged cling to the cathode that is negatively charged. [39]

Essentially, it is a cathodic deposition, as indicated by the equation:



Electrolytic method for heavy metal recovery

5.2 MODERN TECHNOLOGIES FOR REMOVAL OF HEAVY METALS

There are many techniques that are used for heavy metals removal like nano-adsorbent, hydrogels, adsorption, biosorption and many more. [40]

1. PHOTOCATALYSIS

Photocatalysis is a process that uses light to illuminate a semiconductor-electrolyte interface. It is an innovative solution through which environmental contaminants can be quickly and effectively eliminated. [41]

Energy over the semiconductor bandgap causes the creation of electron-hole (e^-/h^+) pairs in the semiconductors' conduction and valence bands. Species in solution with the appropriate redox potential can be reduced or oxidised by these moving charge carriers. The semiconductors TiO_2 , ZnO , CeO_2 , SnO_2 , CdS , and ZnS are among those that are frequently analysed. [42]

2. HYDROGELS

A hydrogel is a network of hydrophilic polymers that is three-dimensional (3D) and maintains its shape by chemical and physical links between its individual chains. The hydrogel's ability to swell in

water and hold a lot of water while preserving its structure is a crucial characteristic. A substance must contain at least 10% water by weight (or volume) to qualify as a hydrogel. [43]

Most of the time, after the stimulus is gone, hydrogel may revert to its original state. Some popular types of hydrogels include those that are pH-sensitive, light-sensitive, electro-sensitive, and temperature-sensitive. [44]

3. MEMBRANE SEPARATION

In the membrane separation process, a semipermeable membrane is pressed under a lot of pressure to separate particular components from the solution. This technique can be divided into four categories based on pore size: ultrafiltration (UF), reverse osmosis (RO), nanofiltration (NF) and micro-filtration (MF) [45]. Diffusion is the process through which molecules or ions travel across a membrane, and the pace of diffusion relies on several factors, including pressure, membrane permeability, temperature and the total amount of molecules or ions in the solution. Adsorption, sieving, and the electrostatic phenomena are the three fundamental concepts that primarily govern the membrane separation process. [46]

4. ELECTRODIALYSIS

One of the most cost-effective new technologies is electrodialysis (ED), which uses electrically driven ion-exchange membranes to remove ions from aqueous solutions. In addition to eliminating even the lowest quantities of metal ions from the effluents, the process also has the benefit of producing effluent water that may be recycled. [47] In order to concentrate and extract Nickel (Ni) and its salts from synthetic effluent based on industrial nickel-plating process, as well as to remove organic molecules from the additives, a research lab-scale ED system is used. Using a three-compartmental electrodialysis approach at a low pH with the electrodes isolated from the sample by ion-exchange membranes, simultaneous recovery of heavy metals and phosphorus has been accomplished. [48]

5. NANO – ADSORBENTS

Many studies have been devoted to the development of high-performance, low-cost nano-adsorbents for the removal of heavy metals from wastewater. The most popular and widely used adsorbents have been Zeolite, activated carbon, nanotubes of carbon, and graphene. The removal effectiveness of these adsorbents has been affected by changes to their size, shape, physical makeup, and chemical composition. [49]

6. BIOSORPTION

Biosorption is now regarded as an effective and environmentally acceptable alternative method for heavy metals removal from wastewater effluent produced by various businesses. Metal ions are bound to the outermost layer of a biosorbent during the physiologically chemical process known as biosorption [50]. Yeasts, algae, bacteria, biopolymers, fungi, agricultural and industrial wastes are examples of potential metal sorbents. Even smaller amounts of heavy metals can be removed through biosorption, which is also a key method for their recovery. [51]

6. REMOVAL OF HEAVY METAL THROUGH ADSORPTION

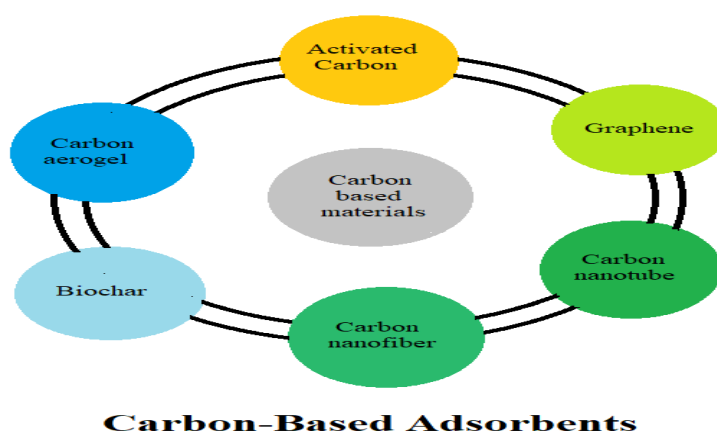
The adsorption process depends on various factors such as the characteristics of the adsorbent and heavy metals, as well as operational conditions like temperature, pH, adsorbent quantity, adsorption duration, and the initial concentration of metal ions [52].

Typically, the adsorbent surface can attract and retain heavy metal ions. This approach is considered cost-effective, efficient in removing contaminants, and easy to execute with the additional benefit of being able to regenerate the adsorbed metal ions. Various techniques have been developed for the purification of wastewater, which are described in the following sections. [53]

Carbon-based adsorbents

Carbon-based nano porous adsorbents, specifically activated carbons (ACs), carbon nanotubes (CNTs), and graphene (GN), are extensively used in heavy metal removal applications due to their exceptional surface area (ranging from 500 to 1500 m²/g). To enhance the adsorption capacity of heavy metals, the carbon surface can be modified by introducing functional groups such as carboxyl, phenyl, and lactone groups [54].

The most commonly used methods for modifying the surface include nitrogenation, oxidation, and sulfuration, which improve the specific surface area, pore structure, adsorption capacity, thermal stability, and mechanical strength. The cost of the adsorbent materials should be taken into consideration when selecting the most suitable adsorbents. [55]



When the surface of the adsorbent is modified, its surface area may decrease while the number of surface functional groups may increase. This modification can lead to an increase in the adsorption of metal ions [56]. The adsorption uptake can be enhanced by increasing the surface area of the adsorbent, the quantity of adsorbent used, the initial concentration of metal ions, and the contact time. Although multi-wall carbon nanotubes (MWCNTs) are commonly used for heavy metal removal, they tend to aggregate quickly in aqueous solutions due to their high hydrophobicity, which can lead to a decrease in their adsorption potential. [57]

There is insufficient literature available on the quantitative assessment of the functional groups' contribution to heavy metal ion sorption. Additionally, the current surface modification methods require high heat/pressure, strong acid/base solutions, or intensive oxidation/reduction reactions, which can be complex and expensive. As a result, the use of carbon-based adsorbents in industrial applications is restricted. To address this issue, researchers should develop new surface modification techniques that are cost-effective, environmentally friendly, and innovative. [58]

Chitosan-based adsorbents

Chitosan (CS) is a natural polymer with adsorptive properties, owing to the presence of amino ($-NH_2$) and hydroxyl ($-OH$) groups, that makes it suitable for removing pollutants from wastewater. However, its low mechanical strength and poor stability lead to inefficient regeneration. Furthermore, CS in its powder or flake form is not ideal due to low porosity, low surface area, resistance to mass transfer, and high crystallinity [59]. Researchers have suggested various structural and chemical modifications to address these issues. For instance, cross-linking chemical modification can enhance the strength of CS by connecting the polymer chains and functional groups. However, this approach may decrease the uptake of pollutants. [60]

Chemical modification techniques, such as grafting, can increase the adsorption capacity of chitosan (CS) by covalently bonding functional groups (e.g., amine and hydroxyl) to the polymer backbone. Additionally, researchers have suggested combining CS with other adsorbent materials to improve its adsorption capacity, mechanical strength, and thermal stability. Moreover, the ion-imprinting technique has been used to create

adsorbents that exhibit high selectivity for target metal ions.[61]

The ability of CS to remove heavy metal ions is mainly determined by the protonation or non-protonation of its amine and phosphoric groups, which can affect the pH of the wastewater. However, unmodified CS-based adsorbents have low reusability due to various factors, such as strong metal-ion-adsorbent bonding, low thermal and chemical stability, poor mechanical strength, incomplete desorption, reduced adsorbate-adsorbent interaction, and limited availability of adsorption sites. Therefore, there is a need to explore alternative regeneration methods and modifications that can enhance the reusability of CS-based adsorbents. [62]

Mineral adsorbents

Mineral-based adsorbents, including zeolite, silica, and clay, have emerged as promising low-cost options for water purification. Among these, clay exhibits excellent cation exchange capacity, selectivity, surface hydrophilicity, swelling/expanding capacity, and electronegativity [63]. To further enhance its adsorption efficiency, acid washing, thermal treatment, and pillar bearing can be used to increase pore size, volume, and specific surface area. The adsorption process is primarily governed by physical adsorption, chemical adsorption, and ion exchange mechanisms, while parameters such as pH, temperature, adsorption time, and adsorbent dosage also play crucial roles. An increase in pH and decrease in initial concentration can significantly improve the adsorption removal efficiency.[64]

The use of natural minerals can be a cost-effective solution for water treatment. However, their removal efficiency may decrease over time, making it necessary to explore modification methods like calcination and impregnation to enhance their performance. These modifications, though, can add costs to the process and release new chemical agents into the environment [65]. An alternative method is grafting functional groups onto the minerals, which can produce eco-friendly and multifunctional adsorbents that can effectively treat different types of wastewaters. Additionally, the preparation of two-dimensional nanosheets and one-dimensional nanotubes-based clay adsorbents could lead to the development of innovative, low-cost, and highly efficient adsorbents. [66]

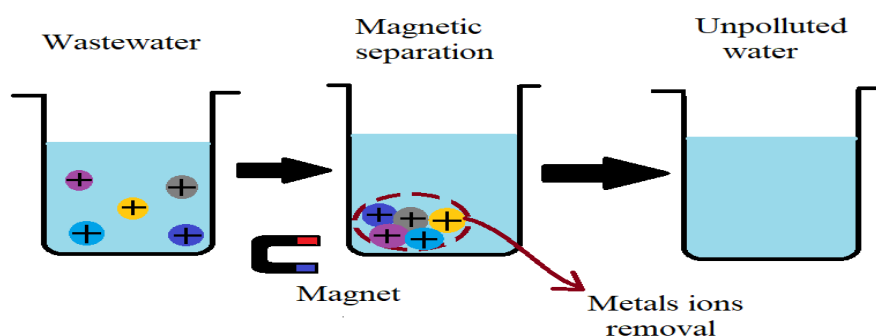
Magnetic adsorbents

Magnetic adsorbents are a unique class of materials that contain iron particles, particularly magnetic nanoparticles like Fe_3O_4 . Chitosan, polymers,

starch, biomass, or carbon can all be used to create the material matrix. Surface charge, redox activity, and magnetic field strength all have an impact on the adsorption process. They offer several advantages, including as low cost, simple synthesis, excellent surface charge, and reusability [67]. Zero-valent iron nanoparticles (ZVI NPs), iron oxides including hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄), and spinel ferrites are just a few of the magnetic adsorbents that have been suggested in the literature. Surface shape and the adsorbent's magnetic properties are just two examples of the many variables that affect the mechanism and kinetics of the sorption process [68]. Experimental conditions like pH, irradiation time, adsorbent concentration, wastewater temperature, and initial pollutant dosage also affect the adsorption process. The iron particles present in

the adsorbent significantly enhances the removal of metal ions from effluents.[69]

Several research studies have explored the use of Fe₃O₄ particles coated to remove heavy metal ions. Three commonly employed methods are co-precipitation, high-gravity technology, and grafting. Among these methods, grafting is often preferred due to its flexibility and simplicity. However, its effectiveness depends on the availability of active hydroxyl and functional groups on the surface of Fe₃O₄ particles. Despite its advantages, the resulting adsorbents from the grafting method have not proven to be cyclically stable, thereby impeding its commercialization. [70]



Adsorption process through magnetic adsorption

Biosorbents

The presence of various functional groups, such as carboxyl, amino, hydroxyl, phosphate, and thiol, on the surface of a biosorbent can facilitate the biosorption process. Typically, pollutants interact with the surface of the biosorbent through different mechanisms, including electrostatic interaction, aggregation, complexation /coordination, microprecipitation, ion exchange, reduction, or oxidation [71]. The surface charge density of the biosorbent and the ionization of its functional groups are influenced by the pH of the solution. When the pH is low, cations tend to be stable and can bind to the biosorbent surface. Conversely, at higher pH values, the solubility of metal cations reduces, which could lead to a precipitation phenomenon. [72]

The quantity of biosorbent used plays a crucial role in determining the efficiency of pollutant removal since it provides more available biosorption sites.

The biosorbent's capacity can be increased at elevated temperatures due to several factors, such as decreased solution viscosity, a reduction in Gibbs free energy, and bond rupturing [73]. These factors lead to an increase in the collision frequency between the biosorbent and metal ions, thus enhancing the biosorbent's active sites and resulting in a higher affinity for pollutant removal. However, at higher temperatures, the bonding force between the biosorbent and pollutants may decrease, leading to a reduction in the biosorbent's sorption uptake. Additionally, studies have shown that increasing the mixing agitation rate leads to an increase in removal efficiency. [74]

Metal-organic frameworks adsorbents

Metal-organic frameworks (MOFs) are typically produced through reticular synthesis, which involves strong bonding between metal ions and organic linkers. Many MOFs have been proposed

by researchers; however, it has been observed that most of the organic ligands used to create MOFs which are expensive and toxic [75]. Zirconium-MOFs (such as UiO-66) are a promising class of nanostructured materials for sorption applications due to their ability to easily incorporate functional groups and their hydrolytic-thermal stability, including amine, carboxylic, hydroxyl, and oxygen, or by using the cross-linking method. By creating composite-based MOF adsorbents, further improvements in the adsorption capacity of MOFs can be achieved. [76]

Even though MOFs possess impressive features and can efficiently eliminate heavy metal ions, some target metals may not be accessible due to the presence of micropores. Additionally, their stability in water is usually low, and MOFs formed using Mn, Fe, and Cu have exhibited poor chemical stability [77]. Consequently, more investigations are required to modify the structure of MOFs and increase their size to make them suitable for industrial wastewater applications. Furthermore, various techniques for enhancing the stability and sorption kinetics of MOFs should be proposed and used. [78]

7. CONCLUSION

In conclusion, heavy metal contamination in wastewater is a growing concern for environmental and public health. Adsorption has emerged as a promising technique for removing heavy metals from wastewater due to its efficiency, cost-effectiveness, and ease of operation. Various adsorbents, such as activated carbon, zeolites, and clay minerals, have been extensively studied for their effectiveness in removing heavy metals from wastewater.

The adsorption process can be influenced by various factors, including pH, temperature, initial metal concentration, and contact time. Therefore, optimization of these parameters is necessary to achieve maximum adsorption efficiency.

Overall, adsorption offers a sustainable and viable solution for removing heavy metals from wastewater. It has the potential to minimize the environmental and health risks associated with heavy metal pollution. Further research and development of advanced adsorbents and optimization of the adsorption process are needed to enhance the efficiency of heavy metal removal from wastewater.

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