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ENVIRONMENTAL TOXICOLOGY OF HEAVY METALS: CHEMICAL STRATEGIES FOR MITIGATION

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Abstract

The environmental toxicology of heavy metals poses significant challenges due to their persistence, bioaccumulation, and severe health and ecological impacts. Heavy metals such as lead, mercury, cadmium, and arsenic enter the environment through industrial activities, mining, and agricultural runoff, contaminating water, soil, and air. Their removal is difficult as they do not degrade naturally, and traditional remediation methods, including chemical precipitation and adsorption, often suffer from inefficiency, high costs, and secondary pollution. To address these challenges, advanced chemical strategies such as nanotechnology-based adsorbents, bioremediation using microorganisms, and green synthesis of functional materials have been developed for heavy metal sequestration. Additionally, phytoremediation and chelation therapy have shown potential in reducing toxicity in contaminated sites and living organisms. Despite these advancements, limitations such as scalability, environmental compatibility, and regulatory constraints hinder widespread implementation. Future research should focus on developing sustainable, cost-effective, and eco-friendly remediation techniques, integrating artificial intelligence for process optimization, and strengthening policy frameworks to regulate heavy metal discharge. Collaboration among scientists, policymakers, and industries is crucial for implementing large-scale solutions. A comprehensive approach that combines scientific innovation, environmental management, and policy reforms is essential to mitigating heavy metal toxicity, ensuring environmental sustainability, and protecting public health.

Keywords: *Heavy Metal Toxicity, Environmental Remediation, Nanotechnology-Based Adsorbents, Bioremediation Strategies.*

Introduction

Heavy metals belong to a category of elements found in the environment having high atomic weight ranging from 63.5 to 200.6 and a density greater than 4000 kg/m3 [1]. Over 50 elements on the periodic table have been identified as HMs which comprise transition metals, metalloids, lanthanides and actinides. Some of them include tin, zinc, boron, mercury, copper, nickel, cadmium, cobalt, vanadium, strontium, titanium, arsenic, lead, molybdenum, and chromium. About 17 of these HMs have been classified as extremely lethal and relatively accessible. It is obvious that selected HMs such as iron, boron, copper, nickel and zinc are vital for plant growth in trace concentrations, however, at concentrations beyond the maximum concentration limit (MCL), they become lethal to both plants and animals. The largest availability of HMs can be found in soil and aquatic systems and sparsely in the atmosphere. Soil pollution due to HMs occurs due to entry of industrial wastewater, sewage sludge, weathering of soil minerals and fertilizers. Research has shown that HMs not only cause soil pollution but also negatively affect food production, quality and health. Even low concentrations of some HMs can harm plants, while others may accumulate in plant tissues with no apparent adverse effects on yield. Growing plants in HMs-contaminated areas can lead to changes in their metabolism, physiology and biochemistry, resulting in decreased growth, metal accumulation, and reduced biomass generation. When studying the toxicity of HMs in plants, it is essential to consider their perpetual impact and molecular behavior. Most studies have been conducted in vitro or hydroponic culture, using high metal concentrations in growth media. The toxicity of a HM is dependent on its oxidation state, with Cr (VI) being the most lethal form of Cr, typically occurring as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions in association with oxygen. In contrast, Cr (III) is less mobile and toxic, predominantly held to organic material in water and soil [2]. The ability of HMs to persist in the soil in bioavailable forms to roots is impacted by desorption, complexation and adsorption in the soil, which is dependent on the soil structure and pH. Heavy metals are reported to have greater mobility in acidic soils [3].

Natural

Igneous and sedimentary rocks are regarded as the most common natural sources of heavy metals [3]. The parent material, from which they were originally derived, is the main source of HMs in soils. The Earth's crust is composed of sedimentary rocks to a small extent (approximately 5%) and 95% igneous rocks. Different concentrations of HMs are present in igneous and sedimentary rocks (Table 1). HMs naturally arise in the soil as a result of the weathering process because they originate in the Earth's crust. HMs in rocks may be released into the soil environment as a result of a variety of natural processes, such as erosion, leaching, volcanic eruptions, biological processes, terrestrial processes, and surface winds [4].

Anthropogenic

Anthropogenic generally indicates sources that are man-made. The concentrations of heavy metals (HMs) in agricultural soil in environments are increased by anthropogenic activities such as smelting and mining, burning fossil fuels for energy, disposing of municipal waste , applying fertilizer [5], using pesticides, and irrigating sewage

Industrial

Heavy metals are released into the environment as a result of rising human activity, such as industrial advancements. Eventually, these contaminants build up in the soil, especially in rapidly industrializing areas. Some industrial sources of heavy metals are.

Lead

Combustion of fossil fuels, paints, and pigments; application of lead in gasoline, fertilizers, solid waste, incineration of industrial waste, explosives, ceramics, and dishware, solid waste combustion, paints and pigments, industrial dust and fumes, manufacturing of lead-acid batteries, pesticides, mining and metallurgy, some types of PVC, urban runoff.

Nickel

Industrial dust, electroplating, production of iron and steel, food processing industries, chemical industries, incineration of waste, fertilizers, industrial aerosols, mining and metallurgy, battery, and combustion of coal [6].

Chromium

The textile industry, metal plating, paints and pigments, rubber, photography, tanning, chemical industry, leather industry, industrial dust and fumes, fertilizers, mining, and metallurgy [40,41].

Mercury

industrial wastewater, fossil fuel combustion, fluorescent bulbs, chloral Kali, scientific instruments, production of chemicals, mercury arc lamps, industrial dust, and fumes, incineration of municipal wastes, pesticides, fertilizers, solid waste combustion, smelting and metallurgy, electrical switches, explosive, rubber and plastics, mercury products (mercury amalgam, thermometers, batteries), cellulose, mining[7].

Copper

Textile industry, plating, paints and pigments, rayon, mining and metallurgy, pesticides, mining and metallurgy, explosives, electrical and electronics waste.

Agricultural

The agricultural sector has many potential sources, including fertilizer, pesticides, livestock dung, and wastewater[8] . Agri culture and industry both contribute to heavy metal pollution in agricultural soil and plants, particularly in areas close to cement and electroplating companies. That is to say, the soil's surface is an ideal location for accumulating heavy metals, which the plant can then take in through its roots and vascular system together with water Bioaccumulation of pesticides in food chains, caused by careless usage, poses a significant threat to mammals and other non-target species[9]. Plant parts, soil, air, and water can all retain pesticide residues for long periods [10] .3.2.2.1. Fertilizer. Both organic (natural) and inorganic (synthetic) fertilizers are sources of HMs. After the anaerobic digestion (AD) procedure, ammonium fertilizers (sulfate and nitrate) are created as organic or biofertilizers [11]. Chemically made or synthetic fertilizers are another name for inorganic fertilizers, which are composed of both inorganic and chemical components. The chemical designation of arsenic (As), a naturally occurring and abundant element of the Earth's crust, is metalloid due to its metallic and nonmetallic qualities. Both organic and inorganic forms of As are found in soil, with the latter being a very toxic form. Bio-fertilizers, liming materials, and phosphate fertilizers are the most common inorganic fertilizer types responsible for HMs release in agricultural soil and subsequent uptake by plants . 3.2.2.2. Pesticide. Pesticides are harmful substances that can be created synthetically or naturally. They can also be hazardous compound combinations. Insecticides, bactericides, and fungicides are frequently used in agricultural fields to control harmful weed, fungus, bacterial, and insect infestations [12]. In recent years, around 2 million tons of pesticides have been used globally, with 47.5% of those being used as herbicides, 17.5% as fungicides, 5.5% as other pesticides, and 29.5% as insecticides. Table 2 presents the four categories in order of increasing toxicity, from least to most hazardous, with a corresponding level of toxicity. Vinegar, citrus trees, and other perennial crops have seen a faster accumulation of Cu due to the application of fungicides based on copper. Due to the degradation of soil quality and phytotoxicity caused by Cu-contaminated soil, crop production potential is also decreased. Because surface runoff or stormwater transports more Cu to recipient water bodies, it also contributes to water pollution[13]. Mineral resources and elements such as copper, chromium, iron, manganese, and zinc, among others, are essential for both animals and humans because they are involved in a variety of metabolic functions, enzyme activities, receptor sites, hormonal function, and protein transport at specific concentrations[14]. Another group of elements, such as arsenic, cadmium, lead, and mercury, are non-essential and play no useful role in plants, animals, or people. They also serve no nutritional purpose since they are exceedingly poisonous [15]. To set quality standards and identify the hazards to human health and food safety, it is required to describe the sources and amounts of heavy metals in soil. Environmental pollution caused by heavy metals is persistent, covert, and long-term [16]. Because metals are nonbiodegradable and have a lengthy half-life, biological species are unable to decompose them, and they remain in their body parts and surroundings, posing health risks . Bioaccumulation of heavy metals in vegetables poses a health hazard due to their potential to transfer from polluted land and water into the food chain [15] . Soil properties are crucial in food production, and heavy metal pollution of this critical resource, as well as their subsequent absorption and bioaccumulation in food crops, poses substantial environmental and health concerns, especially in poor countries. Heavy metal concentrations are influenced by soil type, plant genotype, and their interactions [17]. In comparison to organic manure, mineral fertilizers contain increased concentrations of heavy metals; as a consequence, the use of mineral fertilizers leads in increased levels of heavy metal pollution in soil [18].Arsenic causes epigenetic alterations, damage to DNA, changes in the p53 protein's expression, histone modifications, DNA methylation, and reduced p21 expression (Fig. 2) [19]. Arsenic poisoning raises the risk of cancer by attaching to DNA-binding proteins and slowing down the DNA repair process [20]. Lead is a carcinogenic substance that causes damage to the DNA repair mechanism, cellular tumor regulating genes, and chromosomal structure and sequence by releasing ROS (Fig. 2). It disrupts transcription by shifting zinc from certain regulatory proteins[21]. (Silber geld et al., 2000). Mercury's peroxidative activity generates a significant quantity of reactive oxygen species (ROS), which can aid protumor genic signaling and cancerous cells growth. ROS can contribute to carcinogenesis by damaging cellular proteins, lipids, and DNA, resulting in cell damage[22]. Nickel works as a carcinogen via controlling a variety of carcinogenic mechanisms, including gene regulation, transcription factor management, and free radical generation. It controls the expression of particular long non-coding RNAs, mRNAs, and microRNAs. It participates in the methylation of the promoter and the downregulation of gene 3 (MEG3) to increase the modulation of hypoxia-inducible factor-1, both of which contribute to carcinogenesis [23]. The objective of this review is to explore and evaluate chemical strategies for mitigating the environmental toxicity of heavy metals, focusing on innovative approaches that address their persistence, bioaccumulation, and adverse effects on ecosystems and human health. Heavy metals such as lead, mercury, cadmium, and arsenic are known for their toxicological impacts, including oxidative stress, DNA damage, and disruption of enzymatic processes, leading to severe health and ecological consequences. Despite existing remediation techniques, many approaches are limited by high costs, inefficiency at low concentrations, and potential secondary pollution. Current methods such as adsorption, precipitation, and chelation often lack scalability or sustainability, while bioremediation strategies face challenges in adaptability to diverse environmental conditions. Moreover, the application of advanced materials like nanotechnology and green chemistry remains underexplored in addressing heavy metal toxicity effectively. This review identifies the novelty of integrating innovative chemical strategies, such as hybrid techniques and eco-friendly materials, to develop cost-effective, scalable, and sustainable solutions for heavy metal mitigation. By bridging these gaps, the study aims to provide a comprehensive understanding of emerging methods and their potential to transform environmental management practices.

2 Mechanisms of heavy metal toxicity

Heavy metal-induced oxidative stress and oxidation of biological molecules

Certain heavy metals are known to generate free radicals which may lead to oxidative stress and cause other cellular damages [24]. The mechanism of free radical generation is specific to the type of heavy metal.

Iron

Iron is a useful heavy metal in the human body as it is a constituent of certain biological molecules like hemoglobin and is involved in various physiological activities. However, in its free state, iron is one of the heavy metals generally known to generate hydroxyl radical (OH•) as shown below by the Fenton reaction.

$$\mathrm{Fe}^{3+}+\mathrm{O}_2^{-}\rightarrow\mathrm{Fe}^{2+}+\mathrm{O}_2 \qquad \text{E1}$$

$$\mathrm{Fe}^{2+}+\mathrm{H}_2\mathrm{O}_2\rightarrow\mathrm{Fe}^{3+}+\mathrm{OH}\cdot+\mathrm{OH}^{-}\,(\text{Fenton reaction}) \qquad \text{E2}$$

Net reaction (Haber-Weiss reaction):

$O2^{-}+H2O2\rightarrow OH^{-}+OH\cdot+O2$ E3

In addition to the above reactions, the following reactions below can also occur:

$OH\cdot H2O2\rightarrow H2O+H^{+}+O2\cdot^{-}$ E4
$OH\cdot+Fe2+\rightarrow Fe3^{+}+OH^{-}$ E5
$LOOH+Fe2+\rightarrow Fe3^{+}+LO^{-}+OH\cdot$ E6

Hydroxyl radical (OH•) is the most common free radical generated by the oxidation of iron. OH• is capable of reacting with biological molecules such as proteins, lipids, and DNA damaging them. When OH• reacts with guanine, a nitrogenous base of nucleic acids, it leads to the generation of 8-oxo-7,8-dihydro-20-deoxyguanosine (8-oxo-dG) and 2,6-diamino-5-formamido-4-hydroxypyrimidine (FAPy-G), in which the former is a good marker for oxidative damage [23].

It is well documented that metal-induced generation of oxygen-reactive species can attack polyunsaturated fatty acids such as phospholipids. The first of such observation was first presented by Bucher et al. [25] who showed that iron-generated OH• can oxidize lipid membranes through a process known as lipid peroxidation. Following his experimental observations, he proposed the following mechanism:

Steps of lipid peroxidation:

Initiation: $Lipid+R\cdot/OH\cdot\rightarrow Lipid\cdot$ E7
Propagation: $Lipid\cdot+O2\rightarrow Lipid-OO\cdot$ E8
$Lipid-OO+Lipid\cdot\rightarrow Lipid-OOH+Lipid\cdot$ E9
Termination: $Lipid\cdot+Lipid\cdot\rightarrow Lipid-Lipid$ E10
$Lipid-OO\cdot+Lipid\cdot\rightarrow Lipid-OO-Lipid$ E11

At the initiation stage, the radical (R•)/OH• attacks the lipid membrane to form a radial lipid. This radical lipid further propagates the formation of peroxyl lipid radical by reacting with a dioxygen molecule or with a lipid. This reaction further promotes damage to the lipid molecule. At the termination stage, two radical lipid molecules and/or a peroxyl lipid radical react to form a stable lipid molecule. The major aldehyde product of lipid peroxidation is malondialdehyde and it serves as a marker for lipid peroxidation. Generally, proteins are not easily damaged by $H2O2$ and other simple oxidants unless transition metals are present. Thus, protein damage are usually metal-catalyzed and involves oxidative scission, tyrosine cross-links, loss of histidine residues, the introduction of carbonyl groups, and the formation of protein-centered alkyl (R•), alkoxyl (RO•), and alkyl peroxyl (ROO•) radicals [26].

Health impacts of heavy metals:

Health effects of cadmium toxicity

The organs most affected by cadmium intoxication are consistent with the routes of exposure (Stankiewicz et al. 2023; ATSDR 2010). They involve the respiratory system and gastrointestinal tract. Occupational exposure to cadmium may result in adverse health effects, including various chronic diseases (Fig. 2). Acute inhalation of cadmium is manifested by symptoms resembling flu (fever, body pain), and chronic **exposure is predominantly caused by lung and kidney diseases.**

Cadmium and the respiratory system

Clinical manifestations: Accumulated evidence has revealed that the inhalation of cadmium can cause chronic obstructive pulmonary disease (COPD), a chronic inflammatory condition that causes airflow restriction and breathing problems, sometimes termed chronic bronchitis or emphysema [27]. Air pollution by cadmium and smoking are typical causes of COPD. Several animal studies have well-documented cadmium-induced lung toxicity. Cadmium intoxication, which is associated with pulmonary inflammation and inhalation of cadmium aerosol (1.6 mg/m3 a day) over 6 weeks, results in pulmonary damage in rats. This and other animal pulmonary toxicity studies proposed that reduced lung function in smokers may also be related to cadmium contained in cigarette smoke (~ 2 µg of cadmium/ cigarette), among other factors [28].A mouse model study confirmed that increased pathological scores and alveolar destruction indicators, including airway wall thickness, are consistent with long-term Cd exposure. Cross-sectional studies in male adults revealed that a high cadmium content in the blood is associated with the incidence of COPD [29]. Pathologically altered pulmonary function in COPD patients exposed to cadmium has been attributed to, to some extent, a reduction in telomerase activity. As expected, COPD patients of greater age and smoking habits are more prone to suffer from CD associated declines in pulmonary function. Interestingly, one study reported no correlation between cadmium exposure and altered pulmonary function in children. If we accept that cadmium causes cancer, then lung cancer is the most likely diagnosis. Given that occupational workers are often exposed to several heavy metals with carcinogenic properties (e.g., cadmium, arsenic, and lead), it is difficult to evaluate the effect of cadmium itself. In addition, other risk factors, such as smoking, genetic predisposition to cancer, eating habits, age, physical activity, and other factors, may be important. The level of cadmium in the blood of smokers may correlate with the early stages of lung cancer development. In addition to lung cancer, some studies have reported a potential link between cadmium exposure and kidney and prostate cancers. The molecular mechanism of cadmium-induced pulmonary damage: This type of damage is caused by Cd exposure and involves the upregulation of inflammatory cytokines, including tumor necrosis factor-α (TNF-α), interleukins (IL1β, IL-6, IL-8, and IL-10), and transforming growth factor-β (TGF-β) [30]. The transmembrane protein pulmonary E-cadherin, which is involved in cellular adhesion, was downregulated in cadmium-exposed mice; conversely, several mesenchymal markers, including N-cadherin (implicated in cancer metastasis), vimentin (class III intermediate filaments), and α-smooth muscle actin (α-SMA), were markedly upregulated. Long-term cadmium exposure in mice results in the deposition of extracellular matrix (ECM)-containing collagen around small airways. These results confirmed that the decline in COPD-associated lung function is caused by long-term cadmium exposure in mice. Lung macrophages play important roles in the inflammatory response to injury and the repair of injury. Cadmium induced injury (100 nanograms/kg) in mice results in the polarization of macrophages (a process of the production of distinct functional phenotypes) to a proinflammatory M1 phenotype [31]. In addition, cadmium-induced toxicity enhanced the glycolytic function of macrophages, and the extracellular acidification rate manifested as the cellular release of acidic substances into the extracellular space.

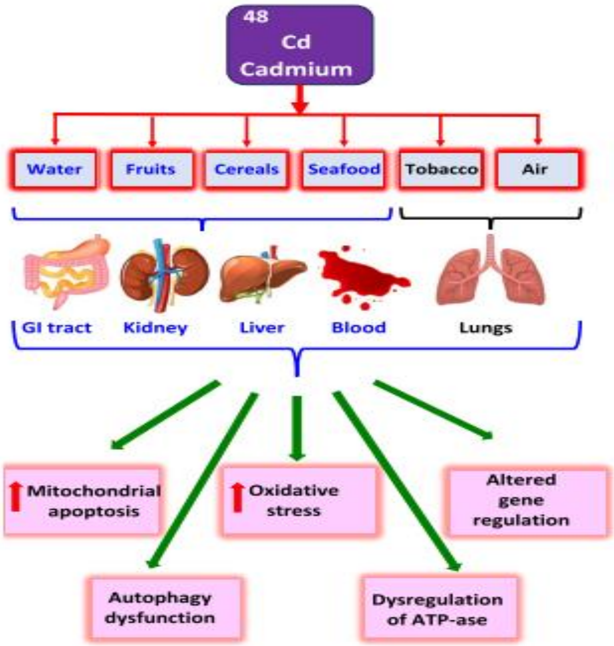

Figure 1: Sources and effects of cadmium toxicity

Mercury

For many years, Hg toxicity was related to the central nervous system. However, increasing evidence suggests that methylmercury (MeHg) exposure may increase the risk of adverse cardiovascular effects on populations [32]. Hg-mediated vascular effects result in elevated oxidative stress and inflammation, as well as decreased oxidative defense. The profile of elevated stressor and minimized defense can lead to thrombosis, mitochondrial dysfunction, and autoxidation of the mitochondrial inner membrane. Another toxic effect of Hg can occur through the inactivation of paraoxons. Paraoxons activity is necessary for protection against lipid oxidation, Hgmediated inhibition will lead to a dysfunctional high-density lipoprotein (HDL) and to decrease the delivery of reverse cholesterol to the liver. Pathological outcomes associated with Hg exposure and changes in lipid profile include atherosclerosis, myocardial infarction, and CVDs. Hg toxicity is indeed strongly associated with hypertension, coronary heart disease, myocardial infarction, carotid artery occlusion, and atherosclerosis. Valera et al. [33] and da Cunha Martins et al. [34] have reported studies on blood pressure (BP) and heart rate variability (HRV) among Quebec native populations that are indirectly exposed to Hg and MeHg. These studies have shown that exposure to Hg or MeHg harm BP and HRV in Eskimo adults. In contrast, exposure to MeHg during childhood will affect only HRV among Nunavik Inuit children without eliciting changes in BP [35]. The primary adverse cardiovascular effect observed in humans after exposure to MeHg has been increased BP [36] . Grandjean et al. [37] investigated whether childhood heart functions were affected by exposure to MeHg through seafood, and exposure of MeHg was associated with decreased sympathetic low frequency and parasympathetic high-frequency modulation of HRV.

Heavy metals in the environment

Heavy metals naturally occur in the environment and are vital for survival, but they may become hazardous when they accumulate in organisms. A few of the most frequent heavy metals that contaminate the environment include mercury, cadmium, arsenic, chromium, nickel, copper, and lead [38]. Cadmium is released into the atmosphere as a result of natural or manmade activities and animals and humans can be exposed to it differently. Cadmium pollution of the aquatic environment occurs through absorption, industrial waste, and surface runoff into sediments soil and sediments. People can be poisoned by cadmium via ingesting food, breathing air, or drinking water rich in the metal. Cadmium does not have any attributes that are helpful for plant growth and metabolic processes [39]. Mercury is an extremely hazardous heavy metal that may be found in biosphere. Due to human activities, it has also become a widespread contaminant and is increasing in the atmosphere. Mercury converts to the highly toxic methylmercury when in contact with aquatic sediments[40]. Methylmercury enters the human body through the food chain via fish, seafood, and wildlife, which become contaminated after ingestion of toxic microorganisms. It penetrates the circulation after being absorbed into the human body and causes a variety of neurological problems[41] . Lead is a non-biodegradable metal that is available in nature and found in relatively low amounts. Atmospheric lead levels are increasing continuously because of the human activities including manufacturing, mining, and fossil fuel burning. Lead is toxic to the human body when exposed to amounts greater than the optimum. Children are at higher risk of lead poisoning; when they come into contact with dust laden with environmental lead, the severity of poisoning increases [42][43]. Manganese, the most plentiful of the toxic heavy metals, is found in various oxidation states in nature. During combustion of methylcyclopentadienyl manganese tricarbonyl (MMT), an additive in gasoline, manganese oxides are emitted into the air. Although manganese is required for a variety of physiological activities, excessive consumption results in substantial toxicity[43]. Chromium is a cancerous and toxic element. In the environment, it exists in two stable oxidation states: chromium (III) and chromium (IV) (VI). Chromium (III) is a less hazardous form of chromium (VI). They can interconvert to each other during industrial operations. However, conversion of chromium (VI) to chromium (III) is less harmful to the environment because the latter is lower in toxicity. Chromium is used in many industries that pose a threat to regional climates. In comparison to natural chromium emissions from the environment, ferrochrome industry emissions are at the highest level (Fig. 1) [44]. Cobalt is found in abundance across the environment, such as vegetation, soils, rocks, and water and is utilized to make alloys. Although its rate of discharge is low, it is highly dangerous to humans. Cobalt affects the human body in both beneficial and harmful aspects. The small amounts of cobalt usually have no negative consequences, but massive discharges into the environment can cause fatalities . Nickel is a naturally abundant element and has extensive industrial uses. It is emitted from both natural and anthropogenic sources into the atmosphere . It has many adverse effects on humans, and causes allergies, nasal and lung cancer, and kidney and cardiovascular diseases owing to the inhalation of contaminated air . Copper is recognized as a vital micronutrient for living organisms. It has a role in the plants' normal physiological functions, such as chlorophyll formation, photosynthesis, and carbohydrate and protein metabolism. Copper deficiency alters important metabolic processes, and elevated exposure causes toxicity. Zinc is a fundamental and omnipresent metal. It is associated with plenty of enzymatic reactions via acting as a cofactor. Zinc toxicity depends on the manner and quantity of exposure. Smelting and mining are major the sources of zinc. A large amount of zinc emitted into the environment originates from activities.

Figure 2: Diagrammatic explanation of heavy metals in the environment

Methods

Several conventional treatment methods, such as chemical precipitation, coagulation and flocculation, adsorption, ion exchange, solvent extraction, neutralization, membrane separation, and electrochemical methods, can remove heavy metals from inorganic effluents (Figure 15.2). The various treatment strategies and methodologies used for heavy metal removal are discussed in the following sections.

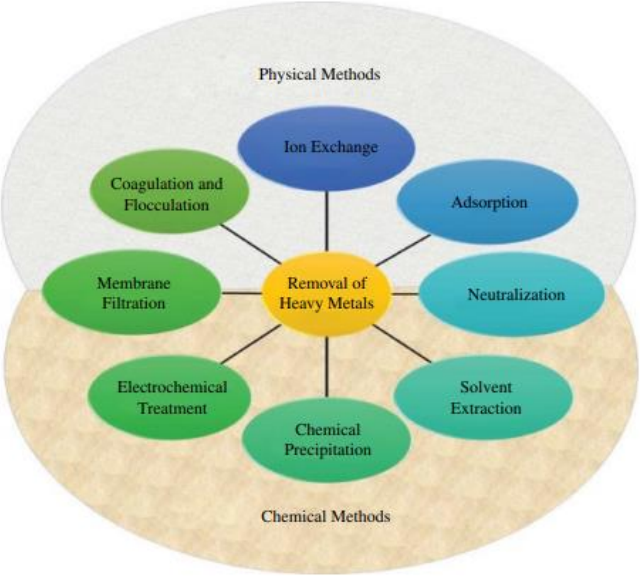

Figure 3: Physical and chemical methods used for the removal of heavy metal ions

Physical Methods for Heavy Metal Removal

Membrane Filtration

In wastewater treatment, various types of porous and thin-film composite membranes are used. There are different types of driving forces regulating membrane processes such as low pressure (microfiltration, ultrafiltration, and distillation), high pressure (nanofiltration, reverse osmosis), and osmotic pressure (forward osmosis, electrodialysis, liquid membrane, etc.). Principle factors applied to the application of the membrane process are pore size, pore distribution, degree of hydrophilicity, surface charge, solution flow, and presence of functional groups. These factors play a crucial role in the interpretation of the overall membrane process of water production rate and heavy metal removal efficiency. The performance of the membrane is generally determined by its flux rate and selectivity. Cellulose acetate, polyamide, polysulfide, etc. are porous membranes used in this process where solution flow under pressure and withdrawing the membrane releases water at atmospheric pressure. For reverse osmosis (RO), the applied pressure must always be greater than osmotic pressure for sufficient water flux. Membrane separation technology is governed by steric hindrance mechanisms or size exclusion, Donnan exclusion (charge–charge repulsion) effect, and adsorptive ability toward the contaminants. Membrane filtration has received appreciable recognition for the treatment of inorganic effluents such as heavy metals, and it can also eliminate organic compounds and suspended solids . This technology has gathered more attention and has become a favorable approach to heavy metal removal due to its cost-effectiveness and high efficiency . For selective separation of heavy metals, multiple membrane processes have been developed to reduce the cost and pollution load. Metal ions like Cu2+, Ni2+, Cr(VI), and As(V) have been successfully removed by RO and nanofiltration (NF). The removal of metal ions through ultrafiltration (UF) can be accomplished with the help of chemicals during the separation process, they are known as micellar-enhanced UF (MEUF) and polymer-enhanced UF (PEUF) . MEUF is a type of physicochemical membrane separation method that adds anionic surfactant into wastewater which agglomerates and forms micelles. The electrostatic force is the main factor through which heavy metals are trapped in the outer part of the micelle and remaining untapped pass through the ultrafiltration membrane. The advantages of this method include high removal efficiency, high flux, and low energy cost, whereas the disadvantage is the high operating cost. Water-soluble polymers in wastewater are used in PEUF, as they help in the elimination of small solute molecules that cannot be removed by conventional ultrafiltration. Ultrafiltration uses a permeable membrane to eliminate heavy metals, macromolecules, and suspended solids from an inorganic solution based on the molecular weight of eliminating compounds (1000–100

000Da) and pore size of a membrane (5–20nm). It can attain a removal efficiency of 90%. According to the study of Kosarek (1981), an integrated UF process with a chelating ligand successfully achieved the removal of As(V), Cd(II), Pb(II), Hg(II), Ni(II), and Se(II) from electroplating wastewater. showed the effective utilization of the reverse osmosis membrane to remove chromium and cyanide from metal-plating wastewater[45]. According to the study of, the charged ultrafiltration membrane was used for the elimination of Cu(II), Ni(II), and Zn(II) ions from electroplating water [46]. A nanofiber membrane based on poly(vinyl alcohol-co-ethylene) synthesized by activating with cyanuric chloride and covalently connecting with iminodiacetic acid demonstrated enhanced removal of copper, zinc, nickel, and cobalt (Figure 15.3)

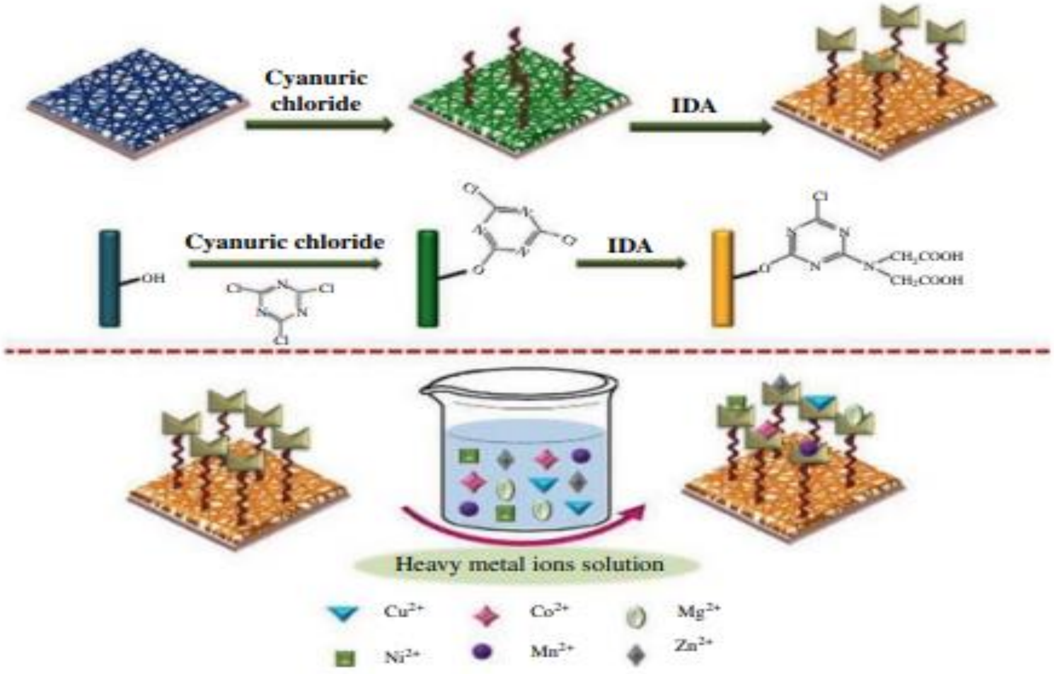

Figure 4: Membrane filtration method produced by Dutta and De (2017). (Used with permission from the Royal Society of Chemistry.

Chemical Methods for Heavy Metal Removal

Solvent Extraction

One of the most acceptable and established processes in hydrometallurgy is solvent extraction, which has been used in the successful hydrometallurgical processing of cobalt, nickel, copper, zinc, uranium, molybdenum, vanadium, tungsten, zirconium, niobium, hafnium, indium, germanium, gallium, platinum group metals, boron, reprocessing nuclear fuels, decontamination of wet-process phosphoric acid, nitric acid recovery, etc. In the present scenario, several stable extractants are available that exhibit better selectivity for metal ions following eco-friendly processing routes (Figure 15.9). In the processing of the metal separation method, organophosphorus has often been used as an extractant. The recovery of zinc and copper has been done successfully from sulfuric acid of low pH using di-(2-ethylhexyl)-phosphoric acid (D2EHPA) as an extractant. It also demonstrates the removal of nickel from aqueous sulfate solutions at pH range 6–7 and the extraction of chromium from aqueous sulfuric acid (Kongolo et al. 2003). Utilization of D2EHPA and Acorga M5640 (a hydroxy oxime derivative) effectively separates nickel from cobalt at lower pH. Using D2EHPA as an extractant, precipitation of copper and chromium was done at the initial level and later nickel sulfate was generated from pure raffinate solvent extraction aqueous solution via the salt crystallization method. For better stripping efficiency, the modifier has been used, in the case of chromium, the stripping mixture has the composition of NaOH and H2O2, while for other metals, sufficient H2SO4 or sulfate salt solution will be good enough for stripping . Cyanex 272 is also an organophosphorus used for the extraction of Fe, Zn, Cr, Cu, and Ni from sulfuric and/or sulfate solutions. It also demonstrates the successful separation of cobalt from nickel around 99.4% at pH 6. According to the study of Juang and Huang 2003, zinc extraction has dominated the diffusion at the initial stage of extraction, whereas the limiting step for copper extraction depends on experimental conditions such as the prominent role of aqueous layer diffusion at lower metal concentration, high carrier concentrations, and high aqueous pH. The Kelex 100® has been proved as a chelating extranet of Ga (III) and Ge (IV). The selectivity of Kelex 100 is good in a strongly basic solution for the separation of gallium/aluminum. It demonstrates successful metal recovery around 60% at pH1.5±0.1, 2.0±0.1, and 3.1±0.1 for cadmium, zinc, and chromium, respectively, indicating that cadmium has been extracted at lower pH in comparison with zinc and chromium .

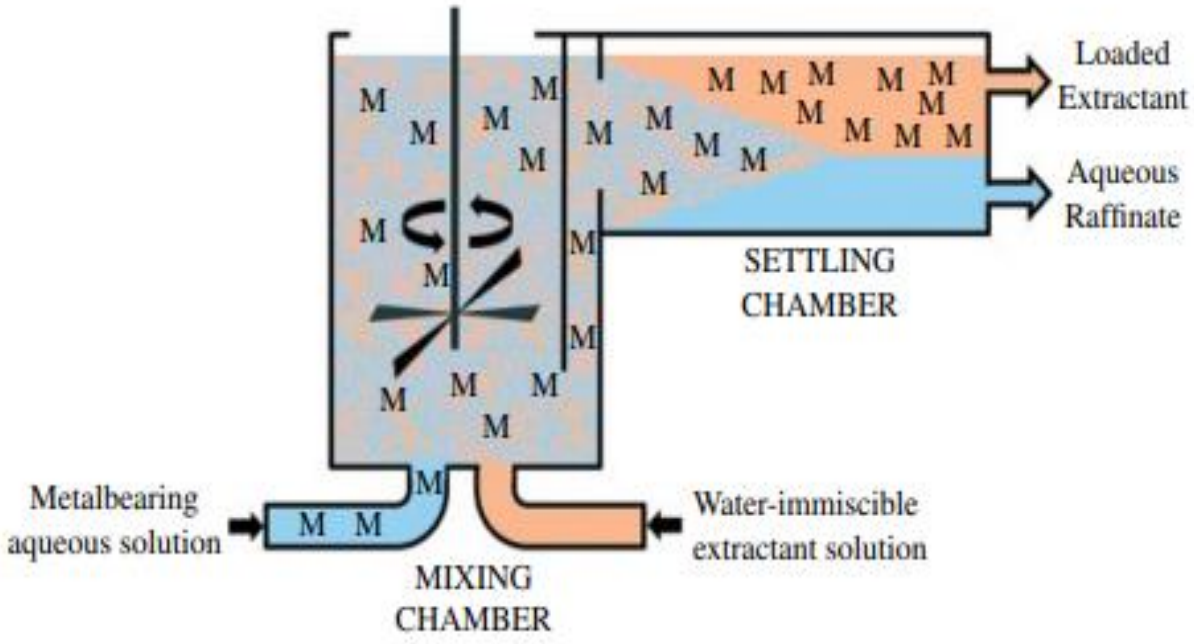

Figure 5: Schematic representation of a mixer-settler for continuous solvent extraction operation produced by Wilson et al. (2014). (Used with permission from the Royal Society of Chemistry.)

Lead poisoning and chelation therapy

The common people are exposed to lead and its compounds by lead-related industries such as automotive and battery manufacturing, refining, and smelting. Lead inhibits several biological processes and is hazardous to the nervous system, heart, kidneys, and gastrointestinal tract, with the most affected nervous system. Lead also disrupts brain development in children, causing cognitive impairments. Children are more sensitive to lead exposure even at low levels because of high absorption in the gastrointestinal tract and permeability of the BBB. Lead affects neurotransmission by altering Ca2+-associated activity, which leads to excitotoxicity. Lead also affects glial cell (astrocyte, and oligodendrocyte) activity, resulting in demyelination. Clinical manifestation of lead toxicity symptoms includes headache, anemia, abdominal distress, and in severe conditions, convulsions, coma, and death [47][48]. Succimer, BAL and CaNa2EDTA are primarily used for the chelation of lead. CaNa2EDTA only removes extracellular lead, and its effectiveness increases when combined with BAL. Co-treatment with CaNa2EDTA and MiADMSA showed better biochemical and clinical outcomes than monotherapy against subacute lead toxicity in the rat model. Treatment with α-lipoic acid in combination with a thiol chelator reduces oxidative stress and brain lead concentration in rats.

Nanomaterials for Heavy

Metals Removal Nanomaterials can be used to remove heavy metals from wastewater by using the adsorption method on their surfaces. To remove heavy metal ions from wastewater, nanomaterials must meet the following criteria: nontoxic nanomaterials should be used; the nanomaterials should provide high adsorption capacities and selectivity to low pollutant concentration; the pollutant could be easily removed from the nano-adsorbent surface; and adsorbents should be considerably recyclable. In recent years, nanomaterials such as zeolite, carbonaceous, chitosan, polymer-based ferrite, magnetic, bimetallic, metal oxide, metallic, etc., have been used to remove heavy metals from wastewater. Various nanomaterials are described and explored in detail in the following sections based on their fundamental material and importance for heavy metal removal.

Chitosan-Based Nanomaterials

The polysaccharide chitosan nanoparticles have been derived from naturally occurring sources, such as shellfish and crustacean shells (e.g., crabs, prawns, shrimp, and beaks of cephalopods). Chitosan is a hydrophilic polymer that is non-toxic, biodegradable, bio-renewable, biocompatible, and biodegradable. When chitin is hydrolyzed in alkaline circumstances (e.g., concentrated NaOH), it yields chitosan . Chitosan can also be generated via enzyme hydrolysis in the presence of chitin deacetylase [49] (Figure 2). The chemical and mechanical modification of its unique properties generates novel properties that facilitate its utilization in different fields. Because of its superior solubility in water and organic solvents, as well as the presence of a significant number of –NH2 and –OH groups, chitosan has garnered increased interest in the water purification industry, where it may chelate hazardous contaminants such as dyes and heavy metals. A study found that the chemical changes in chitosan and chelation improve the sorption in addition to the selectivity capability of the compound by grafting additional functional groups onto the compound's backbone. Chitosan's backbone has been modified to incorporate a new functional group, which adjusts the pH range for metal sorption, enhances the density of sorption sites, and modifies the composition of sorption sites to improve the sorption selectivity for the targeted metals[50] . Dubey et al. developed carbon nanoparticles (CANPs) for the adsorption of Hg2+ ions in water [101]. Ions of alginate and Chitosan electrostatically react with both calcium and tripolyphosphate ions owing to the presence of negative and positive charges on chitosan and alginate ions. This investigation discovered a substantially higher level of maximal adsorptive power for ions of Hg2+ recorded by 217.4 mg/g at 30 ◦C CA Nanoparticles. In another study, ZnO/chitosan core–shell nanocomposite was synthesized, which successfully separated copper ions, cadmium ions, and lead ions from water in order: Pb2+ > Cd2+ > Cu2+ . By the same token, a similar compositing technique was achieved to create a nanocomposite of TiO2/chitosan nanoparticles, which showed a high adsorption capacity for divalent ions of lead and copper. Esmaeili and Khushnasiba functionalized chitosan nanoparticles with alginate to prepare an alginate/chitosan nanocomposite adsorbent. The prepared adsorbent removed 94.9% of Ni+2 from aqueous solution . The chitosan–alginate nanocomposite was synthesized by microemulsion method. The synthesized biopolymers were applied to remove Hg2+ from water, with promising results. The high interaction among differently charged contaminants in water, negatively charged alginate and positively charged chitosan, allowed an adsorption capacity of 217.40 mg/g of Hg+2, which was quite high . A hierarchy of porous three-dimensional carbon materials was synthesized by Yuan et al., who used chitosan as a carbon/nitrogen source to do so . The results demonstrated that HNC has a very high adsorption capacity for lead 2+ and cadmium 2+ in an aqueous environment, which is consistent with previous findings. A photocatalytic process, according to the authors, is responsible for the adsorption of Pb2+ onto HNC materials, which is generated by the coordination and electrostatic contact between the ions of Pb2+ and the O- and N-containing functional groups of HNC substances.

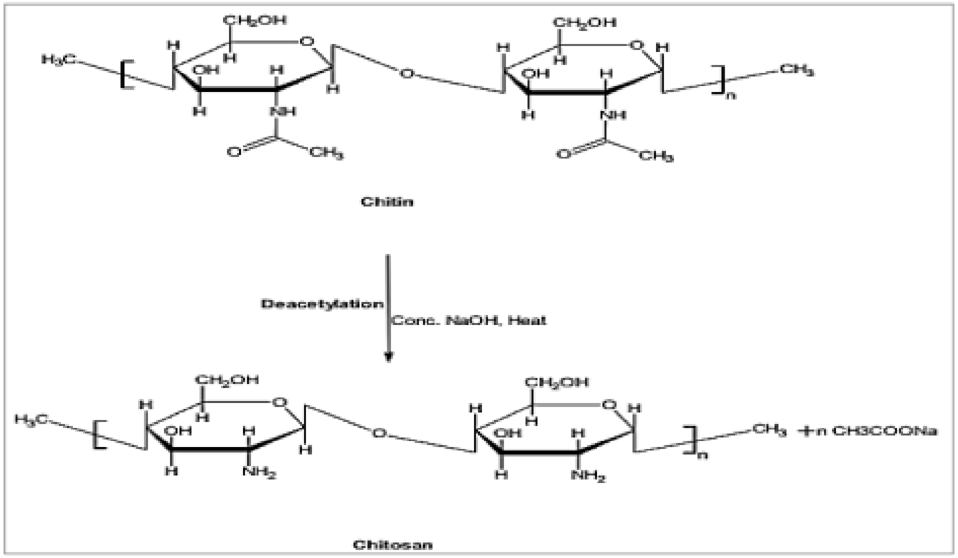

Figure 6: Deacetylation of chitin to chitosan. Adapted with permission from.

Lingling Liu et al 2019 demonstrated that The heavy metals in water has caused serious damage to the health of animals and human beings, it is considered to be one of the most serious environmental pollutants. Nanotechnology is one of most effective ways to remove heavy metal ions. It is applied to the treatment of heavy metal wastewater and it includes adsorption and membrane separation. This chapter describes the basic principles of adsorption and membranes. In addition, two critical topics are discussed. One comprises the adsorption materials and their modification method, the adsorption mechanism, and adsorption efficiency. The other comprises the performance and selection of membrane materials, membrane fouling, the methods of cleaning and regenerating the membrane, engineering application, and process design. More importantly, nanotechnology has been successfully applied to engineering by immobilizing nanomaterials on special carriers and organic membranes.

Challenges and limitations:

Environmental toxicology of heavy metals presents significant challenges due to their persistence, bioaccumulation, and adverse effects on ecosystems and human health. Heavy metals such as lead, mercury, cadmium, and arsenic can enter the environment through industrial discharge, mining activities, and agricultural runoff, leading to contamination of water, soil, and air. One of the major limitations in addressing heavy metal toxicity is the difficulty in their complete removal from the environment, as they do not degrade like organic pollutants. Additionally, their complex interactions with biological systems can result in long-term toxicity, affecting multiple trophic levels. Traditional remediation techniques, such as chemical precipitation, ion exchange, and adsorption, often suffer from inefficiency, high cost, and secondary pollution. To mitigate these challenges, advanced chemical strategies have been developed, including nanotechnology-based adsorbents, bioremediation using microorganisms, and green synthesis of functional materials for heavy metal sequestration. Chelation therapy and phytoremediation have also shown promise in reducing heavy metal toxicity in living organisms and contaminated sites. However, the implementation of these strategies is often hindered by factors such as scalability, environmental compatibility, and regulatory constraints. Future research should focus on sustainable, cost-effective, and eco-friendly approaches to mitigate heavy metal pollution while ensuring minimal ecological disruption.

Future perspective:

The environmental toxicology of heavy metals should focus on developing sustainable, cost-effective, and highly efficient mitigation strategies that minimize ecological disruption. Advancements in nanotechnology and biomaterials hold promise for enhancing heavy metal remediation through innovative adsorbents and catalysts with high selectivity and reusability. Integrating artificial intelligence and machine learning can optimize remediation processes by predicting contamination patterns and improving treatment efficiency. Additionally, genetically engineered microorganisms and plants offer potential for bioremediation with enhanced metal uptake and degradation capabilities. Green chemistry approaches, including eco-friendly chelating agents and bio-based sorbents, should be prioritized to reduce secondary pollution. Policy frameworks must also be strengthened to regulate heavy metal discharge and promote cleaner industrial practices. Collaboration between scientists, policymakers, and industries is essential to implement large-scale, environmentally sustainable solutions. Future studies should also explore the long-term ecological impacts of heavy metal contamination and remediation efforts to ensure a holistic approach to environmental protection.

Conclusion:

The environmental toxicology of heavy metals remains a critical challenge due to their persistence, bioaccumulation, and harmful effects on ecosystems and human health. Conventional remediation techniques often fall short in terms of efficiency, cost-effectiveness, and environmental safety. However, advancements in nanotechnology, bioremediation, and green chemistry offer promising solutions for mitigating heavy metal pollution. Future efforts should focus on developing sustainable and scalable strategies that minimize ecological disruption while effectively removing contaminants. Additionally, strengthening regulatory policies and fostering interdisciplinary collaboration will be essential in addressing this global issue. A comprehensive and proactive approach integrating scientific innovation, environmental management, and policy reforms is crucial to mitigating heavy metal toxicity and ensuring a safer and healthier environment.

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