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# Heavy metal contamination in water matrices its ecotoxicology and adsorption based removal strategies

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## Abstract

Global wastewater generation and its total pollutant load are rising due to population expansion, faster urbanisation, and economic development. Heavy metals, toxic in low concentrations and possessing a low level of degradability, are considered more persistent and pose more detrimental effects on the water matrices than other pollutants. Its bioaccumulation and ecotoxicological effects increase toxicity for humans and marine biota. Hence, it's imperative to remove heavy metals from water. Various methods have been discussed for removing heavy metals from water based on their advantages and disadvantages. Adsorption-based removal strategies are widely used due to their consistently enhanced removal effectiveness, decreased costs, and ease and simplicity in developing innovative adsorbents. In this study, the adsorption capacity of different adsorbents in the removal of heavy metals has been discussed. Mechanisms involving the removal of heavy metals from water by diverse adsorbent materials were also summarised.

**Keywords**: Heavy Metals, Ecotoxicology, Adsorbents, Adsorption, wastewater treatment

## Introduction

Water is the earth's most vital resource and deserves immediate attention. Every aspect of the water cycle is seeing an increase in water pollution. The World Health Organisation projects that by 2025, over four billion people will live without access to adequate clean water. By 2030, the health and livelihoods of 4.8 billion people could be at risk if current water quality monitoring is not improved. Global wastewater generation and its total pollutant load are increasing due to population growth, rapid urbanization, and economic development (1). The growing problem of water pollution worldwide is a result of several pollutants, the most common of which are pesticides, heavy metals, petroleum products, pharmaceuticals, dyes, and organic and inorganic materials that can dissolve in water. Heavy metals refer to metals that are harmful even in trace quantities due to their hazardous characteristics; they exert a considerable detrimental impact on the environment and human health, making them a critical area of investigation. Various sources are considered for the heavy metal contamination in water. Natural phenomena, such as volcanic eruptions, and anthropogenic activities, including mining, the combustion of fossil fuels, agricultural runoff, the release of industrial effluents, municipal wastewater, and the use of pesticides containing salts of heavy metals (2), are some of the ways heavy metals enter water. Industrial effluent discharge is considered the primary route for heavy metal contamination of water bodies, posing a severe ecotoxicological threat to aquatic and freshwater ecosystems. Heavy metals are potent neurotoxins in the fish species. When heavy metals interact with chemical stimuli in fish, they disrupt the fish's ability to communicate with its environment, causing deformities in the fish species, both in natural populations and laboratory settings. The deformities include stunted growth,, and organ damage. These deformities act as effective indicators of environmental heavy metal contamination (3). Heavy metal contamination disrupts the biochemical, phytochemical functions of human, animals and plants. For instance when heavy metal enter human body through food or water it interrupts the enzymatic or metabolic pathway resulting in cognitive disorders, immune system related disorders, kidney damage, cardiovascular illness skin irratation and also induce cancer since most of the heavy metals are listed as carcinogenic (4). Hence heavy metal removal from wastewater before its discharge into water bodies is crucial. Various methods are explored for removal of heavy metals from waste water such as membrane filtration (5), ion exchange (6), adsorption (7), coagulation or flocculation (8), chemical precipitation (9), floatation (10), bioremediation (11). All these methods have their advantages and disadvantages. Chemical precipitation method requires more chemicals, and the removal of heavy metals is limited (12). Coagulation or flocculation methods involve the usage of chemicals in large quantities, which increases capital cost, leads to the production of a high volume of sludge, and causes difficulties in scaling up (13); in the case of Ion Exchange Limited metal removal, high resin usage, and the overall cost is high (14). Bioremediation involves maintaining and managing microorganisms, which is a time-consuming and slow process. Conversely, adsorption has emerged as the predominant approach for removing heavy metals from wastewater (15). Adsorption is a process in which the atoms, molecules, ions, or dissolved solids from the liquids grip onto the surface of the solid through various mechanism like electrostatic attraction, chemisorption, complexation, ion exchange, hydrogen bonding, redox reactions. The adsorption technique is favoured due to its consistently enhanced removal effectiveness, decreased costs, and ease and simplicity in developing innovative adsorbents (16). The potential success of adsorption of heavy metals depends mainly on the type of adsorbent material used, surface area, porosity, surface functional groups and its affinity to metal ions. In recent years Various innovative adsorbents were engineered or synthesized like activated carbon (17), agricultural waste (18), nanocomposites (19), biochar based adsorbents (20), metal organic frameworks (21). These materials offer tailored structure in case of pore, surface area, porosity and functional groups which improves adsorption capacity, kinetics, selectivity and reusability compared to the other conventional adsorbents for removing heavy metals form water. This review examines the source, ecotoxicological impacts of heavy metal on human and aquatic organism involved in the adsorption of most toxic heavy metal like cadmium, chromium, mercury, arsenic, lead and copper. Each heavy metal exhibits unique adsorptive behaviour and possess different operational parameters like pH, contact time, dose, metal ion concentration. The review also provides details on adsorption mechanism involved in the removal of heavy metal from water. Understanding of mechanism helps in curation of engineered adsorbents for each heavy metal with specific parameters. The discussion focuses on recent literature and experimental findings like pH, adsorbent dose, initial concentration, contact time and offering a comparative analysis of adsorption capacity of different materials under varied experimental conditions. The final section draws conclusion from the surveyed literature and provides future perspective aiming to build the gap between the batch studies and real-world applications. The main emphasis is placed on the development of sustainable material, synthesis methods, regeneration and its reusability of adsorbents. To summarize the review provides comprehensive understanding of heavy metal contamination and adsorption-based innovative remediation methods for metal ion removal.

## Sources of Heavy metals in water

Heavy metals are naturally present in the environment, but human activities have significantly increased their levels in water matrices. Copper (Cu), chromium (Cr), zinc (Zn), cadmium (Cd), arsenic (As), mercury (Hg), and lead (Pb) are listed as the most hazardous and toxic heavy metals by USEPA. WHO and EPA have determined the permissible limit of heavy metals in water, and it's listed in (Table 1 & Fig. 1). Lead (Pb) is the most commonly found heavy metal in the environment in relatively small amounts. It enters water matrices mostly through anthropogenic activities that include smelting, used as fuels, aerosols, batteries, mining, metal plating, pesticides and agricultural fertilizers (22). Chromium(Cr) is a naturally occurring element in the Earth's crust. The Earth's crust contains chromium content above 200 mg kg$^{-1}$. Chromium exists in various forms like Cr(VI) is considered to more toxic and contaminate water due its prevalent use in various industries. The concentration of Cr(VI) increased in water matrices due to its usage in the industries like tanning, steel slags, chrome plating, textiles dyeing, stainless steel welding, paints, inks, plastic pigments, wood-preservation (23). Copper(Cu) is the most prevalent heavy metal found in various rocks and minerals in nature. It is also the third most widely used heavy metal in the world and the second most toxic metal, after mercury, when it contaminates drinking water (24). Copper exists in various forms, among which Cu(II) has a wide range of applications, although it has relatively adverse effects. Its industrial applications

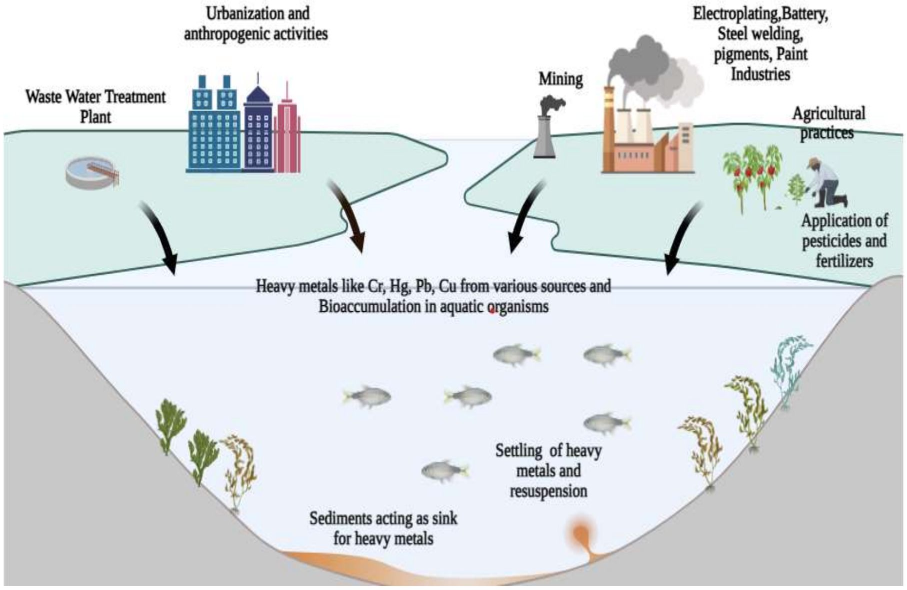

**Fig 1:** Source of Heavy Metal Contamination in Water Matrices

**Table 1:** Permissible limits of heavy metals in drinking water allowed by the United States Environmental Protection Agency (USEPA) and the World Health Organisation (WHO) (30) (31)

| S. No | Heavy metals | Permissible limit by UESPA in (ppm) | Permissible limit by WHO in (ppm) |
|---|---|---|---|
| 1 | Chromium | 0.1 | 0.05 |
| 2 | Lead | 0.01 | 0.05 |
| 3 | Mercury | 0.001 | 0.002 |
| 4 | Copper | 2.0 | 1.30 |
| 5 | Arsenic | 0.010 | 0.01 |
| 6 | Cadmium | 0.002 | 0.01 |

include the steel industry, electroplating, the dyes and pesticides industry, the petroleum refining industry, paints, and explosives. Its usage in these industries is a crucial way through which it enters the water stream (25). Arsenic (As) is naturally present in the form of mineral deposits in nature. It is present in sediments, rocks, and volcanic ash. The elevated levels of arsenic in water are due to anthropogenic activity, biological processes, and geochemical processes. The anthropogenic source of arsenic in water is due to industrial uses like mining, and use of arsenic in agriculture, like arsenic fungicides, herbicides, and wood preservatives (26). Mercury (Hg) is considered one of the ten leading chemicals of concern by the WHO. The occurrence of mercury in water can be attributed to both anthropogenic and natural sources. The anthropogenic sources include cement, gold, iron, and steel production (27), Natural sources include earthquakes, volcanic eruptions, and forest fires. (28). Cadmium (Cd) naturally present in weathering rocks and contamination in water occurs mainly due to industrial activities like steel works, dyes, fertilizers, paper mills, pesticide, welding, electroplating, petroleum refinery (29).

## Ecotoxicological impacts of Heavy metals and its toxicity in humans

Heavy metal pollution adversely affects plant and animal biodiversity in water ecosystems. Bioaccumulation is the biggest concern in these cases, where aquatic organisms absorb heavy metals from water, sediment, or food over time. The heavy metals accumulate in their organs faster than they can be eliminated, resulting in toxic effects and potential harm to the entire food chain (32). Idrees et al., (33), reported the toxicity of heavy metals like Chromium (Cr), Cadmium (Cb), Lead (Pb) in river water of Kosi located in Rampur, Uttar Pradesh, India. The freshwater fish *Channa punctatus* was collected from the river and studied accumulation of metals in the organs was found in the kidney of the fish with the concentration of 0.076 ± 0.208 for Cr 0.482 ± 0.059 for Cd, and 0.127 ± 0.705 for Pb showing more accumulation of Cd and Cr than Pb. Ecotoxicology studies on the river Tamiraparani water concentration of Cr, Cb and Cd was found to high in the sediments and organs of fish *Dawkinsia filamentosa* from the samples collected from the river Tamiraparani located in Tamil Nadu. The accumulation of the metals in the gills and liver was observed. Histological examination of the fish selected from the five sites of the river showed the *D. filamentosa* has atrophy in gill filaments, accumulation of leucocytes, lamellar aneurysm, cellular hypertrophy, edema, blood congestion in blood vessels and damage in epithelial lining and examination of the liver showed irregular shaped hepatocytes, disintegration of cell boundaries, nuclear degeneration, accumulation of leukocytes, leukocyte infiltration showing sever hepatotoxic effects. Presence of heavy metals in sediments is more than water acting as a sink for the heavy metal accumulation, facilitating the long-term presence of toxic metals in water leading to the accumulation of metals in the organs of fish causing severe organ damage and impaired growth (34). Chromium bioaccumulation was studied in fish *Cyprinus carpio* where the fish was exposed to 96 hours of chromium chloride at sub lethal concentration. The bioaccumulation was found in the organs in following order gills, intestine, muscle, skin, bones. The damage in spleen and intestine was noted. Increase in haemoglobin, red blood cells, decrease in blood platelets, white blood cells, marker for liver dysfunction was noted. Exposure of chromium in fish lead to change in the haematological and biochemical changes in the fish with affecting major organs (35). Lead contamination in fish during their early growth stage affects was studied using *Danio rerio* embryo and post fertilization at different pb concentration for 96 hours in controlled study. The exposure affected and impacted the development of zebrafish embryo by inducing embryo coagulation, it also reduced the burst activity and number of movements of the embryo and muscle twitching. The hatched larvae exhibited cardiovascular effects leading to increased blood flow, inhibition of endothelial cell growth, oxidative stress, major antioxidant gene coding enzyme were dysregulated, inhibition of catalase that is responsible for protection against oxidative damage, reduced heart rate indicating the toxic effects of lead in the zebra fish (36). Copper contamination in water has ill effects in the aquatic organism's lab-controlled study on *Labeo rohita* to determine the histopathological and haematological alteration. When fish was exposed to copper and results found were significant increase in leukocyte, and decrease in red blood cells, total protein, albumin and globulin decreased significantly. Organs like gills, liver and kidney showed inflammation, brain tissue damage, neuron necrosis, intracellular edema, cytoplasmic vacuolization and congestion (37). Arsenic toxicity in aquatic organisms was studies using *Pangasianodon hypophthalmus* haemoglobin, white blood cells, red blood cells underwent severe impact, DNA damage, growth of the fish affected when exposed to arsenic, growth related hormones, tumour necrosis factor and interleukin was upregulated, increased cortisol, detoxifying pathway were affected, bioaccumulation of arsenic was higher in liver and the kidney tissues (38). Mercury contamination in water has ill effects leading to accumulation in organs the study on zebra fish was done to understand the abnormalities in the zebrafish larvae and embryo. The zebra fish was exposed to mercury for 96 hours at a particular concentration and the results showed the morphological malformation like spine and tail deformities, pericardial edema, pericardial edema, changes in pigmentation, enzyme important to maintain the redox system showed a significant increase indicating a induction of protective response due to increase in the mercury toxicity and fluctuation in the levels of PP1 which is critical regulator for embryonic development in fish (39). Toxicity of heavy metals in human occur through various routes like ingestion through food, inhalation by industrial fumes or dust, skin contact through contact with heavy metal contaminated site. For instance, ingestion of electroplating water led to the gastrointestinal irritation, acute liver and kidney damage, necrosis of liver cell, myocardial damage, increase in white blood cell and decrease in lymphocyte count (40). Cadmium inhalation through dust led to the accumulation in the respiratory pathways like lungs and development of lung diseases, digestive system, kidney, binds to red blood cells. The prolonged exposure results in chronic bronchitis (41). Chronic exposure of mercury led to anorexia, weight loss, muscular weakness, damage in central system, kidney, tremors in eye muscles, eye lids and limbs (42). The persistent threat of heavy metal and its toxicity on human health and aquatic systems underscores the necessity of immediate intervention in controlling the contamination of heavy metals in water matrices, public awareness, and sustainable pollution control practices (Fig. 2).

## Heavy metal toxicity and its removal from water by adsorption

Bioaccumulation, biomagnification, and bioconcentration are serious issues faced by humans, plants, and other organisms when they come into contact with heavy metals; hence, the emergence of technology for removing heavy metals from the environment has been a priority for many years (32). The most commonly used physicochemical treatment methods for removing heavy metals from water include precipitation (43), membrane filtration (44), coagulation (45), ultrafiltration (46), nanofiltration (47), reverse osmosis (48), Ion exchange, photocatalysis, flotation, adsorption (49) and microbial Bioremediation (15). Conventional Methods have various limitations; coagulation has high sludge formation and aggravates the separation problem by moving the hazardous chemicals to the solid phase, and is inefficient in eliminating low concentrations of metal ions (50). The removal rate limits flotation, and it's

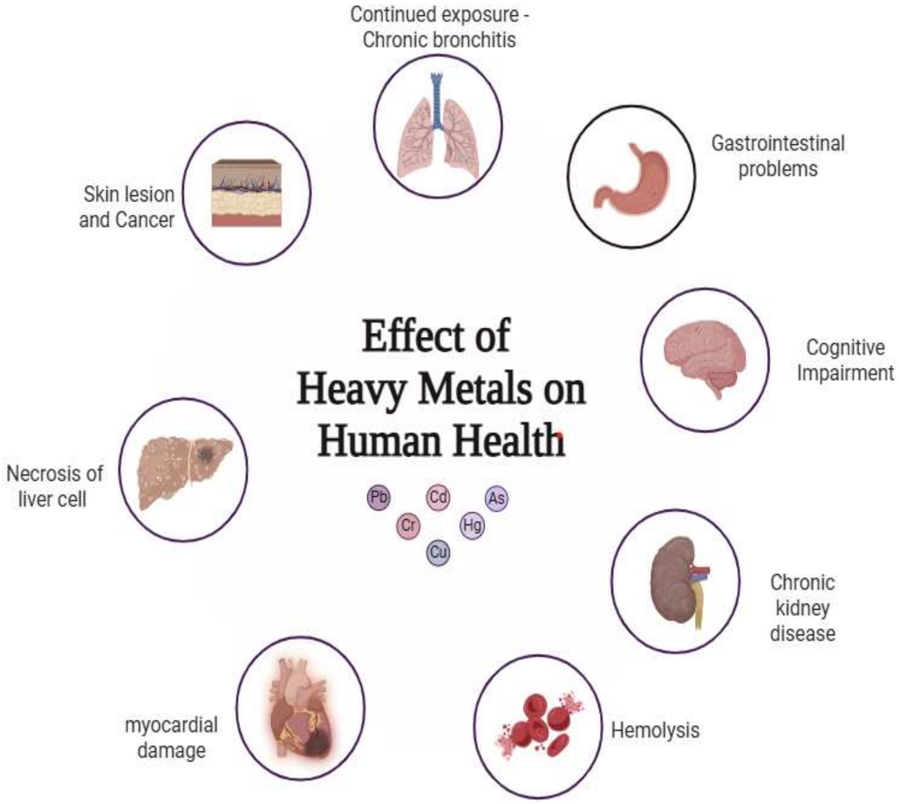

**Fig 2:** Toxicity and Effects of Heavy Metals on Human Health due to prolonged Exposure

in effective when applied to high concentrations of metals in water. Furthermore, the absence of biosurfactants limits the process due to elevated toxicity. In Reverse osmosis, the use of high pressure leads to membrane fouling and breaks down when the contaminants build up on the membrane surface (51). Extended processing time and less practicality are the disadvantages of the photocatalysis technique (52). Due to various limitations in physicochemical processes, Adsorption has been regarded as the most effective approach for removing heavy metals from water, and it is the preferred method due to its effectiveness, economic feasibility, technological viability, low maintenance, procedural simplicity, reusability of adsorbents. Adsorption involves the transfer of a pollutant, such as heavy metals, from an aqueous solution to the surface of the adsorbent, where heavy metal ions are attached through physical or chemical interactions (53). Adsorbents possess numerous advantageous characteristics, such as efficient transport and kinetics, enhanced selectivity for rapid separation, thermal, chemical, and mechanical stability, resistance to fouling, regenerative capacity, minimal solubility in contact with liquids, extensive surface area, high efficacy, suitable pore size and volume, consistency, viability, accessibility, easy regeneration methods, affordability, minimal environmental impact. (31). Various engineered or innovative adsorbents were discussed in terms of their nature of the of raw materials utilized to obtain adsorbents that are suitable for specific heavy metal. The following subsections (4.1-4.6) present recent studies on the adsorption of individual heavy metals using diverse adsorbents, highlighting their adsorption capacity, versatile synthesis and modification methods, optimized parameters, and reusability, providing a information that can be considered when development of adsorbents used in the application in real-world water treatment systems.

### *Chromium*

Chromium is a widely used heavy metal with numerous industrial applications, resulting in increased contamination in water matrices. Hexavalent chromium (Cr(VI)) is the most prominent form of chromium present in different states like $HCrO_4^-$, $CrO_4^{2-}$, or $Cr_2O_7^{2-}$, depending on the pH of the solution. Due to its anionic nature and high solubility, even at lower concentrations, the removal of hexavalent chromium from water matrices has been challenging. However, adsorption has proven to be an effective method among various remediation strategies. Various operational parameters, including initial concentration, pH, adsorbent dosage, and contact time, influence Cr(VI) removal from water. A wide range of simple to innovative adsorbents has been developed for the effective adsorption of Cr(VI) from water. Table 2 presents a comprehensive overview of recent studies on various adsorbents developed for the removal of Cr(VI), ranging from simple biochar to innovative metal-organic frameworks incorporating nanoparticles. Table 2 also provides detailed information about the synthesis method, modifications involved, and parameters optimized to achieve higher Cr(VI) removal, offering a consolidated advancement in the removal of Cr(VI) from aqueous solutions. Most of the adsorbents synthesized were obtained from green waste, including water hyacinth, rice straw, olive pomace, eucalyptus twigs, and peanut. These biomasses are rich in lignocellulosic content, which has many functional groups that can undergo carbonization and favor surface modification. The use of waste materials and their development into value-added materials for environmental remediation aligns with the Sustainable and eco-friendly approach. Islam et al., (54) used rice straw Zeng H et al., (55) utilized eucalyptus twigs and leaves Alouiz et al., (56) used olive pomace. Innovative and engineered raw materials like nanoparticles, nanocomposites, and chitosan-based adsorbents were developed by Irshad et al., (57), Niu et al., (58), Hu et al., (59) providing increased surface area, porosity, and enhanced functional groups that help in improving the removal efficiency of Cr(VI). Modification and various synthesis methods are employed to tailor the adsorbent and achieve a higher adsorption capacity. Pyrolysis was the most commonly used method for synthesizing biochar. The two-step pyrolysis method, with chemical activation using phosphoric acid ($H_3PO_4$), was preferred to increase the surface area, porosity, and addition of functional groups on the surface of the biochar. Activated eucalyptus biochar (AC), teff based activated carbon (TSAC), olive pomace activated carbon were activated prior to pyrolysis with phosphoric acid. The chemical activation before pyrolysis and after pyrolysis increased the surface area by five times and a considerable increase in pore density and pore size also was noted in case of Activated eucalyptus biochar and increase surface area was noted in olive pomace activated carbon. FTIR analysis confirmed the presence of hydroxyl, carboxyl, aromatic and phosphate groups. The presence of oxygenated groups and aromatic and aliphatic groups helps in the metal binding. The phosphoric acid activation introduces and enhances P-O and C-O which aids in the adsorption of Cr(VI). Qu et al., (60) developed an innovative adsorbent using water hyacinth powder as raw material which involves one-step doping microwave-assisted pyrolysis activation. the release of gas on the surface of the material created more pores and folds making it more porous and giving space for the Iron ($Fe^0$) particles to spreads without clumping. New

**Table 2**: Chromium Removal from Water Using Different Adsorbents

| S. No | Adsorbent material | Source/ Type | Modification/ synthesis method | Optimum parameters | Adsorption capacity (mg/g) | Isotherm Model/ kinetics | Reusability | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | ZnBDC/ CSC composite | Zn-MOF + Chitosan | Citrate Crosslinked, Zn-MOF coated | pH- 5 Initial concentration -100mg/L Contact time-25 min | 225 ± 4 mg/g | Langmuir, pseudo-first-order kinetics | 85% | (58) |
| 2 | Activated Eucalyptus Biochar (AC) | Eucalyptus twigs and leaves | Phosphoric acid activation + pyrolysis @500 °C | pH-2, initial concentration – 100 mg/L | - | Pseudo-second order kinetics | - | (55) |
| 3 | Fe/N co-doped porous hydro char, $MP_1HC_{MW}$ | Water hyacinth powder | One-step N doping, microwave-assisted pyrolysis activation | pH - 3.66 initial concentration - 100 mg/L contact time-120 minutes | 274.34 mg/g | Sips, Avrami kinetic model | 73.91 % | (60) |
| 4 | Iron-modified rice straw biochar (FMRSB) | Rice straw | $FeCl_3·6H_2O$, $FeSO_4·7H_2O$ | pH- 3 initial concentration - 20 mg/L contact time of 180 min | 45.5mg/g | Sips model, pseudo-second order kinetics | - | (54) |
| 5 | Magnetic Biochar ($MBC_{PH}$) | Peanut husk | Impregnation of iron oxide onto peanut husk followed by Pyrolysis | pH- 2 Initial concentration -50mg/L Contact time-180 minutes | 75.5 mg/g | Pseudo-second order kinetics | 71.79% | (62) |
| 6 | Zinc oxide nanoparticles | *Ficus benghalensis* | green synthesis | pH-4 initial concentration -30mg/L contact time-240 minutes | 46 mg/g | Langmuir, | - | (57) |
| 7 | Teff Straw-Based Activated Carbon (TSAC) | *Eragrostis teff* straw | Synthesised using phosphoric acid (H□PO□) followed by calcination at high temperature | pH -2 initial concentration -20mg/L contact time-60 minutes | 49.285 mg/g | Langmuir, Freundlich, pseudo-second-order model | - | (63) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 8 | Cucurbituril-modified magnetic chitosan microspheres (CB/MS) | Magnetic chitosan | CB on magnetic chitosan by hydrothermal | pH range- 2-8 | 297.3 mg/g | Langmuir, Pseudo-second order kinetics | 83.2 % | (59) |
| 9 | *Sesbania bispinosa* biochar (SBBC) nanocomposite | *Sesbania bispinosa* | Impregnated with Cu-oxide Mn-oxide | pH- 4<br>initial concentration - 50mg/L<br>contact time-120 minutes | 75 mg/g | Freundlich pseudo-second-order kinetics | 89.6 % | (64) |
| 10 | Activated carbon | Olive pomace | Activation using phosphoric acid and heat treatment using a muffle furnace | pH-2<br>contact time-120 minutes | 68.659 mg/g . | Freundlich, pseudo-second order kinetics | - | (56) |

nitrogen-containing functional groups are also formed on the surface and this active sites better adsorb and bind to the Cr(VI) ions, achieving adsorption capacity of 274.34 mg/g. Adsorption process mainly depends upon the parameters like pH, initial concentration, adsorbent dose, contact time. the Cr(VI) adsorption studies were carried out typically between pH 2-4 where the Cr(VI) exists in $HCrO_4$. Chromium ions, with a negative charge, are electrostatically attracted to the positively charged surface of the adsorbent in acidic conditions. Consequently, at lowered pH levels, enhanced adsorption efficacy was noted, whereas an increase in pH corresponded with a decline in adsorption efficiency (61). The adsorption of chromium ion also attained equilibrium between the contact time 120-180 minutes is due to the various modification in the surface of the adsorbent which could be the reason for the efficient adsorption of Cr(VI) in moderate contact time. Adsorption capacity across the studies ranged from 11.91 mg/g to 297.7 mg/g. Cucurbituril-modified magnetic chitosan microspheres (CB/MS) developed by Hu et al., (59) have the highest adsorption capacity with introduction of CB onto to chitosan which lead to increase in the specific surface area and favourable for the increased capture of the Cr(VI) ions. Kinetic studies and equilibrium data showed the adsorption of Cr(VI) followed pseudo-second order and Langmuir model indicating that chemisorption occurs between the Cr(VI) and the surface electron donating functional groups leading to monolayer adsorption on the homogenous surface. Reusability studies were conducted to determine the long term usability of the adsorbent *Sesbania bispinosa* biochar (SBBC) nanocomposite developed by Tariq et al., (64) showed Cr removal of 89.1% for the first cycle and slightly decreased to 81.60% for the fourth cycle and also showed stability with less leaching the metals from the composite. The studies reviewed showed the different range of adsorbents that has shown favourable for the adsorption of Chromium from aqueous solution. the comprehensive understanding of this parameter is essential for developing more advanced adsorbents that are more effective in water treatment.

### ***Copper***

Copper exists in three forms: Cu(0), Cu(I), and Cu(II), with Cu(II) being the most hazardous and prevalent in the environment. It had a wide range of applications in various industrial sectors, leading to toxic Cr(II) in the industrial effluent stream. Copper also infiltrates surface and groundwater systems in aquatic environments and may subsequently contaminate drinking water, posing a risk to human health. Cu(II) pollution has increased in the global marine environment and is recognised as a significant heavy metal pollutant owing to associated health risks (25). Table 3 provides a detailed summary of the different adsorbents that were developed for the removal of Cu(II) from water matrices by adsorption. Among the reported adsorbents natural materials and novel engineered composites have been explored. For example, sawdust-chitosan nanocomposite beads, chitosan montmorillonite composite aerogel (CS-MMT), Cellulose-zeolite hydrogel, novel collagen-based (SA/BHC)@TE aerogel, Carboxymethyl cellulose CMC) these innovative adsorbents utilized the combined benefits of biopolymers like chitosan, cellulose, collagen and materials like sawdust, montmorillonite and zeolite. These materials are sustainable and have metal-binding capacity due to the presence of surface functional groups like amino, carbonyl, amide, phenolic, and hydroxyl (65) (66) (67) (68) (69). Additionally biochar obtained from *Ascophyllum nodosum* by slow pyrolysis with different increasing pyrolysis temperature lead to the increase in the carbon content, aromaticity, high specific surface area and porosity with maximum adsorption capacity of 223 mg/g and Gum seyal thermochemically modified by pyrolysis followed by chemical modification using ammonium pyrrolidine dithiocarbonate (APDC) lead to the increase in the mesoporous which was critical for the adsorption of Cu(II) with increased adsorption capacity of 211.24 mg/g. other notable methods used for the synthesis of adsorbents were Coprecipitation, Hydrothermal synthesis, sol-gel method, crosslinking synthesis or modification (70) (71) (72) (66) (73). Notable synthesis method through which an adsorption capacity of 397.1 mg/g was mechanical force assisted green synthesis of Carboxymethyl cellulose (CMC). The green synthesis method used was alkaline treatment using sodium hydroxide (NaOH) to disrupt the highly crystalline structure of cellulose which was confirmed by X-Ray Diffraction (XRD) followed by the mechanical force assisted synthesis which uses shear, compression and extrusion force in closed plasticizing machine in absence of solvents leading to increase in the degree of substitution to 0.9 which significantly increase the surface-active sites and adsorption capacity (69). Alginate based adsorbent developed by Hao et al., (72) was obtained by crosslinking and merging of two metal ions like Fe(III) and Al(III) with sodium alginate, sodium graphene oxide and montmorillonite which showed a high specific surface area of 429.75 m2 /g it was due to metal ion Fe(III) ability to form coordination with more ligands due to large radius and creating a strong cross-linking effect. The introduction of metal ions with varying coordination configurations allows for effective control over the slit structure and pore density of the adsorbents, and improved the selectivity for copper ion adsorption and exhibited an adsorption capacity of 116.44 mg/g. The studies indicate that synthesis method and modification methods also play a crucial role in the increased adsorption of Cu(II). In case of operating parameters, the maximum adsorption of Cu(II) occurred between 5-6 in acidic conditions, indicating the $H^+$ ions are limited and protonation increases and complexation of Cu(II) with surface functional groups and pH less than 6 leads to the precipitation of Cu(II) and limiting adsorption leading to decreased adsorption efficiency (72). Isotherm and kinetic studies were conducted to understand the metal-adsorbent interactions. Most of the adsorbents in Table 3 followed Langmuir monolayer adsorption on a homogeneous surface. Cellulose zeolite hydrogel, carboxymethyl cellulose (CMC) followed the Freundlich isotherm, indicating adsorption of Cu(II) occurs in multi molecular layer (67). In case

**Table 3**: Copper removal from water using different adsorbents

| S. No | Adsorbent material | Source/ Type | Modification/ synthesis method | Optimum parameters | Adsorption capacity (mg/g) | Isotherm Model/ kinetics | Reusability | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | Sawdust-Chitosan Nanocomposite beads | Sawdust, chitosan | - | pH- 5<br>Initial concentration -50mg/L<br>Contact time- 70 min | 7.32 mg/g | Freundlich | - | (65) |
| 2 | Ascophyllum nodosum-derived Biochar | Ascophyllum nodosum seaweed | Slow pyrolysis at different temperatures | pH-5,<br>initial concentration -100 mg/L<br>contact time- 350 minutes | 223 mg/g | Langmuir | - | (70) |
| 3 | Chitosan-montmorillonite composite aerogel (CS-MMT) | Montmorillonite, Chitosan | Sol gel method | pH - 6 | 86.95 mg/g | Langmuir, pseudo-second order kinetics | 85% | (66) |
| 4 | Alginate-based adsorbent | Fe-GMS | Crosslinking modification with $Fe^{3+}$ /$Al^{3+}$ | pH- 6<br>adsorbent dose- 0.04g/L | 116.44 mg/g | Langmuir, pseudo-first order kinetics | 81.80 % | (72) |
| 5 | Cellulose-zeolite hydrogel ($RH_4Z_4$) | Rice husk | Crosslinking synthesis using NaOH/urea + zeolite (4:2 ratio) | pH-6<br>contact time- 480 minutes | 10.77 mg g–1 | Pseudo-first order, Freundlich | - | (67) |
| 6 | magnetic gamma alumina nanoparticles (MGAl-NPs) | Aluminium nitrate ($Al(NO_3)_3$) iron oxide ($Fe_2O_3$) | Co-precipitation Hydrothermal synthesis | pH- 5<br>initial concentration - 50mg/L<br>adsorbent dose-0.1g | 34.48 mg/g | Langmuir, Pseudo-second order | 97.1% | (73) |
| 7 | Modified Gum Seyal biochar (BC APDC) | Gum seyal | Pyrolysis (muffle furnace), chemical modification using ammonium pyrrolidine Di thiocarbamate (APDC) | pH-5 | 211.24 mg/g | Langmuir, pseudo-second-order | 60.26 % | (71) |

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|---|---|---|---|---|---|---|---|---|
| 8 | Novel collagen-based (SA/BHC) @TE aerogel | Sodium Alginate, Bovine Hide Collagen, Tannin Extract | Hydrogen bonding, crosslinking | pH-6<br>contact time-90minutes<br>adsorbent dose-40mg | - | pseudo-second-order | 80 % | (68) |
| 9 | mercaptopropionyl corn straw (MPCS) | Corn straw | Alkali pretreatment, modification using the sulfhydryl group | pH-5<br>initial concentration-50mg/L<br>contact time-80 minutes | 8.25 mg/g | Langmuir, pseudo-second-order | 98.34% | (74) |
| 10 | Carboxymethyl cellulose CMC) | α-Cellulose | Mechanical force-assisted green synthesis | Initial concentration-850 mg/L | 397.1 mg/g | Freundlich | - | (69) |

of kinetic studies most of the adsorbents followed pseudo-second order kinetics, signifying the adsorption followed chemisorption in which the functional groups form a strong, irreversible bond with the metal during adsorption. The regeneration efficiency of an adsorbent is a critical metric for assessing its practical efficacy. Effective adsorbent materials provide not only a high adsorption capacity but also significant reusability and stability. Magnetic gamma alumina nanoparticles (MGAl-NPs) showed regeneration efficiency of 97.1% after three consecutive adsorption-desorption cycle. Similarly, mercaptopropionyl corn straw (MPCS) adsorbent exhibited a reusability of 98.34% after five cycles, indicating a stability, high reusability efficiency, and increased adsorption capacity (73) (74). The reviewed studies on different adsorbents for the removal of Cu(II) from water matrices depends on the various parameters from synthesis methods to operating conditions. Key observation was that the choice of the adsorbent must balance preparation complexity, reusability and adsorption capacity. Both natural material and innovative adsorbents are explained to understand the depth and behaviour of the adsorbents used for the adsorption of Cu(II). This information could help in the cost effective and sustainable development of more complex and engineered adsorbents with better adsorption capacity and reusability and more fit for practical applications.

### ***Cadmium***

Cadmium is a non-essential heavy metal that is toxic even in lower concentration. Cadmium heavy metal contamination in water is rapidly increasing due to the human activities since cadmium has wide range of usage in the industry while its sources and contamination routes are discussed earlier, this section mainly focuses on Table 4 where different adsorbent that are designed specifically for the removal of cadmium and its adsorption performance are discussed. The adsorbents discussed in the table are vastly diverse like nanocomposites, agricultural waste, nano zeolite composites, insect waste derived adsorbent, metal organic framework and most commonly used activated charcoal. The synthesis and modification methods involved in the development of these engineered adsorbents are the most crucial factor to enhance the adsorption of $Cd^{2+}$ ions. Magnetic tea waste biochar (MTWBC) was synthesized by pyrolysis followed by impregnation of biochar

**Table 4**: Cadmium removal from water using different adsorbents

| S. No | Adsorbent material | Source/ Type | Modification/ synthesis method | Optimum parameters | Adsorption capacity (mg/g) | Isotherm Model/ kinetics | Reusability | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | Nanozeolite-Y/xanthan gum (GZX) | Rice straw | Nanozeolite crosslinking with $Fe^{3+}$ modified using glutamine | pH- 6<br>Initial concentration -50mg/L<br>Contact time-50 min | 339.1 mg/g | Langmuir, pseudo-second-order | - | (77) |
| 2 | Magnetic tea waste biochar (MTWBC) | Tea waste | Pyrolysis followed by impregnation with $FeCl_3$ | pH-8<br>Contact time-360 minutes<br>Adsorbent dose-2g/L | 812.74 mg/g | Tempkin, Modified Freundlich kinetic | 8.73% | (75) |
| 3 | Fe-Ca modified biochar (FeCa-BC) $Fe_4Ca_1BC$ | Wheat straw | Pyrolysis followed by modification using $Fe(NO3)_3\cdot 9H_2O + CaCl_2$ | pH-7 | 76.70 mg/g, | Pseudo-second-order | - | (82) |
| 4 | Mealworm Frass(MF) | mealworm frass | - | pH-6<br>contact time-30 minutes<br>adsorbent dose-8g/L | 48.1 mg/g, | Langmuir, pseudo-second order kinetics | 90% | (83) |
| 5 | Chitosan@*fig* Branch Biochar | Fig branch, chitosan | Pyrolysis, modified using chitosan | pH-6<br>initial concentration -100mg/L<br>contact time-90minutes | 62.25 mg/g | Langmuir, pseudo-second order | 92.3% | (79) |
| 6 | A Novel 3D N-, S-rich GO composite | Graphene oxide, 2-mercapto-1,3,4-thiadiazole (MTD) | one-step facile hydrothermal method | pH-7<br>contact time-40mintues | 37.176 mg/L | Langmuir, pseudo-second order | >92% | (80) |
| 7 | Sulfur-functionalized sawdust biochar Na2S2O3+ SDB350 | Sawdust, Sulphuric acid, sodium sulfide | Pyrolysis, modification by immersion of biochar | pH- 5<br>contact time-5 minutes | 34.14 mg/g | Langmuir, pseudo-second-order model | - | (84) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 8 | oxidant-modified biochar (OMB) | *Platanus orientalis* Linn (POL) leaves | Pyrolysis followed by modification using oxidizing agent | pH-6 | 52.5 mg $g^{-1}$ | Langmuir, pseudo-second order | - | (85) |
| 9 | TMU-5 Metal Organic Framework (MOF) | N,N'-(2,5-bis pyridyl)-*hexa*-3,4-diaza-2,4-diene (4-bpdh) | Sonochemical synthesis, coated with silica layer | pH-6<br>initial concentration - 20mg/L<br>adsorbent dose-15mg/L | 635 mg/g | Langmuir | - | (76) |
| 10 | Activated charcoal | commercial | - | pH-5<br>contact time-60 minutes | 682.5 mg g−1 | Langmuir<br>pseudo-second-order kinetics | - | (78) |

with ferric chloride ($FeCl_3$). Process conditions of pyrolysis like temperature, duration of pyrolysis followed by differing concentration of ferric chloride for impregnation of biochar were optimized using Response surface methodology to obtain high removal efficiency of cadmium. The optimized parameters for pyrolysis were a temperature of 200ºC for 4 hours followed by impregnation with a 0.9 g/g concentration of ferric chloride which showed an 80% removal of $Cd^{2+}$.

The functional groups like hydroxyl, carbonyl, amino, carboxyl on the surface were enhanced during pyrolysis assisted impregnation. The specific surface area was around 15 $m^2/g$ with presence of mesopore and the paramagnetic properties of the adsorbent was also confirmed by S shaped curve obtained from Vibrating Sample Magnetometry (VSM). The crucial optimization of adsorbent showed a maximum adsorption capacity of 812.7mg/g of $Cd^{2+}$ ions which is twenty five times more higher than the adsorption capacity of biochar produced from similar agricultural waste (75). Ul Mehdi et al., (76) utilized a Sono chemical synthesis followed by silica coating for the development of highly innovative silica-coated metal-organic framework (SiO2@TMU-5). The coating of MOF using silica led to the development of the larger pores with pore size up to 17.15 nm which perfectly captures the cadmium during the adsorption process and showed an excellent adsorption capacity of 635 mg/g. other notable synthesis or modification methods used for the development of the adsorbents are nano zeolite crosslinking with $Fe^{3+}$ and modification using glutamine in developing Nanozeolite-Y/xanthan gum (GZX) which also showed a adsorption capacity of 339.1 mg/g. crosslinking of adsorbent with amino acid like glutamine increased the stability of the adsorbent and also strengths the adsorbent material structure (77). Though synthesised adsorbents showed an impressive adsorption capacity, implying the importance of tailored functionalization and surface engineering, it is mandatory to analyze its performance with commercially available adsorbents. Among which the activated carbon was most used material due to availability, low cost, and performed well in the water treatment studies. For instance, activated carbon showed an adsorption capacity of 682.5 mg/g (78), which is the second highest in the reported adsorption studies in Table 4, despite the superior adsorption capacity of the engineered materials commercial material also showed significant efficiency and industrial relevance. Other important parameters like pH, initial concentration, contact time, adsorbent dosage were also optimized to achieve higher removal efficiency of cadmium from water. Optimum pH value for cadmium adsorption lies between the range 5-7, indicating the influence of surface charge and metal speciation. Cadmium exists as $Cd^{2+}$ when pH is <7 and when pH is raised from 3 to 6 the surface tends to become less protonated surface leading to the drop in $H_3O^+$ and during adsorption competition for site between $H_3O^+$ and $Cd^{2+}$ favouring more adsorption of $Cd^{2+}$ ions. When the pH is increased above 7 the precipitation of cadmium occurs leading to decrease in the adsorption capacity, so the adsorption of cadmium is more efficient in slightly acidic to neutral pH conditions (77). Contact time varied from 50-360 minutes for different adsorbents it was due to the initial rapid uptake of $Cd^{2+}$ ions followed adsorption of the metal ions based on the presence of pores. Isotherm studies showed the best fit to be Langmuir model in most of the engineered adsorbent and commercial activated carbon indicating a homogenous monolayer adsorption due to presence of uniform and stable pores. Temkin model was considered to be the best fit for Magnetic tea waste biochar (MTWBC) with possess maximum adsorption capacity among the reported engineered adsorbents indicates the possibility of multilayer adsorption due to presence of diverse porous and heterogenous surface in the biochar. The varying difference in the fitting model also provides a deep insight in the structural complexity of the adsorbents and its interaction with cadmium during adsorption (79) (80) (75). Kinetic studies mostly followed pseudo-second order, indicating chemisorption as the mechanism behind the adsorption of $Cd^{2+}$ implying the adsorption is not only physical interaction but the formation of surface bonding between the adsorbent and $Cd^{2+}$ which can be attributed to the presence of surface functional groups. The regeneration studies mostly not reported but the data provides a viability of adsorbent and its scability in industrial applications. Chitosan@*fig* Branch Biochar showed an impressive reusability of 92.3% (79). Overall, the comparative evaluation gives key information for developing practical adsorbents for cadmium removal.

### *Lead*

Lead (Pb(II)) is a type of heavy metal ion that is detrimental to the ecological environment and the food chain. The wastewater containing Pb(II) ions has emerged as a critical and challenging aspect of environmental protection. A recent study indicated that the electroplating sector, metal smelting, automotive fuel combustion, and pesticide application are the primary sources of Pb(II) effluent. Consequently, it is imperative to adopt viable and sustainable methods for the removal of Pb(II) ions from industrial effluent (81). Adsorption is one of the cost-effective and sustainable methods for removing lead from wastewater, and it is primarily discussed in exploring different adsorbents that are engineered, scalable, and practical, as shown in Table 5. Diverse range of adsorbents were included in Table 5 to understand the efficiency of adsorbent in Pb(II) removal from aqueous solutions. It includes carbon-based adsorbent, nanocomposites, novel organic covalent framework, biopolymer-based adsorbents. Carbon-based adsorbents include Rice Straw Biochar, *Prosopis juliflora* biochar, Red mud-modified biochar (AMHC-C5R5), pinewood biochar (86) (87) (88). Here the raw materials used for the development of the carbon-based adsorbents mostly are agricultural waste like rice husk, corn cob, pinewood. Carbon-based materials are more extensively explored due to their low cost, high porosity, and ease of modification and surface functionalization. Red mud-modified biochar (AMHC-C5R5) developed using corn cob and red mud. The synthesis method adopted was microwave-assisted hydrothermal carbonization (MHTC), followed by $K_2CO_3$ activation. MHTC enhances the crystallinity, char production, and thermal stability while preserving carbon and oxygen content further activation using potassium

**Table 5**: Lead removal from water using different adsorbents

| S. No | Adsorbent material | Source/ Type | Modification/ synthesis method | Optimum parameters | Adsorption capacity (mg/g) | Isotherm Model/ kinetics | Reusability | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | magnetic carbon (MBC) | Pine cone | Pyrolysis | pH -7 | 123.38 mg/g | Langmuir, pseudo-second order | - | (90) |
| 2 | Cellulose nanofiber alginate hydrogel beads | Cellulose nanofiber (CNF), sodium alginate beads | Simple crosslinking | pH- 4.2<br>initial concentration - 300 mg/L<br>contact time-180 min | 318.47 mg g | Langmuir, pseudo-second order | >80% | (92) |
| 3 | nanocomposite GO/CMC/FeNPs | Carboxymethylcellulose (CMC) graphene oxide (GO) iron nanoparticles (FeNPs) | Hydrothermal synthesis | pH-6<br>contact time-30 minutes | 1850 mg/g | Pseudo-second order | - | (91) |
| 4 | Powdered activated carbon (PAC-5) | Granular activated carbon, nitric acid ($HNO_3$ ) | Acid functionalization | - | 28.70 mg/g | Langmuir | - | (96) |
| 5 | Novel covalent organic framework | Tetrafluoroterephthalonitrile, Hydroxylamine hydrochloride and anhydrous potassium carbonate | Amidoxime modification | pH- 5<br>initial concentration - >400 mg/L<br>adsorbent dose- 10mg/L | 368.68 mg/g | Langmuir | 14.05 % | (93) |
| 6 | Araucaria gum/calcium alginate composite beads (CR11) | Araucaria heterophylla tree's gum, calcium alginate | Bead formation using calcium alginate crosslinking | pH-6<br>initial concentration - 200 mg/L<br>Adsorbent dose- 3 g/L | 149.95 mg/g | Langmuir Pseudo-second-order | 5% | (94) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 7 | Rice Straw Biochar | Rice straw | Soxhlet extraction, pyrolysis | initial concentration - 20mg/L adsorbent dose- 10mg | 183.8 mg/g | Langmuir, pseudo-second order | - | (86) |
| 8 | Red mud-modified biochar (AMHC-C5R5) | Corn cob, red mud | microwave-assisted hydrothermal carbonization<br>$K_2CO_3$ activation | pH-4<br>Adsorbent dose- 1g/L | 197.83 mg/g | Freundlich, pseudo-second order | 78.46 % | (88) |
| 9 | *Prosopis juliflora* biochar nitric acid modified | *Prosopis juliflora* | pristine, phosphoric, and nitric acid modification | - | 18.72 mg $g^{-1}$ | Freundlich, pseudo-second-order | - | (87) |
| 10 | Pinewood biochar dispersed with greigite and magnetite nanoparticles | Pinewood, greigite, magnetite nanoparticles | Co-precipitation method | pH-5 contact time- 120 minutes | 138.9 mg/g | Langmuir, pseudo-second-order | - | (89) |

carbonate enriches the pore structure and surface groups, and it demonstrated an adsorption capacity of 197.83 mg/g (88). Biochar derived from agricultural waste showed great potential in Pb(II) removal, but its recovery has always remained a challenge; hence, studies where magnetic properties are incorporated for the ease of its recovery pinewood biochar dispersed with greigite and magnetite nanoparticles (89) and magnetic pine cone developed from a pine cone incorporated with ferrous sulfate heptahydrate ($FeSO_4 \cdot 7\,H_2O$), ferric chloride hexahydrate ($FeCl_3 \cdot 6\,H_2O$) (90) were also developed to improve the recovery of the adsorbent after adsorption of Pb(II). Though agricultural waste derived biochar with modification and functionalization offers notable adsorption in the removal of Pb(II) it is always outdone by engineered and innovative adsorbents developed using nanocomposites, covalent organic frameworks and hydrogel beads for instance, adsorbents developed using carboxymethylcellulose (CMC), graphene oxide (GO), iron nanoparticles (FeNPs) showed an excellent adsorption capacity of 1850 mg/g which is very high in the removal of Pb(II) by adsorption. The synthesis method hydrothermal carbonization played a crucial role in the enhancing the surface making it more porous with large pores which is of 10μm with composite material having a covalent bond between the CMC, GO and FeNPs (91). Zhao et al., (92) developed Cellulose nanofiber alginate hydrogel beads involving simple crosslinking leading to formation of high specific surface area and porosity and presence of more carboxyl and hydroxyl as surface functional groups provides more active sites which made the adsorption of Pb(II) more efficient with adsorption capacity of 318.47 mg/g. Xiang et al., (93) novel covalent organic framework which are high porous, crystalline, and offers ease of functionalization. It exhibited an adsorption capacity of 368.68 mg/g high removal efficiency was attributed to the presence of high specific surface area of 189.824 $m^2$ /g. The operational parameters pH, adsorbent dose, initial concentration, contact are very important criteria to obtain high adsorption capacity. Majority of reviewed studies the adsorption of Pb(II) was done in the pH range 4 to 7 that is slightly acidic to neutral. At lower acidic pH levels there are more of $H^+$ ions which compete with Pb(II) site and hence adsorption occurs in the range that are not more acidic (92). Initial concentration of Pb(II) varied from the range 200mg/L to 400mg/L the range varying from low to high helps in understanding adsorbent efficiency in the removal of low and high level of heavy metal lead contamination. Mostly engineered or surface modified materials like were able to efficiently adsorb high concentration of Pb(II) (94). Optimized contact time ranged from 30-180 minutes. Equilibrium time of 30 minutes which was faster was reported for nanocomposite due to the presence of its high specific surface area, pore volume and high porosity (90, 91). Isotherm and kinetic modelling were done to understand the mechanism involved in the removal of Pb(II). Langmuir isotherm was reported in the all the studies indicating monolayer adsorption where the adsorbate forms a single layer around the adsorbent. Pseudo second order kinetics was reported in most of the reviewed studies (86) (88) (92). High regeneration efficiency achieved for reported adsorbents were 80% after multiple cycles for most of the adsorbents developed from the agricultural waste and biopolymers (92). On the contrary most of the advanced adsorbents showed less reusability of 14.5% for novel covalent framework and 5% for alginate base adsorbent showing strong irreversible bond between the adsorbent and Pb(II) (93) (94). Various adsorbents, from natural to innovative engineered adsorbents, were reported to understand material property and parameter optimization for the effective adsorption of Pb(II) from water.

***Arsenic***

The Agency for Toxic Substances and Disease Registry (ATSDR) has listed arsenic as the first element followed by other heavy metals like lead and mercury. This list comprises 275 chemicals, prioritised according to their significance as risks to human health. Inorganic arsenic species are more toxic than organic species. Ar(III) is more hazardous than Ar(V) (95). Adsorption a promising technique, was utilized to eliminate arsenic from water due to eco-friendly, cost effective and ease in the developed of versatile adsorbents modifications.

Table 6 gives detailed information above the latest studies on adsorption of arsenic. The table mainly focus on the parameters like source of the raw material used for the adsorbent synthesis, modification methods used, optimal parameters utilized in the studies, kinetics, isotherm studies and percentage of reusability. source of raw material used for the adsorbent developed includes agricultural waste derived biochar's, biopolymers, nanoparticles, metal oxides, and unusual source like marble waste was also explored. Use of a different range of raw materials for the adsorbents promotes circular economy of creating waste into value-added products. The reported studies showed a broad range of variation in the adsorption capacity based on operational parameters, synthesis method and adsorbent composition. The highest adsorption capacity for the removal of Ar(III) reported in the Table 6 was Succinic acid-modified Magnesium–Iron Layered Double Hydroxide (SA/MgFe-LDH) of 181.3 mg/g. layered double hydroxide, which is an anionic clay, was also a nanomaterial synthesised using the precursor magnesium oxide. Followed by the addition of succinic acid and hydrothermal treatment. Succinic acid was mainly used to control the crystal growth in a radial form and dope the crystal with carboxylate ions ($RCOO^-$). The radial form of the crystal altered the pore structure and increased the active sites on the surface of the adsorbent. BET confirmed the presence of mesopores. Since the adsorption capacity is greatly influenced by the presence of active sites and surface morphology and pore density, the synthesis method played a crucial role in increasing the

**Table 6**: Arsenic removal from water using different adsorbents

| S. No | Adsorbent material | Source/ Type | Modification/ synthesis method | Optimum parameters | Adsorption capacity (mg/g) | Isotherm Model/ kinetics | Reusability | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | nanoscale zero-valent iron embedded on polyaniline reinforced with sodium alginate hydrogel microbeads (PANI-SA/ZVI ) | Sodium alginate, alanine, and iron chloride | Chemical synthesis followed by ionic crosslinking | pH range-4-6<br>contact time-180 minutes<br>adsorbent dose-80mg | 104.167mg/g | Pseudo-first order | 86.61 % | (101) |
| 2 | Silver nanoparticles and Fe-Ce mixed oxide supported on polymeric anion exchanger (FeO(OH)-HCO-Ag-D201) | Goethite (α-FeO(OH)), Hydrous ceric oxide ($CeO_2$•$H_2O$), Silver nanoparticles (AgNPs) | Encapsulation | pH range-8-9<br>initial concentration -<br>adsorbent dose- | 40.12 mg/g | Langmuir<br>Pseudo-second-order | - | (100) |
| 3 | bimetallic zinc-iron-modified biochar (1Zn-1Fe-1SBC) | Sugarcane bagasse, zinc chloride, iron chloride | Pyrolysis, impregnation | pH-5<br>adsorbent dose- 0.2g/L |  | Langmuir<br>Pseudo-first order | - | (104) |
| 4 | $H_3PO_4$-modified Tea Waste biochar (MTWB) | Tea waste, phosphoric acid | Acid modification | pH-8<br>adsorbent dose-0.08g<br>initial concentration - 1mg/L | 37.432 mg/g. | Freundlich,<br>Pseudo-second order | - | (102) |
| 5 | Iron-modified biochar from As-enriched *P. vittata* (FAs-BC) | *Pteris vittata* | Pyrolysis, $FeCl_3$ modification | pH-7 | 70.9 mg/g) | Pseudo-second order | 71.1 % | (98) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 6 | Succinic acid-modified Magnesium–Iron Layered Double Hydroxide (SA/MgFe-LDH) | Magnesium oxide, Iron(III) nitrate nonahydrate – $Fe(NO_3)_3 \cdot 9H_2O$, Succinic Acid) | Co-precipitation, addition of succinic acid, and hydrothermal treatment | pH range-3-8.5 | 181.3 mg/g | Freundlich, Elovich, Intrinsic Model. | - | (97) |
| 7 | marble waste powder | Raw marble waste powder | - | Contact time-60mintues<br>Adsorbent dose-3g/L<br>Initial concentration-0.25mg/L | 0.386218 mg/g | Liu, non-linear pseudo second order | 70.20% | (105) |
| 8 | Bagasse-Mn-Al (B-Mn-Al) | Sugarcane bagasse, magnesium, aluminium metal | Pyrolysis, impregnation, and coprecipitation. | pH-2<br>initial concentration - 496 µg/L.<br>contact time-65 minutes<br>adsorbent dose-1.375 g/L | 55.0964 mg/g | Langmuir, pseudo-second order | - | (106) |
| 9 | Novel Advanced graphene oxide | sodium nitrate, potassium permanganate, graphene oxide powder | Modified Hummer method | A ratio of 1 g of $NaNO_3$ and 6.6 g of $KMnO_4$ used to synthesize 1 g of graphite<br>pH-4 | 70.66 mg/g | Langmuir, | - | (99) |
| 10 | Ball-milled natural pyrite coupled with sulfite | Natural pyrite, | Ball milling using 50 g agate balls (diameter of 10 mm) | pH-6<br>Adsorbent dose-0.5 g/L<br>Catalyst dose-0.05 g/L | 37.64 mg/g<br>73.43 mg/g | Langmuir, pseudo-first order | - | (107) |

adsorption capacity and also in the increased removal efficiency of arsenic (97). Iron-modified biochar from As-enriched *P. vittata* (FAs-BC) was another novel adsorbent developed from the plant *Pteris vittata*. Iron-modified biochar was synthesised using pyrolysis followed by modification using $Fecl_3$. Functional groups involved in the adsorption of Arsenic was hydroxyl group indicating surface functional group complexation and showed an adsorption capacity of 70.9 mg/g (98). Novel graphene oxide (GO) developed by modified hummer method showed an adsorption capacity of 70.66 mg/g. optimization of the GO was done using RSM, including two factors: sodium nitrate and potassium permanganate. The use of strong oxidizing agents increased the surface oxygenated functional groups. These groups act as the active interaction site for arsenic ions (99). The other synthesis and modification method discussed in Table 6 were encapsulation, coprecipitation, ionic crosslinking and acid modification (100) (97) (101) (102). This modification often led to the increased efficiency in the adsorption of the arsenic. Optimum condition reported for the adsorption of arsenic in the Table 6 are pH, adsorbent dose, initial concentration, contact time. The optimum pH range for arsenic adsorption was from 4-7, which is an acidic to basic range. Under very acidic conditions (pH < 3), the efficacy of adsorption declines due to proton competition, leading to a reduction in available active adsorption sites. At moderate acidic pH values, the pentavalent form of arsenate can exist as $H_2AsO_4^-$ or $HAsO_4^{2-}$, which exhibits a stronger propensity to bind than arsenite. The efficacy of arsenic removal improves with increasing pH (101). The shortest contact time of 60 minutes were noted for marble waste powder, though it did not show impressive adsorption capacity. Bagasse-Mn-Al (B-Mn-Al) developed from sugarcane bagasse showed an notable contact time of 65 minutes with an initial concentration at very limited range of 496 µg/L and adsorption capacity of 55mg/g (103). Arsenic adsorption studies were mostly carried out using Arsenic(III) and Arsenic(V). Isotherm modelling and kinetic studies were done. Langmuir isotherm and pseudo-second order was the best fit to most of the adsorbents, indicating monolayer adsorption and rate limiting step to be chemical adsorption. Reusability data was not presented for most of the adsorbents listed in the Table 6. Nanoscale zero-valent iron embedded on polyaniline reinforced with sodium alginate hydrogel microbeads (PANI-SA/ZVI ) after subsequent three cycles showed a reusability of 86.61% indicating the reusage of the adsorbent (101). Iron-modified biochar from As-enriched *P. vittata* (FAs-BC) managed to obtain 71.1% after 5 cycles indicating the sustainability of the adsorbent and its reusability (98). The comparative analysis of the various adsorbent for arsenic removal indicates that different materials demonstrated favourable adsorption capacity. The adsorption of arsenic also mainly dependent on the optimum parameters. Different synthesis method like ball milling, modified hummer method was adopted to increase adsorption capacity by increased surface area, surface functional groups and pore volume through which the removal efficiency of arsenic was improved. To summarize the reviewed adsorption studies gave a detailed explanation of the arsenic removal from water by adsorption and need for the future scope of research to carried out on real time water samples to further develop sustainable adsorbents.

### *Mercury*

Mercury is characterised as a persistent and toxic metal that exhibits a high ability for bioaccumulation. After entering the environment, it can disperse to locations far from its source and persist for up to 360 days; hence, its removal is very much mandatory from water. Adsorption is the most commonly preferred method for removing heavy metals, such as mercury, due to its minimal energy consumption, absence of secondary pollutants, and alignment with the principles of sustainability (103). Table 7 presents a compilation of various innovative adsorbent materials, including natural clay, nanocomposites, and bio-based adsorbents, each possessing unique properties and applications in mercury adsorption. The listed adsorbents have been modified using different approaches, exhibiting diverse variations in surface functionalisation, pore diversity, and their mechanisms of interaction with mercury ions. Natural kaolin clay, biopolymers, metal-organic frameworks, and nanocomposites are some of the adsorbents listed in Table 7, along with detailed experimental conditions. The synthesis method plays a key role in increasing the adsorption capacity. For instance, metal-organic framework (MOF88), which was synthesised by following defect engineering and post-modification, exhibited an incredible adsorption capacity of 957.94 mg/g. Formic

**Table 7**: Mercury removal from water using different adsorbents

| S. No | Adsorbent material | Source/ Type | Modification/ synthesis method | Optimum parameters | Adsorption capacity (mg/g) | Isotherm Model/ kinetics | Reusability | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | modified kaolin (K-SLS) | Kaolin, Sodium lauryl sulfate (SLS), Sodium Dodecylbenzene sulfonate (SDBS) | Pulverization, surface chemical modification | Contact time-90 minutes | 17.77 mg/g, | Sips model<br>Pseudo-second order | - | (114) |
| 2 | functionalized metal-organic framework (MOF-808) | thiol, oxime, and thiourea, metal-organic framework | Post-synthesis modification, defect engineering | pH-7 | 957.94 mg/g | Langmuir,<br>Pseudo-second order, | 81.37% | (108) |
| 3 | Novel nanofibrous membrane (CPP) | polycaprolactone (PCL), chitosan (CS) | Electro spinning | pH-6<br>adsorbent dose-0.02g<br>contact time-60 minutes | 393.04 mg/g. | Langmuir, pseudo-second order. | 88.4 % | (109) |
| 4 | Novel Chitosan-coated superparamagnetic iron oxide nanoparticles | Chitosan, Iron(III) chloride, Iron(II) chloride tetrahydrate | chemical co-precipitation method, coating of chitosan | pH-6<br>adsorbent dose-10 mg/mL<br>contact time-40 minutes | 62.958 mg/g | Langmuir, pseudo-second order | - | (113) |
| 5 | Bio-Polymeric Blended Nanocomposite | Chitosan, silica nanoparticles, guar-gum | Sol-gel, stirring, sonication, freeze drying | pH-12<br>initial concentration- 50mg/L<br>contact time-90 minutes<br>adsorbent dose-50mg | 36 mg/g | Langmuir,<br>Pseudo-second order | 58% | (112) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | Activated carbon blended with fresh pistachio green shell powder | fresh pistachio green shell, activated carbon powder | Acid activation, | pH-6.13 initial concentration- 36.68 g/L fresh pistachio shell powder dosage-9.21 g/L activated carbon dosage-7.25 g/L contact time -78 min | 3.392 mg/g | Langmuir | 74% | (115) |
| 7 | Natural kaolin (NK) clay | Kaolin clay | - | pH - 6.81 contact time-90 minutes | 10.964 mg/g | Langmuir isotherm model, pseudo second order | 91.36% | (116) |
| 8 | Nanoporous biochar | Rice straw biogas residue | Hydrothermal carbonization, chemical activation using KOH | | 209.65 mg/g | Langmuir isotherm model, pseudo second order | - | (103) |
| 9 | Recycled Tetra Pak waste | Tetra Pak waste | pyrolysis | pH-4 Adsorbent dose- 0.4 g/L | 215.7 mg/g | Sips, pseudo first order | - | (110) |
| 10 | Porous activated carbon from walnut shells | Walnut shell | Chemical activation, pyrolysis | pH-2.1 | 214.1 mg/g. | Langmuir, pseudo-second order | - | (111) |

acid was used as a modulator to create a missing linkers defect in the surface of the MOF using 1-(4-carboxyphenyl)-2- 2-thiourea (CPT). CPT, as it contains carboxylic acid and thiourea, features sulfur and nitrogen atoms that have a higher affinity for mercury ions. This modification was performed after the synthesis of MOF. BET analysis confirmed the presence of micropores and mesopores. Sulfur and nitrogen had uniform dispersion with an octahedral structure, and they introduced a novel functional group, the thiol group(-SH). When the concentration of CPT was increased, the adsorption capacity also increased, indicating that the functional groups contributed to the enhanced adsorption of Hg+ ions (108). Electrospinning was another notable synthesis method used in the fabrication of the novel nanofibrous membrane (CPP). The source involves chitosan, a biopolymer, and polycaprolactone (PCL) at a ratio 8:2(w/w) and concentration of

15%(w/v). The key parameters enhanced by electrospinning are the crystalline structure, which provides a larger surface area, and the exposure of functional groups, including carbonyl, amine, and hydroxyl, that increases the interaction with Hg(II) ions. The increased surface area was confirmed by BET, with a high specific surface area of 62.17 m²/g, featuring a microporous and mesoporous structure. Functional groups responsible for mercury adsorption are oxygen and nitrogen containing groups due to increased O1 peaks intensity. These critical changes and functionalization in the adsorbent led to an excellent adsorption capacity of 393.04 mg/g of mercury ions (109). Carbonized materials developed from waste like biogas rice straw residue, Tetra Pak waste, and walnut shells also showed good removal efficiency. The most common methods used for the synthesis of adsorbents were pyrolysis, hydrothermal carbonization assisted with chemical activation, or modification (110) (103) (111). Nanoporous biochar developed a high specific surface area from 273.26 to 2372.51 $m^2$/g and increased pore volume. The presence of micropores and mesopores contributed to the increased adsorption of mercury ions with an adsorption capacity of 209.65 mg/g (103). In case of Tetra Pak waste, the main functional groups involved in the adsorption of mercury were oxygen-containing groups like hydroxyl (OH), carboxyl (COOH), calcium-oxygen bond(C-O), inducing a complexation between the adsorbent and mercury ion that increased the removal efficiency. Tetra Pak waste showed an adsorption capacity of 215.7 mg/g (110). Porous activated carbon from walnut shells was another carbonized adsorbent reported in the Table 7. The adsorbent was prepared using walnut shell as a carbon source, followed by chemical activation using $K_2CO_3$. Pyrolysis after chemical activation increased the specific surface area 1046.9 $m^2$ /g which led to more uptake of mercury ion and the adsorbent exhibited an adsorption capacity of 214.1 mg/g (111). The optimum conditions for achieving maximum removal efficiency are pH, initial concentration, adsorbent dose and contact time. for mercury adsorption the optimum pH range was between 4-6. Bio-Polymeric Blended Nanocomposite showed better removal efficiency around 12 but had only 36mg/g adsorption capacity (112). Contact time of 40 minutes was achieved for Novel Chitosan-coated superparamagnetic iron oxide nanoparticles indicating that adsorption equilibrium was attained with short span of time with notable adsorption capacity of 62.958 mg/g (113). Isotherm and kinetic studies were done to understand the underlying mechanism for the adsorption of mercury ions. Most of the adsorbents followed the Langmuir isotherm, indicating a monolayer adsorption. Modified kaolin and Tetra Pak waste adsorbent best fitted with sips model indicating that heterogenous surface was leading to difference in the adsorption of the mercury based on the active sites (114). Pseudo-second order kinetics was mostly followed by the adsorbents, suggesting chemisorption. Reusability of the adsorbents is also an important criterion when designing an adsorbent. Natural kaolin (NK) clay showed a high reusability of 91.4% (103), which exhibits sustainability and scale-up properties. Various adsorbent and its synthesis methods were discussed for adsorption of mercury.

## Mechanism involved in the removal of heavy metals from water

Adsorption of metal ions are usually classified into physisorption and chemisorption. Physisorption is the surface interaction between adsorbent and adsorbate where the adsorbate forms a bond with adsorbate due to weak Vanderwal's force or electrostatic interaction making it reversible. On the contrary chemisorption occurs where the adsorbent and adsorbate form a strong irreversible chemical bond like ionic or covalent making it more specific interaction exhibiting precipitation, pore adsorption, simple diffusion, intra-particle diffusion, hydrogen bonding, ion exchange, and redox reaction (49). The important factors that control the mechanism are the metal

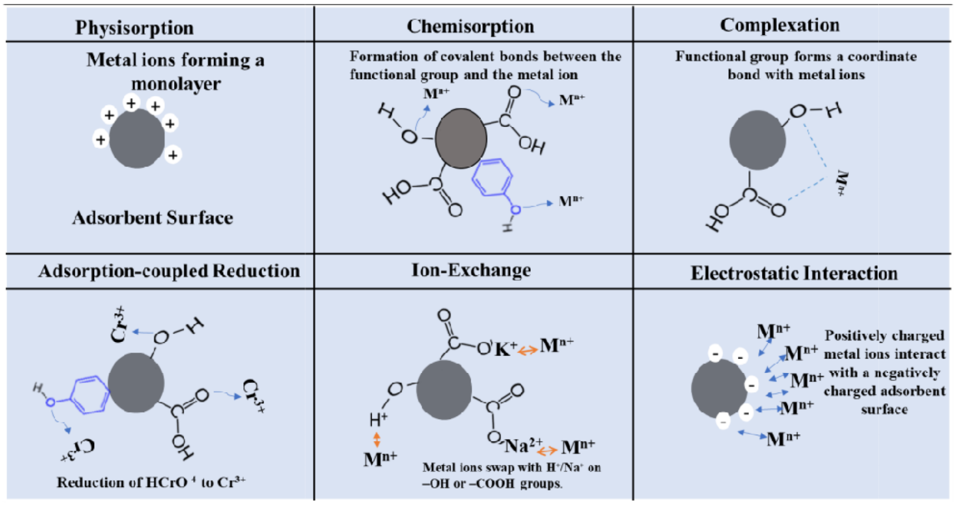

**Fig 3:** Mechanism involved in the adsorption of Heavy Metals

speciation state, adsorbent nature and its properties, adsorbent surface and type of the functional groups present, operation parameters like pH, initial concentration, adsorbent dose, contact time and availability of the binding site. Different adsorbents materials used are natural materials, nanoparticles, nanocomposites, engineered meta organic frameworks (Fig. 3). Electrostatic interaction is the primary mechanism where the adsorbent surface is negatively charged which readily adsorbs the positively charged metal ions. The interaction occurs when the deprotonation of the surface functional groups occurs and increasing surface negativity leading to adsorption of positively charged metal ions it is pH dependent and occurs at the initial stages of adsorption (55). Complexation where the metals ions form a stable bond with the surface functional groups like hydroxyl, carbonyl, amide, thiol groups the bonds formed are stable contribute to the specificity and strength of metal binding (91, 110). Adsorption coupled reduction where the surface functional groups reduce the toxic heavy metal to its non-toxic forms its mostly observed in chromium where Cr(VI) was reduced to Cr(III). Redox reaction is facilitated by the reducing functional groups or the electron donating species present of the surface of the adsorbent (117). Hydrogen bonding also occurs during adsorption due to the presence of oxygen-containing functional groups that act as an electron donor it mostly occurs when natural material is used as the adsorbent and it's also not considered as the primary mechanism it occurs during the initial stages of adsorption before the strong interaction between the adsorbent and adsorbate occurs (76) (108). Precipitation occurs at certain pH when the metal ions form a precipitate when it interacts with functional group present on the surface of the adsorbent (97). Ion exchange happens when the metal ion is replaced with the ions present on the surface of the adsorbent it most commonly occurs on the adsorbent that has ionizable functional groups(66, 68). Therefore, the deep understanding of the underlying mechanism helps to facilitate a tailored adsorbents to support sustainable treatment strategies for heavy metal removal.

## Conclusion

Heavy metal contamination in water has been a bigger global issue due to its persistence, toxicity, bioaccumulation, and toxicity. Anthropogenic activities like mining, electroplating, steel industry, welding, pesticide industry, agricultural runoffs and its improper water disposal increased the heavy metal contamination in water bodies posing a serious risk to ecosystem and human health. Persistence of heavy metal and accumulation in aquatic organisms, and plants and animals and its biomagnification in food chain also affect organisms in various trophic levels. The ecotoxicological effect of heavy metals influences the biochemical, physiological and metabolic pathways of the aquatic organisms. These organisms undergo oxidative stress, DNA damage, fluctuation in enzymes important for growth deformations in organs during development, accumulation of heavy metals in major organs and increased mortality leading to biodiversity loss and disruption in aquatic ecosystem. The prolonged exposure of heavy metals in humans also led adverse health effects. Organs like kidney, liver, lungs are affected. Carcinogenic effects of heavy metals led to the skin, lung cancers. Neurological disorders, bone damage is also noted. Various strategies were adopted adsorption emerged as the widely used method due to its environment friendly nature and adaptability with wide range of adsorbents tailored based on the pollutants. Various adsorbents like biochar, metal oxide, nanoparticles, activated carbon demonstrated an excellent removal efficiency in different heavy metals under diverse operational conditions. The effectiveness of the adsorbent also based on the surface area, pore density, pore volume, functional groups and its interaction mechanism between the adsorbent and the metal ion. Understanding of various mechanisms like chemisorption, electrostatic interaction, and complexation helps in adsorbent design and its efficient use in the removal of heavy metals. To summarize, to eliminate heavy metal contamination in water, choosing a suitable removal strategy requires a proper understanding of source, ecotoxicological effects and its toxic effects in humans. Continued research in developing novel, cost effective, suitable, high-performing adsorbents essential to meet the growing demand for water treatment. The integration of adsorption technology with other treatment methods and the real-world field testing of the developed adsorbents could provide a way for scalable and sustainable water treatment solution.

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