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Low-Cost Adsorbents and Nanomaterials for Removal of Heavy Metals from Contaminated Water: Review

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Abstract: **Worldwide concern has been raised about the contamination of heavy metals and their harmful impacts on both environment and human health. Numerous technologies have been changing throughout time to address this issue. Among the most practical and economical techniques, adsorption is still used to treat wastewater that is contaminated with heavy metals. From a review of the literature, numerous adsorbents' and their adsorption abilities were evaluated. In addition to that producing novel adsorbents such as metal-organic frameworks (MOFs) and nanocomposite for the elimination of heavy metals from polluted water was focused. Although the expense of regeneration is significant, there are numerous commercial, industrial, and environmental advantages to reducing the use of fresh adsorbent. This review makes an effort to give a thorough overview of various modified adsorbents, their efficiency, and nanotechnology based strategies for separating contaminants from wastewater. Future perspective and heavy metal removal opportunities were disused in the manuscript. Additionally, it is implied that nanomaterial and nanocomposite have demonstrated remarkable attention for the reduction of these heavy metals.**

Keywords: **Heavy metals, environment, adsorption, wastewater, nanomaterial, nanocomposite.**

I. INTRODUCTION

Because watery plants and animals are bio-accumulating metals has an impact on metabolic dysfunction and long-term physiological impacts are generated by human populations. Environmental researchers and organizations committed to reducing water pollution are particularly worried about this issue. [1-3].

Water is an essential source of energy and life, even if many people throughout the world have a shortage of clean drinking water and fresh water. Extreme water pollution and nearby soil contamination are largely the results of the fast increase in population growth, industrialization, a fast increase in population urbanization. The main causes of freshwater contamination can include runoff from agricultural areas, dumping of industrial effluent, the discharge of sanitation waste that hasn't been treated, and harmful toxic pollution. It is well known that water poisoning causes between 70 and 80 percent of all illnesses in underdeveloped nations, particularly in vulnerable populations like children and women [4-5]. Because they are harmful and accumulate throughout the food chain, heavy metal contamination of aquatic habitats is a concern that affects the environment globally.

Heavy metals in groundwater, aquatic environments, industries, and even treated wastewater are the main contaminants. Consumers are at risk from drinking water containing heavy metals. Pb, Cr, Cu, Zn, Cd, Hg, and other metals can harm bones, neurons, and the liver [6]. They can also block the functional groups of essential enzymes. Natural sources of metal ions in water include anthropogenic activities such as solid garbage management and industrial effluents, as well as the leaching of ore deposits. With the quick rise of industrial activity over time, there was a considerable rise in the number of heavy metals in the water system.

An adsorbent is typically considered to be economical if it takes minimal processing, is "low-cost.", is plentiful in nature, or is a waste and by-product obtained from another company. Additionally, increased sorption capacity can make up for the expense of additional processing. Following A summary of some of the literature includes stated adsorption capacities that are highlighted, when possible, to give an idea of sorbent efficiency.

In order to remove heavy metals from contaminated water, novel adsorbents such metal-organic frameworks (MOFs) and nanocomposite are being developed, which were discussed in this review. The stated adsorption techniques are highlighted whenever there is an opportunity to discuss a plan for adsorbent efficiency. The results of this study can therefore be used to design advanced, ecologically safe, and economically viable processes for application in water treatment technologies. Providing the readers with clear comprehension and indication of how to proceed with further research.

Current Wastewater Treatment Technologies

Chemical precipitation, ion exchangers, chemical oxidation/reduction, electro dialysis, UV filtration and reverse osmosis are only a few of the traditional techniques used in aqueous solutions to eliminate metal ions (Figure 1). However, these traditional methods have their intrinsic drawbacks (Table 1), including delicate operating environments, lower efficiency, the formation of secondary sludge, and the expense of disposal [7]. Adsorption technology, on the other hand, has drawn a lot of interest because of its benefits. Since early antiquity, applied adsorption science has been a topic of interest. Only a select few rare specialists employed some carbon-based materials, such as charcoals [8].

The build-up of a property of a material that is at the intersection of two phases, such as liquid and solid or gas, is known as adsorption. The substance on which adsorption occurs is known as the adsorbent, while "adsorbate" is the substance that builds up at the interface. The adsorption technique has also been extensively utilized to remove gases from the atmosphere and solutes from solutions. Unbalanced attraction forces exist at the surface of solids, and these forces are what cause adsorption. Physical adsorption is used to describe situations when the adsorption is brought on by weak van der Waals forces. Additionally, adsorbent and adsorbate molecules may form a chemical connection; Chemisorption is the name for this kind of adsorption. [9-11].

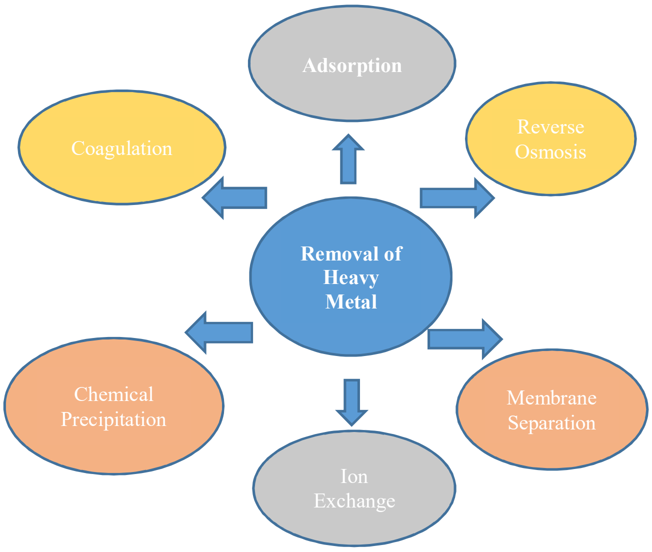

Figure 1: Traditional Methods for separation of heavy metals from wastewater

TABLE 1
Discussing various wastewater treatment systems

Technique	Advantage	Disadvantage	Reference
Inorganic precipitation	(i) Simplification (ii) low capital expenditure (iii) adapted to handle large concentrations of heavy metal ions	(i) Low metal ion concentration turns ineffective (ii) not sensible (iii) the production of a lot of sludge	[12-15]
Ion-exchange	Ion-exchange	(i) Because of chemical reagent renewal, secondary contamination may result. (ii) It is too expensive to use on a wide scale for treating a lot of wastewater.	[16]
Membrane filtration	Membrane filtration	(i) Expensive and difficult procedure (ii) Heavy metal removal has been hampered by membrane fouling.	[17-18]
Adsorption	(i) Because of its expensive price, AC is rarely used in adsorption. (ii) To remove heavy metal ions, various inexpensive adsorbents have been created and put to the test. (iii) A relatively recent technique called bio-sorption has shown great promise for removing heavy metals from wastewater.	(i) removing heavy metals from low-concentration wastewater (ii) The kind of adsorbents used determines the efficacy of adsorption.	[19-20]

Adsorbents Mechanism

In comparison to traditional approaches, the adsorption process is inexpensive, has a very cheap cost of operation, and produces less pollution when hazardous metal is extracted. Adsorption techniques are thought to be environmentally favorable because sorbents can be recycled and utilized multiple times for efficient removal [21-22]. Price effectiveness, a high surface area, a wide range of pore sizes, the existence of a functional moiety, and the sorbent's polar properties are the main factors that must be taken into consideration when choosing an adsorbent. Understanding the adsorption process is so crucial. Adsorption is a mechanism of mass transport whereby a solute from the solution builds up on the adsorbent's surface, which is usually a solid [23].

Table 2 shows the adsorption capabilities and experimental conditions of inexpensive absorbent for removing heavy metals. There are two different types of forces at work between the adsorbent and the adsorbate, namely physical and chemical interactions. Physical forces have no characteristics. Since they are weak and adsorbed molecules can adhere to adsorbents wherever they are. By covalent or electrostatic bonding, adsorbate adheres to adsorbents in chemical adsorption, which is particular in nature hydrogen bonds, dispersion interactions, and van der Waals are the driving mechanisms for physical adsorption.

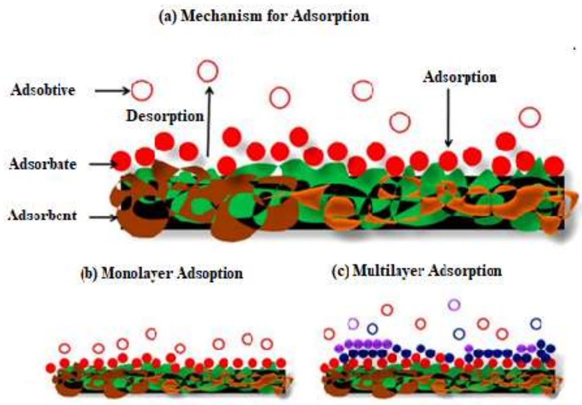

Figure 2: (a) The general mechanism for the adsorption, (b) monolayer adsorption, and (c) multilayer adsorption [23].

TABLE 2
Adsorption capabilities and experimental conditions of inexpensive absorbent for removing heavy metals.

Adsorbent	Adsorbate	Adsorption isotherm	Kinetics	Adsorption capacity (mg/g)	Reference
Sugarcane cellulose	Zn^{2+}	Langmuir	Pseudo second	558.9	[24]
Shell cashew	Zn^{2+}	Langmuir	Pseudo second	455.7	[25]
Banana peel	Pb^{2+}	Langmuir	–	2.18	[26]
Watermelon rind	Pb^{2+}	Langmuir	Pseudo second	98.06	[27]
Lemon peel	Co^{2+}	Langmuir	Pseudo second	22	[28-29]
FT Onion skin	Pb^{2+}	Langmuir	Pseudo first	200	[30]
Cucumber peels	Pb^{2+}	Langmuir	Pseudo second	133.6	[31]
Date tree leaves	Pb^{2+}	Temkins	Pseudo second	58.83	[32]
Lemon peel	Co^{2+}	Langmuir	Pseudo second	22	[33]
Cassava	$Co^{2+, Zn2+}$	Freundlich	Pseudo First	55.8	[34]
Modified Cassava	Co^{2+}, Zn^{2+}	Freundlich	Pseudo First	559.8	[35]
Moss	Co^{2+}, Zn^{2+}	Langmuir	Pseudo First	14	[36]
Biochar from rice straw	Zn^{2+}	Langmuir	Pseudo Second	38.6	[37]
Modified peanut hull hydrochar	Pb^{2+}	Langmuir	-	22.38	[38]
ZnCl2 activated grapefruit +	Pb^{2+}	Freundlich	–	12.73	[39]
Carbon activated from pine cones	Pb^{2+}	Langmuir	Pseudo second	27.53	[40]
modified orange peel	Pb^{2+}	Langmuir	Pseudo second	141.84	[41-43]
Natural bentonite	Zn^{2+}	Langmuir	pseudo second	68.49	[44-46]
natural zeolite	Zn^{2+}	Langmuir	Pseudo second	53.64	[47]
Carb	Co^{2+}	-	Pseudo first	10.46	[48]
Carbon Activated from Van apple	Pb^{2+},Zn^{2+}	Langmuir	Pseudo second	15.96	[49-50]

				11.72	

Future Perspective and Heavy Metal Removal Opportunities

The bio adsorbents used to remove copper, cadmium, and chromium are excellent substitutes for commercially available adsorbents since they are inexpensive and effective. According to research work done so far, after modification, the removal efficiency of adsorbents for sewage removal of heavy metals increased [51]. Less effort has, however, been done in this regard. Therefore, our future goals include improving the removal efficiency of bio adsorbents after modification (with the least amount of acid, base, and heat required, nanomaterials), regeneration of adsorbents, metal ion recovery, and commercial application of bio adsorbents [52]. The difficulty of the method used to remove heavy metals from wastewater maintaining a pH that is adequate for adsorption may need significant amounts of bio adsorbents and additional chemicals.

TABLE 3
Adsorption capabilities of nanocomposites under experimental heavy metal removal conditions

Adsorbent	Adsorbate	Adsorption isotherm	Kinetics	Adsorption capacity (mg/g)	Reference
Nanostructure alumina	Pb^{2+}	Freundlich and Langmuir	Pseudo second	125	[56]
ZnO	Zn^{2+}	Langmuir	Pseudo second	357	[57]
Functionalized CNT	Zn^{2+}	Freundlich	Pseudo second	1.05	[58]
Graphene oxide/PAMAM dendrimers	Pb^{2+}	-	Pseudo second	568.18	[59]
GO-NH_2	Co^{2+}	Langmuir	Pseudo second	116.35	[60]
Glycol-GO	Pb^{2+}	-	-	146	[61]
Fe_3O_4/bentonite Nanocomposite	Co^{2+}	Langmuir	Pseudo second	18.76	[62]
Calcareous clay (RY)	Pb^{2+}, Zn^{2+}	-	-	37.85 13.37	[63]
Lignin-containing nanofibers	Pb^{2+}	-	-	37	[64-65]
Poly-ammonium dithiocarbamate (PADTC)	Zn^{2+}	Langmuir	Pseudo second	226.7	[66]
Tin antimonite (SnSb)	Co^{2+}	Freundlich	Pseudo second	38.3	[67]
Iron oxide	Co^{2+}	Langmuir	-	10.6	[68]
EDTA-Magnetic-GO	Pb^{2+}	Langmuir	Pseudo second	508.4	[69-70]
Graphene Oxide	Zn^{2+}	Langmuir	Pseudo second	345	[71]
PAMpDA nanoparticles poly (aniline-com-phenylenediamine)	Co^{2+}	Langmuir	Pseudo second	86.2	[72]
Zeolite-Nanoscale Zero Valent Iron (Z-NZVI)	Pb^{2+}	Langmuir	Pseudo second	85.37	[73]
Nano hydroxyapatite	Pb^{2+}	Langmuir	–	1000	[74]
Goethite(nano)	Co^{2+}	Freundlich	Pseudo second	86.85	[75]
Zeolite-Nanoscale Zero Valent Iron (Z-NZVI)	Pb^{2+}	Langmuir	Pseudo second	85.37	[76]
Nitrogen-doped magnetic CNTs	Cr^{+3}	Langmuir	-	638.56	[77]

Nanomaterials and Nanocomposites

Other than the typical synthetic nanoparticles used as adsorbents, Metal-organic framework (MOF), graphene oxides, and other novel materials investigated for their ability to absorb heavy metals. It is well known that nanoparticles and nanoparticle-incorporated nanocomposites have high strength, large surfaces, variable non-corrosive surface chemistry properties, and oxygen on their surfaces [53]. Graphene and graphene oxides, metal oxides, single- and multi-walled CNTs, and other nanoparticles are frequently employed for inclusion. Metal ions, clusters, and organic ligands are all part of the crystalline structure of MOFs. It has been discovered that MOFs and modified MOFs have a good chance of removing multivalent and divalent heavy metals from wastewater. Table 3 provides a quick summary of the various nanocomposites and MOFs that have been investigated for their capacity to adsorb as well as the ideal conditions for maximizing the removal of the adsorbate ions. According to Wang et al lead (II) ions have a significant affinity for NH_2 - Zr-MOF as a result of their attraction to the amine group's single electron. The NH_2 functionalized MOF and lead (II) have high electronegativity, which makes it simple to create stable complexes and improve removal [54-55]. As they closely interact PAMpDA@Fe_3O_4 nanocomposite and PAMpDA are paired with the adsorbent's amine and imine group. Copolymers, according to Zare et al, are efficient in removing Co^{2+} [78-81]. Reactive N-H and NH_2 groups and phenylene rings on each side of the copolymer chain of PAMpDA give it a very high degree of chemical flexibility. Mohammad and Tonight studied the metal ion adsorption capability of CNTs, and their results demonstrated a considerable dependence on their entire functional groups including surface acidity. Functional group types and numbers depend on the oxidation method, and CNT morphologies (the degree of surface imperfections), which are mostly related to their manufacturing method and their precursors [82-83].

The results of this study could be used to develop an economical and environmentally friendly heavy metal ion removal technique for use in water treatment technologies [84-90].

II. Conclusion

A thorough analysis of studies using both standard and unconventional adsorbents to cope with the adsorption of heavy metals that were published in the previous ten years was conducted. For the elimination of cobalt, zinc, and lead (II) (III), numerous new adsorbents were employed. The adsorption and experimental parameters capabilities were used to compare the research. Because zinc is used in so many different industries, the removal of zinc from wastewater is a highly researched topic. Numerous physical, chemical, and biological techniques have been researched with positive outcomes. The initial concentration, pH, and contact time are three variables that have an impact on the elimination % of adsorbate during adsorption.

However, as wastewater treatment must often be a low-cost plan for its majority acceptance, we should be forced to design more affordable technologies. To achieve this goal, more effort from researchers and technologists is needed. The synthesis of high metal adsorption adsorbent capacities (Cd, Pb, and Cr) without burdening the finished product is possible by using modifying agents in adsorbent or using nanocomposites. The manufacturing of modified adsorbents from solid waste is a viable alternative to the disposal of this trash and even allows for the addition of value to waste that is typically disposed of.

Additionally, the nanocomposites-based materials outperformed other unmodified and modified adsorbents in terms of efficiency. However, compared to the traditional adsorbents, the modified adsorbents' have adsorption capabilities were significantly higher. The technique was used because the environmental conditions kept throughout the preparation have a big influence on the properties and effectiveness of the nanoparticles. However, further research is necessary to fully comprehend their harmful impacts on the environment, health, and appropriate disposal. But there aren't many publications in this field of inquiry that concentrate on the economic value of using these adsorbents and their cost-effectiveness. Therefore, future research might be done to show the economic value of employing these adsorbents to remove heavy metals through cost analysis.

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