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RESEARCH PAPER

Applications of Nano Composites for Heavy Metal Removal from Water by Adsorption: Mini Review

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ABSTRACT

The increasing contamination of water by various heavy metals has emerged as a pressing global issue, threatening human health, aquatic ecosystems, and agricultural sustainability. These heavy metals are required to remove through cost effective and efficient removal approaches due to their toxicity, persistence and bioaccumulation. This review explores the transformative potential of nanocomposites as advanced adsorbents for heavy metal elimination. By investigating their synthesis, characterization, and functional classifications, the study highlights how these materials outperform conventional methods through enhanced surface properties and adsorption efficiency. A comparative analysis of adsorption mechanisms, such as ion exchange, electrostatic interactions, and complexation, is addressed, alongside evaluations of critical operational parameters like pH, contact time, and percentage removal. Additionally, the paper also outlines the limitations of current nanocomposite technologies, such as scalability challenges and environmental concerns, while potential future options for the removal of heavy metals. This review sets the groundwork for future nanomaterials developed to address global water decontamination by extending knowledge in this field.

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INTRODUCTION

One of the most essential needs for life is water. It is like lifeblood of our earth. It is silent hero, maintaining our universe from cellular processes to global ecosystem. Around 0.3% of the water resources in this world are drinkable[1]. Unfortunately, water pollution is now the most pressing global issue and it is urgent need to evaluate water management policy to tackle this problem[2]. Both developed and developing countries are facing this issue. Multiple organic and inorganic contaminants emitted from both natural and anthropogenic sources have caused the quality of water supplies to deteriorate drastically. When undesirable water bodies spread across a water system, the quality of the water changes, leading to water pollution[3-14]. There are many factors which can contribute

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to water pollution. Rapidly growing population, fast industrialization, expanding urbanization, and inappropriate use of natural resources have all had a detrimental impact on water quality in recent decades[15]. More than 1500 substances have been identified as contaminants[16]. Organic matter, nutrients, drugs. and cosmetics, poly- and perfluoroalkyl compounds, chemicals, heavy metals, dyes, radioactive materials, plastic items, nanoparticles, and pathogens are the contaminants of the primary concern[17, 18]. Among these contaminants, heavy metals are the most toxic pollutants due to their poisonous nature and chemical reactivity. These heavy metals (Zn, Pb, Cu, Cd, Cr, Ni, Hg, Ag etc.) enter into water supplies directly or indirectly[19]. These metals remain in the environment for longer time as they are non-biodegradable and have various oxidation states. Heavy metals have potential to cover long distances in the environment. Therefore, it is very important to eliminate all these pollutants especially heavy metals from wastewater before they are released into water supplies.

A number of techniques have been reported for waste water treatment, including adsorption membrane filtration, precipitation flocculation, Coagulation, electrolytic extraction, Fenton's process, ion exchange, reverse osmosis, Constructed Wetlands, biological removal, and reduction[20-22]. These methodologies, however, have certain limitations and challenges associated with their applications in water treatment [23-28]. High cost, less efficiency, production of waste as by-product, low reliability, expensive equipment, and complex operating system are some drawbacks of these listed techniques. Besides these techniques, adsorption is one of the best and simple method used for the elimination of the heavy metals from water [4-11, 13, 14, 29-40]. The adsorption approach for removing contaminants has been found to be highly efficient, economical, and simple to use.

Various materials are employed for heavy metals removal from water. Nanoscale materials are widely used to treat water. These materials have unique properties because of their tiny size and high surface area to volume ratio. Due to these characteristics, nanocomposites exhibit high removal efficiency. Alongside their large surface area, nanocomposites show exceptional catalytic properties which make them suitable adsorbents for heavy metals removal from water. Their large surface area provides greater number of active sites for species to be removed. Therefore, they are the best materials for heavy metal decontamination.

The objectives of this review are to address an urgent need for effective and sustainable solutions for heavy metal contamination in water. This includes exploring the latest advancements in the synthesis, structural characterization, and applications of nanocomposites for the adsorptive removal of heavy metals from aqueous solutions, evaluating the adsorption mechanisms, such as diffusion, electrostatic interactions, and redox reactions, Investigating the factors influencing adsorption performance, including pH, contact time, and surface modifications. Identifying the most efficient nanocomposite materials based on adsorption capacity, removal efficiency, and recyclibility to provide a comparative framework for material selection is main objective of this study. This review also discusses critical analysis of practical limitations of nanocomposite applications, such as high production costs, environmental concerns, and scalability, and suggesting possible solutions for overcoming these barriers. This paper also proposes innovative strategies for developing eco-friendly and cost-effective nanocomposites that can work efficiently and align perfectly with the global standards.

This review distinguishes itself by offering a multidisciplinary approach on the use of novel and efficient nanocomposites for heavy metal removal, bridging gaps between material science, environmental engineering, and sustainable development. Unlike previous studies, this paper compares the adsorption efficiencies of nanocomposites extensively and relates them to their structural and functional properties. Additionally, it offers an extensive review of the adsorption mechanisms, explaining the role of complexation, surface contacts, and redox processes in high removal percentage. The paper also presents the idea of integrating nanocomposites into hybrid water treatment systems to optimize their potential. In order to ensure that future advancements in water purification technologies are in line with the Sustainable Development Goals of the UN, this study provides a bedrock for future developments by addressing economic and environmental challenges and suggesting directions for green synthesis and recyclability.

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HEAVY METALS

Among all these toxic substances, heavy metals have the most adverse effect on environment because their concentration in water, soil and air is increasing tremendously as a result of anthropogenic activities. Any metal, irrespective of its density or atomic mass, that is hazardous is considered a heavy metal[41]. Some lighter elements such as aluminium, arsenic, selenium and metalloids are harmful for environment and considered as heavy metals while some heavy metals such as gold is non-toxic[42]. According to United States Environmental Protection Agency (USEPA), heavy metals can be arranged on the basis of maximum contaminant level (MCL) in following order[43]. Zinc (0.80) > Copper (0.25) > Nickel (0.20) > Chromium (0.05) > Arsenic (0.050) > Cadmium (0.01) > Lead (0.006) > Mercury (0.00003)

Heavy metals can be classified into two main categories on the basis of their importance for plant and animal growth. Group 1 consists of elements such as B, Cu, Fe, Mo, Ni, and Zn which are considered vital for the plant and animal development. These metals become toxic when their concentration exceeds to a certain limit. Group 2 consists of As, Cd, Hg, and Pb which are not important for the animal and plants growth[44].

Rapid industrialization and urbanization along with extensive use of fertilizers and pesticides have posed serious threats to the environment due to increasing heavy metals concentration in our ecosystem[45]. Some of the primary sources of heavy metal pollution are Industries such as metal processing, electroplating, and chemical manufacturing often use and release heavy metals into the air, water, and soil, Improper disposal of electronic waste, batteries, auto-mobiles, and other metal-containing products can lead to heavy metal contamination of soil and water. Activities like leaching, dust emissions, wastewater discharge and natural activities such as Burning fossil fuels like coal and oil, volcanic eruption, metal corrosion, soil erosion, geological weathering release heavy metals into the atmosphere, which can then be deposited in soil and water bodies[46].

Industrial effluent containing heavy metals have high solubility in water and get mixed with water and soil which alters the composition of these natural medium[47]. These heavy metals are non-biodegradable in nature so they mix with water and soil and cause contamination of the food chain[48]. The pollution caused by these heavy metals are mostly long lasting, adverse and irreversible in nature. Prolonged intake of heavy metals may cause internal abnormalities as body begins to accumulate these toxic substances and use as required elements[49]. Arsenic, lead, mercury, and cadmium are the heavy metals that the World Health Organization (WHO) has included among the top 10 toxic substances because of their high toxicity and ecological resilience[50]. The biotoxicity of the heavy metals like zinc, copper, lead, arsenic, aluminium, and mercury are diarrhea, tremors, gastrointestinal disorders, vomiting, paralysis, depression, liver damage, insomnia, carcinogen, rheumatoid arthritis, stomatitis, renal disorder, depression, nausea, convulsion and pneumonia[51]. Apart from humans, animals and plants are also severely affected by these toxic heavy metals. High lead concentration in soil decreases soil efficiency while low lead concentration can cease biological mechanisms like transpiration, photosynthesis and mitosis which result in dark green color of the leaves and short roots[52].

NANOCOMPOSITE

Due to all these adverse effects of heavy metals, several materials are employed for the removal of the heavy metals. This review paper will focus on nanocomposites. The term “nano-composite material” developed over time to include a wide range of systems, including one, two, three, and amorphous materials, which are composed of specifically different components and assembled at the nanoscale[53]. Nanocomposites are the materials with nanoscale structure that enhance the macroscopic properties of the substance [54-56]. The nanocomposite material is a customized modern materials with the ability to remove fillers from a number of different substrates[54]. Nanocomposite are actually nanomaterials that integrate more than one distinct components to produce a composite, at least one dimension in nano range (1nm=10^{-9}m), which has the finest characteristics of each component. Nanoparticles such as clay, metals, carbon nanotubes serve as filler in nanocomposites. Nanocomposite have advance properties and advantages[57]. 1) Only a small concentration of nano-filler is required to enhances their properties. 2) These materials are lighter in weight as compared to other composites. 3) Nanocomposites have improved properties that

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depends upon size such as thermal, chemical, mechanical, optical, magnetic and electrical properties.

Nanocomposite based purification

Conventional water treatment techniques such as coagulation-flocculation, reverse osmosis, chemical precipitation and ion exchange have some drawbacks which make them less suitable for removal of pollutants from water. Treatment techniques like chemical precipitation and coagulation-flocculation produce hazardous byproducts as waste and require high cost for operation[58]. Reverse osmosis is somehow effective while it is also expensive technique in terms of fueling, costly energy demand and high priced membrane[59]. Because of the limited applications of current water treatment technologies, it is now significant to develop and create novel and efficient materials at a low cost which offer improved characteristics, high efficiency and less cost.

Nanocomposites are proved to be an efficient and novel materials for the decontamination of water and strong alternatives for the removal of toxic contaminants[60]. Compared to conventional techniques, nanocomposites which are made up of nanoparticles embedded in a matrix, exhibit improved membrane filtration, catalytic activity, and adsorption properties[61]. Heavy metals, organic dyes, and microbes are just a few of the pollutants that nanocomposites can successfully remove due to their massive surface area, tailored chemical compositions, and effective extraction techniques[62, 63]. Different types of nanocomposites degrade different type of pollutants [24, 27, 34, 55, 64-74]. Metal oxide based nanocomposites like TiO_2-ZnO, TiO2-Graphene, ZnO-Ag, Fe_3O_4 remove organic pollutants from water in the presence of light[75]. Carbon-based nanocomposites such as carbon nanotubes, graphene oxide exhibit a high potential to adsorb organic dyes and heavy metals[76-78]. Polymer-based nanocomposites (Chitosan- Fe_3O_4, PVA-TiO_2, PVA-Ag) display antibacterial characteristics, making them useful for detoxification applications[79, 80].

Adsorption

Upto the start of 21st century, eradication of pollutant especially dyes and heavy metals involved only basic water purification processes such as equalization and sedimentation[81]. There is need to develop treatment methods of water that are more economical and reliable. Among the number of available methods, adsorption has emerged as a superior, preferred and prominent technique[31]. The surface phenomenon in which accumulation of particular component at the surface or at the interface between two phases occurs is called adsorption[82]. Simple operation, high effectiveness[83], cost effective, no production of toxic byproducts[84], production of high quality treated effluent, resistance for harmful

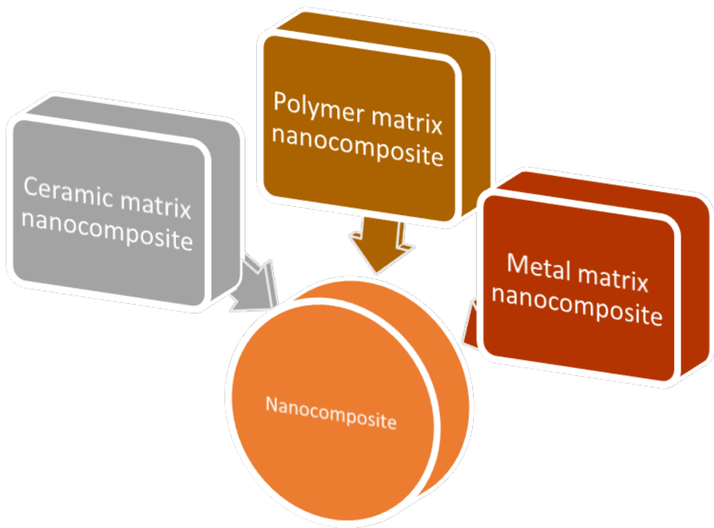

Fig. 1. Classification of nanocomposite on the basis of matrix.

chemicals[85], small maintenance, exceptional versatility, [86], capability of treatment of highly concentrated colourants[31], regeneration and use of adsorbent again and again are some of the unique characteristics of adsorption process which make this process the best and the most reliable among all other methods available. Adsorbents may adsorb heavy metal ions present in water through chemical or physical attraction. Chemical adsorption is more reliable for the removal of heavy metals because heavy metals ions are strongly attracted towards functional groups present on the surface of the adsorbent[43].

Role of nanocomposite in water treatment through adsorption

Water contamination is increasing day-by-day and heavy metals are playing their role dangerously due to their toxic nature, chemical and physical stability, and bioaccumulation. Nanocomposites are now appealing materials for the removal of heavy metals from water through adsorption because of their unique physiochemical characteristics. These nanocomposites can remove highly toxic heavy metals with high percentage removal at very low concentration[87].

Synthesis of nanocomposites

Nanocomposites are made up of matrix (polymer, metal) and nanofiller (nanomaterials, nanotubes). This interaction between matrix and nanofiller give unique properties to nanocomposites such as improved thermal. electrical, and mechanical properties. Nanocomposites can be synthesized by various ways, however, their synthesis methods are broadly divided into top down and bottom up approaches. Table 1 describes the comprehensive outlook of synthesis, properties, and applications of the nanocomposites types.

The top-down approach uses mechanical and physical techniques to break down bulk materials into nanoscale structures. Commonly employed methods include ball milling, laser ablation, and mechanical milling. For instance, mechanical milling

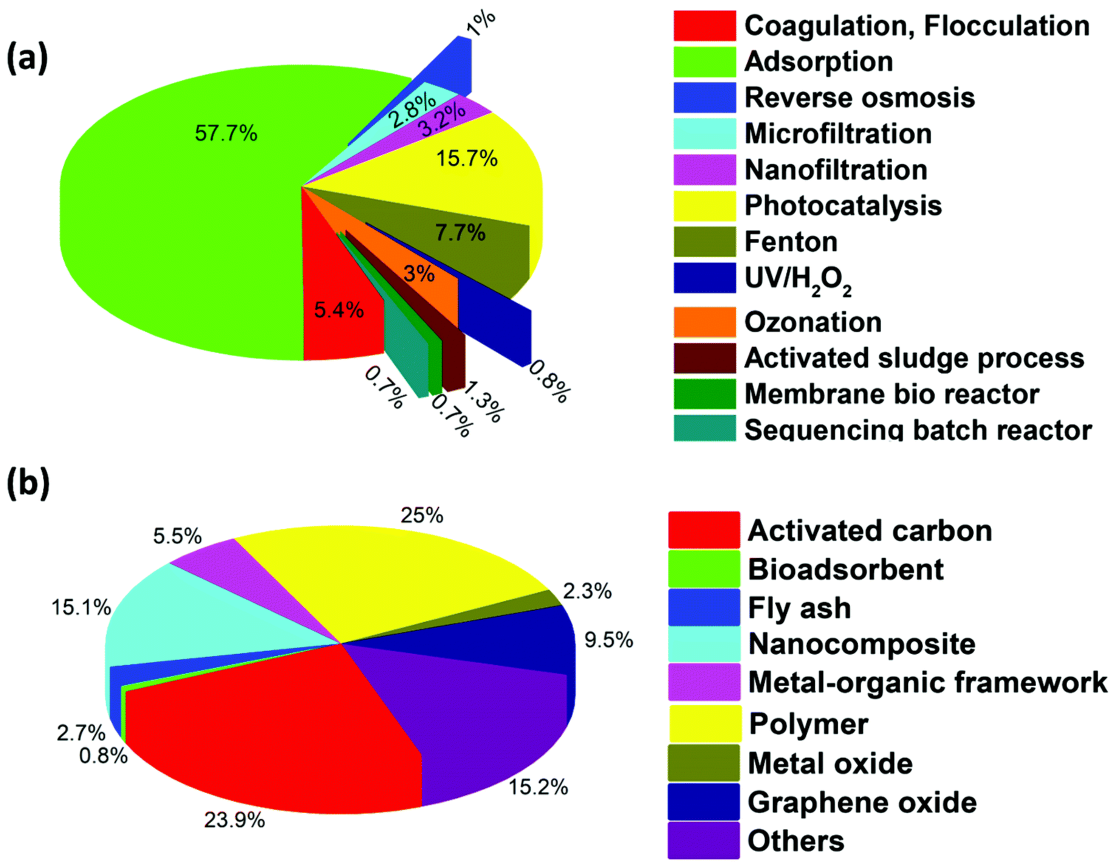

Fig. 2. Recent advances in removal of heavy metals by adsorption (a) and nanocomposites (b).

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reduces the size of bulk materials into nano-range while preserving their structural and chemical strength by using extremely powerful crushing. By directing high-energy lasers onto a substance and forcing it to evaporate into tiny particles, laser ablation produces nanoparticles[88]. Even though these techniques work smoothly, these methods frequently demand high amount of energy[89]. While the bottom-up approach employs chemical or biological processes to assemble nanostructures from atomic or molecular precursors. Common techniques include co-precipitation, sol-gel synthesis, and hydrothermal techniques. Sol-gel produces nanocomposites with uniform size and shape by hydrolyzing and condensing monomers. Metal oxide nanocomposites are synthesized most effectively by co-precipitation, whereas hydrothermal techniques produce homogeneous, highly crystalline nanostructures under controlled pressure and temperature[90].

Characterization of nanocomposites

Mechanical charcterization

Nanocomposites are characterized mechanicallly through various theoritical and empirical approaches. These techniques determine mechanical parameters of the nanocomposites. These analysing techniques include Compression analysis, tensile analysis, the Flexure analysis, the Hardness analysis, Dynamic Mechanical analysis (DMA), Universal testing machine (UTM), the Shear test, impact test and many others[91].

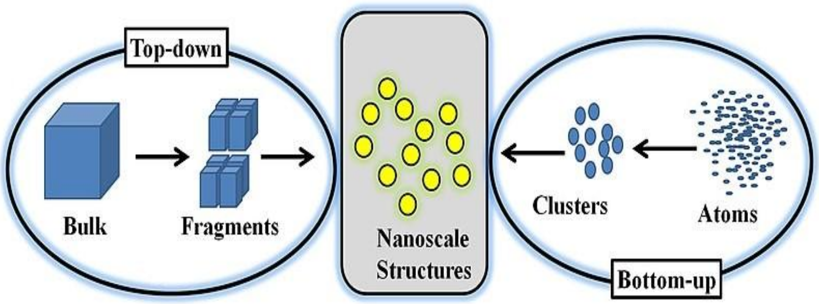

Fig. 3. Schematic representation of top-down and bottom-up approach.

Table 1. Summary of nanocomposite types.

Type of nanocomposite	Synthesis techniques	Examples	Properties	Applications	Reference
Polymer nanocomposites	In-situ, solution blending, sol-gel	Clay, graphene, carbon nanotubes	Thermal stability, better toughness, increased moisture resistance	Automotive industry, packaging, electronic	[91]
Ceramic nanocomposites	Hot pressing, sintering, sol-gel	Aluminium-zirconia, Alumina polymer	High stiffness, improved chemical stability, thermal conduscivity	Composites, energy storage applications, electronics	[92]
Metal matrix nanocomposites	In-situ, mechanical alloying, powder metalluragy	Aluminium-alumina, magnesium carbon nanotubes	Hardness, wear resistance, corrison resistance, stifness	Biomedical industry, aeroscpace, defence, automative industry	[93]
Carbon-based nanocomposites	Chemical vapor deposition, physical vapor deposition,	Graphene epoxy, CNT-polyamide, CF epoxy	High stiffness, chemical and thermal stability	Sensors, electronics, energy storage	[94]
Semiconductor nanocomposites	CVD, PVD, sol-gel	ZnS-quantum dots, ZnO-CdS	Catalytics properties, optical properties	Solar cells, catalysts, sensors	[95]
Biopolymer nanocomposites	Melt mixing, in-situ, polymerization	Starch-clay, chitosin-silver	Antimacrobial activity, barrier capacity, thermal stability	Agriculture, packaging, biomedical applications	[96]

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The durability of particular material in real world applications can be estimated from mechanical tests of various components. UTM determines compressive and tensile strength, whereas DMA investigates viscoelastic behavior under oscillatory stress. As nanocomposites are uniformly distributed, adding nano fillers to matrix often results in higher mechanical strength and stiffness. For example, graphene and the substrate material have a strong interfacial interaction, as a result, graphene oxide-based nanocomposites offer excellent tensile strength. A single test cannot assess mechanical strengths of target material since various materials interact differently to a particular set of conditions.

Thermal characterization

The aim of thermal characterization of nanocomposites is to examine how the materials behave under varying conditions of heat, temperature, and moisture in order to evaluate parameters such as melting points, coefficients of expansion, glass transition temperatures, dilations, heat stresses, strains, and thermomechanical characteristics, etc. Various experimental and theoretical investigations were conducted to test heat resistance and thermal stability of the materials. These tests include the Thermo-Gravimetric Analysis (TGA), Thermo-Mechanical Analysis (TMA), the Differential Scanning Calorimetry (DSC), the Hygroscopicity Test and the Melt Index Rheology Analysis (MI-RA)[91-93].

DSC determines crystallization points, glass transition, and melting points, giving insights into thermal changes. TGA examines loss in weight as an index of temperature, providing thermal degradation temperatures and material stability. Polymer-based nanocomposites often show enhanced heat stability because fillers hinder the mobility of the polymer chains. These characterizations are helpful in determining the suitability of these nanocomposite materials for industrials applications where temperature varies significantly. These tests are helpful in giving a broad picture of how the material would break down or transform under particular events.

Chemical characterization

Chemical composition, number and type of bonds, chemical stability and reactivity of the nanocomposites can be identified by various chemical characterization techniques. These

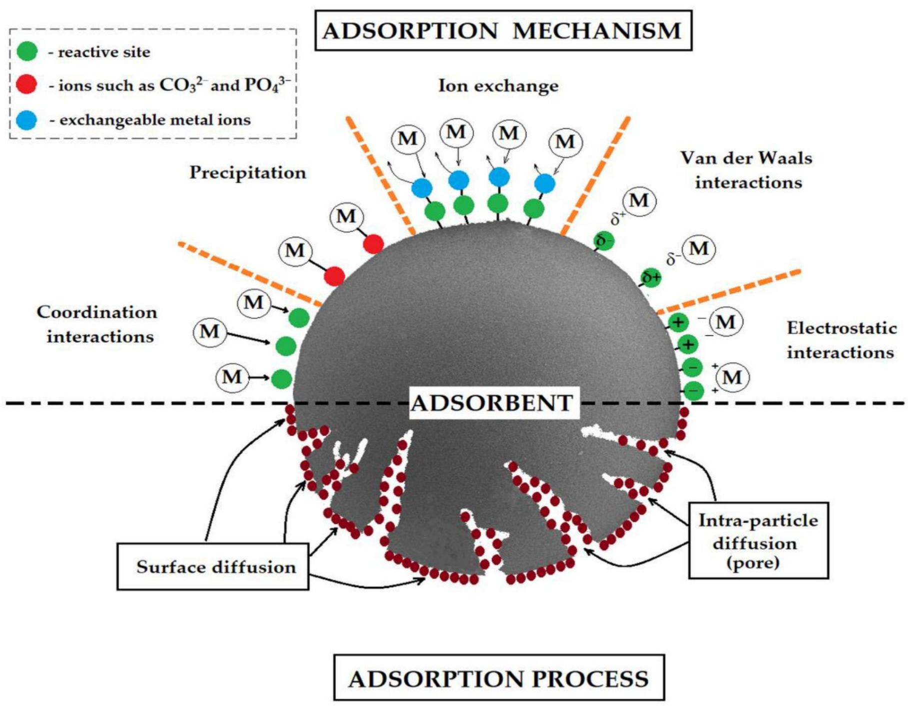

Fig. 4. Visual representation of possible heavy metals adsorption mechanism.

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techniques include X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Absorption Spectroscopy (XAS), the Fourier Transform Infra-Red (FTIR) Spectroscopy[94], Electron-Paramagnetic Resonance (EPR) Spectroscopy, the Raman Spectroscopy and the Energy Dispersive Spectroscopy (EDS), Mass spectrometry, X-ray Photoelectron Spectroscopy (XPS)[95, 96].

FT-IR determines particular functional groups vibrations of nanocomposites [33, 35, 97-99] while XPS gives detail about composition and varying oxidation states. Glow discharge spectrometry and induced coupled plasma spectroscopy are 2 techniques that are currently effective in determining the deposited layer's surface concentration[91]. These techniques are especially beneficial for understanding how chemical interactions, such as covalent bonds or hydrogen interactions, between nanomaterials and matrix components affect adsorption capacities in water treatment applications.

To optimize the performance and customize nanocomposites for particular uses, an intensive understanding of the mechanical, thermal, and chemical characteristics, achieved through integrating these methods, is necessary.

ADSORPTION MECHANISM OF HEAVY METALS USING NANOCOMPOSITES

Nanocomposites have showed high removal efficiency of heavy metals through adsorption process due to their unique properties such as large surface area, better selectivity, and high adsorption capacity. Table 2 shows adsorption capacity of different nanocomposites for heavy metals. Adsorption mechanism of heavy metals using nanocomposites involves physical and chemical adsorption approaches.

In diffusion mechanism, heavy metals from solution move onto the surface of the adsorbent through diffusion and get adsorbed on the active sites (pores) of the nanocomposites materials (adsorbent). Weak Vander waal forces develop between heavy metals ions and adsorbent surface[100]. In porous nanocomposites, such as metal organic based nanocomposites, where diffusion through small pores is critical, this technique is commonly used. There are two stages of diffusion: intra-particle diffusion (movement within porous structures) and external diffusion (displacement to the outside surface of the material). Adsorptive removal of Pb(II) on activated CN tubes is example of surface adsorption[101].

Some nanocomposites have negatively charged functional group (-OH^-, -$COOH^-$, -NH_2) on their surface which attract positively charged heavy metals ions in solution. The chemical reactions between nanocomposite and heavy metal ions are highly pH sensitive because the electrical charge on the surface of nanocomposite varies with pH. Electrostatic interaction between functional

Table 2. Applications of nanocomposites for the adsorptive removal of heavy metals.

Nanocomposite	Heavy metal	pH	Contact time (min)	Adsorption capacity (mg/g)	% Removal	Reference
ZnO-CNT	Cd(II)	6.0	90	135	91.5	[114]
Chitosan-TiO_2	Cr(VI)	3.0	60	165.3	88	[115]
GO-Fe_3O_4	Pb(II)	5.5	120	200	95.5	[116]
MnO_2-GO	As(III)	7.0	180	240	93	[117]
CNF-Fe_3O_4	Cu(II)	6.0	100	150.5	90	[118]
Silica-embedded Ag	Hg(II)	5.0	60	205	94.7	[119]
MOF-199 composite	Zn(II)	6.8	105	175	85	[120]
ZnO-SiO_2	Cu(II)	5.7	90	146	85.5	[121]
TiO_2-CeO_2	Cr(VI)	7.0	100	180	91	[122]
Ag-Al_2O_3	Pb(II)	6.5	125	250	96	[123]
Lignin-$Mg(OH)_2$	Ni(II), Pb(II), Cd(II)	7	90	88	91	[124]

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groups of nanocomposites and heavy metal ions cause removal of heavy metals from aqueous solution e.g. removal of Cu(II) through graphene oxide[102]. Chitosan-based nanocomposites effectively removed heavy metal from water due to interaction between NH_2 and OH functional groups and heavy metals ions[103]. This mechanism is particularly useful for heavy metals with low concentration as electrostatic interaction increases rapidly at initial stage.

In ion exchange mechanism, Heavy metal ions in solution are replaced by positively charged ions such as Na^+, K^+, Mg^{+2} present on surface of the nanocomposite. These cations don't cause water pollution. This type of mechanism is very effective in layered nano range materials like zeolites and clay. These cations don't cause water pollution. Na^+ of zeolite are exchanged by Pb(II) is an example of ion exchange mechanism[104]. Due to its reversible nature, this mechanism is particular effective.

In complexation, some nanocomposites have functional groups such as carboxyl and amine on their surface which form coordination complex with heavy metal ions. This method is extremely specific to the selected metal's and the nanocomposite's chemical compositions. This phenomenon results in elimination of the heavy metals from water. In [105], thiol-functionalized carbon nanotubes form stable complexes with Hg(II) ions, radically enhancing their removal capability. Chitosan based nanocomposites form stable complexes with Cr(III) in water[106].

The redox mechanism involves a chemical reaction which takes place between heavy metal and surface of the adsorbent, making heavy metals less toxic. Surface of the nanocomposite acts as oxidizing or reducing agent. This method is specific with metals having variable oxidation state such as Cr(VI). Fe_2O_3 nanocomposite materials reduces Cr(IV) to Cr(III)[107].

CONCLUSION AND FUTURE OUTLOOK

Heavy metals contamination is common form of global water pollution. Several human and natural activities produce heavy metals such as Cu, Fe, Mo, Ni, Pb, Cd, Hg, Cr. All these metals cause serious issues for aquatic and terrestrial ecosystem. Addressing this issue requires efficient, scalable, and environmentally friendly solutions. Nanocomposites are highly efficient materials for removal of heavy metals from aqueous solution due to their high surface area, porosity, and multifunctional reactivity. The review highlights the exceptional adsorption capacities of nanocomposites like ZnO-CNT, GO-Fe_3O_4, MnO_2-GO, CNF-Fe_3O_4, Ag-Al_2O_3, and TiO_2-CeO_2, which achieve removal efficiencies higher than 90% for several metals, including lead, cadmium, and chromium. Adsorption is superior technique because of high efficiency, affordability and reliability. Despite these advancements and developments, many challenges such as the high cost of synthesis, variability, and limited environmental sustainability of current nanocomposites remain significant. An interdisciplinary approach that combines innovations in material science with economical and environmentally friendly production techniques is needed to overcome these barriers. The future of water treatment proposes improved efficiency, lower cost, and environmental compatibility through the incorporation of nanocomposites with cutting-edge methods like photocatalysis or hybrid filtration methods.

In future, Nanocomposites have the potential to advance economical, effective, and ecological solutions for water purification. In order to reduce the impact on the environment, new research should focus on developing green synthesis techniques that make use of biopolymers, agricultural waste, and renewable resources. It will be significant to improve the adsorption capacity of nanocomposites through making structural changes such as enlarging their surface area, adjusting their pore size, and functionalizing their surfaces with certain chemical groups. Additionally, the effectiveness of water treatment could potentially be increased by incorporating nanocomposites into hybrid systems that include adsorption, photocatalysis, and modified filtration systems. Another critical area of attention is the life cycle analysis of these materials, emphasizing recyclability and biodegradability to reduce additional contamination. With the goal to scale up these breakthroughs for practical uses and make sure that future nanocomposites meet the objectives of environmental sustainability and economic growth, cooperation across the academic, industrial, and regulatory sectors will be crucial.

CONFLICT OF INTEREST

The authors declare that there is no conflict

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of interests regarding the publication of this manuscript.

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