Review on Removal of Heavy Metals from Wastewater Using Spinel Nano Ferrites

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Abstract
Water pollution, exacerbated by industrial activities, urbanization, and inadequate waste management, seriously affects ecosystems and human health. Heavy metals, including lead, mercury, and cadmium, are of particular concern due to their environmental toxicity and persistence. They can enter water sources through natural processes and human activities, accumulating in organisms and leading to bioaccumulation and biomagnification in the food chain. The authors highlight the emerging use of spinel ferrite nanoparticles (SFNPs) for removing heavy metals from wastewater. SFNPs have unique properties, such as high surface area and magnetic characteristics, making them promising materials for addressing water treatment challenges. The review underscores the potential of SFNPs in improving water quality and managing wastewater effectively.

Keywords: Heavy Metals, Rare-Earth, Spinel Ferrite Nanoparticles, Water Pollution

1. Introduction

1.1 Water Pollution

Water pollution is a pressing environmental problem that profoundly impacts biodiversity, ecosystem functioning, and human well-being. Various anthropogenic activities, including industrial discharges, agricultural runoff, urbanization, and improper waste disposal, cause water pollution. From these sources, pollutants enter water bodies, from heavy metals and pesticides to pharmaceuticals and microplastics. The UN General Assembly recognizes clean drinking water as a fundamental right [1]. However, guaranteeing water purity is becoming increasingly difficult with rapid industrialization and globalization. Pollutants accumulate in water bodies and food webs, ultimately threatening organisms and humans. The consequences of water pollution are far-reaching and diverse. Contaminated water endangers human health, leads to waterborne diseases, and has long-term health consequences. In addition, aquatic ecosystems suffer from habitat degradation, loss of biodiversity, and impaired water quality, threatening the survival of many species. Economic impacts, such as reduced access to clean water and lower productivity in sectors that rely on water resources, compound the social costs of water pollution.

1.2 Heavy Metals as Water Pollutants

Heavy metals are metallic elements with high atomic weights and densities. These elements are typically located in the middle and bottom parts of the periodic table and possess properties such as conductivity and malleability. Though there is no strict definition of heavy metals, they are generally considered to include elements like lead, mercury, cadmium, arsenic, chromium, nickel, etc. While some heavy metals are essential micronutrients for organisms in small amounts, they can be toxic at higher concentrations [2].

Clean drinking water is essential for the preservation of life and good health. However, in the age of the industrial boom and the increasing environmental pollution that accompanies it, access to clean drinking water is a distant dream for many. Many harmful pollutants are irresponsibly discharged into water bodies and pose a significant risk to humans, animals, plants, and the environment. Among these pollutants, heavy metals are extremely toxic and can harm human health [3]. Heavy metals enter the environment through both natural processes and human activities. Heavy metals occur naturally in the earth's crust and can seep into water sources through geological processes. For example, rocks and soils containing heavy metal minerals can weather over time and release these metals into groundwater and surface waters [4][5][6]. Human activities such as industrial processes, mining, agriculture, and urbanization can significantly increase the concentration of heavy metals in water. Industrial effluents, mining effluents, and agricultural practices containing pesticides and fertilizers are common pathways through which heavy metals enter water bodies [2]. Unlike organic pollutants, heavy metals do not degrade or break down over time. Once released into the environment, they persist for long periods and can accumulate in sediments, soils, and living organisms, including aquatic plants and animals. Heavy metals also have the potential to bioaccumulate in the food chain. Organisms such as algae, plankton, and aquatic plants absorb these metals from water and accumulate them in their tissues. When higher trophic levels consume lower trophic organisms, accumulated heavy metals are transferred and concentrated in a process called biomagnification. This can lead to high levels of heavy metals in organisms at the top of the food chain, including humans [3].

1.3 Health Hazards of Heavy Metals

Four of the 10 substances listed by WHO as Chemicals of Major Public Health Concern are heavy metals [7]. While these metals are essential to the human body in minuscule quantities, ingesting them in higher quantities poses serious risks to human health. These metals can enter the body through ingestion, inhalation, or dermal contact. Once inside the body, they can accumulate in tissues and organs, leading to various health problems [8]. Unchecked consumption of heavy metals can lead to a variety of health problems, including neurological disorders, kidney damage, respiratory issues, cardiovascular diseases, and various cancers [8][9][10]. Heavy metals, such as lead, mercury, and arsenic, can cause neurological damage, including impaired cognitive function, memory loss, tremors, and in severe cases, paralysis [9][10][11]. In men, exposure can result in low sperm count and volume. Prenatal exposure to heavy metals, particularly lead and mercury, can lead to birth defects, developmental delays, and even abortion of the fetus [9][12]. Heavy metals can accumulate in the liver, kidneys, and lungs, leading to organ damage and dysfunction [9][13]. Chronic exposure to certain heavy metals has been associated with an increased risk of cancer, as these metals can disrupt normal cellular processes. Lung, liver, kidney, and skin cancer are among the types of cancer that can develop [10][14][15][19][21]. Ingestion of heavy metals through contaminated food or water can cause gastrointestinal issues such as nausea, vomiting, abdominal pain, and diarrhoea [18]. Exposure to certain heavy metals can also cause allergic skin reactions, dermatitis, and other skin disorders [13][14][20]. The table below summarises various heavy metal sources, side effects, and consumption guidelines.

Heavy Metal	Metal Ion	Sources	Side Effects on Human Health	Guideline Value (according to WHO)	Reference no.
Lead (Pb)	Pb (II)	• Naturally in Earth's crust • Plumbing systems • Mining and smelting • Pesticides	• Kidney and brain damage • Reduction in sperm count • Miscarriage and premature birth • Abortion of fetus.	0.01 mg/l	[9][12]
Mercury (Hg)	Hg (II)	• Industrial waste • Fish consumption • Fungicides	• Dermatitis • Kidney damage • Pink disease • Lung damage	0.006 mg/l	[13][10]
Arsenic (As)	As (III) and As (V)	• Earth's crust • Contaminated water • Industrial waste • Tobacco	• Skin lesions • Blackfoot disease • Diabetes • Cancer of the bladder and lungs	0.01 mg/l	[11][14]
Cadmium (Cd)	Cd (II)	• Soil and rocks • Cigarette smoke • Battery manufacturing • Welding	• Lungs, breast, prostate cancer • Stroke • Pulmonary edema	0.003 mg/l	[15][16] [17]
Chromium (Cr)	Cr (VI)	• Anthropogenic activities • Pigment industry • Hip and knee prosthetics	• DNA damage • Hypersensitivity • Nasal irritation and ulcer	0.05 mg/l	[18]
Nickel (Ni)	Ni (II)	• Soil • Volcano eruptions • Chemical and food industry	• Lung cancer • Asthma • Cardiovascular diseases	0.07 mg/l	[19]
Barium (Ba)	Ba (II)	• Natural Sources • Petroleum industry • Pharmaceutics	• Paralysis • Renal failure • Elevated blood pressure	1.3 mg/l	[20]

Zinc (Zn)	Zn (II)	• Mining activities • Industrial waste • Sewage and wastewater	• Anxiety • Atrial Strokes • Hypertension • Cancer	5.00 mg/l	[21]

Table 1: Heavy metal sources, side effects, and consumption guidelines

2. Spinel Ferrite Nanoparticles and Their Properties

Nanoparticles are particles having at least one dimension in the nanometer, i.e. 1-100 nm range [22]. Recently, spinel ferrite nanoparticles (SFNPs) have garnered considerable interest as promising materials for removing heavy metals from water. This interest is attributed to their unique properties, which include a high surface area, chemical stability, and adjustable magnetic characteristics.

SFNPs are special materials that can be represented by the chemical notation AB_2O_4. In this notation, A and B denote positively charged metal ions in tetrahedral (A site) and octahedral (B site) positions, respectively. Spinel ferrites are formed when a trivalent cation (Fe^{3+}) is combined with another binary metallic cation, such as Mn^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and so on [23]. The properties of ferrites are significantly influenced by the types, quantities, and positions of these metallic cations in the crystal arrangement [24]. Ferrites possess unique properties such as improved saturation magnetization, excellent electrical resistivity, superparamagnetism, and high chemical stability, making them much more effective than their bulk counterparts [25].

2.1 Magnetic Properties

Spinel ferrite nanoparticles (SFNPs) exhibit strong magnetic properties because of transition metal ions in their crystal lattice. The magnetic properties of SFNPs are significantly influenced by their size and shape. When the size of the nanoparticles decreases, their magnetic properties change, leading to phenomena such as superparamagnetism. This means the nanoparticles only exhibit magnetic behaviour in an external magnetic field. The magnetic properties of SFNPs can be adjusted by changing parameters such as particle size, composition, and synthesis method, making it possible to customize magnetic properties for specific applications [23].

2.2 Adsorption

SFNPs are well-suited for removing metallic ions due to their inherent ability to adsorb metals. Due to their nanoscale dimensions, spinel ferrite nanoparticles typically have a high surface area-to-volume ratio. This increased surface area provides more active sites for adsorption, enhancing their adsorption capacity for various contaminants. SFNPs can adsorb contaminants through multiple mechanisms, including electrostatic interactions, ion exchange, surface complexation, chemical bonding, and physical adsorption, making them a good candidate for removing toxic heavy metal pollutants from water [26].

2.3 Easy Recovery and Reuse

SFNPs are a popular choice for wastewater treatment because they can be regenerated and reused with the same efficiency as before. These nanoparticles possess superior magnetic properties, which makes them easily removable from water by applying an external magnetic field. Unlike other methods, this magnetic separation process is more straightforward, efficient, and economical. Furthermore, the recovered nanoparticles can be reintroduced into the adsorption system to remove contaminants from new solutions, making the process more sustainable [27].

3. Spinel Ferrite Nanoparticles for Removing Heavy Metals From Wastewater

The rise in industrialization and population growth has released harmful pollutants, including heavy metal ions, pesticides, detergents, dyes, and volatile organic compounds, into water bodies without proper assessment. These pollutants can cause severe health problems such as neurological damage, cardiovascular issues, genetic mutations, and cancer in both animals and humans. Various water treatment techniques, such as electrolysis, filtration, and chemical oxidation, have been employed to combat this issue. However, these methods have limitations such as insufficient removal of pollutants, low adsorption affinity, difficulty in recovering adsorbents, and high expenses. As a result, the current adsorbents used in water treatment are not very efficient. Therefore, there is a need for adsorbents that are economically friendly, effective, and easy to recover and reuse. SFNPs have been researched as a potential solution due to their excellent physical and chemical properties, including high surface-to-volume ratio, superparamagnetism, and exceptional adsorption capacity [28]. SFNPs such as $MnFe_2O_4$ and $CoFe_2O_4$ successfully removed As (V) with high degrading efficiency of 96% and 92% respectively [29]. $NiFe_2O_4$ alone was able to remove various toxic heavy metals like Cr (VI), Pb (II), and Cd (II) with an impressive efficiency of 89%, 79%, and 87%, respectively [30]. A 98.5% degrading efficiency was obtained for removing Pb (II) by Cu-doped $MgFe_2O_4$ [31]. Ca-doped Ni-Zn ferrites were successfully able to remove 98.25% and 51% of Cd (II) and Cr (VI) respectively [32]. Zn (II) was degraded with an efficiency of 70% and 60% by $MnFe_2O_4$ and $CoFe_2O_4$ respectively [33]. The table below lists the removal efficiency of various spinel ferrites for heavy metals.

S.No.	Spinel Ferrite	Heavy Metal	Removal Efficiency	Particle Size	Reference No.
1.	$MnFe_2O_4$ and $CoFe_2O_4$	As (V)	96% and 92%	30 nm and 75 nm	[29]
2.	$NiFe_2O_4$	Cr (VI), Pb (II), and Cd (II)	89%, 79%, and 87%	30.254 nm	[30]
3.	$Cu_{0.5}Mg_{0.5}Fe_2O_4$	Pb (II)	98.5%	29.5 nm	[31]
4.	$Ca_xNi_{0.4}Zn_{0.6-x}Fe_2O_4$	Cd (II) and Cr (VI)	98.25% and 51%	24 nm – 38 nm	[32]
5.	$MnFe_2O_4$ and $CoFe_2O_4$	Zn (II)	70% and 60%	20 nm – 80 nm	[33]
6.	$NiFe_2O_4$	Pb (II) and Cd (II)	97% and 80%	30-50 nm	[34]
7.	$CoFe_2O_4$	Cr (VI)	89.92%	15 nm – 23 nm	[35]
8.	$CuFe_2O_4$, Zn-$CuFe_2O_4$, and Co-$CuFe_2O_4$	Cr (VI)	54%, 90%, and 93%	79 nm, 66 nm, and 56 nm	[36]

9.	$MnFe_2O_4$	Cr (VI)	59.35%	100 nm	[37]
10.	$CuFe_2O_4$	Ba (II)	68%	32.4 nm	[38]
11.	$CoFe_2O_4$	Pb (II) and Zn (II)	96% and 92 %	27.82 nm	[39]
12.	$Zn_{0.2}Ni_{0.8}Fe_2O_4$	Cr (VI)	87.9%	14.9 nm	[40]
13.	$CoSm_{0.025}Fe_{1.975}O_4)_{0.9}G_{0.1}$	Pb (II)	99.8%	29 nm	[41]
14.	$(Mg_{0.4}Co_{0.4}Mn_{0.2})Fe_{2-2x}Sm_xSn_xO_4$	Cr(III), Fe(III), and Zn(II)	93.3%, 98.8%, and 80.6%	20.28 to 13.31 nm	[42]

Table 2: Heavy metals removal using rare-earth doped spinel nano ferrites

4. Advantages of Spinel Ferrite Nanoparticles

Spinel ferrite nanoparticles (SFNPs) offer significant benefits for wastewater treatment due to their strong magnetic properties, large surface area, and chemical stability. They are affordable and can be easily separated from treated water using a magnetic field, efficiently removing various pollutants, including dyes, heavy metals, and organic contaminants. Furthermore, SFNPs are readily reusable and regenerative, making them a cost-effective option for water purification [43].

Key advantages of spinel ferrite nanoparticles for wastewater treatment:

4.1 Magnetic separation

A major advantage of these materials is their magnetic property, which enables easy separation from treated water using a magnetic field. This feature simplifies the purification process and reduces the risk of secondary pollution from the adsorbent, contributing to cleaner, safer water solutions [44].

4.2 High adsorption capacity

SFNPs have high adsorption capacity due to their large surface area filled with active sites that bind pollutants. This makes them effective at removing heavy metals and contaminants from water, contributing to cleaner aquatic environments [45].

4.3 Chemical stability

The pH level of a solution affects heavy metal ions and the surface charge of the adsorbent, influencing its adsorption capacity. Higher pH values can lead to metal hydroxide precipitation, reducing the availability of metal ions for adsorption. Spinel ferrites are stable across various pH conditions, making them effective for wastewater treatment [46]

4.3 Customizable properties

By varying the metal composition of the spinel ferrite, the surface properties and adsorption selectivity can be tailored to target specific pollutants [47].

4.4 Regeneration and reusability

SFNPs can be easily regenerated and reused multiple times by simple magnetic separation and washing, significantly reducing the cost of treatment. The magnetic properties of spinel ferrites enable them to be easily separated from the substrate or reaction product with an external magnet, making it a more environmentally friendly option [48].

4.5 Cost-effective

Compared to other nanomaterials, spinel ferrites are relatively inexpensive to synthesize, making them a cost-efficient option for wastewater treatment **[49].**

5. Limitation of SFNPs

Using SFNPs for wastewater treatment can be difficult because most laboratories formulate synthetic wastewater instead of real wastewater. To fully understand the effects of genuine wastewater and potential solutions, all components of real wastewater must be used in experiments. When reusing regenerated nano adsorbents in adsorption-desorption cycles, the adsorption capacity of the material may decrease over time. Once the adsorbent is completely worn out, it should be replaced with fresh material, and the used SFNPs should be disposed of as solid waste. However, SFNPs can be mobile and highly reactive, posing risks to humans, biological systems, and the environment. Therefore, their handling and management must be taken into consideration. As nanoparticles can interact with the environment differently and react with various chemicals, their management must be strictly regulated to ensure environmental safety. However, the literature has limited information on managing discarded nanoparticles, and further research is needed [50] [51].

6. Conclusion

Water pollution significantly threatens environmental sustainability and human well-being, necessitating comprehensive research and effective management strategies. In conclusion, the use of SFNPs for the removal of heavy metals from wastewater holds significant promise. These heavy metals pose a high risk to ecological and public health concerns due to their toxic properties, and addressing their widespread presence in the environment is the need of the hour. The superior magnetic and adsorption properties of SFNPs make them a much better choice for tackling the issue of heavy metal pollution. Their recoverability and reusability lead to reduced costs compared to traditional methods. However, we still need to study their toxicity, which can harm human health. Their management and disposal after they have been used should be done properly so that it doesn't cause further damage to the environment. There is also a need to broaden the research horizon and extensively study the potential of SFNPs for removing all heavy metals.

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