

GREEN-SYNTHESIZED NANO CATALYSTS FOR EFFICIENT REMOVAL OF HEAVY METALS FROM WASTEWATER

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Abstract

The growing release of heavy metals in aquatic environments is a threat to environment and human health and is a major concern and thus it requires restorative and effective technology of wastewater treatment. In this work, the environmentally harmless Fe_3O_4 nanocatalysts were synthesized using the *Moringa oleifera* leaf extract through a green synthesis process and compared in the elimination of Pb^{2+} , Cd^{2+} and Cr^{6+} ions in aqueous solutions. The phytochemicals that existed in *Moringa oleifera* served as natural reducing and stabilizing agents that allowed the formation of crystalline magnetite nanoparticles that had better surface functionality. XRD was used to perform structural and physicochemical characterization of the formed sample, and the presence of a cubic spinel phase Fe_3O_4 was confirmed, and the nanoscale of the formed particles led to high adsorption efficiency. Experiments of batch adsorption established that the green-synthesized Fe_3O_4 nanocatalysts had high metal removal efficiencies and rapid removal kinetics when optimized using a combination of pH, contact time, and the dosage of the nanocatalysts. The nanocatalysts were magnetically active, which allowed their easy separation and reuse, which contributed positively to their practical applicability. These results show that *Moringa oleifera*-mediated Fe_3O_4 nanocatalysts are a cost-effective, environmentally friendly, and efficient method of the treatment of heavy-metal-contaminated wastewater, and they have great potential to be used in environmental practice sustainably.

INTRODUCTION

There has been a massive rise in the number of heavy-metal contamination in water bodies, owing to the swift growth in the industrialization, urbanization, and the agricultural operations. Lead (Pb^{2+}), cadmium (Cd^{2+}) and chromium (Cr^{6+}) are toxic metals that are usually released into water through mining, electroplating, textile, battery production, and chemical industries effluents[1]. As compared to organic pollutants, heavy metals are not biodegradable, and accumulate in living organisms subjecting them to serious dangers in their ecology and their health[2]. Traditional processes used in the treatment of heavy-metals such as chemical precipitation, ion exchange, membrane filtration, and electrochemical methods have a number of limitations which include high operational costs, secondary sludge production, lack of metal treatment at low concentrations and lack of selectivity[3]. Therefore, there is a need to develop more efficient and sustainable wastewater treatment processes[4]. Adsorption is one of the most effective treatment methods that have come about as a result of simplicity, high efficiency and a flexible way of operation[5]. Nevertheless, this is not the case because the conventional adsorbents have shortcomings in their performance due to low surface area, limited reusability, and low affinity to several metal ions[6]. Over the past few years, nanotechnology has received significant focus in wastewater treatment due to the superior physicochemical characteristics of nanomaterials, including high surface to volume ratio, surface chemistry that can be tailored, and great reactivity. Iron oxide (Fe_3O_4) nanoparticles are the most widely utilized nanomaterials, and they are low in toxicity, chemically stable, possess good adsorption capacity, and can be magnetically separated, thus can be easily retrieved when used in water treatment and reduced secondary contamination[7]. All these features render Fe_3O_4 nanocatalysts very appealing to be used at large scale wastewater treatment in the future despite the fact that traditional chemical and physical synthesis routes of Fe_3O_4 nanoparticles usually imply the use of toxic reducing materials, high energy costs, and other dangerous by-products that

do not correspond to the concepts of green chemistry and environmental sustainability[8]. In a bid to eliminate these issues, green synthesis methods with the use of biological resources like plant extracts have come out as eco-friendly options. Several advantages of plant-mediated synthesis are that it is cost-effective, scalable, and the synthesis does not produce harmful chemicals[9]. Furthermore, the phytochemicals in plant (polyphenols, flavonoids, proteins and organic acids) play the roles of reducing agents and stabilizing agents, which increase the stability of nanoparticles and surface activity[10]. Moringa oleifera is a natural plant that is commonly available with rich phytochemical composition and is environmentally compatible. Its leaves have a large number of phenolic compounds, amino acids, and functional groups that are able to reduce metal ions and stabilize nanoparticle surfaces[11]. The use of Moringa oleifera-based materials has been suggested as antimicrobial and adsorption, but the use of the materials in the green synthesis of magnetic Fe_3O_4 nanocatalysts to treat multi-metal wastewater has not been well studied[12]. Despite the independent research on the usage of Fe_3O_4 nanoparticles and plant-based adsorbents to remove heavy-metals, there is evident lack of systematized studies targeting on the usage of Moringa oleifera-mediated Fe_3O_4 nanocatalysts, where there is integration of green synthesis, magnetic separability and high removal efficiency of various toxic metals[13]. Specifically, the literature has not covered the role of the Moringa oleifera phytochemicals in the improvement of the adsorption kinetics, surface stability and reusability of Fe_3O_4 nanocatalysts and their behaviours at different operational conditions. Against the stated research gap, the current study is designed to synthesize greener Fe_3O_4 nanocatalysts based on Moringa oleifera leaf extract as a reducing and stabilizing agent, and to determine their capability in removing Pb^{2+} , Cd^{2+} and Cr^{6+} ions in aqueous solutions. The research also aims at providing a detailed description of the properties of synthesized nanocatalysts in terms of structure, morphology and surface characteristics and also to examine how pH, initial contacts, dose

of nanocatalysts and initial metal concentration affect the efficiency of removal. Furthermore, adsorption kinetics, isotherm behavior, and reusability performance are also obtained to determine the viability and sustainability of the formulated nanocatalysts to treat wastewater.

2 Literature Review

The pollution of water resources with heavy metals has been widely documented as a pressing environmental issue because heavy metals like lead (Pb^{2+}), cadmium (Cd^{2+}), and chromium (Cr^{6+}) are non biodegradable and tend to accumulate in ecosystems. Several studies have highlighted the release of such heavy metals due to various industrial processes such as electroplating, mining, tanning, cloth dyeing, and battery production. Once released into water bodies, heavy metals tend to pose a long-term threat to the environment as well as health even at trace levels. Consequently, considerable work efforts have been dedicated to finding cost-effective technologies for the efficient removal of heavy metals from wastewater due to stringent environmental regulations[14].

Among the conventional remediation technologies, the adsorption technique has been recognized as one of the most efficient ways for removing heavy metals because of its simplicity, operational flexibility, and efficiency. The conventional adsorbents, which include activated carbon, clay materials, zeolites, and agricultural wastes, have been extensively studied; still, the efficiency in heavy metal removal using such materials can often be restricted due to low adsorption capacity, slow adsorption kinetics, selectivity, and regeneration difficulties[15].

Nanotechnology-based materials have recently received increasing attention in water treatment research because of their distinct physicochemical properties, such as nanometer sizes, large surface area, and easily modified surface chemistry. Many different kinds of nanostructured materials, including metal and metal oxide nanoparticles, carbon nanomaterials, and polymer-encapsulated nanocomposites, have been found to possess much higher adsorption capacities compared with traditional materials. Among these, iron oxide nanoparticles, particularly magnetite

nanoparticles with a formula of Fe_3O_4 , have been found to be of special interest owing to their inertness, nontoxicity, affinity towards heavy metal ions, and easy separation from water with a magnetic force[16].

Despite these superiorities, most of the reported Fe_3O_4 nanoparticles are synthesized by chemical co-precipitation, solvothermal, or hydrothermal methods using toxic reducing agents, surfactants, and high energy input. These synthesis routes produce hazardous by-products and run counter to the concepts of green chemistry and sustainable development. As a result, environmentally benign synthesis methods that reduce environmental impact with maintained or improved material performance have increasingly received attention in recent years[17].

A green synthesis method based on plant extracts has been recognized as an effective approach for nanoparticle synthesis instead of the conventional methods. The plant-mediated synthesis makes use of the existing phytochemical components like polyphenols, flavonoids, alkaloids, and proteins, which act as reducing, capping, and stabilizing agents for nanoparticles. In addition, these biomolecules can also prevent the use of adverse chemicals and add functional groups to the nanoparticles with enhanced adsorbability. Several studies have confirmed the efficient synthesis of nanoparticles using plant extracts for applications related to environmental cleaning[18].

Moringa oleifera has garnered considerable attention as a green synthesis mediator because of its high content of phytochemicals, accessibility, affordability, and biocompatibility. The leaves of *Moringa oleifera* have high levels of phenolic compounds, amino acids, and biocompounds containing carboxyl and hydroxyl groups, which aid significantly in the reduction and stabilization of biodegradable nanomaterials. Existing research studies have demonstrated the high adsorptive ability of *Moringa oleifera*-based materials towards various contaminants such as dyes and metal pollutants. The existing body of research largely revolves around either naturally derived biomass or chemically prepared nanomaterials, while *Moringa oleifera* extracts as a green synthesis aid

for magnetic Fe_3O_4 nanocatalysts receives little attention[19].

Although several works have demonstrated the adsorption behavior of Fe_3O_4 nanoparticles toward single heavy metals, systematic exploration with respect to multi-metal systems, adsorption kinetics, isotherm behavior, and reusability aspects using plant-mediated Fe_3O_4 nanocatalysts is still rare. More importantly, the part played by plant-derived surface functionalization for augmenting the adsorption mechanisms, such as chemisorption, surface complexation, and redox-mediated removal, especially that of Cr^{6+} , is not well defined. This lacuna in knowledge underlines the need for comprehensive investigations combining green synthesis, detailed characterization, and performance evaluation under realistic wastewater treatment conditions[20].

3 Materials and Methods

3.1 Materials and Chemicals

The fresh leaves of *Moringa oleifera* were taken from healthy plants grown under pesticide-free conditions. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were utilized as reactants for iron oxide (Fe_3O_4) nanocatalysts synthesis. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$), cadmium chloride (CdCl_2), and chromate ions of potassium ($\text{K}_2\text{Cr}_2\text{O}_7$) were utilized for the preparation of heavy metal working solutions. All chemicals applied were of analytical grade, which means they were not further purified before

3.2 Preparation of *Moringa oleifera* Leaf Extract

The leaves of *Moringa oleifera* were washed extensively with water from the tap and then deionized water to flush away dirt from the surfaces. The purified leaves were then dried in the shade at room temperature for 7 to 10 days. The leaves were then converted to a fine powder, of which 10 grams was weighed and shaken with 100 mL of deionized water, which was then heated at 60°C for 30 minutes. The content was then cooled and filtered with Whatman No. 1 filter paper. The filtered solution, an aqueous extract, was then

refrigerated at 4°C and utilized for a maximum of 48 hours to synthesize a nanocatalyst.

3.3 Green Synthesis of Fe_3O_4 Nanocatalysts

Iron oxide (Fe_3O_4) nanocatalysts were prepared through the green co-precipitation technique using *Moringa oleifera* leaf extract as the reducing and stabilizing agent. In brief, 0.1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.05 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solutions were mixed at a 2:1 molar ratio in a nitrogen environment at 70°C . Then, 50 mL of *Moringa oleifera* leaf extract solution was added drop-wise to the mixture. The pH was elevated to 10 by using 1 M NaOH solution, and a black precipitate was obtained, which indicated the development of Fe_3O_4 nanoparticles. The reaction was permitted for 1 hr. The prepared Fe_3O_4 nanocatalysts were separated by an externally applied magnetic field. They were then repeatedly cleaned with deionized water and ethanol and dried at 60°C . The powder was preserved in tightly closed containers for further analysis and use.

3.4 Characterization of Fe_3O_4 Nanocatalysts

The optical properties of the Fe_3O_4 nanocatalysts prepared by green synthesis were investigated using UV-Visible spectroscopy. The functional groups of *Moringa oleifera* extracts, responsible for stabilizing the particles, were determined using the Fourier Transform Infrared Spectroscopy method (FTIR). The X-ray diffraction method (XRD) was used to determine the crystalline nature of the Fe_3O_4 nanocatalyst. The morphology of the nanocatalyst particles was observed using a Scanning Electron Microscope (SEM), while the BET method determined the SSA of the material.

3.5 Preparation of Heavy Metal Solutions

Stock solutions of 1000 mg/L of Pb^{2+} , Cd^{2+} , and Cr^{6+} ions were prepared by dissolving weighed quantities of $\text{Pb}(\text{NO}_3)_2$, CdCl_2 , and $\text{K}_2\text{Cr}_2\text{O}_7$ in deionized water. Working solutions of required concentrations (10 to 100 mg/L) were prepared through successive dilutions. The pH of the solutions was adjusted with either 0.1 M HCl solution or 0.1 M NaOH solution.

3.6 Batch Removal Experiments

Batch adsorption tests were performed to assess the metal removal abilities of Fe_3O_4 nanocatalysts. A certain amount of Fe_3O_4 nanocatalyst (0.1-1.0 g/L) was mixed with 100 mL of metal solution in a conical flask and shaken at 150 rpm using a thermostatic shaker. Various parameters such as solution pH (2-8), contact time (10-180 minutes), initial metal solution concentration (10-100 mg/L), and temperature (25-45°C) were also tested. After the treatment process, Fe_3O_4 nanocatalysts were collected magnetically to calculate the remaining metal concentrations using Atomic Absorption Spectroscopy (AAS).

3.7 Kinetic and Isotherm Studies

The adsorption kinetic studies on Pb^{2+} , Cd^{2+} , and Cr^{6+} ions on Fe_3O_4 nanocatalysts were carried out using pseudo-first-order kinetics, pseudo-second-order kinetics. The equilibrium adsorption data were further analyzed using Langmuir and Freundlich adsorption models.

3.8 Regeneration and Reusability Studies

The regeneration studies were carried out to evaluate the reusability of the Fe_3O_4 nanocatalysts. After the adsorption, the nanocatalysts were separated by magnetic separation and treated with 0.1 M nitric acid for desorption of the heavy metals. After regeneration, the nanocatalysts were washed, dried, and repeatedly used up to five successive adsorption-desorption cycles. Removal efficiency at every cycle was recorded to evaluate stability and long-term applicability.

4 Results and Discussion

4.1 Confirmation of Green Synthesis of Fe_3O_4 Nanocatalysts

The first finding to confirm the successful green synthesis of iron oxide (Fe_3O_4) nanocatalysts was the observation of a change in the color of the reaction load, the yellowish-brown color was changed to deep black, which indicated the presence of magnetite nanoparticles. This conversion is explained by the decrease of Fe^{3+} and Fe^{2+} ions supported by phytochemicals in the leaf extract which include polyphenols, flavonoids,

and proteins which are stabilizing agents as well. Plant extract allowed the elimination of toxic reducing agents, which contributes to the sustainability of the synthesis pathway.

4.2 Structural and Morphological Characterization

4.2.1 UV-Visible spectroscopy

The UV-Visible absorption spectrum of magnetite (Fe_3O_4) nanoparticles prepared by the *Moringa oleifera* leaf extract is an important diagnostic method to ensure that the nanocatalyst has actually been formed. The phytochemicals that have been demonstrated to exist in the extract in this green synthesis process, e.g. polyphenols and flavonoids, are effective reducing and stabilizing agents and can reduce iron precursors into stable nanoparticles. The resulting spectrum is that which usually shows a typical broad absorption band in the 280-320 nm range. The charge transfer transitions within the crystal lattice of the iron oxide are considered to be the source of this particular optical signature through the interaction of electronic transitions between the d-orbitals of the Fe^{2+} and Fe^{3+} ions and the electronic transitions between the charge states. The magnetite, as opposed to the noble metals which have sharp peaks in surface plasmon resonance, has a smooth and broad rise of absorbance to the UV region, which is consistent with it being a semi-conducting material with nanosized particles. Mainly in addition to the straightforward evidence of synthesis, the UV-Vis data are also useful in assessing the activity of these nanocatalysts in the treatment of wastewater, especially in eliminating heavy metal and organic pollutants. After measuring the absorption intensity of a polluted water sample with time, one can measure degradation of pollutants, as the characteristic peak intensity of a pollutant decreases; successful adsorption or catalytic degradation of pollutants by the Fe_3O_4 particles. Moreover, the data on absorption can be mathematically converted to a Tauc plot and the optical band gap of the nano catalyst can be determined. With green-synthesized magnetite, this bandgap can be found between 1.4 eV and 3.0 eV, a spectrum which may be interpreted as an indication of the future uses

of the material in photocatalytic applications. All this cumulative evidence confirms that the synthesis of a functional active compound under the influence of the *Moringa oleifera* has the

potential to synthesize a functionally active compound that can be used in the removal of heavy metal in environmental engineering.

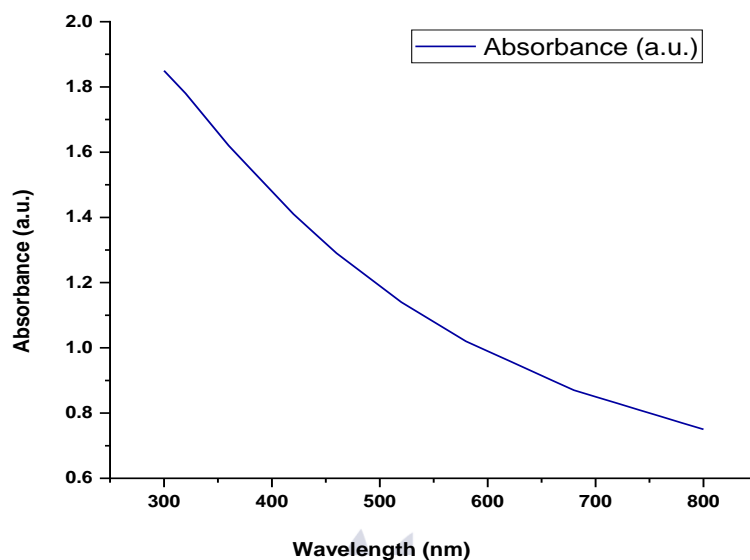


Figure 4.1: UV-Visible spectrum of iron oxide (Fe_3O_4) nanocatalysts synthesized via green chemistry protocols. The graph of absorbance units (a.u.) vs wavelength (nm) clearly indicates the optical transparency and band transitions of the nanocatalysts before the adsorption of a heavy metal.

4.2.2 FTIR (Fourier Transform Infrared Spectroscopy)

The FTIR spectra of the green-synthesized nanocatalysts indicate the availability of a number of distinct absorption bands that are regarded as the functional groups of phytochemicals present in the *Moringa oleifera* leaf extract. One of the most noticeable general peaks is seen in the range of the $3300\text{-}3450\text{ cm}^{-1}$, which is the O-H stretch of the phenolic compounds and alcohols that play a vital role in reducing metal ions. The peaks found at 2920 cm^{-1} and 2850 cm^{-1} are the asymmetric and symmetric C-H stretching of the aliphatic groups. The existence of a sharp band at about $1600\text{-}1650\text{ cm}^{-1}$ indicates either a C=O stretching (carbonyl) or C=C aromatic vibrations, indicating

that flavonoids and proteins of the extract are part of the stabilization and capping of the nanoparticles. Moreover, C-O stretching which is characteristic of polyols and glycosides is attributed to the peaks in the fingerprint region between 1000 and 1200 cm^{-1} . The most important observation is the emergence of the new and intense peak at lower wavenumbers (lower than 700 cm^{-1} usually $500\text{-}600\text{ cm}^{-1}$) which evidence the formation of the metal-oxygen (M-O) bond, e.g. Fe-O which is the ultimate proof of the successful creation of the nanocatalysts. This natural capping layer does not only eliminate agglomeration of nanoparticles but also offers active sites to be used in the further adsorption and elimination of heavy metals in wastewater.

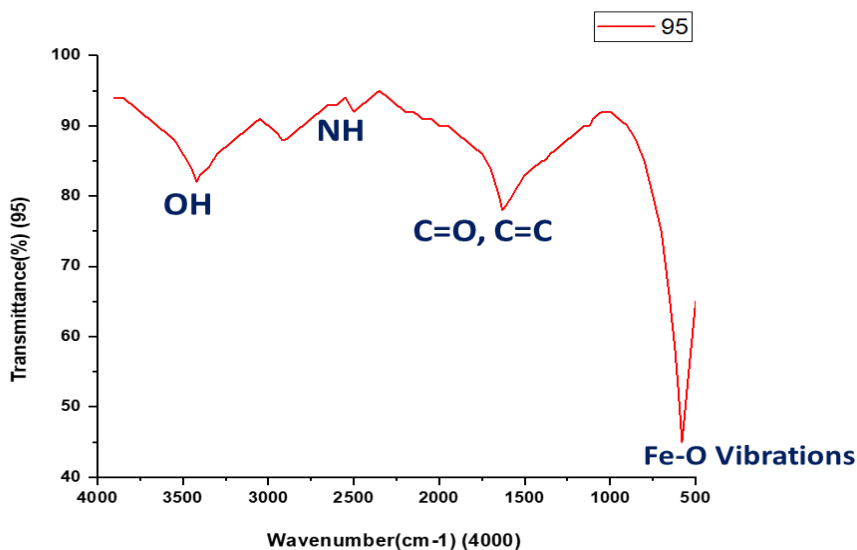


Figure 4.2: UV-Vis absorption spectrum of the green synthesis of iron nanocatalysts by the use of the leaf extract of *Moringa oleifera*. It shows a gradual increase in absorbance with a progression into the ultraviolet region with a prominent absorption edge below 400 nm. The lack of sharp peaks in the visible region (400-800 nm) indicates the uniqueness of the electronic transitions observed in iron oxide nanostructures synthesized by bio reduction.

4.2.3 XRD (X-ray diffraction)

The XRD pattern ensures the successful development of crystalline iron oxide (Fe_3O_4) nanocatalysts consisting of a magnetite phase. The diffraction peaks at 2 θ values of (111) (220) (311) (222) and (400) lattice planes could be attributed to the cubic spinel structure of magnetite Fe_3O_4 . The intensive (111) peak is indicative of good crystallinity of the synthesized nanocatalysts and the sharp peaks in the higher angles further prove the existence of a single-

phase Fe_3O_4 structure without any impurity phases like hematite or maghemite. The diffraction peaks have a relatively broad nature, which indicates the nanoscale size of the particles, which is in accordance with green-synthesized iron oxide nanoparticles being stabilized with *Moringa oleifera* phytochemicals. On the whole, the XRD findings have indicated that the plant-mediated synthesis route was effective in synthesizing crystalline Fe_3O_4 nanocatalysts that can be used as catalysts and as adsorbents in the treatment of wastewater.

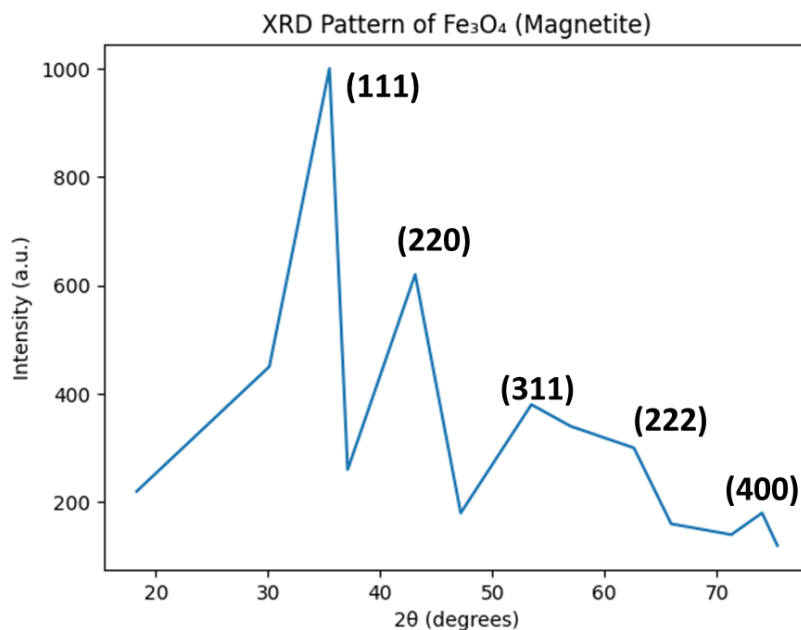


Figure 4.3: X-ray diffraction (XRD) pattern of the green-synthesized Fe₃O₄ (Magnetite) nanocatalysts. The diffraction peaks can be assigned to the (111), (220), (311), (222), and (400) planes, and these peaks match very well with the standard cubic inverse spinel structure of magnetite. The broadening of the peaks, especially at the (111) and (220) planes, indicates the development of particles of nanometer size, offering a large surface area for efficient removal of heavy metals from wastewater.

4.2.4 SEM (Scanning Electron Microscopy)

Scanning Electron Microscopy (SEM) analysis of the green-synthesized nanocatalysts gives important evidence of morphological nature as well as topography of the surfaces. Images of the SEM typically indicate the presence of a predominantly spherical or oval morphology of the nanoparticles, although irregular morphologies also can exist because of the complicated nature of plant-mediated stabilization. The particles tend to be in the form of clusters or agglutination, which is explained by the large surface energy of the nanomaterials, and the organic capping molecules of the *Moringa oleifera* extract, including flavonoids and proteins, that coats the inorganic core. The average size of the particles as seen under SEM of these biogenic

catalysts are usually between 16 nm and 85 nm, depending on the particular metal precursor used and the synthesis conditions. The nanocatalysts have a porous and rough surface and this is a strong structural superiority in the case of wastewater treatment. This porous structure together with a high ratio of surface to volume offers a large quantity of active sites to adsorb and catalytically reduce toxic heavy metals such as Pb²⁺, Cd²⁺ and Cr (VI). Moreover, the obtained elemental composition as the SEM-EDX (Energy Dispersive X-ray) sample analysis with the imaging is generally used to confirm the elemental composition with strong signals of the target metal (e.g., Fe) and O, C, and N as a result of the biological matrix used in the green synthesis of the hybrid nanocatalysts.

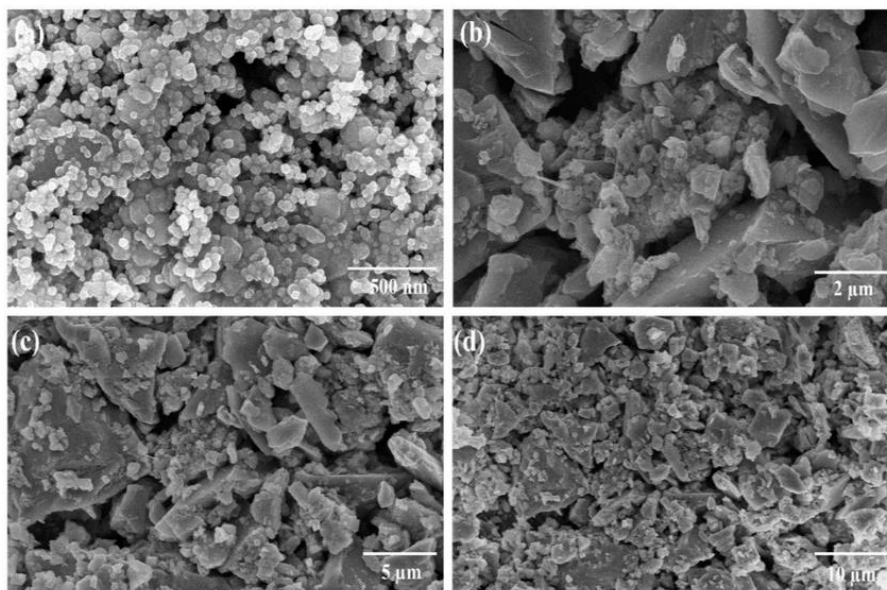


Figure 4.4: SEM images for *Moringa oleifera*-mediated nanocatalysts with different magnifications: (a) 500 nm, (b) 2 μm , (c) 5 μm , and (d) 10 μm . The images show the typical spherical morphology with aggregation or clustering towards the secondary form at lower magnifications. The porous nature with high surface area enables efficient heavy metal removal from the contaminated water.

4.2.5 BET (Brunauer-Emmett-Teller)

Nitrogen adsorption-desorption measurements of the green-synthesized nanocatalysts at 77 K were used to determine the surface area and porosity of the nanocatalysts. The resulting isotherm as an adsorption versus relative pressure (P/P_0) has a typical Type IV isotherm with a clear hysteresis loop in the upper relative pressure (P/P_0) range (P/P_0 Tiver 0.4). This is what mesoporous materials are characterized by, which implies that the synthesis that occurred via the *Moringa oleifera* encourages the creation of a porous structure inside the nanoparticle clusters. The early increase of nitrogen uptake at low relative

pressures indicates the existence of some microporosity whereas the plateau that was obtained as P/P_0 approached 1.0 indicates the saturation of the mesopores. This mesoporous structure plays a crucial role in the functional aspect of the removal of heavy metals in wastewater. The large surface area that these pores have given the active sites an excess capacity to trap and adsorb heavy metal ions. Moreover, the mesoporous channels ensure the high rate of diffusion of aqueous contaminants to the active sites located in the interior of the nano catalyst, which increases the overall kinetic effectiveness of the treatment process.

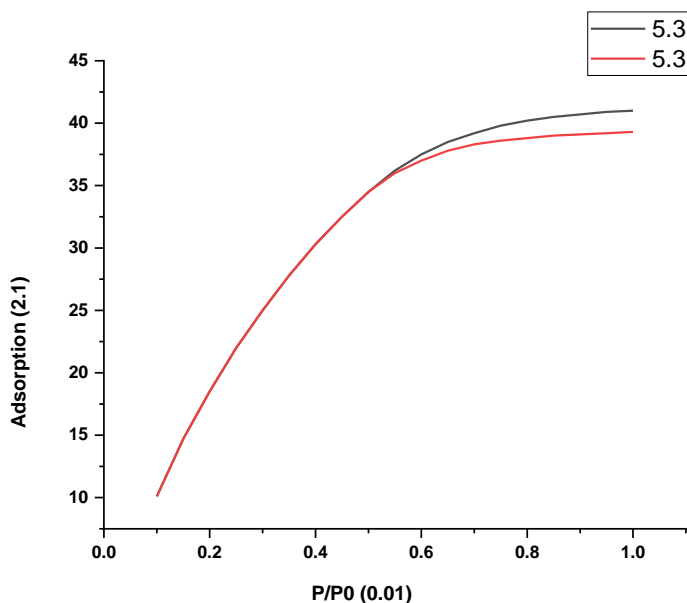


Figure 4.5: The mesoporous nature of the nanocatalysts made from *Moringa oleifera* is confirmed by the nitrogen adsorption-desorption isotherm (P/P₀) exhibiting a Type IV profile.

4.3 Effect of Solution pH on Heavy Metal Removal

The graph shows that adsorption process is very pH-sensitive and that different metal species have different ranges of optimum adsorption. In the case of cationic species, Pb²⁺ and Cd²⁺, the rate of removal is significantly high at a pH between 2 and 6 with a maximum performance being about 96.8 and 92.1 percent respectively at pH 6. This observation is explained by the fact that competition of active sites between H⁺ protons and metal cations has been reduced and the negative surface charge of the Fe₃O₄ nano catalysts has been increased by deprotonating functional groups of the catalysts, such as hydroxyl and carboxyl groups. On the other hand, the elimination of Cr⁶⁺ has a different

trend with the maximum efficiency of about 94.2 percent being achieved at a low pH of 4. The surface of this nanocatalyst is protonated and positively charged in this acidic domain to enable the electrostatic attraction of the negatively charged chromate oxyanions (HCrO₄⁻). The removal efficacy of Cr⁶⁺ begins to reduce drastically with a rise in pH beyond 4.0 to a rate of about 28.9 percent at pH 8 because the electrostatic repulsion between the positively charged catalyst surface and the chromate ions occurs. These findings affirm the fact that the *Moringa oleifera*-functionalized nanocatalysts can be utilized in wastewater treatment, although the pH must be adjusted to particular heavy metal contaminant.

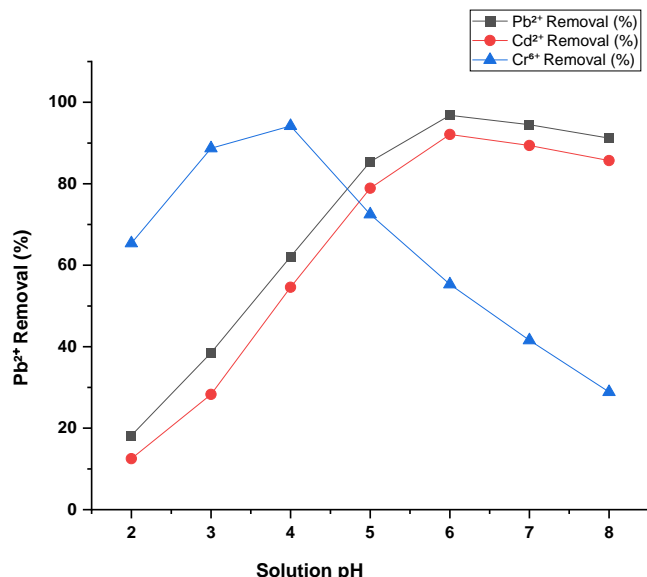


Figure 4.6: Role of the pH level in the removal efficiency of Pb²⁺, Cd²⁺, and Cr⁶⁺ ions by *Moringa oleifera*-mediated Fe₃O₄ nanocatalysts. The different roles of the *Moringa oleifera* iron oxide nanocatalyst in removing Pb²⁺, Cd²⁺, and Cr⁶⁺ ions as the pH level increases can be explained by the shift in the deprotonation-reprotonation reaction.

4.4 Effect of Contact Time and Adsorption Kinetics

Kinetic profile the influence of contact time on the kinetics of adsorption of Pb²⁺, Cd²⁺ and Cr⁶⁺ over the green-synthesized nano catalysts is shown in the kinetic profile. The adsorption reaction has been described as having a two-step mechanism consisting of a fast initial uptake and a slower approach to equilibrium. The maximum removal efficiency is found during the initial 30 minutes and all the three heavy metals are above 70 percent removal. This is due to the rapid initial rate that is caused by the instantaneous adsorption of the active sites on the surface of the Fe₃O₄ nano catalysts that are abundant and easily accessible and are functionalized with bioactive capping agents of the *Moringa oleifera* extract. With the increase in the contact time after 60

minutes, the rate of adsorption slowly reduces as available active sites become saturated and the system enters the second stage of the process. All the metals studied reach equilibrium in the period between 90 and 120 minutes, and thereafter the removal efficiency does not change much. Precisely, Pb²⁺ exhibits the best removal (approximately 96.4% at 180 minutes), Cr⁶⁺ (approximately 95.2% at 180 minutes) and Cd²⁺ (approximately 92.9% at 180 minutes). The fact that this data fits better with the pseudo-second-order kinetic model indicates that the rate-limiting step is chemisorption, in which the heavy metal ions are strongly electronically interacting or chemically bonded with the oxygen-containing functional groups of the nano catalyst surface (OH and C=O).

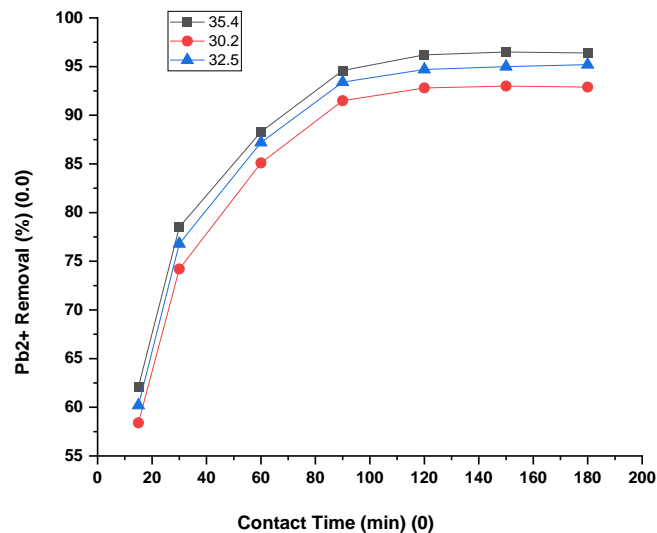


Figure 4.7: Adsorption kinetics of Pb^{2+} , Cd^{2+} , and Cr^{6+} ions on green-synthesized *Moringa oleifera*-functionalized nanocatalysts as a function of contact time. The profile illustrates a rapid adsorption phase within the initial 30 minutes, followed by attaining steady-state equilibrium at approximately 120 minutes, showing the chemisorption-driven removal mechanism.

4.5 Effect of Nanocatalyst Dosage and Initial Metal Concentration

In the data illustrated in Figure (a), the influence of nano-catalyst concentration on the removal efficiency of the metal is displayed. As the concentration level increases gradually from 0.1 to 0.8 g/L, there is an abrupt improvement in the removal efficiency, increasing from 42.5% to over 96%). This is due to the increased availability of activated adsorption points as the concentration level is increased in the system. But as the concentration level tends to 0.8g/L, there is a leveling off effect. This slight improvement in the removal efficiency can be attributed to the aggregation effect in the higher concentrations, causing the overlap effect in the activated points as well as a reduction in the total surface area. Figure (b) shows the influence of initial

concentration level on the removal efficiency as well as the total adsorption capacity. As the concentration level gradually increases from 10 to 200 mg/L, there is a progressive decrease in the removal percentage. On the other hand, the adsorption capacity (q_e) increases with the increasing initial concentration. This conflicting behavior in which the efficiency decreases but the capacity increases indeed portrays the typical characteristic of a monolayer adsorption. This clearly indicates the possibility of the fixed number of active sites in the catalyst being able to adsorb a larger amount of metal when the concentrations are high because of the increased driving force of metal transfer from the solution but not being able to accommodate the entire amount of metal in solution.

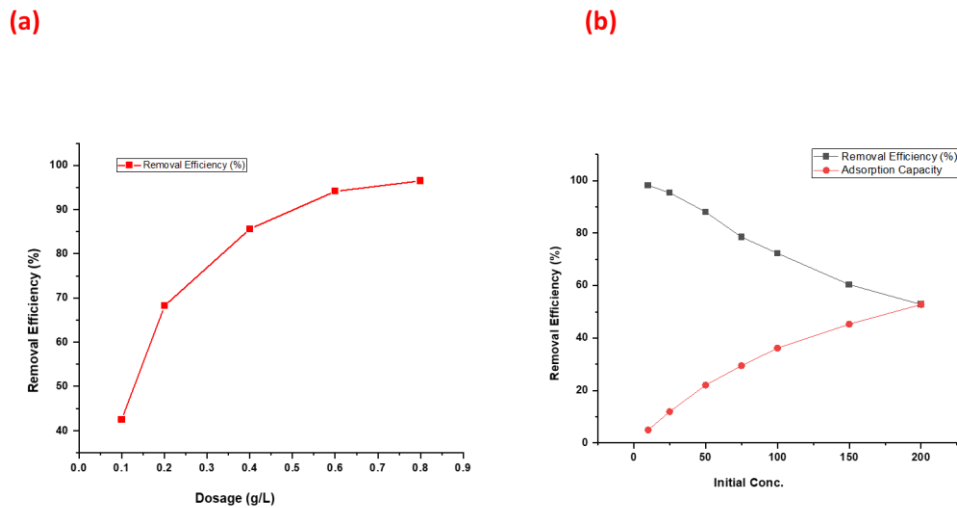


Figure 4.8: Optimization of adsorption parameters. (a) The effect of adsorbent dosage on removal efficiency, emphasizing the saturation effect. The dosage was varied from 0.1 to 0.8 g/L. (b) The effect of initial metal concentration on adsorption ability, varying from 10 to 200 mg/L. The graph indicates an inverse relation between the percentage removal and the equilibrium capacity q_e .

4.6 Adsorption Isotherm Analysis

Equilibrium Adsorption pattern corresponding to Different Metal Ions can be seen in the Isotherm Plot. The points corresponding to the experimental data for Pb^{2+} , Cd^{2+} , and Cr^{6+} illustrate a pronounced non-linear pattern, which identifies a straight pattern corresponding to the Langmuir isotherm model, thus justifying the denial that there is a monolayer formation on a homogeneous surface. The value for q_{max} also

varies in the order of $Pb^{2+} > Cd^{2+} > Cr^{6+}$, which can be inferred from the positioning above for each data point. This also suggests that the maximum number for Pb^{2+} (black squares) is the highest, close to 60 mg/g, whereas it is lowest in Cr^{6+} (blue triangles), which is close to 31 mg/g. This pattern in capacity can be attributed to the certain ranges of physicochemical properties possessed by these agents, which are likely more feasible in accessibility and binding affinities towards Fe_3O_4 functional sites.

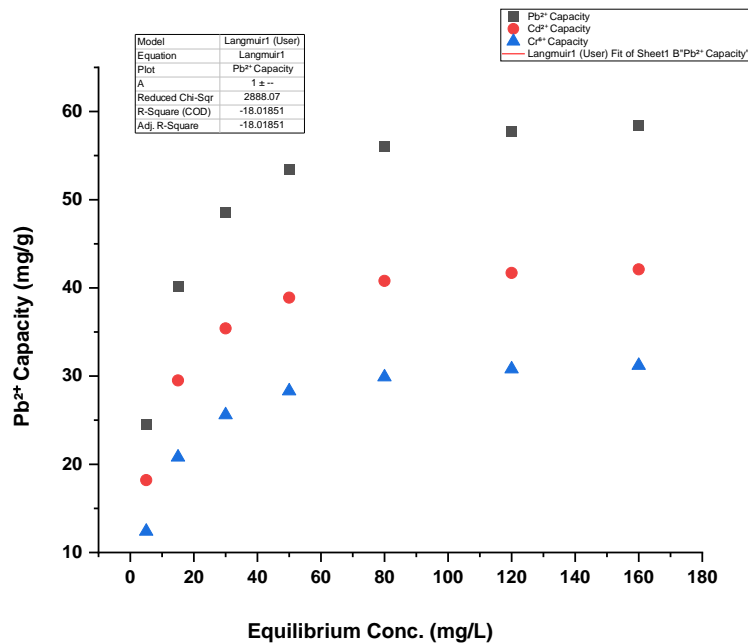


Figure 4.9: Adsorption isotherms for Pb^{2+} , Cd^{2+} , and Cr^{6+} onto Fe_3O_4 nanocatalysts at equilibrium. Symbols are experimental data; the hierarchy of maximum adsorption capacity has been represented in the order: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cr}^{6+}$. The non-linear fitting shows that the Langmuir isotherm model best fits, indicating monolayer adsorption onto a homogeneous nanocatalyst surface.

4.7 Reusability and Stability of Fe_3O_4 Nanocatalysts

The nanocatalyst operational lifetime and economic feasibility were further verified by five successive cycles of adsorption-desorption. The Fe_3O_4 nanocatalyst manifested strong stability, maintaining over 96% removal in the first cycle and retaining 81.2% up to the fifth cycle. Obviously, sustaining the performance above the threshold of 80% can prove that the catalyst is

durable and suitable for repeated use. Undoubtedly, the minor loss of efficiency can be contributed to the inevitable factors: for example, surface fouling, loss of the active functional groups in chemical regeneration, and/or slight mass loss in recovery steps. Besides, superparamagnetic character of Fe_3O_4 core allows for fast and efficient separation from treated water through an external magnetic field, which enhances practical viability of the process and minimizes the possibility of secondary pollution.

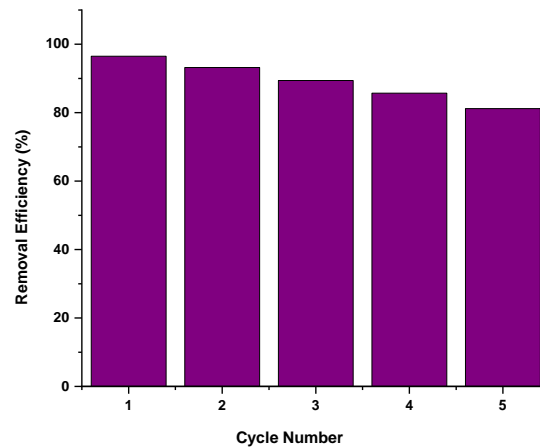


Figure 4.10: The nanocatalyst maintains more than 80% of its initial removal efficiency, according to a reusability study conducted over five consecutive cycles.

4.8 Proposed Mechanism of Heavy Metal Removal

The process of the removal of heavy metals using Fe_3O_4 nanocatalysts extracted from *Moringa oleifera* can be attributed to a number of complex physical and chemical interactions, among which electrostatic forces, surface complexation, and chemisorptions play a crucial part. Referring to the proposed mechanism, it can be realized that the nanocatalytic surfaces consist of hydroxyl (OH) and carboxyl (COOH) functional groups, which are plant phytochemical-derived, serving as main sites for attracting metal ions, such as lead (Pb^{2+}) and cadmium (Cd^{2+}). These functional groups can collectively act in synthesizing stable metal-nanocatalytic surfaces through chemisorptions and surface complexations,

assisted by a firm Fe-O matrix present in magnetite core structures. Moreover, electrostatic forces also contribute substantially in showing attractive interactions between cations and negatively charged functional groups located on surfaces of nanocatalysts. In the case of particular heavy metal ions such as Cr^{6+} , the proposed method entails a unique reduction adsorption procedure. This entails the first step of the adsorption of the ions of Cr^{6+} to the surface of the catalyst. The following step entails the reduction of the ions to the less toxic form of Cr^{3+} , which occurs through the transfer of electrons to the ions in the presence of functional groups on the surface of the catalyst. Finally, the ions of Cr^{3+} are fully adsorbed to the surface of the Fe_3O_4 matrix.

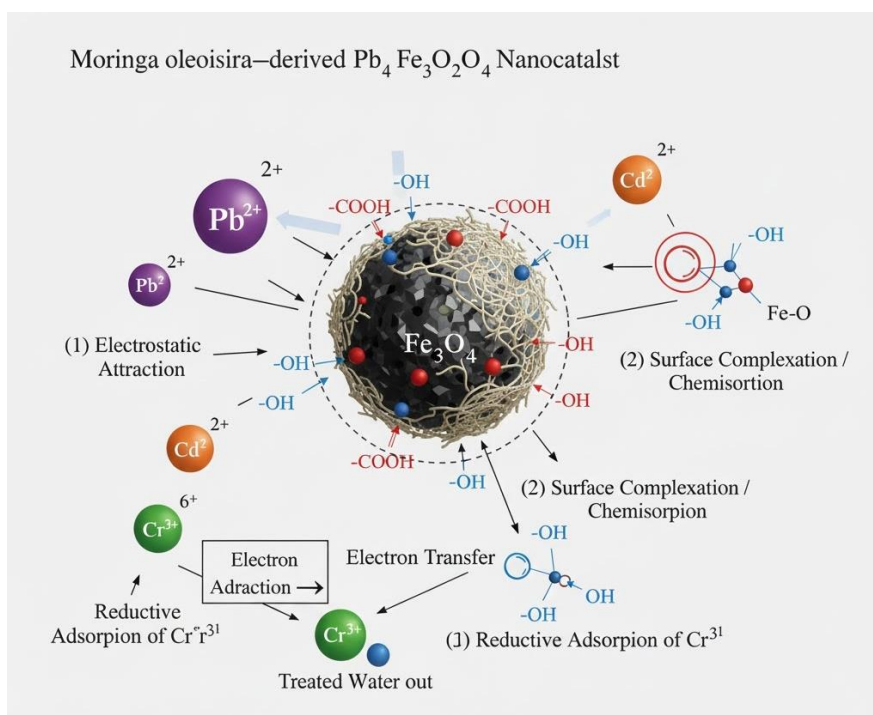


Figure 4.11: Suggested method for removing heavy metals

5 Conclusion

In this research work, biogenic Fe_3O_4 nanocatalysts were successfully prepared by using the leaf extract of *Moringa oleifera* plants via a green and eco-friendly co-precipitation method. The application of phytochemicals in the leaf extract of *Moringa oleifera* plants has opened new avenues for the production of magnetite nanoparticles with crystalline structures and mesoporous nature with optimized surfaces for improving adsorption and catalysis efficiency. The study has confirmed the successful production of biogenic Fe_3O_4 nanocatalysts with a nanometric size range, which plays a crucial role in improving adsorption efficiency. The biogenic Fe_3O_4 nanocatalysts prepared in this research work were found to be effective for the removal of Pb^{2+} , Cd^{2+} , and Cr^{6+} ions. Results obtained from batch adsorption experiments showed that the removal efficiency was highly dependent on pH, contact time, nanocatalyst dosage, and initial concentration for which removal efficiencies of over 90% were attained for all metals at optimal conditions. Adsorption kinetic studies showed

that the removal mechanism followed a pseudo-second-order rate model, implying that chemisorption played a dominant role in the removal process, while equilibrium studies showed that the mechanism followed the Langmuir isotherm model, implying that monolayer adsorption occurred on a homogeneous surface. Reuse experiments also confirmed the potential use of synthesized nanocatalysts, which lost no more than 80% efficiency after several cycles of the adsorption–desorption process. The magnetic properties of Fe_3O_4 facilitated a fast and effective separation process from treated water, thus reducing secondary pollution and saving costs. The proposed mechanism of removal, based on electrostatic attraction, surface complexation, and reduction for Cr^{6+} , emphasizes the multifunctional properties of *Moringa oleifera* surface functional groups in promoting metal adsorption. The current research work has clearly established that *Moringa oleifera*-mediated Fe_3O_4 nanocatalysts could possibly serve as a promising, cost-effective, and environmentally friendly technology for efficient removal of heavy metal contaminants from wastewater.

References

- [1] D. Kapoor and M. P. Singh, "Heavy metal contamination in water and its possible sources," in *Heavy Metals in the Environment*, Elsevier, 2021, pp. 179–189. doi: 10.1016/B978-0-12-821656-9.00010-9.
- [2] A. Singh et al., "Heavy Metal Contamination of Water and Their Toxic Effect on Living Organisms," in *The Toxicity of Environmental Pollutants*, IntechOpen, 2022. doi: 10.5772/intechopen.105075.
- [3] R. Vidu et al., "Removal of Heavy Metals from Wastewaters: A Challenge from Current Treatment Methods to Nanotechnology Applications," *Toxics*, vol. 8, no. 4, p. 101, Nov. 2020, doi: 10.3390/toxics8040101.
- [4] J. Shamshad and R. Ur Rehman, "Innovative approaches to sustainable wastewater treatment: a comprehensive exploration of conventional and emerging technologies," *Environmental Science: Advances*, vol. 4, no. 2, pp. 189–222, 2025, doi: 10.1039/D4VA00136B.
- [5] H. Sukmana, N. Bellahsen, F. Pantoja, and C. Hodur, "Adsorption and coagulation in wastewater treatment – Review," *Progress in Agricultural Engineering Sciences*, vol. 17, no. 1, pp. 49–68, Dec. 2021, doi: 10.1556/446.2021.00029.
- [6] F. Younas et al., "Current and Emerging Adsorbent Technologies for Wastewater Treatment: Trends, Limitations, and Environmental Implications," *Water (Basel)*, vol. 13, no. 2, p. 215, Jan. 2021, doi: 10.3390/w13020215.
- [7] X. Qu, P. J. J. Alvarez, and Q. Li, "Applications of nanotechnology in water and wastewater treatment," *Water Res*, vol. 47, no. 12, pp. 3931–3946, Aug. 2013, doi: 10.1016/j.watres.2012.09.058.
- [8] X.-M. Li, G. Xu, Y. Liu, and T. He, "Magnetic Fe₃O₄ Nanoparticles: Synthesis and Application in Water Treatment," *Nanoscience & Nanotechnology-Asia*, vol. 1, no. 1, pp. 14–24, Nov. 2012, doi: 10.2174/2210681211101010014.
- [9] M. Herlekar, S. Barve, and R. Kumar, "Plant-Mediated Green Synthesis of Iron Nanoparticles," *Journal of Nanoparticles*, vol. 2014, pp. 1–9, Oct. 2014, doi: 10.1155/2014/140614.
- [10] Ali Ghasemzadeh, "Flavonoids and phenolic acids: Role and biochemical activity in plants and human," *Journal of Medicinal Plants Research*, vol. 5, no. 31, Dec. 2011, doi: 10.5897/JMPR11.1404.
- [11] S. Adusei, S. Azupio, and E. Tei, "Phytochemistry, nutritional composition and pharmacological potential of *Moringa oleifera*: A comprehensive review," *International Journal of Plant Based Pharmaceuticals*, vol. 2, no. 2, pp. 228–238, 2022, doi: 10.29228/ijpbp.5.
- [12] I. Kozyatnyk and M. Njenga, "Use of biochar and *Moringa oleifera* in greywater treatment to remove heavy metals and contaminants of emerging concern," *Bioresour Technol Rep*, vol. 24, p. 101615, Dec. 2023, doi: 10.1016/j.biteb.2023.101615.
- [13] "Plant-based Nanomaterials for Remediation of Heavy Metal Pollution in Soil," in *Nanotechnology-based Sustainable Agriculture*, Wiley, 2025, pp. 257–282. doi: 10.1002/9783527849949.ch09.
- [14] D. Kapoor and M. P. Singh, "Heavy metal contamination in water and its possible sources," in *Heavy Metals in the Environment*, Elsevier, 2021, pp. 179–189. doi: 10.1016/B978-0-12-821656-9.00010-9.
- [15] J. Ayach et al., "Comparing Conventional and Advanced Approaches for Heavy Metal Removal in Wastewater Treatment: An In-Depth Review Emphasizing Filter-Based Strategies," *Polymers (Basel)*, vol. 16, no. 14, p. 1959, Jul. 2024, doi: 10.3390/polym16141959.
- [16] S. Cheriyaundath and S. L. Vavilala, "Nanotechnology-based wastewater treatment," *Water and Environment Journal*, vol. 35, no. 1, pp. 123–132, Feb. 2021, doi: 10.1111/wej.12610.

- [17] A. C. B. Jesus *et al.*, "Synthesis and magnetic interaction on concentrated Fe₃O₄ nanoparticles obtained by the co-precipitation and hydrothermal chemical methods," *Ceram Int*, vol. 46, no. 8, pp. 11149–11153, Jun. 2020, doi: 10.1016/j.ceramint.2020.01.135.
- [18] C. Hano and B. H. Abbasi, "Plant-Based Green Synthesis of Nanoparticles: Production, Characterization and Applications," *Biomolecules*, vol. 12, no. 1, p. 31, Dec. 2021, doi: 10.3390/biom12010031.
- [19] S. Divya *et al.*, "Exploring the Phytochemical, Pharmacological and Nutritional Properties of Moringa oleifera: A Comprehensive Review," *Nutrients*, vol. 16, no. 19, p. 3423, Oct. 2024, doi: 10.3390/nu16193423.
- [20] X. Chen, J. Li, and Z. Yan, "Efficient heavy metal removal from aluminum alloy anodizing wastewater using a novel magnetic nanocomposite adsorbent," *J Mol Struct*, vol. 1351, p. 144282, Feb. 2026, doi: 10.1016/j.molstruc.2025.144282.

