Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Surface-Engineered Fe_3O_4/Graphene Oxide/Polymer Magnetic Nanocomposites for Efficient and Reusable Removal of Pb^{2+} and Cd^{2+} from Wastewater

Martin Ouma Osemba

mouma@associates.mku.ac.ke

Mount Kenya University https://orcid.org/0009-0007-2045-4746

Adrián Chávez Huerta

Zulian Institute of Technological Research (INZIT), Venezuela

Research Article

Keywords: Magnetic nanocomposites, Fe_3O_4, graphene oxide, chitosan, Pb^{2+} removal, Cd^{2+} removal, adsorption kinetics, wastewater treatment, magnetic separation, reusability

Posted Date: March 31st, 2026

DOI: https://doi.org/10.21203/rs.3.rs-9248702/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Additional Declarations: The authors declare no competing interests.

Abstract

The development of efficient and recyclable adsorbents for heavy metal removal remains a critical challenge in wastewater treatment. In this study, surface-engineered Fe_3O_4 based magnetic nanocomposites functionalized with graphene oxide (GO) and chitosan were synthesized and evaluated for the adsorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions. Fe_3O_4 nanoparticles were prepared via a co-precipitation method and subsequently integrated with GO sheets, followed by polymer functionalization to introduce abundant oxygen and nitrogen containing functional groups. Structural and physicochemical characterization using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning and transmission electron microscopy (SEM/TEM), Brunauer–Emmett–Teller (BET) surface analysis, and vibrating sample magnetometry (VSM) confirmed the successful formation of a porous, magnetically responsive nanocomposite. Batch adsorption experiments conducted under varying conditions of pH 2–8, contact time of 0–120 minutes, initial metal ion concentration of 10–200 mg L^{-1}, and temperature of 298–318 K revealed that the adsorption process followed the Langmuir isotherm model, with maximum adsorption capacities of 182.4 mg g^{-1} for Pb^{2+} and 136.7 mg g^{-1} for Cd^{2+}. Kinetic analysis showed that the adsorption followed a pseudo-second-order model, indicating chemisorption. Thermodynamic parameters confirmed that the adsorption was spontaneous and endothermic. Notably, the nanocomposite retained over 85% efficiency after six adsorption–desorption cycles, demonstrating excellent reusability. The enhanced performance is attributed to the synergistic effects of GO and chitosan functionalization, providing high surface area and abundant active sites. These findings suggest that the developed nanocomposite is a promising candidate for sustainable wastewater treatment.

1. Introduction

Water contamination by heavy metals such as Pb^{2+} and Cd^{2+} remains a major environmental concern due to their toxicity, persistence, and bioaccumulation (Nthwane et al., 2025). Conventional treatment methods often suffer from inefficiency at low concentrations, high cost, and secondary pollution (Osemba & Maghanga, 2025). Adsorption has emerged as a preferred method due to its simplicity, efficiency, and economic feasibility (Rashid et al., 2021). Magnetic nanomaterials, particularly Fe_3O_4 nanoparticles, offer unique advantages such as high surface area and easy magnetic recovery (Nguyen et al., 2021). However, their practical application is limited by aggregation and insufficient surface functionality (Ganapathe et al., 2020). Surface modification using graphene oxide (GO) and polymers such as chitosan has proven effective in enhancing adsorption performance by introducing functional groups and improving dispersion (Zameran et al., 2025). In this work, a ternary Fe_3O_4/GO/chitosan nanocomposite was synthesized and evaluated for efficient removal of Pb^{2+} and Cd^{2+} ions. The study focuses on adsorption behavior, mechanism, and reusability, providing insights into its potential for real-world applications.

2. Experimental Section

All chemicals used in this study were of analytical grade and employed without further purification. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.999%) and ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$, 99.999%) served as precursors for Fe_3O_4 nanoparticles. Chitosan (medium molecular weight, 75–85% deacetylated) was used as a polymeric functionalizing agent, and graphene oxide (GO) powder was employed as a high surface area support. Lead nitrate ($Pb(NO_3)_2$) and cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$) were used to prepare metal ion solutions. All solutions were prepared using deionized water. Fe_3O_4 nanoparticles were synthesized via a co-precipitation method. Briefly, 5.40 g of $FeCl_3 \cdot 6H_2O$ and 2.78 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 100 mL of deionized water under a nitrogen atmosphere to prevent oxidation, and the solution was heated to 80°C with continuous stirring. 50 mL of 2.0 M Sodium hydroxide was added dropwise until the pH reached approximately 10, resulting in the formation of a black Fe_3O_4 precipitate. The reaction was maintained at 80°C for 60 minutes to ensure complete nanoparticle formation. The Fe_3O_4 nanoparticles were then magnetically separated, washed three times with deionized water and twice with ethanol, and dried at 60°C for 12 hours, yielding 3.0 g of Fe_3O_4. The Fe_3O_4 nanoparticles were subsequently integrated with GO sheets to improve dispersion and introduce additional adsorption sites. For this, 0.50 g of graphene oxide was dispersed in 200 mL of deionized water using ultrasonication at 40 kHz and 200 W for 60 minutes. 2.0 g Fe_3O_4 nanoparticles were then slowly added to the GO suspension and stirred at room temperature for 12 hours, followed by ultrasonication for 30 minutes to enhance anchoring. The resulting Fe_3O_4/GO composite was magnetically separated, washed with deionized water, and dried at 60°C for 12 hours. Chitosan functionalization was performed to obtain the final Fe_3O_4/GO/chitosan nanocomposite. One gram of chitosan was dissolved in 100 mL of 1% (v/v) acetic acid under stirring for 6 hours to form a viscous solution. The 2.0 g Fe_3O_4/GO composite was added gradually to this solution and stirred at 50°C for 8 hours to ensure uniform coating. The pH of the mixture was adjusted to approximately 9 using 0.5 M NaOH, inducing precipitation of chitosan onto the composite surface. The final nanocomposite was magnetically separated, washed until neutral pH, and dried at 60°C for 12 hours. The approximate weight composition of the final material was Fe_3O_4: GO: chitosan ≈ 70:15:15. The entire synthesis procedure is illustrated schematically in Fig. 1, which shows the stepwise formation of Fe_3O_4 nanoparticles, their integration with GO sheets, and subsequent chitosan coating to yield the ternary magnetic nanocomposite.

Batch adsorption experiments were conducted to evaluate the removal of Pb^{2+} and Cd^{2+} ions. Stock solutions of 1000 mg L^{-1} were prepared from $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$, and working solutions (10–200 mg L^{-1}) were obtained by dilution. In each experiment, 0.05 g of the Fe_3O_4/GO/chitosan nanocomposite was added to 50 mL of metal ion solution, and the pH was adjusted between 2 and 8 using 0.1 M HCl or NaOH. The suspensions were agitated at 150 rpm at temperatures of 298, 308, or 318 K for contact times of 0–120 minutes. Following adsorption, the nanocomposite was separated magnetically, and residual metal concentrations were analyzed using AAS or ICP-OES. Adsorption capacities were calculated using:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \text{.....Eq. 1}$$

where C_0 and C_e are initial and equilibrium metal concentrations (mg L^{-1}), V is solution volume (0.05 L), and m is adsorbent mass (0.05 g). Reusability tests were performed by treating the used nanocomposite with 50 mL of 0.1 M HCl for 60 minutes, washing with deionized water until neutral pH, drying at 60°C for 6 hours, and reusing it in subsequent adsorption cycles. This adsorption–desorption process was repeated six times to assess stability and regeneration efficiency.

3. Results and Discussion

The successful synthesis of the Fe_3O_4/GO/chitosan magnetic nanocomposite was confirmed through a combination of structural, morphological, and physicochemical analyses. The X-ray diffraction (XRD) patterns of the synthesized Fe_3O_4 nanoparticles displayed characteristic peaks at 2θ values of 30.2°, 35.5°, 43.2°, 53.5°, 57.1°, and 62.7°, corresponding to the (220), (311), (400), (422), (511), and (440) crystal planes of cubic spinel Fe_3O_4, confirming successful formation of crystalline magnetite. After integration with graphene oxide and chitosan, these peaks were slightly broadened and reduced in intensity, indicating partial surface functionalization without disrupting the crystalline structure. Fourier transform infrared (FTIR) spectroscopy further confirmed the presence of functional groups critical for adsorption. Pure Fe_3O_4 exhibited a strong band at 580 cm^{-1}, corresponding to Fe–O stretching vibrations. In the Fe_3O_4/GO/chitosan nanocomposite, additional bands appeared at 3420 cm^{-1} (O–H and N–H stretching), 1635 cm^{-1} (C = O stretching), 1385 cm^{-1} (C–N bending), and 1090 cm^{-1} (C–O–C stretching), confirming the successful incorporation of oxygen- and nitrogen-containing functional groups from GO and chitosan. These functional groups are essential for binding Pb^{2+} and Cd^{2+} ions through electrostatic interaction, surface complexation, and chelation. Morphological analysis by scanning and transmission electron microscopy (SEM and TEM) revealed that Fe_3O_4 nanoparticles were nearly spherical, with an average diameter of 12.9 nm, and were uniformly dispersed on the GO sheets (Fig. 2). The chitosan coating was observed as a thin, uniform layer enveloping the Fe_3O_4/GO composite, reducing aggregation and providing additional active sites. Brunauer–Emmett–Teller (BET) analysis showed a significant increase in specific surface area from 65 $m^2\ g^{-1}$ for bare Fe_3O_4 to 142 $m^2\ g^{-1}$ for the Fe_3O_4/GO/chitosan nanocomposite, highlighting the effectiveness of surface engineering in creating a porous structure favourable for adsorption. Vibrating sample magnetometry (VSM) measurements confirmed strong superparamagnetic behavior, with a saturation magnetization of 52 emu g^{-1}, enabling facile magnetic separation after adsorption. The adsorption performance of the nanocomposite was strongly influenced by pH as shown in Fig. 2, adsorption capacities for both Pb^{2+} and Cd^{2+} increased sharply from pH 2 to pH 5.5, reaching maximum values of 182.4 mg g^{-1} for Pb^{2+} and 136.7 mg g^{-1} for Cd^{2+}. At low pH, protonation of surface functional groups reduced electrostatic attraction to metal cations, whereas at optimal pH, deprotonated –OH, –COOH, and $–NH_2$ groups facilitated strong complexation with the metal ions. Adsorption declined slightly at pH below 6 due to possible hydrolysis of metal ions. The equilibrium adsorption data were best described by the Langmuir isotherm model, indicating monolayer adsorption onto a homogeneous surface with finite binding sites. The separation factor (R_L) values ranged from 0.03 to 0.57 for Pb^{2+} and 0.05 to 0.63 for Cd^{2+}, confirming favourable adsorption. Freundlich isotherm analysis showed lower correlation coefficients, consistent with the dominant monolayer adsorption mechanism. Kinetic studies revealed that the adsorption process followed a pseudo-second-order model, with correlation coefficients (R^2) exceeding 0.998 for both metal ions. The calculated rate constants indicated rapid adsorption, with equilibrium achieved within 60 minutes. This behavior suggests chemisorption involving electron sharing or exchange between surface functional groups and the metal ions, in agreement with the FTIR analysis. Thermodynamic parameters further supported the spontaneous and endothermic nature of the adsorption process. The Gibbs free energy changes (ΔG°) ranged from − 19.8 to − 22.5 kJ mol^{-1} for Pb^{2+} and − 16.3 to − 18.9 kJ mol^{-1} for Cd^{2+} across 298–318 K, while the positive enthalpy changes (ΔH° = 23.4 kJ mol^{-1} for Pb^{2+}; 19.1 kJ mol^{-1} for Cd^{2+}) confirmed endothermic adsorption. The positive entropy changes (ΔS°) suggested increased disorder at the solid–solution interface during adsorption.

The proposed adsorption mechanism is illustrated in Fig. 2. Pb^{2+} and Cd^{2+} ions are initially attracted to the negatively charged surface through electrostatic interaction, followed by surface complexation with oxygen and nitrogen containing functional groups and chelation by chitosan chains. This synergistic effect between Fe_3O_4, GO, and chitosan enhances adsorption capacity and selectivity. Reusability studies demonstrated excellent stability and practical applicability. After six adsorption–desorption cycles using 0.1 M HCl for regeneration, the nanocomposite retained over 85% of its initial adsorption capacity for both Pb^{2+} and Cd^{2+}, confirming the robustness of the material and the efficiency of magnetic separation. Overall, the high adsorption capacity, rapid kinetics, and strong reusability of the Fe_3O_4/GO/chitosan nanocomposite are attributed to the combined effects of increased surface area, abundant functional groups, and strong magnetic response. These results indicated that surface engineered magnetic nanocomposites are promising candidates for sustainable and efficient removal of toxic heavy metals from wastewater.

4. Conclusion

A surface-engineered Fe_3O_4/GO/chitosan magnetic nanocomposite was successfully developed for efficient removal of Pb^{2+} and Cd^{2+} from wastewater. The material exhibited high adsorption capacity, rapid kinetics, and excellent magnetic separability. The adsorption process followed Langmuir isotherm and pseudo-second-order kinetics, indicating monolayer chemisorption. Importantly, the nanocomposite demonstrated strong reusability, maintaining high performance over multiple cycles. The synergistic combination of Fe_3O_4, GO, and chitosan significantly enhanced adsorption efficiency, making the material a promising candidate for sustainable wastewater treatment.

References

1. Ganapathe, L. S., Mohamed, M. A., Mohamad Yunus, R., & Berhanuddin, D. D. (2020). Magnetite (Fe3O4) nanoparticles in biomedical application: From synthesis to surface functionalisation. *Magnetochemistry*, *6*(4), 68.

2. Nguyen, M. D., Tran, H.-V., Xu, S., & Lee, T. R. (2021). Fe3O4 nanoparticles: Structures, synthesis, magnetic properties, surface functionalization, and emerging applications. *Applied Sciences*, *11*(23), 11301.
3. Nthwane, Y. B., Fouda-Mbanga, B. G., Thwala, M., & Pillay, K. (2025). A comprehensive review of heavy metals (Pb^{2+} , Cd^{2+} , Ni^{2+}) removal from wastewater using low-cost adsorbents and possible revalorisation of spent adsorbents in blood fingerprint application. *Environmental Technology*, *46*(3), 414–430. https://doi.org/10.1080/09593330.2024.2358450
4. Osemba, M., & Maghanga, J. (2025). Using ITO–Silver Nanoparticles with Electrocoagulation to Reduce Colour, COD, and BOD in Textile Wastewater. *Mount Kenya University*. https://www.researchgate.net/profile/Martin-Osemba/publication/398679807_Using_ITO-Silver_Nanoparticles_with_Electrocoagulation_to_Reduce_Colour_COD_and_BOD_in_Textile_Wastewater/links/693fbeb40c98040d481def8d/Using-ITO-Silver-Nanoparticles-with-Electrocoagulation-to-Reduce-Colour-COD-and-BOD-in-Textile-Wastewater.pdf
5. Rashid, R., Shafiq, I., Akhter, P., Iqbal, M. J., & Hussain, M. (2021). A state-of-the-art review on wastewater treatment techniques: The effectiveness of adsorption method. *Environmental Science and Pollution Research*, *28*(8), 9050–9066. https://doi.org/10.1007/s11356-021-12395-x
6. Zameran, N. I., Md Saleh, N., & Nazirah, N. H. (2025). Graphene-based magnetic covalent organic frameworks and deep eutectic solvent functionalized adsorbents for polycyclic aromatic hydrocarbons: A review. *Royal Society Open Science*, *12*(10). https://royalsocietypublishing.org/rsos/article/12/10/251102/236079

Figures

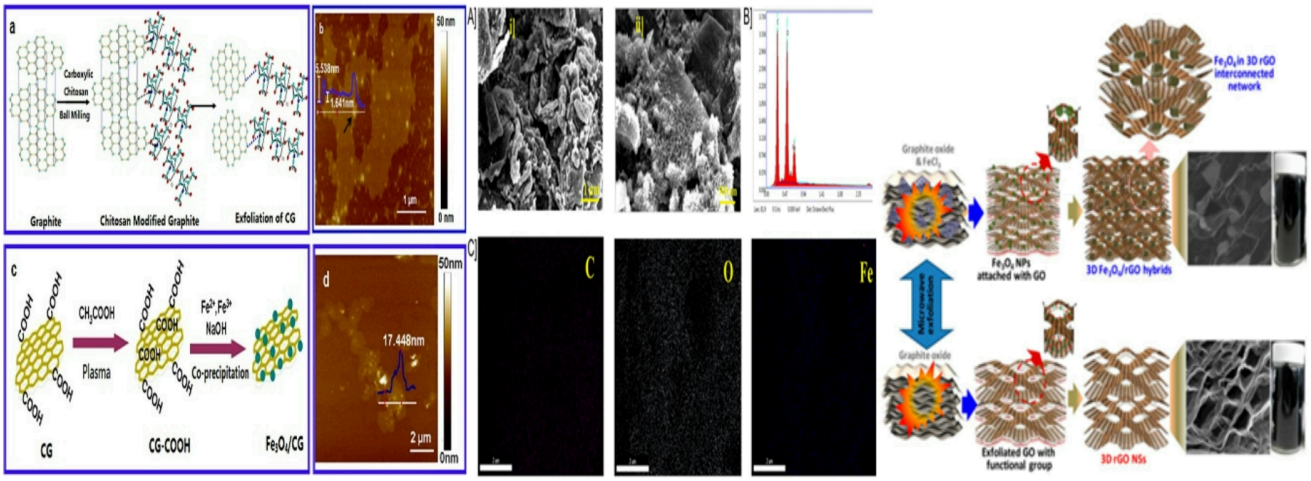

Figure 1

Schematic illustration of the synthesis of Fe_3O_4/GO/chitosan magnetic nanocomposite. (i) Co-precipitation of Fe_3O_4 nanoparticles, (ii) anchoring onto graphene oxide sheets, and (iii) surface functionalization with chitosan.

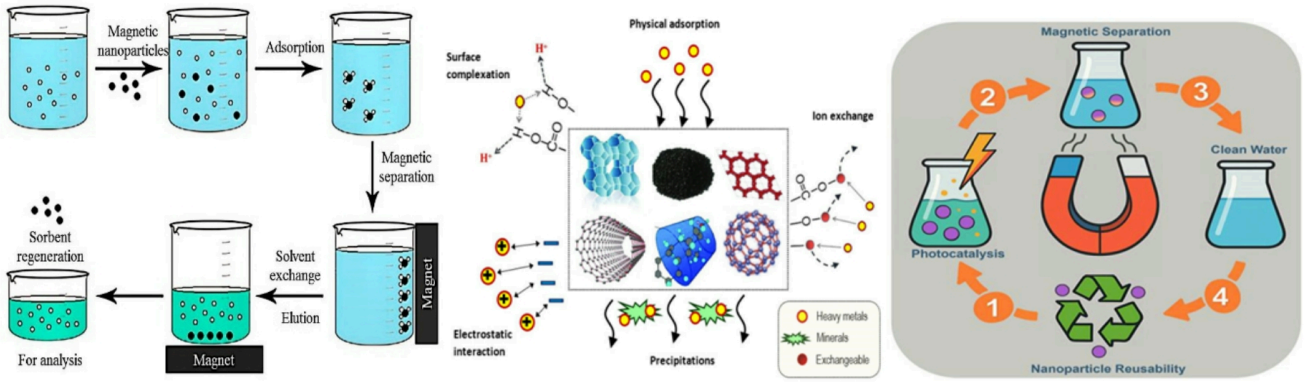

Figure 2

Proposed adsorption mechanism of Pb^{2+} and Cd^{2+} onto Fe_3O_4/GO/chitosan nanocomposite.