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Kinetic Study of Heavy Metals Removal from Pharmaceutical Wastewater Using Geopolymer/Fe_3O_4 Nanocomposite

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ABSTRACT

The pharmaceutical industry, while essential for public health, is a significant contributor to environmental pollution due to the generation of wastewater containing heavy metals. The nanocomposite was characterized using X-ray diffraction (XRD), High-resolution scanning electron microscopy (HRSEM)/energy dispersive spectroscopy (EDS) and Fourier transmission infrared spectroscopy (FTIR). The XRD analysis of the nanocomposite identified indexed as (220), (311), (400), (422), (511), (440), (620), and (533) with respective 2θ values of 32.8°, 35.7°, 44.5°, 53.4°, 57.7°, 64.1°, 71.8°, and 75.1°, can be attributed to the diffraction patterns of Fe_3O_4 crystals, as per the standard data (JCPDS number, 00–43-0317). Additionally, a sharp and intense peak at $2\theta = 26.90°$ corresponds to the presence of amorphous SiO_2 within the matrix sample. The HRSEM image of the nanocomposite exhibited spherical-shaped structures of geopolymer/Fe_3O_4, and some irregular shapes. The effects of the contact time, temperature and dosage on the removal percentage of heavy metal ions were studied. The kinetics and thermodynamics of heavy metal adsorption onto the nanocomposites were investigated, providing insights into the adsorption mechanisms and efficiency. The results indicated that the adsorption process followed pseudo-second-order kinetics, suggesting chemisorption as the dominant mechanism. Thermodynamic studies demonstrated that the adsorption of heavy metals onto the nanocomposites was spontaneous and exothermic, indicating the feasibility and efficiency of the process. The findings of this research contribute to the development of innovative and eco-friendly approaches to mitigate the impact of heavy metals in industrial wastewater, promoting both environmental sustainability and regulatory compliance in the pharmaceutical sector.

Keywords: Environmental, Heavy, Metal, Nanocomposites, Pharmaceutical, Wastewater

INTRODUCTION

The pharmaceutical industry plays a vital role in healthcare by producing a wide range of essential medicines and healthcare products. However, the manufacturing processes in this industry generate significant amounts of wastewater, often containing various pollutants, including heavy metals (Okoro *et al*. 2023). The discharge of heavy metal-contaminated wastewater into the environment severely threatens to aquatic ecosystems and human health. The removal of heavy metals from pharmaceutical wastewater is a critical environmental challenge that requires innovative and effective solutions (Mathew *et al.* 2022).

Heavy metals, such as lead (Pb), cadmium (Cd), and copper (Cu), are known to be toxic and can have detrimental effects on the environment and living organisms. These metals are persistent and can accumulate in biological systems, causing various health problems, including cancer, organ damage, and neurological disorders (Mathew *et al.* 2023). The pharmaceutical industry uses heavy metals in several processes, and these can find their way into wastewater discharges. Therefore, it is imperative to develop efficient methods for removing

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heavy metals from pharmaceutical wastewater (Abd-Elnabi et al. 2023).

One promising approach for the removal of heavy metals from wastewater is the use of nanocomposite materials. Nanocomposites are advanced materials composed of nanoscale components that combine the unique properties of different materials to achieve superior performance (Inobeme et al. 2023a). Geopolymer/Fe_3O_4 nanocomposites, in particular, have gained significant attention due to their exceptional adsorption properties, magnetic responsiveness, and environmental compatibility (Ethaib et al. 2022).

Geopolymers are inorganic polymers formed by the alkaline activation of aluminosilicate precursors, such as fly ash and metakaolin. They exhibit excellent mechanical and chemical stability, making them suitable for a wide range of environmental applications. Fe_3O_4 (iron(II,III) oxide) nanoparticles are magnetic materials that can be easily separated from the solution using an external magnetic field (Inobeme *et al.* 2023b). When incorporated into geopolymers, Fe_3O_4 nanoparticles create a composite material that can efficiently adsorb heavy metals from wastewater and be easily retrieved for regeneration and reuse (Maged et al. 2023).

The research investigates the adsorption capacity, kinetics, and thermodynamics of the nanocomposite (Inobeme *et al.* 2023c). The results will contribute to the development of a sustainable and effective solution for treating pharmaceutical wastewater contaminated with heavy metals, addressing both environmental concerns and regulatory compliance in the pharmaceutical industry (Raji et al. 2023). In this context, this study aims to explore the potential of geopolymer/Fe_3O_4 nanocomposites for the efficient removal of heavy metals, specifically Pb, Cd, and Cu, from pharmaceutical wastewater.

MATERIAL AND METHODS

Synthesis of ZnO/Fe_3O_4 Nanocomposites

The nanocomposite was prepared via a wet impregnation method. 2.0 g of the synthesized geopolymer nanoparticles was dissolved in 100 cm^3 de-ionized water and stirred for 1 h in a 250 cm^3 beaker using a magnetic stirrer. Exactly 2.0 g of Fe_3O_4 nanoparticles was added to the resultant solution and further stirred for 1 h. The mixture was oven-dried at 105 ^oC for 24 hr and calcined at 450 ^oC for 3 h. The solid sample was pulverized using ceramic mortar and pestle to obtain homogeneous and fine particles (Thoda *et al*., 2023).

X-ray Diffraction

The synthesized samples were characterized with the aid of the powdered X-ray diffraction (XRD) method to determine the extent of graphitization of the samples. Phase identification of the mineral constituents of the samples was done by the XRD. The powdered sample was placed and clipped on the aluminium rectangular sample holder. The diffractograms were recorded in the 2θ range of 20º to 90º and phase identification was established (Mentor *et al.* 2022).

Scanning Electron Microscopy–Energy Dispersive

The morphology of the as-prepared samples will be determined using scanning electron microscopy (SEM). Exactly 0.05 mg will be sprinkled onto carbon adhesives tape and sputter-coated with Au-Pd using Quorum T15OT Analyzer for 5 min. The microscope will be operated with electron high tension at 5 kV for imaging. Scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) will further be used to determine the elemental composition of the synthesized nanoparticles and nanocomposites (Mentor *et al.* 2022, Mathew et al., 2023b).

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Fourier Transform Infrared

Fourier transform infrared spectra (FTIR) of the synthesized samples will be recorded using Perkin-Elmer FTIR spectrometer fitted with a deuterated triglycine sulphate (DTGS) detector covering the frequency range of 500-4000 cm^{-1}. The sample cell will be purged with nitrogen gas throughout data collection to exclude carbon(IV) oxide and water vapour. Ten milligrams (0.01 g) of the dried sample will be dispersed in 200 mg of spectroscopic grade KBr to record the spectra. The sample will be recorded in the range of 500 to 4000 cm^{-1} wavenumber (Mentor *et al.* 2022).

Heavy Metal Determination

Exactly 50.0 cm^3 of the pharmaceutical wastewater sample was measured into a 100 cm^3 beaker with the addition of 15 cm^3 concentrated trioxonitrate (V) solution and heated on a hot plate for 10 min. The solution was allowed to cool, and then deionized water was added and filtered into a 100 cm^3 volumetric flask using Whatman No 42 filter paper. This was then made up to the mark with deionized water and analysis of toxic metals were determined using AAS (Perkin Elmer 200 Atomic Absorption Spectrophotometer) (Sumaila *et al*. 2016; Adamu *et al*. 2017).

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern for the geopolymer/Fe_3O_4 nanocomposite is depicted in Figure 1. Within the XRD pattern of the nanocomposite, noticeable diffraction peaks corresponding to Fe_3O_4 nanoparticles are evident. These peaks, indexed as (220), (311), (400), (422), (511), (440), (620), and (533) with respective 2θ values of 32.8°, 35.7°, 44.5°, 53.4°, 57.7°, 64.1°, 71.8°, and 75.1°, can be attributed to the diffraction patterns of Fe_3O_4 crystals, as per the standard data (JCPDS number, 00–43-0317). Additionally, a sharp and intense peak at $2\theta = 26.90°$ corresponds to the presence of amorphous SiO_2 within the matrix sample.

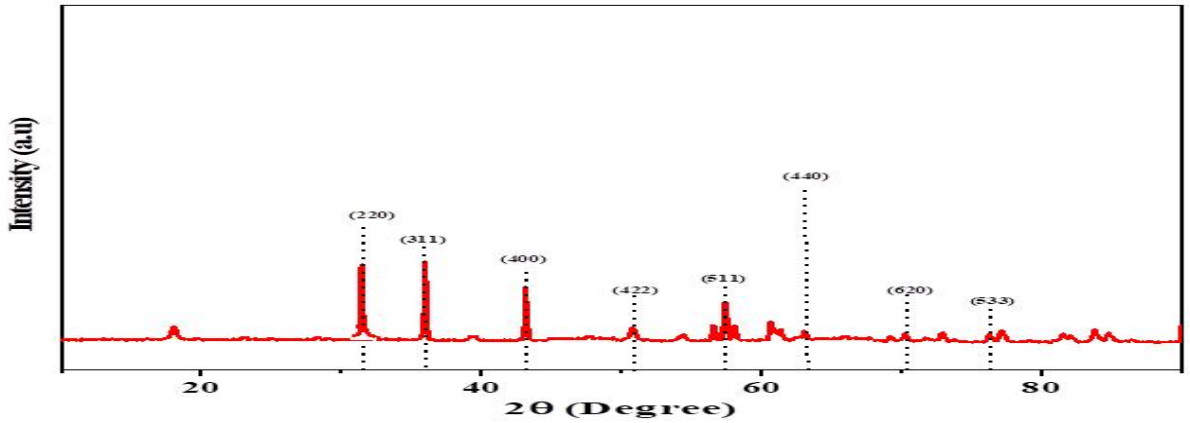

Figure 1: XRD pattern of geopolymer/Fe_3O_4 nanocomposite

Figure 2 displays the High-Resolution Scanning Electron Microscope (HRSEM) images depicting the geopolymer/Fe_3O_4 nanocomposites. These images reveal that the nanoparticles are loosely distributed across the geopolymer's surface. This observation suggests that the geopolymer's surface properties have influenced the deposition of the nanoparticles. It is noticeable that the Fe_3O_4 particles form agglomerations with spherical patterns. This phenomenon can be attributed to the strong attraction between the geopolymer and the Fe_3O_4 nanoparticles. Furthermore, the nanomaterial exhibits a homogeneous distribution, with minimal or no cracks and low porosity. Consequently, it can be inferred that depositing Fe_3O_4 on the geopolymer's surface has the potential to enhance the mechanical properties of the nanomaterial.

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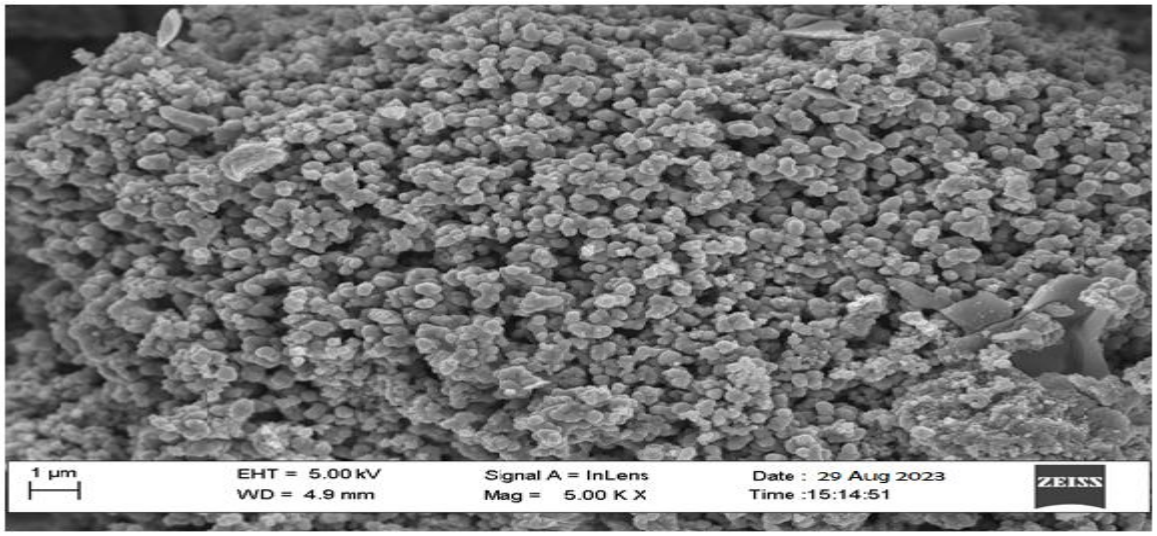

Figure 2: HRSEM image of geopolymer/Fe_3O_4 nanocomposite

In Figure 3, the elemental compositions of the synthesized materials are depicted, confirming the formation of the composite samples. The Energy-Dispersive X-ray Spectroscopy (EDX) results indicate the presence of Al, Si, C, O, and Fe. The presence of C can be attributed to the carbon grid hole used to hold the sample in place.

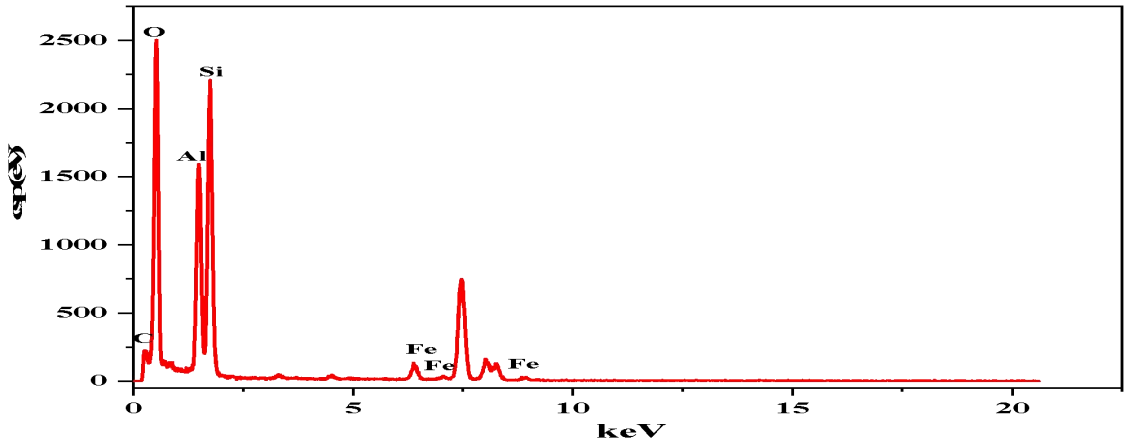

Figure 3: EDX spectrum of geopolymer/Fe_3O_4 nanocomposite

Figure 4 displays the FTIR spectrum of the geopolymer/Fe_3O_4 nanocomposite. The absorption peaks detected at 3450 cm^{-1} are attributed to the stretching vibration of H_2O molecules. This finding suggests the presence of OH groups on the surface of the magnetic nanoparticles and hydroxyl groups within the geopolymer structure. Furthermore, the band observed at around 1635 cm^{-1} signifies the bending mode of H_2O molecules. The existence of SiO_2 in the nanocomposite is verified by the stretching and bending vibrations of Si–O, as evidenced by absorption bands at 814 and 1100 cm^{-1}. Additionally, the band at 510 cm^{-1} corresponds to the bending vibration of SiO_2. The confirmation of Fe_3O_4 nanoparticle formation is supported by the absorption band detected at 552 cm^{-1}, which corresponds to the vibration of metal oxide bonds (Fe–O).

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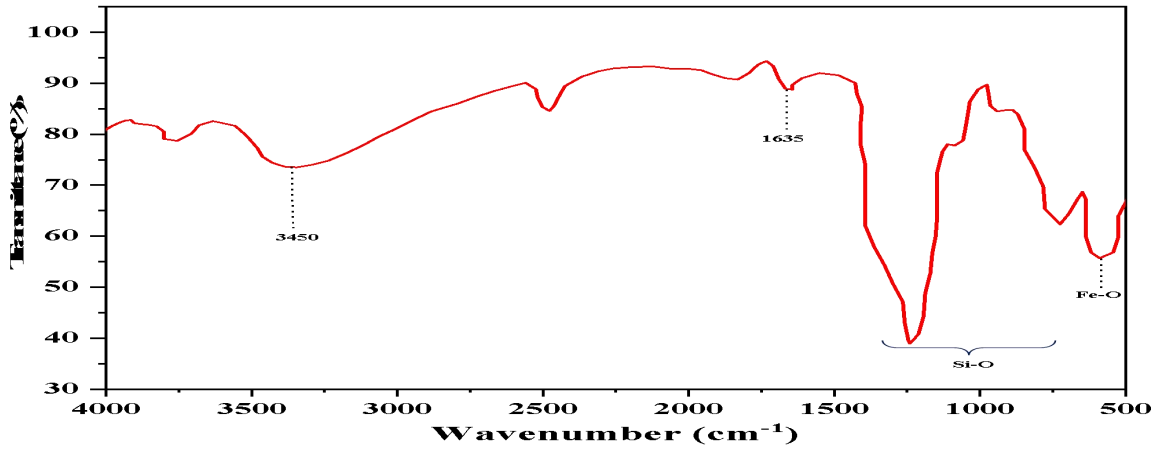

Figure 4: FTIR spectrum of geopolymer/Fe_3O_4 nanocomposite

Figure 5 illustrates the impact of contact time on the adsorption of metal ions using a geopolymer/Fe_3O_4 nanocomposite. The initial phase exhibited rapid adsorption, with removal efficiencies of 65.18% for Fe ions, 60.07% for Cu ions, and 55.35% for Pb ions within the first 25 min. Subsequently, the second phase featured a slower, gradual adsorption process. Following the initial 25 min, a gradual increase was observed, eventually stabilizing after approximately 30 min. In the early stages of adsorption, there were ample adsorption sites on the surface of the adsorbent capable of adsorbing a significant quantity of heavy metal ions. At the 30-minute mark, no further increase or decrease in the adsorption process was observed, indicating equilibrium due to the saturation of adsorption sites. This pattern aligns with findings from prior research on heavy metal adsorption where removal efficiencies of 63.34% for Fe ions, 60.25% for Cu ions, and 58.55% for Pb ions within the first 25 min (Bayuo et al., 2019; Dagde et al., 2023). The swift adsorption of metal ions during the initial phases resulted from the substantial initial concentration gradient between the adsorbate in the solution and the available vacant sites on the adsorbent surface.

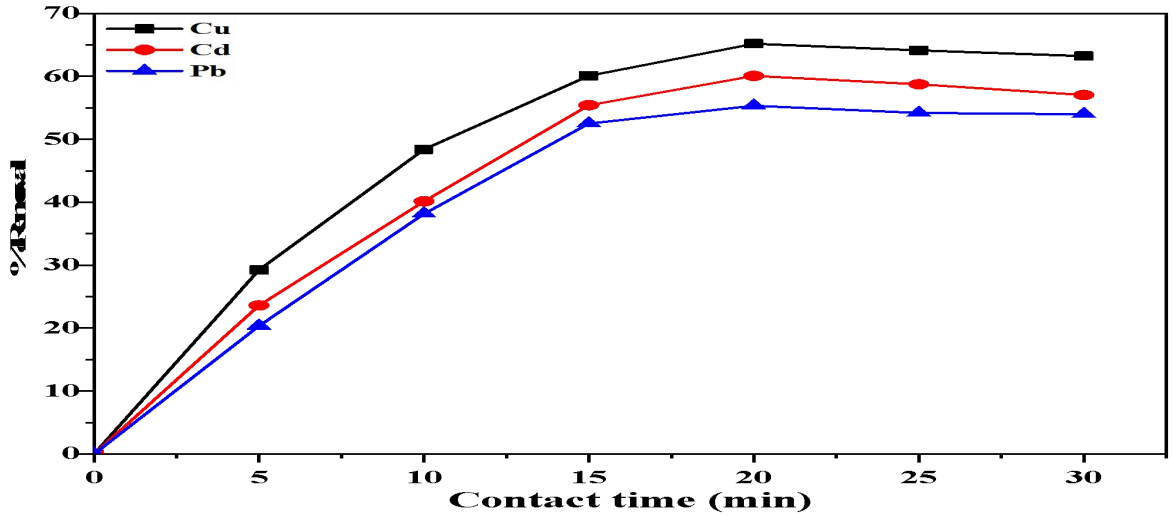

Figure 5: The effect of contact on the removal of Pb, Cd and Cu ion from wastewater

The impact of altering the amount of adsorbent used on the percentage of heavy metal ions adsorbed was investigated in this study, utilizing the as-synthesized adsorbent, a combination of geopolymer and Fe_3O_4, ranging from 0.4 g to 1.4 g (see Figure 6).

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Figure 6 illustrates the relationship between adsorbent dosage and adsorption effectiveness. The experimental data demonstrates that the percentage of adsorption increased from 58.62% to 100% for Cu ions, from 53.15% to 99.02% for Cd ions, and from 50.02% to 96.12% for Pb ions as the adsorbent dosage was raised from 0.4 g to 1.4 g. The observed increase in adsorption with higher adsorbent dosages can be attributed to the inadequate number of adsorbing species in comparison to the larger number of available sites on the adsorbent's surface at higher dosages. This discovery implies that adsorption is nearly directly proportional to the quantity of adsorbent used. Prior research has also noted a substantial number of exchangeable sites at higher adsorbent dosages during the absorption of heavy metal ions (Alasadi et al., 2019; Kumar et al., 2019). This study can be deemed cost-effective and practically relevant because even a small quantity of nano adsorbent has demonstrated reasonable metal ion adsorption percentages from wastewater.

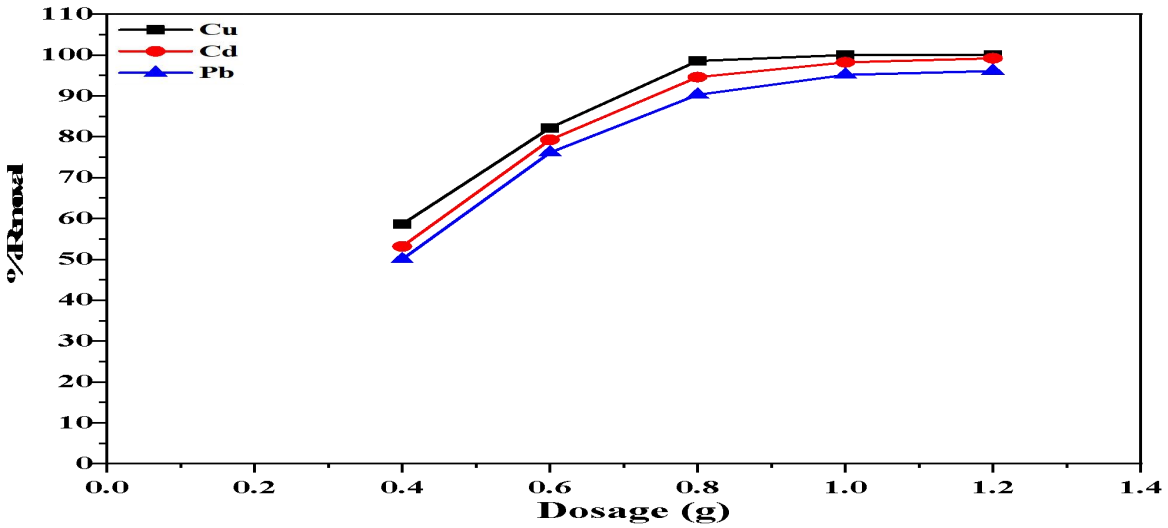

Figure 6: The effect of adsorbent dosage on the removal of Pb, Cd and Cu ion from wastewater

Based on Figure 7, the adsorption of Cd, Cu, and Pb ions exhibited a rapid increase initially as the temperature rose. Specifically, the removal efficiency surged from 38.60% to 82.02% for Cu ions, from 32.70% to 75.21% for Cd ions, and from 30.92% to 72.02% for Pb ions. This uptick in removal efficiency with rising temperature suggests that the process is inherently endothermic. The rationale behind this phenomenon at higher temperatures could be attributed to several factors. Firstly, the increased temperature may enhance the energy available for the adsorption process, facilitating the more efficient transfer of metal ions from the solution to the adsorption sites on the adsorbent material. Additionally, it could lead to an augmentation in the ion exchange capacity of the adsorbent. Moreover, higher temperatures may activate sites on the surface of the adsorbent, consequently generating more effective adsorption sites capable of accommodating a greater quantity of heavy metal ions. This characteristic aligns with the involvement of a chemical reaction or bond in the adsorption process.

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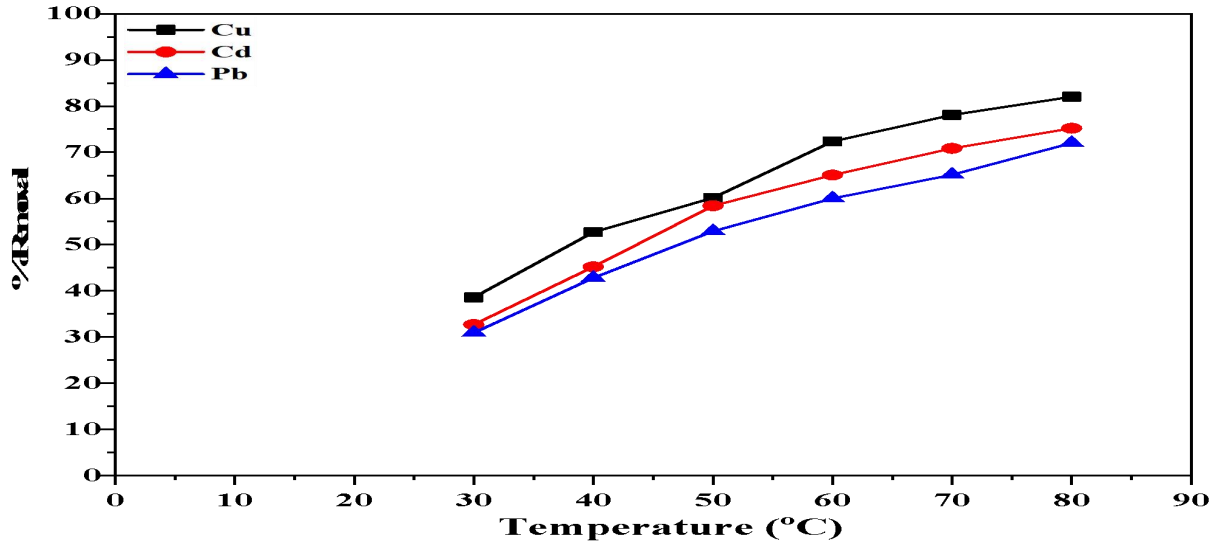

Figure 7: The effect of temperature on the removal of Pb, Cd and Cu ion from wastewater

Adsorption isotherms can be utilized to forecast the fitting parameters and behavior of a sorbent towards various sorption systems. The two most commonly utilized isotherms are the Langmuir and Freundlich adsorption isotherm models. The Freundlich adsorption isotherm was formulated for heterogeneous systems, providing a theoretical framework for multilayer adsorption on the sorbent surface (Musah *et al.* 2022). On the other hand, the Langmuir adsorption isotherm is grounded in the idea that metal ions' adsorption occurs on homogeneous adsorbent surfaces, resulting in a monolayer arrangement of the adsorbed metal ions. Furthermore, it assumes that the energy generated from the adsorption system remains constant. To determine the more suitable model for the adsorption of metal ions, experimental data were fitted into both the Langmuir and Freundlich adsorption isotherm models. The process of metal ion adsorption from wastewater by the adsorbent was explored using the Langmuir and Freundlich adsorption isotherms, as described by Equations (1) and (2).

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2)$$

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (3)$$

where C_e is the equilibrium concentration of substrates in the solution (mg/dm^3), q_e is the adsorption capacity at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g) and b is the adsorption equilibrium constant (L/mg). K_f and n are known as Freundlich constants, and they play important roles in describing the adsorption process. The parameter 'n' offers insights into the level of favorability of the adsorption process. The R^2 values for metal ions, ranging from 0.9890 to 0.9923, are remarkably close to unity when the data is fitted into the Langmuir isotherm. In contrast, the R^2 values obtained from the Freundlich adsorption isotherm, falling between 0.9780 and 0.9899, are comparatively lower. These findings align with those of Ren et al. (2023), who also reported similar outcomes. This robustly suggests that the adsorption process of metal ions onto the surface of the prepared geopolymer/Fe_3O_4 nanocomposites is more strongly associated with the Langmuir adsorption isotherm.

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Table 1: Isotherm models of metal ions removal in wastewater

Isotherm	Parameter	Pb(II)	Cd(II)	Cu(II)
Langmuir	$\mathbf{K_L}$	0.00811	0.0127	0.0194
	$\mathbf{Q_m}$	65.12	70.66	78.02
	$\mathbf{R^2}$	0.9890	0.9902	0.9923
Freundlich	$\mathbf{K_f}$	2.112	3.907	4.505
	n	0.336	0.412	0.539
	$\mathbf{R^2}$	0.9780	0.9803	0.9899

The study of adsorption kinetics plays a crucial role in comprehending adsorption processes. It involves exploring the relationships between the adsorbed metal ions and the time needed for adsorption to occur (Shaba *et al.* 2019). To understand the mechanisms governing adsorption, we conducted research into the adsorptive uptake of metal ions from wastewater using the as-synthesized geopolymer/Fe3O4 at various time intervals. The experimental data obtained were fitted to both the pseudo-first-order model (Equ. 3) and the pseudo-second-order model (Equ. 4).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e and q_t are the amount of metal ion adsorbed per unit mass of the adsorbent (mg/g) at equilibrium time and time t, respectively, k_1 is the pseudo-first-order rate constant and k_2 is the pseudo-second-order rate constant.

According to Table 2, the results indicate that the adsorbent's process for removing metal ions from the wastewater aligns more effectively with the pseudo-second-order reaction model when compared to the pseudo first-order reaction model. This is evident because the degree of fit (R^2) observed is much closer to unity than that of the pseudo first order reaction model (as presented in Table 2). Specifically, the correlation coefficients for the adsorption of Cd, Cu, and Pb ions were 0.9945, 0.9969, and 0.9910, respectively, when utilizing the pseudo-second-order kinetic model. This trend is consistent with the findings reported by Radha et al. (2021). The fact that the adsorption of the studied metal ions aligns better with the pseudo-second-order model suggests that the rate-limiting step of the adsorption process likely involves a chemical sorption process, wherein valency forces come into play through the sharing of electrons between the sorbate and sorbent.

Table 2: Kinetic models of metal ions removal in wastewater

Isotherm	Parameter	Pb(II)	Cd(II)	Cu(II)
Pseudo-first-order	$\mathbf{k_1}$	0.0640	0.0137	0.166
	$\mathbf{q_e}$	37.222	38.742	440.381
	$\mathbf{R^2}$	0.8732	0.8822	0.8991
Pseudo-second-order	$\mathbf{k_2}$	0.761	0.993	1.002
	$\mathbf{q_e}$	83.402	89.250	96.278
	$\mathbf{R^2}$	0.9910	0.9945	0.9969

The thermodynamic parameters, entropy, $\Delta S°$, enthalpy, $\Delta H°$, and the Gibbs free energy, $\Delta G°$ *as presented in Table 3,* were calculated using the following Eqs.(5-7):

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$$K_d = \frac{q_e}{C_e} \quad (5)$$

$$\Delta G = -RT\ln K_d \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

where the values of ΔG, ΔH, and ΔS were measured in kJ/mol, kJ/mol, and J/molK respectively. T is the absolute temperature (K), R is the universal gas constant (8.314 J/molK). The values of ΔH° and ΔS° suggest that the adsorption process is endothermic and spontaneous. The positive value of ΔS° indicates an increase in the degree of freedom for the adsorbed species for metal ions. The negative values of ΔG° for the metal ions confirm that the adsorption process is spontaneous. Moreover, as the temperature rises, the absolute values of ΔG° decrease, which leads to a higher probability of adsorption at elevated temperatures. This observation aligns with the findings reported by Ebisike et al. (2023).

Table 3: Thermodynamic study of metal ions removal in wastewater

Parameter	Temperature (°C)	ΔS (kj/molK)	ΔH (kJ/mol)	ΔG (kJ/mol)
Pb(II)	30	19.98	71.82	-1.78146
	40	19.98	71.82	-2.49966
	50	19.98	71.82	-3.21786
	60	19.98	71.82	-3.93606
	70	19.98	71.82	-4.65426
	80	19.98	71.82	-5.37246
Cd(II)	30	18.34	67.14	-2.00342
	40	18.34	67.14	-2.67482
	50	18.34	67.14	-3.34622
	60	18.34	67.14	-4.01762
	70	18.34	67.14	-4.68902
	80	18.34	67.14	-5.36042
Cu(II)	30	20.4	72.22	-1.48266
	40	20.4	72.22	-2.20486
	50	20.4	72.22	-2.92706
	60	20.4	72.22	-3.64926
	70	20.4	72.22	-4.37146
	80	20.4	72.22	-5.09366

CONCLUSION

The utilization of geopolymer/Fe_3O_4 nanocomposites for the removal of heavy metals from pharmaceutical wastewater has demonstrated promising results and offers a sustainable and efficient solution to address this pressing environmental challenge. The adsorption studies revealed that the geopolymer/Fe_3O_4 nanocomposites possess a high adsorption capacity for heavy metals, specifically Pb, Cd, and Cu, making them effective in reducing heavy metal concentrations in pharmaceutical wastewater. The magnetic responsiveness of the Fe_3O_4 nanoparticles allowed for rapid and easy separation of the nanocomposites from the treated wastewater, simplifying the recovery process and reducing the need for additional separation techniques. Kinetic and thermodynamic analyses indicated that the adsorption process is governed by chemisorption and is both spontaneous and exothermic. This provides valuable insights into the mechanisms involved and the efficiency of the nanocomposites in heavy metal removal. The findings of this study underscore the potential of geopolymer/Fe_3O_4 nanocomposites as an environmentally friendly and effective solution for the removal of heavy metals

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from pharmaceutical wastewater. Overall, this research contributes to the development of innovative and sustainable strategies for mitigating the environmental impact of the pharmaceutical industry, ensuring compliance with environmental regulations, and safeguarding both ecosystems and human health.

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REFERENCES

Abd-Elnabi, M. K., Elkaliny, N. E., Elyazied, M. M., Azab, S. H., Elkhalifa, S. A., Elmasry, and Mahmoud, Y. A.-G. (2023). Toxicity of Heavy Metals and Recent Advances in Their Removal: A Review. *Toxics*, *11*(7), 580.

Adamu A., Iyaka Y. A., Mathew J. T., Inobeme A. and Egharevba H. O. (2017). Assessment of Some Heavy Metal Contamination and analysis of Physicochemical Parameters of Surface Soil within the Vicinity of Minna Railway Station, Niger State, Nigeria. *Journal of Applied Life Sciences International,* 10(1), 1-9.

Alasadi, A., Khaili, F., and Awwad, A. (2019). Adsorption of Cu (II), Ni (II) and Zn (II) ions by nano kaolinite: Thermodynamics and kinetics studies. *Chemistry International*, *5*(4), 258-26.

Bayuo, J., Pelig-Ba, K. B., and Abukari, M. A. (2019). Adsorptive removal of chromium (VI) from aqueous solution unto groundnut shell. *Applied Water Science*, *9*(4), 107.

Dagde, K., Ikenyiri, P., and Yorpah, P. (2023). Application of Gure modified clay for adsorption of heavy metals in polluted underground water. *Chemistry International*, *9*(3), 94-103.

Ebisike, K., Okoronkwo, A. E., Alaneme, K. K., and Akinribide, O. J. (2023). Thermodynamic study of the adsorption of Cd2+ and Ni2+ onto chitosan–silica hybrid aerogel from aqueous solution. *Results in Chemistry*, *5*, 100730.

Ethaib, S., Al-Qutaifia, S., Al-Ansari, N., and Zubaidi, S. L. (2022). Function of Nanomaterials in Removing Heavy Metals for Water and Wastewater Remediation: A Review. *Environments*, *9*(10), 123.

Inobeme, A., Adetunji, C. O., Mathew, J. T., Okonkwo, S., Bamigboye, M. O., Ajai, A. I., Afoso, E. and Inobeme, J. (2023)a. Advanced nanotechnology for the degradation of persistent organic pollutants. In: Shah, M. ed. *Microbial Degradation and Detoxification of Pollutants*. Berlin, Boston: De Gruyter, pp. 51-72.

Inobeme, A., Adetunji, C. O., Maliki, M., Onyeachu, B. I., Kelani, T., Eziukwu, C. A., Olori, E., Mathew, J. T., and Bamigboye, M. O. (2023)b. Strategies to synthesize, advantages, and disadvantages of pharmaceutical nanoparticles. In book: Nanotechnology for Drug Delivery and Pharmaceuticals. Academic Press is an imprint of Elsevier, 371-402.

Inobeme, A., Adetunji, C. O., Mathew, J T., Ajai, A. I., Inobeme, J., Bamigboye, M. O., Onyeaku, S., Maliki, M., Eziukwu, C. and Tawa, K. (2023)c. Nanotechnology for Bioremediation of Heavy Metals. In book: Microbial Technologies in Industrial Wastewater Treatment. Springer Nature Singapore, 19-30.

Maged, A., El-Fattah, H. A., Kamel, R. M., Kharbish, S., and Elgarahy, A. M. (2023). A comprehensive review on sustainable clay-based geopolymers for wastewater treatment: circular economy and future

DOI: 10.56892/bima.v7i4.539

outlook. *Environmental monitoring and assessment*, *195*(6), 693.

Mathew, J. T, Mamman, A; Musah, M, Azeh, Y, Inobeme, A,Umar, M. T, Otori, A. A, Shaba, E. Y, Muhammed, A. I and Yisa, P. S. (2022). Assessment of Selected Heavy Metal Content on Dumpsites Soil and Vegetables Grown in Muwo Metropolis, Niger State, Nigeria. *Journal of Applied Sciences and Environmental management*, 26(9), 1473-1478.

Mathew, J. T., Adetunji, C. O., Inobeme, A., Musah, M., Azeh, Y., Otori, A.A., Shaba, E. Y., Mamman, A. and Tanko, E. (2023)a. Removal of Heavy Metals Using Bio-remedial Techniques. Springer Nature Switzerland AG 2023 M. P. Shah (ed.), Modern Approaches in Waste Bioremediation, 117-130.

Mathew, J. T., Musah, M., Azeh, Y. and Muhammed, M. (2023)b. Adsorptive Removal of Selected Toxic Metals from Pharmaceutical Wastewater using Fe_3O_4/ZnO Nanocomposite, *Dutse Journal of Pure and Applied Sciences*, 9(4a), 236- 248.

Mentor, S., Cummings, F., and Fisher, D. (2022). Preparation of biological monolayers for producing high-resolution scanning electron micrographs. *PloS one*, *17*(7), e0266943.

Musah, M., Azeh, Y., Mathew, J. T., Umar, M.T., Abdulhamid, Z. and Muhammad, A. I. (2022). Adsorption Kinetics and Isotherm Models: A Review. Caliphate Journal of Science and Technology, 1, 20-26.

Okoro, H. K., Orosun, M. M., Oriade, F. A., Momoh-Salami, T. M., Ogunkunle, C. O., Adeniyi, A. G., Zvinowanda, C., and Ngila, J. C. (2023). Potentially Toxic Elements in Pharmaceutical Industrial Effluents: A Review on Risk Assessment, Treatment, and Management for Human Health. *Sustainability*, *15*(8), 6974.

Kumar, G. V. S. R., Malla, K. A., Yerra, B., and Srinivasa Rao, K. (2019). Removal of Cu (II) using three low-cost adsorbents and prediction of adsorption using artificial neural networks. *Applied Water Science*, *9*, 1-9.

Radha, E., Gomathi, T., Sudha, P. N., Latha, S., Ghfar, A. A., and Hossain, N. (2021). Adsorption studies on removal of Pb (II) and Cd (II) ions using chitosan derived copoymeric blend. *Biomass Conversion and Biorefinery*, 1-16.

Raji, Z., Karim, A., Karam, A., and Khalloufi, S. (2023). Adsorption of Heavy Metals: Mechanisms, Kinetics, and Applications of Various Adsorbents in Wastewater Remediation—A Review. *Waste*, *1*(3), 775–805.

Ren, J., Wang, C., Zhang, H., Liu, X., Yang, T., Zheng, W., ... and Ma, Y. (2023). Magnetic Core@ Shell Fe3O4@ Polypyrrole@ Sodium Dodecyl Sulfate Composite for Enhanced Selective Removal of Dyestuffs and Heavy Metal Ions from Complex Wastewater. *Langmuir*, *39*(29), 10098-10111.

Shaba, E.Y., Mathew, J.T, Musah, M., and Agboba, E.I. (2019). The Kinetic and Thermodynamic Study of the Removal of Selected heavy Metals from a Nigerian Brewery Wastewater Using Activated Carbon from Cheese Wood (alstonia boonei). "Theme: Sustainable Energy in hanging limate: The Role of Science and Technology", in 2nd School of Physical Sciences Biennial International Conference Futminna 2019, on 24th -27th June, Minna, Niger State.

Sumaila A. Enenchel D. E. Mathew J. T. and Okaraga A. S. (2016). Synthesis and Characterization of Prymethamine-Sulphadoxine Metal Complexes. *African Journal of Science and Research.* 1(5), 63 – 66.

DOI: 10.56892/bima.v7i4.539

Thoda, O., Moschovi, A.M., Sakkas, K.M., Polyzou, E. and Yakoumis, I. (2023). Highly Active under VIS Light M/TiO_2 Photocatalysts Prepared by Single-Step Synthesis. Applied Science, 13, 6858.