CuFe$_2$O$_4$@ hydroxyapatite composite for the environmental remediation of some heavy metal ions: Synthesis and characterization

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**ABSTRACT**
Tailoring highly efficient adsorbents for environmental remediation is a great challenge key. This paper reports the synthesis of nanostructured pure hydroxyapatite and hydroxyapatite coupled with copper ferrite CuFe$_2$O$_4$@HAp by simple routes for utilizing in the capture of some heavy metal ions like Fe(II) and Al(III) ions. The prepared CuFe$_2$O$_4$@HAp has the advantage of the feasible removal of the adsorbent materials after the treatment process by just exposing them to an external magnetic field. The obtained adsorbent has been characterized by several techniques; XRD patterns showed the high purity of the materials. Moreover, the morphological study by TEM revealed the size of the nanoparticles with a needlelike shape that had a length of 21.9 to 44.04 nm and a cross-sectional dimension of 7.15 to 7.83 nm. Factors like contact time, pH, and the initial concentration have been investigated. Furthermore, different isotherm and kinetic models have been also simulated to study the adsorption performance of CuFe$_2$O$_4$@HAp. The obtained results revealed that this adsorbent could be a promising, safe, and sustainable inexpensive material for the wastewater treatment processes.

**Introduction**

The diversity of deleterious toxic pollutants existing in the wastewater leads to a serious threat to the ecosystem. Heavy metals are essential for all living organisms, but when exclusive being below the standard levels approved by the World Health Organization. Heavy metal pollutants mainly resulted from the intensive industrial discharging of electronic factories of cables, batteries, metal plating, and steal mining ones. Beyond, it is of global concern due to improper disposal. Heavy metal ions are one of the serious pollutants that threaten the human, animals, and plants due to their nonbiodegradability, biological accumulation, and their toxicity even at low concentration (Ansari, Vahedi, Tavakoli, Khooobi, & Faramarzi, 2019; Kaur & Roy, 2021). Continuous intake of heavy metals even in trace amounts could accumulate causing anemia, disorders of the nervous system, mental retardation, kidney damage (Pehlivan, Altun, Cetin, & Iqbal Bhanger, 2009).

It is infamous that exposure to several elements has a remarkable impact on human health. Iron and aluminum were chosen for this study since iron is considered vital for humans’ life whereas having apparent relationships with numerous diseases such as heart disease, cancer, and insulin sensitivity. Concurrently, aluminum is being widely used daily whilst it interferes with several biological processes including its controversial role in Alzheimer’s disease (Peto, 2010).

To date, several techniques have been developed for heavy metals from water solutions, including coagulation/filtration, electrocoagulation, ion exchange, reverse osmosis, membrane separation, nanofiltration, and adsorption. Amongst, adsorption has received more attentiveness owing to its being cost-effective, easy to operate besides the wide availability of adsorbents. (Wu et al., 2018)

Recently, nanotechnology has progressed in the synthesis of NPs and their composites using various methods and precursors. Among the numerous NPs, magnetic nanoparticles (MNPs) have shown great potency in fields such as medicine, cancer therapeutic, bio-sensing, agriculture, and the environment (Ali et al., 2021; Bhatt et al., 2020).

Hydroxyapatite HAp (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) is a calcium phosphate-based material with a hexagonal structure where the OH group could be replaced by F$^-$, CO$_3^{2-}$, SO$_4^{2-}$, Br$^-$ and PO$_4^{3-}$. The remarkable HAp’s structure revealed high thermal stability, ion exchange properties, adsorption capacity, low water solubility, non-toxicity, and acid-base adjustment capability (Ibrahim, Labaki, Giraudon, & Lamonier, 2020). It is considered the main component of bone and teeth that give them the hardness and strength features. HAp has been utilized for several applications like bone repairing material, pharmaceutical industries (Weerasuriya, Wijesinghe, & Rajapakse, 2017), hydroxyapatite chromatographic columns separation of
nucleic acids and proteins (Cummings, Snyder, & Brisack, 2009). Moreover, HAp and its derivatives have been previously reported to exhibit high adsorption potential for the remediation of wastewater and contaminated soil from various pollutants (Karthikeyan, Nikitha, Pandi, Meenakshi, & Park, 2021; Yuan, Gu, Xia, Zhao, & Wang, 2022).

HAp can be obtained either by chemical methods like precipitation, sol-gel, hydrothermal, microwave, or from biological sources such as animal bones, mineral rocks, eggshells, muscle shells, and bio-waste (Bee & Hamid, 2020). The surface characteristics of nano-HAp such as porosity, surface charge, functional groups, hydrophilicity, and acidity/basicity provide it with specific properties that promote its usage in the removal of soil and wastewater pollutants.

Hydroxyapatite revealed a high practical efficiency for the removal of different anions, cations, and organic pollutants in addition to being a highly effective photocatalyst upon doping with different oxides for the photodegradation of organic dyes. Improving the properties of HAp could be boosted by doping with other materials like graphene, carbon nanotubes (Wang et al., 2017), magneto nanoparticles (MNPs) (Pai, Kini, & Selvaraj, 2021). Nanostructured copper ferrite CuFe$_2$O$_4$ is a material with ferromagnetic properties that find different applications due to exhibiting unique thermal and chemical stability, surface hydroxyl groups, and the narrow bandgap (Golshan, Kakavandi, Ahmadi, & Azizi, 2018; Rocha et al., 2019). Therefore, coupling HAp with CuFe$_2$O$_4$ might be an effective route to get a highly efficient magnetic adsorbent. Magnetic nanoparticles are an economical, rapid, and efficient choice for pollutant remediation. The nano-magnetic adsorbents are being widely used for wastewater treatment since they can dispose of a large mass of wastewater pollutants in a very short period of time.

In this study, nano-hydroxyapatite HAp and CuFe$_2$O$_4$ decorated HAp has been synthesized, characterized and thoroughly studied for the removal of some heavy metal ions by sorption technique. The influence of initial heavy metal ion concentration, contact time, pH of the medium has been comprehensively studied to get obtained the optimum conditions for high adsorption efficacy. The kinetic models and the adsorption isotherm have been also investigated.

**Experimental**

**Synthesis of HAp and CuFe$_2$O$_4$@HAp nanopowder**

Hydroxyapatite nanostructured was prepared by the traditional precipitation method using (NH$_4$)$_2$HPO$_4$ and Ca(NO$_3$)$_2$·4H$_2$O as starting materials (Nazeer, Yilgor, Yagci, Unal, & Yilgor, 2017), while ammonia solution was used to adjust the pH of the medium. A suspension of Ca(NO$_3$)$_2$·4H$_2$O (Sigma-Aldrich, 116.05 gm in distilled water) was stirred at room temperature 25 °C, then a solution of (NH$_4$)$_2$HPO$_4$ (Sigma-Aldrich, 39.6 gm dissolved in distilled water) was added drop-wise to the suspension whereas, the pH was adjusted to 11. The resulting precipitate was then centrifuged at 3000 rpm, filtered, washed with distilled water and then dried at 70 °C for 3 h. The following reaction explains the mechanism of HAp synthesis:

$$10\text{Ca(NO}_3\text{)}_2\cdot 4\text{H}_2\text{O} + 6\text{NH}_4\text{HPO}_4 + 8\text{NH}_3\text{OH} \rightarrow \text{Ca}_{10} \text{(PO}_4\text{)}_6 \text{(OH)}_$_2$ + 20\text{NH}_4\text{NO}_3 + 20\text{H}_2\text{O}$$

Copper ferrite, CuFe$_2$O$_4$, was synthesized via the sol-gel technique, where 0.5 mole of ferric chloride FeCl$_3$ (Sigma-Aldrich) and 0.25 mole of copper chloride CuCl$_2$ (Sigma-Aldrich) were dissolved in 250 ml distilled water to form a transparent solution. Then, 5 g of cetyltrimethyl ammonium bromide (CTAB), dissolved in 100 ml hot water, was added to this solution, and was followed by stirring for one hour. The addition of CTAB, as a cationic surfactant, is to control the nanoparticle shape and size by bounding to emerging crystal faces selectively and more strongly. After that, 1 M NaOH was added dropwise until a brown solution was formed and the pH value of the medium was adjusted to 9 m and then the sol-form was stirred for 2 hours.

The next step was aging for 5-days till condensation of sol particles into solid-gel nanoparticles. Finally, the mixture was then filtrated and washed repeatedly with distilled water so as to remove residual chloride particles until giving (-ve) test with silver nitrate solution. The final precipitate was dried at 100 °C, then it was calcined at 550 °C to enhance the crystallinity of the composite. In order to get 10 % CuFe$_2$O$_4$@HAp, a ratio of (1:9 g) of (Cu ferrite: NHAp) was suspended in distilled water (50 ml) then stirred for an hour, filtrated, and dried at a temperature of 100 °C.

**Characterization of the synthesized nanoparticles**

X-ray diffraction (XRD) patterns were obtained using a diffractometer (Siemens-Brucker D5000) with Cu-Ka radiation of (K-Alpha 1 [Å] = 1.54060) in the interval 10° ≤ 2θ ≤ 80° for qualitative analysis of the nanopowders. FT-IR spectra were performed by KBr pellet technique using Perkins-Elmer spectrophotometer (Pye-Unicam Sp-883) at 4000 and 400 cm$^{-1}$. The morphological structure and the particle size determination were also investigated by transmission electron microscope TEM (JEOL JEM-2100 with an accelerating voltage of 200 KV). The surface area of the adsorbent samples and the pore size distribution were studied using (adsorption/desorption data analysis – Bel Sorpt Max, Japan). Firstly, degassing the samples for one h at 150 °C was carried out, then the
adsorption/desorption isotherm with nitrogen was performed at 300 °C. BET (Brunauer-Emmett-Teller) method was used for the specific surface area determination.

**Adsorption experiments**

Stock solutions of 1000 ppm iron (II) and 1000 ppm aluminum (III) were prepared by dissolving the corresponding weights of Mohr's Salt – ammonium iron sulfate (NH₄)₂Fe(SO₄)₉ · 6H₂O and potassium aluminum sulfate dodecahydrate KAl(SO₄)₂ · 12H₂O, respectively as sources of Al(III) and Fe(II) ions, in distilled water and using fresh dilutions for each experiment. The effect of the initial metal ion concentration on the removal percentage was investigated using a 1 g l⁻¹ fixed adsorbent dose and stirring for 2 hours at a temperature of 25 °C. A 50 ml of metal-ion solutions with initial concentrations ranged between 10 and 25 mg l⁻¹ were shacked at 135 rpm. The removal percentage was determined by measuring the metal-ion concentrations before and after treatment using Inductively Coupled Plasma (ICP), Optima 5300 DV-Perkin-Elmer. The removal percentage is calculated using Equation 1, as follows:

\[
\%\text{Removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

where \(C_0\) is the initial concentration of the metal ion (mg l⁻¹); \(C_e\) is the metal ion concentration after adsorption (mg l⁻¹).

Equation 2 is used to calculate the material’s adsorption capacity \(q_e\) at equilibrium (metal /dry adsorbent, mg g⁻¹).

\[
q_e = (C_0 - C_e) \frac{V}{w}
\]

where \(V\) is the solution volume (in liter) and \(w\) is the weight of the adsorbent (in gram). The effect of altering the pH on the adsorption efficiency was studied by adjusting the pH of the aqueous solution between 2 and 8 via a pH-meter model HI 8014 (HANNA instruments) using 0.01 M HCl and 0.01 M NaOH. Then the flasks were adapted on a shaker for 60 min equilibration time at 25 ± 1°C. The effect of contact time on the uptake of Fe²⁺ and Al³⁺ was investigated by preparing using a dry adsorbent dose of (0.05 g) at the natural pH 7, where, Samples were collected at 5 to 120 min time intervals.

**Results and discussion**

**Characterization of nano-HAp and CuFe₂O₄@HAp**

The XRD pattern of pure nano-HAp and CuFe₂O₄@HAp has been displayed in Figure 1. The nano-HAp exhibited a hexagonal system structure with (P63/m space group) that showed main diffraction peaks at \(2\theta = 26.3, 28.3, 30.15, 32.2, 35.2,\) and 49.2, which regarded to the ICDD card no. 01-073-0293. The high intensity and the degree of sharpness of the diffraction peaks are attributed to the perfect crystallinity and the smaller size obtained of the HAp nanoparticles, which was confirmed by the TEM. The hydroxyapatite structure showed crystallographic stability after combining with copper ferrite nanoparticles which have obviously depicted in Figure 1. As shown, there are some extra peaks that were appeared for the composite sample at \(2\theta = 17.8, 22.3\) which were regarded to the presence of copper ferrite nanoparticles.

FTIR spectra showed the different characteristic bands of both HAp and CuFe₂O₄@HAp in the wavenumber between 4000 and 400 cm⁻¹ to investigate the functional groups, as displayed in Figure 2. The characteristic peak

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**Figure 1.** XRD pattern of the synthesized HAp and CuFe₂O₄@HAp nanomaterials.
presented at 1034 cm\(^{-1}\) is attributed to the stretching vibrations of PO\(_4^{3-}\), while the bands at 602 and 564 cm\(^{-1}\) have corresponded to PO\(_4^{3-}\) bending vibrations as previously mentioned (Ahmed et al., 2021). Moreover, there was an abroad band at 3437.3 cm\(^{-1}\), which was regarded as the stretching vibration mode of the OH\(^-\) group. The peak with small intensity around 1637 and 1380 cm\(^{-1}\) could be assigned to the bending mode of surface adsorbed water molecules and carbon dioxide from the air during the synthesis process (Wang, Lv, Wang, Sun, & Tsang, 2021).

Morphological studies and particle size determination were conducted by the transmission electron microscope (TEM). Nano-HAp showed the prevalence of nanoparticles with a needlelike shape that had a length of 21.9 to 44.04 nm and the cross-sectional dimensions of 7.15 to 7.83 nm, as presented in Figure 3(a & b). Upon coupling with the ferrite-based material, cubic-like particles, regarding the CuFe\(_2\)O\(_4\), have been observed with some accumulation, which has particle size around 40 nm, Figure 3(c & d).

**Figure 2.** FTIR spectra of the synthesized HAp and CuFe\(_2\)O\(_4\)@HAp nanomaterials.

**Figure 3.** TEM of the synthesized HAp (a&b) and CuFe\(_2\)O\(_4\)@HAp (c&d) nanomaterials.
Brunauer-Emmett-Teller (BET) analysis was conducted by N$_2$ adsorption/desorption isothermic curves to study the surface properties. Determining the surface area, average pore size, and mean pore diameter is essential for studying the properties of the synthesized HAp-based adsorbents. Figure 4(a) revealed that the surface area increased from 31 to 58 m$^2$ g$^{-1}$ for the pure HAp upon coupling with copper ferrite. HAp and CuFe$_2$O$_4$@HAp demonstrated a type IV isotherm that confirms a mesoporous structure (2–50 nm) and depicted the formation of monolayer adsorption mechanism and the performance of capillary condensation (Estrada-Flores, Martínez-Luévanos, Pérez-Berumen, García-Cerda, & Flores-Guia, 2020). Figure 4(b) illustrates the results of pore size distribution showing that HAp and CuFe$_2$O$_4$@HAp conveyed a narrow distribution ranged 5–10 and 30–35 nm, respectively. Generally, adsorbents with a considerable surface area, and pore size could have more accessible active sites for pollutants binding (Ahmed et al., 2021). It could be deduced that coupling ferrite with HAp is a good influence on the enhancement of the pore size to be a more promising adsorbent so as to improve the trapping of the pollutants into the pores.

**Adsorption performance experiments**

As a matter of fact, from the aforementioned characterization results, it was found that the adsorption properties of HAp were enhanced after being coupled with copper ferrite which leads to the choose CuFe$_2$O$_4$ @HAp for further adsorption experiments of Al (III) and Fe (II) ions as an example of heavy metal ion pollutants. Factors such as initial ion concentration, pH, and contact time were investigated to evaluate the adsorption performance of Al (III) and Fe (II) ions onto the synthesized adsorbents.

**Effect of initial ion concentration**

The initial metal ion concentration performs a fundamental role in the adsorption efficiency. This may be attributed to the fact that the metal ions are being adsorbed on the active adsorbent sites of the adsorbent material. Hence, increasing the metal ions concentration causes saturation of the adsorbent and consequently blocks its active sites. By further increasing the metal ions concentration, no more adsorption will occur due to the active site’s saturation (Iconaru et al., 2018; Negm, Abd El Wahed, Hassan, & Abou Kana, 2018). Figure 5(a) illustrates that the adsorption capacity increased pointedly by increasing the equilibrium concentration of Al (III) and Fe (II) metal ions ranging from 0 mg l$^{-1}$ to 50 mg l$^{-1}$. The maximum values for the adsorption capacities are 49 mg g$^{-1}$ and 88.5 mg g$^{-1}$ for Al (III) and Fe (II) metal ions, respectively. This indicates that the increase in the initial concentrations of heavy metal ions participates in the enhancement of the motive to increase the adsorption capacity until the adsorption sites reach saturation. The resulted data were then fitted in Freundlich and Langmuir scale to further characterize the adsorption behaviors.

**Effect of the pH**

Hydrogen-ion concentration is considered an influential parameter in the adsorption process that could significantly affect the surface charge of any adsorbent. The dependence of the adsorption behavior on pH value is attributed to the metal ion solubility and the
ionization charge of the surface functional groups as hydroxyl, phosphate, carboxylate, and amino. The hydroxyapatite-based adsorbent possesses negatively charged functional groups (PO4-3 and OH-) that allow the adsorbent to provide probable binding sites for cations. Figure 5(b) showed the effect of pH on the adsorption capacity of the copper ferrite/hydroxyapatite material to the metal ions under study. By decreasing the pH, metal ion adsorption was decreased owing to the positive charge intensity generated on the binding sites. The hydrogen ions compete in an effective way with metal ions for binding on the active sites, and therefore the Al (III) removal did not exceed 27.1%. For the iron ion, at pH even lower than 4, it begins to precipitate as hydroxides (Morgan & Lahav, 2007). Conversely, upon increasing the pH value, the removal percent reached 99% at pH 6 due to the higher negative-charge intensity that electrostatically attracts positive ions. Afterward, the efficiency decreased steadily due to the repulsion forces between the positive-charge adsorbed ions and the remaining surrounding non-adsorbed ions. Hence, a pH value of 6 was chosen for the determination of the optimum adsorption conditions.

**Effect of contact time**

The contact time is a vital factor in the environmental-scale adsorption systems. Accordingly, the effect of contact time on the adsorption performance of Al(III) and Fe(II) ions on the synthesized adsorbent has been studied as depicted in Figure 5(c). There was a gradual increment in the adsorption capacity for the first 60 min, which afterward reached a state of equilibrium. This might be attributed to the strong motivation toward the available active sites that were saturated gradually with time. Thus, 60 min was selected for the optimum adsorption conditions.

**Adsorption isotherms**

To further understand the adsorption behavior of the prepared copper ferrite/HAp, the resulting data was studied by two different isotherms; Langmuir and Freundlich isotherms models. Adsorption isotherms help in designing a suitable sorption system that describes the adsorption process.

**Langmuir isotherm model.** Langmuir isotherm postulates the absence of any interaction between the adsorbent and adsorbate molecules (Langmuir, 1918; Li, Zhang, Li, Liu, & Yan, 2021). Moreover, it assumed the formation of monolayer-adsorption can be basically achieved on a uniform-homogeneous adsorbent surface by applying the Langmuir equation

\[
q_e = \frac{Q_0kC_e}{1 + kC_e}
\]  

By rearranging the equation to the common linear form it will be:

\[
\frac{C_e}{q_e} = \frac{1}{Q_0k} + \frac{C_e}{Q_0}
\]

Where \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)) of metal ions; \(q_e\) is the quantity of adsorbed metal-ion per unit mass of adsorbent (mg g\(^{-1}\)); \(Q_0\)
is qe for a complete monolayer (mg g⁻¹), a constant related to sorption capacity; and k is a constant related to the affinity of the binding sites and energy of adsorption (L mg⁻¹); K represents the sorption enthalpy that changes with the temperature where a high K value indicates high affinity. The maximum sorption capacity (Q₀) illustrates that the coverage of sorbent with sorbate is a monolayer.

The relevant parameters of the adsorption on CuFe₂O₄@HAp are listed in Table 1. Figure 6(a) shows the relationship between Ce/qe and Ce as a straight line with slope (1/Q₀) and intercept (1/KQ₀), where the Q₀ and k constants were determined. This pointed out that the adsorption proceeded according to Langmuir’s isotherm and was limited mainly to the monolayer formation. Binding constant (K) followed the order Al³⁺ > Fe²⁺ at a constant temperature, which is relevant to the interactive nature and strength. Whereas, the metal-ions sorption onto CuFe₂O₄@HAp clearly followed the order of Fe²⁺ > Al³⁺ for Q₀-values. This might be attributed to a kind of magnetism that occurred between iron ions and the adsorbent CuFe₂O₄@HAp surface. The equilibrium dimensionless constant (RL) represents the degree of appropriateness of CuFe₂O₄@HAp toward the metal ions under study, which refers to a separation factor or equilibrium parameter:

\[ RL = \frac{1}{1 + KC_0} \]  

where \( C_0 \) is the initial ion concentration and K is the equilibrium constant. The value of RL designates the type of the isotherm to be unfavorable (1 < RL), linear (RL = 1), favorable (0 < RL < 1) or irreversible (RL = 0). Values of this investigation were found to be 0.024 and 0.008 for Al(III) and Fe(II), respectively, indicating the favorable process at the experimental temperature.

**Freundlich isotherm model.** On the other hand, the Freundlich isotherm model postulates that the non-ideal adsorption takes place on heterogeneous surfaces forming a multilayer adsorption system (Freundlich, 1907; Shikuku & Mishra, 2021). It can be characterized mathematically by the heterogeneity factor (1/n).

Freundlich model is expressed by the following equation:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

where, \((KF)\) is Freundlich constant (mg g⁻¹)/(L mg⁻¹) and \(n\) is heterogeneity factor. The KF and \(1/n\) values are related to the adsorption capacity and intensity, respectively which varies with the extent of heterogeneity of the surface of the material used (adsorbent).

Basically, the adsorption process is convenient when \(1/n\) values fall between 0.1 and 1. By employing this model to the obtained data, a plot of ln qe with ln Ce gave a straight line was formed where the intercept and the slope can be used to determine the KF and \(1/n\) values, respectively. At \(n < 1\), adsorption can be deemed a chemical process; otherwise, it is a physical mechanism.

The obtained results revealed that \(n\)-values higher than 1 indicated a physical process with a consequent decrease in the \(R_2\) values in the order Al³⁺ > Fe²⁺ as shown in Figure 6(b). However, as shown in Table 1, the regression coefficient of correlation values (R²) for the Langmuir model was greater than that for

### Table 1. Langmuir & Freundlich isotherms and pseudo-first order & pseudo-second order kinetic models of the adsorption of Al(III) and Fe(II) ions on CuFe₂O₄@HAp. qe (mg g⁻¹), K (min⁻¹), K₂ (g mg⁻¹min⁻¹).

| Metal ion | qe | K | R² | 1/n | K₁ | R² | K₂ | qe | R₁ | K₂ | qe | R₂ |
|-----------|----|---|----|-----|----|----|----|----|----|----|----|----|
| Fe        | 91.7 | 0.40 | 0.99 | 0.385 | 23.75 | 0.52 | 0.009 | 36.7 | 0.99 | 0.001 | 78.1 | 0.97 |
| Al        | 49.2 | 1.99 | 0.99 | 0.139 | 27.33 | 0.64 | 0.013 | 13.5 | 0.96 | -0.063 | 47.8 | 0.99 |

**Figure 6.** Adsorption isotherms of Fe (II) and Al (III) on NMHAp at 25°C (a) Langmuir and (b) Freundlich.
Freundlich model in both heavy metal ions which describes the monolayer adsorption on homogenously distributed active sites on the surface of CuFe₂O₄@HAp.

Adsortion kinetics

To further explore the effect of the adsorption time of Al(III) and Fe(II) ions on the synthesized CuFe₂O₄@HAp, the first- and second-order kinetic models were simulated.

**Pseudo-first-order adsorption kinetic model.** The pseudo-first-order model can be illustrated using Equation (7):

$$\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t$$

where, $k_1$ is the rate constant of pseudo-first-order ($\text{min}^{-1}$), $q_e$ and $q_t$ represent the values of amount adsorbed at time (t) and at equilibrium, respectively. The kinetic parameters were determined by plotting log ($q_e - q_t$) vs. (t) as shown in Figure 7(a). The model validity is inspected by fitting $R_2$ in addition to the consistency between $q_e$ measured and estimated values where $K_1$ and $q_e$ values were calculated using their intercept and slope. The resulting $q_e$-values were 36.76 mg g⁻¹ ($R_2 = 0.99$) and 13.75 mg g⁻¹ ($R_2 = 0.96$), for Al(III) and Fe(II) ions, respectively.

**Pseudo-second-order adsorption kinetic model.** The pseudo-second-order model can be illustrated using the following equation (8) (Karthikeyan et al., 2021):

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t$$

where, $k_2$ is the rate constant of pseudo-second-order ($\text{min}^{-1}$), $q_e$ and $q_t$ represent the values of the adsorbed amount at the time (t) and at equilibrium, respectively. The kinetic parameters were determined by plotting log ($q_e - q_t$) vs. (t) as shown in Figure 7(b). The model validity is inspected by fitting $R_2$ in addition to the consistency between $q_e$ measured and the estimated values where $K_1$ and $q_e$ values were calculated using their intercept and slope. The resulting $q_e$-values were 36.76 mg g⁻¹ ($R_2 = 0.99$) and 13.75 mg g⁻¹ ($R_2 = 0.96$) for Al(III) and Fe(II) ions, respectively.

**Adsorption thermodynamics**

Various thermodynamic parameters are pivotal and should be considered to determine the spontaneity of a process including entropy change ($\Delta S^*$), enthalpy change ($\Delta H^*$), and free energy change ($\Delta G^*$). The temperature has a considerable impact on the adsorption process. Accordingly, the diffusion rate of the adsorbed molecules into the adsorbent (external layer and the internal pores) increases by increasing temperature. The thermodynamic parameters of the adsorption process were both obtained experimentally and estimated using Equations (9–11) at temperatures 298, 308, 318, and 328 K (Azlan, Wan Saime, & Lai Ken, 2009):

$$K_c = \frac{C_{ad}}{C_e}$$

$$\Delta G^* = -RT \ln K_c$$

$$\ln K_c = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}$$

where, $K_c$ is the equilibrium constant, $C_{ad}$ (mg l⁻¹) is the concentration of metal ion adsorbed on the solid surface at equilibrium, while $C_e$ (mg l⁻¹) is the equilibrium concentration of metal ions in the solution, $R$ (8.314 J Kmol⁻¹) is the universal gas constant and $T$ (Kelvin) is the absolute temperature.

The slope and intercept of the Van’t Hoff plot were used to obtain $\Delta H^*$ and $\Delta S^*$ values, respectively as shown in Figure 8. The data in Table 2 demonstrated that at all temperatures $|\Delta H^*| < |T\Delta S^*|$ indicating that entropic changes dominate the adsorption process rather than enthalpic changes. Generally, the change in free energy for physisorption lied in between $-20$ and $0$ kJ mol⁻¹, while that of chemisorption lied in between $-80$ and $-400$ kJ mol⁻¹ (Nnaji, Agim, Mama, Emenike, & Ogarekpe, 2021). The obtained $\Delta G^*$ results at 25 °C were −3.964 and −0.991 kJ mol⁻¹ for Al and Fe.

![Figure 7](image-url). Pseudo-first-order (a) and Pseudo-second-order (b) kinetic models of the uptake of Fe (II) and Al (III) on NMHAp.
ions, respectively. The negative $\Delta G ^{\circ}$ values indicate a physisorption-spontaneous nature of the adsorption process. It was evident from the recorded elevation in $\Delta G ^{\circ}$ value by the temperature that higher temperatures are more favored for the adsorption process.

### Table 2. Thermodynamic parameters of Al(III) and Fe(II) ions adsorption on CuFe$_2$O$_4$@HAp.

| Metal ion | $T$ (K) | $K_c$ | $R^2$ | $\Delta G^{\circ}$ (KJ/mol) | $\Delta S^{\circ}$ (KJ/mol) | $\Delta H^{\circ}$ (KJ/mol) | $T \Delta S^{\circ}$ (KJ/mol) |
|-----------|---------|-------|-------|-----------------------------|-----------------------------|-----------------------------|---------------------------------|
| Fe(II)    | 298     | 1.5   | 0.97  | $-0.991$                    | $0.058$                     | $15.67$                     | $17.28$                         |
|           | 308     | 2.3   |       | $-2.191$                    | $-2.908$                    |                             |                                 |
|           | 318     | 3.1   |       | $-4.008$                    |                             |                             |                                 |
|           | 328     | 4.3   |       | $-3.964$                    | $0.193$                     | $50.598$                    | $57.51$                         |
| Al(III)   | 298     | 5.01  | 0.99  | $-3.964$                    | $0.193$                     | $50.598$                    | $57.51$                         |
|           | 308     | 49.1  |       | $-11.368$                   |                             |                             |                                 |
|           | 318     | 77.3  |       | $-12.54$                    |                             |                             |                                 |
|           | 328     | 108.14|       |                              |                             |                             | $63.30$                         |

### Table 3. Removal efficiency of CuFe$_2$O$_4$@HAp adsorbent using wastewater samples.

| Metal ion | Sample 1 | Sample 2 | Sample 3 |
|-----------|----------|----------|----------|
|           | Before   | After    | Before   | After    | Before   | After    | Removal |
| Al        | 0.169    | 0.009    | 94.6     | 0.296    | 0.026    | 91.2     | 0.575   | 0.029   | 94.9    |
| Fe        | 0.188    | 0.039    | 79.2     | 0.218    | 0.013    | 96.6     | 0.078   | 0.001   | 98.7    |
| Cd        | 0.940    | 0.006    | 93.6     | 0.089    | 0.003    | 91.2     | 0.075   | 0.029   | 94.9    |
| Ni        | 0.008    | 0.007    | 91.2     | 0.010    | 0.006    | 40.0     | 0.009   | 0.005   | 44.4    |
| Cu        | 0.125    | 0.005    | 96.0     | 0.147    | 0.018    | 87.7     | 0.064   | 0.009   | 85.9    |
| Pb        | 0.010    | 0.009    | 10.0     | 0.006    | 0.005    | 16.6     | 0.003   | 0.002   | 33.3    |

On the other hand, the obtained values of $\Delta H ^{\circ}$ were 15.69 KJ mol$^{-1}$ and 50.59 KJ mol$^{-1}$ for both Al(III) and Fe(II) ions on the CuFe$_2$O$_4$@HAp, respectively. The positive values of $\Delta H ^{\circ}$ indicated the endothermic behavior of the adsorption process on the CuFe$_2$O$_4$@HAp surface. While $\Delta S ^{\circ}$ showed values of 0.058 KJ mol$^{-1}$ K$^{-1}$ and 0.193 KJ mol$^{-1}$ K$^{-1}$ for Al(III) and Fe(II) ions, respectively. As a result of the positive entropy $\Delta S ^{\circ}$ values, arising in the randomness degree at

the solid/liquid interface is expected and therefore suggested high affinity of CuFe$_2$O$_4$@HAp for the ions under study.

### CuFe$_2$O$_4$@HAp adsorbent for removal of metal ions from industrial wastewater samples

Three wastewater samples obtained from the outlet of iron and steel factories were used to investigate the removal efficiency of the studied adsorbent. Metal ion concentrations were determined before and after treatment with the CuFe$_2$O$_4$@HAp adsorbent. The results of the detected metal ions are recorded in Table 3. The removal efficiency percentage ranged between about 91–95% and 79–99% for Al(III) and Fe(II), respectively which indicates the higher efficiency of the studied adsorbent toward the remediation of metal ions. Moreover, a small negligible interference was observed from the other pollutants toward the selectivity of the adsorbent and adsorbates understudy confirming the eligibility of CuFe$_2$O$_4$@HAp as an effective water remediation material.

### Conclusion

In this study, nanostructured CuFe$_2$O$_4$@HAp has been successfully synthesized via the traditional precipitation and the sol-gel techniques for the HAp and CuFe$_2$O$_4$, respectively. The synthesized CuFe$_2$O$_4$@HAp has been characterized by several techniques (XRD, FTIR, BET and TEM). Afterward, its adsorption potential for the removal of some heavy metal ions like Fe(II) and Al(III) ions was investigated in addition to exploring
the effect of initial metal concentrations, contact time, and pH, on the adsorption process. The following findings were acquired

- The composite was able to remove about 98.9% and 72.5% of Fe(II) and Al(III) ions, respectively under optimum reaction conditions (pH of 5 and equilibrium time 60 min). The equilibrium data of adsorption are fitted with the Langmuir and pseudo-second order kinetic models.
- The resulting high adsorbing capacity of CuFe2O4 @HAp revealed that it can be readily applied as a promising, environmentally friendly, low-cost, productive adsorbent for metal ion removal from polluted water.

Acknowledgments
The authors are thankful for the support of the Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center (NWRC), Egypt for giving all the facilities to do this work.

Disclosure statement
No potential conflict of interest was reported by the author(s).

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