

RESEARCH ARTICLE

Hydroxyapatite as an Effective Adsorbent for Cu^{2+} and Ni^{2+} : Study on Adsorption and Metal Recovery by Electrochemical Deposition in Deep Eutectic Solvent

Thi Phuong Thao Le¹ | Thi Duyen Le¹ | Thu Phuong Nguyen² | Tien Dung Cong³ 

¹Department of Chemistry, BSASD Research Group, HiTech-CEAE Research Team, Hanoi University of Mining and Geology, Hanoi, Vietnam | ²Institute for Tropical Technology, Vietnam Academy of Science and Technology, Hanoi, Vietnam | ³Department of Chemistry, BSASD Research Group, Hanoi University of Mining and Geology, Hanoi, Vietnam

Correspondence: Tien Dung Cong (congtiendung@humg.edu.vn)

Received: 21 September 2025 | **Revised:** 3 February 2026 | **Accepted:** 19 February 2026

Keywords: adsorbent | copper and nickel removal | deep eutectic solvent | electrodeposition recovery | hydroxyapatite

ABSTRACT

Heavy metal pollution is a global environmental challenge. Removal of heavy metal ions by recyclable adsorbents and metal recovery by environmentally friendly methods are of high importance. In this study, hydroxyapatite (HAp) was synthesized and employed for the removal of copper (Cu^{2+}) and nickel (Ni^{2+}) ions from aqueous solutions. The adsorption behavior of both metal ions was systematically investigated under various conditions, including changes in pH, contact time, initial concentration, and adsorbent dosage. The adsorption capacity and efficiency for Cu^{2+} were measured at 49.53 mg.g^{-1} and 99.06%, respectively, while for Ni^{2+} , the values were 12.15 mg.g^{-1} and 80.99%. Adsorption isotherm analysis indicated a good fitting with Redlich–Peterson models, while kinetic studies confirmed that the process followed the pseudo-second-order models, suggesting chemisorption involvement. Furthermore, desorption of metal ions and recovery of elemental Cu and Ni were conducted via electrodeposition in a choline chloride–urea (reline) deep eutectic solvent. Under optimal electrolysis conditions (current density of 7.5 mA.cm^{-2} , 10-hour duration, 0.1 g metal-loaded HAp, and 60°C), recovery efficiencies reached 94.63% for copper and 94.80% for nickel. The regenerated HAp retained significant adsorption performance, with capacities of 39.25 mg.g^{-1} for Cu^{2+} and 11.18 mg.g^{-1} for Ni^{2+} , corresponding to removal efficiencies of 78.49% and 74.60%, respectively. Synthesized HAp could be potentially an effective, recyclable adsorbent for the treatment and recovery of heavy metals from wastewater.

1 | Introduction

The increasing discharge of heavy metals into aquatic environments due to industrial activities such as mining, electroplating, battery manufacturing, and metal refining has become a serious global concern [1]. Among these, Cu^{2+} and Ni^{2+} are two commonly encountered transition metal ions that exhibit toxic effects on aquatic ecosystems and human health when present above permissible limits. Exposure to excess copper can lead to liver and kidney dysfunction [2], while nickel is a known allergen and potential carcinogen [3]. Owing to their nonbiodegradable nature and high toxicity, the removal and recovery of Cu^{2+} and Ni^{2+} from wastewater are crucial for environmental protection and resource sustainability. Conventional treatment methods—such as chemical

precipitation, ion exchange, membrane separation, and electrochemical techniques—often suffer from high operational costs, sludge generation, or limited selectivity [4]. Therefore, developing cost-effective, efficient, and recyclable materials for heavy metal remediation is of great practical and environmental significance.

Hydroxyapatite (HAp), with the chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, has attracted increasing attention as a promising adsorbent for heavy metal removal due to its low solubility, biocompatibility, high ion exchange capacity, and structural affinity for divalent metal cations. Its ability to remove various heavy metals—such as Pb^{2+} , Cd^{2+} , Cu^{2+} , and Ni^{2+} —has been reported in numerous studies [2, 5–9]. The unique crystal structure of HAp allows for ion exchange between calcium and metal cations, as well as surface

complexation and precipitation mechanisms, contributing to its high adsorption efficiency. Additionally, the nanostructured form of HAp with high surface area enhances its reactive sites, further improving its adsorption capacity. These properties, coupled with its availability and environmental safety, make HAp a viable candidate for heavy metal remediation from contaminated water sources. However, the full potential of HAp as a recyclable adsorbent, especially regarding desorption and metal recovery, remains underexplored and requires further investigation.

In addition to effective removal, the ability to recover valuable metals and regenerate the adsorbent is essential for advancing sustainable water treatment technologies. Recycling copper and nickel not only mitigates environmental hazards but also contributes to the circular economy by recovering useful resources. Conventional recovery methods often rely on harsh chemicals or generate secondary pollutants, highlighting the need for green recovery approaches. Electrodeposition, particularly in environmentally friendly media such as deep eutectic solvents (DESs), offers an efficient, low-toxicity, and selective route for metal recovery [10]. Among these, reline (a mixture of choline chloride and urea) has been widely studied for its tunable physicochemical properties, thermal stability, and compatibility with metal salts. Furthermore, the regeneration of HAp after desorption ensures continued use of the material in multiple cycles, improving process economics and reducing waste. Assessing the reusability of HAp after recovery processes is thus critical to validate its role as a practical and recyclable adsorbent.

Although several publications have mentioned Cu^{2+} and Ni^{2+} adsorption by HAp-based materials [6, 11–17], there are no papers spontaneously researching adsorption, desorption, and metal recovery to recycle HAp materials to date. This study aims to evaluate the performance of HAp as a multifunctional material for the adsorption of Cu^{2+} and Ni^{2+} ions from aqueous media, as well as to investigate the desorption simultaneously recovering these metals and regenerating absorbed HAp material. The research focuses on determining the optimal adsorption conditions including pH, adsorption time, initial concentration, and dosage for both metals. Adsorption isotherms and kinetic models are applied to understand the mechanisms involved in metal uptake. Furthermore, the study investigates the desorption of adsorbed metals and their electrochemical recovery via electrodeposition in reline electrolyte under controlled conditions. The efficiency of the regenerated HAp in subsequent adsorption cycles is also examined. By integrating adsorption, recovery, and regeneration into a single approach, this work contributes to the development of ecofriendly and resource-efficient strategies for wastewater treatment, with implications for both environmental protection and metal resource management.

2 | Experimental Section

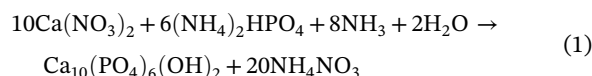
2.1 | Preparation of Metal Ion Solutions and Reline Solvent

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were analytical-grade reagents obtained from Merck (Germany). Choline chloride

(ChCl, $\geq 98\%$) and urea (U, 98%) were purchased from Sigma-Aldrich. The DES, commonly referred to as reline, was prepared by mixing ChCl and urea at a molar ratio of 1:2. The solid mixture was stirred continuously for 3 h at 60°C . A homogeneous, transparent solution was formed, consistent with methods previously reported [18, 19].

2.2 | Synthesis of HAp

HAp powder was prepared via a chemical precipitation route in aqueous medium utilizing calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), and ammonia (NH_3) as precursors [19]. The synthesis reaction is shown in Equation (1). A 0.3 M solution of $(\text{NH}_4)_2\text{HPO}_4$ was slowly added dropwise to a 0.5 M $\text{Ca}(\text{NO}_3)_2$ solution at a constant rate of 1 mL/min under continuous stirring at 800 rpm. The pH of the reaction was maintained between 10 and 12 by adding concentrated NH_3 solution. After the complete addition of phosphate, the reaction mixture was stirred for an additional 2 h, then aged at room temperature for 15 h. The resulting precipitate was repeatedly washed with distilled water until neutral pH was achieved using centrifugation at 4000 rpm. The purified product was then dried at 80°C for 24 h and finely ground to obtain uniform HAp powder [7].



2.3 | Adsorption of Cu^{2+} and Ni^{2+} onto HAp

The adsorption of Cu^{2+} and Ni^{2+} onto HAp was performed by adding HAp to 50 mL of metal ion solution and stirring at 400 rpm. Key parameters such as contact time (10–120 min), pH (2.35–7.0), HAp dose (0.3–1.0 g), and initial metal concentration (20–80 $\text{mg}\cdot\text{L}^{-1}$) were varied to evaluate adsorption behavior. After filtration, residual metal concentrations were measured by the inductively coupled plasma mass spectroscopy (ICP-MS) method on ICAP Q ICP-MS instrument (Thermo Scientific, Germany). Adsorption capacity (Q , $\text{mg}\cdot\text{g}^{-1}$) and efficiency (H , %) were calculated using [16, 20]:

$$Q = (C_0 - C) \cdot V/m \quad (2)$$

$$H = (C_0 - C) \cdot 100/C_0 \quad (3)$$

where, C_0 and C ($\text{mg}\cdot\text{L}^{-1}$) are initial and final concentrations, V (L) is solution volume, and m (g) is HAp mass.

2.4 | Adsorption Isotherms and Kinetics

Equilibrium data were fitted to Langmuir, Freundlich, and Redlich–Peterson models (Equations (4)–(6)) to describe the adsorption mechanism [21, 22].

$$\text{Langmuir non-linear equation: } Q_e = Q_m \cdot \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

$$\text{Freundlich non-linear equation: } Q_e = K_F \cdot C_e^{1/n} \quad (5)$$

$$\text{Redlich-Peterson non-linear equation } Q_e = \frac{K_{RP}C_e}{1 + a_{RP}.C_e^b} \quad (6)$$

where, C_e (mg.L⁻¹) presents the M²⁺ concentration at equilibrium, Q (mg.g⁻¹) indicates the adsorption capacity at equilibrium, Q_m (mg.g⁻¹) is the maximum adsorption capacity, K_L is the Langmuir coefficient, K_F and n are the Freundlich constants, K_{RP} is the Redlich-Peterson constant, a_{RP} is the Redlich-Peterson equilibrium constant, and b is the exponent of the Redlich-Peterson model.

Kinetic behavior was analyzed using pseudo-first-order and pseudo-second-order models (Equations (7) and (8)) to determine the adsorption rates and mechanisms [23].

$$\text{The pseudo-first-order non-linear model: } Q_t = Q_e \cdot (1 - e^{-k_1 \cdot t}) \quad (7)$$

$$\text{The pseudo-second-order non-linear model: } Q_e = \frac{k_2 \cdot Q_e^2 \cdot t}{1 + k_2 \cdot Q_e \cdot t} \quad (8)$$

in which, Q_e (mg.g⁻¹) and Q_t (mg.g⁻¹) are the adsorption capacity at equilibrium and at the time t , respectively; k_1 (min⁻¹) and k_2 (g.mg⁻¹.min⁻¹) are the first-order rate constant and the second-order rate constant, respectively.

2.5 | Desorption of Metal Ions in DES

Cyclic voltammetry (CV) of Cu²⁺, Ni²⁺, and M-HAp in reline was conducted to investigate the electrochemical properties of Cu²⁺ and Ni²⁺ ions under measurement conditions and find out the position of oxidation and reduction peaks of the metals. Based on that, the voltage required to precipitate metal is determined. CV measurements were performed using an Autolab PGSTAT20 potentiostat with a three-electrode setup: a gold working electrode (0.0201 cm²), an Ag/AgCl reference electrode, and a platinum grid counter electrode. For M²⁺/reline systems, 5 mL of reline containing 0.005 M Cu²⁺ or Ni²⁺ was used as the electrolyte. For M-HAp/reline systems, 0.5 g of Cu- or Ni-loaded HAp was dispersed in 5 mL of reline. CV was conducted in the range of -0.2 to -1.6 V at a scan rate of 0.02 V/s (Table 1).

Metal desorption from M-HAp and simultaneous recovery via electroplating were carried out in a three-electrode electrolysis cell using a gold plate (1 cm²) as the working electrode. The M-HAp/reline suspension was stirred at 60°C under N₂ purging. Electrolysis was conducted at ≤ -0.4 V for Cu²⁺ and -0.6 V

for Ni²⁺. Key variables studied included current density (1–7.5 mA.cm⁻²), electrolysis time (1–12 h), and M-HAp mass (0.1–0.3 g). After electrolysis, solids were filtered, washed, dried, and analyzed by ICP-MS to determine remaining metal content.

2.6 | Characterization Methods

The scanning electron microscope (SEM) images, combined with energy dispersive X-ray scattering spectroscopy (EDS) using the FEI Quanta 450 device, were used to determine the morphology and composition of the HAp and M-HAp materials. X-ray diffraction (XRD) measurements were conducted with a Siemens D5005 machine to confirm the phase composition of both HAp and M-HAp. The surface morphology and composition of Au electrodes were examined before and after the electrolysis process through SEM images and EDS results. The structure of the materials was investigated using Fourier transform infrared spectra (FT-IR) from a Nicolet iS10 instrument (Thermo Scientific, USA). The Brunauer, Emmett, and Teller (BET) method, utilizing a TriStar II Plus analyzer, was employed to determine specific surface area.

The point of zero charge (pH_{pzc}) for HAp was measured by the pH drift method [6, 24, 25]. This involved adding 0.2 g of HAp to 50 mL of 0.01 M KCl (99%, Merk), with various initial pH values (pH₀) adjusted by 0.01 M HCl (37%, Merk) or NaOH (99%, Merk). After stirring at a speed of 800 rpm for 30 min and filtering, the final pH values (pH_s) of the solution were recorded to calculate the difference in initial and final pH values (ΔpH = pH₀ - pH_s). The variation of ΔpH with pH₀ was illustrated in a graph. The pH_{pzc} was identified as the point of pH₀ at which the ΔpH equals zero.

3 | Results and Discussion

3.1 | Characteristics of Synthesized HAp

The SEM image in Figure 1a reveals that the synthesized HAp exhibits a rod-like nanostructure. These rod-shaped crystallites are characteristic of HAp synthesized via aqueous precipitation methods and indicate a high surface-to-volume ratio, which is favorable for adsorption applications [26]. The morphology supports efficient interaction with metal ions due to the abundant active surface sites and potential ion-exchange pathways. Figure 1b presents the nitrogen adsorption-desorption isotherm of HAp, which corresponds to a type IV isotherm with a hysteresis loop, indicative of mesoporous structure [27]. The isotherm shows a steep uptake at higher relative pressures ($P/P_0 > 0.8$), confirming capillary condensation in mesopores [28]. The BET-specific surface area was determined to be 91.42 m²/g, which is relatively high for HAp materials synthesized. These results demonstrate that the synthesized HAp possesses favorable structural and textural properties for potential use as an effective adsorbent.

Through the utilization of the pH drift method, the pH_{pzc} of synthesized HAp was determined by plotting the difference in pH (ΔpH = pH₀ - pH_s) against pH₀. It was shown in Figure 2 that the pH_{pzc} of HAp was 7.34. The pH_{pzc} of HAp-based materials could range from 5.8 to 10, depending on the synthesis conditions [12, 14, 29, 30]. According to Smičiklas et al. [29],

TABLE 1 | CV scanning parameters of 0.005 M M²⁺ and 0.5 g M-HAp in reline.

Parameter	Value	Parameter	Value
WE	Au (S = 0.0201 cm ²)	Potential range	-0.2 ÷ -1.6 (V)
RE	Ag/AgCl/Cl ⁻	Potential step	0.005 V
CE	Pt grid	Scanning rate	0.02 V/s
		V _{reline}	5 mL

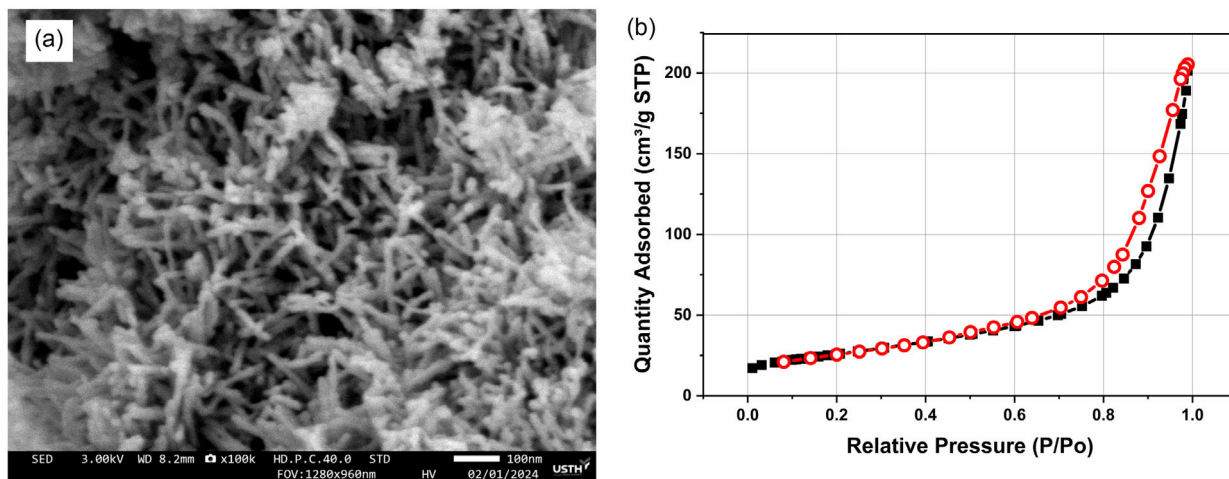


FIGURE 1 | SEM image (a) and BET result and (b) of synthesized HAP powder.

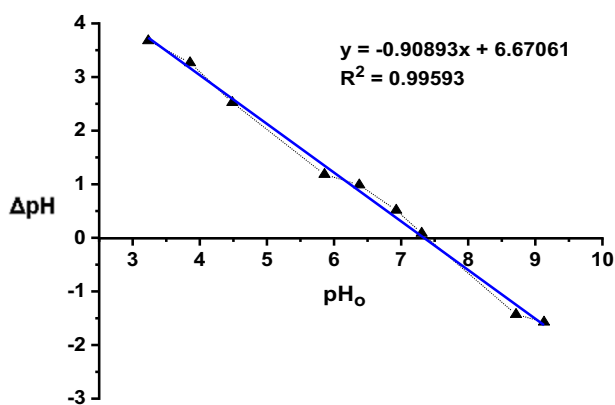


FIGURE 2 | pH_{pzc} of synthesized HAP powder.

materials with a higher pH_{pzc} may exhibit increased sorption of metal ions due to possessing a greater excess of negative charge on their surface. As the pH_{pzc} is an indicator of the net charge of HAP, the obtained result means that the surface of synthesized HAP becomes predominantly positive at $\text{pH} < 7.34$, while above this value, the surface will be negatively charged. For this reason, it may have a strong influence on the adsorption behavior of synthesized HAP in the solution at a different pH.

3.2 | Cu^{2+} , Ni^{2+} Adsorption on Synthesized HAP

3.2.1 | Effect of Factors on Adsorption Efficiency and Capacity

Figure 3 illustrates the influence of contact time on the adsorption efficiency (H) and capacity (Q) of Cu^{2+} and Ni^{2+} ions onto HAP synthesized. For Cu^{2+} , at an initial concentration of 50 mg.L^{-1} , pH 5.35, and 0.03 g of HAP, both Q and H rapidly increased within the first 60 min, reaching near-equilibrium values of $\sim 74 \text{ mg.g}^{-1}$ and $\sim 99\%$, respectively. This rapid uptake suggests strong interaction between Cu^{2+} ions and available active sites on HAP. After 60 min, the curves plateau, indicating saturation of adsorption sites and equilibrium attained. For Ni^{2+} , under the same initial concentration but at pH 5.57 and 0.05 g HAP, Q and H increased sharply up to 60 min, achieving maximum values of $\sim 25 \text{ mg.g}^{-1}$ and $\sim 87\%$. The adsorption rate was slightly slower compared to Cu^{2+} , possibly due to the lower affinity or slower diffusion of Ni^{2+} into HAP's porous structure. Beyond 60 min, only marginal increases were observed, confirming equilibrium established. These results suggest that 60 min is sufficient for efficient removal of both Cu^{2+} and Ni^{2+} using HAP.

Figure 4 presents the effect of initial pH on the adsorption behavior of Cu^{2+} and Ni^{2+} ions onto synthesized HAP. The results showed that the adsorption amount of both Cu^{2+} and Ni^{2+} ions

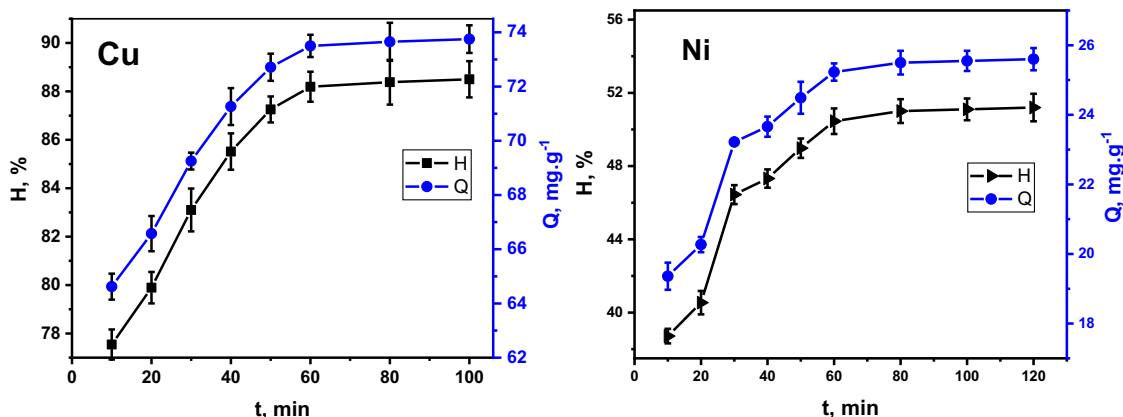


FIGURE 3 | Effect of contact time to adsorption efficiency and capacity of Cu^{2+} ($C_{\text{Cu}^{2+}} = 50 \text{ mg.L}^{-1}$, $T = 25^\circ\text{C}$, $\text{pH} = 5.35$, $m_{\text{HAP}} = 0.03 \text{ g}$) and Ni^{2+} ($C_{\text{Ni}^{2+}} = 50 \text{ mg.L}^{-1}$, $T = 25^\circ\text{C}$, $\text{pH} = 5.57$, $m_{\text{HAP}} = 0.05 \text{ g}$).

on HAp increased with the increase in solution pH, indicating a strong effect of pH on the adsorption ability as mentioned in the above section. This finding is consistent with that obtained in previous research on the adsorption behavior of copper and nickel ions on magnetic HAp [15] and kaolinite [31]. For Cu^{2+} (Figure 4a), at a constant adsorbent mass of 0.03 g, 50 mg.L^{-1} initial concentration, and 60-min contact time, both adsorption efficiency (H) and capacity (Q) increase significantly with rising pH from 2.5 to 5.35. The adsorption capacity reaches a maximum of $\sim 81.4 \text{ mg.g}^{-1}$, with nearly 100% removal efficiency, indicating enhanced electrostatic attraction and surface complexation under near-neutral conditions. Below pH 4.0, the lower adsorption is likely due to competition between H^+ ions and Cu^{2+} for active sites. Similarly, Figure 4b shows that for Ni^{2+} (0.05 g HAp), adsorption improves as pH increases from 2.5 to 5.57, with Q rising from $\sim 11 \text{ mg.g}^{-1}$ to $\sim 35 \text{ mg.g}^{-1}$ and H exceeding 70%. At low pH, protonation of the HAp surface suppresses Ni^{2+} binding, while at higher pH values, reduced competition from H^+ and increased availability of binding sites enhance metal uptake [32]. All investigated pH ranges were lower than $\text{pH}_{\text{pzc}} = 7.34$, leading to the positively net charged surface, which was unfavorable for the adsorption of Cu^{2+} and Ni^{2+} . It suggested that, besides electrostatic interaction, surface complexation should play an important role in the

adsorption process. Although a high pH solution ($>\text{pH}_{\text{pzc}}$) could make the negatively net charged surface, which is favorable for adsorption, the metal precipitation should occur under that condition. In order to avoid metal precipitation, the pH of the solution was chosen at 5.35 and 5.57 for the next investigation of Cu^{2+} and Ni^{2+} adsorption, respectively.

Figure 5 illustrates how varying the mass of HAp influences the adsorption of Cu^{2+} and Ni^{2+} ions. In Figure 5a, for Cu^{2+} ($C_0 = 50 \text{ mg.L}^{-1}$, pH 5.35, $t = 60 \text{ min}$), the adsorption efficiency (H) increases sharply with HAp mass, reaching nearly 100% at 0.05 g. However, the adsorption capacity (Q) decreases significantly from $\sim 130 \text{ mg.g}^{-1}$ at 0.01 g to $\sim 25 \text{ mg.g}^{-1}$ at 0.1 g. This inverse trend results from the fixed amount of Cu^{2+} in solution: increasing HAp mass provides more active sites, improving efficiency, but reduces Q due to fewer Cu^{2+} ions per gram of adsorbent. Similarly, Figure 5b shows that for Ni^{2+} ($C_0 = 50 \text{ mg.L}^{-1}$, pH 5.57, $t = 60 \text{ min}$), H increases with HAp mass, peaking at $\sim 40\%$ with 0.1 g, while Q decreases from $\sim 39 \text{ mg.g}^{-1}$ to $\sim 12 \text{ mg.g}^{-1}$. The lower overall efficiency for Ni^{2+} compared to Cu^{2+} suggests weaker interaction with HAp. These results confirm that adsorption efficiency benefits from increased adsorbent mass, while capacity per gram decreases due to dilution of available metal ions across more active sites.

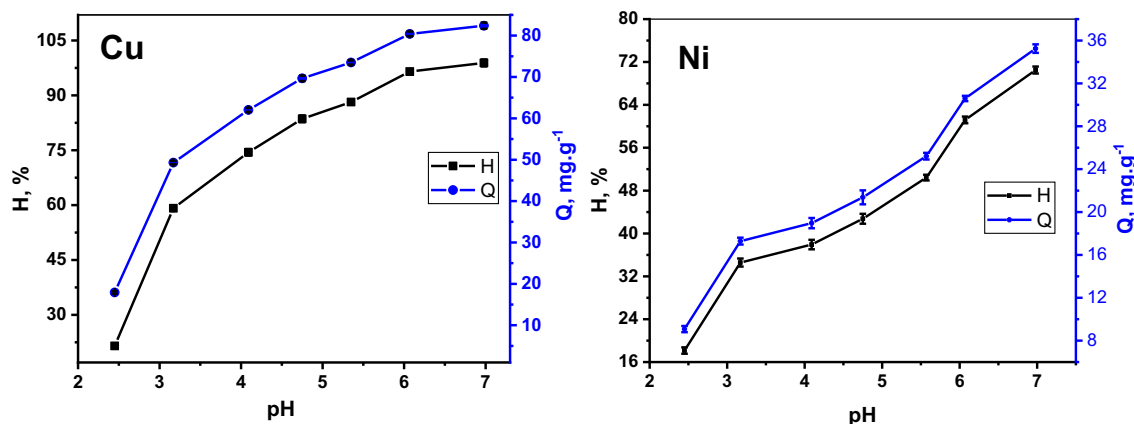


FIGURE 4 | The influence of pH on the adsorption capacity and efficiency of Cu^{2+} ($m_{\text{HAp}} = 0.03 \text{ g}$, $C_{\text{Cu}^{2+}} = 50 \text{ mg.L}^{-1}$, $T = 25^\circ\text{C}$, $t = 60 \text{ min}$) and Ni^{2+} ($m_{\text{HAp}} = 0.05 \text{ g}$, $C_{\text{Ni}^{2+}} = 50 \text{ mg.L}^{-1}$, $T = 25^\circ\text{C}$, $t = 60 \text{ min}$).

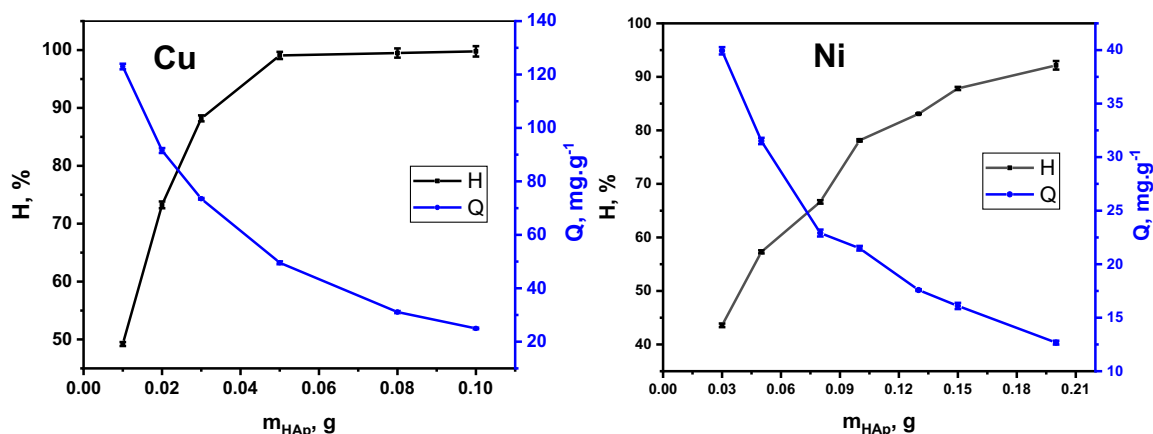


FIGURE 5 | The effect of HAp mass on the adsorption capacity and efficiency of Cu^{2+} ($C_{\text{Cu}^{2+}} = 50 \text{ mg.L}^{-1}$, $T = 25^\circ\text{C}$, $t = 60 \text{ min}$, pH = 5.35) and Ni^{2+} ($C_{\text{Ni}^{2+}} = 50 \text{ mg.L}^{-1}$, $T = 25^\circ\text{C}$, $t = 60 \text{ min}$, pH = 5.57).

Figure 6 illustrates the effect of increasing initial metal ion concentrations on the adsorption behavior of synthesized HAp for Cu^{2+} and Ni^{2+} . For Cu^{2+} (0.05 g HAp, pH 5.35, $t = 60$ min), both adsorption capacity (Q) and efficiency (H) increase steadily with initial concentration ranging from 10 to 80 mg.L^{-1} . Q reaches approximately 76 mg.g^{-1} at the highest concentration, and H continues to rise, suggesting that Cu^{2+} ions remain in excess relative to the available binding sites, favoring continued uptake without site saturation within the investigated range. In contrast, Figure 6 shows that for Ni^{2+} (0.1 g HAp, pH 5.57), adsorption capacity increases with initial concentration up to $\sim 17.5 \text{ mg.g}^{-1}$ at 30 mg.L^{-1} , beyond which it plateaus, indicating saturation of available adsorption sites. Correspondingly, adsorption efficiency (H) rises rapidly at low concentrations and levels off above 30 mg.L^{-1} , reflecting a balance between available Ni^{2+} and HAp active sites. These results demonstrate that Cu^{2+} exhibits a stronger interaction and higher loading potential with HAp compared to Ni^{2+} under similar conditions. This is similar to that of papers observing the adsorption of Cu^{2+} and Ni^{2+} [32–35]. According to Mobasherpour et al. [36], OH^- and PO_4^{3-} groups presented on the HAp surface are Lewis bases. Both Cu^{2+} and Ni^{2+} ions are borderline acids, which could interact with these Lewis bases. However, Cu^{2+} with a larger radius (0.073 nm) compared to that of Ni^{2+} (0.069 nm) could result in a more stable connection with the OH^- and PO_4^{3-} groups presented on the HAp surface [37–39]. This is one of the reasons explaining the greater

adsorption capacity for Cu^{2+} rather than Ni^{2+} on synthesized HAp. Moreover, the hydration energy value of the Cu^{2+} ion (-2100 kJ/mol) is lower than that of Ni^{2+} ion (-2105 kJ/mol) [40], giving Cu^{2+} more chance to escape the hydration layers to cooperate with functional groups of the HAp surface than Ni^{2+} .

3.2.2 | Adsorption Isotherms of Cu^{2+} and Ni^{2+} Ions on HAp

Figure 7 and Table 2 illustrate the adsorption isotherms of Cu^{2+} and Ni^{2+} ions on synthesized HAp, modeled using Langmuir, Freundlich, and Redlich–Peterson equations. The high extent of approximation of a model was confirmed by both the highest value of adjusted R-square (R^2), and the smallest value of sum of squared errors (SSEs) [41]. For Cu^{2+} (Figure 7a), the Langmuir model provided a good fit with a high adjusted R^2 of 0.98852 and SSE of 37.249, indicating monolayer adsorption onto a homogeneous surface. The maximum adsorption capacity (Q_m) was 81.31 mg.g^{-1} , and the Langmuir constant (K_L) was 2.82 L.mg^{-1} , suggesting strong binding affinity. The Freundlich model showed a lower fit ($R^2 = 0.87142$ and $\text{SSE} = 417.2599$), although the value of $n = 3.21$ (>1) confirms favorable adsorption. The Redlich–Peterson model yielded the best correlation ($R^2 = 0.98899$ and $\text{SSE} = 29.78717$), bridging both Langmuir and Freundlich behaviors with $b \approx 1.07$, further validating the dominant monolayer adsorption mechanism with slight heterogeneity [41, 42].

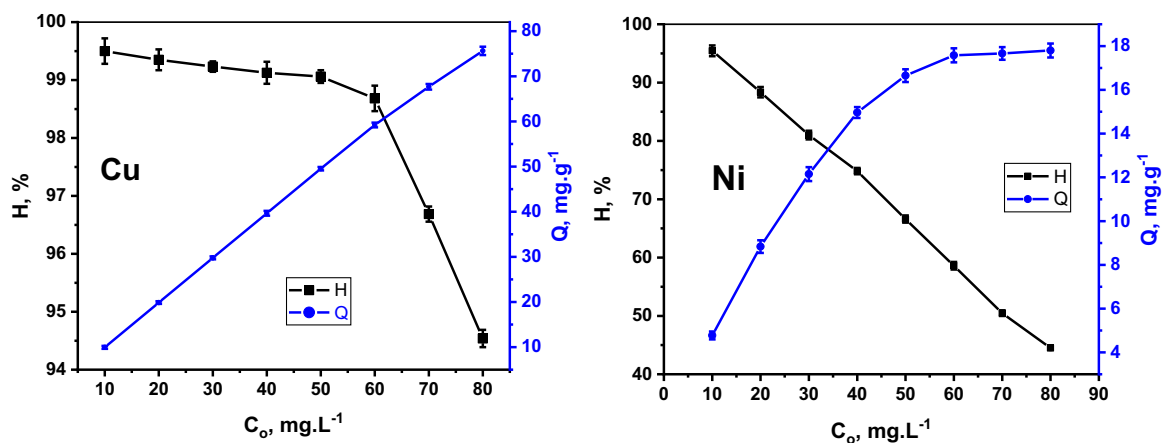


FIGURE 6 | The influence of the initial concentration of Cu^{2+} ($m_{\text{HAp}} = 0.05 \text{ g}$, $\text{pH} = 5.35$, $T = 25^\circ\text{C}$, $t = 60$ min) and Ni^{2+} ($m_{\text{HAp}} = 0.1 \text{ g}$, $\text{pH}_0 = 5.57$, $T = 25^\circ\text{C}$, $t = 60$ min) on the adsorption capacity and efficiency.

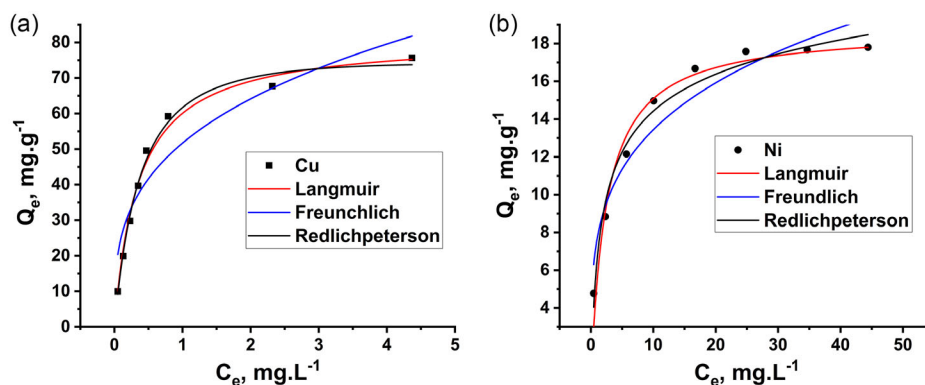


FIGURE 7 | Adsorption isotherms of Cu^{2+} (a) and Ni^{2+} (b) at 25°C according to Langmuir, Freundlich, and Redlich–Peterson models.

TABLE 2 | Q_m , K_L , K_F , n , K_{RP} , a_{RP} , and b parameters of the Langmuir, Freundlich, and Redlich–Peterson models for the Cu^{2+} and Ni^{2+} adsorption process.

Langmuir	Q_m	K_L	Adj- R^2	SSE	Chi-square (χ^2)	
Cu ²	81.31 ± 2.42	2.82 ± 0.26	0.9885	37.249	6.208	
Ni ²⁺	18.78 ± 0.61	0.40 ± 0.07	0.9665	4.779	0.796	
Freundlich	K_F	n	Adj-R ²			
Cu ²	51.67 ± 3.25	3.21 ± 0.52	0.8714	417.259	69.543	
Ni ²⁺	7.64 ± 0.73	0.24 ± 0.03	0.9320	9.530	1.588	
Redlich–Peterson	K_{RP}	a_{RP}	b	Adj- R^2	SSE	Chi-square (χ^2)
Cu ²	201.17 ± 26.15	2.26 ± 0.49	1.067 ± 0.063	0.9889	29.787	5.957
Ni ²⁺	13.77 ± 4.56	1.10 ± 0.53	0.887 ± 0.045	0.9764	2.756	0.551

For Ni^{2+} (Figure 7b), the Langmuir model also fitted well ($R^2 = 0.9665$ and $\text{SSE} = 4.77912$), with $Q_m = 18.78 \text{ mg.g}^{-1}$ and $K_L = 0.41 \text{ L.mg}^{-1}$, indicating weaker interaction compared to Cu^{2+} . The Freundlich model had a good fit ($R^2 = 0.93208$ and $\text{SSE} = 9.53051$), but the low value of $n = 0.24 (<1)$ suggests unfavorable or limited multilayer adsorption. The Redlich–Peterson model again showed superior agreement ($R^2 = 0.97642$ and $\text{SSE} = 2.75689$), with $b \approx 0.89$, supporting a hybrid adsorption mechanism that involves both monolayer and heterogeneous surface interactions. Overall, the combined Langmuir and Freundlich model (Redlich–Peterson) was well fitted to the adsorption of Cu^{2+} and Ni^{2+} ions on synthesized HAp.

The adsorption capacity of materials based on HAp for Cu^{2+} and Ni^{2+} varies significantly depending on material nature, synthesis method, and structural modification. The Cu^{2+} and Ni^{2+} maximum adsorption capacity of several materials based on HAp was given in the Table 3. In the current study, the synthesized HAp exhibited a maximum Cu^{2+} adsorption capacity (Q_m) of 81.31 mg.g^{-1} and Ni^{2+} capacity of 18.78 mg.g^{-1} , placing it among the highly effective unmodified HAp materials. For Cu^{2+} , the Q_m value of 81.31 mg.g^{-1} is higher than that of HAp derived from Bio-Rad (30.72 mg.g^{-1}) [4] and apatite ore (69.59 mg.g^{-1}) [5–9], but slightly lower than commercial Alfa-Aesar HAp (96.64 mg.g^{-1}) [1]. This indicates that the synthesized HAp offers competitive performance, potentially enhanced by its nanostructure and high surface area. For Ni^{2+} , the synthesized HAp shows moderate capacity (18.78 mg.g^{-1}) compared to other modified HAp-based materials. While it surpasses the unmodified HAp in Ref. [9] (46.17 mg.g^{-1}), it is significantly outperformed by functionalized composites such as HAp nanoparticles impregnated on apple pomace (100 mg.g^{-1}) [17], CHA/MFC hybrid (119 mg.g^{-1}) [44], and HAp/ Fe_3O_4 /CS composite (112.36 mg.g^{-1}) [45]. These modifications likely improve dispersion, surface chemistry, and availability of functional groups, boosting Ni^{2+} affinity. Overall, the synthesized HAp shows strong Cu^{2+} adsorption and moderate Ni^{2+} uptake, with potential for further enhancement through surface functionalization or composite formation.

3.2.3 | Kinetics of the adsorption process of Cu^{2+} and Ni^{2+}

Figure 8 and Table 4 show the kinetic modeling of Cu^{2+} and Ni^{2+} adsorption onto synthesized HAp using pseudo-first-order and pseudo-second-order models. For Cu^{2+} (Figure 8a), the

TABLE 3 | The Cu^{2+} and Ni^{2+} maximum adsorption capacity of several materials based on HAp.

Materials	Q_{max} (mg.g^{-1})		Ref.
	Cu^{2+}	Ni^{2+}	
HAp (Bio-Rad)	30.72		[4]
HAp (Alfa-Aesar)	96.64		[1]
HAp (Apatite ore)	69.59		[5–9]
HAp (Bovine bone)	25.7		[43]
HAp (This work)	81.3	18.8	
HAp (Eggshell)	10.58	9.5	[32]
HAp		46.17	[9]
HAp (impregnated on apple pomace)		100	[17]
CHA/MFC (carbonated HAp/modified microfibrillated cellulose)		2.021 mmol.g ⁻¹ (119 mg.g ⁻¹)	[44]
HAp/ Fe_3O_4 /CS		112.36	[45]

experimental equilibrium adsorption capacity ($Q_{e,\text{exp}}$) was 73.75 mg.g^{-1} . The pseudo-second-order model provided a higher R^2 of 0.87999 and a smaller SSE of 8.87507 than the pseudo-first-order model ($R^2 = 0.50501$ and $\text{SSE} = 36.60525$), with a calculated Q_e value of 74.80 mg.g^{-1} , closely matching the experimental data. Similarly, for Ni^{2+} (Figure 8b), the pseudo-second-order model also gave a higher R^2 value (0.90865) and lower SSE (3.52116) than the pseudo-first-order model ($R^2 = 0.66662$ and $\text{SSE} = 12.84978$), and its predicted Q_e (26.58 mg.g^{-1}) aligned well with the experimental Q_e (25.60 mg.g^{-1}). The results measured indicate that the adsorption of Cu^{2+} and Ni^{2+} is better described by the pseudo-second-order model. These results are highly consistent with some literature published about heavy metal adsorption kinetics on HAp-based material’s surface [8, 12, 20, 46]. The superior fit of the pseudo-second-order model for both ions suggests that the adsorption process is likely controlled by chemical interaction involving electron sharing, covalent bonding, or ion exchange between the metal ions and functional groups on the HAp surface rather than by simple diffusion or mass transfer

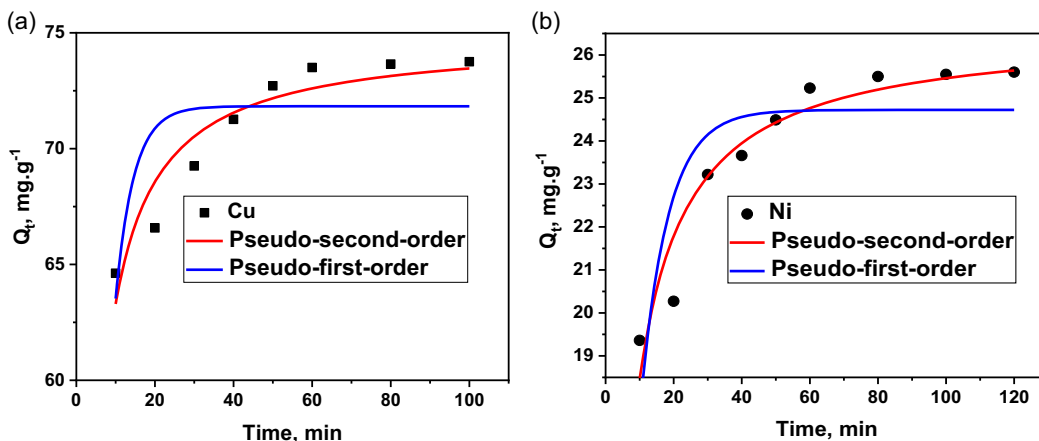


FIGURE 8 | Adsorption data modeled using pseudo-first-order law and pseudo-second-order law of Cu^{2+} (a) and Ni^{2+} (b).

TABLE 4 | The values of k and Q_e follow pseudo-first-order kinetic and pseudo-second-order kinetic.

	Pseudo-first-order kinetic					Pseudo-second-order kinetic					$Q_{e \text{ exp}}$
	Q_e , mg.g^{-1}	k_1 , min^{-1}	R^2	SSE	Chi-square	Q_e , mg.g^{-1}	k_2 , $\text{g.mg}^{-1}.\text{min}^{-1}$	R^2	SSE	Chi-square	
Cu^{2+}	71.83	0.215	0.5051	36.6052	6.1008	74.79	0.007	0.8799	8.8750	1.4791	73.75
Ni^{2+}	24.72	0.125	0.6666	12.8497	1.8356	26.58	0.008	0.9086	3.5211	0.5030	25.60

[11]. In other words, chemical adsorption plays an important role for Cu^{2+} and Ni^{2+} adsorption on HAp.

3.2.4 | Characterization of HAp before and after Adsorption Process

FT-IR, XRD, and SEM-EDS were employed to characterize HAp powder both before and after the adsorption procedure. The FT-IR spectra indicated that the Cu^{2+} adsorption procedure as well as the Ni^{2+} adsorption procedure did not modify the functional groups present in the HAp (Figure 9a). The absorption bands at 1089, 1032, 962, 603, and 567 cm^{-1} are representative of the PO_4^{3-} group in HAp [47, 48]. The absorption band located at 873 cm^{-1} is the characteristic of the P-OH bond. The absorption bands at 3452 and 1637 cm^{-1} presented for free water. The XRD

patterns for HAp, Cu-HAp, and Ni-HAp samples were similar (Figure 9b). The diffraction angles of $2\theta = 31.74^\circ$ and 25.83° symbolized for HAp materials [49]. SEM images of Cu-HAp and Ni-HAp, presented in Figure 10a,b, showed the rod-like form of HAp following adsorption. This result indicates that neither the size nor shape of the HAp particle was significantly altered during the adsorption process. The EDS spectra revealed the presence of copper and nickel in HAp during the adsorption process (Figure 10c,d).

The mechanism of the adsorption process was as follows:

M^{2+} (M: Cu, Ni) ions exchange reaction with the Ca^{2+} ions of HAp:

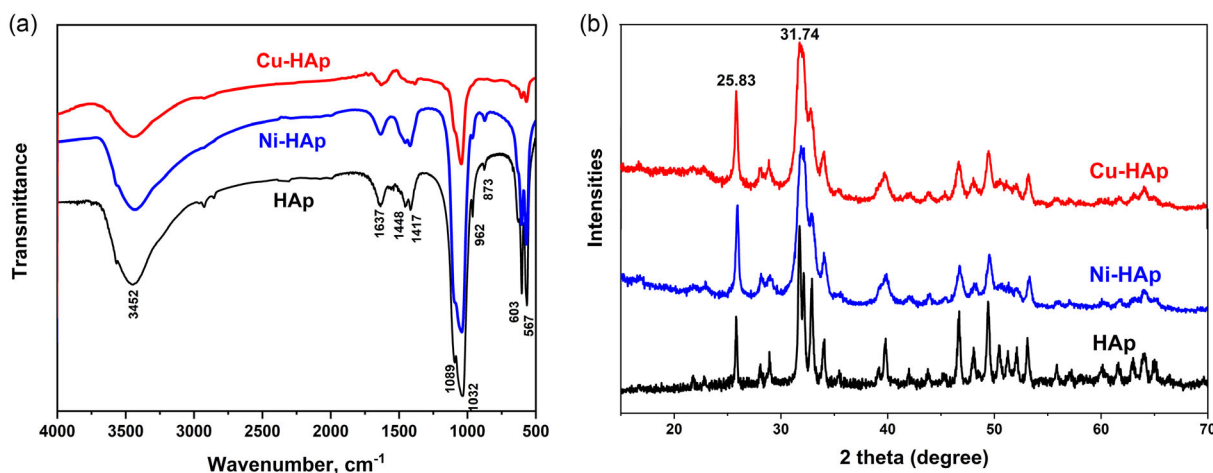
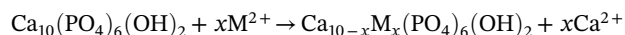


FIGURE 9 | FT-IR spectra (a) and XRD patterns (b) of HAp before and after Cu^{2+} , Ni^{2+} adsorption process.

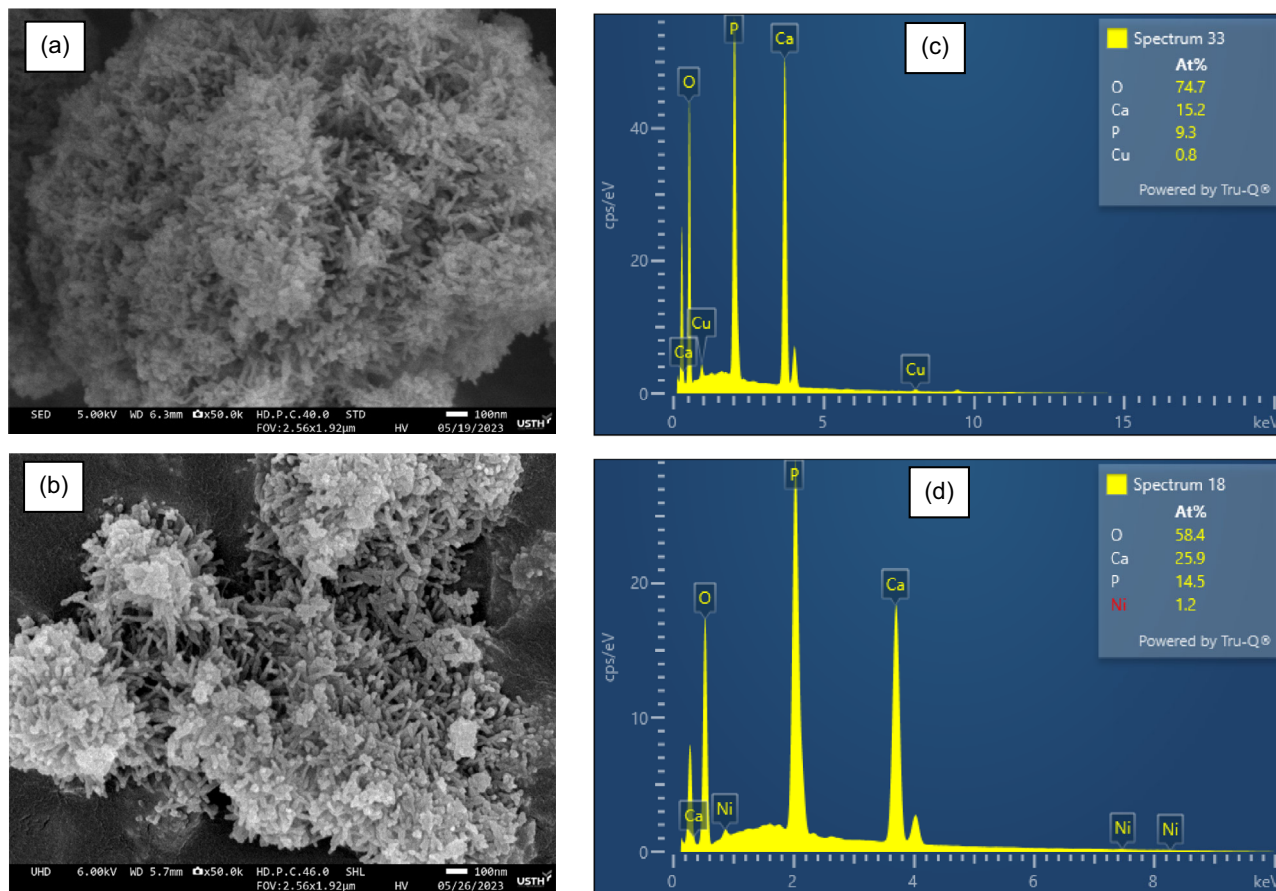
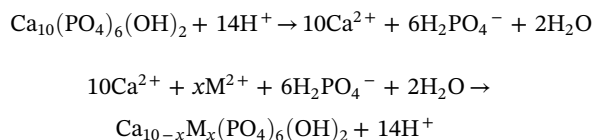


FIGURE 10 | SEM images of Cu-HAP (a), Ni-HAP (b) and EDS spectrums of Cu-HAP (c), and Ni-HAP (d).

Furthermore, at low pH, part of HAP dissolves in aqueous solution containing M^{2+} ions, allowing the following reactions to occur:



3.3 | Desorption of Cu^{2+} , Ni^{2+} , and Recovery of Cu, Ni Metals

3.3.1 | Cyclic Voltammograms of $\text{Cu}(\text{NO}_3)_2$, Cu-HAP, and $\text{Ni}(\text{NO}_3)_2$, Ni-HAP Reline Electrolyte

The CV curves of M^{2+} /reline and M-HAP/reline are shown in Figure 11. Figure 11a illustrates the reduction peak of Cu^{2+} at -0.6 V and the oxidation peak of Cu^0 at -0.4 V. Figure 11c displays the reduction peak of Ni^{2+} at -0.58 V and the oxidation peak of Ni^0 at -0.43 V. It can be seen that the CVs of Ni^{2+} /reline and Ni-HAP/reline are similar. However, there is a slight shift in the copper oxidation-reduction peaks between Cu^{2+} /reline and Cu-HAP/reline. The electrochemical processes occurring during CV scanning can be described in two stages as follows:

Stage 1: M^{2+} ions in M-HAP react with Cl^- ions of reline to form a MCl_n^{2-n} complex and then be reduced to M metal on the Au electrode's surface: $\text{MCl}_n^{2-n} + 2e^- \rightarrow \text{M} + n\text{Cl}^-$

Stage 2: Stripping M metal to M^{2+} : $\text{M} - 2e^- \rightarrow M^{2+}$

The CV results of Cu-HAP and Ni-HAP in reline liquid indicated that M^{2+} can be desorbed out of M-HAP and subsequently reduced to M metal on the cathode surface in reline solvent. This process allows for the recovery and reuse of HAP material. The electrolysis can be carried out at a potential ≤ -0.4 V to obtain Cu metal and at a potential ≤ -0.6 V for Ni metal. This is supported by SEM images and EDS results of the Au electrode surface before and after the electrolysis of M-HAP powder in the reline solvent (Figures 12 and 13).

Before electrolysis, the Au electrode surface is smooth, primarily composed of Au, with small amounts of Al and Si present (Figure 12). After electrolysis, the surface of the Au electrode undergoes a noticeable change (as shown in the SEM images in Figure 13a,c) due to the precipitation of Cu and Ni. The presence of Cu and Ni on the Au electrode surface is demonstrated by the appearance of their peaks in the EDS spectra (Figure 13b,d, respectively). The peaks corresponding to the M metals are significantly lower than the peak for Au, reflecting the minimal amount of M metal that has precipitated on the Au electrode compared to the overall quantity of the electrode.

The mechanism of the desorption process was as follows:

Step 1: Complexation reaction of M^{2+} in M-HAP with Cl^- ion in the reline:

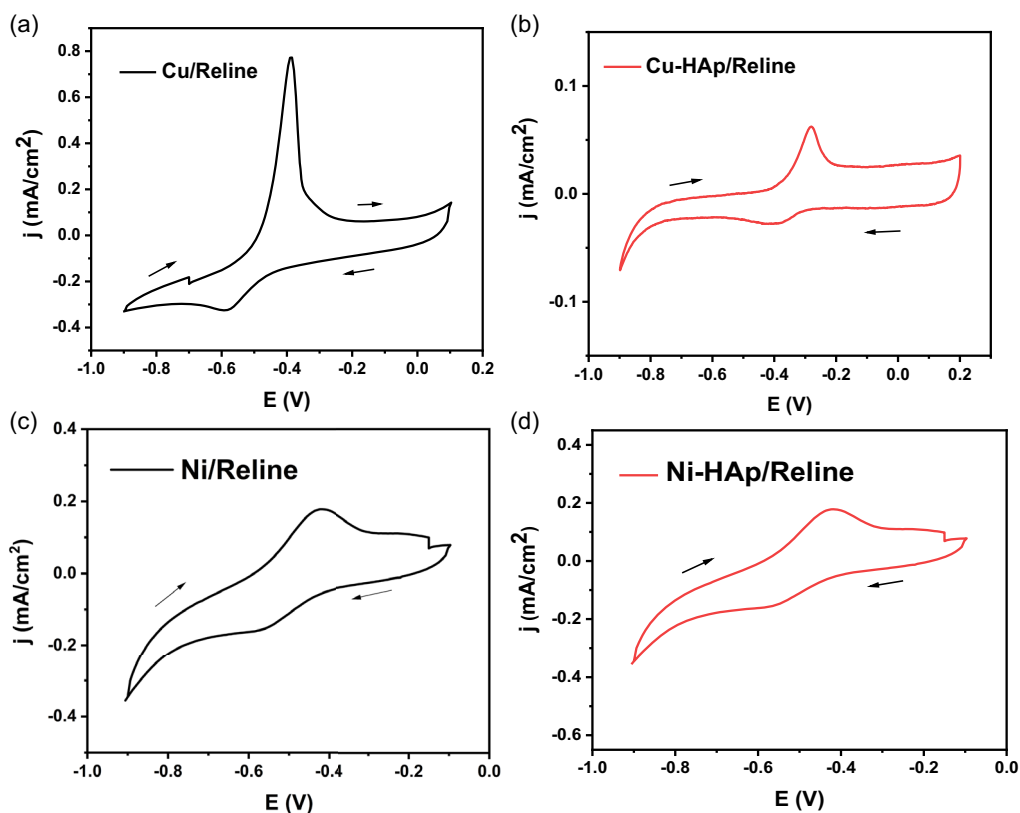


FIGURE 11 | CV curves of Cu^{2+} /reline (a), Cu-HAp/reline (b), Ni^{2+} /reline (c), and Ni-HAp/reline (d).

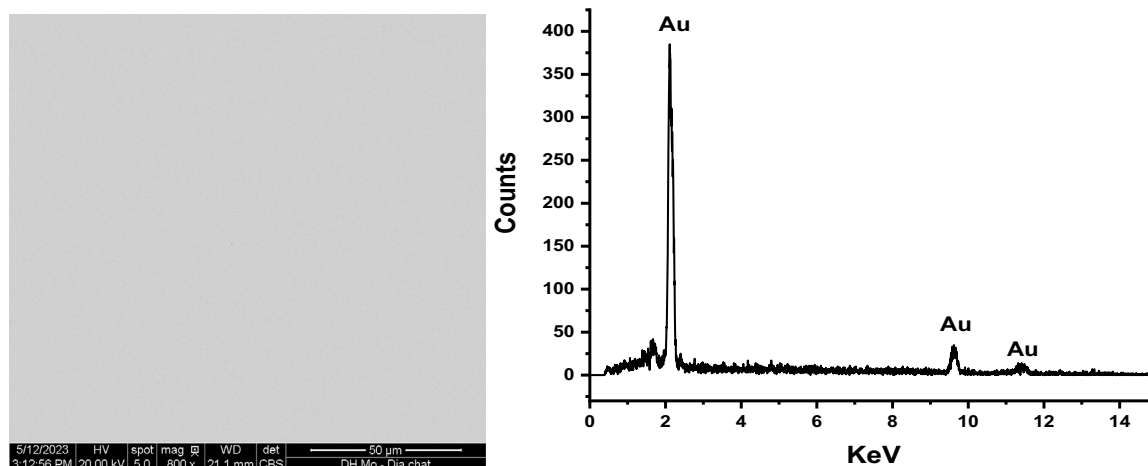
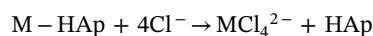
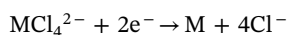


FIGURE 12 | SEM-EDS result of the surface of the Au electrode before electrolysis.



Step 2: The reduction of M^{2+} in the MCl_4^{2-} complex to M metal, which precipitates on the surface of the Au electrode:



3.3.2 | Effect of Electrolytic Parameters on Recovery Efficiency of Copper and Nickel

3.3.2.1 | Influence of Applied Current Density. Experiments used for investigating the influence of current density on the deposition efficiency of metal M on the cathode were carried out under the following conditions: electrolysis time of 5 h,

temperature of 60°C, M-HAp mass of 0.3 g, and current density varying from 1 to 7.5 mA.cm⁻². The results are shown in Table 5. The results show that, as the current density increases, the reduction rate of M^{2+} (in MCl_n^{2-n}) increases, leading to an increase in the amount of M precipitated on the cathode; thus, the electrolysis efficiency increases correspondingly. The highest values of Cu and Ni recovery efficiency were achieved at a current density of 7.5 mA.cm⁻², which were 70.13% and 73.69%, respectively.

3.3.2.2 | Influence of M-HAp Mass. The effect of M-HAp mass on the recovery efficiencies of M was investigated under the following experimental conditions: an electrolysis time of

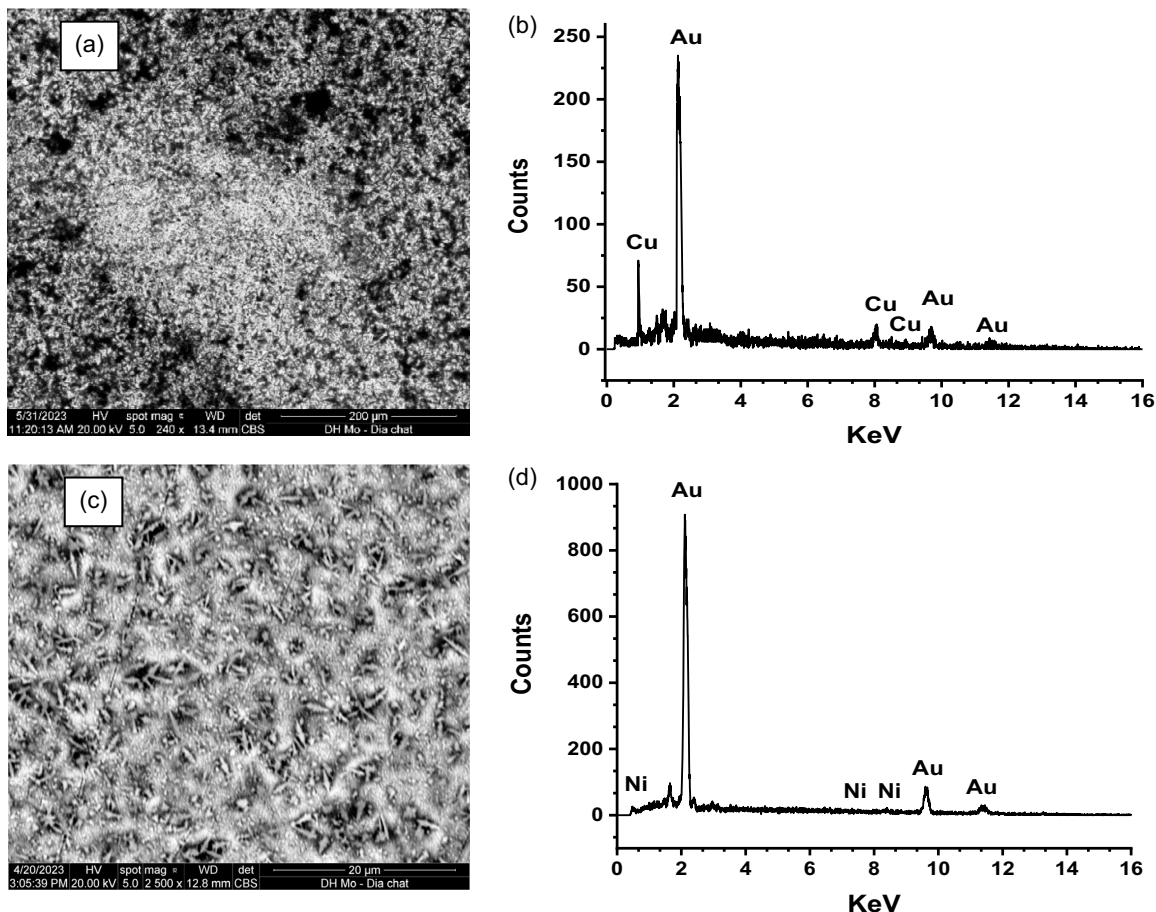


FIGURE 13 | SEM-EDS results of the surface of the Au electrode after electrolysis of Cu-HAp (a,b) and Ni-HAp (c,d).

TABLE 5 | The recovery efficiency of M (H %) from 0.3 g M-HAp at different applied current densities for 5 h of electrolysis.

j , mA/cm ²		1	2	3	5	7.5
H %	Cu	46.68 ± 0.57	55.96 ± 0.75	62.54 ± 0.78	66.51 ± 0.83	70.13 ± 1.01
	Ni	51.37 ± 0.67	62.94 ± 0.80	69.48 ± 0.82	72.40 ± 0.93	73.69 ± 1.03

5 h, a temperature of 60°C, a current density of 7.5 mA.cm⁻², and varying M-HAp mass from 0.1 to 0.3 g. The results presented in Table 6 indicate that as the mass of M-HAp increases, the recovery efficiency of M decreases. This phenomenon can be explained as follows: as the mass of M-HAp powder increases, the amount of M²⁺ supplied also increases, resulting in a greater amount of M precipitated. However, the increase in the amount of M precipitate is less than the increase in M available in M-HAp, which leads to a decrease in recovery efficiency. The recovery efficiency for Cu and Ni reached their highest level of 86.60% and 88.53%, respectively, when the mass of M-HAp used was 0.1 g.

3.3.2.3 | Influence of Electrolysis Time. To investigate the effect of electrolysis time on the recovery efficiency of M metal, experiments were conducted at a current density of 7.5 mA.cm⁻² and a temperature of 60°C, using 0.1 g of M-HAp. The results, presented in Table 7, indicated that the recovery efficiency M increases with the longer electrolysis time. However, to achieve a high recovery efficiency of M in a short duration, an electrolysis

TABLE 6 | The recovery efficiency of M with different M-HAp masses at 7.5 mA.cm⁻² applied current density for 5 h of electrolysis.

m , g		0.1	0.2	0.3
H %	Cu	86.60 ± 0.89	78.53 ± 1.22	70.13 ± 1.26
	Ni	88.53 ± 1.12	79.60 ± 0.95	73.69 ± 0.86

time of 10 h is suitable. Under these conditions, the recovery efficiencies of Cu and Ni reached 94.63% and 94.80%, respectively.

3.4 | Regeneration of Material

After electrolysis, HAp powder is filtered, thoroughly washed with double-distilled water and dried for use in the next step. The regenerative ability of the HAp material is evaluated by examining its physicochemical properties and ability to reabsorb heavy metal ions.

TABLE 7 | The recovery efficiency of M from 0.1 g M-HAp at different electrolysis times.

t, h		2	3	4	5	7	10	12
H %	Cu	72.68 ± 0.23	77.79 ± 0.73	81.41 ± 0.65	86.60 ± 0.98	92.54 ± 0.81	94.63 ± 1.05	95.14 ± 0.92
	Ni	78.32 ± 1.20	82.51 ± 0.93	85.85 ± 0.98	88.53 ± 1.02	92.64 ± 1.21	94.80 ± 0.97	95.30 ± 1.22

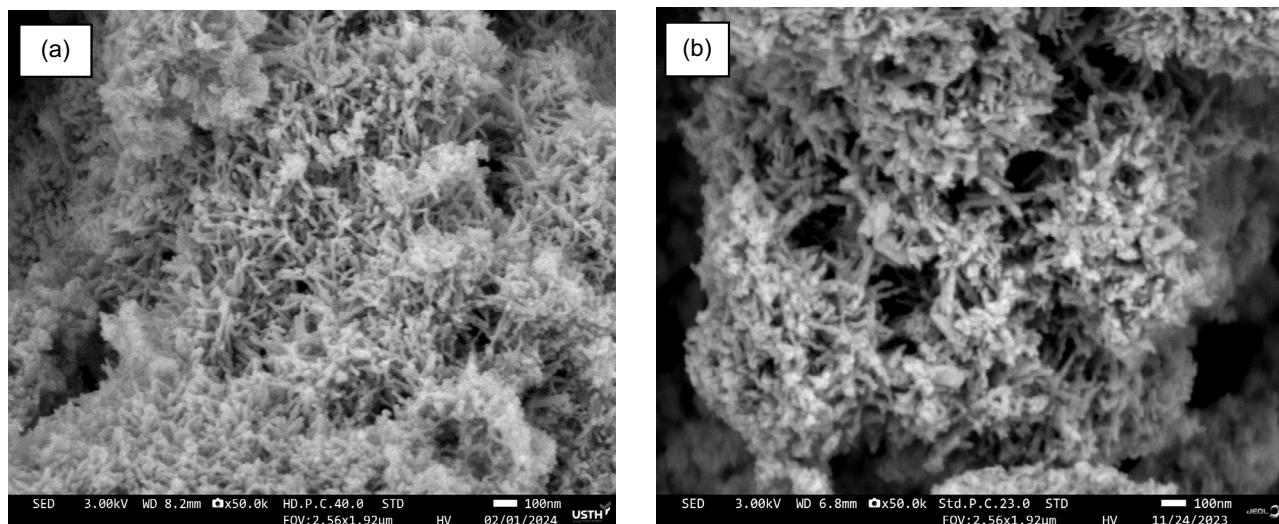


FIGURE 14 | SEM images of original HAp (a) and regenerated HAp (b).

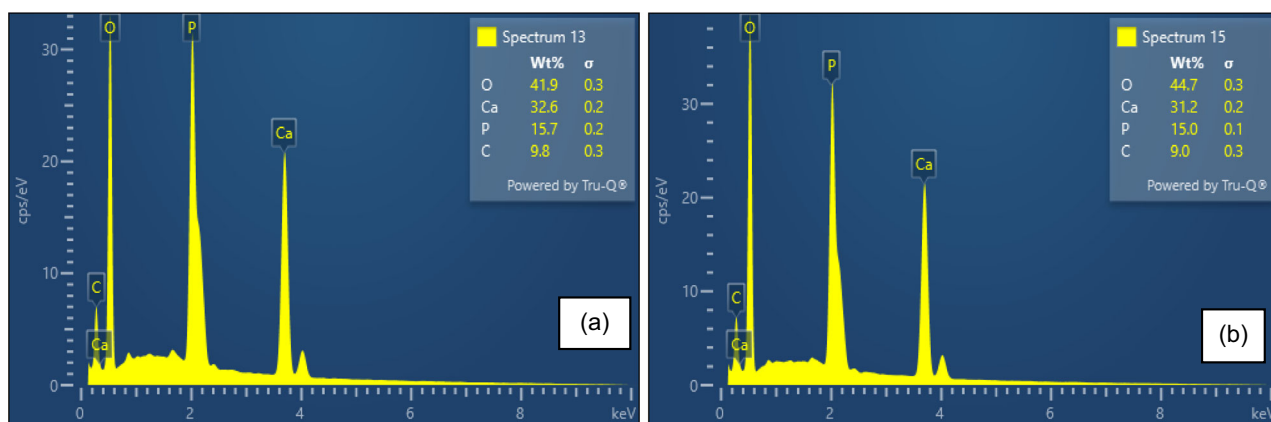


FIGURE 15 | EDS spectra of original HAp (a) and regenerated HAp (b).

3.4.1 | The Physicochemical Properties of Regenerated HAp

The HAp material after desorption exhibits a fibrous structure similar to that of the original HAp material, as shown in the SEM image in Figure 14. The EDS spectrum (Figure 15) identifies the primary components of the regenerated HAp material, which consist solely of Ca, O, and P elements as the HAp material before adsorption. FT-IR spectra (Figure 16) reveal that the HAp material remains unchanged following the adsorption-desorption process.

3.4.2 | Adsorption Capacity and Efficiency of Regenerated HAp

The adsorption procedure of the recycled HAp material for Cu^{2+} and Ni^{2+} was carried out under the optimal conditions

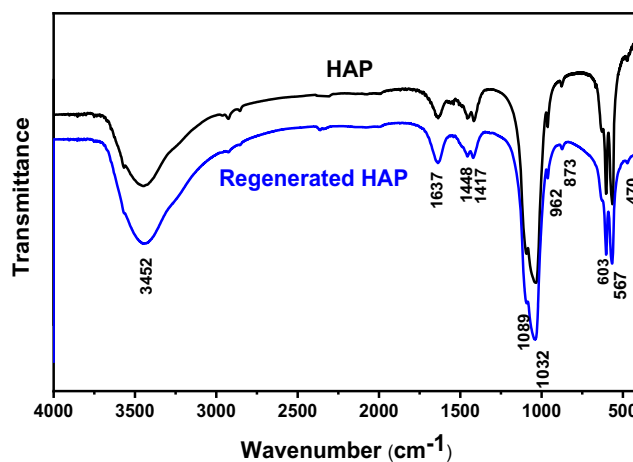


FIGURE 16 | FT-IR spectra of original HAp and regenerated HAp.

TABLE 8 | The adsorption capacity and adsorption efficiency of regenerated HAp for heavy metal ions.

M ²⁺	Contact time, min	pH	HAp mass, g	Initial M ²⁺ concentration C ₀ , mg.L ⁻¹	M ²⁺ concentration after adsorption C _e , mg.L ⁻¹	Adsorption capacity, mg.g ⁻¹	Adsorption efficiency, %
Cu ²⁺	60	5.35	0.05	50	10.754	39.25	78.49
Ni ²⁺	60	5.57	0.10	30	7.621	11.18	74.60

determined during the investigation of the adsorption process using the original HAp material. The experimental conditions and adsorption results are shown in Table 8.

The results presented in Table 8 show that the adsorption efficiency and adsorption capacity of the recycled HAp material for Cu²⁺ reached 78.49% and 39.25 mg.g⁻¹, while for Ni²⁺, the values were 75.80% and 11.37 mg.g⁻¹, respectively. Although these values are lower than those of the original HAp material (with 99.06% and 49.5 mg.g⁻¹ for Cu²⁺ and 80.99% and 12.15 mg.g⁻¹ for Ni²⁺), they still demonstrate effective adsorption by the regenerated HAp material for both Cu²⁺ and Ni²⁺. These results indicate that the HAp material almost retains its original properties after the adsorption-desorption process and can potentially be reused in subsequent adsorption applications.

4 | Conclusion

Synthesized HAp serves not only as an effective adsorbent for removing Cu²⁺ and Ni²⁺ ions from aqueous solutions but also facilitates the subsequent desorption and recovery of copper and nickel metals from the loaded HAp. Optimal conditions for Cu²⁺ removal were found at pH 5.35, 50 mg.L⁻¹ initial concentration, 0.05 g HAp in 50 mL solution, and a contact time of 60 min, achieving a maximum adsorption capacity of 49.53 mg.g⁻¹ and an efficiency of 99.06%. For Ni²⁺, optimal performance was observed at pH 5.57, 30 mg.L⁻¹ initial concentration, 0.1 g/50 mL dosage, and 60 min contact time, yielding a capacity of 12.15 mg.g⁻¹ and 80.99% efficiency. Using an electrodeposition approach, copper and nickel were simultaneously desorbed from the adsorbed HAp material in a reline DES. Notably, the recovery of both metals was achieved simultaneously as well. Under optimal conditions, the results indicated that it is possible to recover 94.83% of copper and 94.80% of nickel. Experimental data demonstrated that the adsorption process for Cu²⁺ and Ni²⁺ ions using HAp powder adhered to the pseudo-second-order kinetic model and followed the Redlich–Peterson isotherm model. The HAp adsorbent can be reused after the desorption process, making it a potentially environmentally friendly and cost-effective solution for the removal of heavy metals from aqueous solutions.

Author Contributions

Thi Phuong Thao Le: investigation (equal), writing – original draft (equal). **Thi Duyen Le** investigation (equal), methodology (lead), supervision (lead), writing original draft (equal). **Thu Phuong Nguyen** formal analysis (lead), visualization (lead). **Tien Dung Cong**

investigation (equal), writing – original draft (equal), writing – review & editing (equal).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. J. Briffa, E. Sinagra, and R. Blundell, “Heavy Metal Pollution in the Environment and Their Toxicological Effects on Humans,” *Heliyon* 6 (2020): e04691.
2. A. Corami, F. D’Acapito, S. Mignardi, and V. Ferrini, “Removal of Cu from Aqueous Solutions by Synthetic Hydroxyapatite: EXAFS Investigation,” *Materials Science and Engineering: B* 149 (2008): 209–213.
3. N. P. Raval, P. U. Shah, and N. K. Shah, “Adsorptive Removal of Nickel(II) Ions from Aqueous Environment: A Review,” *Journal of Environmental Management* 179 (2016): 1–20.
4. O. Dagdag, T. W. Quadri, R. Haldhar, et al., “In Heavy Metals in the Environment: Management Strategies for Global Pollution,” *American Chemical Society* 1456 (2023): 3–24.
5. F. Fernane, M. O. Mecherri, P. Sharrock, M. Hadioui, H. Lounici, and M. Fedoroff, “Sorption of Cadmium and Copper Ions on Natural and Synthetic Hydroxylapatite Particles,” *Materials Characterization* 59 (2008): 554–559.
6. P. T. Nguyen, X. T. Nguyen, T. V. Nguyen, et al., “Treatment of Cd²⁺ and Cu²⁺ Ions Using Modified Apatite Ore,” *Journal of Chemistry* 1 (2020): 6527197.
7. D. T. Le, T. P. T. Le, H. T. Do, et al., “Fabrication of Porous Hydroxyapatite Granules as an Effective Adsorbent for the Removal of Aqueous Pb(II) Ions,” *Journal of Chemistry* 1 (2019): 8620181.
8. T. Nguyen, T. Dinh, T. N. Pham, N. T. Phuong, and C. Buess-Herman, “Adsorption Behavior of Cd²⁺ Ions Using Hydroxyapatite (HAp) Powder,” *Green Processing and Synthesis* 7 (2018): 409–416.
9. I. Mobasherpour, E. Salahi, and M. Pazouki, “Removal of Nickel (II) from Aqueous Solutions by Using Nano-Crystalline Calcium Hydroxyapatite,” *Journal of Saudi Chemical Society* 15 (2011): 105–112.
10. A. Shishov, A. Bulatov, M. Locatelli, S. Carradori, and V. Andruch, “Application of Deep Eutectic Solvents in Analytical Chemistry. A Review,” *Microchemical journal* 135 (2017): 33–38.
11. H. Wu, L. Ling, T. Wang, et al., “Temperature-Directed Morphological Tuning of Hydroxyapatite Nanowires and Dual-Stage Mechanism for Pb(II) Adsorption,” *Environmental Research* 287 (2025): 123145.
12. L. Jian, W. Botao, Z. Tianyou, L. Tiancheng, and J. Lijuan, “Waste-to-Resource Synthesis of Hydroxyapatite from Sludge and Eggshell for High-Capacity Copper Remediation in Wastewater,” *Journal of Water Process Engineering* 77 (2025): 108310.

13. S. Kato, S. Kagawa, K. Saito, and M. Ogasawara, "Incorporation and Deposition Behaviors of Cu and Ni Ions into Hydroxyapatite Channels by Heat Treatment," *Journal of Physics and Chemistry of Solids* 177 (2023): 111287.
14. E. A. Ofudje, A. E. Adedapo, O. B. Oladeji, E. F. Sodiya, F. H. Ibadin, and D. Zhang, "Nano-Rod Hydroxyapatite for the Uptake of Nickel Ions: Effect of Sintering Behaviour on Adsorption Parameters," *Journal of Environmental Chemical Engineering* 9 (2021): 105931.
15. D. N. Thanh, P. Novák, J. Vejpravova, H. N. Vu, J. Lederer, and T. Munshi, "Removal of Copper and Nickel from Water Using Nanocomposite of Magnetic Hydroxyapatite Nanorods," *Journal of Magnetism and Magnetic Materials* 456 (2018): 451–460.
16. Y. Si, J. Huo, Y. Hengbo, and A. Wang, "Adsorption Kinetics, Isotherms, and Thermodynamics of Cr(III), Pb(II), and Cu(II) on Porous Hydroxyapatite Nanoparticles," *Journal of Nanoscience and Nanotechnology* 18 (2018): 3484–3491.
17. P. Chand and Y. B. Pakade, "Synthesis and Characterization of Hydroxyapatite Nanoparticles Impregnated on Apple Pomace to Enhanced Adsorption of Pb(II), Cd(II), and Ni(II) Ions from Aqueous Solution," *Environmental Science and Pollution Research* 22 (2015): 10919–10929.
18. Q. Rayée, T. Doneux, and C. Buess-Herman, "Underpotential Deposition of Silver on Gold from Deep Eutectic Electrolytes," *Electrochimica Acta* 237 (2017): 127–132.
19. L. T. Duyen, C. T. Dung, D. T. M. Thanh, and N. T. Phuong, "Adsorption–desorption of Zn²⁺ Ions Using Hydroxyapatite and Recovery of Zinc by Electrochemical Precipitation Method into Deep Eutectic Solvent," *Polyhedron* 261 (2024): 117126.
20. N. Gupta, A. K. Kushwaha, and M. C. Chattopadhyaya, "Adsorption Studies of Cationic Dyes onto Ashoka (Saraca Asoca) Leaf Powder," *Journal of the Taiwan Institute of Chemical Engineers* 43 (2012): 125–613.
21. C. Rabbat, A. Pinna, Y. Andres, A. Villot, and S. Awad, "Adsorption of Ibuprofen from Aqueous Solution onto a Raw and Steam-Activated Biochar Derived from Recycled Textiles Insulation Panels at End-of-Life: Kinetic, Isotherm and Fixed-Bed Experiments," *Journal of Water Process Engineering* 53 (2023): 103830.
22. H. N. Tran, E. C. Lima, R.-S. Juang, J.-C. Bollinger, and H.-P. Chao, "Thermodynamic Parameters of Liquid-phase Adsorption Process Calculated from Different Equilibrium Constants Related to Adsorption Isotherms: A Comparison Study," *Journal of Environmental Chemical Engineering* 9 (2021): 106674.
23. W. Dou, Z. Deng, J. Fan, et al., "Enhanced Adsorption Performance of La(III) and Y(III) on Kaolinite by Oxalic Acid Intercalation Expansion Method," *Applied Clay Science* 229 (2022): 106693.
24. D. Prahas, Y. Kartika, N. Indraswati, and S. Ismadji, "Activated Carbon from Jackfruit Peel Waste by H₃PO₄ Chemical Activation: Pore Structure and Surface Chemistry Characterization," *Chemical Engineering Journal* 140 (2008): 32–42.
25. M. Kosmulski, "The pH Dependent Surface Charging and Points of Zero Charge. X. Update," *Advances in Colloid and Interface Science* 319 (2023): 102973.
26. V. Dhand, K. Y. Rhee, and S.-J. Park, "The Facile and Low Temperature Synthesis of Nanophase Hydroxyapatite Crystals Using Wet Chemistry," *Materials Science and Engineering: C* 36 (2014): 152–159.
27. S. Storck, H. Bretinger, and W. F. Maier, "Characterization of Micro- and Mesoporous Solids by Physisorption Methods and Pore-Size Analysis," *Applied Catalysis A* 174 (1998): 137–146.
28. T. Horikawa, D. D. Do, and D. Nicholson, "Capillary Condensation of Adsorbates in Porous Materials," *Advances in Colloid and Interface Science* 169 (2011): 40–58.
29. I. Smičiklas, A. Onjia, and S. Raičević, "Experimental Design Approach in the Synthesis of Hydroxyapatite by Neutralization Method," *Separation and Purification Technology* 44 (2005): 97–102.
30. B. Bouzar, N.-E. Abriak, and M. Benzerzour, "Sustainable Reuse of Mineral Waste: Synthesis and Comprehensive Characterization of Hydroxyapatite (HAP)," *Green Technologies and Sustainability* 4 (2026): 100315.
31. K. G. Bhattacharyya and S. S. Gupta, "Influence of Acid Activation on Adsorption of Ni(II) and Cu(II) on Kaolinite and Montmorillonite: Kinetic and Thermodynamic Study," *Chemical Engineering Journal* 136 (2008): 1–13.
32. O. Ayodele, S. J. Olusegun, O. O. Oluwasina, et al., "Experimental and Theoretical Studies of the Adsorption of Cu and Ni Ions from Wastewater by Hydroxyapatite Derived from Eggshells," *Environmental Nanotechnology, Monitoring and Management* 15 (2021): 100439.
33. S. E. Ebrahim, A. H. Sulaymon, and H. S. Alhares, "Competitive Removal of Cu²⁺, Cd²⁺, Zn²⁺, and Ni²⁺ Ions onto Iron Oxide Nanoparticles from Wastewater," *Desalination and Water Treatment* 57 (2016): 20915–20929.
34. F. Fernane, S. Boudia, and F. Aiouache, "Removal Cu(II) and Ni(II) by Natural and Synthetic Hydroxyapatites: A Comparative Study," *Desalination and Water Treatment* 52 (2014): 2856–2862.
35. A. A. Taha, M. A. Shreadah, A. M. Ahmed, and H. F. Heiba, "Multi-Component Adsorption of Pb(II), Cd(II), and Ni(II) onto Egyptian Na-Activated Bentonite; Equilibrium, Kinetics, Thermodynamics, and Application for Seawater Desalination," *Journal of Environmental Chemical Engineering* 4 (2016): 1166–1180.
36. I. Mobasherpour, E. Salahi, and M. Pazouki, "Comparative of the Removal of Pb²⁺, Cd²⁺ and Ni²⁺ by Nano Crystallite Hydroxyapatite from Aqueous Solutions: Adsorption Isotherm Study," *Arabian Journal of Chemistry* 5 (2012): 439–446.
37. S. Li, X. Zhang, Y. Wang, J. Shen, Y. Wei, and C. Wang, "Diethylenetriaminepentaacetic Acid-Modified Covalent Organic Polymer for Removal of Four Heavy Metal Ions from Wastewater," *Journal of Molecular Structure* 1342 (2025): 142722.
38. T. B. Musso, M. E. Parolo, and G. Pettinari, "PH, Ionic Strength, and Ion Competition Effect on Cu(II) and Ni(II) Sorption by a Na-Bentonite Used as Liner Material," *Polish Journal of Environmental Studies* 28 (2019): 2299–2309.
39. W. Chen, F. Yun, S. Zheng, C. Shi, and J. Han, "In Situ Growth ZIF-8 on Porous Chitosan/Hydroxyapatite Composite Fibers for Ultra-Efficiently Eliminating Lead Ions in Wastewater," *Materials Today Communications* 37 (2023): 107255.
40. X. S. Wang, "Equilibrium and Kinetic Analysis for Cu²⁺ and Ni²⁺ Adsorption Onto Na-Mordenite," *The Open Environmental Pollution & Toxicology Journal* 1 (2009): 107–111.
41. A. I. Ivanets, V. Srivastava, N. V. Kitikova, I. L. Shashkova, and M. Sillanpää, "Non-Apatite Ca-Mg Phosphate Sorbent for Removal of Toxic Metal Ions from Aqueous Solutions," *Journal of Environmental Chemical Engineering* 5 (2017): 2010–2017.
42. S. Wongcharee, B. Kandasamy, P. Govindasamy, et al., "Pig Bone-Derived Biochar from Food Industry Waste for Heavy Metal Remediation: Sustainable Consumption and Production," *Results in Engineering* 28 (2025): 108003.
43. L. Kong, X. Liu, G. Lv, et al., "Copper Adsorption Using Hydroxyapatite Derived from Bovine Bone," *Advances in Civil Engineering* 1 (2022): 1026129.
44. S. Hokkanen, E. Repo, L. J. Westholm, S. Lou, T. Sainio, and M. Sillanpää, "Adsorption of Ni²⁺, Cd²⁺, PO₄³⁻ and NO₃⁻ from Aqueous Solutions by Nanostructured Microfibrillated Cellulose

Modified with Carbonated Hydroxyapatite,” *Chemical Engineering Journal* 252 (2014): 64–74.

45. V. T. Le, V. D. Doan, D. D. Nguyen, et al., “A Novel Cross-Linked Magnetic Hydroxyapatite/Chitosan Composite: Preparation, Characterization, and Application for Ni(II) Ion Removal from Aqueous Solution,” *Water, Air, and Soil Pollution* 229 (2018): 101.

46. N. Butrin, N. Rueangchai, P. Noisong, and S. Sansuk, “Synthesis of Hydroxyapatite/Activated Carbon Composite with Bioactivity Property and Copper Ion Removal Efficiency,” *Materials Today Communications* 40 (2024): 109615.

47. F. Zeng, J. Wang, Y. Wu, et al., “Preparation of Pore Expanded Mesoporous Hydroxyapatite via Auxiliary Solubilizing Template Method,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 441 (2014): 737–743.

48. Y.-W. Lin, S.-Y. Peng, and K.-L. Lin, “Hydrothermal Synthesis of Environmentally-Friendly Hydroxyapatite Using Recycled Waste for Efficient Cd²⁺ Removal from Aqueous Solutions,” *Materials Chemistry and Physics* 334 (2025): 130407.

49. W. Feng, L. Mu-sen, L. Yu-peng, and Q. Yong-xin, “A Simple Sol–gel Technique for Preparing Hydroxyapatite Nanopowders,” *Materials Letters* 59 (2005): 916–919.