

Toxic heavy metals removal from river water using a porous phospho-calcic hydroxyapatite

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Abstract

The process of adsorption of copper ions on synthesized hydroxyapatites (p-HAp) by the wet route has been studied experimentally to make a comparison between the adsorption capacity of our porous phospho-calcic material and the phosphate hydroxyapatite. The specific surface of p-HAp was studied by BET, as well as the characterization of p-HAp by FTIR and XRD showed that the synthetic hydroxyapatite has an apatite phase of crystalline structure which is very interesting for the adsorption of metals. Heavy, the results of the adsorption study obtained that the mechanism of adsorption of Cu²⁺ ions was best described by the pseudo-second-order kinetic model and obeyed the linear models of Langmuir isotherms, continued that the adsorption is done in the surface area of p-HAp. Langmuir model parameters reveal that, the adsorption mechanism of Cu²⁺ is fit with this model. The pseudo-first-order and pseudo-second-order models were also used to determine the adsorption kinetic. The experimental data were well fitted by the pseudo-second-order model. Thermodynamic parameters showed that, the adsorption of Cu²⁺ ion onto the composite surface is a spontaneous and favored at neutral pH and at a temperature little higher than room temperature.

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1. Introduction

The strengthening of water quality standards leads to the development of new methods of treatment [1]. Copper can naturally be in a much higher concentration than the norm which can have many toxic health effects, which are based on its concentration in the blood. Indeed, this metal is responsible for lead poisoning in chronic exposure. It can cause great fatigue, behavioral disturbances, memory, sleep, immune and reproductive systems, but its main target organs are the nervous system, kidneys, and blood [2]. The toxicity of copper metal ions develops by bioaccumulation. The industry is responsible for almost all heavy metal discharges into water, and its environmental impact depends on chemical reactions in the aquatic environment (reactions linked to acidity, alkalinity, temperature, oxygenation ...). For this, several researchers have worked on the removal of metal copper using several methods such as precipitation [3], filtration [4], ion exchange [5], and adsorption [6]. Adsorption is an effective treatment through the use of porous and functionalized systems. Apatites are, in particular, complex systems and have been shown to remove metal ions, such as Cu^{2+} , from aqueous solutions [7]. Thus, in this part, we recall the physicochemical behavior of the metal ions (solute) in the aqueous solution and its environmental consequences as well as the physical, structural, and textural characteristics of the adsorbents to interpret the immobilization of pollutants at the surface of an adsorbent [8]. Therefore, apatites have the advantage of being a good adsorbent of harmful substances whether organic or inorganic. The use of hydroxyapatites as decontamination materials depends on their ability to bind metal ions, and how these toxic elements are trapped. Thus, it is essential to precisely define the mechanism for fixing metal ions by the grafted apatites [9]. In this context, Šljivić et al studied the adsorption of Cu^{2+} ions using zeolite, clay, and diatomaceous earth from Serbia [10]. Kouznetsova et al have developed a new mesoporous aluminosilicate/zeolite composite by the model coprecipitation method and used it for Cu^{2+} adsorption [11], and Xu et al prepared Amino-modified attapulgite (M-ATP) to remove Cu^{2+} from aqueous solution [12]. The objective of our work is to make a comparison of the adsorption capacity of copper metal ions (Cu^{2+}) between commercial hydroxyapatites (CAp) and synthetic hydroxyapatites (p-HAp). A series of adsorption experiments were performed to study the selective adsorption of Cu^{2+} to CAp and p-HAp under different conditions. Simultaneously, the results of experimental and theoretical calculations provide a deep understanding of the atomic and energetic level for the selective adsorption of Cu^{2+} on synthetic and commercial hydroxyapatites.

2. Experimental

2.1. Materials

Hydroxyapatite (p-HAp) synthesized according to our work already published [13], using a modified wet chemical method. The synthesis steps are presented in figure 1. The commercial hydroxyapatite (CAp) used as a crystalline model for comparison was taken from ACROS. CAp was dried for two days at 100 ° C before use.

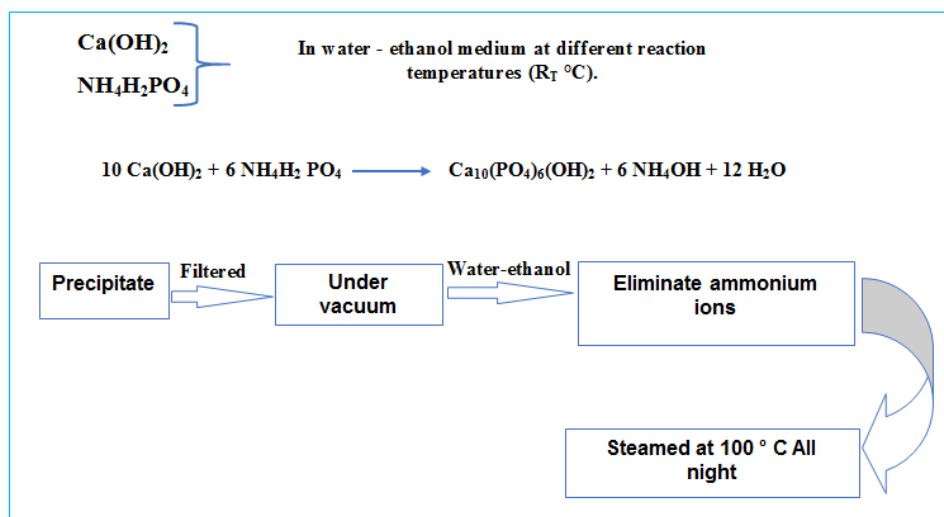


Figure 1. synthesis steps of hydroxyapatite (p-HAp)

2.2. Characterization

Sample of p-HAp was characterized by X-ray powder diffraction (XRD) (Philips PW131 diffractometer, Cu K α radiation) to study their crystal structures. To find out the characteristic bands of the resulting samples infrared spectra were recorded with a resolution of 2 cm⁻¹ on a spectrophotometer; Bruker IFS 66v FT-IR meter. Specific surfaces were calculated according to the Brunauer-Emmett-Teller (BET) method using adsorption data in the relative pressure range of 0.05 to 0.25. The distribution was determined using the Barret-Joyner-Halenda (BJH) approximation in the mesoporous range.

2.3. Experiments of adsorption

Experimental conditions such as 100 ml of total volume, 20 mg / L of initial concentration of copper ions (Cu²⁺), and 2000 mg / L of adsorbent (CAp and p-HAp) were added with a pH=5 was held constant throughout the study. Commercial and synthetic hydroxyapatite were mixed well in solutions of Cu²⁺ in conical flasks. The mixing solutions were placed in the dark for 30 min with adequate agitation to determine their copper (II) ion adsorption capacity. The sampled suspensions were then centrifuged at 4000 rpm for 20 min to remove the adsorbents and then analyzed by an atomic absorption spectrophotometer. Cu²⁺ adsorption ratios were determined using the following equation 1 and 2 :

$$qe = \frac{C_0 - C_e}{m} V \quad (1)$$

2.3.1. Kinetics and equilibrium models

Pseudo-first order and pseudo-second-order Lagrangian models were used for kinetic data analyses. The equilibrium data are evaluated by applying the Freundlich and Langmuir adsorption models. The models and their equations 2 and 5 are as follows:

a. Pseudo-first order

$$\frac{dq_t}{dt} = k_1(q_{e,1} - q_t)^2 \quad (2)$$

Hence, $q_{e,1}$, and q_t show the adsorption capacity of Cu²⁺ (mg / g) at equilibrium and at time t , respectively. K_1 is the rate constant for pseudo-first-order kinetics.

b. Pseudo-second order

$$\frac{dq_t}{dt} = k_2(q_{s,2} - q_t)^2 \quad (3)$$

K_2 is the rate constant for pseudo-second-order kinetics.

c. *Langmuir isotherm model*

$$q_s = q_{s,max} \frac{\beta Ce}{1 + \beta Ce} \quad (4)$$

Hence, $q_{s,max}$ is the maximum absorption capacity of Cu^{2+} (mg / g) and β is the Langmuir constant (L / mg) related to the absorption energy.

d. *Freundlich isotherm model*

$$q_s = K_f Ce^{\left(\frac{1}{n}\right)} \quad (5)$$

K_f is the Freundlich constant correlated with the maximum adsorption capacity, and n represents the adsorption intensity.

3. Results and discussion

3.1. Structural and chemical analysis

Scanning electron microscopy (SEM) allows morphological observations to be made. According to the work already done [13], the synthesized hydroxyapatite consists of small particles which form aggregates (figure 2).

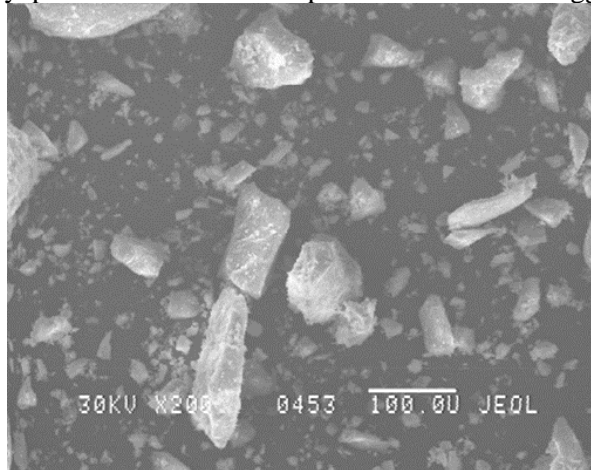


Figure 2. SEM image of hydroxyapatite prepared at 25 ° C and steamed at 100 ° C

X-ray diffraction analysis shows us that p-HAp is poorly crystallized, but the crystal quality increases by increasing the reaction temperature from 25 ° C up to 90 ° C (Table 1), and the analysis also shows that hydroxyapatites consist of a single apatitic phase, and the lines are indexed in the hexagonal system of space group $P6_3/m$.

Table 1. Effect of reaction temperature on crystallinity

Reaction temperature (°C)	(002)	(211)	(300)
25	0.677	2.340	2.741
70	0.355	0.900	0.787
90	0.275	0.666	0.468

An infrared spectroscopic study has already been performed and shows absorption bands around a frequency of 510 cm^{-1} , 1000 , and 3500 cm^{-1} which are attributed to PO_4^{3-} , CO_3^{2-} and OH^- , respectively [13]. In order to know the influence of apatite nanoparticles on the porosity of p-HAp, we established the adsorption-desorption isotherms of N_2 (BET) as well

as the pore distributions on the surface of the hydroxyapatites. According to Table 2, the specific surface of the synthesized hydroxyapatite decreases by increasing the reaction temperature from 25 °C to 90 °C.

Table 2. *Effect of reaction temperature on specific surface of p-HAp*

Reaction temperature (°C)	Specific surface (m ² /g)
25	235
70	151
90	108

3.2. Adsorption studies

3.2.1. Effect of pH

Figure 3 shows the change in pH over time for hydroxyapatite suspensions measured in the presence or absence of Cu²⁺ ions.

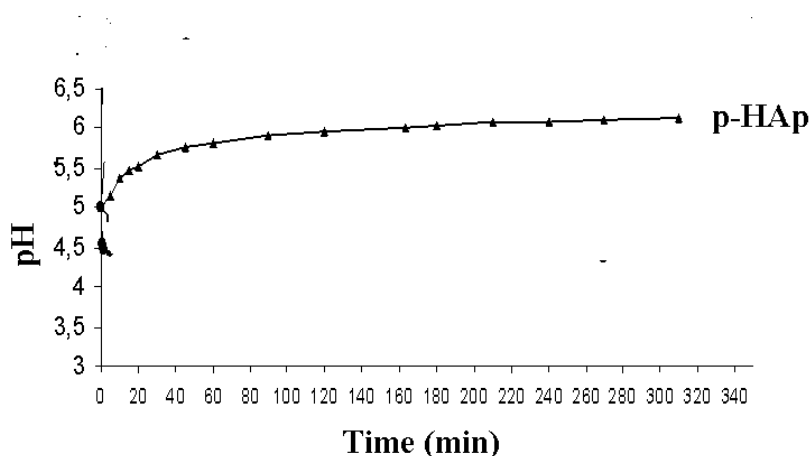


Figure 3. pH variation as a function of time

From figure 3, we observe that the pH of the solution containing hydroxyapatite (p-HAp) and copper (II) ions increases with time, and this increase is due to the release of OH⁻ ions at the cause of the poor dissolution of p-HAp. And the low pH at the start of the process is due to the release of H⁺ in the solution, following the complexation of the Cu²⁺ ions on the surface of p-HAp by the PO₄³⁻ and HPO₄²⁻ groups to form a complex **O₃-P-O-Cu⁺** [14]. The effect of pH has not been studied above pH = 6 due to the precipitation of Cu²⁺ ions as copper hydroxide [15]. Therefore, our experiments were carried out at pH = 5, to avoid any precipitation of these Cu²⁺ ions and their lineage with the actual pH value of the majority of wastewater.

3.2.2. Effect of initial concentration

Figure 4 shows the pattern of the effect of initial Cu²⁺ concentration on the adsorption capacity of synthetic hydroxyapatite (p-HAp) and synthetic hydroxyapatite (CAp).

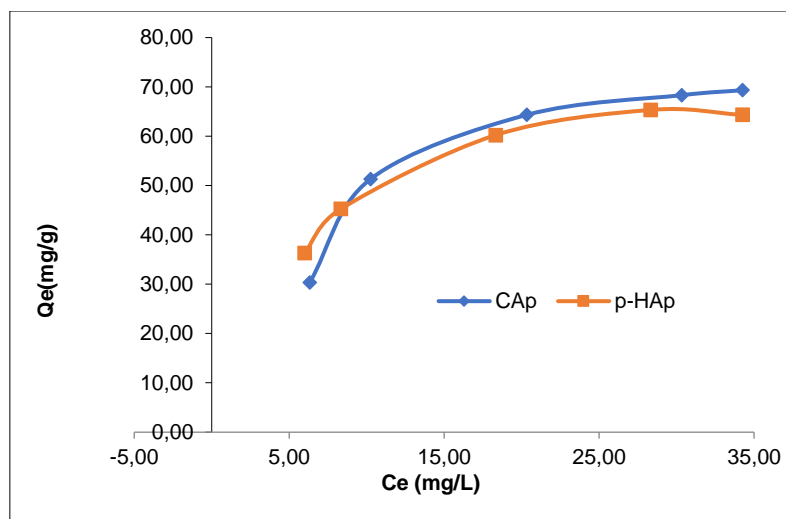


Figure 4. Effect of the initial concentration of Cu^{2+} on adsorption capacity of p-HAp and Cap

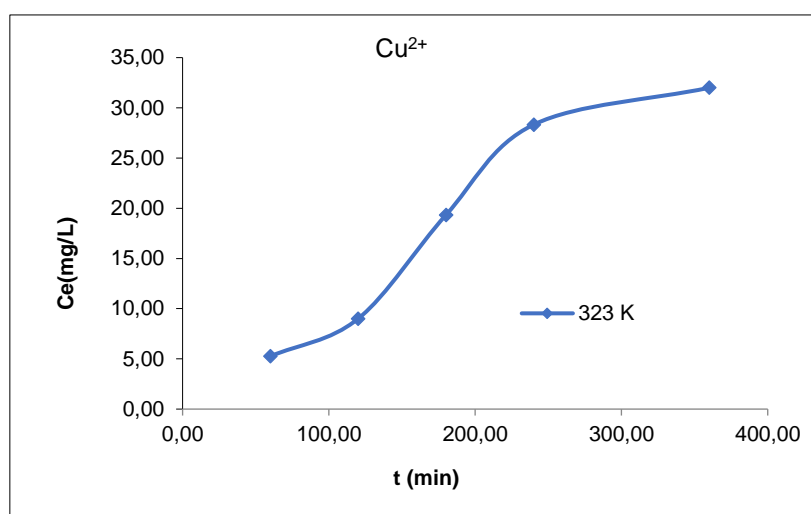


Figure 5. effect of contact time on adsorption of Cu^{2+} by p-HAp

According to figure 4, the adsorbed quantity of Cu^{2+} by synthetic and commercial hydroxyapatite increases by increasing the concentration of pollutant (Copper II) until having saturation at an initial concentration of 6 mmol / L for the two adsorbents (p-HAp and CAP) with a maximum adsorption quantity of 70 mg / g for p-HAp and 60 mg / g for CAP. This study shows that the adsorption capacity of Cu^{2+} by p-HAp is greater than that of CAP. The saturation plateau observed in Figure 4 could be explained by the depletion of all active sites that exist on the surface of each medium [16].

3.2.3. Effect of contact time

The study consists of bringing a volume of 100 mL of a 100 mg / L copper solution at pH = 5 into contact with 0.2 g of p-HAp. The mixture is kept under gentle stirring at room temperature (25 ° C.). Samples were taken at time intervals, then filtered by a micro-filter with a diameter of 0.45 μm and then analyzed by atomic absorption spectrophotometry. In the first minutes, the adsorption kinetics are very fast, after ten minutes equilibrium is reached and then followed by a saturation plateau. The appearance presented in figure 5 could be explained by the fact that the active sites at the start of the adsorption process are available on the surface of p-HAp to fix the Cu^{2+} ions, and this fixation is explained by the large affinity of the p-HAp support for the solute used [17]. To understand the adsorption mechanism and analyze the results found, we used isotherms and kinetic models.

- Kinetics models

To study the phenomenon of pollutant transport in the adsorbent pores, several models such as the diffusion pore model, the homogeneous surface diffusion model, and the heterogeneous diffusion model were applied in a batch system [18].

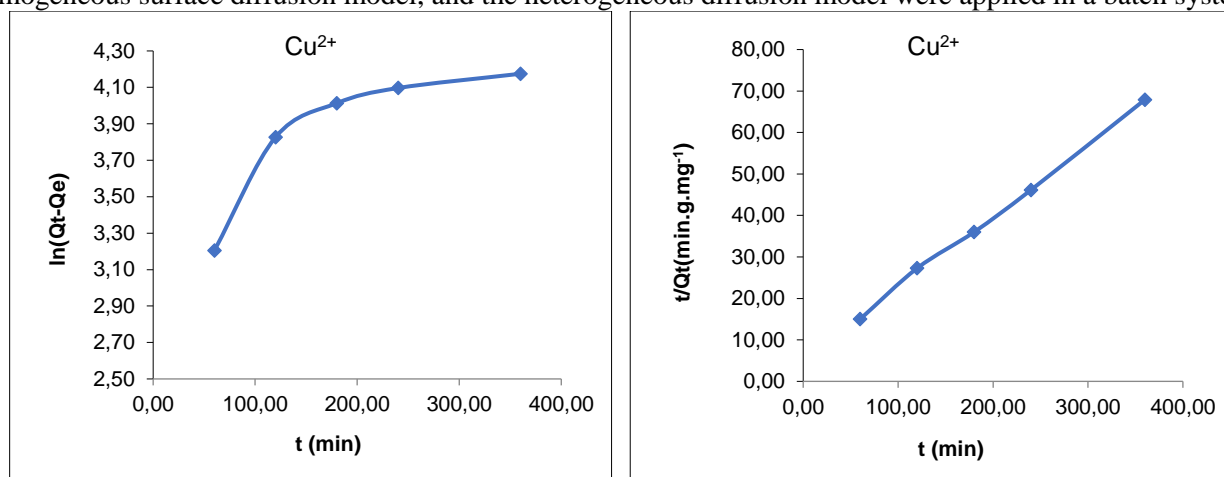


Figure 6. Linear representations of the kinetic model of (a) pseudo-first-order and (b) pseudo-second-order for p-HAp. Fig. 6 groups together the results of linear representations of $\ln(q_e - q_t) = f(t)$ and t/q_t as a function of time relating to the adsorption of copper on synthetic hydroxyapatites. The Cu^{2+} adsorption rate constants on the three supports for pseudo-first-order and second order are determined graphically (Table 3).

From figure 6 and table 3, we find that the pseudo-second-order model represents a good correlation coefficient R^2 (0.9983 close to 1), so it is the reliable one to determine the order of the kinetics of adsorption of Cu^{2+} on p-HAp. Likewise, from the values of q_e presented in Table 3, it can be seen that q_e calculated by the pseudo-second-order model is very close to that determined experimentally for an initial concentration of 12.58 mmol / L in Cu^{2+} ions, which justifies that the adsorption kinetics of Cu^{2+} ions by p-HAp follow the pseudo-second-order model.

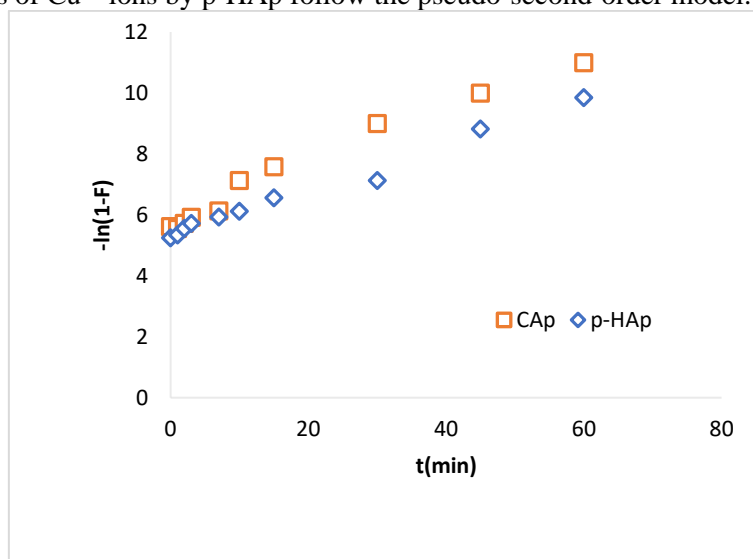


Figure 7. liquid film diffusion model plots for the adsorption of composite based of p-HAp and CAP

- Langmuir and Freundlich isotherm models

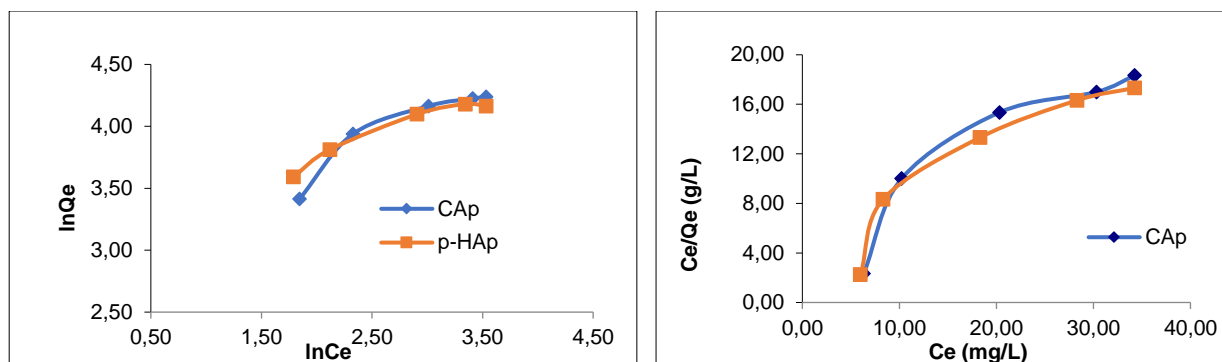


Figure 8. Model of the (a) Langmuir, (b) Freundlich isotherms of p-HAp and CAP

Table 3. Cu^{2+} adsorption parameters on p-HAp and CAP according to the Langmuir and Freundlich models

		p-HAp	CAP
Langmuir isotherm	$q_{e,\max}$	1.92	1.17
	β	1.02	0.76
	R^2	0.9764	0.9591
Freundlich isotherm	$1/n$	0.2128	0.1356
	$\ln K_F$ (L/mg)	0.79	0.38
	R^2	0.8992	0.8298

According to figure 8 and table 3 and based on the value of the linearity (R^2) of the straight lines of the adsorption isotherms of the two models, it can be seen that the value of $q_{e,\max}$ is in good agreement with the experimental values of the adsorbed quantity of Cu^{2+} ions. Therefore, Langmuir's model is most likely to characterize the adsorption of Cu^{2+} p-HAp ions.

3.3. Zero point contaminated pH (pHpzc)

The zero charge point is the pH at which the average surface charge is zero, but this does not mean that there are no positive and negative charges, it means that the numbers of charges in the two categories are identical ($[\text{MO}^-] = [\text{MOH}^{2+}]$). This parameter is very important in adsorption phenomena, especially when electrostatic forces are involved in the mechanisms.

3.3.1. Operating mode

A quick and easy way to determine pHpzc is to use the pH drift method (potentiometric titrations), which consists of placing 60 mg of the material in a 100ml vial containing 20ml of a 0.1 mol/l KNO_3 solution.

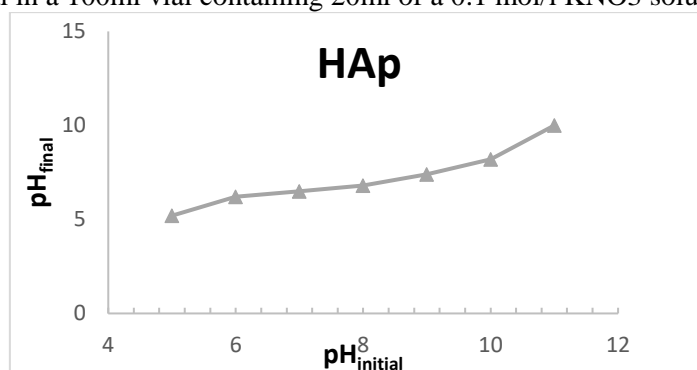


Figure 9. Determination of the pHpzc of the composite material Hap

The initial pH of the solutions is varied between 4 and 11 by adding NaOH and HCl solutions (0.1 mol/l). The suspensions must be kept stirred at room temperature for 6 hours and the final pH is then determined. The pH_{pzc} is the point at which the final pH versus initial pH curve intersects the line pH_{final} = initial pH.

3.3.2. Determination of the zero load point of HAp

The results of the potentiometric titration method for the determination of pH_{pzc} are shown in Figure 9. The first part of the curve, between the initial pH 4 and the initial pH 5, shows that the final pH of the solution increases as the initial pH increases. This can be explained by the fact that the H⁺ ions introduced into solution are consumed by the surface of the material. Between initial pH 6 and initial pH 8 the curve becomes parallel to the x-axis, i.e. the final pH of the solution is stable. Indeed, all H⁺ ions introduced in solution are consumed by the surface of the material until saturation of the sites, then there is a decrease in the final pH, due to the consumption of OH⁻ ions via the deprotonation of the existing sites on the surface of the composite material. The results obtained show that the contamination developed on the surface of the composite material depends on the pH. In fact, for pH values > pH_{pzc}, the surface of the solid is negatively contaminated, which favours the adsorption of cationic species, whereas for pH values < pH_{pzc}, the surface is positively contaminated, favouring the adsorption of anionic species. According to Figure 9 the zero charge point of HAp is pH_{pzc}=6.4. Figure 10 shows the variation of the surface charge of HAp as a function of pH.

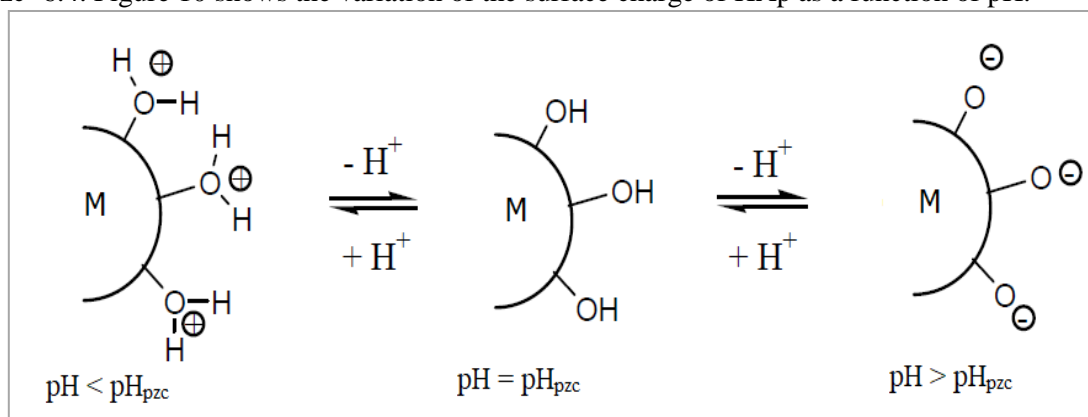


Figure 10. Change in surface contamination of the composite material (M: HAp) as a function of pH

Table 4. The pseudo-second-order model for adsorption of Cu²⁺ ions onto p- Hap and CAp

T (K)	p- HAp			CAp		
	K ₂ (g/mg.min)	Q _{cal} (mg/g)	R ²	K ₂ (g/mg.min)	Q _{cal} (mg/g)	R ²
Cu ²⁺	0.3566	415.3825	0.9765	0.3911	533.5218	0.9645

Table 5. Parameters explain the intra-particle diffusion of Cu²⁺ ions onto p- Hap, and CAp.

p- HAp			CAp			
	K _{id}	Z	R ²	K _{id}	Z	R ²
Cu ²⁺	0.1437	2.7706	0.9520	0.1352	2.8705	0.9523

The results of kinetic models and isotherms give us an idea of the mechanism of adsorption of Cu²⁺ on p-Hap as described in others works for various metallic ions [19- 24]:

- Ion exchange between the Cu^{2+} ions contained in the solution and Ca^{2+} present in the solid. $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + x\text{Cu}^{2+} \rightarrow \text{Ca}_{10-x}\text{Cu}_x(\text{PO}_4)_6(\text{OH})_2 + x\text{Ca}^{2+}$
- The complexation of Cu^{2+} ions at the surface of the apatitic solid by the oxygen of the PO_4^{3-} and HPO_4^{2-} groups. $\text{O}_3\text{P-O-H} + \text{Cu}^{2+} \rightarrow \text{O}_3\text{P-O-Cu}^+ + \text{H}^+$
- Adsorption of Cu^{2+} ions in the pores at the surface of the solid.

Conclusion

In the present study, a comparison between synthesized hydroxyapatite (p-HAp) and commercial hydroxyapatite (CAp) was performed to determine the adsorption capacity of our laboratory-synthesized porous material (p-HAp). The effect of the pH, the contact time, the initial Cu^{2+} concentration were studied to find the optimal adsorption conditions.

The pseudo-second-order kinetic model is more suitable for describing the adsorption of heavy metals p-HAp, and the adsorption isotherms follow the Langmuir isotherms model, which shows that the adsorption takes place on the surface of the p-HAp, i.e. the adsorption process is a monolayer. And the quantity of Cu^{2+} ions adsorbed by p-HAp is greater than that adsorbed by CAp.

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