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Removal Cu(II) and Ni(II) by natural and synthetic hydroxyapatites: a comparative study

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ABSTRACT

The sorption of divalent copper and nickel ions from aqueous solutions on natural and synthetic hydroxyapatites was investigated in batch mode at 25 and 40°C and over metal concentration range of 20–800 mg/L. Effect of initial pH solution was also investigated for two values pH 4.5 and pH 6. The sorption equilibrium data were well fitted by Langmuir's model. Both hydroxyapatites are efficient to remove copper and nickel ions, despite their different compositions and morphologies. The sorption mechanism involved an ion exchange between calcium ions of hydroxyapatite and metal ions along with pronounced precipitation, particularly in case of the synthetic hydroxyapatite. Higher sorption efficiencies were observed with the synthetic hydroxyapatite towards copper ions, similar values for both synthetic and natural hydroxyapatites were found towards Ni ion's sorption and lower values at pH 6.

Keywords: Sorption; Isotherm; Hydroxyapatite; Copper ions; Nickel ions

1. Introduction

The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution, which is a serious cause of water degradation [1]. Numerous metals, such as copper, nickel, chromium, mercury, lead, cadmium, etc. are known to be significantly toxic substances [2]. Sorption technologies, as methods for the removal of heavy metals from wastewaters, have gained much attention in the last decade due to their simplicity, low-cost and high efficiency [3,4]. Various minerals sorbents such as Pb^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} have been evaluated as potential removing agents from aqueous media, such as bentonite, kaolinite, activated carbon and apatite [5–10].

Apatite is the name given to a group of crystals of the general chemical formula $M_{10}(RO_4)X_2$, where R is most generally phosphorus, M could be one of the several metals, although it is usually calcium and X is frequently hydroxide or a halogen, such as fluorine or chlorine [11]. Generally, calcium-hydroxyapatite (Hap) $Ca_{10}(PO_4)_6(OH)_2$ has demonstrated the best removal

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efficiency due to its moderate solubility between highly insoluble and considerably soluble phosphate bearing materials, such as phosphate rock and phosphate fertilizers, respectively [11,12]. It is an ideal material for long term containments because of its high sorption capacity for heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability and despicable cost [13]. Reported data indicate that bivalent metal sorption capacities on Hap, as well as the sorption mechanisms strongly depend on: (1) type of divalent metal, (2) Hap physicochemical properties and (3) other factors, such as metal concentration, solution pH, contact time, etc. [14–17].

It is agreed that sorption of heavy metals occurs on hydroxyapatite at the surface of adsorbent particles through an ion exchange process leading to fixation of toxic metals as insoluble phosphates while calcium ions are released to aqueous solution [17–20]. Sugiyama et al. [21] suggested two general mechanisms for the ability of hydroxyapatite to take up divalent metal cations: (1) the first is concerned with the adsorption of ions on the solid surface followed by their diffusion into hydroxyapatite and the release of cations originally contained within hydroxyapatite (ion–ion exchange mechanism) and (2) the second involves the dissolution of the hydroxyapatite in the aqueous solution containing divalent metals followed by the precipitation or co-precipitation of metal phosphates (dissolution–precipitation mechanism). However, Elouear et al. [22] suggested that the dissolution–precipitation mechanism was operated at a low pH (<4), whereas at a higher pH, the removal of metals is attributed to surface sorption or/and complexation.

Copper and Nickel are reddish metals that occur naturally in the environment [6,8,10,11]. They also occur naturally in plants and animals. Low levels of copper and nickel are essential for maintaining good health while high levels can cause harmful effects, such as nose, mouth or eye's irritations, vomiting, diarrhea, stomach crumps and nausea [23–25]. Nickel is a hard, silvery-white metal used to make stainless steel and other metal alloys. Skin effects are the most common effects in people who are sensitive to nickel. Workers who breathed very large amounts of nickel compounds have developed lung and nasal sinus cancer [10]. It is interesting, therefore, to study interactions of Cu and Ni ions in aqueous solutions with apatites and other insoluble phosphates to predict their adsorption loads, their migrations in liquid and solid phases and associated complex precipitations in natural water during the sorption/desorption process [3,9,25–27].

The aim of the present work is to compare the Cu (II) and Ni (II) ion's removal on natural (consisting of crushed teeth) and synthetic hydroxyapatite in batch mode operation using aqueous solutions of two values of pH and temperatures.

2. Experimental

2.1. Materials and methods

The natural Hap (NHap) originated from a variety of human teeth, which were extracted for prophylactic reasons. NHap was cleaned with a mixture of 10% hydrogen peroxide and sodium hypochlorite for 24 h, rinsed with 1% of nitric acid solution and dried at 30˚C for 24 h. The bleached teeth were grounded in a mortar and then sieved. The sample of 25 and 250 μm size was collected and dried at 60˚C for 8 h.

The synthetic Hap (SHap) was Bio-Rad® calcium phosphate (Bio-Rad®) which was referenced DNA Grade Bio-Gel HTP 130-0420.

The chemical composition of the starting Hap particles was determined by inductively coupled plasma atomic emission spectrometry (ICP/AES), with a Varian Vista spectrometer. The specific surface area was evaluated by N_2 physisorption and calculated according to the BET method with a Coulter-SA3100 device.

2.2. Sorption experiments

The batch sorption experiments were performed in polyethylene bottles containing known amounts of sorbent in a suspension of 50 mL of cupric or nickel nitrate solutions at concentrations ranging from 20 to 800 mg/L and constant agitation of 120 rpm in a horizontal shaker for periods ranging from 0.5 to 24 h. The apatite suspensions were shaken at two temperatures, i.e. 25 and or 40˚C and two pH values of 4.5 and 6. The solutions were filtered using a porosity filter of 0.2 μm pore size and both Cu (or Ni) and Ca contents were then analysed by atomic absorption spectroscopy.

In order to avoid precipitation of copper at $pH > 6$, or hydroxyapatite dissolution at $pH < 3$, the initial pH 4.5 and pH 6 were chosen for further experiments [8,14,18,19]. Both powder NHap and SHap were also analysed by scanning electronic microscopy (SEM) at a magnification of 50,000 of space scale.

The amount of Cu(II) or Ni(II) per unit mass of adsorbent Q in (mg/g) was calculated using Eq. (1):

$$Q = \left(\frac{C_0 - C_f}{m}\right)V \tag{1}$$

where C_0 and C_f are the initial and final metal concentration (mg/L), V is the volume (L) of metal solution used for sorption experiments, and m is the mass of hydroxyapatite used (g), respectively.

3. Results and discussion

3.1. Hap characterization before sorption

Some features of the two apatites are reported in Table 1. The concentration of cations is given as referred to 6 PO_4. It is interesting to see that the NHap presents much lower surface area than the SHap.

SEM observations, illustrated in Figs. 1 and 2, show that NHap exhibits a more heterogeneous morphology and strongly anisotropic surface (Fig. 1). SHap appears as platelets with crystals constituted of small elongated particles separated by pores (Fig. 2).

Table 1
Typical parameters for apatites NHap and SHap

	Specific surface area (m^2/g)	Composition
NHap	1.5	$Ca_{8.92}$ $Na_{0.32}$ $(PO_4)_6$ $(OH)_{1.24}$
SHap	77	$Ca_{8.22}$ $Na_{0.48}$ $(PO_4)_6$ $(OH)_{0.7}$

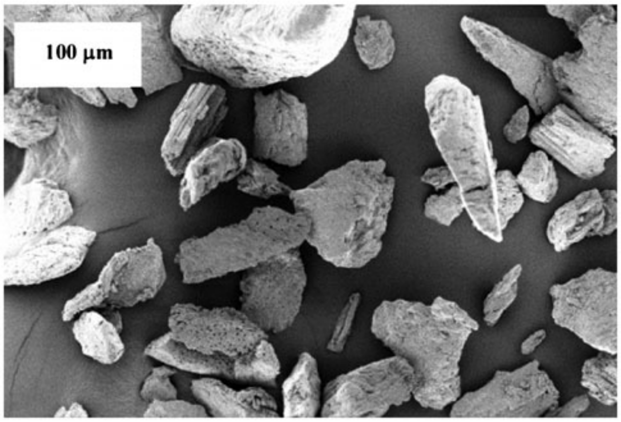

Fig. 1. SEM view of NHap starting material.

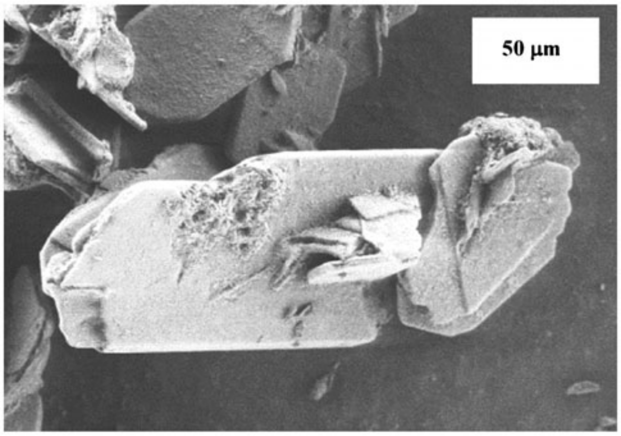

Fig. 2. SEM view of SHap starting material.

3.2. Sorption kinetics

The kinetics of sorption of both Ni(II) and Cu(II) on SHap and NHap are shown in Fig. 3. Although both Hap present different surface area, they exhibited similar kinetic trends before reaching the equilibrium less than 1 and 2 h for Ni(II) and Cu(II), respectively. This denotes that the adsorption process on both Haps was not limited by mass transfer assuming similar adsorption mechanism occurred on both Haps.

3.3. Sorption isotherms

Sorption capabilities of the two hydroxyapatite are drawn in terms of sorption isotherms at equilibrium represented by concentration Q_e of metal (mg per g of Hap) vs. remaining amount of metal in the liquid phase C_e (mg/L) for initial metal concentrations varying from 20 to 800 mg/L.

The equilibrium data of copper and nickel adsorption were explored using the isotherm models of Langmuir, and Freundlich in order to determine the correlation between solid phase and aqueous concentrations at equilibrium. The Langmuir adsorption isotherm can be written as:

$$Q_e = Q_s \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

where Q_s (mg/g) and K_L (L/mg) are Langmuir constants associated with the capacity and energy of adsorption.

In first instance, Langmuir model assumes that sorption occurs in a monolayer where the active sites are identical and energetically equivalent [28].

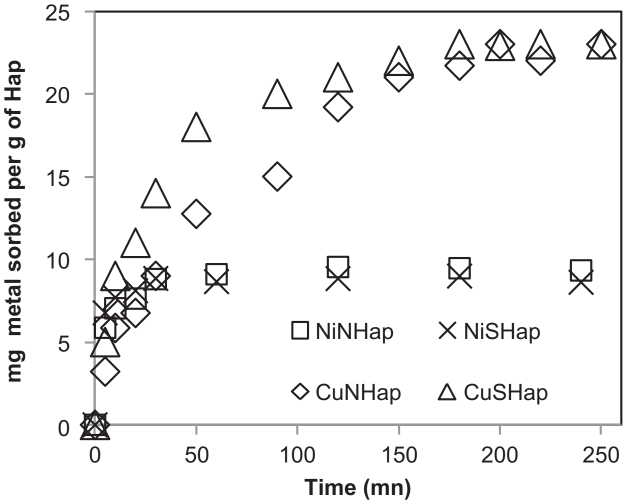

Fig. 3. Kinetic sorption of Cu(II) and Ni(II) ions on SHap and NHap (25°C, 60 ppm and pH 4, 5).

Alternatively, Freundlich model is an empirical expression used to describe a heterogeneous system [28], which is defined as:

$$Q_e = K_F C_e^{1/n} \tag{3}$$

where K_F and $1/n$ are the Freundlich model constants related to the capacity and intensity of the adsorption, respectively.

Examples of equilibrium sorption of Cu(II) trends at pH values of 4.5 and 6 on both NHap and SHap are presented in Figs. 4 and 5 at 25 and 40°C, respecively. Similar trends were also observed for Ni(II) adsorption (not shown).

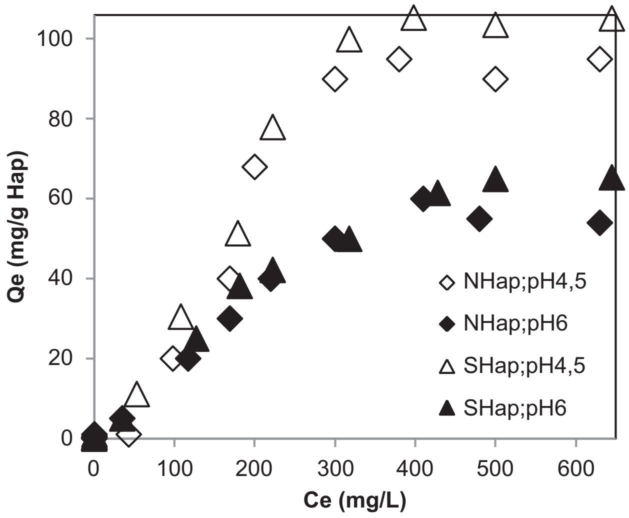

Fig. 4. Isotherm sorption of Cu on both NHap and SHap hydroxyapatite at 25°C.

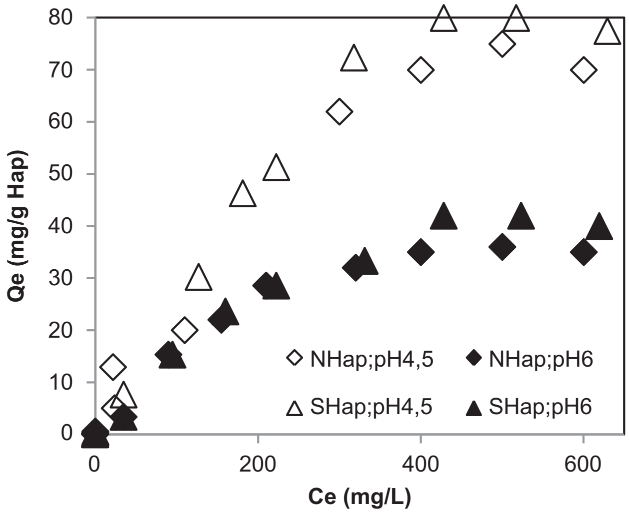

Fig. 5. Isotherm sorption of Cu on both NHap and SHap hydroxyapatite at 40°C.

Figs. 4 and 5 show that increasing temperature and pH has negative effects on adsorption capacities of both NHap and SHap sorbents.

The fit to the linear form of Langmuir and Freundlich models was examined by the calculation of regression values (R^2). Figs. 6 and 7 indicate that the adsorption data for Cu(II) and Ni(II) removal fitted better the Langmuir model than the Freundlich one for NHap and SHap sorbents. Consequently, the sorption of Cu and Ni ions on NHap and SHap follows the Langmuir isotherm model, where the uptake occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules.

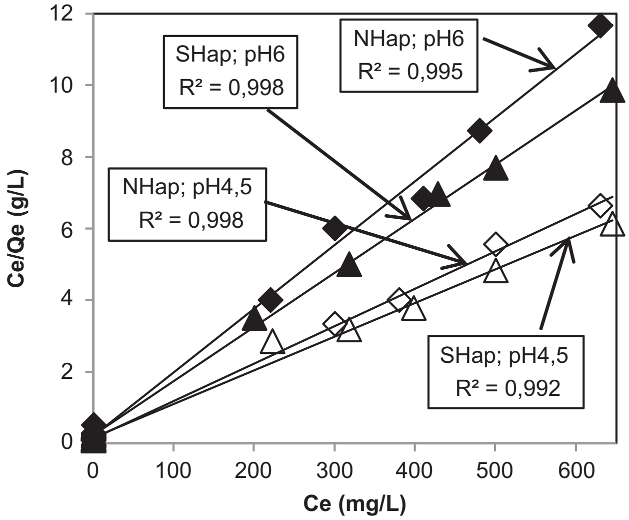

Fig. 6. Linear representation of Langmuir model.

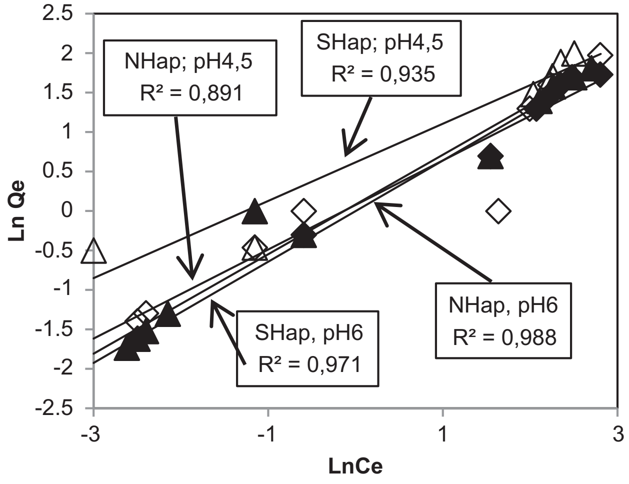

Fig. 7. Linear representation of Freundlich model.

Table 2
Values of sorption capacity Q_s at pH 4, 5 and T = 25°C

	Cu^{2+} on NHap	Ni^{2+} on NHap	Cu^{2+} on SHap	Ni^{2+} on SHap
Q_s (mg/g)	95.24	13.64	106.38	10.94
Q_s (mg/m^2)	63.49	9.09	1.38	0.14

The best recorded values of sorption capacity Q_s (expressed in mg per g and per m^2 of Hap) deduced by fitting experimental data to Langmuir model are given in Table 2 for both Haps at pH 4, 5 and 25°C.

The values of Q_s for Cu(II) and Ni(II) show different trends towards NHap and SHap. SHap exhibits a capacity of Cu(II) which is of magnitude higher than that of NHap while both Haps show roughly similar capacities towards Ni(II). This clearly shows that Haps present selective capacities towards divalent metals. It should be noted that our results of NHap towards Cu^{2+} (95.241 mg/g) is still far higher than that obtained by bone calcination where a capacity of 45.12 mg/g was reported for bone chars of high surface area [8,12].

3.4. Sorption mechanisms

It is well agreed that when sorption of heavy metal's sorption occurs on hydroxyapatite, an ion exchange process takes place leading to the surface fixation of metals as insoluble phosphates against calcium ions release into solution [14,18,19]. Thus, an amount of Cu(II) sorbed on both two Haps vs. an amount of Ca(II) released was investigated as shown in Fig. 8.

It is clear that the NHap released amount of Ca(II) is roughly similar to the amount of uptaken Cu(II) while SHap retained Cu(II) slightly more than Ca(II) released to the solution, particularly at low concentrations. Similar trends were observed with nickel ions (not shown). Thomson et al. [7], who conducted adsorption isotherms of metals from bone char, SHap, phosphate rock and fish bones, found that SHap had higher capacity than the NHap while carbonated synthetic hydroxyapatite released by an exchange process more calcium ions than non-carbonated ones would have done. Herein, the less release of Ca ions in case of SHap would be explained by a potential precipitation of Ca complexes leading to an unbalanced amount between the Cu(II) and Ca ions. However, the analysis of Na ions in solution after sorption showed the low contribution of these ions with calcium ions in the process of exchange with Cu(II) and Ni(II). This observation has already been mentioned by several authors [18,19,29].

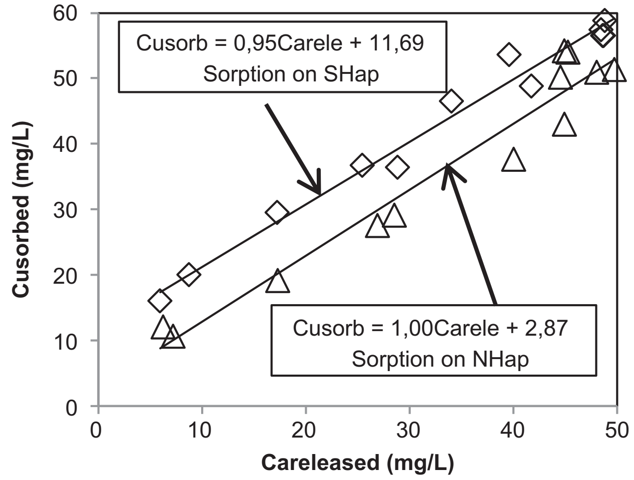

Fig. 8. Amount Cu(II) sorbed on Hap vs. Ca(II) released in solution (T = 25°C and pH = 4.5).

NHap and SHap were examined by SEM after sorption experiments as shown in Figs. 9 and 10. Unlike NHap in Fig. 9, SHap appears to be covered more with crystallites of formed precipitates, which are clearly visible inside the tubuli as shown in Fig. 10. Although this precipitation occurs for Cu(II) ions with both Haps, the resulting morphology of newly formed solid precipitates looks quite different. SEM results are in agreement with Cu(II)/Ca ion balance analysis for both Haps shown in Fig. 8, where a slightly pronounced precipitation occurred along with Cu(II) sorption on SHAp.

A large number of batch experiments suggest sorption processes as the removal mechanism of copper by hydroxyapatite. However, the dissolution of HAP and precipitation of amorphous copper phosphates ($Cu_3(PO_4)_2(s)$) and libethenite ($Cu_2(PO_4)OH(s)$) have also been described [8,13,30–33].

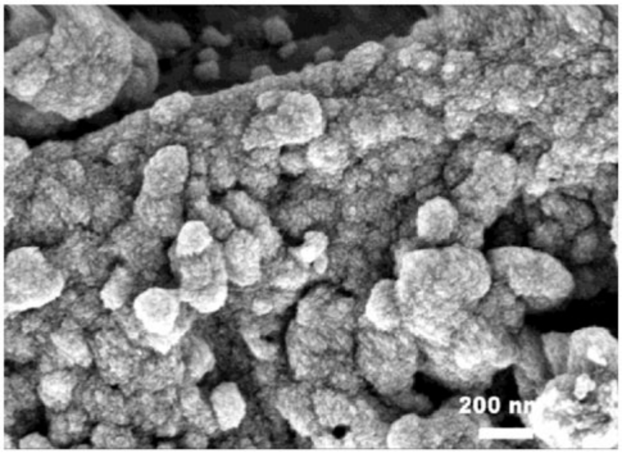

Fig. 9. SEM of NHap after Cu(II) sorption.

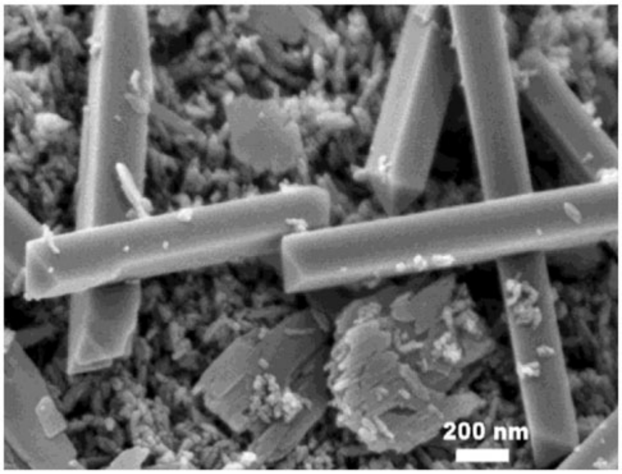

Fig. 10. SEM of SHap after Cu(II) sorption.

4. Conclusion

This study investigated the capability of natural and synthetic hydroxyapatites to sorb Cu(II) and Ni(II) ions from aqueous solutions under batch conditions. Sorption was found promoted at low pH of the aqueous solution. The sorption isotherm data fitted well Langmuir-type isotherms with a standard deviation of 0.99. The sorption mechanism, however, was a function of nature of hydroxyapatite.

The values obtained for Q_s for Cu(II) on NHap, although much lower than that on SHap and other calcined bones, were very promising towards Ni ions opening, therefore, potential applications to waste water decontamination.

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