

# Interactions between calcium phosphate and heavy metal ions in aqueous solution

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**Abstract.** Synthetic and natural calcium phosphates were tested for removal metallic pollution in aqueous solution. Calcium phosphates with Ca/P ratio between 1,33 and 1,67 are fluently called apatite. They have a strong capacity to immobilize metallic ions when they are brought into contact with aqueous solutions.  $\text{Ca}^{2+}$  ions can substituted completely or partly by cations such as metallic ions ( $\text{Ni}^{2+}$ ;  $\text{Cu}^{2+}$ ;  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$ ).  $\text{PO}_4^{3-}$  ions can be replaced by anions such as  $\text{AsO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ , ... etc. Sorption of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solutions on natural (NA) and synthetic (SA) apatite was investigated in batch mode at 25 °C and 40 °C and over metal concentration range of 20–800 mg/L. Other experiments of co-precipitation metal-apatite (metal-TCP) were investigated in static mode at 25 °C. The results characterization of NA and SA apatite by FTIR, SEM, and ICP confirm their composition and apatitic structure. The results confirm efficiency of these calcium phosphates to decontaminate, by adsorption or co-precipitation, metallic ions such as  $\text{Ni}^{2+}$  or  $\text{Cu}^{2+}$  present in aqueous solution at concentrations between 20–800 mg/L.

## INTRODUCTION

Several solid sorbents have been proposed for decontamination of industrial liquid wastes from toxic or radioactive elements. The use of mineral materials such as apatite showed big efficiency for decontamination of industrial waste [1–6]. Apatite is the name given to a group of crystals of the general chemical formula  $\text{M}_{10}(\text{RO}_4)\text{X}_2$ , 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 [7]. One of the most common apatite is calcium hydroxy apatite (Hap), whose theoretical formula is  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Non stoichiometric Hap constitutes the mineral component of hard tissues (bone, dental enamel, etc.) of mammals [6–10].

Study interaction between metal ions such as cadmium, zinc, copper and nickel with apatite is of most interest both for the development of decontamination methods for liquid wastes and for the investigation of processes in human and animal hard tissues [12–14].

The retention mechanisms of heavy metal on apatite include ion exchange with diffusion into the sample, or precipitation of new solid phases, depending on the conditions and the reactivity of the substituted Hap [4–8].

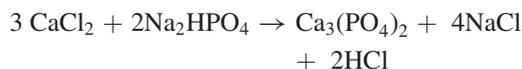
Synthetic and natural phosphates of calcium were tested for reduction metallic pollution in aqueous solution. Sorption experiments of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions such as on apatite were led in batch mode and in aqueous solution. Several operating parameters were studied such as pH (pH4 and pH5), initial concentration of metallic solution (20 to 800 mg/L), and temperature (25 and 40° C). Other experiments were performed by dissolution - precipitation (co precipitation) of apatite with solution of  $\text{Ni}^{2+}$  ions at 25 °C and pH 7.

## 1. EXPERIMENTAL

### 1.1. Materials and methods

The natural apatite (NA) originated from a variety of human teeth, having undergone adequate treatment. After treatment, teeth were calcined at 800 °C for two hours then grounded in a mortar and sieved. The sample of 25 and 250  $\mu\text{m}$  size was collected and used for sorption experiments. The synthetic apatite (SA) was Bio-Rad® calcium phosphate (Bio-Rad®) which was referenced DNA Grade Bio-Gel HTP 130-0420. Chemical composition of the starting apatite particles was determined by inductively coupled plasma atomic emission spectrometry (ICP/AES), with a Varian Vista spectrometer. The specific surface area was evaluated by  $\text{N}_2$  physisorption and calculated according to the BET method with a Coulter-SA3100 device.

The tricalcic phosphate (TCP) with theoretical formula  $\text{Ca}_3(\text{PO}_4)_2$  was prepared by haste at neutral pH. TCP was formed by mixture of  $\text{CaCl}_2$  and  $\text{Na}_2\text{HPO}_4$  according the following equation:



Some features evaluated for NA and SA apatite studied are given in the Table 1 (specific surface evaluated by  $\text{N}_2$ -BET method and composition determined by ICP/AES).

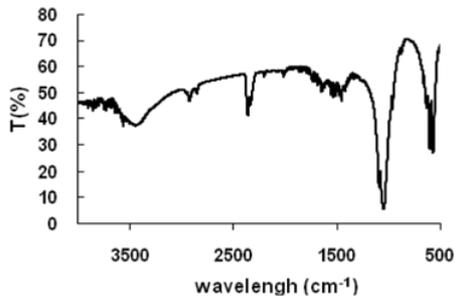
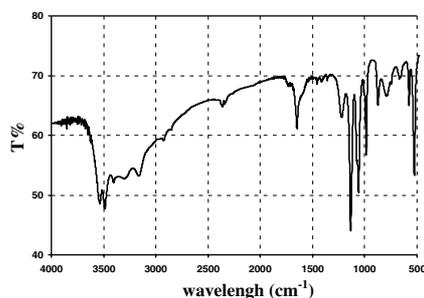
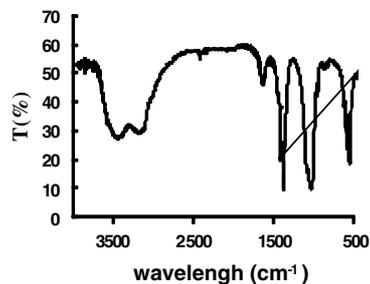
Both powder NA, SA and TCP were also analysed by scanning electronic microscopy (SEM) and by FTIR.

### 1.2. Sorption experiments

Sorption experiments were performed in polyethylene bottles containing known amount of sorbent (with ratio apatite/solution optimised at 4 g/L) in the suspension

**Table 1.** Typical parameters for NA and SA apatites.

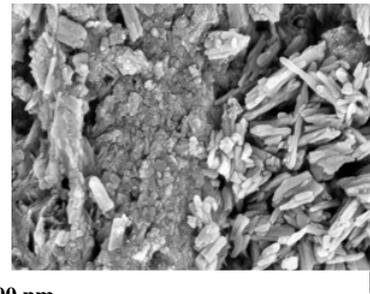
	Specific Surface area (m <sup>2</sup> /g)	Composition
NA	1.5	Ca <sub>8.92</sub> Na <sub>0.32</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>0.7</sub>
SA	77	Ca <sub>8.22</sub> Na <sub>0.48</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>1.24</sub>

**Figure 1.** FTIR Spectrum of NA apatite.**Figure 2.** FTIR Spectrum of SA apatite.**Figure 3.** FTIR spectrum of TCP apatite.

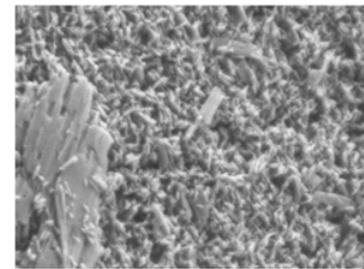
of 50 mL of cupric or nickel nitrate solutions at range concentration between 20 and 800 mg/L and constant agitation for periods ranging from 5 to 600 min. The apatite suspensions were shaken at 25 °C or 40 °C. After time contact, solutions were then filtered on a 0.2 μm porosity filter and analyzed for Cu (or Ni) and Ca by atomic absorption spectroscopy (AAS).

In order to avoid precipitation of nickel or copper hydroxide at pH > 6, or apatite dissolution at pH < 3, the initial pH 4 and pH 5 were chosen for further experiments [5, 11, 15, 16].

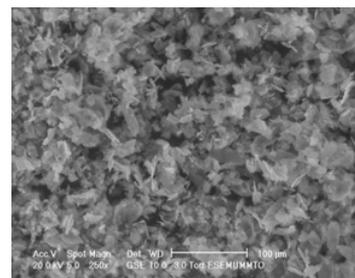
Other experiments were performed by dissolution – precipitation of NA, SA and TCP apatites with solution of Ni<sup>2+</sup> ions. Dissolution of apatite was conducted at pH 2.50 ml of apatite solution was then mixed with 50 ml of metallic solution and stirred for 30 min at 25 °C. Then pH solution was adjusted by adding NaOH solution



200 nm

**Figure 4.** SEM view of NA starting material.

500nm

**Figure 5.** SEM view of SA starting material.**Figure 6.** SEM view of TCP apatite.

until phosphate calcium precipitated. After filtration, the solution was analyzed for Ni by atomic absorption spectroscopy (AAS). Influence of initial amount of NA, SA and TCP on % removal of Ni(II) was just studied.

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

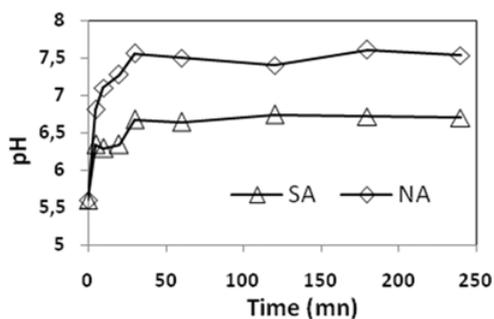
$$Q = \left( \frac{C_0 - C_f}{m} \right) V. \quad (1)$$

Where C<sub>0</sub> and C<sub>f</sub> 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 apatite used (g) respectively.

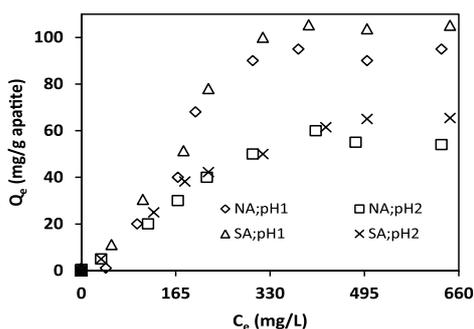
## 2. RESULTS AND DISCUSSION

### 2.1. Results material characterization

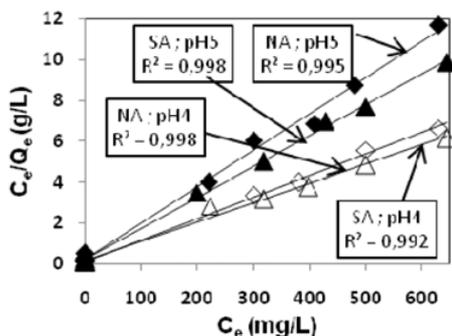
Main results in Table 1 show non stoichiometric hydroxy apatite for NA and SA materials.



**Figure 7.** Evolution pH Ni(II) solution versus time contact between SA and NA apatite (25 °C, 60 ppm, pH<sub>i</sub> 5, 4 g apatite per L solution).



**Figure 8.** Isotherm sorption of Cu on SA and NA at 25 °C for pH<sub>1</sub> = 4 and pH<sub>2</sub> = 5.

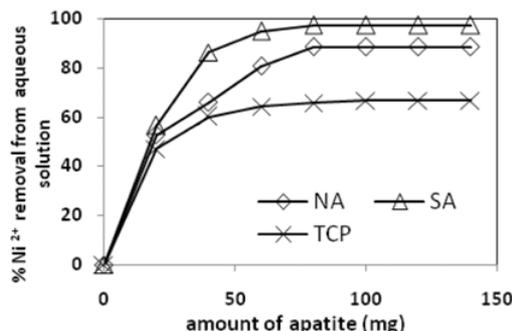


**Figure 9.** Linear representation of Langmuir model for Cu sorption.

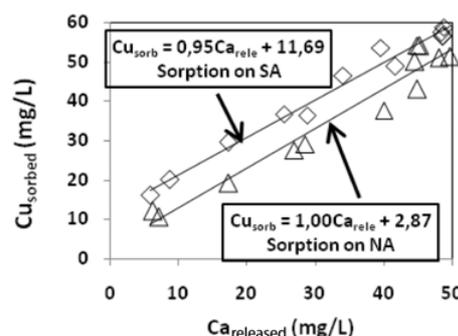
FTIR specter presented on Figures 1 and 2 show presence of the main peaks of phosphates ( $601$  and  $1081\text{ cm}^{-1}$ ) and hydroxides ( $3400\text{ cm}^{-1}$ ). But Figure 3 shows allow presence of these peaks characteristic of hydroxy apatite. However Figures 2 and 3 show a presence of carbonate speak around  $3400\text{ cm}^{-1}$ . SEM observations, illustrated in Figures 4, 5 and 6, show that NA exhibits a more heterogeneous morphology and strongly anisotropic (Fig. 4). SA appears as platelets with crystals constituted of small elongated particles separated by pores (Fig. 4). About TCP, Figure 6 shows precipitate homogenous structure, that indicates calcium phosphate presence in this material. Variation of pH solution seen in Figure 7 shows the buffering effect exerted by SA and NA apatites for contact times beyond 50 mn. Indeed, the hydroxy apatite and apatites are known for their buffering capacity associated with phosphate groups [17].

**Table 2.** Values of sorption capacity  $Q_s$  at pH4 and  $T = 25\text{ }^\circ\text{C}$ .

	$\text{Cu}^{2+}/\text{NA}$	$\text{Ni}^{2+}/\text{NA}$	$\text{Cu}^{2+}/\text{SA}$	$\text{Ni}^{2+}/\text{SA}$
$Q_s(\text{mg/g})$	95.24	13.64	106.38	10.94
$Q_s(\text{mg/m}^2)$	63.49	9.09	1.38	0.14



**Figure 10.** Removal of Ni(II) in aqueous solution by co-precipitation (25 °C, 60ppm).



**Figure 11.** Amount Cu(II) sorbed on apatite versus Ca(II) released in solution ( $T = 25\text{ }^\circ\text{C}$  and  $\text{pH} = 4$ ).

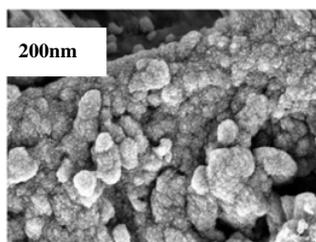
## 2.2. Isotherm sorption

Sorption isotherm represents the sorbed concentration  $Q_e$  (in mg per g of apatite) of the metal after equilibration versus the remaining concentration in the liquid phase  $C_e$  (in  $\text{mg}\cdot\text{L}^{-1}$ ).

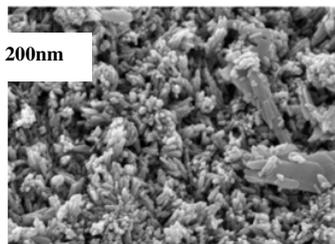
Examples of equilibrium sorption of Cu(II) trends at pH values of 4 and 5 on both NA and SA are presented in Figure 8 at 25 °C. Similar trends were also observed at 40 °C and for Ni(II) adsorption (not shown). Figure 8 show that increasing pH has negative effects on adsorption capacities of both NA and SA sorbents.

The fit to the linear form of Langmuir model (Figure 9) was examined by calculation of regression values ( $R^2$ ). The sorption of Cu and Ni ions on NA and SA follows the Langmuir isotherm model where the uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules [18]. The best recorded values of sorption capacity  $Q_s$  deduced by fitting experimental data to Langmuir model are given in Table 2 for NA and SA at pH4 and 25 °C.

Results of dissolution-precipitation between apatite (NA, SA and TCP) and  $\text{Ni}^{2+}$  are similar to those shown in Figure 10. We note that removal efficiencies of  $\text{Ni}^{2+}$  ions by co precipitation increase as far as amount apatite



**Figure 12.** SEM view of NA material after Cu(II) sorption.



**Figure 13.** SEM view of SA material after Cu(II) sorption.

increases until total elimination at about 60 mg of amount apatite. Low efficiency was shown with TCP.

### 2.3. Sorption mechanisms

When sorption of heavy metals occur on hydroxy apatite, an ion exchange process occurs leading to surface fixation of metals as insoluble phosphates against calcium ions release into solution [5, 11, 16]. Thus, amount of Cu(II) sorbed on NA and SA versus amount of Ca(II) released was investigated as shown in Figure 11. This figure shows that NA released amount of Ca(II) roughly similar to amount of uptake Cu(II) while SA retained Cu(II) slightly more than Ca(II) released to the solution.

Thomson et al. [2], found that synthetic hydroxy apatite had higher capacity than the natural one while carbonated synthetic hydroxy apatite released by an exchange process more calcium ions than non-carbonated ones would have done.

NA and SA were examined by SEM after sorption experiments as shown in Figures 12 and 13. Unlike NA, SA (Fig. 13) appears to be covered more with crystallites of formed precipitates.

## CONCLUSION

This study investigated the capability of natural and synthetic apatites (hydroxy apatites) to sorb Cu(II) and Ni(II) ions from aqueous solutions under batch conditions. Several features can be deduced from this study: Copper and nickel ions are well sorbed; sorption is pH and temperature dependent. Removal of copper or nickel ions from aqueous solutions is efficient on either synthetic or natural Hydroxy apatite but less by co-precipitation of metallic phosphate. 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 hydroxy apatite. The  $Q_s$  values obtained

lead to practical applications of apatite for waste water decontamination.

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