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Study of cobalt adsorption on an oxygenated apatite surface

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Abstract

The aim of this study was to evaluate the effectiveness of the oxygenated apatite (OA) to adsorb cobalt cations in solution. The factors influencing the adsorption, such as initial concentration of the metal in solution, the pH and temperature of the medium, the ionic strength and the temperature of calcination were investigated. The tests of cobalt adsorption show that the fixed amount (32,2 mg/g) is important compared with other matrices adsorbent. This retention capacity increases with increasing the initial concentration of cobalt, the contact time and the adsorbent dose. The optimum pH of adsorption is 6,4 and the ionic strength of the medium has a negative influence on fixation rate of cobalt due to the competitiveness of the electrolytes present in solution with the metal towards the adsorbent active sites. With respect to the calcination at 900 ° C, it reduces the adsorbent power of the AO due to the increase of crystallinity degree and the disappearance of the hydrated layer of apatite. As regards the process of cobalt adsorption, it can be explained by the Langmuir and Freundlich isotherms.

Keywords: oxygenated apatite; adsorption; cobalt.

1. Introduction

The oxygenated apatite (OA) belongs to the family of apatites chemical formula $Ca_{10}(PO_4)_6(OH)_2(O_2)$. It is characterized by a structure containing hexagonal tunnels along the c-axis wherein the inserted molecular oxygen acts as an antibacterial [1]. Its specific surface area relatively large, combined with its ability to exchange cations and/or anions they have made the AO a candidate in the treatment of water polluted by toxic heavy metals such as Cd, Pb, Zn, Cr, Hg, Co …. This matrix also has the advantage of being slightly soluble in a wide pH range (4-9) and thermostable. In addition, poorly crystallized apatites have, on their surface, a hydrated layer poorly organized, but labile, containing inorganic ions as Ca^{2+}, CO_3^{2-}, HPO_4^{2-} and PO_4^{3-}[2], [3]. This hydrated layer that evolves over time, would be responsible of the high reactivity of the apatites surface and gives them a very strong adsorption and ion exchange capacity. These properties could also be related to the presence of relatively mobile ionic species and easily exchangeable in this layer [4], [5]. Various methods have been proposed to purify water contaminated with toxic heavy metals. The solid phase extraction is still one of the most used methods due to the solid phase reusability, the use of non-toxic solvents and the fact that it generates little waste. In the case of the decontamination of polluted waters with cobalt, various inorganic and organic matrices have been proposed among which there are vermiculite [6], zeolite [7], kaolinite [8], manganese oxide hydrate [9], marine green alga [10] and hydroxyapatite [11], [12].

In this paper, we will discuss the results on the evaluation of the effectiveness of cobalt adsorption by AO and the factors that affect the retention, such as the initial concentration of metal in solution, the pH and temperature of the medium, the ionic strength and temperature of the calcinations. We also describe the models that explain the adsorption process.

2. Materials and Methods

2.1. Preparation of oxygenated apatite with a ratio Ca / P of 1.67

In a beaker, 50 ml of hydrogen peroxide 10% was mixed with 1.3740 g of calcium oxide. After dropwise addition of 50 ml of the diluted solution (H_3PO_4 + 10 % [H_2O_2]) on the walls of the beaker, the reaction mixture is kept under vigorous stirring for two hours. The resulting precipitate was then vacuum filtered, dried in an oven and then calcined at 300°C.

2.2. Characterization techniques of the synthesized apatite

The prepared apatite is analyzed by X-ray diffraction (XRD), using Cu-K□ radiation on a XRD Shimadzu 6000 powder diffractometer. The infrared spectra were recorded on a Shimadzu FTIR spectrophotometer type-8400S. Thermogravimetric analysis was performed using a Shimadzu apparatus (type: DTG - DTA-TG simultaneous 60). UV-visible data were obtained using a Shimadzu apparatus (type: UV prob 2,21). The specific surface and the pore distribution were determined respectively by BET (Brunaur, Emmett, Teller) and BJH (Barret, Joyner, Halenda) methods using an instrument Autosorb.

2.3 Experiment and measurement of the adsorbed metal amount

Cobalt chloride (0,35 g) was introduced into a beaker containing 200 ml water. After homogenization of the solution, 1 g of AO was added. The evolution of the cobalt concentration versus the time was followed by UV-Visile. The pH adjustment of the solution is achieved by addition of NH_3 or of HNO_3 (10^{-2} mol/L). The adsorbed amount (**Q**) of cobalt by AO is determined by difference between the initial concentration and the concentration at equilibrium using the following expression: $\mathbf{Q = (Co - Ce).V/m}$; where **m** (g) is mass of AO; **V** (l) is the volume of the solution; $\mathbf{C_o}$ (g/l) is the initial mass concentration of the solute in the liquid phase and $\mathbf{C_e}$ is the mass concentration of the solute concentration at equilibrium.

2.4. Adsorption kinetics

The model used is the HO and McKay (pseudo-second order model) is generally used to describe the adsorption phenomena of chemisorption type [13] and is expressed as the following equation: $\mathbf{t/q_t=1/k_2q_e^2 + t/q_e}$ **;** where **t** (min) is the contact time; $\mathbf{q_t}$ (mg/g) is the uptake of cobalt at time t; $\mathbf{q_e}$ (mg/g) is adsorbed amount at equilibrium and K_2 (g.mg^{-1}.min^{-1}) is the pseudo-second-order rate constant for cobalt in adsorption process.Initial rate constant of the intra-granular diffusion $\mathbf{k_d}$ can be calculated from the following equation [14]: $\mathbf{K_d=q_t/t^{0.5}}$ **;** where **t** (min) is the contact time and $\mathbf{q_t}$ (mg/g) is the uptake of cobalt at time t.

3-Results and Discussion

3.1. Characterization of the adsorbent

The structure of the prepared OA was analyzed using FTIR spectroscopy as shown in figure 1. The infrared absorption bands at 1046 – 1087 cm^{-1} and 962 cm^{-1} (PO_4^{3-}), 3560 cm^{-1} (OH^-), 1450 cm^{-1} (CO_3^{2-}) indicate that the synthesized AO is in a poorly crystalline apatitic form and slightly carbonated.

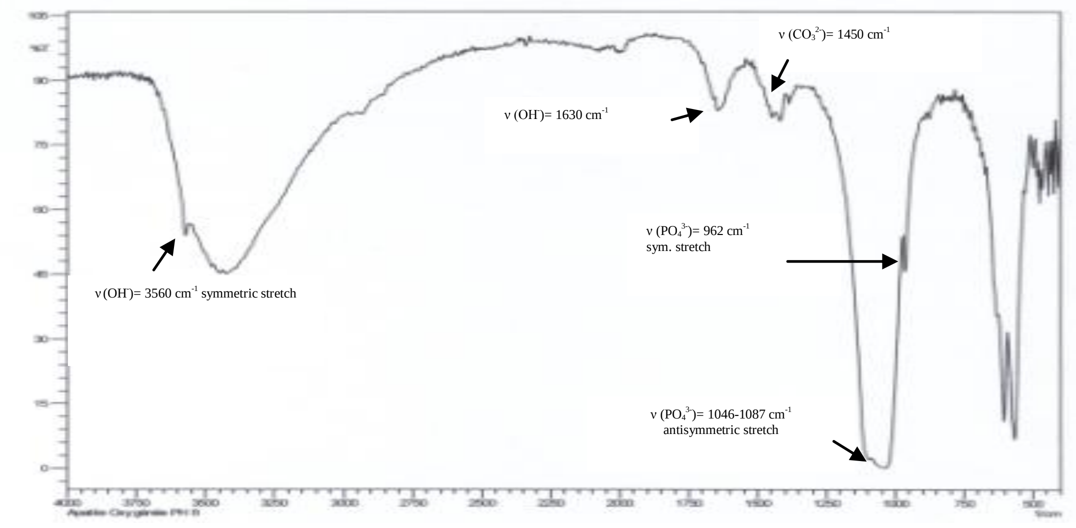


Figure 1: Infrared spectrum of the AO calcined at 300 ° C.

The X-ray diffraction patterns (Figure 2) represent the calcined AO at 300 ° C (**a**) and at 900 ° C (b). It appears from these diagrams that the synthesized product has evolved into a poorly crystallized apatite pure phase (case of **a**) and well crystallized (case of **b**).

The loss of mass and the thermal variations of the AO were followed by TGA and DTA from room temperature to 1000°C under a stream of nitrogen and with a temperature rise rate of 10°C/min. The TGA curve (Figure 3a) shows two mass losses which are very small at the beginning of the thermogram and at 600°C. The first mass loss is attributed to the desorption of water from AO surface. While the second loss, it corresponds to the elimination of residual carbonates (type A) detected by infrared spectroscopy at about1450 cm^{-1}. The substitution possibility of OH^- (hydroxyapatite type A) and/or PO_4^{3-} (hydroxyapatite type B) groups by the carbonate ion (CO_3^{2-}) has been described in the literature [15]. With respect to the DTA curve relating to the porous apatite (Figure 3b), it shows the presence of two exothermic effects occurring close to temperatures respectively of 50°C and beyond 450°C. Both effects correspond successively to the removal of water molecules adsorbed to the surface of this material and the elimination of carbonate ions.

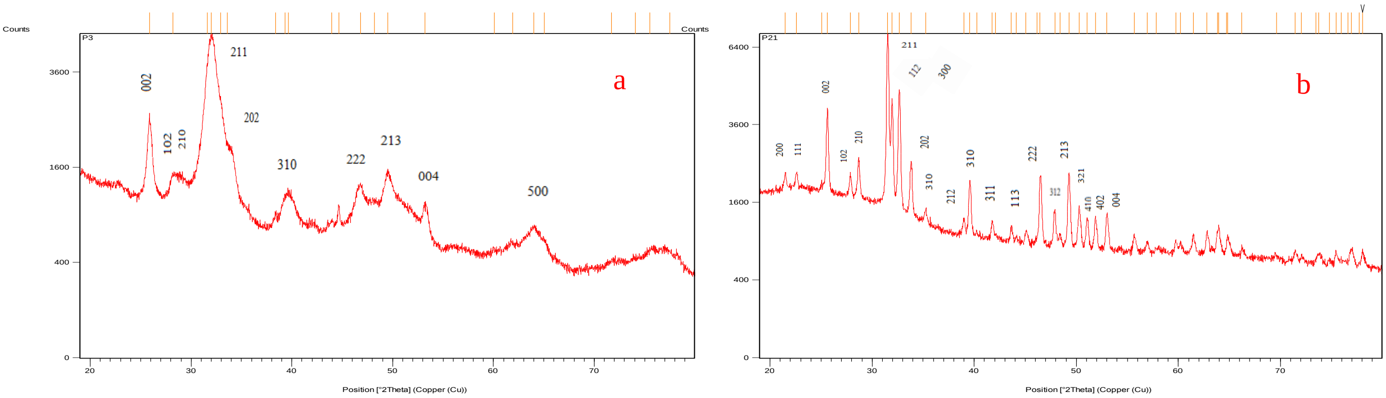


Figure 2: X-ray diffraction spectrum of the AO calcined at 300° C (a) and at 900° C (b).

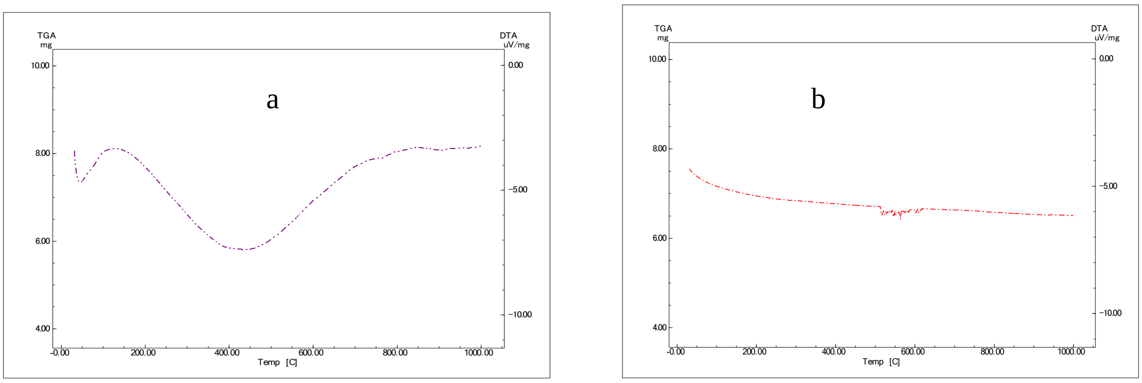


Figure 3: Thermogravimetric analysis (**a**) and Differential thermal analysis (**b**) of OA.

Figure 4 shows the Nitrogen adsorption-desorption isotherm on the oxygenated apatite. The hysteresis loop for the synthesized sample starts at a relative pressure P/P0 greater or equal to that due to hydroxyapatite (P/P_0=0,65). The fact that the hysteresis loop is activated at low relative pressures, we can confirm that the texture of the solid is very hard and well organized and that its mesoporosity is interesting. In addition, the existence of a hysteresis suggesting the presence of mesoporosity in the apatite surface in which a capillary condensation occurs. The measurement results of the specific surface (SS), the pore volume (Vp) and average pore diameter (Dp) of the apatite are given in Table 1.

Table 1: Specific surface area and pore size of the AO

Sample	Specific surface (**m^2/g**)	Porous volume (**cc/g**)	Pore radius (**A**)
Ca/P=1,67	141,6	0,686	50,207

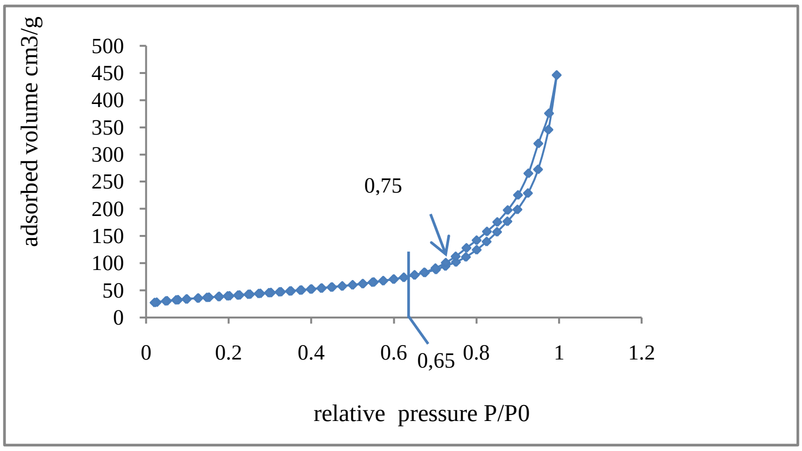


Figure 4: Isotherms of N_2 adsorption-desorption of oxygenated apatite calcined at 300°C.

The morphology observation of the prepared apatite was performed by scanning electron microscopy (SEM). To minimize the effects of load and achieve a resolution of 20 microns, we have worked under low voltage (30 kV). Prior to be analyzed, the powders are deposited onto an adhesive patch of carbon and metallic gold. The obtained images allow to visualize the morphology and grain distribution (Figure 5). We note that the particle size of the apatite is not uniform and it varies from 6 to 11 µm.

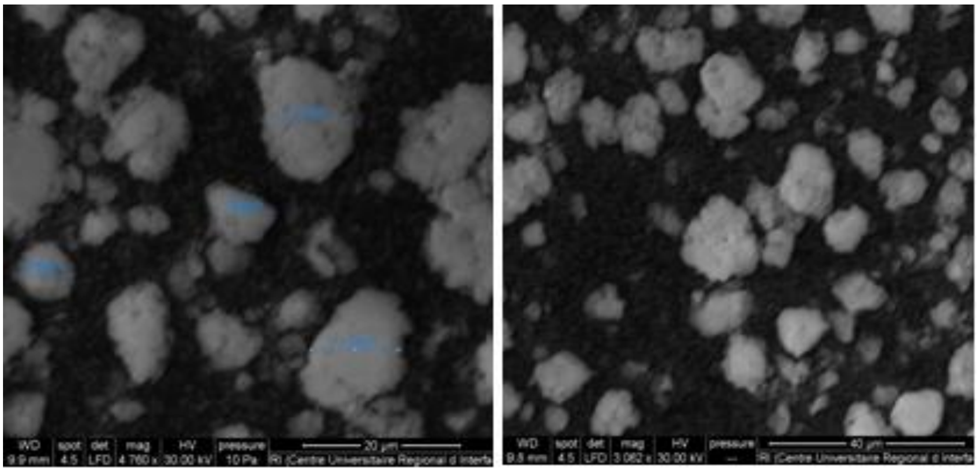


Figure 5: Images of the apatite (calcined at 300 °C) obtained by scanning electron microscopy.

3.2. Kinetic Study of the cobalt adsorption by oxygenated apatite

From Figure 6 (Langmuir model) that shows the cobalt adsorption by the AO versus the contact time, we can deduce that the adsorption took place in two steps: a quick first one which lasted during 60 min with a maximum amount of cobalt adsorption of 24,56 mg/g. The retention process is probably governed by an adsorption mechanism of ions on the apatite surface. A slower second one which starts at 60 min and continued until the end of the experimental period. This reduction of the cobalt adsorption may come from intra-granular distribution of cobalt ions (grain heart exchanges).

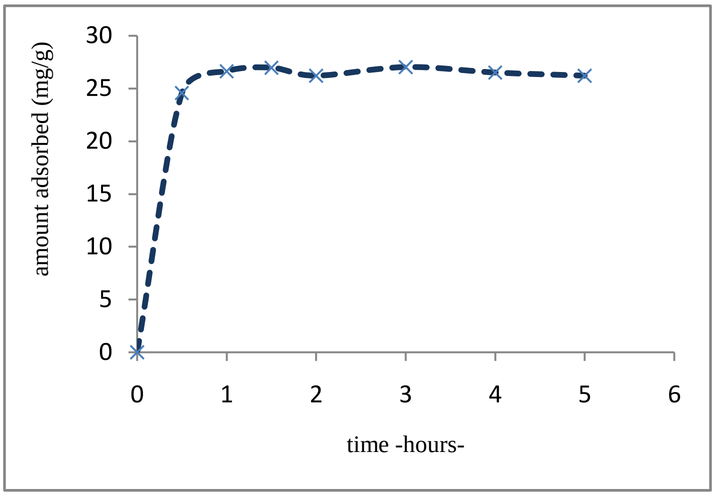


Figure 6: Kinetic of the cobalt adsorption by oxygenated apatite.

3.3. Modeling of adsorption kinetics

The pseudo-second order model was tested to investigate the process of cobalt adsorption by the AO (Figure 7). Kinetic parameters calculated from this model are given in Table 2. It appears from these results that the proposed model is in good agreement with the experimental data and the kinetics of the reaction is pseudo-second order type. We can also say that the chemical adsorption is substantial which means that the bonds existing between the adsorbate and the adsorbent are of medium intensity.

Table 2: Kinetic parameters calculated from the pseudo-second order model for the adsorption of cobalt by AO.

k_2 (g.mg^{-1}.min^{-1})	Q_e (calculated) (mg /g)	Q_e (experimental) (mg / g)	R^2
2,17×10^{-2}	27,25	27,02	0,9996

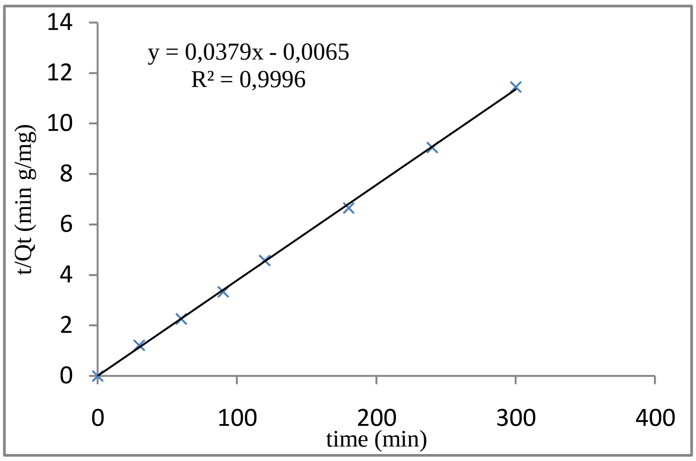


Figure 7: The pseudo-second order model for the adsorption of cobalt by AO.

3.4. Effect of initial cobalt concentration

The apatite adsorption capacity study of the cobalt as a function of the initial mass concentration of metal was examined (Figure 8, Table 3). The duration of the adsorption, the pH of the reaction medium and the mass of oxygenated apatite are respectively 0 to 5 h; 6,4 and 1g. The obtained results (Figure 8) shows that the amount of adsorbed cobalt increases with the increase in the apatite contact time. In terms of the metal adsorption kinetic, it is the same whatever its initial concentration.

Table 3: Amount of adsorbed cobalt (Q_{ads}) as a function of the initial concentration.

Initial concentration (g /L)	Q_{ads} (mg/g)
0,25	20,4
0,375	22,15
0,75	24,6
1,25	25,51
1,75	26,2

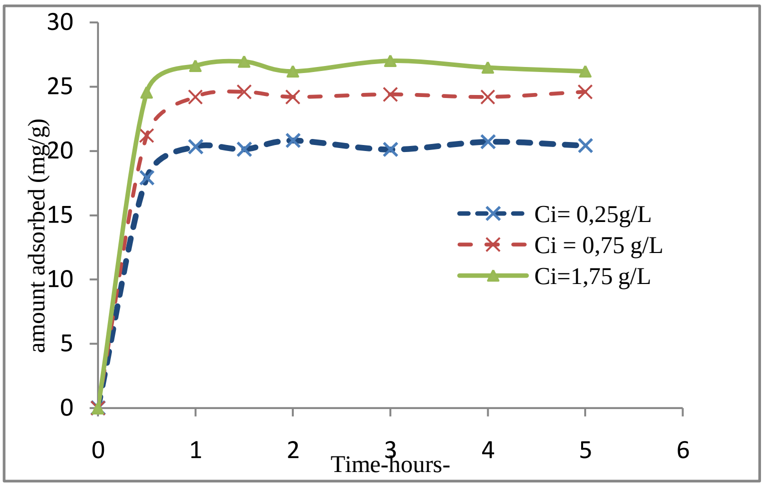


Figure 8: Effect of sorbent dose on cobalt adsorption.

3.5. Intra-granular diffusion modeling

The variation of the adsorbed amount as a function of time square root showed that the curve is formed as a gently sloping right which does not pass through the origin. Indeed, there is a rapid initial adsorption of cobalt ions on the apatite surface which diminishes as the surface is covered. The slow diffusion intra-granular takes place when the covering the outer surface is completed (Figure 9). The rate constant of the intra-granular diffusion (k_d) estimated at 6,86 10^{-2} mg/gmin^{0,5} indicates that it is not the determinant step of the reaction kinetic.

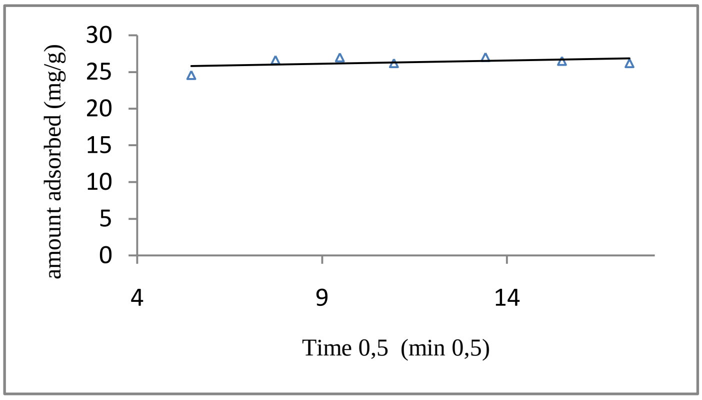


Figure 9: Variation of the adsorbed amount as a function of time square root.

3.6. Freundlich isotherm

The linear form of the Freundlich isotherm shown in figure 10 corresponds to the following expression:
ln Q = ln a+1/n ln Ce ; where **Q** (mg/g) is the adsorbed amount of cobalt at equilibrium; **a** is the empirical constant of the Freundlich isotherm (l/mg); n is the adsorption intensity and **C_e** (mg/l) the cobalt concentration in solution at equilibrium. The values of **a** and **1/n** estimated from the line of Figure 10 are respectively of 2,97 l/mg and 0,1044. These results show that the energy associated with the cobalt adsorption process is important (**1/n** = 0,1044) and chemical adsorption is significant. However, the adsorbent affinity towards the solute remains medium (**a** = 2,97).

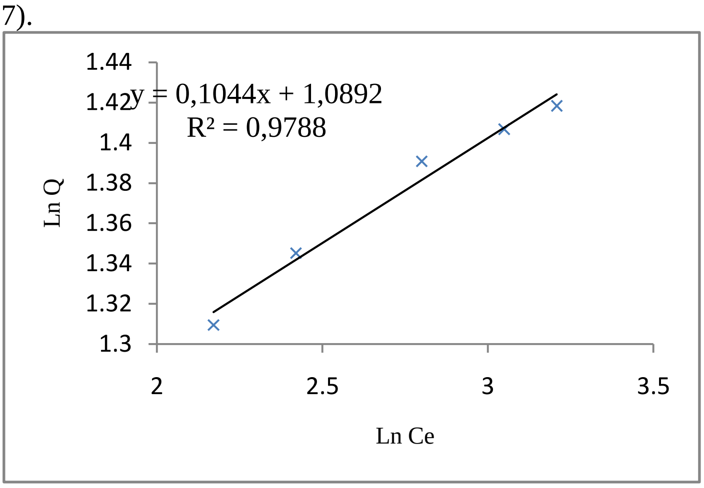


Figure 10: Experimental values of **a** and **1/n** estimated by the Freundlich model

3.7. Effect of initial pH of the solution

The pH of the medium is one of the important variables which significantly affect the extent of adsorption of metal onto the adsorbent. Therefore, cobalt adsorption on the OA as function of the initial pH of the metal solution was studied. The operating conditions are: Contact time is between 0 and 5 h; pH = 4,4; 5,4 and 6,4 and amount of OA = 1g.

From the experimental results, we note that the final pH of the solution is always higher than initially measured and the amount of the adsorbed cobalt is almost constant in this range of pH. A study of the cobalt adsorption by hydroxyapatite (HAP) in an initial pH range of 4-12, showed that the phenomena occurring at the surface of the adsorbent are as follows [16]: for initial pH values below the isoelectric point of the HAP (6,8), there is protons consumption on the surface of this later (sites: PO^- and $CaOH^0$) causing an increase in the final pH. for

the initial pH values above the isoelectric point of the HAP, there is consumption of OH^- ions via deprotonation of $CaOH_2^+$ and POH^0 sites existing on the surface which causes the decrease of final pH, and for pH solution greater than 8, there is precipitation of $Co(OH)_2$.
In our case, the final pH of the solution is always higher than initially measured due to the consumption of protons on the OA surface. This latter is either neutral or negatively charged and cobalt ions adsorption is almost constant (average value = 26,8 mg/g).

3.8. Retention isotherm

In this study, solutions of different cobalt concentrations containing 0,5% of apatite were prepared. After a contact time of 5 hours, the mixture is filtered and the pH of the medium is measured before and after adsorption. Finally, the cobalt concentration is determined by UV-visible spectroscopy. The cobalt isotherm retention reproduced by OA in Figure 11 shows that from an equilibrium concentration of the order of 2,35 g/l (C_i = 2,5 g/l), the maximum value of the adsorbed amount of about 32,2 mg/g is almost reached.

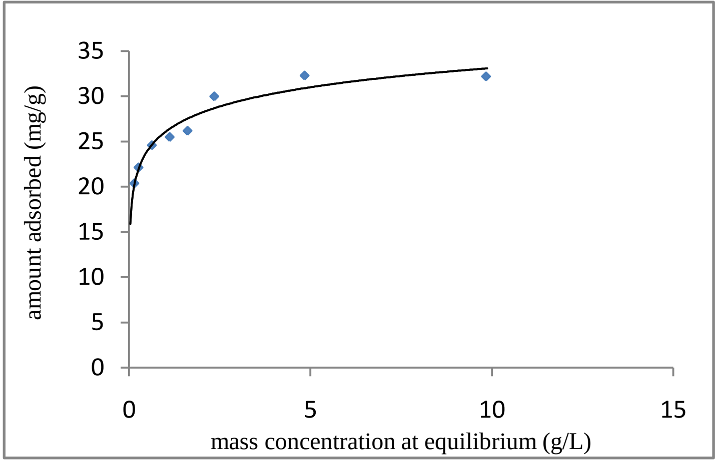


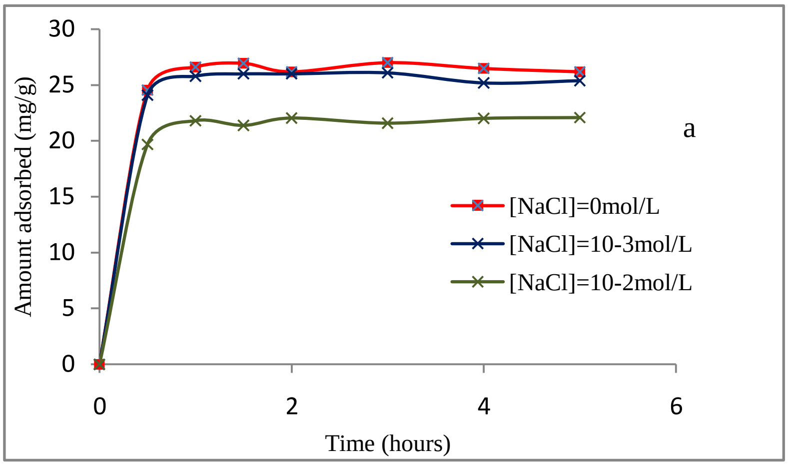
Figure 11: Isotherm retention of different cobalt concentrations.

3.9. Effect of ionic strength

The waste water often contain many ions such as Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, ... It is therefore necessary to study the influence of the presence of certain ions on cobalt removal by apatite material. The effect of ionic strength on the adsorption depends on both the surface of the adsorbent and of the nature of the electrolyte cation. It has been shown, in the case of an adsorption phenomenon governed mainly by an ion exchange mechanism, that an increase in ionic strength of the solution is accompanied by a significant reduction of adsorption capacity [17]. This behavior is attributed to the competition between the inorganic cations for the adsorption sites. It should be noted that the adsorption is affected by the nature of the counterion due to the difference in cation affinities towards the surface of the adsorbent. Figure 12 a shows the cobalt retention by apatite examined at pH = 6,5; room temperature and at different NaCl molarities (10^{-2} et 10^{-3} mol/l) for an initial mass concentration of the cobalt equal to 1,75 g/l. Increasing the salt concentration causes a significant decrease in the adsorption capacity. This behavior is attributed to the competition between the cation of the electrolyte and the cation of cobalt towards retention sites. Cobalt adsorption tests on apatite were performed in the presence of Na^+ and K+ ions at pH 6,5 and room temperature. The obtained retention isotherms are illustrated in Figure 12b. It is found that the retention capacity of the cobalt is influenced by the nature of the compensating cation. It is of the order of 22,1 and 24,4 mg/g for Na^+ and K^+ respectively. The variation of the adsorption capacity appears to be related to the affinity of the inorganic cation for apatite material. The more the cation affinity for OA is large, the more difficult is to displace it by cobalt cation. For the Na^+ ion, the retention capacity of the cobalt is relatively low (22,1 mg/g for Na^+ and 24,4 mg/g for K^+). This seems to be attributed to its affinity towards the active sites of the surface apatite, to its smallest size than K + and to its charge.

3.10. Effect of temperature on the cobalt retention

The cobalt retention tests by AO were performed at three temperatures: 15°C, 25°C and 35°C. The isotherm of cobalt retention by apatite shows that the amount of exchanged cobalt between the adsorbent and the adsorbate remains almost unchanged whatever the temperature. These variations do not appear to be significant. The average value of the adsorption capacity is of the order of 27 mg/g.



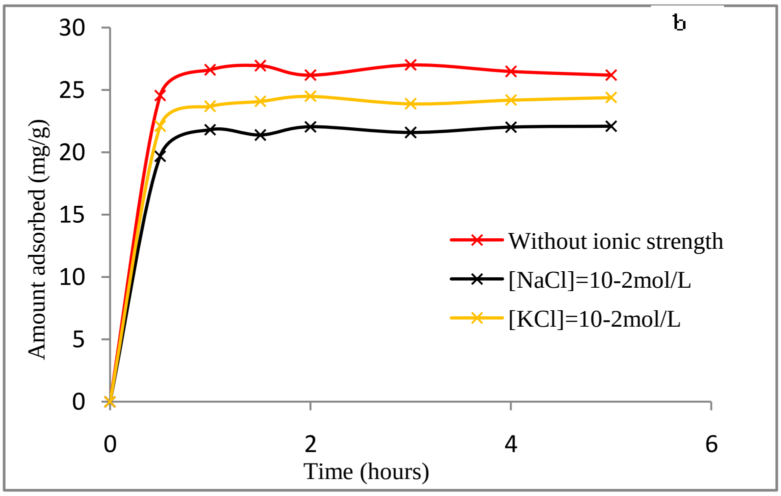


Figure 12: Variation of the amount of adsorbed cobalt versus time for different NaCl molalities (a) and effect of the NaCl-KCl ionic strength on the cobalt adsorption on the OA surface (**b**).

3.11. Effect of calcination temperature on the cobalt adsorption

The isotherms of cobalt retention by apatite calcined at 300 °C and 900 °C are illustrated in Figure 13.

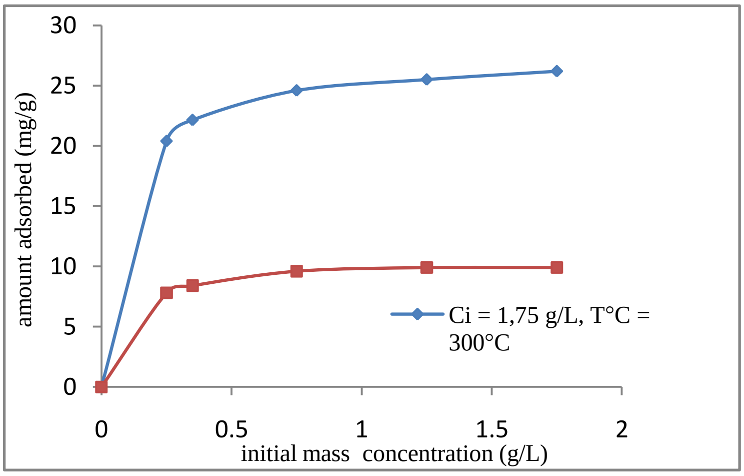


Figure 13: Isotherms of cobalt retention by apatite calcined at 300 °C and 900 °C.

It appears that the retention capacity of the cobalt is influenced by the temperature of calcination. They are of the order of 26,2 and 9,9 mg/g for the samples calcined at 300 °C and 900 °C respectively. The decrease of the adsorption capacity appears to be related to the increase of crystallinity degree and the disappearance of the hydrated layer of apatite (case of calcined apatite 900 °C).

Conclusion

The aim of this study was to evaluate the effectiveness of the oxygenated apatite (OA) to adsorb cobalt cations in solution. The factors influencing the adsorption, such as initial concentration of the metal in solution, the pH and temperature of the medium, the ionic strength and the temperature of calcination were investigated. The tests of cobalt adsorption show that the fixed amount (32,2 mg/g) is important compared with other matrices adsorbent. This retention capacity increases with increasing the initial concentration of cobalt, the contact time and the adsorbent dose. The optimum pH of adsorption is 6,4 and the ionic strength of the medium has a negative influence on fixation rate of cobalt due to the competitiveness of the electrolytes present in solution with the metal towards the adsorbent active sites. With respect to the calcination at 900 ° C, it reduces the adsorbent power of the AO due to the increase of crystallinity degree and the disappearance of the hydrated layer of apatite. As regards the process of cobalt adsorption, it can be explained by the Langmuir and Freundlich isotherms.

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