RESEARCH ARTICLE

ADSORPTION OF FLUORIDES ON DROMEDARY BONES CHARRED AND ENABLED WITH HCL

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ARTICLE INFO	ABSTRACT
	In this study, a new adsorbent has been developed by activating bone dromedary (calcined at 600 °C for 12 hours) with hydrochloric acid (HCl) at different concentrations, which significantly increased capacity for adsorbing fluorides. The effects of activator concentration were studied. The results show that the adsorbent is optimized for a concentration of the activator (HCl) around 0.05M. The adsorption isothermal data were well adjusted by the Freundlich model and the maximum adsorption capacity obtained by the Langmuir model is 17.24 mg / g at 25° C ± 2° C. The adsorption kinetics follows the pseudo second order model and the adsorption equilibrium is reached in 90 minutes.
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INTRODUCTION

Fluorine has a double effect on the living system. While the upper fluoride concentration to 1.5 mg / L leads to skeletal and dental fluorosis, a concentration less than 0.5 mg / L is responsible for tooth decay, because a low fluoride levels helps strengthen enamel (Razbe *et al.,* 2013). Prolonged consumption of water containing fluoride ions in a content of between 1.5 and 4 mg/L causes dental fluorosis. By prolonged exposure to even higher concentrations (4-10mgL-1), the dental fluorosis evolves into a skeletal fluorosis (Mohapatra *et al.,* 2002; Moturi *et al.,* 2002). Some aquifers in Niger, particularly in the regions of Maradi and Zinder, have abnormal levels of fluoride ions. The prolonged consumption of these waters has had serious consequences on the health of certain populations of Maradi. Approximately five thousand (5,000) children were suffering from dental fluorosis, five hundred (500) of them developed skeletal fluorosis. This abnormal presence of fluoride ions has rendered some water sources unsuitable for consumption. This greatly diminishes the already insufficient water resources in these regions (Denise Williams *et al.,* 2002). To reduce the fluoride ion content of drinking water, several processes have been developed (precipitation, ion exchange, reverse osmosis, Donan dialysis, adsorption, membrane processes, etc.)

(Hichour *et al.,* 1999; Saha *et al.,* 2012). For developing countries, including Niger, adsorption is the most appropriate method involving the less instrumentation and the availability of a wide range of pollutant-specific adsorbents (Ali, 2012; Saha *et al.,* 2012). The elimination of fluoride from drinking water by adsorption is currently widely used, given its cost and accessibility. This process is implemented with many materials (clay, activated carbon, calcined bone, etc.). This technique aims for accessibility of rural populations to simple and adapted water purification methods, the exploitation of degraded water resources, the valorization of local materials, the valorization of waste like dromedary bones and the protection of the environment. Charred bones are often used in fluoride adsorption without activation. The objective of this study is to determine the effect of activation of charred dromedary bones on their fluoride adsorption capacity. The activator is hydrochloric acid. According to the work of GOUROUZA *et al.,* the dromedary bone consists essentially of hydroxyapatite of formula $Ca_{10} (OH)_2 (PO_4)_6$ [9].

MATERIALS AND METHODS

Preparation of the adsorbent material: The adsorbent used is dromedary bone. It was prepared by a simple method of carbonization and activation. First, the bone was carbonized at 600 ° C for 12 hours in ceramic crucibles to remove organic

matter and odors. Then, in each of five solutions of hydrochloric acid (HCl) of respective concentrations 0.01M; 0.05 M; 0.1 M; 0.5M and 2M, was introduced 20 g of carbonized dromedary bone (OC) and ground. The OC stays for 24 hours in the HCl solution with stirring. The products of activation were washed with distilled water and dried in an oven at 105 ° C for 24 hours.

Investigation of the conditions of preparation: The effect of the concentration of the activator on the stability of the adsorbent was investigated by determining the content of calcium, fluorides and that of phosphates contained in the supernatant after activation. Calcium was dosed by EDTA titrimetry. Fluoride and phosphate were dosed by colorimetric with a DR 3800 spectrophotometer.

Adsorption experiments: Adsorption experiments were carried out with 0.4 g of adsorbent in 50 ml of fluoride solution (10 mg / l) in 100 ml polyethylene flasks. All adsorption experiments were carried out at room temperature (25 ± 2 ° C) for 24 hours with stirring. After adsorption, the samples were filtered through a 0.45 μm polypropylene membrane fiber and the residual fluoride concentration in the solution was determined by a DR / 3800 molecular absorption spectrophotometer at the wavelength of 580 nm. Fluoride solutions were prepared by dissolving NaF in distilled water. To examine the effect of activator concentration on the adsorption capacity of the activated adsorbent, the five adsorbents obtained after activation (charred and activated bone (OCA)) and no activated OC were used under the same experimental conditions of adsorption.

Adsorption isotherms and kinetic adsorption studies: In this study, Langmuir isotherm, Freundlich isotherm, Lagergren's first and pseudo-second order, and interparticle diffusion were used to interpret the experimental data of the adsorption process. The qe versus Ce curve, ie the adsorption isotherm, has been adjusted with the Langmuir model and the Freundlich model. The adsorption kinetics showed the relationship between the adsorption capacity (qt) and the adsorption time (t) between the start and the equilibrium of the adsorption process, which reflected the adsorption rate. The adsorption curves as a function of time were adjusted to the first and second order kinetic models. The adsorption capacity (qe) was calculated as the amount of fluoride adsorbed per unit mass of the adsorbent.

$$q_e = \frac{(C_0 - Ce)V}{m}$$

Where Co (mg / L) is the initial fluoride concentration and Ce (mg / L) equilibrium fluoride concentration; m (g) is the mass of the adsorbent used; V (L) is the volume of the fluoride solution.

RESULTS AND DISCUSSION

Influence of the concentration of hydrochloric acid on the stability of the OC: Figures (1 and 2) give the fluoride content and calcium content of the supernatant after activation of OC at different concentrations of hydrochloric acid. The results of Figures (1 and 2) show an abnormal presence of calcium and fluoride in the supernatant after activation of OC. This presence of fluorides indicates the presence of fluorinated compounds in the OC. These same results also show that the

calcium or fluoride content in the supernatant increases as the concentration of activator used increases, indicating partial dissolution of the OC during activation. The OC dissolution rate during activation is a function of the concentration of the activator. According to the work of Nezli *et al.,* the alkaline pH of water decreases the chemical activity of calcium and promotes the alteration of fluoride minerals (Nezli *et al.,* 2010). The results of Figures (1 and 2), show that the amount of free fluoride in the supernatant after activation is inversely proportional to the pH of the activator.
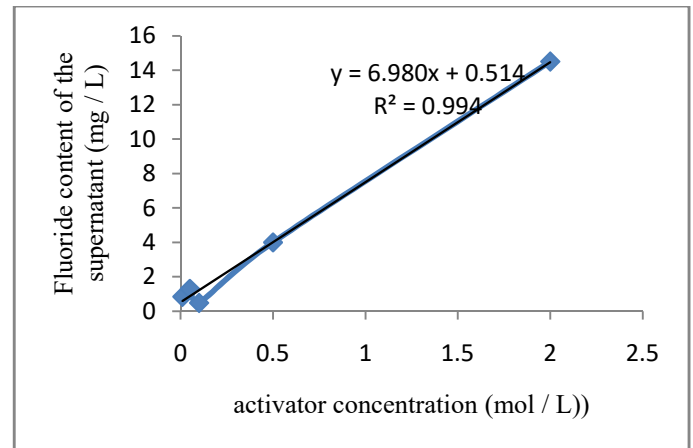

Figure 1. Fluoride content of the supernatant after activation of OC at different concentrations of HCl, OC 20g mass
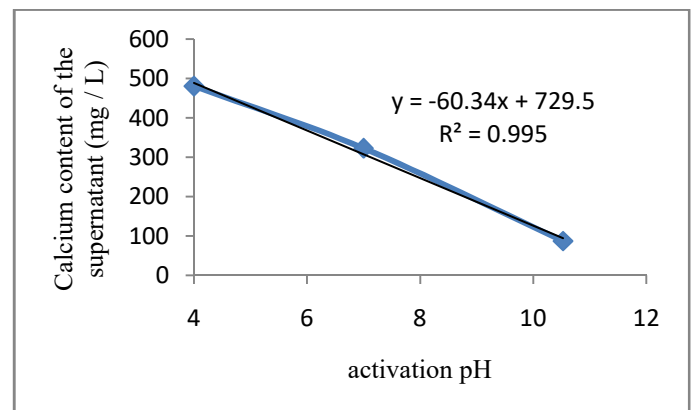

Figure 2. Calcium content of the supernatant after activation of OC at different concentrations of HCl, OC mass 20g
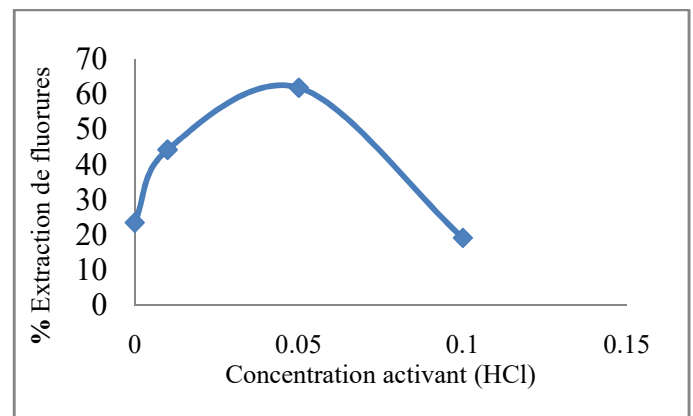

Figure 3. Percentage of fluoride extraction by OCA as a function of activator concentration (adsorbent quantity 0.4 g, fluoride concentration 10 mg L-1 and contact time 24 h)

This indicates that the fluorinated minerals contained in the OC are more stable in alkaline medium than in acid medium.

These results are in agreement with those of J. C. Elliot, who indicate that the solubility of hydroxyapatite depends not only on the initial chemical composition of the samples, but also on the pH of the medium in which it is found (Elliot, 1994). According to the work of Karima ACHELHI, the presence of fluorides in hydroxyapatite decreases its solubility (Karima ACHELHI, 2012). These results make it possible to assume that, when hydroxyapatite containing fluorinated compounds is in an aqueous medium, the fluorinated compounds pass into solution before hydroxyapatite. The phosphate content of the supernatant after activation of the OC at the respective concentrations 0.01 M and 0.05 M are respectively 0.39 mgL-1 and 2.78 mgL-1, which confirms the influence of the concentration of the activating the dissolution rate of the OC during activation.

Effect of activation on the adsorption capacity of fluorides on OCA: Figure 3 gives the percentage of fluoride removal by activated OC with HCl (OCA) at the following concentrations: 0M; 0.01M; 0.05M and 0.1M HCl. The results of figure 3 show that the extraction rate of the OCA is greater than that of the OC when the concentration of the activator (HCl) is between 0.01M and 0.08M. The extraction rate of the OCA is maximum, when the activation takes place has a concentration of HCl close to 0.05M. According to Ma, Y. Shen, *et al.,* the pH of a solution affects the shape of the fluoride as well as the surface charge of the adsorbents (Ma *et al.,* 2014). According to Ma, Y. Shen, *et al.,* the pH of a solution affects the shape of the fluorides in the presence as well as the surface charge of the adsorbents in the aqueous medium (Ma *et al.,* 2014). The rate of fluoride extraction obtained with OCA may be due to: either a change in the surface charge of the OC during activation, or the pH of the aqueous medium during adsorption, or a modification of the form of fluorides in solution. According to F. R. Eirich, the surface charge of a material is a function of the pH of the aqueous medium in which it is found (Eirich, 1977). Let x be the pH of the aqueous solution in which the solid exists under a neutral electric potential:

-if pH <x, the net charge of the material surface is positive;
-if pH> x, the net charge of the material surface is negative.

Optimization of the contact time: It is important to study the effect of the contact time required to achieve equilibrium when designing batch adsorption experiments. In this study, a set of experiments was conducted during adsorbate-adsorbent contact times ranging from 5 min to 90 min, at constant temperature, to evaluate the time required to reach equilibrium. The results in Figure 4 show that the rate of adsorption of fluorides on OCA is maximal in the first 20 min. They also show that the adsorption capacity 4.3 mg / g is reached in 60 min. According to P. Saha *et al.,* the rapid adsorption rate at the initial stage can be explained by an increased availability of the number of active binding sites on the surface of the adsorbent (Saha *et al.,* 2010). The effect of the initial fluoride concentration on OCA extraction percentage is studied at various fluoride concentrations (4; 10; 15; 21; 25 and 33 mg / L), fluoride solution volume (100 ml) OCA mass (0.4 g) at pH 7 and 25 ° C. It is well observed in Figure 5 that as the initial fluoride concentration increases, the percentage of fluoride removal by the OCA increases. The higher extraction capacity at a higher concentration was predictable because, generally, the adsorption capacity of the

adsorbent increases by increasing the initial concentration of the adsorbate.

Adsorption isotherms: The adsorption isotherms give qualitative information on the nature of the solute-surface interaction as well as the specific relationship between the adsorbate concentration and its degree of accumulation on the surface of the adsorbent at constant temperature (Jingru Liu *et al.,* 2013; Macka, 1997). In this study, in order to understand the fluoride adsorption mechanisms on OCA, the equilibrium data were analyzed using the Langmuir and Freundlich isothermal models.
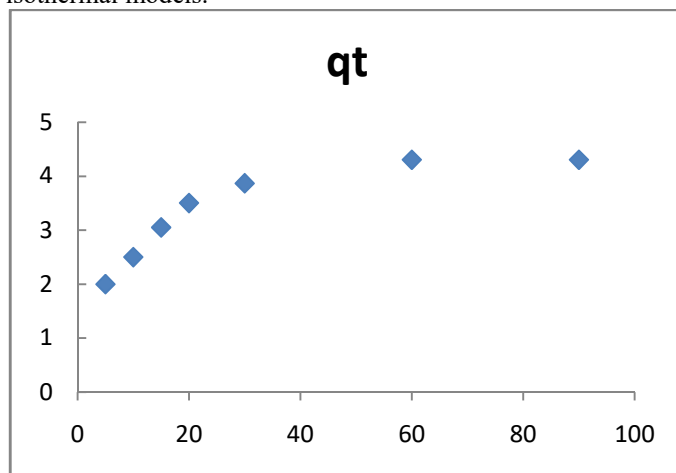

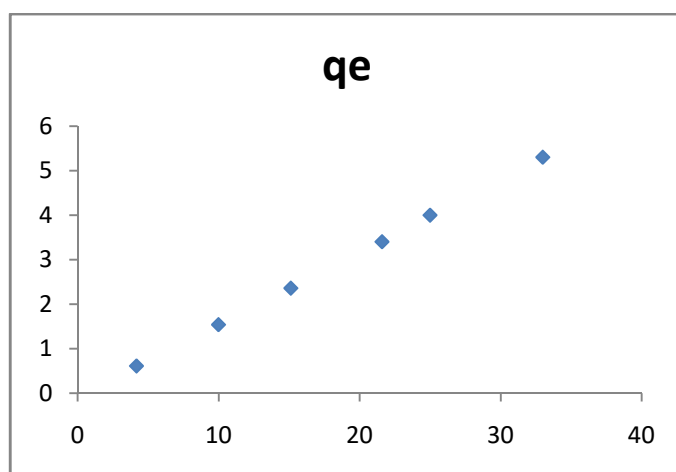
Figure 4. Effect of contact time on adsorption capacity

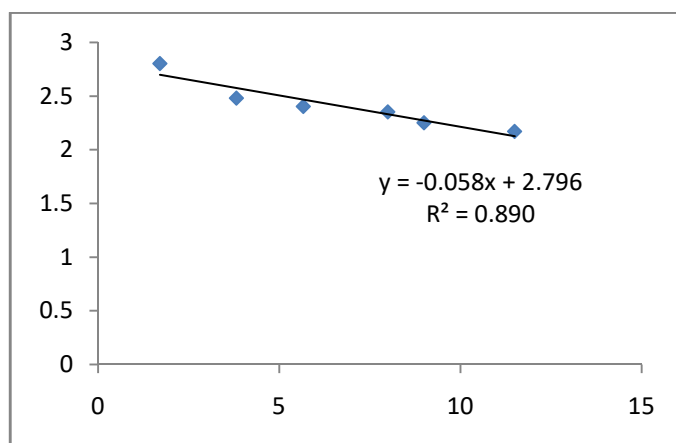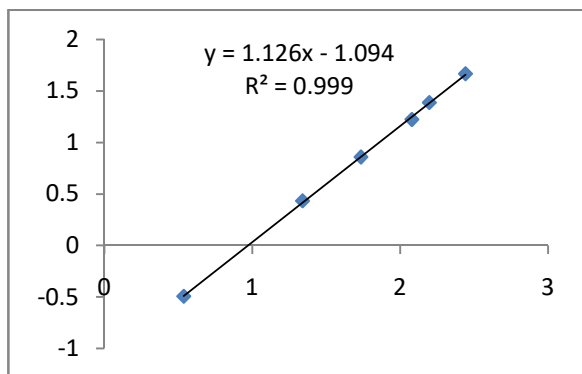**Figure 5. Effect of initial concentration of adsorbate**

Figure 6. Langmuir isotherm of fluoride adsorption on OCA

The adsorption isotherms were obtained from the representation of the amount of fluoride adsorbed on OCA (qe (mg / g)) as a function of the concentration of fluoride in equilibrium solution (Ce (mg / L)) see figures (6 and 7). qe and Ce were obtained from experiments conducted at various fluoride concentrations (4; 10; 15; 21; 25 and 33 mg / L). The parameters listed in Table 1 show that the data fit the Freundlich isothermal model better than the Langmuir model in terms of the higher R^2 of 0.999. According to S.P. Dharupaneedi, *et al.,* this reveals that fluoride adsorption has occurred on heterogeneous OCA surfaces, probably in a multilayered form (Dharupaneedi *et al.,* 2014).

Figure 7. Freundlich isotherm of fluoride adsorption on OCA

Table 1. Parameters of Langmuir and Freundlich isotherms of OCA

Adsorbent	Adsorbate	Freundlich isotherm $lnqe = lnKf + \dfrac{1}{n}lnCe$			Langmuir isotherm $\dfrac{Ce}{qe} = \dfrac{1}{KLqm} + \dfrac{Ce}{qm}$		
		K_F(mg/g)	n	R^2	K_F (L/mg)	q_m (mg/g)	R^2
OCA	F-	0,335	0,888	0,999	0,0207	17,24	0,890

Table 2. Values of kinetic parameters

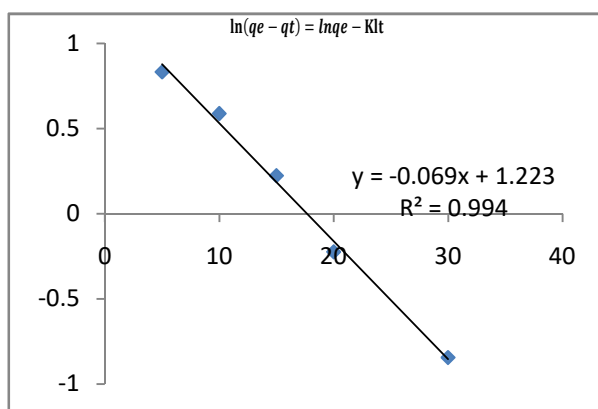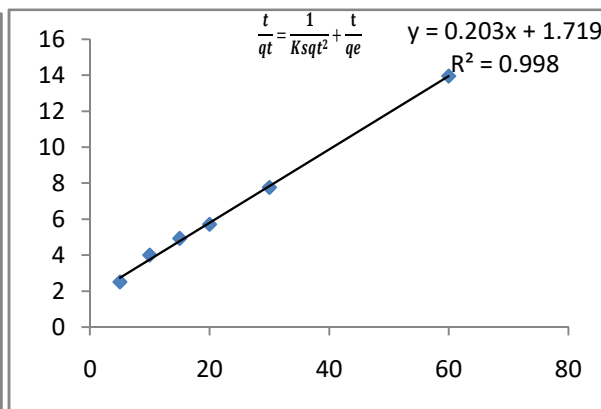| Adsorbent	Adsorbate	Pseudo-first-order model $\mathbf{ln(qe - qt) = lnqe - Klt}$			Pseudo-second-order model $\dfrac{t}{qt} = \dfrac{1}{Ksqt^2} + \dfrac{t}{qe}$			Intra-particle diffusion model $q_t = Kpi\, t^{0.5} + Ci$
		q_e (mg/g)	K_1(min^{-1})	R^2	K_2 (g.mg^{-1}min^{-1})	q_e (mg/g)	R^2	K_1(mg g_1 min$^{0.5}$) C1 (mgg^{-1}) R_1^2 0,675 0,442 0,992 K_2(mg g_1 min$^{0.5}$) C2 (mgg^{-1}) R_2^2 0,235 2,499 0,971
CBCA	As(V)	3,397	0,069	0,994	0,023	4,926	0,998	

Figure 8. First order of Lagargren

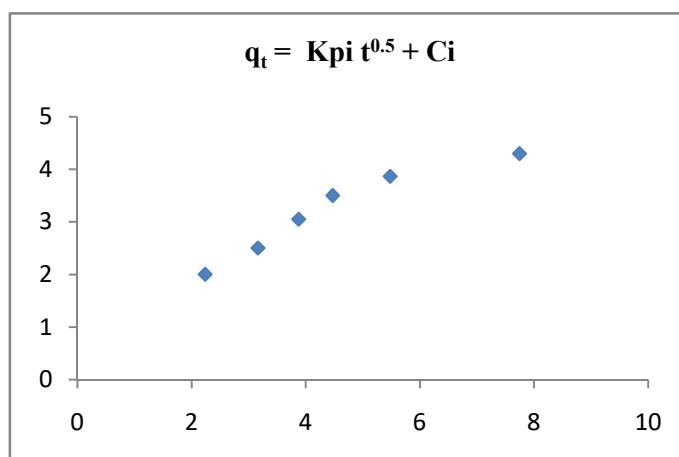**Figure 9. Lagargren's second order**

Figure 10. Interparticular Diffusion

Kinetic studies of adsorption: Given that, the kinetics of fluoride adsorption on OCA is important for the design of appropriate adsorption technologies; pseudo-first-order, pseudo-second-order kinetics and the intra particular diffusion model have been used to adjust the fluoride adsorption data on the OCA to explore the behavior of fluoride adsorption (Hu *et al.,* 2015; Rosales *et al.,* 2015). The pseudo-first order generally applies during the first 20 to 30 minutes of the adsorption process (Ncibi *et al.,* 2008). The equation used to describe the adsorption isotherm (Lagergren, 1988) is:

$$qt = qe(1 - e^{-k1t})$$
$$\ln(qe - qt) = lnqe - \text{Klt}$$

Where qe and qt are, respectively, the amount of fluoride absorbed per unit mass (mg g-1) at equilibrium and at any time t, k1 is the constant of the pseudo-first order adsorption rate (min-1). The kinetic curve of ln (qe - qt) versus t of fluoride adsorption on the studied OCA is shown in Figure 8. The pseudo-second order equation assumes that the process of adsorption involves a chemisorption mechanism. The pseudo-second-order model used is the following (Ho, 1995):

$$\frac{t}{qt} = \frac{1}{Ksqt^2} + \frac{t}{qe}$$

Where qe and qt are, respectively, the amount of fluoride absorbed per unit mass (mg g-1) at equilibrium and at any time t. Ks is the second order frequency constant (g mg-1 min-1). The kinetic curve of t / qt as a function of t of the adsorption of fluorides on the studied OCA is shown in Figure 9. The results in Table 2 show that the adsorption data better fit the pseudo-second order kinetic model, with $R^2 = 0.998$ higher than that of the pseudo-first order kinetic model. In addition, the equilibrium fluoride absorption capacity obtained from the pseudo-second-order kinetic model was almost equal to that obtained experimentally, ie 4.3 mg / g. According to Onyango *et al.,* 2006, then Torres-Pe're *et al.,* 2008, this indicates that chemical adsorption was the step controlling the rate in the fluoride adsorption process and that the fluoride adsorption process depends more on the number of fluorides present in the solution than on free OCA sites on the surface (Onyango *et al.,* 2006; Torres-Pe´ rez *et al.,* 2008). In addition, K1 = 0.675 of the interparticle diffusion model indicates that the fluoride adsorption rate on the OCA was much higher, which is consistent with the equilibrium time results. Figure 9 shows that the adjusted curve of the intraparticle diffusion model can be divided into two linear segments, indicating that the adsorption process followed two steps. According to Rosales *et al.,* Ki1 and Ki2 are related to fluoride adsorption rates during both steps, namely surface adsorption and intraparticular diffusion (Rosales *et al.,* 2015).

Conclusion

In this study, dromedary bone charred and activated with HCl (OCA) and dromedary bone charred but not activated (OC) were applied for fluoride removal from water. The OCA fluoride adsorption capacity obtained experimentally (4.926 mg / g) is significantly higher than that obtained with the non-activated OC (< 1 mg /g).

The OCA has shown good performance in removing fluoride from water. The isothermal data were well adjusted by the Freundlich model, which indicated that fluoride adsorption occurred on heterogeneous OCA surfaces, probably in a multilayered form. The results of this study demonstrate that OCA is a promising adsorbent for the removal of fluoride from aqueous solutions and will allow the upgrading of waters polluted by fluoride is cheaper.

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