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# Elimination of fluoride ions from an aqueous solution with charred beef shoulder blade bones

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## Abstract

This study was centered on the effects of contact time, initial fluoride ions concentration and the adsorbent dose on fluoride ions sorption by charred beef bones. The most efficient sorption system was observed by using 8 g L-1 of calcined bones. The Lagergren pseudo second order model describes the kinetic processes of sorption. That of Freundlich discribes the process of isotherm adsorption. The results of the study showed that the sorption reaction was spontaneous and that the mechanism on the material was chemisorption.

*Keywords:* beef shoulder blade bones; Calcination; Adsorption; Defluoration

## 1. Introduction

The presence of fluoride in drinkable water, within the permissible limits of 0.5-1.0 mg L-1, is beneficial to the production and maintenance of bones and teeth, while excessive consumption of fluoride causes fluorosis of the teeth or the skeleton. It is a chronic disease that manifests itself by a mottling of teeth in mild cases, softening of the bones and nerve damage in severe cases [1, 2]. The former commonly known as dental fluorosis "spotted enamel" was recognized as one of the manifestations of chronic toxicity due to the presence of fluoride in drinkable water [3, 4]. Contamination of groundwater / surface water could either come from natural geological sources or sectors using fluoride compounds as raw materials [5]. Excess of fluoride in drinkable water can be removed by using chemical precipitation and adsorption phenomena on the surfaces of minerals. Materials such as calcium phosphate, charcoal, bone apatite, activated alumina, activated carbon were tested for the removal of fluoride. Recently, hydrotalcite compounds and their calcined materials were used for the same purpose [6, 7]. The hydroxyapatite has ben studied as an adsorbent of fluoride under some conditions [8] by considering the effect of some important parameters such as contact time [9, 10], the adsorbent dose [11], the particles size, the pH of the solution, the presence of other anions and the initial fluoride concentration [12]. The substitution of fluoride ions by OH groups in the hydroxyapatite network was found to be irreversible. It was reported that only apatite and calcium orthophosphate can incorporate fluoride ions [13]. More recent studies have recognized the importance of ion-exchange properties of apatites in a variety of areas. Current methods used to remove fluoride from water can be divided into two categories namely: the precipitation of calcium fluoride and aluminum salts used to remove fluoride from industrial wastewater [14]. However, with a low concentration of fluoride, many sorbents lose their fluoride removal capacity [15]. The lower limit for fluorine reduction by most adsorbents is superior to 2 mg / L [16] and, therefore, they are not suitable for drinkable water, as some of them cannot operate at extreme pH value [17]. Among the adsorbents studied so far, nano-hydroxyapatite (n-PAHs) were considered good adsorbent because of their low cost, and greater capacity of defluorination [18]. The aim of this work was to study systematically parameters such as contact time, initial concentration of fluoride ion and the adsorbent dose to elucidate the fluoride ions sorption behavior by calcined beef bone. Consequently, calcined beef bone flour was prepared and tested for its applicability as an agent of defluorination.

## 2. Materials and methods

### 2.1. *characterization of the adsorbent*

The material used for the adsorption of fluoride was beef scapula calcined at 600 ° C for 20 hours. Before any use, this material was subjected to a series of analyzes including XRD, IR, and BET to characterize it.

### 2.1.1. *Infrared Spectrometer (IR)*

The infrared (IR) spectrum was obtained using a spectrometer" Universal ATR (Attenuated Total Reflectance) PERKIN ELMER over a spectral range of 400-4000cm-1.

### 2.1.2. *Analysis by X-rays diffraction*

The mineralogical composition of the calcined cattle bones was determined by X-ray diffraction using a Bruker X-ray diffractometer (Model D5000) in ɵ/2ɵ mode (Scan 3-15 ° or 3 ° to 30 ° in steps of 0.02 ° for a period of 1s, Cu anticathode , 40 kV - 30 mA).

### 2.1.3. *Nitrogen adsorption- desorption isotherms*

The specific surface area (Total SA), the surface of the micro-pores (micro SA) and pore volume (Total PV) of the calcined cattle bones were determined by adsorption / desorption of nitrogen at 77 K using a SORPTOMATIC 1990 Thermoquest.

### 2.2. *Sorption experiments*

Defluorination studies were conducted to optimize various experimental conditions such as adsorbent dose, initial concentration of fluoride and contact time. The defluorination capacity qe on the adsorbent (charred beef bones) was calculated from the difference between the initial concentration Co and the residual concentration Ct in solution as follows:

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

where m and V are respectively the mass of adsorbent and the volume of the solution. The sorption kinetics isotherms were carried out by adsorption experiments made in batches by mixing 0.2 g adsorbent with 20 ml of sodium fluoride containing 5 mg / L as initial fluoride concentration in polyethylene bottles. Throughout the experiment, the mixture was stirred at a speed of 800 revolutions per minute at room temperature (27 ° C ± 1). The effect of different initial fluoride concentrations 5, 10, 20 and 25 mg / L, different adsorbent doses 1, 2, 4, 6, 8, 10 g / L and different contact times of 5 min to 24 hours on the rate of sorption were studied. The final fluoride concentration was measured using a Chromeleon (c) 1996-2001 Dionex Version 6.80 Build 2212.

## 3. Results and Discussion

### 3.1. Infrared *Spectrometer (IR)*

IR spectrum (Figure 1) shows bands in the range of 1100-1000 cm -1 (stretching mode) characteristic of mineral phases of calcified tissues such as bone or teeth. calcium hydroxyapatite, Ca10 (PO4) 6 (OH) 2, is their main inorganic constituent [20,21]. The band at 962 cm -1 is attributed to bending and stretching vibrations (P-O) group of PO43-and that at 1087 cm-1 is attributed to the $CaCO_3$ group [22, 23]. According to Elliott, 1994, these indicate that the $CO3^{2-}$ ions are not structural but adsorbed on the apatite surface [24].

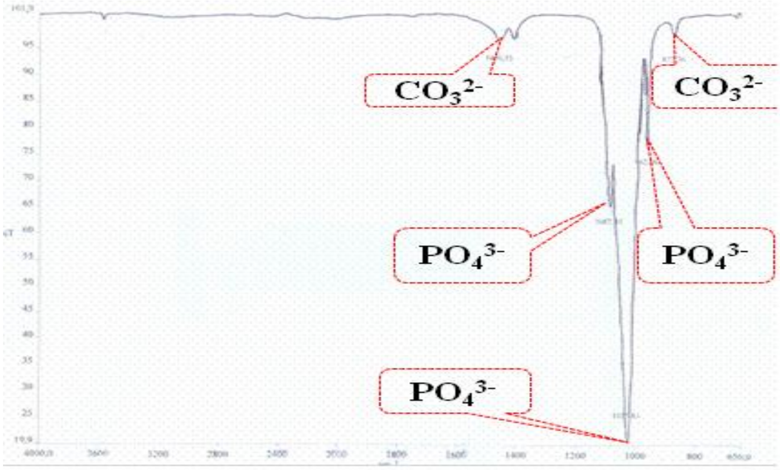

**Figure 1:** IR of calcined beef bone

### 3.2. Analysis *by X-rays diffraction*

Interreticulate spacing in angstrom (Å) around (3.45, 2.82, 2.79, 2.72, 2.64, 2.26, 1.95, 1.88) of the diffractogram, Figure 2 indicates that calcined bone contains hydroxyapatite [19].

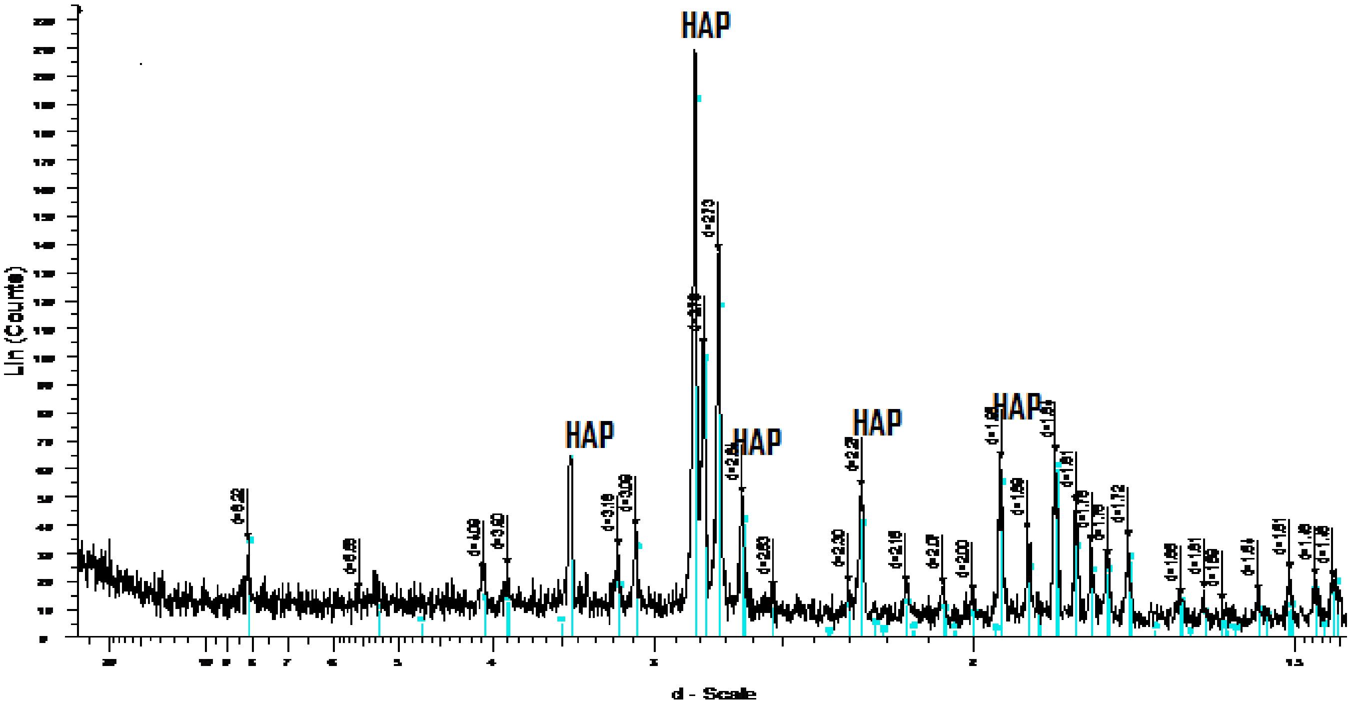

**Figure 2:** XRD diffractogram of the calcined beef bones. HAP = hydroxyapatite

### 3.3. *Nitrogen adsorption- desorption isotherms*

The calcined cattle bone Pore volume (Gurvich) at $p/p^0$ 0,95 is 0,014 $cm^3/g$. It's BET Surface area was 11,32 $m^2/g$, the Micropore volume was 0,0074 $cm^3/g$ and it's total surface area De Boer was 11,66 $m^2/g$.

### *3.4. Effect of contact time on the rate of adsorption*

Figure 3 illustrates the effect of contact time in the range of 5-180 min on the capacity of defluorination of calcined beef bone with 10 mg L-1 as the initial fluoride concentration and 5 g L-1 of adsorbent at room temperature.

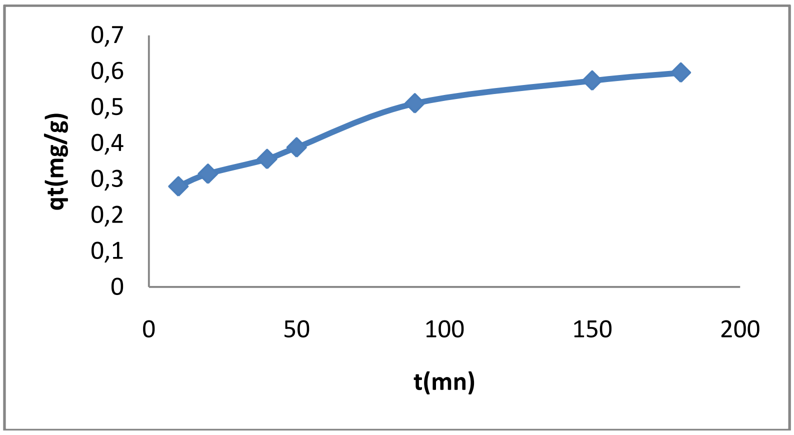

**Figure 3:** effect of contact time on the ability of calcined beef bone defluorination

It shows that the adsorption took place in two stages: an initial rapid phase, which lasted 100 minutes and a slower second phase which continued until the end of the experimental period. The balance was not achieved in a stirring time of 180 min because the sorption was still rising. The amounts of fluoride adsorbed increases with contact time increase. During these 180 minutes, the beef charred bones registered a 0.596 mg / g defluorination capacity.

### *3.5. Effect of adsorbent dose on the rate of adsorption*

Figure 4 shows that the amount of the adsorbent influences the adsorption percentage.

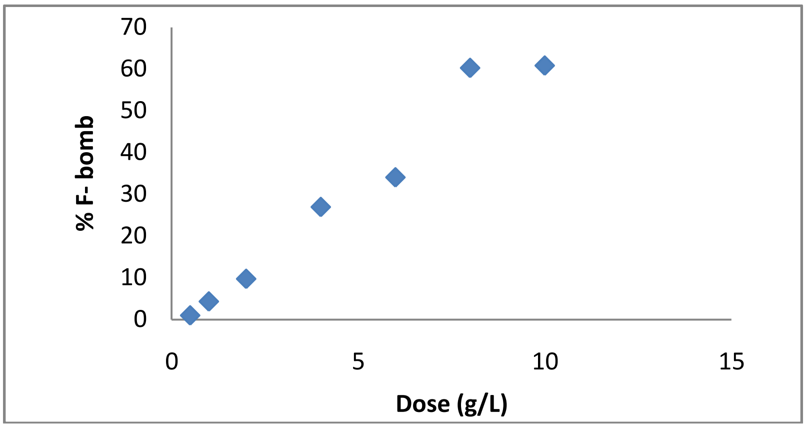

**Figure 4:** Effect of adsorbent dose on percentage extraction of fluoride by bone charred beef

The fluoride adsorption percentage by the calcined beef bone increases with the mass of the adsorbent dose which goes from 0.98 to 60.83% when the dose increases, from 1 to 10 g L-1. When the adsorbent dose increases from 8 to 10 g L-1, the extraction percentage increases from 60.27 to 60.83, indicating that the optimal dose is 8 g L-1 which shows the good charred beef bone adsorption properties.

### *3.6. Effect of initial fluoride concentration on the rate of adsorption*

The initial concentration effect on fluoride adsorption was studied at different initial fluoride concentrations by keeping other parameters constant. The initial concentration effect on the eliminated fluoride quantity at the same tem is shown on Figure 5.

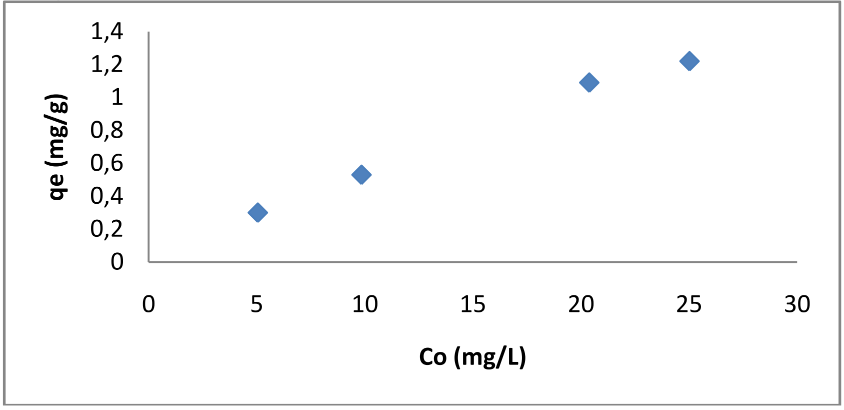

**Figure 5:** Effect of initial fluoride concentration on calcined beef bone adsorption capacity.

It is noticed that the fluoride adsorption capacity (qe) increases with the initial fluoride concentration. This observation is sustained by the availability of an important number of fluoride ions, thereby increasing the availability of fluoride ions to solid-solution interface and adsorption performance.

### *3.7. Adsorption isotherms*

Figure 6 shows the Freundlich isotherm. The constants 1 / n (mg L-1) and kF represent respectively the Freundlich empiric isotherm constant and the charred beef fluride ions sorption intensity [25]. They were calculated from the slope and the intersection of the lnqe representation according to lnCe on Figure 6. Where qe (mgg-1) is the amount of adsorbed fluoride per unit weight of adsorbent at equilibrium and Ce (mg l-1) the fluoride concentration of the solution at equilibrium.

The value of 1 / n is between 0 and 1 and that of n between 1 and 10 (see Table 1), this situation indicates that conditions were favorable for adsorption. The constants qm and KL of Langmuir isotherm (Figure 7) shown in Table 1 were calculated from the slope and intercept of the curve Ce / qe as a function of Ce [26].

The values of regression coefficients (R2) listed in Table 1 were used to find the suitable model. The low value of the correlation coefficient R2 of the Langmuir isotherm indicates its non applicability. The high correlation coefficient R2 of Figure 8 shows the applicability of the Freundlich isotherm. The applicability of the isotherm can be tested by calculating the separation constant RL [27]. The separation parameter (RL) is calculated from the Langmuir adsorption constant using the following equation:

$$R_L = \frac{1}{(1+K_L C_0)} \quad (2)$$

Where $R_L$ is the separation factor, $K_L$ the Langmuir adsorption constant (LMG-1) and Co-F (mg L-1) the initial concentration.

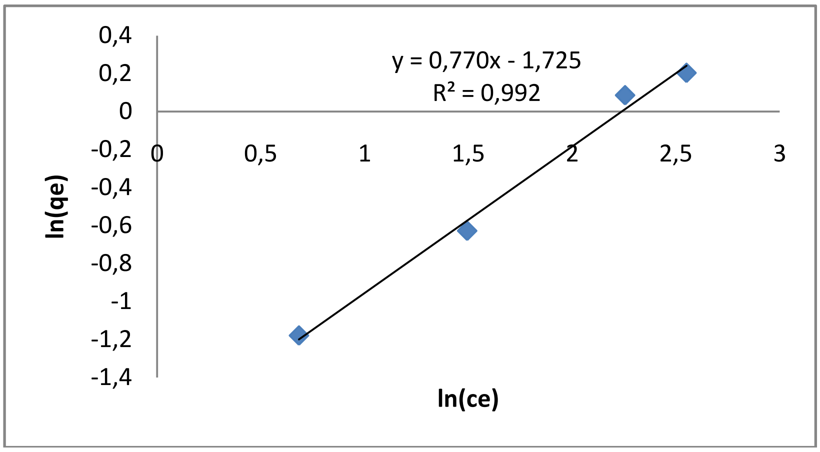

**Figure 6:** Freundlich isotherm of fluoride sorption by charred beef bone

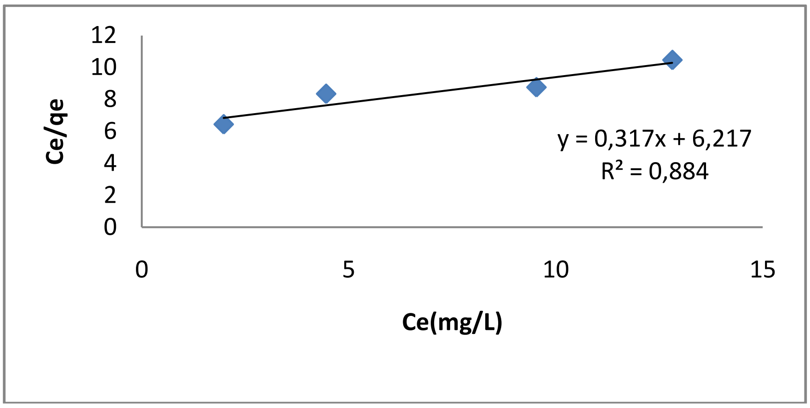

**Figure 7:** Langmuir isotherm of fluoride sorption by charred beef bone

$R_L$ value obtained was 0.748 between 0 and 1 and confirmed that the conditions were favorable for adsorption. The R2 highest value of the Freundlich isotherm on that of Langmuir indicated the relevance of the Freundlich isotherm compared to that of Langmuir [28]. Consequently the physic-chemical adsorption takes place on heterogeneous surfaces [29]. The value of adsorption intensity (n) superior to one means that the forces in the surface layer are attractive [30].

**Table 1:** Isotherms parameters of the sample at 300K

| **adsorbate** | **adsorbent** | **Langmuir** | | | **Freundlich** | | |
|---|---|---|---|---|---|---|---|
| | | **$q_m$ (mg/g)** | **$K_L$ (L/mg)** | **$R^2$** | **$K_f$ (L/mg)** | **1/n** | **$R^2$** |
| **fluoride** | **calcined bones** | **3,154** | **0,05** | **0,884** | **0,178** | **0,77** | **0,992** |

### *3.8. Thermodynamic investigations*

The variation of the Gibbs energy of adsorption ΔG ° was calculated in the same manner as in the literature [31, 32]. The value of ΔG ° obtained is-2864 kJ mol-1. It indicates that the sorption reaction is spontaneous.

### *3.9. Sorption kinetics*

Two kinetic models (pseudo-first order and pseudo-second order by Lagergren) based on the reaction and diffusion were applied to test the physical conditions of the experimental data.

#### *3.9.1. Models of Lagergren*

The pseudo first-order [33] and the pseudo-second order of Lagergren models [34] were tested to interpret the experimental data of adsorption process. The pseudo-first order model:

$$Ln(q_e - q_t) = Lnq_e - K_1 t \quad (3)$$

where q1 (MGG-1) is the maximum adsorption capacity of the pseudo-first order and K1 (min-1) the rate constant of the pseudo-first order in the fluorides adsorption process is shown on Figure 8.

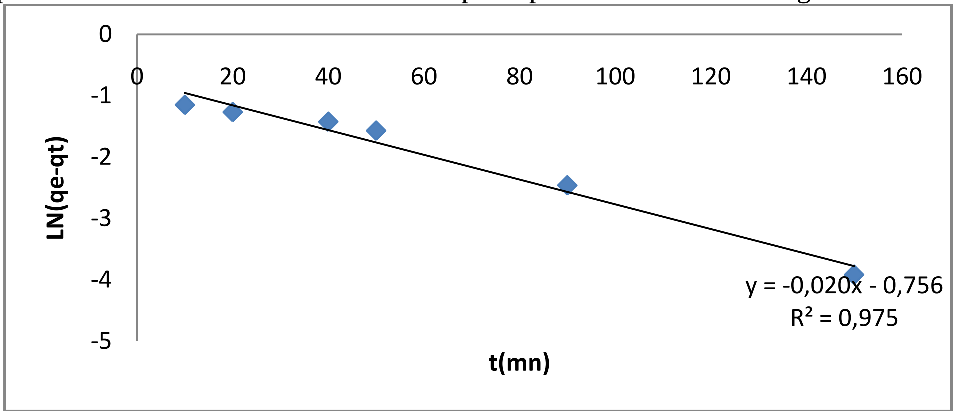

**Figure 8:** Lagergren first order isotherm

The slope of the curve ln (q1-qt) according to t Lagergren pseudo-first order [33] under different experimental conditions gives the value of the rate constant. The linear plot of ln (qe-qt) according to t in Figure 10 indicates the applicability of Lagergren equation.

The pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{K_e q_e^2} + \frac{t}{q_e} \quad (4)$$

where $q_2$ (mgg$^{-1}$) is the maximum adsorption capacity of the pseudo-second order and K2 (g (mg min) -1) the rate constant of the pseudo-second order for fluorides adsorption process (Figure 9).

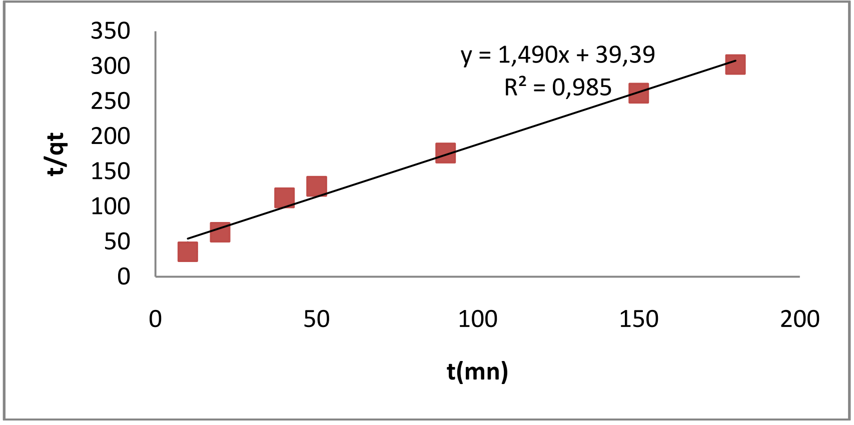

**Figure 9:** Lagergren pseudo-second order isotherm

The plot of Lagergren pseudo-second order t / qt according to t [35] (Figure 9) gave an R2 value greater than the pseudo-first order (see Table 2), indicating the applicability of the second order model. The rate of sorption follows the kinetic of Lagergren pseudo-second order model and is produced by the diffusion in the pores.

**Table 2:** Lagergren fluoride sorption constants per calcined beef bone Co-F [10 mg L-1] and adsorbent dose 5 g L-1.

| **adsorbate** | **adsorbent** | **Pseudo first ordre** | | | **Pseudo second ordre** | | |
|---|---|---|---|---|---|---|---|
| **fluoride** | **Calcined ox bone** | **$q_1$(mgg$^{-1}$)** | **$K_1$ ( min-1)** | **$R^2$** | **$q_2$ (mgg$^{-1}$)** | **$K_2$ g (mg min)$^{-1}$** | **$R^2$** |
| **Co[10 mg L$^{-1}$]** | **Co[5 g L$^{-1}$]** | **0,469** | **0,02** | **0,975** | **0,671** | **0,056** | **0,985** |

### *3.9.2. Elovich model*

The Elovich rate equation is used in the chemisorption kinetics of gases on solids. However, some researchers have applied this model to solid-liquid sorption systems [36]. This model is represented in the linear form (Figure 10) by the following equation:

$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t$ (5)

where qt ($mgg^{-1}$) is the amount of fluoride ions adsorbed by the calcined bone at time t (h); a (mgg-1h-1) the fluoride ions sorption constant and b (gmg-1) fluoride ions desorption constant.

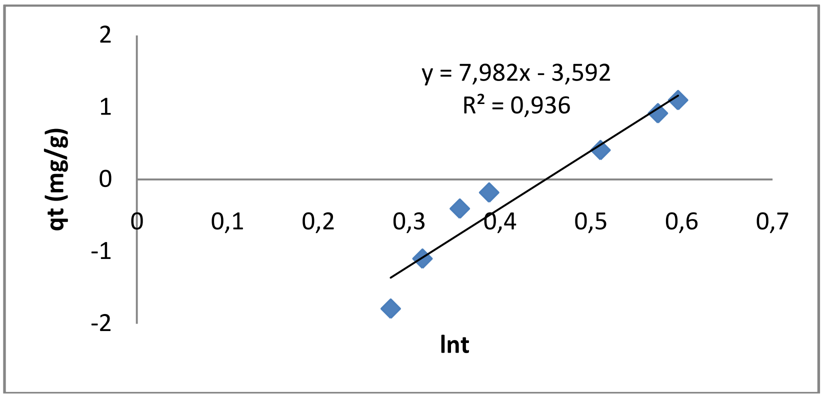

**Figure 10:** Elovich model

The sorption and desorption constants values obtained are (a) and (b) a = 1.293 mg g-1 h-1, b = 0.125 gmg-1. The relatively low value of the correlation coefficient R2 = 0.936 shows that the model is not well adapted to the experimental data.

### *3.9.3. Diffusion models*

The transfer of solute Sorption process in a solid-liquid is controlled either by diffusion in the pores [37] or by inter-particle diffusion [38, 39]. The model of mass transfer by inter-particle diffusion is used to understand the process of fluoride sorption by the calcined beef bone [40]. The expression of sorption rate is given by the following equation:

$q_t = K_P t^{0.5}$ (6)

Where qt (mg g-1) is the amount of adsorbed fluoride per g of adsorbent at time t. Weber and Morris [41] reported that if the particle diffusion is involved in the sorption process, the amount of adsorbate adsorbed per unit of adsorbent in comparison with the square root of time would result in a linear relationship. On Figure 11 indicating relationship qt according to $t^{0,5}$, there are three linear segments with the time of fluoride sorption per calcined bone.

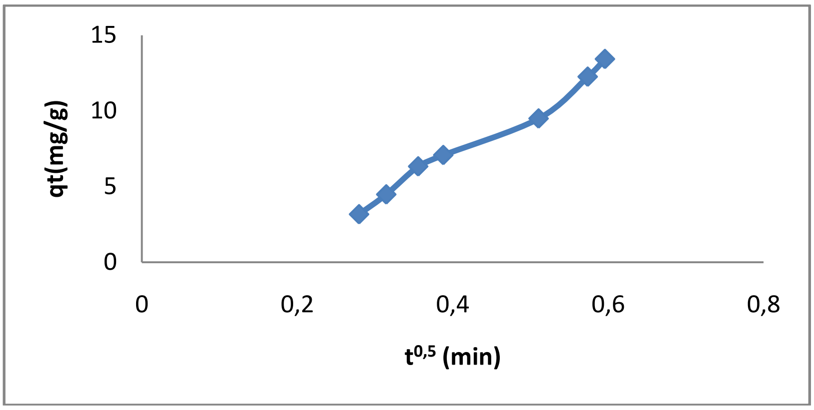

**Figure 11:** sorption capacity as a function of the square root of contact time

According to the intraparticle diffusion model, the first segment is interpreted as a diffusion limit of fluoride film on the surface of the bone. The second linear segment indicates an internal fluoride diffusion, corresponding to the migration of fluoride from the surface of the calcined bone to the intraparticle active sites. The third segment indicates a fluoride chemisorption on the active sites [42]. F-ions then diffuse in the intermediate layers to replace the OH-ions. This shows that the particle diffusion is involved in the sorption process but is not the only mechanism limiting and that other mechanisms are involved. The slope of the linear relationship lnqt according to lnt$^{1/2}$ representes the interparticle diffusion rate constant Kp (mg g-1 min-0.5).

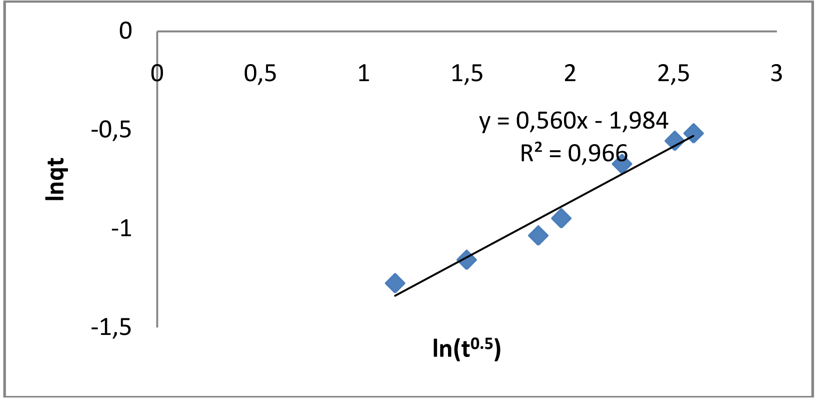

**Figure 12:** mass transfer model by interparticle diffusion

The shape of the curve (Fig.12) yielded the rate constant of interparticle diffusion of the fluoride adsorption on ox scapula calcined bone. It is: Kp = 0.56 mg g-1 min-0.5. The calcined bone flour used in this study contains calcite. In calcite, fluoride replaces CO32-, as shown in the equation below and the positions of Ca 2 + are quite unchanged [43].

$2F^- + CaCO_{3\,(s)} \leftrightarrow CaF_{2(s)} + CO_3^{2-}$ K = 200

The volume of CaF2 being smaller than that of the replacement reaction CaCO3 leaves more porosity. Thus, ions -F may diffuse into the particles and CO32- may also diffuse out the calcite particles. Therefore, fluoride may interact with CO32- inside calcite [44].

### *3.10. Fluoride sorption mechanism*

The solution pH is an important parameter that controls the sorption process due to the ionization of surface functional groups and the alteration of the solution composition.

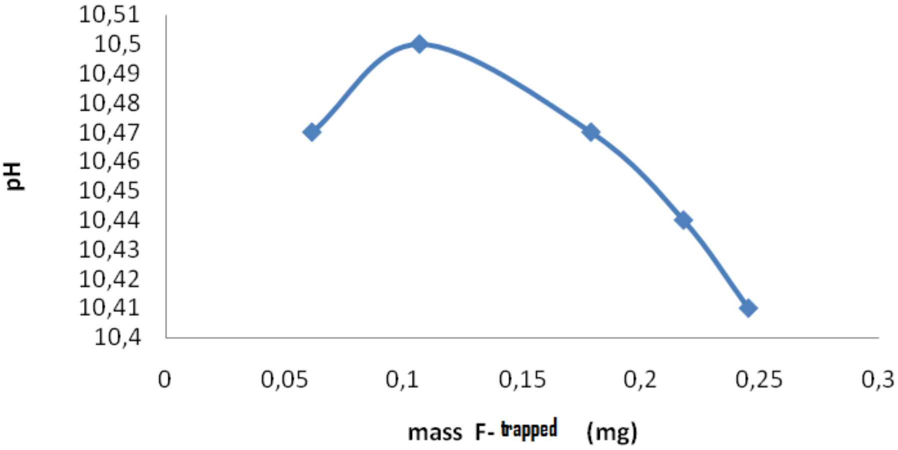

**Figure 13:** pH of the supernatant (F-, calcined bones) after 24 hours of contact time

Figure 13 shows a downward trend of the pH of the solution at equilibrium when the mass of fluoride adsorbed exceeds 0.1 mg. In aqueous solution and only at pH> 4 can the insoluble forms CaHPO4 • 2H2O and Ca5 (PO4) 3OH of hydroxyapatite be present [28]. The stability constant of fluoroapatite (log K = 54.6) being greater than that of hydroxyapatite (log K = 40.4) [29], the chemical adsorption of the fluorides can be explained by the following reaction:

$Ca_5(PO_4)_3OH + F^- \leftrightarrow Ca_5(PO_4)_3F + OH^-$

Fluoroapatite is formed between pH 5 and 10, while the hydroxyapatite is the predominant specie at pH> 7. This may explain the downward trend of the pH of the supernatant at equilibrium (Figure 13) when the mass of fluoride trapped exceeds 0.1 mg.

## Conclusion

The results of the characterization indicate that the calcined cattle bone is composed of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ and $CaCO_3$ calcite.

The results of adsorption show that the beef calcined bone is a precursor material appropriate for the defluorination of aqueous solutions. It was found that the mass of fluoride adsorbed on the adsorbent depends on the dose of adsorbent, the initial fluoride concentration and the contact time. The increasing of the initial concentration of fluoride or the contact time results in an increasing defluorination capacity. The results obtained from adsorption isotherms were well described by the Freundlich model. This fact indicates that sorption is heterogeneous and that the sorption reaction follows the Lagergren pseudo-second order kinetics. The adsorption reaction is spontaneous on the adsorbent. The results of this study show that the calcined ox bone is a potential material that could be used for the treatment of fluoride ions contaminated water.

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