

Use of calcined camel bones for water fluoridation of five boreholes in the Maradi region, Niger

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Abstract

The presence of fluorides in drinking water has become a major concern worldwide due to their chronic carcinogenic behavior for humans. The development of easily accessible and environmentally friendly disposal strategies is therefore a challenge for scientists. Camel bones calcined at different temperatures and then activated with HCl at different concentrations were used for the removal of fluorides ions from an aqueous solution. The effect of activate concentration, initial adsorbate concentration, contact time and adsorption process were studied. In addition to these previous parameters, the influence of co-existing ions on the adsorption capacity of fluorides ions was investigated. The optimal dose on calcined and activated camel bones is 16g / L with a maximum adsorption capacity of 0.63 mg / g. After optimization of this parameter an application on natural waters was realized. The study showed that the calcined and activated dromedary or camel bone is a promising adsorbent for the removal of fluorides ions from fluoridated or contaminated or drinking water.

Keywords: Bone; Camel; Calcinations; Activation; Adsorption; Fluoride

1. Introduction

The importance of water in human life continues to grow. The supply of good quality water is becoming increasingly difficult due to population growth, living standards, rapid development of industrial technologies and pollution problems. The pollution problem concerns both surface and groundwater. The high levels of fluoride recorded in some groundwaters make them unfit for consumption, which reduces the water resources of riparian populations [1].

Fluorides, although playing a prophylactic role in the human body, can lead to toxic effects in high doses. Indeed, their toxicity is proven by their entry into the composition of insecticides and bactericides [2]. The long-term consumption and accumulation of fluoride ions in the body causes harmful effects such as the destruction of tooth enamel, the development of diseases such as heart, psychic, neurological disorders and even genetic mutations [3]. Because of its very strong electronegativity, fluorine is usually in the form of a chemical combination, i.e. bound to other chemical elements. For this reason, the term "fluorides" should be preferred. Fluorides are widespread in nature: soil (minerals), air, water and certain foods (fish, tea...) [4].

Studies have shown that some aquifers in Niger, particularly in the Maradi and Zinder regions, have abnormal levels of fluorides ions, which make them unfit for consumption [5].

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In October 1998, an internal report of the SNE (current SEEN), reported fluoride levels in the hydrogeological aquifer of Tibiri province of Gobir, about ten kilometers from the city of Maradi, four to five times higher than that recommended by the World Health Organization (WHO) which is 0.8 mg L⁻¹ in hot areas [5]. Due to the prolonged consumption of fluoridated water from this Tibiri hydrogeological aquifer, about five hundred (500) children are affected by osteodental and skeletal fluorosis [5].

To reduce the fluoride ion content of contaminated water, several treatment processes are available. Among these processes are: precipitation, adsorption and membrane processes [6].

The removal of fluorides ions from drinking water by adsorption is currently widely used and involves many materials. This fluorides ions adsorption technique aims to collect local materials (camel bone) and degraded water resources. This is how we opted in this study, for the adsorption of fluoride ions by camel bones, calcined and activated.

In this study, we used the fluorides ions adsorption technique by collecting local materials camel bones and degraded water resources. We proceeded to the treatment process through adsorption of fluorides ions by camel bones that have been calcined and activated,

The objective of this study is to assess the ability of fluoride ions to be eliminated by calcined and activated camel bones in order to develop a semi-artisanal fluoridation system that populations could appropriate.

2. Materials and methods

2.1. Materials

2.1.1. Characterization of the adsorbent: camel bone

The adsorbent used is camel bone. This material has already been characterized [7]. The results of the characterization showed that the camel bone consists essentially of hydroxyapatite with the formula $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. Before use, the camel bone was crushed, calcined, activated with hydrochloric acid and washed with distilled water to remove impurities. It is then dried in an oven (103-105°C) for 24 hours.

2.1.2. Analytical reagents

The analytical reagents used are:

- Sodium fluoride, NaF used as a source of fluoride ions;
- The SPADNS reagent (red zirconium lacquer solution of red color) used for the determination of fluoride ions;
- Calcone carboxylic acid used as an indicator of calcium ions (CAT 947-99)
- Ethylene diamine tetraacetate, which was used to titrate calcium ions;
- Sodium hydroxide, NaOH and hydrochloric acid, HCl used to adjust the pH during the first activation of calcined bones;
- Vanadomolybdate solution used for the determination of phosphorus.
- Potassium hydroxide, KOH was also used during the determination of calcium ions to adjust the pH, i.e. to bring it between 12 and 13.

2.1.3. Basic equipment

Balance (KERN 572, Max 1210g d = 0.01) for weighing masses (calcined bones and analytical reagents). Magnetic stirrers, beakers, vials, ceramic crucibles, vats.

2.1.4. Heavy equipment

- Oven type to cap (autonomy 6 hours); temperature range from 0 to 1200 °C



Figure 1 Capper oven

Multi parameter (HANNA (pH & EC combo))



Figure 2 Multi parameter HANNA (combo pH & EC)

spectrophotometer



Figure 3 Molecular absorption spectrophotometer DR/2800

2.2. Experimental Protocol

2.2.1. Physico-chemical analyses of camel bones.

Moisture content

The estimation of the water content was carried out on 2 g of camel bones taken and placed in a ceramic crucible. Or: the mass of the camel bone introduced into the crucible and dried in an oven at 105 ° C until its weight remains constant. M_1

After cooling to room temperature, the dried mass is reweighed. The moisture content (% H) can be determined by the following formula:

$$\%H = \frac{M_3 - M_2}{M_1} \times 100 \quad (1)$$

M_1 : Initial mass of the camel bone introduced into the crucible in (g).

M_2 : Mass of the crucible filled after drying in (g).

M_3 : Mass of the crucible filled before drying in (g).

The ash rate

2g of camel bone sample are dried in an oven at 105 ° C for 24 hours. Then, the crucibles containing the previously dried sample are calcined in a furnace at 600 ° C for 4 hours. After cooling to room temperature, the crucible is weighed again. The ash content (% C) is calculated as follows:

$$\%C = \frac{P_3 - P_2}{P_1} \times 100 \quad (2)$$

P_1 : The initial mass of camel bones used in (g).

P_2 : The mass of the crucible containing the camel bone after calcination in (g).

P_3 : The mass of the crucible filled before calcination in (g).

Fixed carbon content.

Fixed carbon is the carbon remaining after removal of volatile matter and ash. It is determined from the formula

$$C_F = 100 - (V + C) \quad (3)$$

V: Volatile matter expressed as a percentage by mass of the dry sample.

C : Ash content expressed as a percentage by mass of the dry sample.

Calcination of camel bones

The bones were calcined to 600 degrees for 12 hours in ceramic crucibles. In order to eliminate organic matter and odors but also to increase the specific surface.

Activation of charred bones

- Activation by pH fixation

The pH of the calcined bone plus distilled water mixture is equal to 10.5.

The objective of this activation is to act on the charge of the surface of the calcined bone by keeping it in a solution of lower pH than that obtained with distilled water.

Two pH values were used: pH = 4 and pH = 7.

To achieve these pH (4 and 7), in a mixture of 40g of calcined bone and 500 mL of distilled water of initial pH 10 , 5 hydrochloric acid was introduced. The whole is put under agitation.

pH was monitored for five (5) days.

The activated product is cleared of all its free ions by several washes with distilled water then dried in the oven at 105 °C for 24 hours.

- Activation of calcined bones with hydrochloric acid solutions

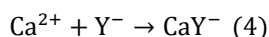
The calcined bones were activated with 0.01 M, 0.05 M, 0.1 M, 0.5 M, 2 M hydrochloric acid solutions. The mixture of calcined bone and hydrochloric acid is stirred for 24 hours. The activated product is washed several times with distilled water to remove impurities and then dried in an oven at 105 °C for 24 hours.

Determination of calcium ions after activation

We measured the calcium of the supernatant after activation to find out whether hydroxyapatite is dissolved or not during activation.

- Calcium is dosed as follows:

50 ml of the supernatant is introduced into a 500 mL flask. Then, successively, 2 mL of KOH (8N) and 0.2 mg of calcium indicator (cat 947-99). While stirring, we add EDTA which is the titrant. Equivalence is achieved when the color turns blue. The complexation of Ca²⁺ ions is done according to the equation:



2.2.2. Determination of phosphate

As in the case of calcium, to find out whether hydroxyapatite is dissolved or not during the second activation, we measured the phosphorus of the supernatant after activation. The supernatant resulting from the activations with hydrochloric acid solutions of concentrations 0.05 M and 0.01 M are recovered, filtered and then determined to determine the phosphate ion content. The procedure is as follows:

Place 20 mL of the supernatant in a 25 mL volumetric flask, add 1 mL of ascorbic acid solution and the reading after calibration.

- Principle of dosing

In an acidic medium and in the presence of ammonium molybdate, orthophosphates give a phosphomolybdic complex reduced by ascorbic acid which develops a blue coloration.

Fluoride ion adsorption operation

To make the adsorption of fluoride ions on the calcined bone and activated or not activated, we proceeded as follows:

In a 100 mL Erlenmeyer was introduced 0.4 g of calcined and activated bones and then 50 mL of sodium fluoride (NaF) solution. The mixture is stirred for 24 hours.

Determination of fluoride ions after adsorption

The adsorption supernatant is filtered with filter paper. The residual fluorides ions content is determined by molecular absorption spectrophotometry with a DR/2800.

- Principle of dosing

The supernatant is first filtered. The fluorides ions are complexed with the SPADNS reagent (red zirconium lake solution of red color). The latter forms with fluorides ions a colorless zirconium-fluoride complex (ZrF). The residual staining of the SPADNS reagent is measured by molecular absorption spectrophotometry with DR/2800 at a wavelength of 580 nm.

Optimization of adsorption parameters

The effect of adsorbent mass and contact time on adsorption capacity were studied.

Additions of counter-ions (Cl⁻ and SO₄²⁻, NO₃⁻, PO₄²⁻)

It is likely that the presence of significant contents of chloride, sulfate and nitrate anions has an influence on the retention of fluoride anions on calcined and activated camel bones. Excess fluorides ions in drinking water coexist with other salts. Their elimination should take into account the influence of other salts present in the same medium. This part of our study consists of evaluating the adsorption of fluoride ions in the presence of other ions. The effect of the presence of competing anions such as Cl⁻, NO₃⁻, and SO₄²⁻ on the percentage of extraction of F⁻ ions by calcined and activated camel bones is studied using different concentrations 10, 20, 30 and 40 mg. L⁻¹ of the competing anion.

Natural waters used

Water samples containing fluorides that were collected from a fluoridated endemic area to test the suitability of the adsorbent for field conditions. Water samples from 5 boreholes were taken from different villages (kouka-biyar, babankori, Sabon-machi, Malam-kaka and Dakoro) in the Maradi region. The simplest approach is to rinse and fill the 500 ml sterile polyethylene vials prepared in the laboratory with water from the casing at the exit of the borehole. pH and conductivity were measured at the sampling site. Transport of samples from the site to the laboratory was carried out away from light and at low temperatures in glacial. The anion contents of each water sample were determined in the laboratory according to the protocol developed by AFNOR (1986). pH and conductivity were measured by a multi-parameter HANNA device (pH & EC combo).

3. Results and discussions

- The ash rate

$$\%C = \frac{M_3 - M_2}{M_1} * 100 \quad (5)$$

$$10\% = \frac{49,63 - 49,43}{2} * 100 \quad (6)$$

The ash rate thus obtained is low. Indeed, our adsorbent has a significant effect. A high ash content decreases the specific surface, and makes the activation process difficult because they clog the pores of the carbon structure.

- Fixed carbon

$$C_F = 100 - (V + C) \quad (7)$$

$$C_F = 100 - (10 + 3) = 87 \% \quad (8)$$

The balance of immediate analyses shows that the bones of calcined camel bones have a low ash content, and a fixed carbon content of 87%. This implies that calcined camel bones is a potential precursor to the manufacture of an adsorbent with low ash production. Similar results have been reported

3.1. Experimental results

From the initial masses (m_i) of the fluoride ions (NaF solution) and those of the solutions of the mixture (NaF and activated calcined bone) after adsorption (m_f), the trapped m_p , m_f masses (m_i), the extraction percentages (P_e) and the trapped quantities (q_p) were calculated using the following equations: m_p , P_e , q_p

$$m_p = m_i - m_f \quad (9)$$

$$P_e = \frac{m_f \times 100}{m_i} \quad (10)$$

$$q_p = \frac{m_p \times 100}{m_o} \quad (11)$$

Where m_o denotes the mass of camel bones calcined after activation.

The masses, m_p, m_f, m_i, m_o , are expressed in milligrams (mg)

3.2. Calcium content released as a function of the pH of the mixture

Figure 4 shows the evolution of the calcium content released as a function of the final pH after HCl activation.

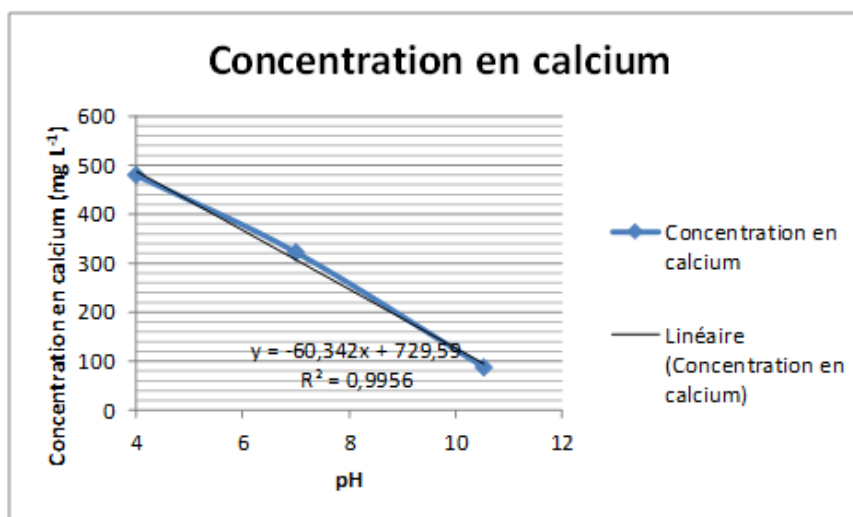


Figure 4 Amount of calcium released as a function of final pH

This figure shows that the lower the final pH, the higher the calcium content released.

The correlation coefficient ($R^2 = 0.9956$) shows that there is a strong correlation between the final pH after activation and the calcium content released.

According to Claire CHAÏRAT [8] during the treatment of hydroxyapatite with hydrochloric acid, calcium is released preferentially by ion exchange Ca^{2+} / H^+ . The activated product is depleted of calcium. This depletion is attributed to a Ca^{2+}/H^+ ion exchange reaction involving protons in the aqueous solution. The result is a mineral surface depleted in calcium and enriched with protons.

According to Karima [9], the free calcium content when the pH decreases is due on the one hand to the protonation of the surface of the apatite and on the other hand to its partial dissolution.

The equation for the partial dissolution of hydroxyapatite in the HCl solution is:



The increase in calcium content released when pH decreases is therefore due on the one hand to the partial dissolution of hydroxyapatite and on the other hand to ion exchange Ca^{2+}/H^+ .

3.3. Phosphorus content released as a function of the concentration of acid used for activation

The phosphorus content released by calcined bones during their activation by hydrochloric acid at concentrations 0.01 M and 0.05 M respectively are 0.39 mg L⁻¹ and 2.78 mg L⁻¹. These results show that the level of phosphorus released is a function of the concentration of the acid used for activation.

The phosphorus and calcium levels released into the supernatant after activation of the calcined bones show that hydroxyapatite is dissolved during activation.

3.4. Effect of final pH of activation on fluoride ion extraction percentage

Figure 5 shows the effect of the final pH of activation on the percentage of fluoride ion extraction. The fluoride solution used at a concentration of 5 mg.L⁻¹.

Two samples were activated, one at final pH 4 and the other at final pH 7.

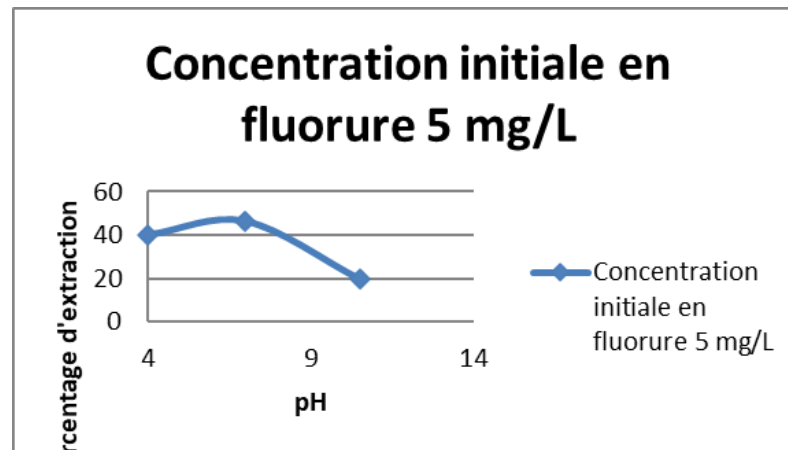


Figure 5 Percentage of fluoride ion extraction as a function of final pH of activation (amount of adsorbent 0.4 g, concentration of fluoride ions 5 mg L⁻¹ and contact time 24 h)

With the material not activated at pH = 10.5 the extraction percentage is 19%.

With the activated material at pH = 7, the percentage of extraction of fluoride ions is 46% With the material activated at pH = 4 the percentage of extraction of fluoride ions is 40%.

These results show that the final pH of activation has an influence on the percentage of fluoride ion extraction.

According to Bolger, the acidic or basic character of a surface is expressed in relation to its isoelectric point or zero charge point, defined as the pH of the aqueous solution in which the solid exists under a neutral electric potential.

- If pH < at the isoelectric point then the net charge is positive
- If pH > at the isoelectric point then the net charge is negative

For a pH of the solution higher than the isoelectric point, the surface of the adsorbent is negatively charged which favors the adsorption of cations. For a pH of the solution below the isoelectric point, the retention of the anions is favored because of the positive charge of the adsorbent. Larbi el hammari [10] showed that the apatitic surface can be modified by the action of phosphoric acid without affecting the crystal structure of the apatite and the morphology of the particles.

The extraction percentages at final activation pH 4 and final activation pH 7 are higher than that of the non-activated sample of pH = 10.5. These percentages show that, when the final pH of activation is less than 10.5, the surface tends to charge positively, favoring the adsorption of fluoride ions.

The percentage of adsorption of fluoride ions by hydroxyapatites Ca₁₀(PO₄)₆(OH)₂ contained in bone also depends on parameters such as grain size, porosity and crystallinity [10]. The samples used in our experiment come from the same sample so it is assumed that these calcined bones have the same structure, porosity and crystallinity.

The ability of bones to retain fluoride ions in water comes from the presence in its structure of hydroxyapatite Ca₁₀(PO₄)₆(OH)₂, as hydroxyl groups can be replaced by fluoride ions [2, 10, 11,12].

3.5. Effect of the concentration of hydrochloric acid used for activation on the percentage of fluoride ion extraction

Five calcined bone samples of 20 g each were activated with hydrochloric acid of concentration 0.01 respectively; 0,05; 0,1; 0,5 and 2 M.

Samples activated with hydrochloric acid of concentration 0.5 and 2 M respectively in distilled water release fluoride ions with concentrations of 4 mg L⁻¹ and 14.5 mg L⁻¹ respectively. Due to the high levels of fluoride released in distilled water by the latter, they were not used for adsorption.

Samples activated with hydrochloric acid at concentrations, 0.01; 0.05 and 0.1 M in distilled water also release fluoride ions as shown in Figure 15 but with low contents. These samples were used for adsorption.

The presence of fluoride ions in the mixture (calcined and activated bone plus distilled water) indicates the presence of fluorinated compounds in the calcined bone. According to Nezli et al, alkaline pH and bicarbonate hardness of water decrease the chemical activity of calcium and promote the alteration of fluorinated minerals, which induces the solubility of fluoride [13]. The fluoride ion contents obtained by introducing calcined and hydrochloric acid-activated bones into distilled water also indicate that acidic pH also decreases the chemical activity of calcium and promotes the alteration of fluorinated minerals, inducing their solubility.

Figure 6 shows the content of fluoride ions released in the water distilled by the calcined and activated bone as a function of the concentration of the acid used for activation.

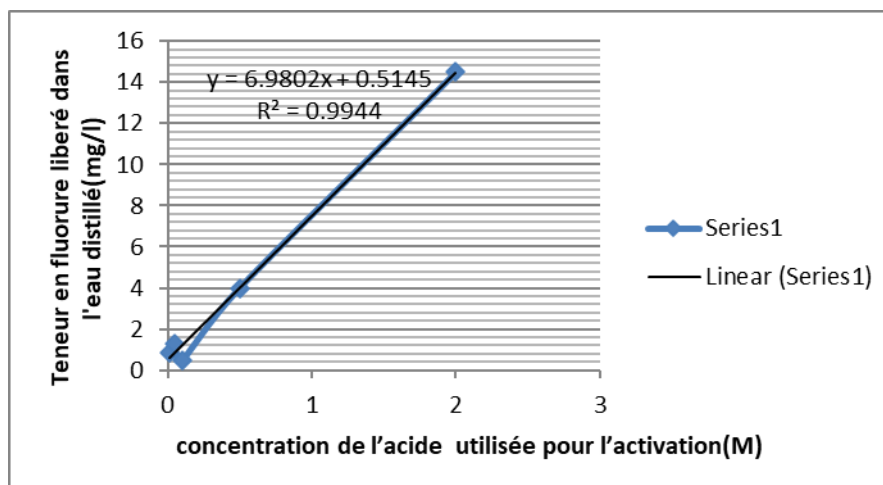


Figure 6 Fluoride ion content released in distilled water by the activated sample as a function of the concentration of acid used for activation (amount of adsorbent 0.4 g, 50 mL distilled water and contact time 24 h)

These results show that the content of fluoride ions released is proportional to the concentration of hydrochloric acid used for activation. They also show that activation of calcined bones with hydrochloric acid at concentrations above 0.5 M destroys hydroxyapatite in calcined bone and weakens fluoroapatite in bone. This may explain the high levels of calcium and phosphate ions obtained in the supernatant of calcined and activated bones at higher acid concentrations. It may also explain the high levels of fluoride ions released in distilled water from calcined bones and activated at concentrations 0.5 and 2 M.

Figure 7 shows the percentage of fluoride ion extraction from acid-activated samples at acid concentrations 0.01 M, 0.05 M and 0.1 M.

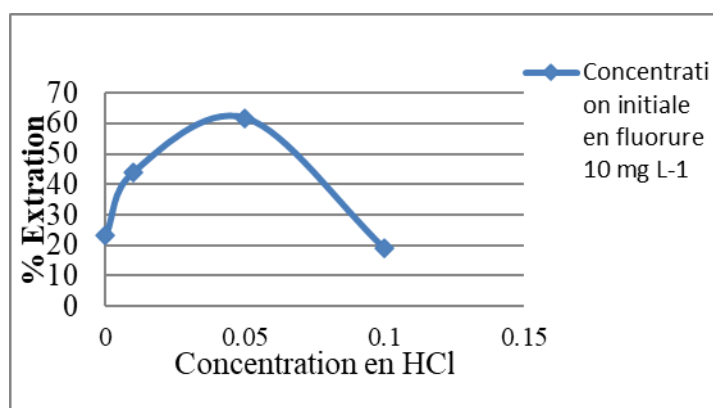


Figure 7 Percentage of fluoride ion extraction as a function of acid concentration used for calcined bone activation (amount of adsorbent 0.4 g, fluoride ion concentration 10 mgL⁻¹ and contact time 24 h)

Sodium fluoride solution used for adsorption at a concentration of 10 mgL⁻¹. Figure 7 shows that:

- With the non-activated sample, the percentage of extraction of fluoride ions is 23%.
- with the sample activated with hydrochloric acid of concentration 0.01 M the percentage of extraction of fluoride ions is 44%.
- with the sample activated with hydrochloric acid of concentration 0.05 M the percentage of extraction of fluoride ions is 61.76%.
- with the sample activated with hydrochloric acid of concentration 0.1 M the percentage of extraction of fluoride ions is 19%.
- The percentages of extraction of fluoride ions obtained with calcined bones and activated with hydrochloric acid at a concentration less than or equal to 0,05 M were greater than that of the non-activated sample.

These extraction percentages show that the activation of the camel bone calcined with hydrochloric acid of concentration less than or equal to 0.05 M modifies the charge of the surface of the latter. This charge becomes more positive, favoring the adsorption of anions in general, therefore fluoride ions.

Camel bones calcined and activated with hydrochloric acid at a concentration greater than 0.5 M are a potential source of fluoride ion pollution of water.

3.6. Optimization of contact time

In this study, a set of experiments was performed for adsorbate-adsorbent contact times ranging from 15 min to 90 min, at constant temperature, to evaluate the time required to reach equilibrium. The results of Figure 8 show that the adsorption rate of F⁻ ions on calcined bones is maximum in the first 15 min. They also show that the time required to reach equilibrium is 75 min. This variation in speed over time reflects distinct phases of the sorption phenomenon. During the first phase (0 to 15 min), the high intensity of the speed may be due to the easy access to the external sites of the adsorbent. The decrease in speed, between 15 and 75 min, can be explained by the saturation of external sites and the migration of F⁻ ions from the surface to the sites of the internal pores [14].

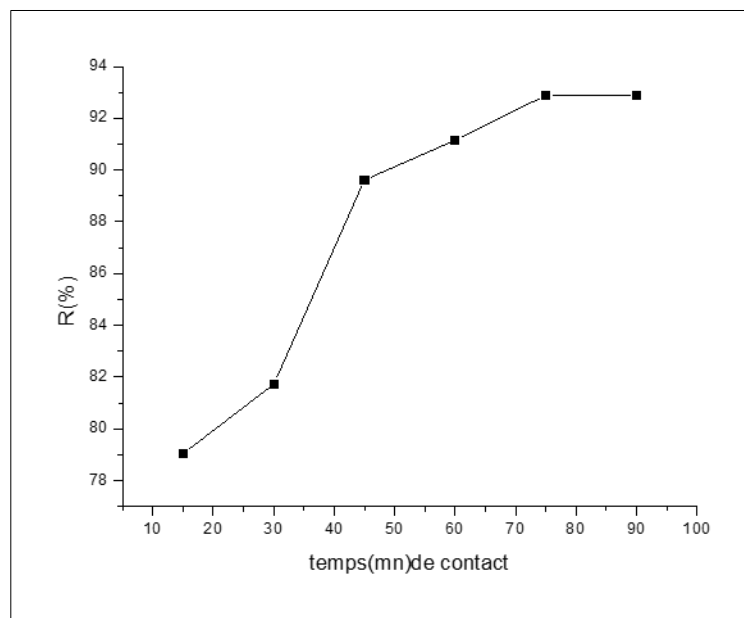


Figure 8 Percentage of extraction of F⁻ ions by calcine and activated bones as a function of contact time. ([F⁻] = 5mg. L⁻¹, pH = 7, adsorbent dose 0.4g, calcination temperature 600 ° C, [HCl] activating = 0, 05 M).

3.7. Effect of the dose of the adsorbent

The dose of the adsorbent is an important parameter because of its efficacy (% elimination) and the amount of F⁻ adsorbed per unit weight of adsorbent (q_e). Adsorption tests of F⁻ ions on calcined and activated bones were performed using different masses (0.4, 0.6, 0.8; 1 and 1.2g) of the adsorbent, volume solution F⁻ (50 ml), [F⁻] = 5 mg L⁻¹ at pH 7 and 25 ° C. The results in Figure 9 show that the percentage of extraction of F⁻ ions increases as the dose of the adsorbent increases. They also show that the best adsorption capabilities are obtained at low doses. The increase in the percentage

of extraction of F^- as the dose of the adsorbent increases is mainly due to an increase in the specific surface area of adsorption thus putting more active retention sites [15] Figure 9 shows that beyond (16g / L) of activated bones, the percentage of extraction of F^- ions changes very little. This small change in the percentage observed at high doses of the adsorbent is probably due to (1) the availability of less active sites at the end of the adsorption process and/or (2) the difficulty of F^- ions first to penetrate the adsorbent, while F^- ions partially cover surface sites [16].

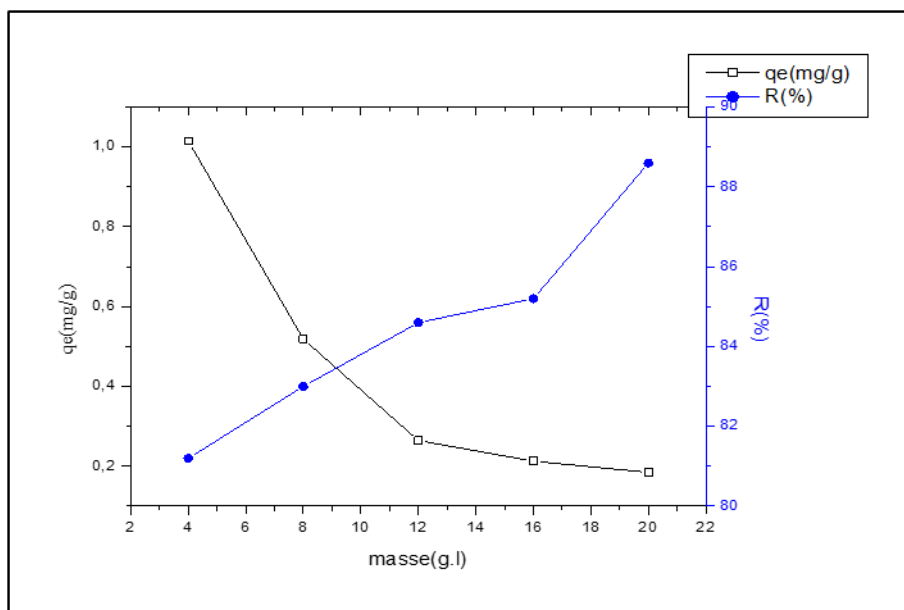


Figure 9 Percentage of extraction of F^- ions by the adsorbent as a function of the dose of the adsorbent

3.8. Effect of initial concentration of F^- ions

Generally, the adsorption capacity of the adsorbent increases by increasing the initial concentration of the adsorbate molecules. The effect of the initial concentration of F^- ions on the percentage of extraction of F^- ions by calcine and activated bone is studied at different concentrations of F^- (3, 5, 70 and 10 $mg L^{-1}$). For this is considered a volume of 50 ml of solution F^- , a mass of the adsorbent equivalent to 0.4g, a pH of 7 and a temperature of 25 ° C. It is well observed in Figure 10, that as the initial concentration of F^- ions increases, the percentage of extraction of the latter by the adsorbent increases in parallel.

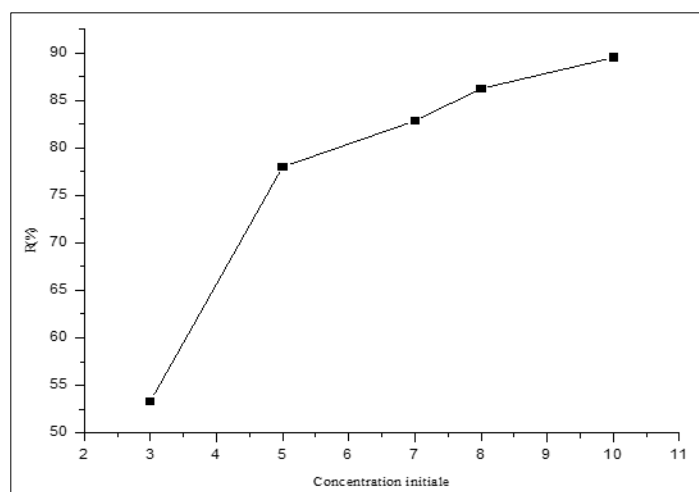


Figure 10 Effect of the initial concentration of F^- ions on the adsorption rate. (pH = 7, mass of adsorbent 0.4g. L^{-1} , calcination temperature 600°C, [HCl] activating = 0.05M).

Two phenomena can explain this variation in the percentage of extraction of F^- ions by the calcine bones of camel when the initial concentration of F^- ions varies. First phenomenon, when the concentration of the adsorbent increases, the

number of collisions between the F^- ions and the functional groups of the adsorbent also increases. This leads to an increase in adsorption capacity [17]. Second phenomenon, in the presence of a high concentration of F^- , the diffusion forces of F^- towards the surface of the adsorbent become significantly higher which favors the processes of intra-particle diffusion [18].

3.9. Effect of the presence of competing anions

The results of Figure 11 show that the presence of competing anions (Cl^- , NO_3^- , SO_4^{2-}) greatly lowers the percentage of extraction of F^- ions by calcine and activated bones. These results also show the order of influence of competing anions on the percentage of extraction of F^- ions by calcine and activated bones: $NO_3^- > Cl^- > SO_4^{2-}$. According to [19], the classification of the radii of hydrated anions (Cl^- , NO_3^- , SO_4^{2-}) is: $r(SO_4^{2-}) > r(Cl^-) > r(NO_3^-)$. In the presence of Cl^- , NO_3^- , and SO_4^{2-} anions, the adsorption of F^- ions on calcine and activated bones is competitive. The selectivity of calcine and activated bones is correlated with the size of the adsorbate. The variation of the percentage of extraction of F^- by our adsorbent as a function of the concentration of the competing anion observed in Figure 11 may be due to a shift in the equilibrium of the adsorption of F^- by the adsorbent towards the fixation of the competing anion and the release of F^- . However, above a certain concentration, the decrease in the extraction of fluoride ions is stopped and the extraction yield remains constant. This means that only a part of the adsorption sites is not selective and can be occupied by other anions.

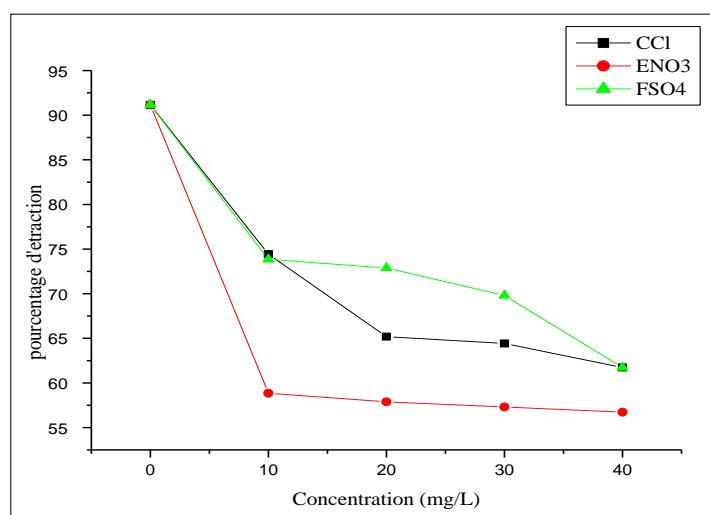


Figure 11 The effect of the presence of competing anions (Cl^- , NO_3^- , SO_4^{2-}) on the percentage of extraction of F^- ions by calcine and activated camel bones. ($[F^-] = 5 \text{ mg L}^{-1}$, $\text{pH} = 7$, mass dose of the adsorbent $0, 4 \text{ g L}^{-1}$, calcination temperature 600°C , $[HCl]$ activating = 0.05 M)

3.10. Application of calcine and activated camel bones in natural waters

Table 1 Results of the use of calcine and activated camel bones (0.4 g/L) for the removal of fluoride ions from borehole water in the Maradi region (Niger)

Village	ph	$[SO_4^{2-}]$ (mg/L)	$[NO_3^-]$ (mg/L)	$[Cl^-]$ (mg/L)	$[PO_4^{2-}]$ (mg/L)	$[F^-]$ before adsorption (mg/L)	$[F^-]$ after adsorption (mg/L)
Banbakori	7.11	5.72	30.00	40.82	0.38	2.15	1.14
Dakoro	7.01	4.8	24.00	23.07	0.42	1.80	0.15
Malamkaka	7.03	16.6	50.00	44.37	0.51	2.48	0.15
Sabonmachi	6.79	2.00	25.00	28.50	0.29	1.94	0.70
Kouka biyar	6.70	10.20	9.00	24.85	0.18	1.99	0.61

Table 1 shows the results obtained by comparing the fluoride concentration of water samples before and after the adsorption test on calcine and activated camel bones. Some final concentrations after adsorption are below the WHO

standard, compared to the initial concentrations of water samples from these 5 villages. our adsorbent has a retention of more than 65% of fluoride. It should be noted that the F^- content rate varies from village to village. The highest fluoride retention rate is still observed in both synthetic and natural water with calcined and activated camel bone. The elimination of fluoride in natural waters shows a much higher retention in Malamkaka than in other villages. This yield is higher than that in synthetic water for the same amount of bone of camel calcined and activated because of the possible presence of competing anions in natural water. This has been shown in the study of [20] where the retention of fluorides increases in the presence of competing anion ions. These samples from waters in the endemic area have a fluoride concentration above 1.80 mg/L, above the WHO guideline value of 1.5 mg/L for drinking water (WHO, 2004). While after treatment, the trough concentrations are less than 1.14 mg/L.

4. Conclusion

The results of this study show that activation by pH fixation as well as that carried out with a hydrochloric acid solution of concentration less than or equal to 0.05 M improve the percentage of fluoride ion extraction by calcined camel bones.

However, when the calcined bones are activated with a hydrochloric acid solution of concentration greater than 0.05 M the activated product is not suitable for adsorption because of the high levels of fluoride ions they release in distilled water. They become a potential source of fluoride ion pollution.

The phosphorus and calcium levels of the supernatant after activation show that activation caused partial dissolution of hydroxyapatite in the calcined bones.

The high levels of fluoride ions respectively 4 mg L⁻¹ and 14 mg L⁻¹ of the mixtures (calcined and activated bones with hydrochloric acid at concentrations 0.5 M and 2 M respectively in distilled water) indicate the presence of fluoroapatite in calcined bones. They also indicate that activation of calcined bone with hydrochloric acid at concentrations greater than or equal to 0.5 M destabilizes the fluoroapatite it contains and makes it more soluble in water. The effectiveness of defluorination depends particularly on the calcination temperature of the adsorbent, the concentration of the activate (HCl), the pH of the F^- solution and the mass of the adsorbent material. The competitiveness of counter ions (NO_3^- , Cl^- , SO_4^{2-}) vis-à-vis the removal of F^- ions depends on the following factors:- The radius of the hydrated ion considered. Indeed, the classification according to selectivity follows the following order $NO_3^- > Cl^- > SO_4^{2-}$; the quantity of counterions particularly nitrates and / or chlorides. The technical feasibility of removing fluoride ions from fluoride-laden water by adsorption to calcined and activated camel bones has been demonstrated. Given the abundance of this local material, its low-cost accessibility and adsorption capacity, it can be said that camel bones calcined and activated either at a pH less than 10 or by hydrochloric acid solutions of less than or equal to 0.05 M may be promising materials.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they have no competing

References

- [1] Annane, Q., (2011). Improvement of the defluoridation technique by the new bipolar electrocoagulation process. Thesis of magister of chemistry university Tizi-Ouzou Algeria faculty of science department of chemistry
- [2] Comlan dovonon L F, Soclo H, Gbaguidi M A N and Youssao A. (2011). Use of calcined bones in fluoridation of contaminated water: Experimental determination of optimal calcination temperature and bone particle size. Int. J. Biol. Chem. Sci. 5(4): 1712-1726
- [3] Zobeidi A and messiatfa A, (2010), rate status in waters and Main foods consumed in the willaya el-oued fluorides reviewed. Sci. background. App., vol. 2 no. 2 97-106.

- [4] Fluoride: what's new? Press contact: Marylin Herrmann, tel. 02 648 09 4 and 04 388 45 84, fax 04 388 45 86 – e-mail: marylin.h@skynet.be – Design Peekaboo~www.sourirepourtous.be - Fondation pour la Santé Dentaire
- [5] Denise Williams, Abdoulaye Ibbo, Daddy, (2002) Too much fluoride in water: 500 children with disabilities Article 2823 Niger d
- [6] Hichour M, Persin F, Sandeau J, Molénat J et. Gavach C, (1999) ; D efluoridation of water by Donnan dialysis and electro dialysis" Revue des sciences de l'eau / Journal of Water Science, vol. 12, n° 4, p. 671-686. Available sur [http:// pp. 671-686](http://pp.671-686). Available on <http://www.erudit.org/apropos/utilisation.html>
- [7] Samb F, (2004) problem of fluoride in drinking water supply in Senegal analysis of the situation proposal of the solution. Graduation project for the degree of Design Engineering
- [8] Claire CHAÏRAT (2005) experimental study of the kinetics and mechanisms of alteration of apatitic minerals doctoral thesis UNIVERSITY TOULOUSE III – PAUL SABATIERUFR: SVT
- [9] Karima ACHELHI (2012) Zirconia hydroxyapatite organo-apatites and nanocomposites for metal scavenging MOHAMMED V UNIVERSITY – AGDAL FACULTY OF SCIENCES RABAT Doctoral thesis in cotutelle with the Pierre and Marie Curie University of Paris Order No.:2573
- [10] Larbi EL HAMMARI (2007) Synthesis and physico-chemical studies of porous calcium phosphates grafted by organic molecules: structure and adsorption process Mohammed Vagdal UniversityThe Faculty of Rabat Sciences Doctoral Thesis Order No.: 2362
- [11] Mohamed Ndong, Coudou Mar-Diop, Falou Samb, El hadji Ngom, Oumar Sock (2009) Fluorine adsorption by calcined bones: Study of batch regeneration by sodium hydroxide after saturation J. Soc. Ouest-Afr. Chim. (2009) 027;1-7
- [12] Codou MAR DIOP (2011) use of calcined bones for the defluoridation of drinking water in rural areas of Senegal Cheick Anta Diop University of Dakar (UCAD) RESCIF.
- [13] Nezli I E , djabri L and djidel M (2010), origins and speciation of fluoride in the waters of the surface aquifer of the Ouargla basin (Algerian northern Sahara) Laboratory for the Protection of Ecosystems in Arid and Semi-Arid Zones, Kasdi Merbah Ouargla University, BP 511, Ouargla 30000 (Algeria). P143
- [14] H. Massai1, L. A. Nlondok1, C. Tcheka, B. B. Loura, Ileana DenisaNistor and J. M. Ketcha (2015) Kinetic and Batch Equilibrium Adsorption of Nickel (II) and Copper (II) Ions from Aqueous Solution Onto Activated Carbon Prepared from BalanitesaegyptiacaShells.American Chemical Science Journal6 (1): 38-50, 2015, Article no. ACSj.2015.035ISSN: 2249-0205.
- [15] Dbik, A., El Messaoudi, N., & Lacherai, A. (2014). Valorisation of wood dates stones of a variety of palm tree of Tinghir region (Morocco): Application to eliminate methylene blue. J. Mater. Approximately. Sci, 5, 2510-2514
- [16] Balouch, A., Kolachi, M., Talpur, F. N., Khan, H., & Bhangar, M. I. (2013). Sorption kinetics, isotherm and thermodynamic modeling of defluoridation of ground water using natural adsorbents. American Journal of Analytical Chemistry, 4(5), 221.
- [17] Guo, Q., & Reardon, E. J. (2012). Fluoride removal from water by meixnerite and its calcination product. Applied Clay Science, 56, 7-15.
- [18] Lenoble, V. (2003). Arsenic removal for drinking water production: chemical oxidation and adsorption on innovative solid substrates (Doctoral dissertation, University of Limoges).
- [19] Bernard, M. (1996). Usual general and mineral chemistry.
- [20] Kusrini, E., Sofyan, N., Suwartha, N., Yesya, G., & Priadi, C. R. (2015). Chitosan-praseodymium complex for adsorption of fluoride ions from water. Journal of Rare Earths, 33(10), 1104-1113.