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Adsorption Tests of Fluoride Ions by Raw Clays and Activated with Hydrochloric Acid and Application to Natural Waters



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ABSTRACT

The objective of this study is to test the capacity of raw and activated clays from three quarries in the municipality of Tanout in region of Zinder (Niger) in the elimination of fluoride ions. The methodology is based on tests with synthetic waters containing fluoride ions by playing on certain parameters (contact time, pH, mass, concentration and temperature) and natural waters from certain boreholes of the same region while maintaining the optimized parameters. The results obtained show that raw and activated clays adsorb fluoride ions well with more affinity towards activated clays. Removal capacities increase with contact time and concentration, but decrease with pH, mass and temperature. The fluoride ions contained in the waters of Belbedji and Koundoumawa are more eliminated with affordable yields (39.86 to 70.41%). These results also show that these Tanout clays are potential materials for the defluoridation of natural waters in Zinder region.



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INTRODUCTION

Groundwater is one of the main sources of consumption water supply for the population in most parts of the world [1]. However, studies have shown water contamination by fluoride ions in several countries [2, 3, 4]. Generally, these ions are frequent in sedimentary basins, in areas of crystalline bases and in volcanic regions [2]. So, in groundwater, they come from the dissolution of these formations that may contain minerals such as fluorite (CaF_2), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) [5], sellaite (MgF_2) [6], muscovite, tourmaline and the volcanic activity itself generating fluorinated gaseous inputs [2]. These ions have beneficial and harmful effects on health depending on the concentrations and the duration of exposure [7 - 12]. Their harmful effects in organism, lead to the destruction of teeth enamel, the development of diseases such as osteoporosis, heart and mental disorders, skin cancers and even genetic effects [11]. In Niger, this problem was observed in Tibiri in Maradi region where more than 424 victims of malformations of the lower limbs, wrists and cranial lesion and more than 500 victims of massive destruction of dental enamel were counted [13]. Due to this worldwide problem, many techniques at laboratory and industrial scales have been developed, but adsorption remains the simplest and easiest to implement. This technique uses solid materials as an adsorbent. And in recent years several types of materials have been tested using this technique [14], but given the economic reality of developing countries and environmental concerns, the use of materials of natural origin such as clays are very attractive. Some have shown their ability and others their inability. In Niger, the only study carried out on bentonite from Tahoua region showed its incapacity in its natural state [15]. It is for this reason that this study is carried out, which aims to test natural and activated clays from the municipality of Tanout in Zinder region in the elimination of fluoride ions. To our knowledge, these clays have never been tested in adsorption.

MATERIAL AND METHODS

Adsorbents (raw and activated clays with HCl)

The raw clays used were sampled in three different quarries in Tanout township of Zinder region (Niger). An orange clay (Arg1-B), a red (Arg2-B) and a green (Arg3-B). These clays were chemically activated with an activating agent HCl of 2M concentration at a temperature of 60°C and a stirring time of 3 hours. After this activation step, the samples were washed thoroughly

with hot distilled water until a negative test was obtained with AgNO_3 to eliminate the Cl^- ions, then dried in an oven at a temperature of 80°C . The clays resulting from this activation were named Arg1-2C, Arg2-2C and Arg3-2C for orange, red and green clay respectively (Figure 1).

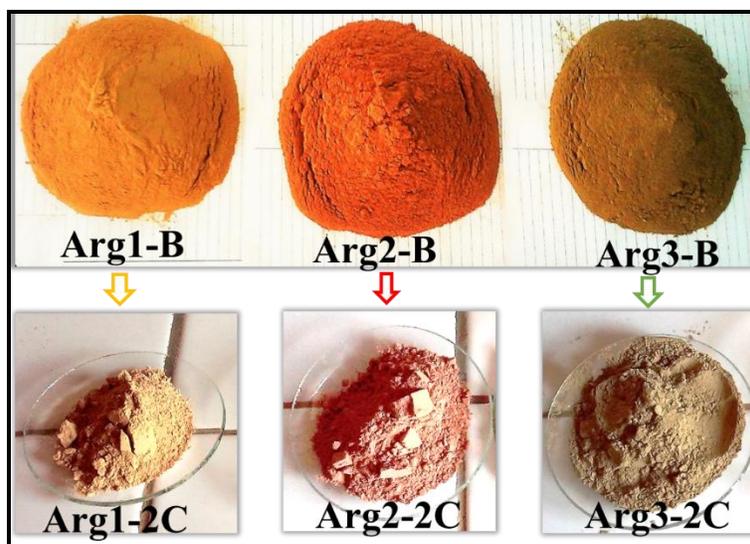


Figure 1: raw and activated clays with HCl

Preparation of the stock solution of F^- ions

A stock solution of F^- 1 g.L^{-1} ions was prepared by dissolving 2.210 g of NaF (sodium fluoride) in 1 L of distilled water contained in a plastic flask. An analysis solution with a concentration of 2 mg.L^{-1} was prepared from the stock solution. Adsorption experiments were performed in 500 ml plastic beakers on magnetic stirrers at room temperature without pH adjustment. The effects of contact time, pH, adsorbent mass, concentration and temperature were studied.

Effect of contact time

The adsorption capacity of F^- ions was monitored by testing a dose of 2 g of raw and activated clays with 400 ml of a solution of F^- ions with a concentration of 2 mg.L^{-1} under magnetic stirring at $500 \text{ rpm} \cdot \text{min}^{-1}$. Samples were taken to determine the residual concentrations at all times while taking care to put the adsorbent back into the solution after filtration. The filtrations were carried out on Wattman filter papers of $0.45 \mu\text{m}$ porosity and the residual concentrations were determined using a molecular absorption spectrophotometer by the SPADNS method. The amount and percentage of adsorption were calculated by the following formulas:

$$q_t = \frac{(C_i - C_f) \times V}{m} \text{ (mg.g}^{-1}\text{)} \quad (1)$$

$$r \text{ (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

With C_i : initial concentration and C_f : final concentration after adsorption

This step makes it possible to really determine the time at which the adsorption of the F^- ions has reached its maximum in order to vary the different parameters for possible analyses.

Mass Effect of Adsorbents

By maintaining the times at which adsorption reached its maximum for the six clays (three raw and three activated), various masses (0.5; 1; 1.5; 2; 2.5 g) were brought into contact with 100 ml of the F^- ion solution, still keeping the same conditions as before (room temperature, without pH adjustment, at 500 rpm). After filtration, the residual concentrations were determined by spectrophotometry. This step makes it possible to determine the optimal mass which better adsorbs the F^- ions.

Effect of initial concentration of fluoride ions

For the concentration effect, the process is the same but, varying the concentration of the F^- ions (1.5; 2; 2.5; 3; 3.5 mg.L^{-1}) and keeping the mass 0.5 g adsorbents.

Effect of pH

The effect of pH was studied by adjusting the pH of the synthetic solution of F^- ions by solutions of NaOH (0.1 N) and HCl (0.1 N). Three solutions (of pH 5, 7 and 9) were used in this study and the experiments were carried out under the same conditions ($V = 100 \text{ ml}$, $C = 2 \text{ mg.L}^{-1}$, $m = 0.5 \text{ g}$, $v = 500 \text{ rpm}$ and ambient temperature).

Effect of temperature

As for the thermodynamic studies, they were still carried out in plastic beakers and maintaining the same conditions as before, but varying the temperature (30, 40 and 50 °C) while controlling it using a thermometer.

Application on natural waters

The adsorption experiments were carried out while maintaining the physicochemical parameters of the natural waters (pH, concentration and temperature) of Koundoumawa, Garagoumsa, Belbedji and Kantché structures and the parameters optimized from the synthetic solutions (mass and contact). Optimal masses of 0.625 g of adsorbents were brought into contact with 100 ml of natural waters with stirring at 500 rpm. After reaction and filtration, the residual concentrations were determined by spectrophotometry.

RESULTS AND DISCUSSION

Results

Characteristics of raw clays

Table 1 presents some characteristics of raw clays.

Table 1: Some characteristics of raw clays

Oxides	Arg1-B	Arg2-B	Arg3-B
SiO ₂	68.1	83.2	56.1
Al ₂ O ₃	17.02	7.04	14.3
Fe ₂ O ₃	7.6	3.35	8.06
SiO ₂ /Al ₂ O ₃	4.001	11.818	3.923
BET specific surface (m ² .g ⁻¹)	444.1	418.4	437.8

Arg1-B and Arg2-B clays have been previously characterized on the mineralogical, structural, textural and physicochemical levels [16, 17].

Effect of contact time

Figure 2 presents the results of the effect of the contact time of the F⁻ ion elimination test by the raw and activated clays. This figure shows that the equilibrium is reached for all the clays at 120 min. Thus, activated clays have higher adsorption capacities than raw clays. Similarly, in the raw state Arg2-B has more affinity for F⁻ ions than the other two clays, but unlike in the activated state where it is Arg3-2C. Indeed, the process of the amount adsorbed as a function of time is

carried out in two stages: a first which is characterized by rapid adsorption in the first 50 min and a second which is carried out slowly until equilibrium.

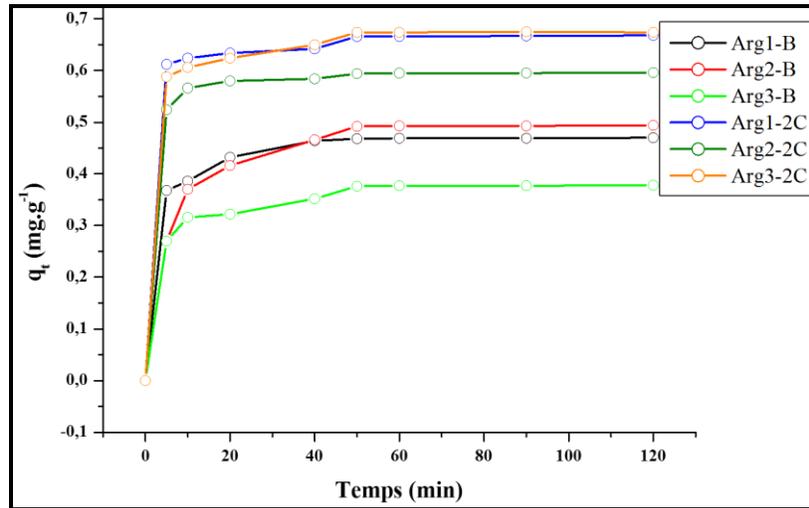


Figure 2: Effect of contact time of adsorption of F⁻ ions on clays

Effect of initial concentration of fluoride ions

The effect of the initial concentration of F⁻ ions on adsorption by clays is presented in Figure 3. It can be seen that the adsorption capacity of clays increases with the increase in the concentration of F⁻ ions. No plateau was detected in the range of concentrations that we studied apart from Arg3-2C, which shows a decrease in adsorption capacity at a concentration of 3 mg.L⁻¹.

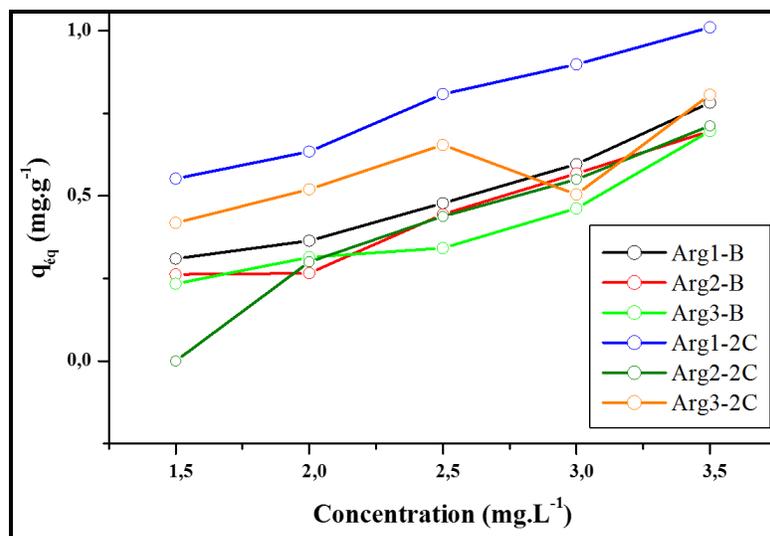


Figure 3: Effect of concentration on the adsorption of F⁻ ions by clays

Mass Effect of Adsorbents

The results of the adsorbent mass effect on the adsorption of F^- ions by the clays are presented in Figure 4. It is apparent from this figure that the increase in the mass of the clays leads to a decrease in the capacity of adsorption of F^- ions and that activated clays adsorb better than raw clays for the same concentration and the same contact time. Thus, in the interval of the masses studied, no plateau was detected. In addition, the removal efficiency increases with the increase in the mass of these clays.

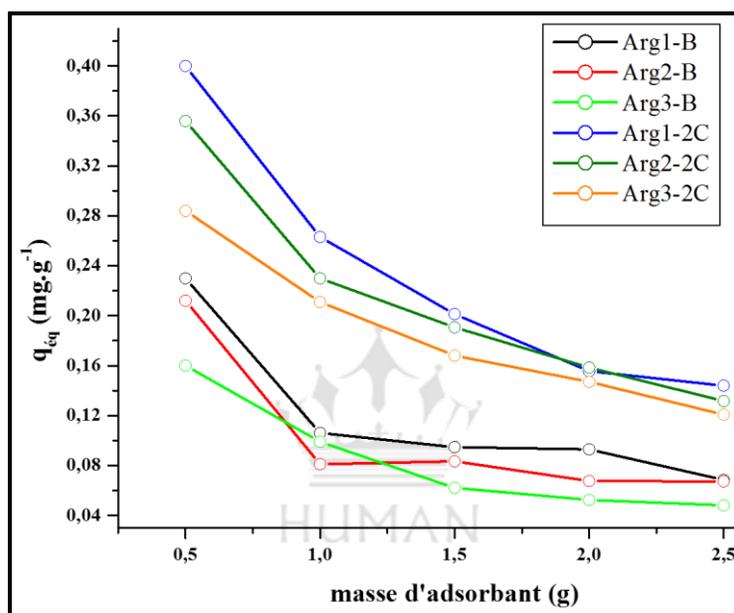


Figure 4: Effect of adsorbent mass on the adsorption of F^- ions

pH Effect of Initial Concentration

The results of the variation of the pH of the initial solution on the adsorption of F^- ions by clays are given in Figure 5. It shows that the adsorption of F^- ions takes place more in an acidic medium than in a basic one and that, clays activated with hydrochloric acid have more affinities relating to F^- ions than raw clays.

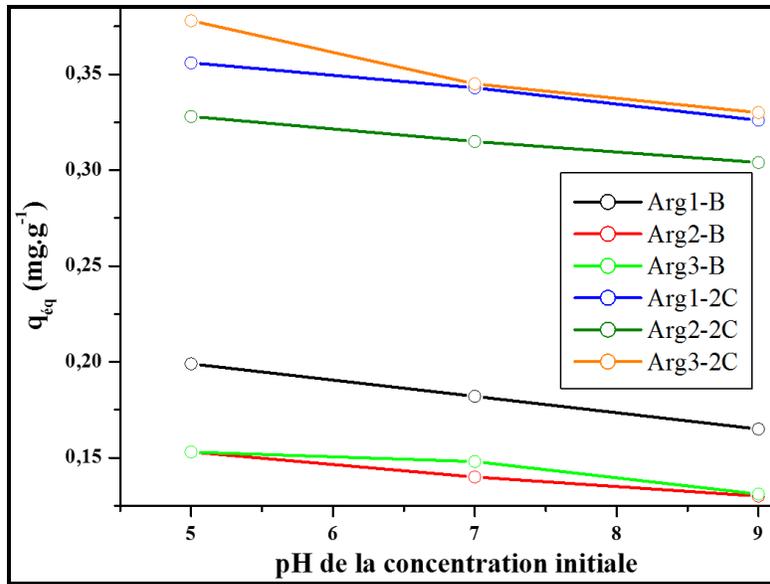


Figure 5: Effect of the pH of the initial concentration on the adsorption of F⁻ ions

Effect of temperature

In general, the increase in temperature leads to a decrease in the adsorption capacity of F⁻ ions by raw and activated clays (Figure 6). Thus, activated clays have more affinity for F⁻ ions than raw clays.

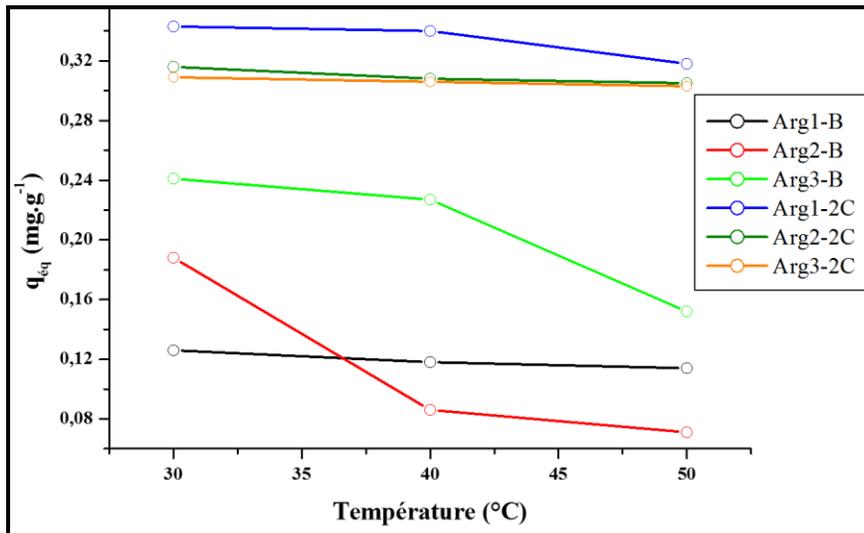


Figure 6: Effect of temperature on the adsorption of F⁻ ions

Application on natural waters

The results obtained from the elimination of the F⁻ ions contained in the natural waters of Zinder region by raw and activated clays are presented in Figure 7. This figure shows that the F⁻ ions contained in the waters of Belbedji are more eliminated, then come respectively those of the waters of Koundoumawa, Garagoumsa and Kantché. Thus, Arg3-2C better adsorbs the F⁻ ions of these waters, except those of Belbedji where they are better adsorbed by Arg1-B. Removal efficiencies are reported in Table 2.

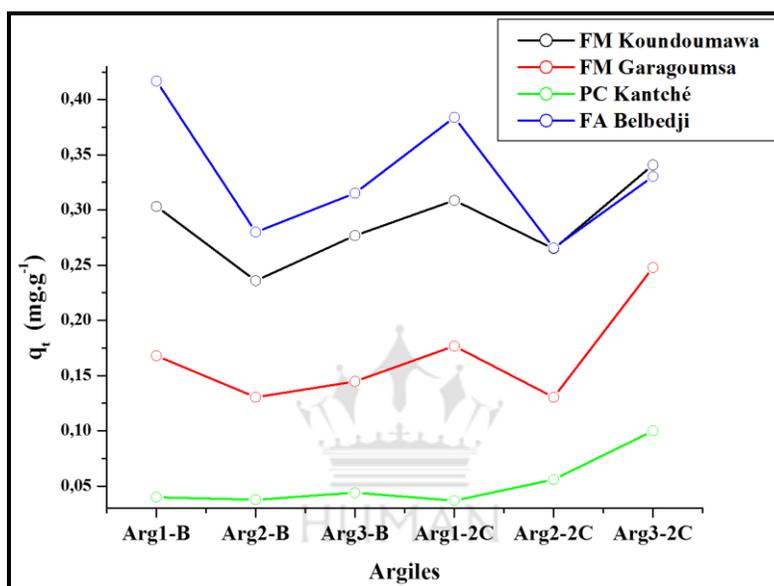


Figure 7: Application of elimination of F⁻ ions on natural waters by clays

Table 2: Efficiency (%) of removal of F⁻ ions from natural waters

Argiles	Koundoumawa	Garagoumsa	Kantché	Belbedji
Arg1-B	51,22	38,32	11,36	70,41
Arg2-B	39,86	29,74	10,68	47,3
Arg3-B	46,76	33,03	12,5	53,24
Arg1-2C	52,16	40,33	10,45	64,86
Arg2-2C	44,73	29,74	15,91	44,86
Arg3-2C	57,57	56,57	28,41	55,81

This table shows that the elimination yields vary according to the type of clay and the physico-chemical composition of the water containing the F^- ions. But, overall waters of Kantché have the lowest removal efficiency.

DISCUSSION

Effect of contact time

The adsorption of F^- ions observed by all clays in a rapid manner in the first 50 min, could probably be due to the abundance and availability of active sites on the surface of these clay materials. Indeed, the slow step observed, could be mainly due to the progression of occupation and the saturation of these active sites, which would undoubtedly lead to an inefficiency of adsorption of these ions by these clays and or a change in the pH. in the reaction medium. However, the strong affinity of activated clays with respect to F^- ions, exceeding that of raw clays, could be attributable to the acid sites which are born after acid activation of these raw clays likely to increase their adsorption capacity and/or their specific surface (SS). Thus, the equilibrium time of 120 min obtained in this study exceeds that of *Gourouza* [18] on clays from Tahoua region. This difference would be mainly due to the high SS of our materials which exceeds that found by this author, or to the different mineral elements contained in our clay samples and/or to acid activation. On the other hand, the good affinity of Arg2-B to F^- ions could probably be due to its intrinsic properties (such as its high microporous SS, its microporous volume, its micropore size and its high SiO_2 content) which exceed those of two other raw clays. Because these characteristics are essential for good adsorption and the F^- ions strongly attack the SiO_2 . So the more the SiO_2 level increases, the more the F^- ions will be adsorbed.

Effect of the initial concentration of F^- ions

The increase of the adsorption capacity of F^- ions by raw and activated clays observed when the initial concentration increases, could be due to the availability and abundance of reaction sites likely to adsorb more F^- ions. as long as they are available locally. Indeed, the non-observation of the saturation plateau in the range of concentrations studied was probably due to the fact that the saturation rate of these clays is not reached and that they could adsorb larger quantities of F^- ions. So it would have been necessary to increase the concentrations to define the saturation threshold. This observation was also made by *Gourouza* and *Errais* [18, 19] during the adsorption of F^-

ions by Sabon Karé clay and the adsorption of anionic dyes on Fouchana clays respectively. This supports our hypothesis. But, unlike the results found by *Nasr* [20] which do not show effective change by bone and cuttlefish.

Mass Effect of Adsorbents

The decrease in the adsorption capacity of clays observed during the elimination of F^- ions when the mass increases, could be due to the non-saturation of the reaction sites during adsorption, or to the interaction of particles resulting from the high quantity of these clays obstructing the adsorption of these F^- ions, because the adsorption capacity depends on the mass, and the more the mass increases, the more the capacity decreases. But, the increase in adsorption efficiency could be due to the availability of reaction sites. Similar results have been reported by *Nasr* and by *Mourabet* [20, 21]. Our hypothesis on the decrease in adsorption capacity corroborates those made by *Gourouza* and by *Mourabet* [18, 21].

pH Effect of Initial Concentration

The decrease in the adsorption capacity of F^- ions observed when passing from the acid medium to the basic medium, would probably be linked to the pH_{PCN} of these clays which play a crucial role in the adsorption of F^- ions in the solid-liquid interface. So when in an acid medium (below the pH_{PCN}), these clays acquire positive charges likely to promote a strong attraction towards F^- ions, which would lead to an increase in the adsorption capacity. But, unlike in a basic medium (above the pH_{PCN}) where these clays will acquire negative charges likely to repel these F^- ions, which would lead to a reduction in the adsorption capacity. Similar results were reported by *Mourabet* [21]. Thus, the high adsorption rates of activated clays observed could be due to the increase of their adsorption sites and the SS they could develop after acid activation.

Effect of temperature

The decrease in the adsorption capacity of F^- ions on clays when the temperature increases could be due to the destabilization of the physical forces involved or to the change in the degree of oxidation of certain constituent elements of these clays which could better adsorb these ions in the unoxidized state. This indicates the endothermic character of adsorption of F^- ions on the

surface of these clays. This same phenomenon was observed in the case of the adsorption of anionic dyes on Fouchana clay [19].

Application on natural waters

The high percentage of elimination of F^- ions from the waters of Belbedji by the raw and activated clays could be explained by the fact that these waters have a higher concentration exceeding that of the other structures. This will allow the different available reaction sites of these clays to adsorb the maximum of F^- ions, as has been found in the case of synthetic solutions, that increasing the concentration of F^- ion leads to an increase in the adsorption capacity of these clays. This observation is identical for the other structures which are in perfect agreement with their initial concentrations of F^- ions. But, as the waters of Koundoumawa and Belbedji have the same initial concentration and those of Belbedji have a higher percentage of elimination, this could be due to the difference in the physico-chemical composition of these waters, including certain elements (HCO_3^- or Na^+) contained in the waters of Koundoumawa could compete with the F^- ions or have an influence on their adsorptions respectively. The increase in pH observed after adsorption could be attributable to the fact that the F^- ions react with the positive charges of the clay surfaces, which will undoubtedly lead to its increase. Our results differ from those obtained by *Diop* [22] who found acidic pH values after adsorption on montmorillonite. This difference would probably be due to the fact that our clays are made up of several minerals and trace elements in addition to montmorillonite which can adsorb F^- ions to the detriment of the other ions present in the waters of these structures.

CONCLUSION

The various F^- ion elimination tests carried out on raw and activated clays have shown the possibility of these clays adsorbing these ions. From a performance point of view, the chemically activated clays showed more affinity towards these ions than the raw clays. And equilibrium is reached at 120 min for all the clays. Thus, we have shown in particular the possibility of natural clays in the raw state without any activation to adsorb these ions with yields of more than 50% in the natural waters of Belbedji and Koundoumawa. Which is a bit difficult in the literature. So, these clays would be potential materials for the adsorption of these ions.

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