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Sustainable approach to recover the hull waste of balanitesoegyptiaca for the removal of fluoride from water

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ABSTRACT: The presence of fluoride in water has become a major concern worldwide because of its chronic human carcinogenic behavior. Developing easily accessible and environmentally friendly disposal strategies is therefore a challenge for scientists. Heme-activated balaniteoegyptiaca shell carbon has been studied for its ability to adsorb fluorine from aqueous solutions. The kinetics and adsorption capacity of activated carbon were evaluated. The effect of various parameters, such as activator concentration, initial fluoride concentration, pH, and contact time on the sorption process was studied. The influence of the addition of co-existing ions on the adsorption of fluorine has also been studied. Thermodynamic parameters such as "ΔG◦", "ΔH◦" and ΔS◦ were calculated to understand the nature of the sorption. A field study was conducted with fluorine-containing water samples that were collected from a fluoridated endemic area to test the suitability of the adsorbent for field conditions.

I. INTRODUCTION

Millions of people suffer from fluorosis due to high levels of fluoride in their drinking water. The problem is more serious in rural communities and small urban communities, especially in third world countries [1]. In Niger, this problem is common in places such as Maradi, Zinder and Tillaberi [].The effect of fluoride on human health depends on its concentration in drinking water and on the total amount ingested. Excessive ingestion of fluoride above the World Health Organization (WHO) limits (> 1.5 mg / L) may lead to dental fluorosis and / or skeletal influenza [2]. Therefore, it is imperative to correct excess fluoride in the drinking water. The removal of fluoride from water can be achieved by various physicochemical and biological methods [3]. Adsorption is one of the most effective technologies for the removal of fluoride from drinking water compared to other technologies such as reverse osmosis [4],nanofiltration[5], electrodialysis[6,7] and Donnan Dialysis [8]. In addition to the adsorption properties, establishing the adsorption mechanisms of fluorine is also necessary for the industrial design of new adsorbents [9]. In recent years, considerable attention has been devoted to the development of new, cost-effective natural materials for the removal of fluoride from water, such as wheat straw, sawdust, sugar cane carbon, bone charcoal, limonum-treated citrus (lemon), reported by Yadav et al. [10], and Rojas-Mayorga et al. [11] and Tomar et al. [12]. The local agri-food industry produces large waste stocks that can be used for water treatment. This is the case for example of hulls oegyptiacabalanites. Thismaterial is inexpensive, very available both from a point of view of quantities that proximity to the regions of the water to be treated. The current work aims to explore the feasibility of removing F- ions from aqueous solution from the hull of calcinedoenyaptiaca (CBC) or calcined and activated (CBCA) balanites. We have developed this new adsorbent CBCA by simple method of calcination and activation. The removal of fluorine from the aqueous solution by CBCA has been studied and discussed.
The purpose of this study is to describe and examine the mechanism of adsorption of F- ions on CBCA, based on the experimental results obtained.

II. MATERIALS AND METHODS

A. Preparation of the absorbent

The adsorbent used is a natural waste (the shell of balanitesoegyptiaca (CB)). CBA was calcined at different temperatures (400 ° C, 500 ° C, 600 ° C and 700 ° C). Each calcination product was divided into five fractions. Four fractions were activated with hydrochloric acid (HCl) at different concentrations (0.5M, 1M, 2M and 3M).

B. Preparation of the solution F-

In this work, solutions of F- ions were prepared from NaF powder and distilled water. The solutions used for the adsorption studies have a pH adjusted by 0.1M HCl or 0.1M NaOH.

C. Adsorption experiments

The sorption experiments were carried out in 100 ml polyethylene beakers. Each time, 50 ml of CF-concentration solution (NaF) and one mass of the adsorbent were introduced into the beaker. The mixture (adsorbent-solution F-) is stirred for a time t. The residual fluoride ion content Ce is determined by molecular absorption spectrophotometry, with a HACH, DR / 3900 at the wavelength of 580 nm.

D. Optimization of adsorption parameters

The influence of the calcination temperature (400 ° C., 500 ° C., 600 ° C. and 700 ° C.), the concentration of the acid used (0.5M, 1M, 2M and 3M) and the pH of the adsorbed solution (2-10), have been studied. The effect on the adsorption capacity of the solids of the mass of the adsorbent (4 to 20 g / L) was studied. The contact time required to reach equilibrium was determined using different contact times (15, 30, 45, 60, 75 and 90 min). To check the sensitivity of the supports to the presence of other anions, adsorption were carried out in the presence of competing anions (Cl -, NO 3, SO42 -) using different concentrations (10, 20, 30 and 40 mg / L) of the competing anion. Finally, the influence of the temperature of the experiment on the percentage of extraction of F-ions by the solid CBCA was studied, carrying out the adsorption at three different temperatures (298K, 318K and 323K).

E. Calculations

The adsorption capacity of F- on CBCA at time t (qt (mg / g)) as well as at equilibrium (qe (mg / g)) was calculated on the basis of the following equations:

$$\boldsymbol{q_t} = \frac{(\mathrm{C_0 - Ct})\mathrm{V}}{\mathrm{m}} \; (1) \qquad \boldsymbol{q_e} = \frac{(\mathrm{C_0 - Ce})\mathrm{V}}{\mathrm{m}} (2)$$

The percentage of F- eliminated R (%) was calculated from the following equation:

$$\boldsymbol{R} = \frac{(\boldsymbol{C_0} - \boldsymbol{Ce})\mathbf{100}}{\boldsymbol{C0}}$$

Where Co (mg.L-1) is the initial concentration of F- and Ce (mg.L-1) F-concentration at equilibrium; m (g) is the mass of the adsorbent used; V (L) is the volume of the solution of F-.

F. Adsorption isotherms and kinetic adsorption studies

There are several equations of isotherms available to analyze the experimental data of the adsorption equilibrium. In this study, Langmuir, Freundlich, Elovich isotherms, and Lagergren's first and second-order pseudo-order were used to interpret experimental data from adsorption processes.

G. Physico-chemical characteristics

The zero point of load (PZC) is a valuable parameter for a good understanding of the contact between the surface of the CBCA and F-. In addition, the concept of PZC also suggests the availability of OH- (pH> PZC) or H + ions (pH <PZC) on the surface of the adsorbent. CBCA PZC was determined by the salt addition method as indicated in the literature [13]. Briefly, 50 ml of 0.1 M solution of KNO3 was transferred to six 100 ml Erlenmeyer flasks. The initial pH of these solutions was adjusted to 2.0, 4.0, 6.0, 8.0, 10 and 12 by adding 0.1 M HNO3 / NaOH and then 200 mg CBCA was

added to each vial. These flasks were stirred in a water bath for 2 h at room temperature and allowed to equilibrate for 48 h. These suspensions were centrifuged and the final pH of each supernatant was noted. The CBCA PZC was calculated from the curve between the initial pH and the final pH. The point at which the final pH curve crosses the initial pH gave PZC. The FTIR has been used for the identification of CBCA surface functions. The spectrum was carried out using a PERKIN ELMER Universal ATR (Attenuated Total Reflectance) spectrometer over a spectral range of 500-4000 cm -1. Texture parameters of the hull of Balanitescalcined at 700 ° C were determined using an ASAP 2420 V2.09 (V2.09 J).

III. RESULTS AND DISCUSSIONS

A. Physic-chemical characteristics

The texture parameters of the 700 ° C calcined flask of Balanites calculated from the N_2 adsorption isotherms at -196 ° C are: BET Surface Area (S_{BET}) = 167 m² / g; pore volume (V_t) = 0.093 cm³ / g; micropore volume (V_{DR}) = 0.052 cc / g; mesopore volume (V_{Mes}) = V_t - V_{DR} = 0.041 cm³ / g; % mesopores = (V_{Mes} / V_t) * 100 = 44; % micropores = (V_{DR} / V_t) * 100 = 66.

The PZC value of the CBC powder is 7 (Figure 1), this indicates that the adsorption of F- is favored at pH < 7 (G. C. Velazquez-Peña et al, 2014) [13].

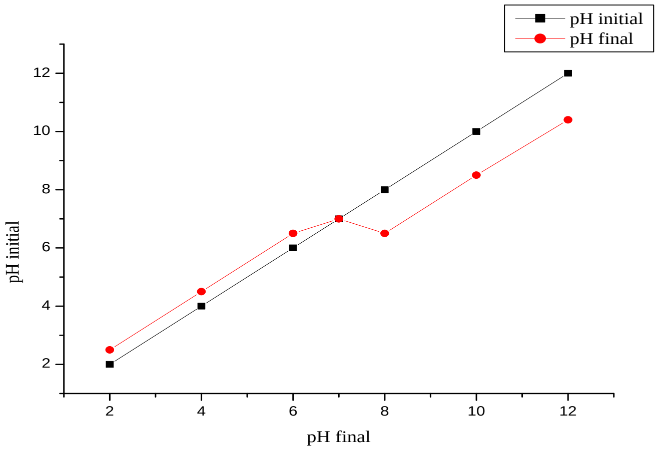


Figure 1: Determination of PZC of the CBCA

As shown in Figure 2, the peak observed at 3452 cm-1 can be attributed to the presence of a hydroxyl (OH) group [14]. The peak at 857 cm-1 corresponds to the out-of-plane strain O-H [15]. The wave number of 1272 cm-1 indicates the presence of a strong C-F bond [16]. The intensity of this band increases after adsorption, indicating the adsorption of fluoride on the CBCA. After adsorption, the modification of the band around 1272 cm -1 indicates that the hydroxyl groups on the adsorbent surface played a role in the adsorption. The peaks at 867 cm-1 and 796 cm-1 indicate that hydrogen bonding is enhanced due to the fact that the adsorbed fluoride has electronegativity greater than that of oxygen in the formation of a hydrogen bond [17].

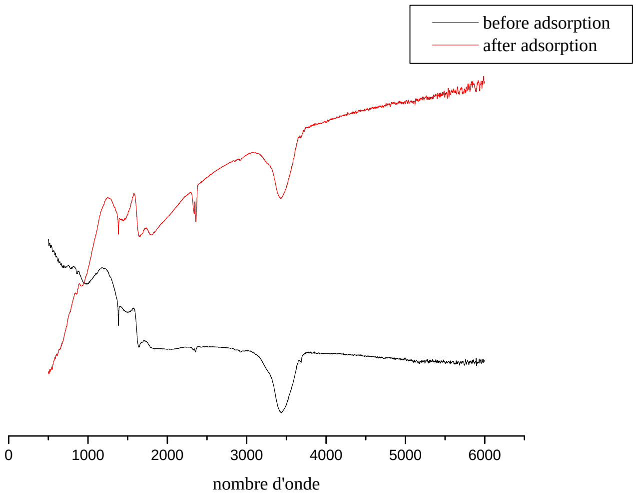


Figure 2: FTIR of CBCA before and after adsorption

B. Optimization of the concentration of the activating agent

The hull of calcined but not activated (CBC) oenyptiacabalanites does not adsorb F$^-$. The effect of activation of calcinedbalanite shell (CBC) with HCl acid on its ability to adsorb F$^-$ was investigated using different concentrations of HCl (0.5M, 1M, 2M and 3M). The results (Figure 2) show that the adsorption capacity of F$^-$ on CBCA increases as the concentration of the activating agent (HCl) increases. They also show that 3M is a good concentration of activator (HCl) for better adsorption of F$^-$ on CBCA. According to M.N. Alaya, et al, [18], calcination creates pores. But, the combustion of the hull produces tar vapor. The deposit of tarred substances (vapor) fills some pores, or at least blocks them with disorganized carbon. Activation develops the porous structure of a material. From the foregoing, the increase in the adsorption capacity of F$^-$ on CBCA as the concentration of the activating agent increases can be explained by an increase in the porous surface following activation, and or removing deposition of tarred substances (vapor) filling certain pores.

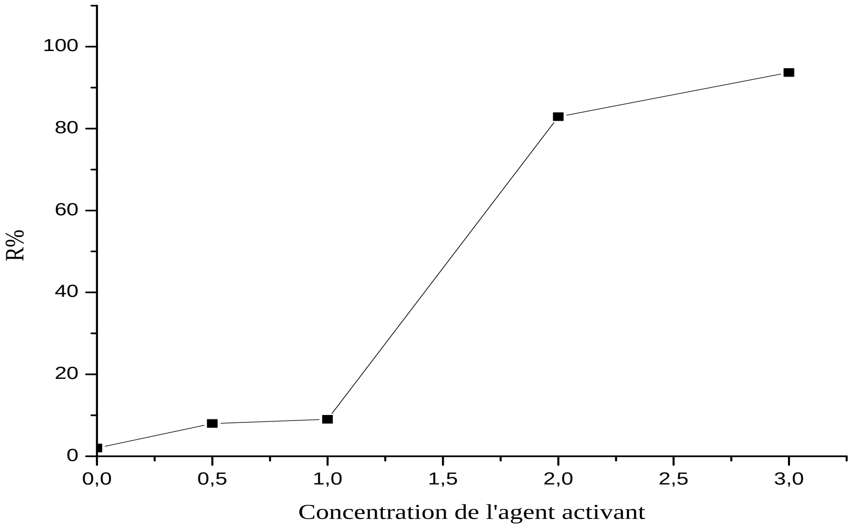


Figure 3: effect of the concentration of the activating agent on the adsorption capacity of the F$^-$ ions on CBCA ([F$^-$] = 5 mg.L^{-1}, pH = 7, adsorbent dose 4g.L^{-1}, temperature calcination 700 ° C; contact time)

C. Optimization of the calcination temperature

To determine the effect of the calcining temperature of CB on its adsorption capacity of F- ions, adsorption experiments were carried out on calcined CB at different temperatures (400 ° C, 500 ° C, 600 ° C). C and 700 ° C) and systematically activated with 3M HCl. The results of Figure 1 show that the adsorption capacity of F-ions on CBCA begins to increase when the temperature exceeds 500 ° C and increases as the calcination temperature increases. In the case of calcination of Theobroma cacao, [19] showed that the pore diameter and pore volumes of the monolith were increased as the calcination temperature increased. CB is a lignocellulosic. Therefore, the increase in the adsorptive capacity of F-ions on CBCA as the calcination temperature increases may be due to an increase in pore diameter and volume during calcinations [20] have shown that with certain lignocellulosic materials, calcination temperatures above 700 ° C produce coal with too small micropore volumes. Fisal Ahmad et al., [19] have also shown that lignocellulosic calcination at 500-700 ° C can alter the surface charge with the departure of the H and O atoms, in the light of the above, 700 ° C. can be considered as the maximum CB calcination temperature for this study for better adsorption of F- ions.

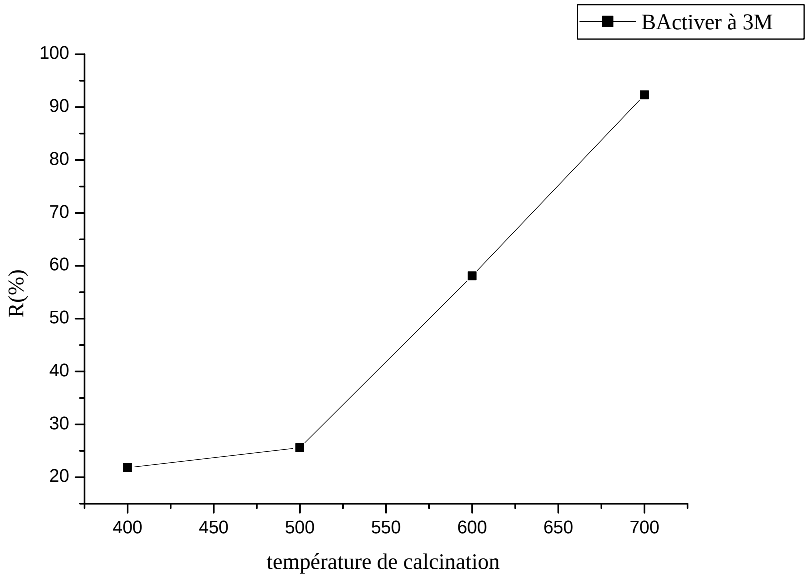


Figure 4: percent extraction of F^- ions by CBCA as a function of the calcination temperature of CB ($[F^-]$ = 5 mg.L^{-1}, pH = 7, adsorbent dose 4g.L^{-1}, [HCl] activating = 3 M, contact time).

D. PH optimization of F-solution

The effect of the pH of the medium on the ability to extract F-ions on CBCA was studied using different solutions of F- pH 2 to 10. The results of Figure 3 show that the pH of the solution F- has an influence on the percentage of extraction of F- ions by CBCA. If $2 \leq pH \leq 7$ the percentage of extraction of F- ions by CBCA is practically constant, about 82%. On the other hand, if $7 < pH \leq 10$, as the pH of the F-solution increases, the percentage of extraction decreases.According to Garg et al., [21], the pH controls the adsorption capacity of an adsorbent for the sequestration of ions from a solution due to its influence on the surface properties of the adsorbent and the ionic forms of the pollutants in the solutions. Figure 4 indicates that the zero charge point of the CBCA is obtained at pH 7 [22]. The surface has acquired a positive charge at pH values below 7. Therefore, the adsorption of F- at this pH level is mainly due to the electrostatic attraction between the positively charged surface and the negatively charged F-ions and the dominance of chemisorption. As the pH increases, the surface has acquired negative charges, physisorption dominates, therefore the percentage of extraction of F- ions decreases.

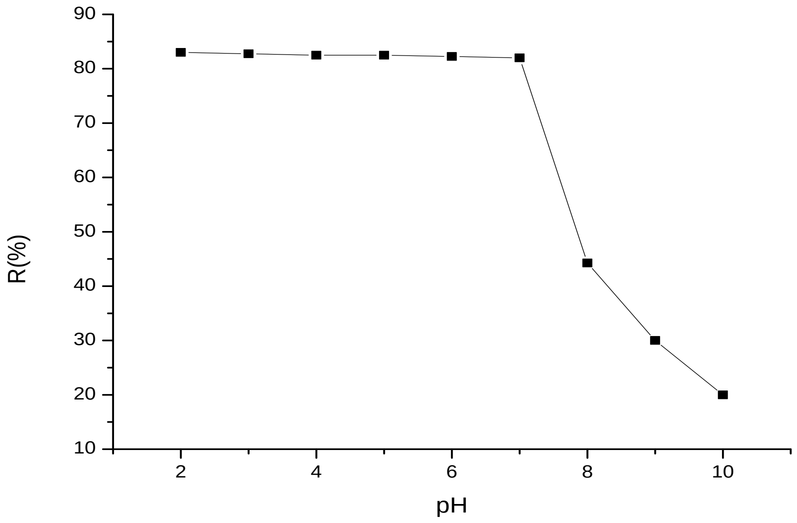


Figure 5: Percentage extraction of F$^-$ions by CBCA as a function of the pH of the medium ([F-] = 5 mg.L^{-1}, adsorbent dose 4g.L^{-1}, calcination temperature 700 ° C., [HCl] activating = 3M, contact time:)

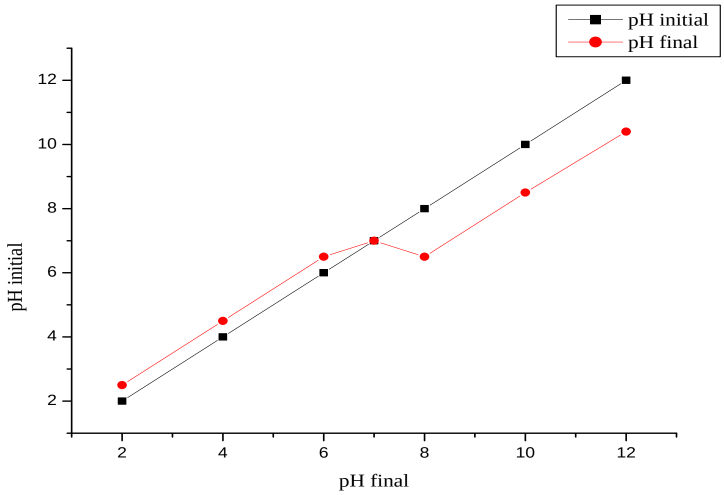


Figure 6: Determination of the null load point of the CBCA. ([F$^-$] = 5 mg.L^{-1}, pH = 7, adsorbent dose 4g.L^{-1}, calcination temperature 700 ° C., [HCl] = 3M).

E. Optimization of the 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 6 show that the adsorption rate of F-ions on CBCA is maximal in the first 15 min. They also show that the time required to reach balance is 75 min. This variation of the speed over time reflects distinct phases of the sorption phenomenon. During the first phase (0 to 15 min), the high intensity of the velocity may be due to the easy access to the external sites of the adsorbent. The decrease in velocity, 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 internal pores.

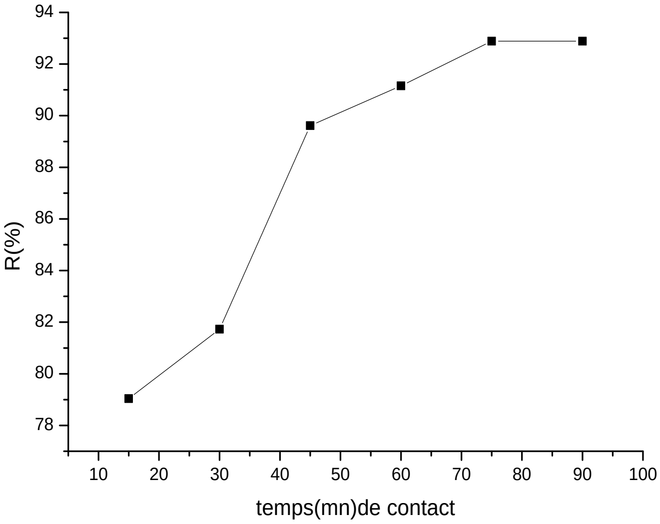


Figure 7: Percentage extraction of F$^-$ions by CBCA as a function of contact time. ([F$^-$] = 5 mg.L^{-1}, pH = 7, adsorbent dose 4g.L^{-1}, calcination temperature 700 ° C., [HCl] activator = 3M).

F. Effect of CBCA dose

The dose of the adsorbent is an important parameter because of its efficiency (% removal) and the amount of F- adsorbed per unit weight of adsorbent (qt). Adsorption tests of F-ions on CBCA were carried out using different masses (0.2, 0.4, 0.6, 0.8, 1 and 1.2 g) of CBCA, solution volume F- (50). ml), [F-] = 5mg / L at pH 7 and 25 ° C. The results of Figure 6 show that the percentage of extraction of F- ions increases as the dose of CBCA increases. They also show that the best adsorption capacities are obtained at a low dose. The increase in F-extraction percentage as the dose of CBCA increases is mainly due to an increase in adsorption surface area thus putting more active retention sites [23], . It can be seen (Figure 7) that, beyond (16 g / L) of CBCA, the percentage of extraction of the F- ions evolves very little. This small percentage change observed at high doses of CBCA is probably due to the availability of less active sites at the end of the adsorption process and / or the difficulty of F-edge ions in penetrating the adsorbent, while F- ions partially cover surface sites [24, 25, 26]. The results in Figure 6 indicate that the optimal dose of CBCA for extraction of F- ions is 16g / L.

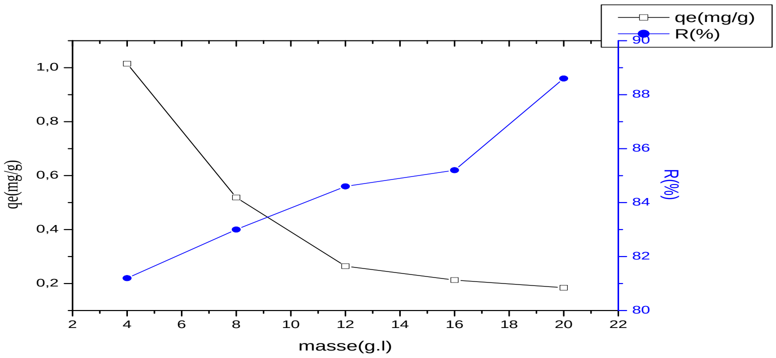


Figure 8: Percentage extraction of F□ ions by CBCA as a function of the dose of CBCA. ([F-] = 5 mg.L^{-1}, pH = 7, calcination temperature 700 ° C., [HCl] activating = 3M)

G. Effect of initial concentration of F^-

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^- on the percentage of extraction of the latter by CBCA is studied at various concentrations of F^- (3, 5, 70 and 10 mg / L), solution volume F^- (50 ml), mass CBCA (0.4 g) at pH 7 and 25 ° C. It is well observed (Figure 6) that as the initial concentration of F^- increases the percentage of extraction of these by CBCA increases. Two phenomena can explain this variation of the percentage of extraction of F^- by CBCA when the initial concentration of F^- varies. First phenomenon, when the concentration of F^- increases, the number of collisions between the F^- molecules and the functional groups of CBCA also increase, resulting in an increase in the adsorption capacity [27, 28, 29, 30]. Secondly, in the presence of a high F^- en concentration, the diffusion forces from F^- to CBCA become much higher, which favors intraparticular diffusion phenomena.

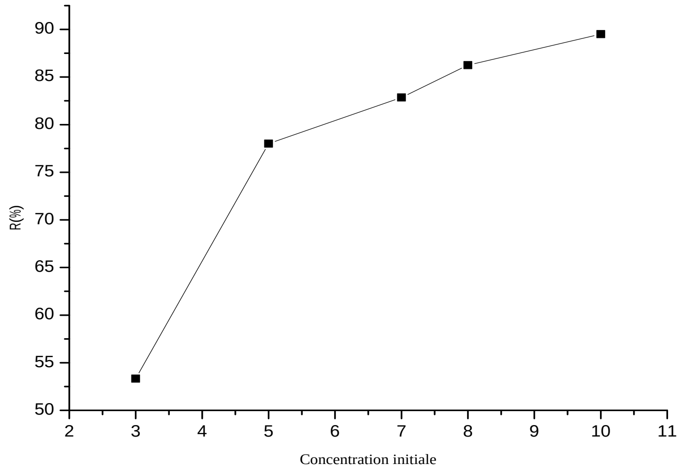


Figure 9: Effect of the initial concentration of F^- on the adsorption capacity (pH = 7, adsorbent dose $4 g.L^{-1}$, calcination temperature 700 ° C., [HCl] activating = 3M).

H. Effect of the presence of competing anions

The effect of the presence of competing anions (Cl^-, NO_3^-, SO_4^{2-}) on the percentage of extraction of F^- by CBCA is studied using different concentrations of 10, 20, 30 and 40 mg / L of competitor anion. The results (Fig. 8) show that the presence of competing anions (Cl^-, NO_3^-, $SO_4^{2-)}$ strongly lowers the percentage of F^- extraction by CBCA. They also show that the order of influence of the competing anions on the percentage of extraction of the F^- by CBCA is: NO_3^- >Cl^-> SO_4^{2-}. According to Bernard et al, (1996), the classification of the radii of the hydrated anions (Cl^-, NO_3^-, SO_4^{2-}) is: r (SO_4^{2-})> r (Cl-)> r (NO_3^-). In the presence of anions (Cl^-, NO_3^-, SO_4^{2-}), the adsorption of F- on CBCA competes with that of (Cl^-, NO_3^--, SO_4^{2-}) and the selectivity of CBCA is correlated with the size of the adsorbate. The variation of the percentage of extraction of F- by CBCA as a function of the concentration of the competing anion observed (Fig. 8) can be due to a displacement of the equilibrium of the adsorption of F- by CBCA towards the fixation of the competitor anion and the release of F- [31]. However, beyond a certain concentration, the reduction of the fluoride extraction 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.

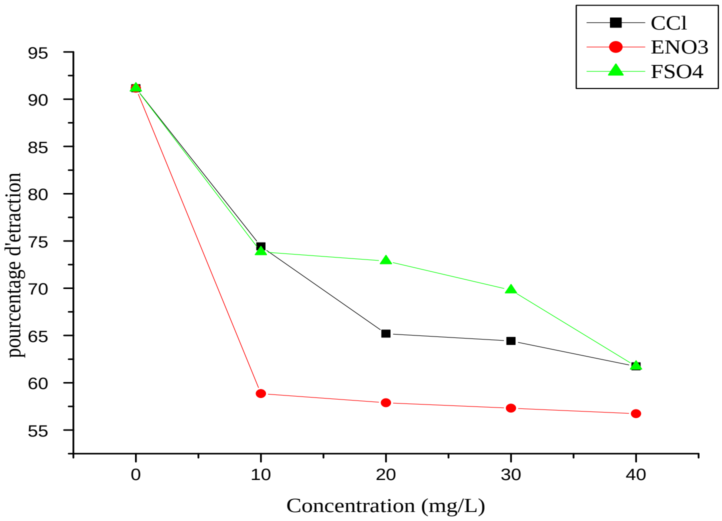


Figure 10: The effect of the presence of competing anions (Cl^-, NO_3^-, SO_4^{2-}) on the percentage of extraction of F^- by CBCA ($[F^-]$ = 5 mg.L^{-1} pH = 7, adsorbent dose 4g.L^{-1}, calcination temperature 700 ° C., [HCl] activator = 3M).

CBCA has been applied in the extraction of F- ions from some drilling water, see Table 1.

Table 1: Effect of the use of CBCA for fluoride removal from drilling water in the Maradi region (Niger). (4g.L^{-1} CBCA, 700 ° C)

Village	pH	$[SO_4^{2□}]$ (mg/L)	$[NO_3^{□}]$ (mg/L)	$[Cl^{□}]$ (mg/L)	$[PO_4^{2□}]$ (mg/L)	$[F^{□}]$ avant adsorption (mg/L)	$[F^{□}]$ après adsorption (mg/L)	Abattage %
Banbakori	7,11	5,72	30	40,825	0, 38	2,15	1,14	
Dakoro	7,01	4,8	24	23,075	0,42	1,80	0,15	
Malamkaka	7,03	16,6	50	44,375	0,51	2,48	0,88	
Sabonmachi	6,79	2	25	28,5	0,29	1,94	0,70	
Koukabiyar	6,70	10,2	9	24,85	0,18	1,99	0,61	

It is not clear why it works better with Malamkaka water than with Banbakori water while the concentration of anions is higher.

I. Thermodynamic study

The influence of temperature on the percentage of adsorption of F^- by CBCA is studied by carrying out the adsorption at three temperatures (298K, 318K and 323K). The thermodynamic parameters (ΔH, ΔS and ΔG) of the adsorption reaction of F^- on CBCA were determined from the following equations (BOUBERKA et al., 2005):

$$K_d = \frac{q_e}{C_e} \Delta G = -RTlnK_d$$

$$lnK_d = \left(\frac{\Delta S°}{R}\right) - \left(\frac{\Delta H°}{R}\right) \times \frac{1}{T}$$

Where Kd is the adsorption distribution coefficient, ΔS the entropy variation, ΔH the enthalpy change of the adsorption reaction, ΔG the Gibbs free enthalpy, qe the adsorption capacity of F^- on CBCA (mg / g), T (K) is the temperature at which the experiment was performed, R (J mol-1 K-1) the perfect gas constant. The values of ΔH and ΔS were determined from the slope and the intersection with the ordinate axis of the curve, lnKd as a function of 1 / T. As shown (Figure 9), the variation of the temperature (298K, 318K, and 323K) of the experiment has a significant influence on the percentage of adsorption of F^- on CBCA only if the contact time (CBCA-F^-) is greater than 45 minutes. Figure 9 also shows that beyond 60 min of contact time, the percentage of F^- on CBCA adsorption increases as the temperature increases. According to S. Aytas et al., [32], the increase in the adsorption capacity with temperature is attributable either to the increase in the number of active surface sites available for adsorption on the adsorbent, or to the desolvation of the adsorbates and decreasing the thickness of the boundary layer surrounding the adsorbent at the temperature, so that the mass transfer resistance of the adsorbate in the boundary layer decreases. The values of the thermodynamic parameters (ΔH; ΔS and ΔG) of the adsorption of F^- on CBCA are given in Table 2. The negative values of Gibbs free enthalpy obtained at different temperatures show that the adsorption process F^- on CBCA is spontaneous and the degree of spontaneity of the adsorption reaction increases as the temperature of the experiment increases. The positive value of ΔH indicates that the process of adsorption is endothermic. According to S. Aytas et al., [32], positive ΔS promotes the complexation and stability of F- adsorption on CBCA.

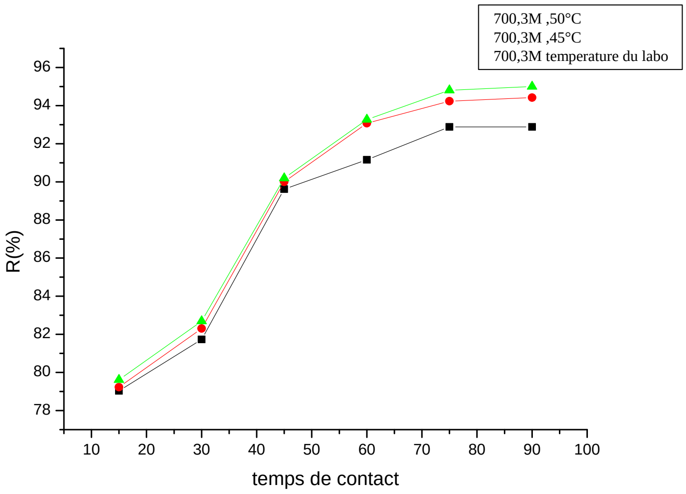


Figure 11: Effect of the temperature of the experiments on the percentage of extraction of F^-ions by CBCA ($[F^-]$ = 5 mg.L^{-1}, pH = 7, adsorbent dose 4g.L^{-1}, calcination temperature 700 ° C, [HCl] activating = 3M).

Table 2: Thermodynamic parameters of fluoride sorption on CBCA

Température(K)	ΔH(KJ)	ΔS(KJ)	ΔG(KJ)
298	0,44	12,574	-0,638
318			-1,373
323			-1,476

J. Adsorption isotherms

The adsorption isotherms provide 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 constant temperature adsorbent [33, 34]. In this study, in order to understand the adsorption mechanisms of F^- On CBCA ions, the equilibrium data were analyzed using the Langmuir and Freundlich isothermal models. The adsorption isotherms were obtained from the representation of the amount of F^- adsorbed on CBCA (qe (mgg^{-1})) as a function of the concentration of F- in equilibrium solution (Ce (mg.L^{-1})). qe and Ce were obtained from experiments at various concentrations of F- (3, 5, 70 and 10 mg.L^{-1}).

The Langmuir isothermal model is based on the assumption that the adsorption process is monolayer on the surface of the adsorbent and that there is no interaction between adsorbed and free molecules in the solution [35]. The Langmuir equation is applied to quantify the adsorption capacity of the adsorbent when all the adsorption sites are of equal binding energy. In this study, the Langmuir isotherm model is used on the one hand, to demonstrate a monolayer adsorbate distribution inside the adsorbent and on the other hand, to represent the equilibrium distribution of F^- between CBCA and the solution. To describe the Langmuir adsorption isotherm, the following equation is used [36]:

$$\frac{\boldsymbol{Ce}}{\boldsymbol{qe}} = \frac{\mathbf{1}}{\boldsymbol{KLqm}} + \frac{\mathbf{Ce}}{\boldsymbol{qm}}$$

Where qe (mg / g) is the amount of F-adsorbed on CBCA at equilibrium; This (mg / L) is the concentration of F^- at equilibrium; qm (mg / g) is the maximum adsorption capacity of F^- by CBCA; K_L ($L.mol^{-1}$) is the Langmuir constant exponentially proportional to the heat of adsorption and related to the adsorption intensity. The Ce/qe en function curve of Ce should be linear if Langmuir adsorption is applicable (G Wang et al, 2009) [37].

The Freundlich isothermal model describes a heterogeneous adsorption process and assuming different sites with several adsorption energies [J. Su, et al, 2011) [38]. The Freundlich model is suitable for the description of multilayer adsorption with interaction between adsorbed molecules [39]. In this study, the Freundlich model is chosen to estimate the adsorption intensity of F^- on the surface of the CBCA [40]. The equation used to describe the Freundlich adsorption isotherm is as follows [41]:

$$\boldsymbol{lnqe} = \boldsymbol{lnKf} + \frac{\mathbf{1}}{\boldsymbol{n}}\boldsymbol{lnCe}$$

Where q_e ($mg.g^{-1}$) is the amount of F^-adsorbed on CBCA at equilibrium; this ($mg.L^{-1}$) is the concentration of F- at equilibrium; K_f ($mg.g^{-1}$) is the Freundlich constant associated with the adsorption capacity; 1/n is the Freundlich constant associated with the adsorption affinity.

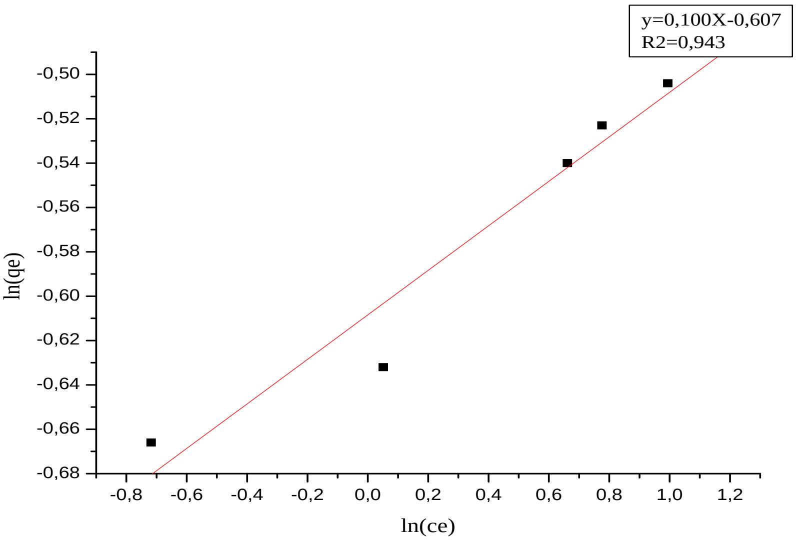


Figure 12: Freundlich isotherm of the adsorption of F^- on CBCA, ($[F^-]$ = 5 $mg.L^{-1}$, pH = 7, adsorbent dose $4g.L^{-1}$, calcination temperature 700 ° C., [HCl] activating = 3M).

Figure 10 shows the Freundlich isotherm. The constants of this isotherm 1/n and k_f ($L.mg^{-1}$) respectively the empirical constant of the Freundlich isotherm and the intensity of the adsorption of F^- on CBCA were calculated respectively from the slope and the intersection with the y-axis of the representation of ln (q_e) in function ln (Ce).

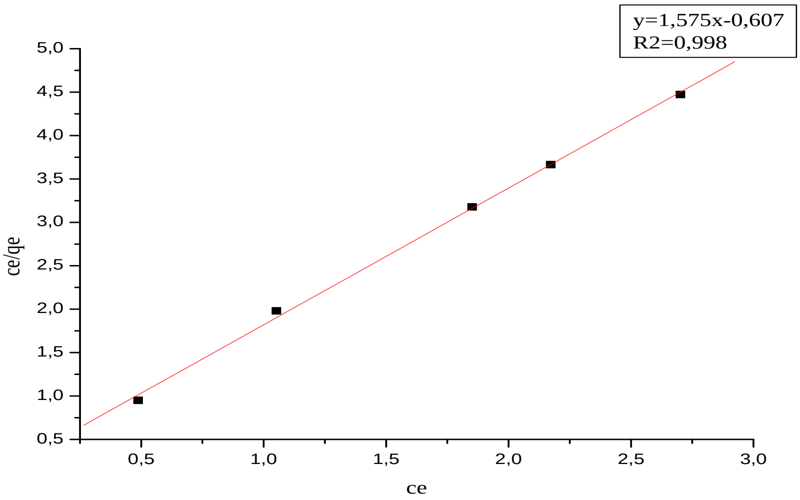


Figure 13: Langmuir isotherm of the adsorption of F^- on CBCA, ([F-] = 5 mg.L^{-1}, pH = 7, adsorbent dose 4g.L^{-1}, calcination temperature 700 ° C., [HCl] activating = 3M).

Table 2: Langmuir and Freundlich isotherm parameters of fluoride sorption on CBCA

adsorbent	adsorbate	Freundlich isotherm			Langmuir isotherm		
		K_F(mg.g^{-1})	1/n	R^2	K_F (L.mg^{-1})	q_m (mg.g^{-1})	R^2
CBCA	F^-	0,545	0,1	0,943	6,454	0,635	0,998

There is no significant difference between the correlation factor values of the Freundlich model (R^2 = 0.943) and that of the Langmuir model (R^2 = 0.998). According to W. Fritz, et al, (1981), the adsorption process seems to have a mixed behavior of these two models that could well be described as a pseudo-multilayer adsorption. According to G. Annadurai, et al, [42], this situation indicates that the adsorption of F^- on CBCA is a complex adsorption process with an uneven energy distribution due to different groups of surface with different levels of activation energy for the adsorption process and an interaction between adsorbate. The high correlation coefficient R^2 of Langmuir compared to that of Freundlich indicates that the Langmuir isotherm model could better correctly describe the measured equilibrium adsorption data. That is, monolayer adsorption plays a major role in the adsorption process. According to V.K. Gupta et al [43], the value of 1/n being less than 1, the adsorption of F^- on CBCA is favorable.

K. Kinetic studies of adsorption

On the basis of the results obtained from the adsorption experiments of F^- on CBCA at constant temperature and monitoring the adsorbed amount with time (Figure 5), the adsorption kinetics of F^- on CBCA is studied with the kinetic models pseudo first order, pseudo second order, Intraparticle diffusion model and the Elovich model. In published studies, the kinetic model followed by the adsorbent is often analyzed by the correlation coefficient (R^2) with the experimental data [44]. The pseudo-first order is generally used in case of physical adsorption on homogeneous adsorbents [45]. It generally applies during the first 20 to 30 min of the adsorption process [46]. The equation used to describe the adsorption isotherm [47] is:

$$\mathbf{qt} = \boldsymbol{qe}(\mathbf{1} - \boldsymbol{e}^{-\boldsymbol{k1t}})$$

$$\mathbf{ln}(qe - qt) = lnqe - \mathbf{Klt}$$

Where qe and qt are, respectively, the values of the amount of F- absorbed per unit mass (mg g-1) at equilibrium and at any time t, k1 is the constant of the adsorption rate of the pseudo-first order (min-1). Using Lagergren's simple equation, the rate of sorptive interactions can be evaluated [48].

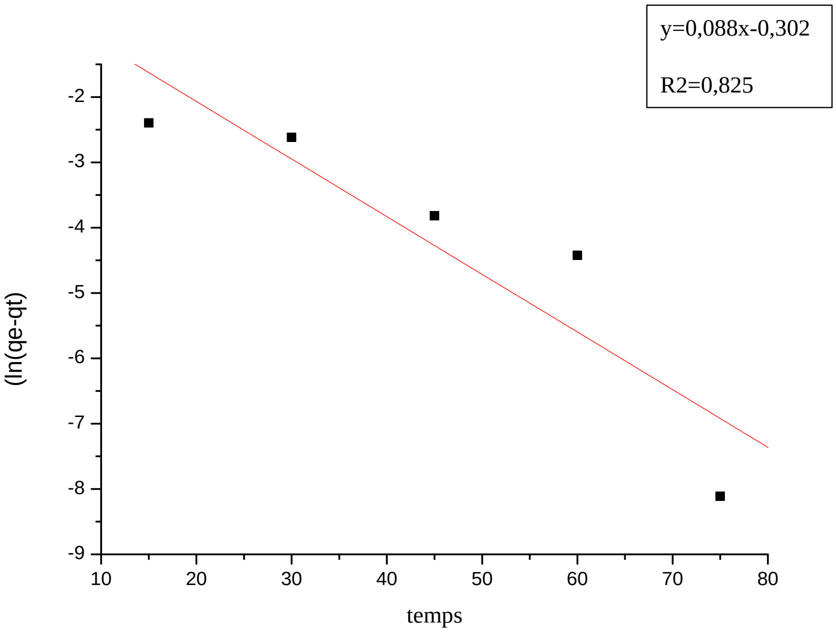


Figure 14: Lagergren first-order isotherm of the adsorption of F^- on CBCA ([F-] = 5 mg.L^{-1}, pH = 7, adsorbent dose 4g.L^{-1}, calcination temperature 700 ° C., [HCl] activating = 3M).

The pseudo-second order equation assumes that the process of adsorption involves a chemisorption mechanism. The pseudo-second-order model used is the following [49]:

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

Where qe and qt are, respectively, the values of the amount of F^- 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 the F^- on CBCA studied is shown in Figure 13:

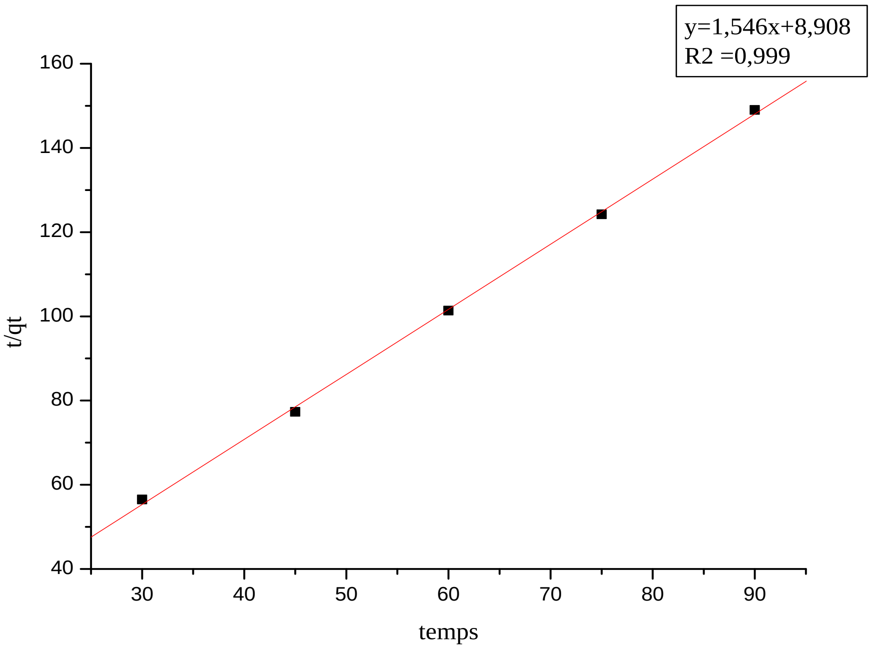


Figure 15: Lagergren pseudo-second order isotherm of ion adsorption on CBCA

The kinetic parameters were determined and tabulated in Table 3. The correlation coefficient R^2 in the pseudo-second-order model (0.999) is significantly higher than that of the pseudo-first-order model (0.875). The correlation with the pseudo-first order kinetic model gave a significantly low value of R^2. Moreover, the qe value calculated in the pseudo-second-order model is closer to the experimental data than that of the Pseudo first-order model, indicating that the kinetic data better fit the pseudo-second-order model than the pseudo-first order model [27]. The mechanism of adsorption is therefore a chemisorption [35]. The chemisorption mechanism is a monolayer, which supports the Langmuir isotherm model because of its high R^2 value.

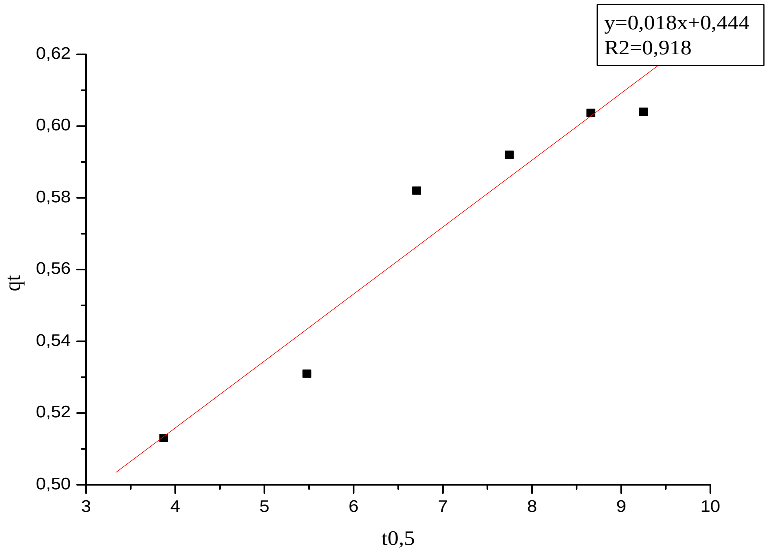
L. Intraparticle diffusion model

In order to understand the mechanisms and steps controlling the kinetics of adsorption, the experimental kinetic results were tested by Weber and Morris's intraparticle diffusion model [50]. According to this theory.

$q_t = \text{Kpi}\, t^{0.5} + \text{Ci}$

Where kpi is the intraparticular diffusion rate. Ci, the interception of phase i gives an idea of the thickness of the boundary layer, that is to say the greater the interception, the greater the effect of the boundary layer is large [51].

If intraparticular scattering occurs, then qt versus $t^{0.5}$ will be linear, and if the plot traverses the origin, the rate limiting process is solely due to intraparticular scattering. Otherwise, another mechanism with intraparticular diffusion is also involved.



The values of Kp and Ci are obtained by linearizing the curve qt = f ($t^{0.5}$). The values of Kp, Ci and the correlation coefficient R^2 obtained are in table 3. The slope of the linear part indicates the rate of the adsorption process [52].The results show that the diffusion rate of F^- in CBCA decreases as the contact time increases. The first stage was completed within 45 minutes, where 88% of the adsorption occurred. The first linear part did not pass near the origin. The linear lines of the second and third steps do not cross the origin. According to K. Mohanty et al, [53] this deviation from the origin could be due to the difference in mass transfer rates in the initial and final stages of adsorption. According to Brijesh S. et al, [54], the observed multi-linearity indicates that different mechanisms are involved in the sorption process.

Table 3: Kinetic parameters of reaction-based

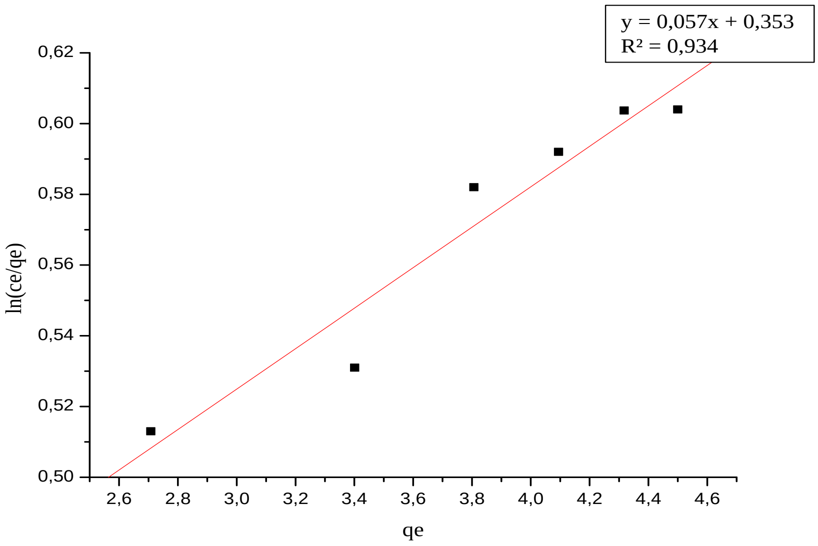
adsorbent	adsorbate	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion model		
		q_e (mg/g)	K_1(min^{-1})	R^2	K_s ($g.mg^{-1}min^{-1}$)	q_e (mg/g)	R^2	K_p(mg g_1 $min^{0.5}$)	Ci (mgg^{-1})	R^2
CBCA	F-	0,739	0,088	0,825	0,04	0,647	0,999	0,018	0,444	0,918

M. Elovich's equation

Elovitch's expression was first used to describe the chemisorption kinetics of gases on solids [55]. Despite this, this model has been widely used and cited in the case of chemisorption kinetics for solid/liquid systems [56]. The Elovitch equation, initially used to express the beginning of the sorption process, long before equilibrium, can be used correctly in case of chemisorption with highly heterogeneous materials [57]. The adsorption of F^- on CBCA is modeled according to the Elovich Model [58] with the equation:

$$q_t = 1/b \ln(ab) + 1/b \ln t$$

Where qt ($mg.g^{-1}$) is the amount of F^- adsorbed on CBCA at time t, a is the initial adsorption rate of the Elovich model ($mg.g^{-1}.min^{-1}$) and b is the extent of the coverage superficial ($g.mg^{-1}$). The equation constants are obtained from the plot of the line qt versus
Ln(t).



. **Figure 17:**Elovich isotherm of F-adsorption on CBCA

Table 4: Elovich parameters of F-ion adsorption on CBCA

a(mg g-1 min-1)	b(g mg-1)	R^2
27,89	17 ,54	0,934

From the value of R^2 (Figure 14), it can be deduced that the Elovich model can be accepted as one of the characteristics of the adsorption reaction. According to C.E. Chitour [59], chemisorption is well described by the Elovich equation, when the adsorption process follows the pseudo-second order. The process of adsorption of F^- on CBCA follows the pseudo-second order, so the adsorption of F^- on CBCA is indeed a chemisorption. According to several authors [60, 61], since the mechanism of fluorine sorption seems to be more related to chemisorption, as mentioned previously, the model of 'Elovich is better for describing kinetic data.

IV. CONCLUSION

In the present study, an activated charcoal obtained from the hull of balanitesoegyptiaca has been produced and used for the removal of F^- from drinking water. The percentage of removal of F^- from natural waters by the CBCA is about 65%. The test results verified that HCl activation increased the performance of CBC as adsorbing F^- in water. At room temperature (25 ° C), optimal adsorption is obtained at acid pH (pH $\leq$ 7). The effectiveness of the defluorination depends particularly on the calcination temperature of the CB, the concentration of the activator (HCl), the pH of the F^- solution, the mass of the adsorbent material, the F^- concentration. The adsorption equilibrium results show that this equilibrium is suitably described by the Freundlich and Langmuir models. The F^- adsorption process on CBCA follows second-order kinetics, with an initial sorption rate of 0.383 g.mg $^{-1}$.min. The competitiveness of the counterions (NO_3^-, Cl^-, $SO_4{}^{2-}$) with respect to the removal of F^- depends on the following factors: the radius of the hydrated ion under consideration. Indeed, the classification according to the selectivity follows the order $NO_3^->Cl^-> SO_4^2$; the quantity of the counterions, particularly in nitrates and / or in chlorides.

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