Removal of Fluoride from aqueous solution using natural Mauritanian clay as low cost adsorbent: A preliminary study

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Abstract

Fluoride removal from aqueous solution by ultrasound-assisted adsorption using natural Mauritanian clay as low cost adsorbent has been studied. The effects of some variables governing the efficiency of the process such as clay adsorbent mass, contact time and pH were investigated using a batch technique. The adsorption kinetic data were analyzed using the Pseudo First Order (PFO) and Pseudo Second Order (PSO) models. The adsorption modeling was carried out using the Langmuir, Freundlich and Redlich-Peterson adsorption models. The correlation coefficient (R^2) between the calculated and the experimental data by nonlinear method were used. For kinetic study, the adsorption process fitted the PSO model and agreed with chemisorption. Langmuir and Redlich-Peterson isotherms represent well the experimental adsorption data. The maximum adsorption capacity from the Langmuir model (q_{max}) was 0.22 mg g^{-1}. The results of the present work showed that natural Mauritanian clay has a good potential for fluoride removal from aqueous solutions via ultrasound-assisted adsorption.

1. Introduction

Fluoride has been classified as one of the potable water contaminants by the World Health Organization (WHO) [1]. The presence of fluoride in water has both beneficial and detrimental implications on human health depending on concentrations. At concentrations below 1mg L^{-1} fluoride helps in prevention of dental caries and development of bones particularly for children below the age of 10 [2;3].

However, excessive consumption of this substance inevitably leads to a number of adverse effects such as dental and skeletal fluorosis, decreased birth rates, lower intelligence quotient, thyroid gland injury and neurological disorders, when it is beyond the maximum permissible limit (1.5 mg L^{-1}) of Fluoride in the drinking water [4].

Therefore, many researchers are trying to focus on various defluoridation techniques such as reverse osmosis, precipitation, membrane filtration, ion exchange and adsorption [5-10]. In addition,

commercial activated carbon has been widely used in water treatment so far. However, the adsorbent activated carbon is cost prohibitive.

Thus, it is important to explore low-cost adsorbent for fluoride removal from aqueous solution. Recently a lot of cost effective adsorbents have been reported to possess fluoride removal capacity such as zeolites [11], natural soil [12], fired clay [13] and fly ash [13].

In this study, the natural and available Mauritanian clay was chosen to investigate its adsorption capacity for fluoride present in aqueous solution using the ultrasound assisted batch operation. Insofar as, many authors have reported that the innovative technologies used in combination with adsorption is sonication [14-16]. The effects of adsorbent mass, contact time and pH on the adsorption efficiency of Fluoride were studied using the batch experiment. The kinetics of Fluoride adsorption on clay was analyzed by Pseudo First Order (PFO) and Pseudo Second Order (PSO) kinetic models. Experimental equilibrium data were fitted to the Langmuir, Freundlich and Redlich-Peterson isotherm models.

2. Methodology

2.1 Adsorbate

Sodium fluoride (NaF), used in this study was of analytical grade and was used without further purification. All other chemicals used in this study were of analytical reagent grade. A stock solution of 1000 mg L^{-1} Fluoride was prepared by dissolving 2.21 g of NaF in 1000 mL of distilled water. Experimental solutions for various experiments are prepared by dilutions of the stock solution.

2.2 Preparation and Characterization of clay adsorbent

The raw clay was taken from Hassi El Ebyed in Moughataa of M'Bout, Wilaya of Gorgol, in Mauritania. The sample was grounded, sieved of the sample powder (< 100 μm), drying in the oven for 24 hours at 60 °C and used as such without any pretreatment. FTIR spectra of clay before and after fluoride adsorption were recorded.

2.3 Batch adsorption studies

Batch experiments were carried out by varying clay adsorbent dosage (0.1-2 g), effect of pH (2, 7 and 12) and contact time (5–60 min). The adsorption isotherms were obtained by varying the initial fluoride concentrations from 0.25 to 10 mg L^{-1}. In all sets of experiments were sonicated by ultrasonic bath Fisherbrand FB15050. At the end of each experiment, the sonicated solution mixture was microfiltered and the residual concentration of fluoride was analyzed by photometer Wagetech 7100. The adsorption uptake at equilibrium time q_e (mg g^{-1}) and percentage of the fluoride removed (%) are expressed by following equations (1) and (2), respectively:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

$$R\,(\%) = \frac{C_i - C_e}{C_i} \times 100 \qquad (2)$$

Where q_e is the fluoride concentration in clay (mg g^{-1}), C_i is the initial fluoride concentration (mg L^{-1}); C_e is the fluoride concentration at equilibrium (mg L^{-1}); V is the solution volume (L) and m is the mass of the clay adsorbent used (g). All batch experiments were conducted in triplicate and the average values are reported.

2.4 Study of adsorption kinetics

PSO and PFO model non linear kinetics were applied to investigate the adsorption data [17]. The nonlinear kinetics PFO and PSO models may be expressed by (3) and (4), respectively:

$$q_t = q_e(1 - \exp^{-k_1 t}) \qquad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (4)$$

Where q_t is the amount of fluoride adsorbed per unit mass of clay (mg g^{-1}) at time t, k_1 (L min^{-1}) is the PFO rate constant, k_2 (mg g^{-1}min^{-1}) is the PSO rate constant for adsorption, q_e (mg g^{-1}) the amount of fluoride adsorbed at equilibrium and t is the contact time (min).

2.5 Adsorption isotherms

Langmuir, Freundlich and Redlich-Peterson models were employed for to evaluate the efficacy of the adsorption process. A monolayer adsorption is defined by the Langmuir model upon the homogeneous surface of the adsorbent [18] and represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (5)$$

Where q_e is the quantity of fluoride adsorbed per unit mass of clay (mg g^{-1}), k_L is the Langmuir constant related to the adsorption capacity (L g^{-1}), C_e is the concentration of fluoride in the solution at equilibrium (mg L^{-1}), q_m is the maximum uptake per unit mass of clay (mg g^{-1}). The factor of separation of Langmuir, R_L is calculated by equation (6):

$$R_L = \frac{1}{(1 + k_L C_0)} \qquad (6)$$

Where C_0 is the highest initial concentration of fluoride and K_L is the Langmuir constant. The R_L value implies the adsorption to be defavourable (R_L>1), linear (R_L=1), favourable (0<R_L<1), or irreversible (R_L=0).

A multilayer adsorption is described by the Freundlich model upon the heterogeneous surface of adsorbent [19] and illustrated as in equation (7):

$$q_e = K_F C_e^{1/n} \qquad (7)$$

Where K_F (mg g^{-1}) (L mg^{-1})^n and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equation [20]. The nonlinear representation of the Redlich–Peterson model is as in equation (8):

$$q_e = \frac{K_{RP}C_e}{1 + \alpha_{RP}C_e^n} \qquad (8)$$

Where K_{RP} (L g^{-1}) and α_{RP} (L mol^{-1}) are the Redlich-Peterson isotherm constants, while n is the exponent, which lies between 0 and 1.

To optimize the design of an adsorption system for the removal of fluoride, it is important to establish the most appropriate correlation for the equilibrium data. The correlation coefficient R^2 values between the calculated and the experimental data by nonlinear method are determined by following equation (9):

$$R^2 = 100\left(1 - \frac{\left\|q_{exp} - q_{mod}\right\|^2}{\left\|q_{exp} - q_{avr}\right\|^2}\right) \qquad (9)$$

Where q_{exp} (mg g^{-1}) is equilibrium capacity from the experimental data, q_{avr} (mg g^{-1}) is equilibrium average capacity from the experimental data and q_{mod} (mg.g^{-1}) is equilibrium from model. So that $R^2 \leq 100$ – the closer the value is to 100, the more perfect is the fit.

3. Results and Discussion

3.1 Clay adsorbent characteristics

The physicochemical results showed pH of 7.95, a low moisture content of 1.49 %, bulk density of 0.83 g mL^{-1}, and loss on ignition of 30.11 %. X Ray-Fluorescence analysis showed that the predominant constituents are Silica (42.1 %) and Aluminium (18.6 %) oxide and other elements considered as impurities [21].

Figure 1 shows FTIR spectra of the clay before and after adsorbate adsorption. The result of the FTIR study of clay adsorbent showed absorption peaks located 3671, 3613, 3504, 1537, 946, 819, 744, 721, 626, 487and 437 cm^{-1} (Figure 1). According to [22], the most of the bands such as 3671 cm^{-1}, 3618 cm^{-1}, 3504 cm^{-1}, 947 cm^{-1}, 819 cm^{-1}, 744 cm^{-1} and 487 cm^{-1} show the presence of kaolinite. The Si–O stretching vibrations were observed at 744 cm^{-1}, 721 cm^{-1}, 487 cm^{-1} and 437 cm^{-1} showing the presence of quartz.
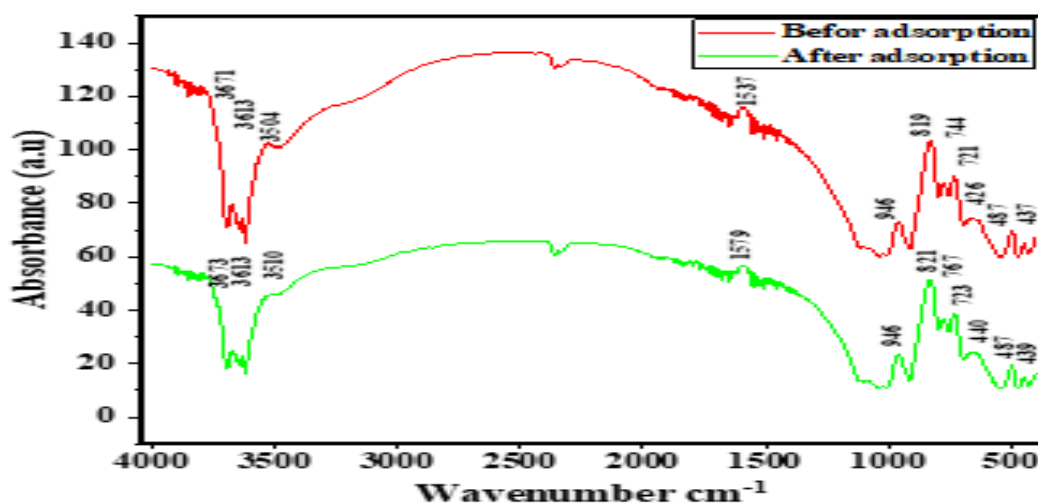

Figure 1. FTIR spectra of clay adsorbent before and after Fluoride adsorption

After fluoride adsorption, the slight shift of peaks was at 1579, 821, 767, 723, 640, 486, 439 cm^{-1} (Figure 1). A slight shift of frequency and a slighter decrease in intensity of some peaks could be attributed to fluoride ions adsorbed to clay adsorbent. The FTIR spectroscopic study after adsorption confirmed that the fluoride ion has a binding ability with the surface of clay adsorbent.

3.2 Effect of adsorbent mass

Variation of mass in the range 0.1–2 g at a fixed fluoride concentration (1 mg L^{-1}) for fluoride removal by clay adsorbent is shown in Figure 2. The results suggest that the increase in the dose of clay adsorbent results in an increase in adsorption, probably due to increase in the retention surface area. Similar phenomenon was reported for fluoride adsorption using natural Bentonite [23]. The optimal clay adsorbent mass obtained is 1 g.
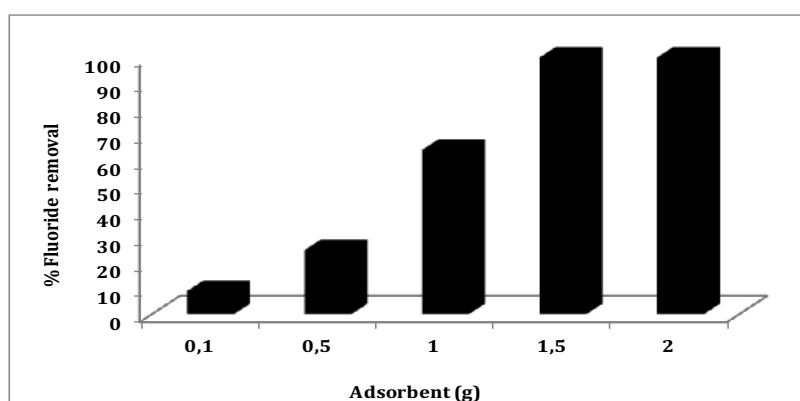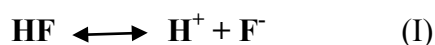

Figure 2. Effect of clay adsorbent mass on the adsorption of Fluoride
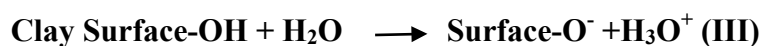
3.3 Effect of pH

The adsorption of fluoride under different pH (2, 7 and 12) is determined for 1 mg L^{-1} of fluoride solution as shown in Figure 3. In Figure 3, the results of pH effect on fluoride removal indicate that the removal efficiency of fluoride increased when the pH of the solution increased from 20 % at pH 2 to 68 % at pH 7. At pH 12, the percentage of the fluoride removed showed a significant decrease (45 %). The lower percentage of fluoride removed obtained at pH 2 indicate the possibility of formation of weakly ionized hydrofluoric acid (HF) [24], according to the following reaction (I) [25]:

$$HF \longleftrightarrow H^+ + F^- \qquad (I)$$

According to [26], the combined effect of both chemical and electrostatic interactions between the oxide surface and fluoride ion, could be responsible for the adsorption reduction. The highest removal efficiency of fluoride adsorption obtained at pH 7 is evaluated at 68 %. The fluoride adsorption could be explained by ion exchange mechanism as shown in reaction [27] (II):

$$\text{Clay Surface-OH}_2^+ + F^- \longrightarrow \text{Clay Surface-F} + H_2O \ (II)$$

However, the reduction of the removal of fluoride adsorption at pH 12 may be due to competition of hydroxyl ions with fluoride for adsorption sites of clay (reaction) (III) [28]:

$$\text{Clay Surface-OH} + H_2O \longrightarrow \text{Surface-O}^- + H_3O^+ \ (III)$$

At pH 12, the electrostatic repulsion between fluoride ions and negatively charged surface sites becomes increases due to the predominant Surface-O⁻ which results in low adsorption of fluoride ions. Similar results were also reported for adsorption of fluoride onto various other adsorbents like Morringa indica based activated carbon [29], Sandalwood [30] and possotia leaf [31].
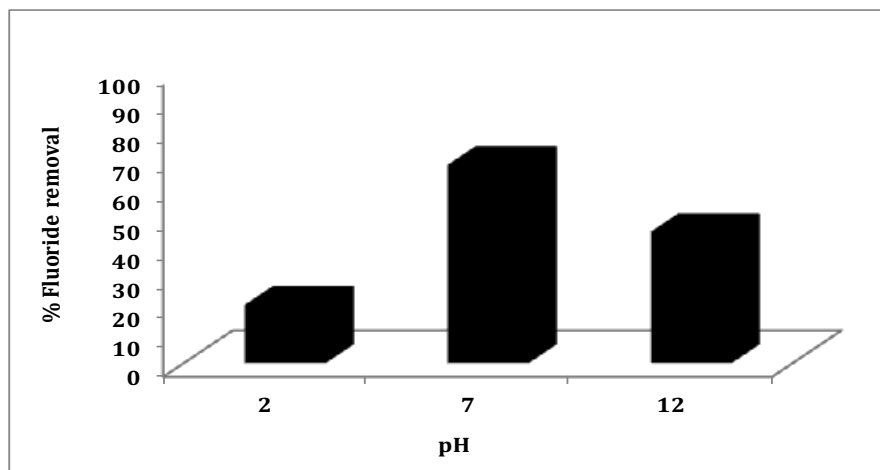

Figure 3. Effect of solution pH on the removal of Fluoride by clay adsorbent

3.4 Kinetic study

The effect of contact time on removal of fluoride (1 and 2 mgL^{-1}) is shown in Figure 4. The removal of fluoride by adsorption on clay adsorbent was found to be rapid and then to slow down with increasing in contact time. At equilibrium 64 and 51 % for 1 and 2 mg L^{-1} respectively are obtained with a contact time of 40 min for clay adsorbent. Therefore a contact time of 40 min is selected for all the equilibrium tests.
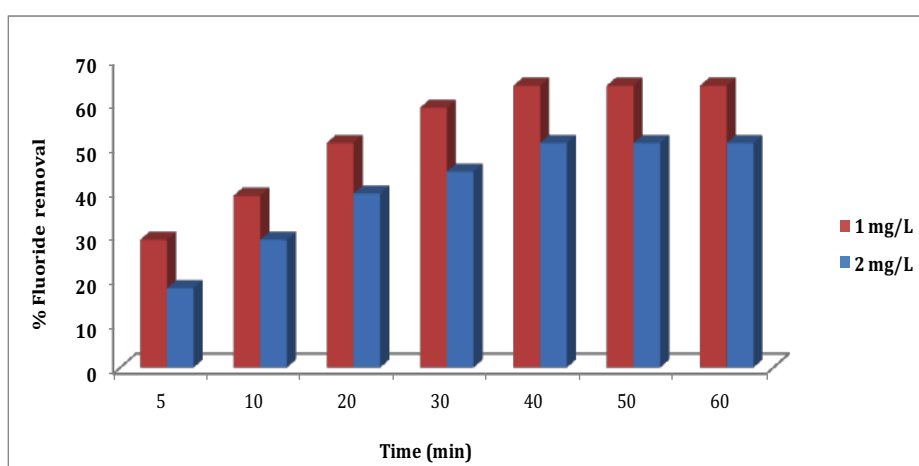

Figure 4. Effect of contact time on the removal of
Fluoride by clay adsorbent

Figure 5 and figure 6 shows that adsorption kinetic data for the adsorption of fluoride onto clay adsorbent. The calculated values were listed in table 1. A high value of R^2 of PSO model was achieved for fluoride, which indicated that this adsorption model is more fitted with the adsorption data, suggesting that the rate controlling step is chemical adsorption [32].
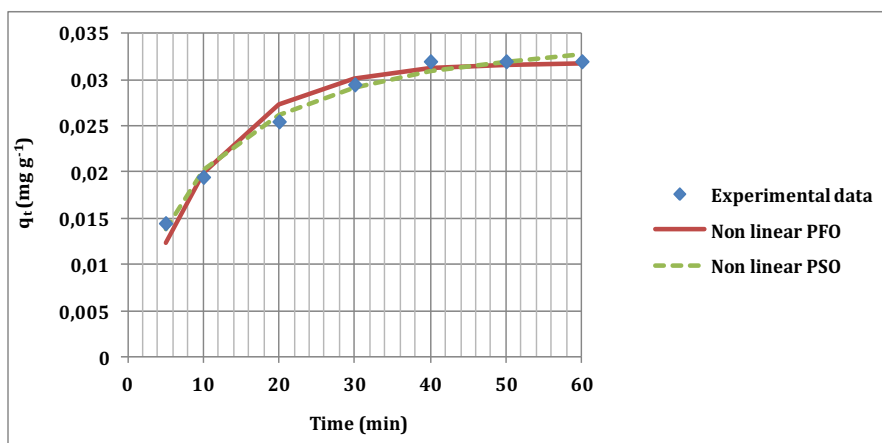
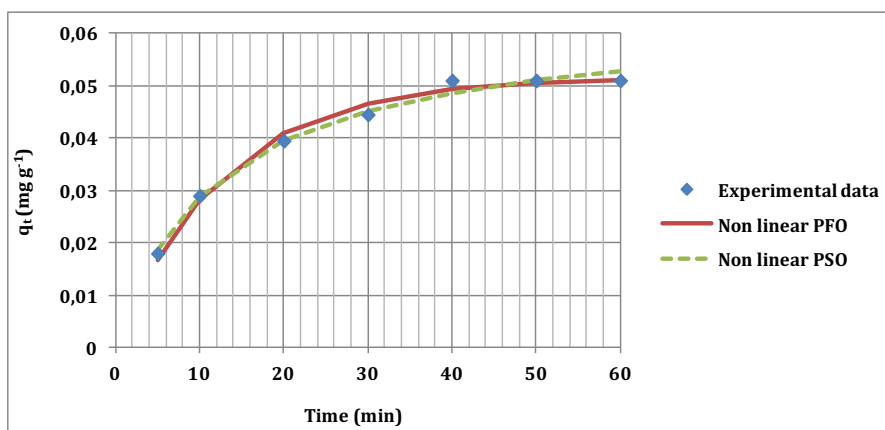**Figure 5.** PFO and PSO non linear for clay adsorbent with initial Fluoride concentration of 1 mg L^{-1}

Figure 6. PFO and PSO non linear for clay adsorbent with initial Fluoride concentration of 2 mg L^{-1}

Table 1: Non-linear kinetic model parameters

Model	Parameters	1 mg L^{-1}	2 mg L^{-1}
	q_{exp}	0.032	0.051
PFO	q_e	0.031	0.051
	K_1	0.098	0.079
	R^2 (%)	97.1	98.8
PSO	q_e	0.037	0.063
	K_2	3.12	1.33
	R^2 (%)	98.9	99.1

3.5 Adsorption isotherms

Figure 7 show the experimental data fitted to non-linear forms of the Langmuir, Freundlich and Redlich–Peterson models for fluoride adsorption by clay adsorbent. The isotherms constants related to three studied models determined from the plots shown in Figure 7 are listed in Table 2. From table 2, the Redlich–Peterson and Langmuir models gave the highest R^2 values showing that the adsorption isotherms of fluoride by clay adsorbent were best described by these two models. The suitability of the Langmuir isotherm to fit the data was confirmed by the exponent value of the Redlich– Peterson model, n, which was equal to 1. Based on the Langmuir isotherm model, the adsorption of fluoride on clay adsorbent is likely to occur via chemisorption due to the monolayer formation [33]. Clay adsorbent is assumed to have homogeneous surface-active sites which are all identical and energetically equivalent.
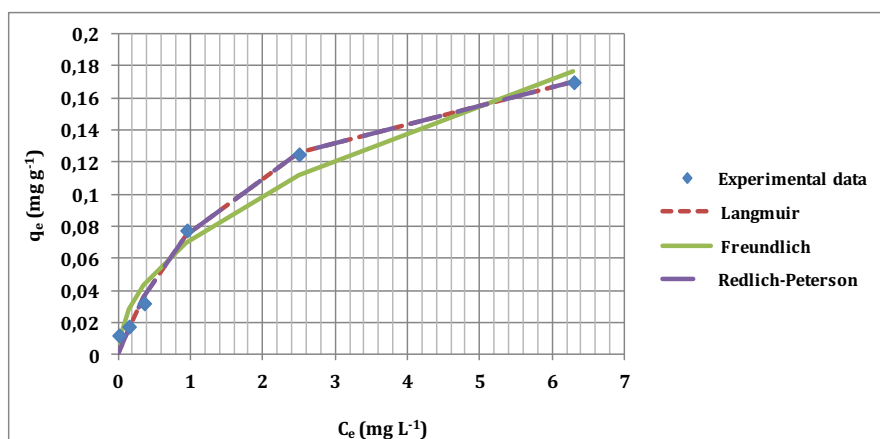
Figure 7. Non- linearized isotherm models for the removal of Fluoride by clay adsorbent

Table 2: Parameters of the Langmuir, Freundlich and Redlich-Peterson isotherms of fluoride by clay adsorbent

Model	Parameters	Values
Langmuir	q_m	0.22
	K_L	0.54
	R_L	0.16
	R^2 (%)	99.3
Freundlich	$1/n$	0.49
	K_F	0.072
	R^2 (%)	97.4
Redlich-Peterson	K_{RP}	0.12
	α_{RP}	0.55
	n	1
	R^2 (%)	99.3

The maximum adsorption capacity (q_m) of 0.22 mg g^{-1} obtained in this study is comparable with the one found by [29], who reported a capacity removal of 0.23 mg g^{-1} of activated carbon prepared from Morringa indica. Additionally, table 3 summarizes the maximum adsorption capacity values reported for other adsorbents in the literature. Comparing them with the results obtained in this work, our natural and Mauritanian clay can be employed as low-cost adsorbent and considered as an alternative to other materials for the fluoride removal. In addition, the values of R_L, K_L and $1/n$ are in between 0 and 1 indicating that the adsorption of fluoride onto clay adsorbent is favorable.

Table 3: Maximum adsorption capacity, q_m, of various adsorbents for Fluoride

Adsorbents	q_m (mgg^{-1})	References
Monmorillonite	0,0450 à 25 °C	[34]
Monmorillonite	0,0470 à 40 °C	[34]
Monmorillonite	0,0528 à 50 °C	[34]
Monmorillonite	0,0557 à 60 °C	[34]
Bleaching powder	0,1308	[35]
Activated clay	0,179	[36]
Raw clay	0,071	[36]
Mauritanian clay	0,22	This work

Conclusion

The adsorption of fluoride from aqueous solutions using available and natural Mauritanian clay has been studied. The obtained results showed that the PSO model fit the experimental data well and agreed with chemisorption. Langmuir and Redlich-Peterson isotherms represent well the experimental adsorption data. The maximum adsorption capacity for fluoride on natural Mauritanian clay adsorbent was found to be 0.22 mg g^{-1}. It can be concluded that the natural Mauritanian clay, without any treatment, may be used as a potential adsorbent for the removal of fluoride from water via ultrasound-assisted adsorption. However, the usability of natural Mauritanian clay for fluoride removal from real water will be tested and for safe use, an additional study of characterization its impurities are required.

Conflict of Interest: The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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