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Kinetics And Equilibrium Studies Of Fluoride Adsorption On Laterite And Kaolinite: Comparative Studies

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ABSTRACT:

The presence of a small amount of fluoride in drinking water is beneficial to human health but a high amount (>1,5 mg/L) has adverse effects. Laterite from Ngaoundere (Cameroon) was tested as a potential adsorbent for removing excess fluoride, and compared with kaolinite. Experiments were carried out by Jar test at room temperature (24 ± 2°C), and the removal efficiencies of these materials studied with respect to time (0 - 180 min), stirring speed (60, 160 and 260 rpm), pH (4 - 10), adsorbent dose (1 – 10 g/L). Results showed that adsorption equilibrium is attained in 60 min and kinetics follows a pseudo-second-order model for both adsorbents used. At different pH and stirring speeds, laterite was better than kaolinite in retaining fluoride. The highest fluoride removal by both adsorbents was obtained at pH 4 – 5. Best adsorption fits were obtained with the Langmuir and Redlich–Peterson isotherms. Upon calcination of Laterite at 550 °C, fluoride adsorption increased up to 50%, showing that heat treatment can be used to improve fluoride adsorption by laterite.

INTRODUCTION

Fluoride pollution of water occurs through different channels which are natural and anthropogenic sources [1]. Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into groundwater sources by the slow natural degradation of fluorine contained in rocks. Fluorine compounds have industrial applications and extensively used in the production of semiconductors and fertilizers. Toxic wastes containing fluoride are generated in all industries using fluoride or its compounds as raw material. Concentrations of fluoride higher than 1.0 – 1.5 mg/L in water, depending on geographic region, can have harmful health effects such as dental and/or skeletal fluorosis, which affects especially children under 9 years. At lower concentrations (below 1mg/L), it can be beneficial in preventing skeletal and dental problems [2]. The World Health Organization (WHO) has set the maximum acceptable concentration of fluoride in drinking water at 1.5 mg/L [3]. Literature review showed that excess fluoride (> 1.5 mg/L) in ground water has been highlighted as a major health hazard in many countries such as India, Ghana, Algeria and the Rift Valley countries in East Africa [4]; [5]. In Cameroon, ground water sources in several volcanic rural areas have concentrations exceeding the WHO limit [6]; [7]. Several defluoridation methods proposed and tested worldwide are mostly based upon the principles of precipitation, adsorption and ion exchange [8]. However the defluoridation methods developed so far lack viability at the end user level due to one or more reasons such as high cost technology, limited efficiency and deteriorated water quality 9. Among the various methods used for defluoridation of water, the adsorption process is widely used and offers satisfactory results and seems to be a more attractive method for the removal of fluoride in terms of cost, simplicity of design and [5]; [10]. In recent years considerable attention has been focused on the study of fluoride removal using natural, synthetic materials such as activated alumina [11], iron oxide [12], activated carbon [13], red mud [14], fired clay [15]. Results from several investigators indicated that adsorbents such as aluminium oxide [11], iron oxide oxide [12] are efficient for fluoride removal due to their high loading capacity and affinity for fluoride ion. However due to their relatively high cost, attention has focused on searching for new lost cost adsorbents [16]. Laterite soil is wide spread in tropical regions and in Cameroon and could be accessible at lower cost; but given the wide variation in composition and properties [17], [18], these have to be tested for fluoride adsorption in each case. In this study, removal of fluoride from aqueous solutions by laterite soil, using the Jar test method as a batch reactor simulation of adsorption by addition of adsorbent under agitation, was investigated and compared with kaolinite. The aim of the study was to evaluate the feasibility of using laterite soil from Ngaoundere (Cameroon) for removing fluoride from water in a batch reactor under different physico-chemical conditions: pH, adsorbent dose, contact time, agitation speed.

MATERIAL AND METHOD

A. *Material*

Laterite material was collected on the campus of the University of Ngaoundere at about 0.5 m of depth from the surface. It was washed several times with distilled water to remove earthy impurities, dried at 105°C for 24 hours and allowed to cool in a desiccator. It was ground using a ball mill. Then the powder was sieved to obtain desired sieve size (≤ 32 µm) for the experiments. Calcined laterite was obtained by heating dry laterite powder in a furnace (Pyrolabo, France) at 550°C for 20 hours. Kaolinite powder obtained from Riedel-de Haën (Germany) was dried at 105 °C in an oven (Heraeus, Germany) and allowed to cool in a desiccator at room temperature. It was used without any further purification.

B. *Batch adsorption Studies*

Adsorption experiments were conducted on a Jar Test bench in 1L beaker. A stock solution of 1000 mg/L fluoride ion was prepared from NaF (Sigma-Aldrich) for the experiments. In a typical run, the beakers were filled with 500 mL of fluoride solution at a predetermined concentration and the pH adjusted to the desired value with either 0.1M NaOH or 0.1M HCl solution. A predetermined amount of adsorbent was then added to each beaker and the mixture homogenized by stirring at a fixed speed. After a given time the agitator was stopped and the flasks removed. The suspension was centrifuged (BIOFUGE Heraeus, Germany) at 950 g, and the residual fluoride concentration in the aqueous solution was measured electrochemically by means of a multiparameter analyser (Consort, Belgium) equipped with a Fluoride ion specific electrode (Elite 201, England). The amount of fluoride adsorbed (q) was calculated as the change in aqueous phase concentration from initial value according to Eq (1)

$$q=\frac{(C_0-C)}{m}\times V \qquad \text{Eq 1.}$$

Where:

C_0 = the initial concentration (mg/L)

C = the concentration (mg/L) at contact time t (min)

V = the solution volume (L)

m = the amount of adsorbent added (g)

RESULT AND DISCUSSION

Characterization of laterite sample

Laterite sample was characterized through physicochemical analyses. Nitrogen adsorption on the laterite used displayed hysteresis similar to type IV isotherms in the IUPAC classification, indicating the presence of pores. Numerous values deduced from the adsorption isotherm are shown on table 1. Laterite used is a mesoporous material and has an average adsorption pore size of 10.879 nm. The cumulative pore volume found on laterite is relatively low, which is coherent with the small surface area obtained on this material (26.925 m^2/g). Recent work on this material [18]. using SEM/microprobe, TEM and XRD, revealed the predominance of kaolinite as base clay mineral with traces of smectite. Surface clusters of iron oxides corresponding to goethite and hematite, and aluminium oxide (gibbsite) and titanium dioxide were also found. The laterite soil has an isoelectric point (iep) located around pH 3

Table 1: Surface characteristics of laterite

Parameters	Value
BET Surface Area	26.925 m^2/g
BJH Adsorption Cumulative Pore Volume of pores between 1.700000 and 300.000000 nm Diameter	0.0664 cm^3/g
Adsorption Average Pore Diameter (4V/A by BET)	10.879 nm
BJH Adsorption Average Pore Diameter (4V/A)	14.725 nm
Median Pore Diameter	1.1745 nm

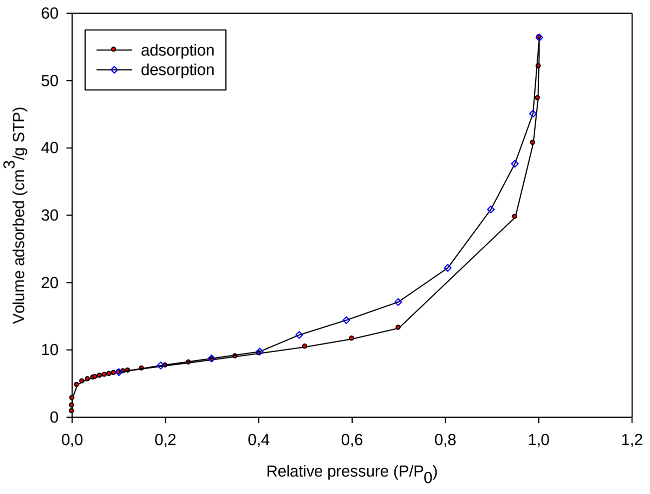

Figure 1: Nitrogen adsorption-desorption at 77 K on laterite.

CONTACT TIME AND ADSORPTION KINETICS

Figure 2 shows the fluoride adsorption kinetic data at pH 4, plotted as adsorption density (mg F/g) as a function of time for three adsorbents.

The values of the adsorption density for the three materials are increasing up to 60 min and there after it remained almost constant indicating the attainment of equilibrium. This time was fixed as minimum contact time was fixed as minimum contact time for the maximum defluoridation of the sorbent used. Fluoride adsorption density increases in the order; kaolinite, laterite and calcined laterite. Calcination of laterite improves fluoride adsorption form 3.14 to 4.66 mg/g, an increment of about 50%. The increased in adsorption density may be explained by the fact that calcination of laterite destroys the structure of kaolinite mineral, making available aluminium oxide formerly coordinated to silica.

Pseudo-first and second-order rate equations were used to model fluoride adsorption kinetics on the laterite, calcined laterite and kaolinite surface. The plot of t/q_t vs t (pseudo-second-order model) gives a straight line with higher correlation coefficient values than with the fit obtained from a straight line plot of log (q_e-q_t) against t (pseudo-first order model). Solid lines in figure 2 are curve fitting results for the pseudo-second order model. Table 1 shows the parameters for both pseudo-first-order model and pseudo-second-order model. As indicated in Table 1, the R^2 values for the pseudo-second order model is significantly greater than those for the pseudo-first order model.

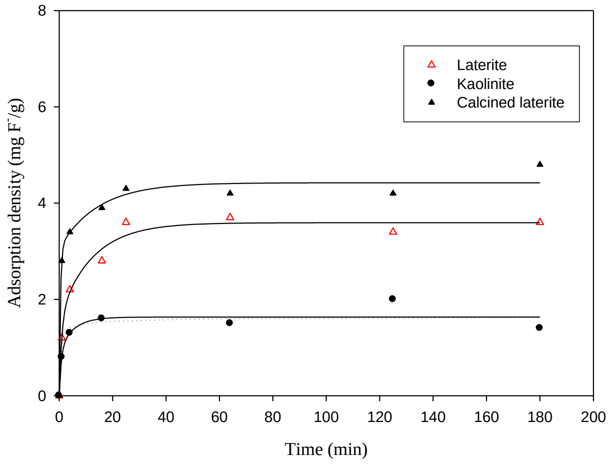

Figure 2. Effect of contact time on fluoride adsorption density on Laterite, Kaolinite and calcined Laterite (stirring speed 260 rpm, pH = 4; initial fluoride concentration = 20 mg/L, adsorbent dose = 1g/L; 24 ± 2°C)

Table 2: Kinetic model parameters.

Kinetics models	Linear form	Parameters	Kaolin	laterite	Calcined laterite
Pseudo-first order	$\log(q_e-q_t)=\log q_e-\frac{K_a}{2.303}t$	R^2	0.310	0.901	0.851
		K_1 (min^{-1})	0.026	0.027	0.073
Pseudo-second order	$\frac{t}{q_t}=\frac{1}{h}+\frac{1}{q_e}$	R^2	0.990	0.992	0.994
		K_2 (g.mg^{-1}.min^{-1})	0.090	0.621	0.930

. EFFECT OF SOLUTION PH

The effect of pH on fluoride adsorption density on laterite and kaolinite was studied at various pH values (ranging from 4 to 10). The curves have the same trend; the adsorption density decreases from 6.07 mg/g to 0.850 mg/g and from 3.65 mg/g to 0.22mg/g, respectively for laterite and kaolin as the solution pH was increased from 4 to 10. These results lend more support to previous findings that the adsorption of anions on clay minerals decreases as the pH of the solution increases [19]. The decrease in adsorption of fluoride with increase in pH has been explained on the basis of decrease of positive charge on the clay minerals [19]. As the pH increased the adsorption density decreased. This is probably due to the competition for adsorption site between fluoride and hydroxyl ions at the clay surface. At all pH, the adsorption density of fluoride on laterite is greater than that on kaolin. The high adsorption capacity of laterite may be attributed to the presence of alumina and iron oxides in this adsorbent.

EFFECT OF ADSORBENT DOSE

The effect of adsorbent dosage on fluoride adsorption on laterite and kaolinite at contact time of 60 min was studied. The results are presented as adsorption density versus adsorbent dosage in Figure 4. The adsorption density decreases from 2.9 mg/g to 0.66 for laterite and from 1 mg/g to 0.08 mg/g for kaolinite. However, it can be seen from Figure 4 that after the dosage of 6 mg/L for the adsorbent used, there was no significant change in the adsorption density of fluoride. This is due to the overlapping of active sites at higher dosage, thus reducing the net surface area [20].

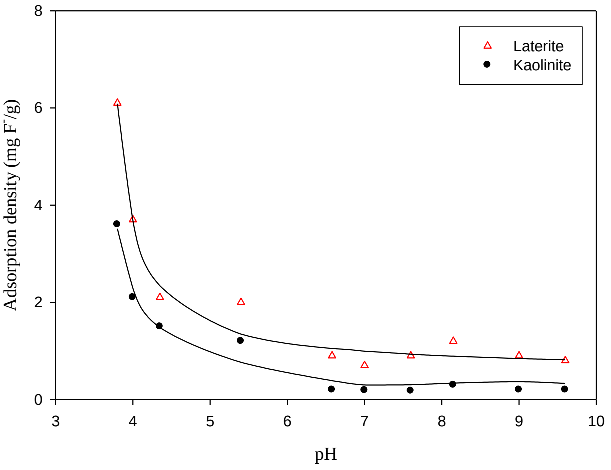

Figure 3. Effect of initial pH on adsorption of fluoride on laterite and kaolinite (stirring speed 260 rpm ; contact time 60 min ; initial fluoride concentration = 20 mg/L, adsorbent concentration = 1g/L, 24 ± 2°C).

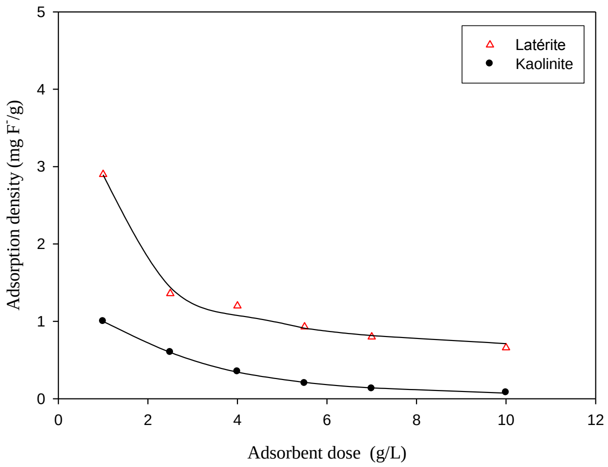

Figure 4. Effect of adsorbent dose on fluoride adsorption (pH= 4, initial fluoride concentration = 20 mg/L and contact time = 60 min)

EFFECT STIRRING SPEED

Results in figure 5 show that for a contact time of 60 min, as Jar test stirring speed rises from 50 to 150 rpm, fluoride adsorption density on kaolinite and laterite is hardly affected, but above 150 rpm adsorption density decreases with increasing stirring speed. Laterite still gives higher adsorption than kaolinite at all three speeds tested. It is suggested that the foregoing observed reduction could be explained by hydrodynamic effects around the adsorbent. It is known that the mechanism of Fluoride adsorption on oxides involves inner sphere and outer sphere complexation, the latter being controlled by electrostatic charge and the former by chemical affinity. At high agitation speeds, outer sphere adsorption will be affected and will tend to decrease [21].

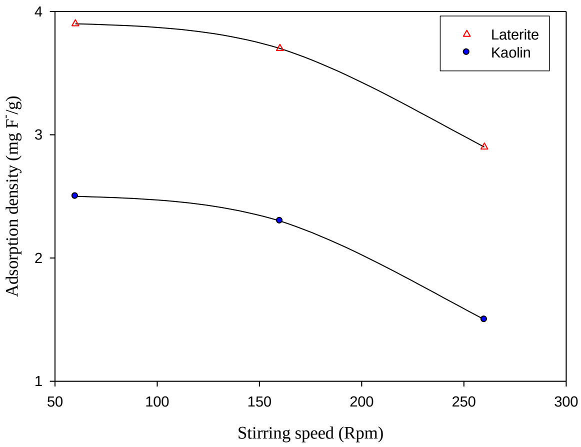

Figure 5. Effect of stirring speed on adsorption density of fluoride on laterite and kaolinite (pH= 4 ; Initial fluoride concentration = 20 mg/L and contact time =60 min)

ADSORPTION ISOTHERMS

Table 2. Isotherms parameters obtained from Langmuir, Freundlich and Redlich-Peterson models for Kaolinite and Laterite.

Isotherm models	**Langmuir**			**Freundlich**			**Redlich-Peterson**			
	X_m (mg/g)	b (L/mg)	R^2	K	1/n	R^2	K_R (L/mg)	a_R (L/mg)	B	R^2
Kaolinite	1.99	0.40	0.97	1.23	0.16	0.42	0.99	-0.56	0.97	0.97
Laterite	3.37	0.32	0.99	0.74	0.42	0.93	0.98	-2.67	0.99	0.94

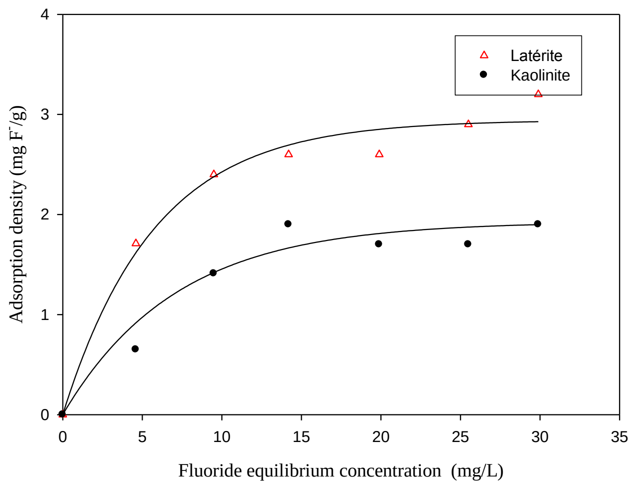

Figure 6. Isotherms on laterite and kaolinite (stirring speed 260 rpm; pH 4; Initial fluoride concentration = 20 mg/L and contact time = 60 min)

Three adsorption isotherms, namely the Langmuir, Freundlich and Redlich-Peterson models, were used to analyse adsorption data and results are presented in figure 5. The equations of these models are as follows:

Linearized Langmuir equation; $\frac{C_e}{q_e} = \frac{1}{X_m * b} + \frac{C_e}{X_m}$ Eq 2

Linearized Freundlich equation; $\log q = \log k + \frac{1}{n} * \log C_e$ Eq 3

Linearized Redlich-Peterson equation; $\log\left[\left(K_R * \frac{C_e}{q_e}\right) - 1\right] = \log a_R + \beta * \log C_e$ Eq 4

Where q_e is the density of adsorption at equilibrium, C_e the fluoride concentration at equilibrium, X_m the maximum adsorption capacity required to form a monolayer (mg/g), b the binding energy constant (L/mg). The empirical parameter n in the Freundlich isotherm represents the adsorption intensity while k (mg/g) represents the adsorption capacity. In the Redlich-Peterson isotherm, K_R is the Redlich–Peterson constant (L/mg), a_R is an empirical constant (L/mg) and β an exponent that lies between 0 and 1.

Constants obtained from Langmuir, Freundlich and Redlich-Peterson models are given in Table 2, where it is seen that Langmuir and Redlich-Peterson models give better fits, with correlations coefficients greater than 0.94. Derived monolayer adsorption capacities, Xm, at pH 4 were respectively, 1.99 mg/g for kaolinite and 3.37 mg/g for laterite. These values are similar to those obtained on clay materials of similar composition, and are in the range (2.2–4.4 mg/g) of that for commercial activated alumina [22].

CONCLUSION

Laterite a geomaterial is abundant in Cameroon. It can be used as an adsorbent for the removal of fluoride from aqueous solutions. Based on the experimental results of this study, the following conclusion can be drawn. Equilibrium time is attained in 60 min for laterite and kaolinite. Experimental data can be described adequately by pseudo order kinetic model for laterite and kaolinite which is its laterite source mineral. The optimum pH of fluoride adsorption for both adsorbent lies between pH 4 and 5. Langmuir, Freundlich and Redlich-Peterson isotherms models were found to fit the equilibrium data well for laterite. However for kaolinite it is the model of Langmuir and Redlich-Peterson. The adsorption capacity of laterite is higher than that of kaolinite and can be improve by heat treatment.

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