Removal of Fluoride from Water by Adsorption onto Fired Clay Pots: Kinetics and Equilibrium Studies

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Excessive fluoride in potable water is a serious health problem in rural areas of many developing countries. Hence, there is a need to find a simple and cost-effective method for water defluoridation in such areas. In the northern part of Cameroon, clay pots are used for cooking food and water storage. The firing of these pots consists of intensive burning using fire wood. They were tested as a potential adsorbent for removing excess fluoride from water. Experiments were carried out in a jar test at room temperature (25 ± 2°C). Effects of contact time (0–90 min), pH (4, 5, 7, 8, and 9), stirring speed (60, 90, 120, and 200 rpm), and ionic strength (0–1000 mg/L) were investigated. Results showed that equilibrium was attained in 10 min whatever the pH. Pseudo-second-order and pore diffusion models described well the adsorption process. The highest amount of fluoride adsorbed (1.6 mg/g) was obtained at pH 4-5 and the optimum stirring speed is 120 rpm. Ionic strength has a significant effect on fluoride adsorption.

1. Introduction

Fluoride ion exists in natural waters and it is an essential micronutrient in humans in preventing dental caries and in facilitating the mineralization of hard tissues if taken at a recommended range of concentration. Higher level of fluoride in groundwater is a worldwide problem [1–3]. The World Health Organization (WHO) has set a guideline of 1.5 mg/L for fluoride in potable water [4]. Concentration higher than this value can lead to fluorosis (dental and/or skeletal) and several types of neurological damage in severe cases [5]. Many methods have been developed for fluoride removal from water such as adsorption [6], ion exchange [7], membrane processes such as reverse osmosis and nanofiltration [8, 9], electrodialysis [10, 11], and precipitation [12]. Among these methods, adsorption is a widely used method for defluoridation which depends on ions (adsorbate) in fluid diffusing to the surface of a solid (adsorbent) when they are bound to the solid surface or are held there by weak intermolecular forces [13]. Adsorption is recognized as the most efficient, promising, and widely used fundamental approach in water and wastewater treatment processes [14]. Different adsorbents such as activated alumina [15], bleaching earth [16], iron oxide [17], activated titanium rich bauxite [18], activated carbon [19], red mud [20], and clay [21, 22] were tested to find out efficient and economically viable defluoridating ones. Among these adsorbents, clay and clay minerals are naturally abundant, renewable, and environmentally sustainable [23–25]. They are considered robust adsorbents [24] due to their low cost, sorption properties, and ion exchange potential. In recent years, considerable amount of work has been done on activation of clay and clay minerals to improve the adsorption capacity and hence removal efficiency [26, 27]. Chemical and physical activation methods are commonly used. However chemical treatment has not always proven to be effective. For example, Ma et al. [28] reported equilibrium fluoride adsorption capacity by granular acid treatment of bentonite of just 0.07 mg/g. That is why some researchers turn to heat treatment which can also increase ions adsorption capacity in clay [29, 30].

Clay pot is made of a mixture of different types of natural clays. The process consists of mixing the different clay fractions, forming the pot, and burning under an intensive wood fire (around 300°C) where they get cooked. During
the firing process (cooking phase) some of them get broken. These broken pots are not useful for water storage but could be used as an adsorbent, because they are primary heated clays. The main objective of this investigation is to study the removal efficiency of fired clay pots powder as a potential adsorbent for fluoride removal under different physicochemical conditions.

2. Materials and Methods

2.1. Materials. Clay pots were collected from Kouladje, a village in the northern part of Cameroon. The firing of these pots consists of its intensive burning using fire wood (Figure 1). The clay powder was obtained after crushing and sieving a clay pot with standardized stainless sieves and the fraction less than 100 μm was collected. All other reagents used in the present study were of analytical grade. A stock solution of fluoride 1000 mg/L was prepared by dissolving appropriate quantity of sodium fluoride (Sigma-Aldrich, USA) in distilled water.

2.2. Characterization of Adsorbent. The surface morphology of the fired clay powder was examined using scanning electron microscopy (Hitachi S-3000H, Japan) microscope with an accelerating voltage of 15 kV. EDAX was also performed on the same device. The specimens were prepared using carbon tape.

2.3. Batch Adsorption Studies. Adsorption experiments were carried out on a jar test (batch mode) at different pH (4, 5, 7, 8, and 9) ionic strengths (0–1000 mg/L) and stirring speed (60, 90, 120, and 200 rpm). In a typical run, beakers (1L) were filled with 500 mL fluoride solution of predetermined concentration, with pH adjusted to the desired value with 0.1 M NaOH or 0.1 M HCl solution. The ionic strength of the solution was also adjusted by adding KNO₃ solution. A predetermined amount of adsorbent was added to the beaker and the resulting suspension was stirred at a fixed speed. After a given time, the stirring stopped, the suspension was centrifuged (BIOFUGE Heraeus, Germany) at 950g, and the supernatant was filtered on a Minisart X50 (Prolabo, France) membrane filter of porosity 0.1μm. The residual fluoride concentration in the aqueous solution was measured by means of a multiparameter analyser (Consort 869, Belgium) equipped with fluoride ion specific electrode (ELITE 201, England).

Isotherm experiments were carried out at pH = 4, by varying fluoride concentration ranging from 1 to 64 mg/L. The amount of fluoride adsorbed (q) was calculated as the change in the aqueous phase concentration from initial value according to

\[ q = \frac{(C_0 - C)}{m} \times V, \]

where \(C_0\) and \(C\) (mg/L) are the initial fluoride concentration and at contact time \(t\) (min), \(V\) (L) is the volume of solution, and \(m\) (mg) is the amount of adsorbent added.

3. Results and Discussion

3.1. Morphological and Elemental Composition of Fired Clay. Clay morphology at different magnification is presented on Figure 2. It is observed from this figure that the morphology of the fired clay is compact with interlayers which are favorable for adsorption phenomena. This compactness of the morphology is due to the effect of the temperature applied on these clays during the firing process of pots. The EDAX spectrum of Figure 3 showed the presence of Na, Mg, Al, Si, Fe, K, and O. Clay is mainly composed of silica as shown in Table 1 and can be explained by the fact that the extraction zone is composed of the sand-clay types [31].

3.2. Kinetic Study. The kinetic study was carried out in an agitated vessel as described earlier by changing the various operating conditions.

3.2.1. Effects of pH. Figure 4 shows a comparison of the amount of fluoride adsorbed at different pH as a function of contact time. The examination of these kinetic curves reveals a rapid adsorption to attain the equilibrium adsorption. In all the pH used, two phases were observed: (a) the first phase, where the adsorption is rapid and appeared within the 10 min contact time; (b) the second phase, where the amount of fluoride adsorbed remained constant after 10 min of contact time, implying that equilibrium was reached. In general, the fast adsorption could be attributed to a surface reaction process. It is also shown in Figure 4 that the adsorption density decreases with the increase of pH. This can be

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**Table 1: Elemental compositions of Kouladje fired clays obtained by EDAX.**

| Elements             | Weight (%) | Atomic (%) |
|----------------------|------------|------------|
| Oxygen (O)           | 40.26      | 55.02      |
| Sodium (Na)          | 0.20       | 0.19       |
| Magnesium (Mg)       | 0.25       | 0.23       |
| Aluminium (Al)       | 3.48       | 2.82       |
| Silicon (Si)         | 51.30      | 39.93      |
| Potassium (K)        | 0.27       | 0.15       |
| Iron (Fe)            | 4.23       | 1.66       |
attributed to competition between hydroxide and fluoride ion having the same charge and similar radius [32]. The maximum adsorption was obtained at the pH 5. The obtained result for maximum adsorption is in agreement with fluoride removal studies on red mud (pH 5.5) [20], refractory grade bauxite (pH 5.5) [33]. Adsorption is also not favored in the acid range; this may be a result of the formation of weakly ionized hydrofluoric acid [20].

The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to test the adsorption kinetics data to investigate the mechanism of adsorption. The pseudo-first-order rate expression of Lagergren is given as [34]

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$$  \hspace{1cm} (2)

where $q_t$ (mg/g) is the amount of adsorbed fluoride at time $t$, $k_1$ (min$^{-1}$) is the rate constant of the first-order reaction, and $q_e$ is the equilibrium sorption uptake derived from extrapolation of experimental data at time $t = \infty$. A straight line of $\log(q_e - q_t)$ versus $t$ suggests the applicability of this kinetic model (Figure 5(a)). $q_e$ and $k_1$ (Table 2) were determined from the intercept and slope of the plot, respectively.

The pseudo-second-order kinetic model [34] is integrated and linearized form has been used:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t$$  \hspace{1cm} (3)

The plot of $t/q_t$ versus $t$ (Figure 5(b)) gave a straight line showing that second-order kinetic model was applicable and $q_t$ and $k_2$ (Table 2) were determined from the slope and intercept of the plot, respectively.

From Table 2, the values of correlation coefficients obtained for the pseudo-first-order reaction were not appropriate to describe the adsorption of fluoride on fired clay. On the contrary, the values of correlation coefficients for pseudo-second-order model were all greater than 0.95 and the adsorption capacities calculated by the model are close to those determined by experiments. Hence, the data was well correlated by the pseudo-second-order model as shown in Figure 5. This fact suggested that the rate of fluoride adsorption
Table 2: Kinetics parameters for adsorption of fluoride on fired clay.

| Initial concentration (mg/L) | First-order model | Second-order model | Intraparticle diffusion model |
|-----------------------------|-------------------|--------------------|------------------------------|
|                             | $q_{e,\text{exp}}$ (mg/g) | $k_1$ (min$^{-1}$) | $q_{e,\text{cal}}$ (mg/g) | $R^2$ | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $q_{e,\text{cal}}$ (mg/g) | $R^2$ | $k_p$ (mg g$^{-1}$ min$^{-0.5}$) | $R^2$ |
| 10                          | 1.40              | 0.25               | 0.87                        | 0.87  | 0.48                         | 1.30                      | 0.97  | 0.45                         | 0.99  |
| 40                          | 2.17              | 0.49               | 0.90                        | 0.90  | 0.28                         | 2.06                      | 0.98  | 0.73                         | 0.98  |

Figure 5: First-order (a) and second-order kinetics modeling of fluoride adsorption on fired clay pots (adsorbent dose 1 g/L, pH = 7, and temperature 25 ± 2°C).

adsorption onto fired clay is dependent on the availability of adsorption sites rather than the adsorbate concentration in solution [35].

To evaluate the limiting rate of the fluoride adsorption on fired clay, the possible contribution of intraparticle diffusion on fluoride adsorption process was explored using Weber-Morris model [36]:

$$q = k_{\text{int}}t^{0.5} + C,$$

where $k_{\text{int}}$ can be calculated from the slope of the plot of $q$ versus $t^{0.5}$. As shown in Figure 6(a), the linear portion of plot is not passing through the origin at each of the tested concentrations, which indicates the fluoride adsorption on fired clay is a complex procedure. Both the surface adsorption as well as intraparticle diffusion contributes to the rate determining step [16, 37].

The data was further used to investigate the slow step occurring in the present adsorption system. The applicability of Bahangam’s equation [38] was tested

$$\log \log \left( \frac{C_0}{C_0 - qm} \right) = \alpha \log t,$$

where $C_0$ is the initial concentration of the adsorbate in solution (mg/L), $V$ is the volume of the solution (L), $m$ is the weight of adsorbent used per liter of solution, $q$ is the amount of adsorbate retained at time $t$, and $\alpha$ (<1) and $k_0$ are constants to the present system which was examined. As such, log log$(C_0/(C_0 - qm))$ was plotted against log$t$ in Figure 6(b). The plot was found to be linear and the correlation coefficients are greater than 0.95 indicating that kinetics confirms Bahangam’s equation and therefore the adsorption of fluoride on fired clay was pore diffusion controlled [37].

3.3. Adsorption Isotherms. Fluoride ion adsorption was carried out at pH 4 and stirring speed of 120 rpm. Two isotherm equations have been applied for this study, Langmuir and Freundlich. The linear form of the Langmuir equation is given by

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b},$$

where $q_e$ and $C_e$ are the equilibrium concentrations of fluoride in the adsorbed (mg/g) and liquid phases (mg/L), respectively. $Q_m$ and $b$ are the Langmuir constants which are related to the adsorption capacity and energy of adsorption, respectively, and can be calculated from the intercept and slope of the linear plot, with $C_e/q_e$ versus $C_e$.

The adsorption equilibrium data was also applied to Freundlich isotherm model. The linear form of the model can be expressed as follows:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e,$$
Figure 6: Intraparticle diffusion model (a) and Bahangam’s equation plot (b) (adsorbent dose 1 g/L, pH = 7, and temperature 25 ± 2°C).

Figure 7: Adsorption isotherms of fluoride on fired clay pots (stirring speed 120 rpm; pH = 4; contact time = 30 min).

Table 3: Langmuir and Freundlich isotherms parameters for the adsorption of fluoride on fired clay pots.

| Models     | Parameters | Parameters | $R^2$ |
|------------|------------|------------|-------|
| Langmuir   | $b$ (L·mg$^{-1}$) | $q_{max}$ (mg/g) | 0.95  |
|            | 0.067      | 4.16       |       |
| Freundlich | $k_f$ (mg/g) | $n$         | 0.98  |
|            | 0.35       | 0.602      |       |

where $q_e$ and $C_e$ are the equilibrium concentration of fluoride in the adsorbed (mg/g) and liquid phases (mg/L), respectively. $k_f$ and $n$ are the Freundlich constants which are related to adsorption capacity and intensity, respectively. These constants can be calculated from the slope and intercept of the linear plot, with log $q_e$ versus log $C_e$.

To show the ability of different isotherms to correlate with experimental results, the theoretical plots from each isotherm have been fitted with the experimental data for adsorption of fluoride on fired clay pots (Figure 7). Langmuir and Freundlich parameters and regression coefficients ($R^2$) are presented in Table 3. From Figure 7, the adsorption data fitted well with Freundlich isotherm model indicating the heterogeneous distribution of active sites on fired clay pot [39]. The value of the correlation coefficient is 0.98, indicating a good mathematical fit. The Langmuir plot model has lower $R^2$ than the Freundlich model. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameters were determined by using the following equation:

$$R = \frac{1}{1 + bC_0},$$

where $C_0$ is the initial concentration and $b$ is the Langmuir isotherm constant.

The value of $R$ varied from 0.93 to 0.19. These values are less than 1, indicating the favorable adsorption of fluoride on fired clay [16].

3.4. Effect Stirring Speed. Effects of stirring speed on the adsorption of fluoride are presented in Figure 8. It is clear from the figure that the adsorption density increases with agitation speed up to 120 rpm and beyond this it is almost constant. The external mass transfer increases with the agitation speed, resulting in an increase in fluoride transport from the bulk to the adsorbent sites and thereby increasing the rate of adsorption. Fluoride adsorption density is almost invariant beyond 120 rpm, as the external mass transfer...
resistance does not decrease appreciably beyond this rpm. Therefore, it was suggested that 120 rpm could be suitable for fluoride adsorption by fired clay and no reduction of fluoride retention was observed as found by Ndi et al. [22].

3.5. Effect of Ionic Strength. The effect of ionic strength on fluoride adsorption was studied by varying the concentration of KNO$_3$ (0–1000 mg/L) (Figure 9). The result showed that the amount of fluoride adsorbed on fired clay pot was significantly affected when the concentration increases from 0 to 1000 mg/L KNO$_3$. The same effect of ionic strength was also observed for the adsorption of Cr(VI) on bentonite [40]. Studying the influence of ionic strength is a simple approach to distinguish between inner sphere and outer sphere surface complexes when direct evidence from microscopic data is absent. According to Hayes et al. [41], if the adsorption is not affected by the variations of the ionic strength, then an inner sphere surface complexation should form, whereas the presence of outer sphere complexes is indicated by changes in adsorption with changing ionic strength. Based on this theory, it is postulated that the adsorption of fluoride on fired clay pots may take place by the formation of outer sphere complexation.

4. Conclusion

Adsorption of fluoride onto fired clay pots from Cameroon has been studied in detail. Fired clay is composed of different oxides. Kinetic studies reveal that equilibrium is attained within 10 min whatever the pH studied. The maximum adsorbed fluoride is 1.3 mg/g at a stirring speed of 120 rpm. Adsorption follows pseudo-second-order and both the surface adsorption and intraparticle diffusion contribute to the rate determining step. Freundlich isotherm fits the adsorption data adequately. The effect of ionic strength has a significant effect on fluoride adsorption.

Being a useless and abundantly available material, fired clay pots can be used for industrial application for removing fluoride from water.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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