STUDY OF DEFLUORIDATION OF WATER USING NATURAL CLAY MINERALS

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Abstract—Fluoride is an essential component in the mineralization of bones and in the formation of dental enamel. Excessive intake may result, however, in teeth mottling and dental and skeletal fluorosis. With an average fluoride concentration of ~2.4 mg L^{-1} in Tunisian drinking water, the present study focused on promoting low-cost materials for removal of excess fluoride. Two Tunisian raw clays were used as adsorbents in a batch process to eliminate excess fluoride ions from drinking water and, thus, avoid fluorosis phenomena. Physicochemical characterization and chemical analysis of the raw clays were carried out using X-ray fluorescence, X-ray diffraction, and the BET method. For fluoride removal, the effects of contact time, adsorbent dose, and pH were evaluated. The optimum defluoridation capacity was at 30 min of contact time, 20 g/L of clay dose, and at pH = 3. The kaolinite tested removed more fluoride than smectite. The selected clay was used successfully to remove fluoride from contaminated water with high concentrations of foreign ions that exceeded the potability limits. Adsorption isotherms revealed that the data fitted well to both the Langmuir and Freundlich adsorption isotherms, thus confirming both monolayer and multilayer adsorption.

Key Words—Adsorption, Fluoride Removal, Isotherm, Natural Clay Minerals, Natural Water.

INTRODUCTION

Contaminants such as fluoride, arising from anthropogenic and natural sources, have become a significant problem. Fluoride can leach into groundwater resources from natural mineral deposits which contain fluoride (*e.g.* fluorapatite, sellaite, fluorspar, and cryolite; Mohaptara *et al.*, 2009). A strong correlation has been established between dental fluorosis and high levels of fluoride in the potable groundwater and surface water (Nyaora *et al.*, 2001; Daw, 2004). Excess fluoride ions in drinking water occur in several regions of Tunisia, particularly in the south, in areas close to the Gafsa Phosphate mining basin. A study of the prevalence of oral disease in 600 school children in Kairouan, central Tunisia, was carried out by Maatouk *et al.* (1998). The study confirmed that Kairouan is an area of endemic fluorosis with a prevalence of 57.7% in 12-year-old school children. In some areas of that city, the fluoride-ion content reached 2.8 mg/L with 98% dental fluorosis (Maatouk *et al.*, 1998, 2006).

Many technologies have been applied to the removal of excess fluoride from water, *e.g.* chemical precipitation (Islam and Patel, 2007), membrane technology (Arora, 2004), flocculation and electrocoagulation (Hu, 2005), ion exchange (Meenakshi and Viswanathan, 2007), and adsorption (Ku *et al.*, 2002). The adsorption

method is the most promising and efficient method for defluoridation of water. Many adsorbents have been tested, *e.g.* metal oxides (Haron *et al.*, 1995; Wajima *et al.*, 2009), activated alumina (Meenakshi *et al.*, 1991), clays (Chaturvedi *et al.*, 1988), zeolites (Dondi and Marsigli, 1997; Sun *et al.*, 2011), and silica gel (Grybas *et al.*, 2011). Defluoridation by adsorption onto cost-effective natural materials is the most commonly utilized method. The use of natural adsorbents is particularly beneficial, both in terms of economics and ecology.

Clays which have large specific surface areas, good chemical and mechanical stability, a layered structure, and large cation exchange capacities (CEC) make the best adsorbents (Gitari *et al.*, 2015). Because of their adsorptive properties, clays can be used in a raw or modified state to create clay-based adsorbents for inorganic contaminants in water (Gitari *et al.*, 2015). The positively charged edge surfaces of the clay minerals at pH < pH$_{PZC}$ (PZC = point of zero charge) explains their high affinity for uptake of negatively charged ions (Vinati *et al.*, 2015).

Numerous water-treatment studies have been carried out, *e.g.* the removal of pesticides (Fushiwaki and Urano, 2001), dyes (Sadki *et al.*, 2014), and heavy metals (Fe, Co, Ni, Cd, and As) (Kashif, 2016; Bentahar *et al.*, 2016).

Defluoridation capacity has also been investigated with clays such as bentonite (Srimurali *et al.*, 1998), kaolinite (Srimurali *et al.*, 1998; Agrawal *et al.*, 2002a; Meenakshi *et al.*, 2008), montmorillonite (Agrawal *et al.*, 2002b; Ramadani *et al.*, 2010); Mg-, Fe-, Al-, and La-exchanged smectite (Kashif, 2016; Thakre *et al.*,

2010; Kaygusuz *et al.*, 2015; Kamble *et al.*, 2009), and organically modified smectite (Gammoudi *et al.*, 2013).

The main objective of the present study was to investigate the capacity of raw Tunisian clays in the defluoridation of natural water. Firstly, the physicochemical characteristics of the raw clays were assessed to check how they might be best used in terms of the defluoridation mechanism. Then, possible optimizations of the raw clays' parameters were investigated. Finally, the defluoridation capacity of the optimized clays for heavily fluorinated water was evaluated. Such insights will be important in terms of enhancing the value of the Tunisian raw clays.

MATERIALS AND METHODS

Materials

Two natural raw clays were used in the present study: A1 was collected from the northwest of Tunisia and A2 from the south of the country. Mineralogical analysis of the raw clays was carried out by X-ray diffraction (XRD) using a Philips X'Pert diffractometer (Malvern PANalytical, Malvern, Worcestershire, UK), with CuKα radiation. The chemical composition was determined by X-ray fluorescence (XRF) using an Axios Wavelength instrument, also from Malvern PANalytical. The specific surface area was measured by the Brunauer-Emmet-Teller (BET) method using a Tristar 3000 device (Micromeritics, Norcross, Georgia, USA). Fourier-transform infrared (FTIR) spectra of clays before and after adsorption were recorded using an IRAffinity-1 instrument (Shimadzu, Columbia, Maryland, USA). The KBr pressed pellet technique was used to record FTIR spectra (clay:KBr ratio = 1:20; at a pressure of 60 kN).

Sodium fluoride (NaF), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were obtained from Sigma-Aldrich (St. Louis, Missouri, USA). 0.1 M HCl and 0.1 M NaOH solutions were used to adjust the pH. All chemicals were of analytical grade and were used without further purification. In the experiments, the solutions were prepared using deionized water with a resistivity of 18 MOhm-cm.

Experimental protocol

The defluoridation experiments were carried out in static conditions (a batch method). Known amounts of raw clay were placed in polypropylene bottles containing fluorinated solutions (prepared from NaF salt in deionized water) with concentrations of 2 mg/L of fluoride. The temperature was fixed using a thermostatic bath at 25ºC. To investigate the effect of contact time, samples were collected from the solutions studied at time intervals of 30−180 min. The concentration of the adsorbent was varied from 5 to 20 g/L, and the initial pH of the solution was adjusted to 3, 4, 5, or 6.

After stirring, the supernatant was withdrawn and filtered using a 0.45 µm syringe-driven filter (Millex-LH, PTFE, Millipore Corp., Burlington, Massachusetts, USA). The amount of fluoride ions removed was calculated from the difference between the initial and final fluoride concentration expressed by equation 1:

$$\text{Fluoride removal } \% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 = the initial concentration and C_e = the equilibrium F^- concentration. The fluoride ion concentration, before and after adsorption, was determined by means of a fluoride ion selective electrode (ISE model no. 6.0502.150, Metrohm, Herisau, Switzerland). The ion meter was calibrated before every use. Before any measurements were made, 10 mL aliquots of experimental solutions were mixed with 10 mL of total ionic strength-adjusting buffer (TISAB I) prepared as suggested by Agrawal *et al.* (2002b).

RESULTS AND DISCUSSION

Characterization of clay samples

The XRD and XRF quantification results (Table 1) revealed that sample A1 is rich in kaolinite while A2 is mainly smectitic. The difference is reflected in the chemical analysis with more SiO_2 and Al_2O_3 measured for A1. A2 contained large amounts of Fe, Ca, Mg, and Na. Phase quantification showed that A1 consists mainly of kaolinite (57%), with a minor amount of illite (8%).

Table 1. Mineralogy and chemical composition of samples A1 and A2 from XRD and XRF measurements.

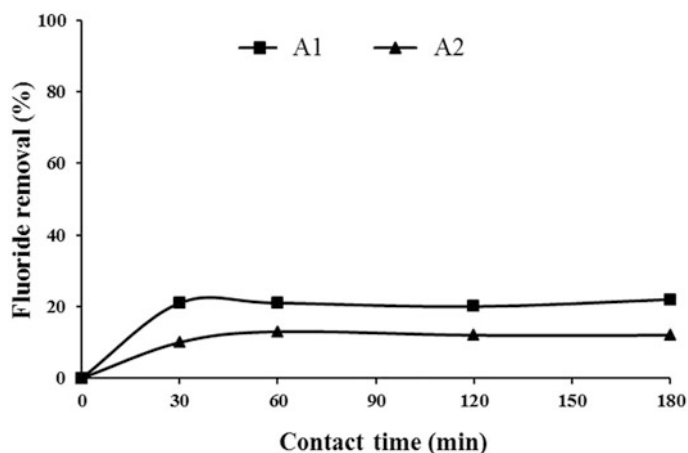| Mineralogy (%) A1		Mineralogy (%) A2		Chemical composition (wt.%) A1		Chemical composition (wt.%) A2	
Kaolinite	57	Smectite	74	SiO_2	56.50	SiO_2	47.74
Illite	8	Kaolinite	9	Al_2O_3	28.03	Al_2O_3	18.59
Quartz	35	Illite	3	Fe_2O_3	1.42	Fe_2O_3	7.39
		calcite	6	CaO	0.19	CaO	3.85
		Quartz	6	MgO	0.38	MgO	1.98
				Cr_2O_3	0.03	Na_2O	1.94
				ZrO_2	0.10	K_2O	1.58
				P_2O_5	0.19	P_2O_5	0.27
				LOI	9.75	LOI	15.3

Figure 1. Variation of fluoride-removal percentage as a function of contact time for samples A1 and A2: ($C_0 = 2$ mg/L; adsorbent amount = 5 g/L; $pH_i = 6 \pm 0.5$; temperature = 25ºC).

The associated mineral was mainly quartz (35%), in agreement with the large amount of SiO_2 reported by the chemical analysis (Table 1).

Sample A2 consists mainly of smectite (74%), with minor amounts of kaolinite (9%), illite (3%), calcite (6%), and quartz (6%). The specific surface area, S_{BET}, was 33 m^2/g for A1 and 86 m^2/g for A2.

Adsorption experiments

Effect of contact time. The adsorption curves (Figure 1) revealed the effect of contact time on fluoride removal by A1 and A2. Initially all adsorbent sites were vacant and the solute concentration gradient was high. The optimum equilibrium was reached after 30 min. Later, fluoride uptake decreased significantly due to the decrease in the number of available adsorption sites (Yadav *et al.*, 2006). For both clays, the adsorption capacity was small (<25%). Kaolinite, however, exhibited about double the capacity of smectite to remove fluoride.

These differences in adsorption capacity may be due to the fact that, initially, at lower PZC, kaolinite presents more positively charged sites (surface-available edge hydroxyls) that could assimilate fluoride ions.

In fact, kaolinite is a better adsorbent of fluoride than smectite because it exhibits more hydroxyl groups on one of the basal planes of the clay, which are the adsorption reaction sites of fluoride ions.

Effect of adsorbent dose. The effect of the amount of adsorbent on the proportion of fluoride removed (Figure 2) is that the removal capacity of sample A1 increased from 21 to 48% and of A2 from 10 to 28%, with an increase in adsorbent dose from 5 to 20 g/L.

The percentage of fluoride removed increased with the increase in clay dose because of the enhanced number of active sites available for adsorption of fluoride ions. A dose of 20 g/L was considered appropriate as this reduced the amount of fluoride to less than the standard for potability.

Effect of pH. In aqueous clay systems, the surface potential is determined by the activity of ions (H^+ or
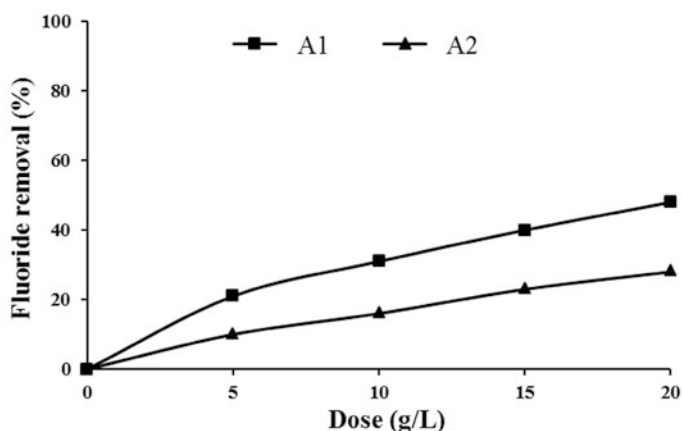

Figure 2. Variation in fluoride-removal percentage as a function of clay dose for samples A1 and A2 ($C_0 = 2$ mg/L; contact time = 30 min; $pH_i = 6 \pm 0.5$; temperature = 25ºC).
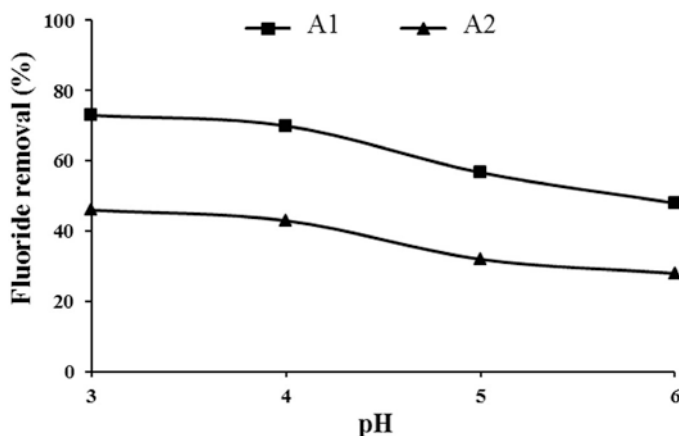
Figure 3. Variation in fluoride-removal percentage as a function of pH for samples A1 and A2 ($C_0 = 2$ mg/L; contact time = 30 min, adsorbent amount = 20 g/L; temperature = 25ºC).

OH⁻) which react with the mineral surface. Thus, pH plays an important role in controlling the adsorption of the fluoride at the clay−solution interface. Such interfaces for acid−base dissociations develop positive and negative charges at the surface (Worrl, 1968).

Defluoridation studies were carried out using both A1 and A2 in acidic media, with the pH ranging from 3 to 6. This pH range was chosen because previous studies suggested that defluoridation is better at pH <7 (Agrawal *et al.*, 2002a).

The plot presented (Figure 3) indicates clearly that the percentage of fluoride removal was influenced by the pH of the medium; the percentage of fluoride removal increased from 48 to 73% for A1 and from 28 to 46% for A2, respectively, over the pH range of 6 to 3.

Greater adsorption at lower pH ranges led to the assumption that chemisorption dominates in this range and physisorption occurs at higher pH ranges (Meenakshi *et al.*, 2008). With increasing pH, the hydroxyl ions which formed at the surface of the clay competed with fluoride ions for exchange sites (Ghorai

and Pant, 2005), resulting in reduced adsorption capacity.

Fluoride uptake in natural water. The uptake of fluoride ions from field samples collected from the city of Metlaoui (Gafsa, southern Tunisia) by the A1 clay was measured. Sample A1 showed a greater fluoride-removal capacity than sample A2. Detailed physico-chemical characteristics of field water from Metlaoui before and after fluoride uptake by A1 clay (Table 2) revealed that the natural water had a relatively high salt content (2.4 g/L). The salinity and sulfate and fluoride contents were greater than allowed by Tunisian potability standards. Following treatment with A1 clay, however, the concentrations of most of the ions present in this water decreased, and the fluoride-ion content decreased from 3.05 to 0.85 mg/L.

The percentage removal of fluoride in field water (72%) was very similar to that of the simulated water (73%) samples, which suggests that A1 clay is selective for fluoride ions. Similarly, the sulfate content remained

Table 2. Physicochemical characteristics of field water before and after fluoride uptake by sample A1.

Field water from Metlaoui	Before treatment	After treatment	Tunisian potability standards (NT 09.14)	WHO sstandards
pH	7.66	5.80	6.5−8	6.5−8
Conductivity (µS/cm) at 25ºC	2820	1670	300−2500	−
TDS (mg/L)	2349	1266	200−2000	1000
Ca^{2+} (mg/L)	208.4	101	300	500
Mg^{2+} (mg/L)	98.7	82	150	−
Na^+ (mg/L)	305.1	233.3	200	200
K^+ (mg/L)	12.43	12.80	−	−
HCO_3^- (mg/L)	366	15.2	−	−
SO_4^{2-} (mg/L)	1049.5	1040.5	600	250
Cl^- (mg/L)	354.5	212.7	600	300
NO_3^- (mg/L)	13	12.4	45	50
F^- (mg/L)	3.05	0.85	0.8	1.5

relatively constant, confirming the selectivity of A1 clay for fluoride. Sulfate ions were the main competitor ions during removal of fluoride.

After treatment with A1 clay, the pH of the solution increased from 3 to 5.80, which may be due to the exchange between fluoride and hydroxide ions in the clays (Thakre *et al.*, 2010).

Indeed, according to Yakub and Soboyejo (2013), kaolinite, which is a hydrated aluminosilicate, can exchange its OH$^-$ ions for F$^-$ ions in the presence of fluoride ions in solution. The exchange was possible because of the similar ionic radii of F$^-$ and OH$^-$, 1.36 Å and 1.40 Å, respectively. In addition, as noticed previously, adsorption of the fluoride ions was possible because of the positively charged surface sites of clays at near-natural pH (Vinati *et al.*, 2015).

To understand the fluoride-adsorption mechanism, FTIR analysis was performed on A1 clay samples before and after adsorption (Figure 4). The FTIR spectra contained the usual kaolinite peaks at 3694 cm^{-1} for inner-surface OH stretching, 3626 cm^{-1} for inner-OH stretching, 1110 and 1033 cm^{-1} for Si-O bending, 695 cm^{-1} for Si−O stretching, 471 and 433 cm^{-1} for Si-O bending, 789 and 753 cm^{-1} for Si-O-Al compounded vibrations, and 433 cm^{-1} and 471 cm^{-1} for Si-O vibrations as described by Meenakshi *et al.* (2008).

The decrease in the intensity of the kaolinite OH stretching modes (Figure 4) in the fluoride-treated A1 at 3694 and 3620 cm^{-1} is direct evidence that the F$^-$ for OH$^-$ anion exchange reaction is in play, in addition to the fluoride adsorption process (Meenakshi *et al.*, 2008).

These results, along with those from Meenakshi *et al.* (2008), demonstrate that the mechanism of removal of fluoride ions can be by a simple exchange with OH$^-$ ions and/or by adsorption to the positively charged sites on the clay surface.

Adsorption isotherm studies

A variety of empirical isotherm models was used to review the experimental fluoride adsorption data. The two most commonly used are the Langmuir and Freundlich isotherms. The Langmuir isotherm is valid for monolayer sorption due to a surface with a finite number of identical sites. The Freundlich adsorption isotherm describes the heterogeneous surface energy by multilayer adsorption.

The linear form of the Freundlich isotherm is given as:

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad (2)$$

where, q_e is the amount of fluoride adsorbed per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of fluoride in the solution (mg/L), K is a measure of the adsorption capacity, and 1/n is the adsorption intensity.

The plot of log q_e *vs.* log C_e shows a good linear relationship, yielding a correlation coefficient of R^2 = 1 (Table 3).

The constants K and n of the Freundlich isotherms (Table 3) are temperature independent, and the adsorption process is favored when the value of n lies between 1 and 10, which is the case in the present study.

The Langmuir isotherm model is represented by equation 3:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e q b} \qquad (3)$$

where q_m is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum adsorption capacity of the adsorbent, and b (L/mg) is the Langmuir isotherm constant that is related to the energy of adsorption (Table 3). The Langmuir isotherm is also expressed in terms of a dimensionless constant separation factor or equilibrium parameter known as R$_L$, presented in equation 4:

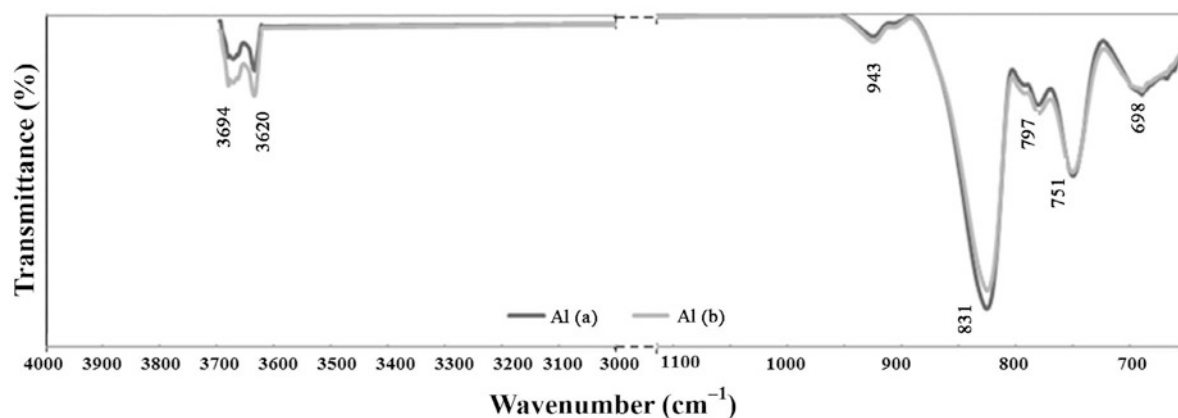$$R_L = \frac{1}{1 + bC_0} \qquad (4)$$

Figure 4. FTIR spectra of sample A1: (a) before and (b) after fluoride uptake.

Table 3. Freundlich and Langmuir isotherm parameters.

Temperature (K)	——— Langmuir isotherm parameters ———				Freundlich isotherm parameters		
	q_m (mg/g)	b (L/mg)	R_L	R^2	K (mg/g)	n	R^2
298	7.87	0.070	0.58	0.983	1.48	1.97	0.993
308	9.68	0.064	0.61	0.982	1	1	1
318	16.05	0.032	0.75	0.989	1.01	0.99	0.999

where b is the Langmuir isotherm constant and C_o is the initial concentration of fluoride (mg/L).

The R_L values obtained (Table 3) were between 0 and 1 which indicates favorable adsorption for the temperature range studied.

Adsorption isotherms revealed that the data fitted well to both the Langmuir and Freundlich adsorption isotherms, confirming both monolayer and multilayer adsorption and best-fit with the Freundlich model.

CONCLUSIONS

The removal of fluoride ions from natural waters using raw kaolinite and smectite from Tunisia in batch experiments was studied. The optimum conditions for fluoride removal were established as: contact time = 30 min, clay dose = 20 g/L, and pH = 3 at room temperature (25°C). A1 kaolinite was more efficient at removing fluoride than A2 smectite. Application of the process on naturally fluorinated water from southern Tunisia was carried out successfully. The proportions of fluoride removed from synthetic water and from natural, fluorinated water were almost identical at 73%. The results indicated that the Tunisian kaolinite has potential for application in defluoridation of natural water.

ACKNOWLEDGMENTS

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