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Physicochemical and Performance Evaluation of Natural and Modified Ire-Ekiti clay: Emerging Substrate in the De-fluoridation of Drinking Water

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ABSTRACT

Potable water is one of the implicit requisites for healthy living. Groundwater is an affordable source of drinking water in most rural areas of Nigeria. One of the major challenges in drinking water quality is fluoride, which dosage above 1.5mg/L has been reported to cause some related health issues. Adsorption methods have proven to be effective in the de-fluoridation of drinking water. However, this works examines the physiochemical and performance evaluation of Ire-Ekiti clay in the de-fluoridation of drinking water. A method-The clay soil was characterized by the determination of Cation Exchange Capacity at pH values of 5.4 and 7.4, organic matter content and x-ray fluorescence analysis. Batch experiments were conducted to evaluate and optimize various operational parameters such as contact time, adsorbent dose, pH and speed of agitation. It was observed that Fe^{3+} modified Ire-Ekiti clay soil had the highest adsorption parameters as 2.5 g/100 mL of Ire-Ekiti clay soil removed up to 65.3% of fluoride from the initial concentration of 2 mg/L at a pH of 6 with a contact time of 25 min and agitation speed of 350 rpm. Therefore Fe^{3+}modified Ire-Ekiti clay soil has potential for application in de-fluoridation of groundwater.

Keywords: *Characterized, performance evaluation, adsorbent, application groundwater.*

INTRODUCTION

Potable water is one of the implicit requisites for healthy living. However, the growing industrialization, and extensive use of a range of chemicals for various human applications, has increased the burden of unwanted pollutants, most especially in developing countries, where they rely on underground water sources for drinking and other domestic applications. Groundwater is widely sourced in Nigeria because of its affordability, although its chemical nature is one of the most important criteria that determines its usefulness for specific need and as a result, not all groundwater is fit for consumption [1].

One of the challenges of drinking water quality include presence of excess fluoride, arsenic and natural organic matters, heavy metals, and variety of pathogens are the major cause of water borne diseases [2]. Although the presence of fluoride in drinking water, within the acceptable limits of less than or equal to 1.5 mg/L, is beneficial for the production and maintenance of healthy bones and teeth, excessive intake of fluoride can cause dental or skeletal fluorosis [3, 4].

It is expedient to make efforts by providing drinking water with fluoride concentration below 1.5 mg/L, because of the health challenges pose by consuming high dosage of fluoride. Meenaksi and Maheshwani [5] reported various de-fluoridation techniques; including adsorption, ion exchange, membrane techniques and precipitation methods. Adsorption methods have proven to be the most effective of all de-fluoridation techniques because of its cost effectiveness; as most of the substrate applied is readily available and easily sourced. A range of materials such as clay soils [6], activated alumina [7], activated carbon [8] and other low cost materials have been evaluated for the de-fluoridation of drinking water.

Modified clay materials have also proven to give satisfactory results in the de-fluoridation of drinking water; such substrates include: Fe^{3+} modified bentonite clay in Republic of South Africa [9] and Al^{3+} modified bentonite clay also in Republic of South Africa [10]. However, it is important to consider the adoption of this technique for the de-fluoridation of drinking water in Nigeria; most especially Ekiti State, where Ire-Ekiti clay soil is relatively abundant. This work evaluates the physicochemical properties of natural and modified Ire-Ekiti clay and their performance evaluation for the de-fluoridation of drinking water.

2. MATERIALS AND METHODS

2.1 Sample collection and preparation: Clay soil was collected from Ire-Ekiti, Ekiti State, Nigeria. A 1000 mg/L fluoride was prepared by dissolving 2.21 g NaF in 1 L of distilled/de-ionized water. 100 mg/L dilution was made by extracting 100mL of the solution in 1000 mL volumetric flask. All reagents used in this study were of analytical grade.

2.2 Preparation of clay soil: Ire-Ekiti clay soil was washed by rinsing with distilled/de-ionized water at a ratio of 1:5 in 1 L beaker, the mixture was stirred for 5 min, and the procedure was repeated twice. The mixtures obtained after rinsing were agitated for 15 min. In a reciprocating shaker and later centrifuged at 200 rpm. The samples were then dried in oven for 12 h at 105°C. The clay samples were milled and passed through a 200 µm sieve.

For the modification of Ire-Ekiti clay soil, anhydrous ZnO and $FeCl_3$ were dissolved in distilled/de-ionized water to produce 0.1 M solutions. 10 g of the clays soils were activated by 0.1 M solution of NaOH prior to the addition of the prepared 0.1 M anhydrous ZnO and $FeCl_3$ in 100 mL volumetric flask, after which their volumes were adjusted to 100 mL. The pH of the mixtures was adjusted to 6.5 and the solution was shaken at 200 rpm on a reciprocating shaker. The mixtures formed precipitate, which were centrifuged and washed with distilled/de-ionized water until the pH of the filtrates were 6.5. The residue was collected and dried in an oven at 105° C for 12 h. Thereafter, the samples were milled into fine

powder

2.3 Physicochemical Analysis: The physicochemical analysis of the natural and Zn^{2+} and Fe^{3+} modified clay soil were evaluated by determination of pH, Organic Matter Content (OMC), Cation Exchange Capacity (CEC) and X-Ray fluorescence techniques. The pH was determined using 1:10 clay/water ratio. 10 g of each of clay samples were weighed into a beaker and suspended in 100 mL of distilled/de-ionized water. The mixture were agitated carefully and allowed to settle for 15 min. The pH was determined by an already calibrated (Buffer 4) Hanna HI pH meter. Organic matter content was determined according to methods of Hong and Teresa [11] while CEC was determined using ammonium acetate method according to Jackson [12]. The bulk chemical composition of the clay samples were determined by X-Ray Fluorescence analysis. Samples were oven-dried at 100°C for 12 h, after which they were crushed to powder. The powdered samples were the mixed with binder (ratio 1:9 in grams of C-wax and EMU powder). The XRF analyses were carried out using a Phillips Analytical PW1480 X-Ray Fluorescence Spectrometer equipped with Rhodium tube as the X-Ray source.

2.4 Batch Adsorption Experiments: The adsorption experiments were carried out for the comparative performance evaluation of natural, Zn^{2+} modified and Fe^{3+} modified Ire Ekiti clay soil. Parameters such as effect of adsorption on contact time, adsorbent dosage, pH and speed of agitation were evaluated to determine the applicability of these substrates for fluoride removal.

Adsorption of fluoride as a function of contact time

100 mL of 10 mg/L F- solution was pipetted into 24, 250 mL bottles and 2 g each of natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay soils were added to each bottles. The mixtures were agitated for 5, 10, 15, 20, 25, 30, 35 min at 200 rpm using a reciprocating shaker. The experiments were carried out in triplicates. After equilibration, the mixtures were centrifuged for 10 min at 300 rpm. The samples were analyzed for F- using an Advanced Electrochemistry meter.

Adsorption of fluoride as a function of adsorbent dosage

The rate of fluoride removal as a function of adsorbent dosages were evaluated by measuring 100 mL of 10 mg/L F- in 21, 250 mL bottles on which different dosages (2.5, 2.25, 2.0, 1.5, 1.0, 0,5, 0.25 g) of natural, Zn^{2+} modified and Fe^{3+} modified clay were added. The mixtures were agitated for 60 min at 200 rpm at room temperature. After equilibration, the mixtures were centrifuged for 10 min at 300 rpm and were later analyzed for F- using Advanced

Electrochemistry meter.

Adsorption of fluoride as a function of pH

The rate of fluoride removal as a function of pH was carried out at pH values of 2, 4, 6, 8, 10, 12 by measuring 100 mL of 10 mg/L of F- in 25, 250 mL bottles. 2 g each of natural, Zn2+ modified and Fe3+ modified Ire-Ekiti clay were added to each bottle while the mixtures were agitated for 60 min at 250 rpm using a reciprocating shaker. After equilibration, the mixtures were centrifuged for 10 min at 300 rpm and F- concentration analyzed with an Advanced Electrochemistry meter.

Adsorption of fluoride as a function of speed of agitation

The rate of fluoride removal as a function of speed of agitation was evaluated by measuring 100 mL of 10 mg/L F- in 18, 250 mL bottles and 2 g each of natural, Zn2+ modified and Fe3+ modified Ire-Ekiti clay soil were added. The mixtures were agitated at 10, 50, 200, 300, 350 and 400 rpm, using a reciprocating shaker. After equilibration, the mixtures were agitated for 10 min at 300 rpm and F- concentration analyzed with an Advanced Electrochemistry meter.

Eq. (1) was used to calculate the percentage fluoride removal.

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

Where C_o is the initial F- concentration and C_e is the equilibrium concentration in mg/L.

3. RESULTS

3.1 Physicochemical parameters

Cation Exchange capacity (CEC) of Ire-Ekiti clay soil was evaluated at pH values of 5.4 and 7.4 (Table 1) in order to determine the capacity of active sites for fluoride adsorption. The results revealed that higher values of CEC were obtained at pH value of 7.4. The concentrations of exchangeable cations in natural Ire-Ekiti clay were obtained as follows; Na^+ (51.40), K^+ (2.68), Ca^{2+} (0.42) and Mg^{2+} (27.22), all in meq/100g at pH vale of 7.4. These values were slightly lower than those obtained from zn^{2+} and Fe^{3+} modified Ire-Ekiti clay. Higher values of Na (58.30), K^+ (2.96), Ca^{2+} (0.62) and Mg^{2+} (29.80), all in meq/100g exchangeable cations were obtained by modification of Ire-Ekiti clay with Fe^{3+}. Table 1 also revealed the percentage organic matter content of natural, Zn^{2+} and Fe^{3+} modified Ire-Ekiti soil; the results showed that pH and modification of clay soil did not affect its organic matter content.

Table 1: The title showed the results of physicochemical parameters of natural and modified Ire-Ekiti clay

Natural	Exchangeable cations				Total CEC(meq/100g)	%OMC
	Na+	K+	Ca2+	Mg2+		
5.4	36.2	1.46	0.42	27.22	65.30	8.9
7.4	51.40	2.68	0.42	27.22	81.72	8.9
Zn2+ modified						
5.4	37.81	1.40	0.58	28.20	67.99	8.9
7.4	56.2	2.80	0.58	28.20	87.78	8.9

Fe3+ modified						
5.4	39.20	1.46	0.62	29.80	71.08	8.9
7.4	58.30	2.96	0.62	29.80	91.68	8.9

Table 2: The title showed chemical composition of natural and modified Ire-Ekiti clay

Parameter	Natural	Zn2+ modified	Fe3+ modified
Al_2O_3 (%w/w)	17.2	16.32	16.30
CaO (%w/w)	0.86	0.73	0.72
Cr_2O_3 (%w/w)	0.02	0.02	0.01
Fe_2O_3 (%w/w)	32.80	33.60	36.80
K_2O (%w/w)	0.30	0.08	0.2
MgO (%w/w)	1.62	1.78	1.22
MnO (%w/w)	0.06	0.08	0.03
P_2O_5 (%w/w)	0.05	0.01	0.03
TiO_2 (%w/w)	0.04	0.01	0.04
SiO_2 (%w/w)	41.80	32.46	26.03

3.2 Chemical composition

The chemical compositions of the natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay soil were determined by x-ray fluorescence spectroscopy (Table 1). It was revealed that natural Ire-Ekiti clay soil was a typical alumina silicate mineral with SiO_2/Al_2O_3 ratio 2.60. Slightly difference ratios of alumina silicate values (2.00 and 1.6) were obtained for Zn^{2+} and Fe^{3+} modified Ire-Ekiti clay soil. Modifications of the clay did not affect aluminosilicate ratio but also concentrations of other chemical composition varied extensively.

3.3 Batch Adsorption Experiments

Influence of contact time on F^- removal

The equilibrium adsorption time was determined by evaluating the rate of adsorption of F^- onto the surfaces of natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay soil at different time ranging from 0-35 min, using 2 g adsorbent at 200 rpm for 60 min (Fig. 1). As observed in Fig. 1, fluoride uptake by natural and modified Ire-Ekiti clay soil increased from initial values; natural (15.6%), Zn^{2+} modified (16.2%) and Fe^{3+} modified (26.2%) at 5 min up to about; natural (34.8%), Zn^{2+} modified (36.2%) and Fe^{3+} modified (56.2%) at 25 min. The rate of surface adsorption of F^- by the natural and modified clay decreased from 25 min., showing that the time for equilibrium adsorption of F^- onto both types of clay adsorbent was 25 min.

Influence of adsorbent dosage on F^- removal

The dosage of adsorbent applied in this study was in the range 0.25-2.5 g, agitated with 10 mg/L F^- for 60 min at 200 rpm. The aim was to determine the equilibrium adsorbent dosage and evaluate the performance of natural and modified Ire-Ekiti clay soil for F^- removal. Figure 2 revealed that F^- removal efficiency increased with mass of adsorbent in natural and modified batch adsorption experiments. For natural and Zn^{2+} modified adsorption, the optimal adsorption 56.9% and 54.9% occurred at dosages of 2.25g and 2.50 g respectively. However, higher concentrations of F^- ions were adsorbed onto the surface of Fe^{3+} modified Ire-Ekiti clay, when compared with natural and Zn^{2+} modified experiments; with optimal adsorption of 65.3% occurring at 2.50 g dosage.
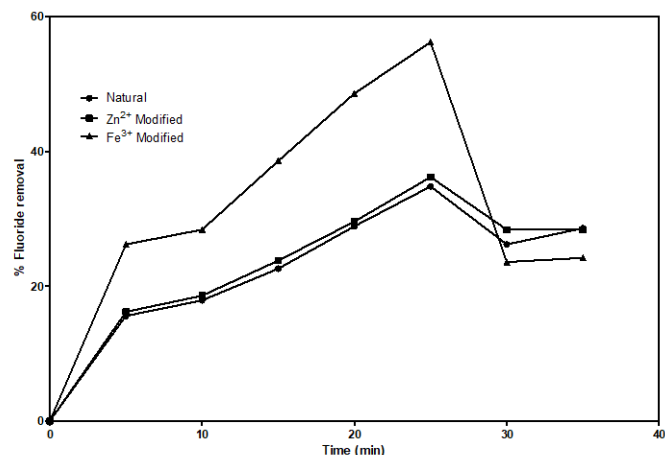

Figure 1: The figure showed the influence of contact time on F^- removal
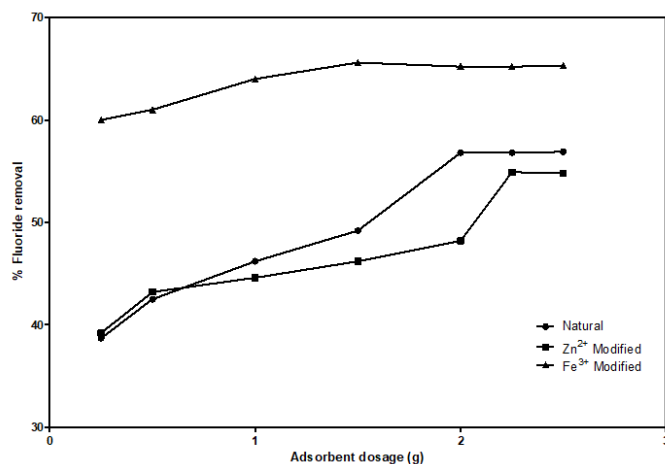

Figure 2: The figure showed the influence of adsorbent dosage on F^- removal

Influence of pH on F^- removal

pH plays a significant role in the control of the surface charge of the adsorbent and in the removal of the adsorbate from the solution. As a result of this, its effect on fluoride adsorption by natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay was evaluated (Fig. 3). In all cases, optimal F^- adsorption occurred at pH value of 6. The optimal F^- adsorption at pH 6 were 48.2%, 56.8% and 59.% for natural, Zn^{2+} and Fe^{3+} modified Ire-Ekiti clay soil respectively. However, modification of clay had positive impacts on the adsorption capacity of the substrate.
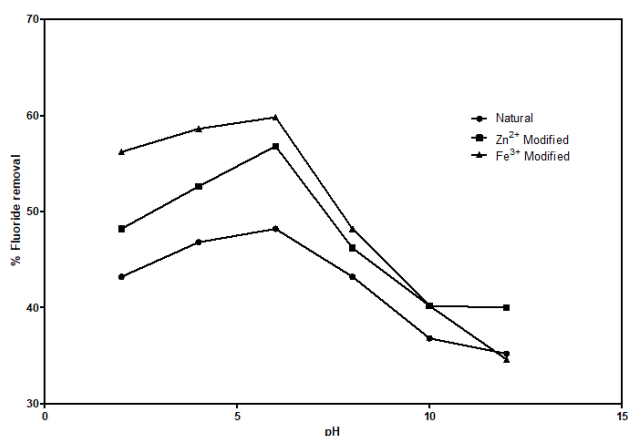

Figure 3: The figure showed the influence of pH on F^- removal
Influence of speed of agitation on F^- removal

The efficiency of adsorption of natural and modified Ire-Ekiti clay soil was evaluated at different speed of agitation of between 50-400 rpm, using 2g of adsorbent in each case. Optimal adsorption occurred at 350 rpm. The adsorption of 46.8% occurred for natural, while for Zn^{2+} modified and Fe^{3+} modified; they are 48.8% and 66.2% respectively.
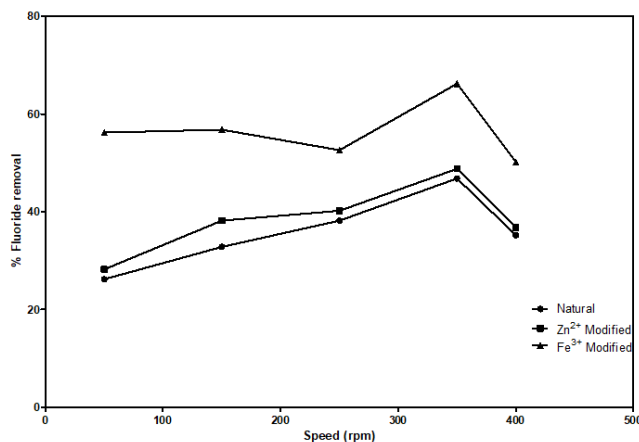

Figure 4: The figure showed influence of speed of agitation on F^- removal

4. DISCUSSION
4.1 Physicochemical parameters
Cation Exchange capacity (CEC) of Ire-Ekiti clay soil was evaluated at pH values of 5.4 and 7.4 (Table 1) in order to determine the capacity of active sites for fluoride adsorption. The results revealed that higher values of CEC were obtained at pH value of 7.4. The concentrations of exchangeable cations in natural Ire-Ekiti clay were obtained as follows; Na^+ (51.40), K^+ (2.68), Ca^{2+} (0.42) and Mg^{2+} (27.22), all in meq/100g at pH vale of 7.4. These values were slightly lower than those obtained from zn^{2+} and Fe^{3+} modified

Ire-Ekiti clay. Higher values of Na (58.30), K^+ (2.96), Ca^{2+} (0.62) and Mg^{2+} (29.80), all in meq/100g exchangeable cations were obtained by modification of Ire-Ekiti clay with Fe^{3+}. CEC is an intrinsic property of soil representing the concentration of negatively charged sites on soil colloids that can exchange cations, the discovery of exchangeable sites on Ire-Ekiti clay soil could be a major breakthrough towards the application of its natural and modified substrates in the adsorption process. Fluoride has tendency to bond with these cations, and as a result could provide possible pathways for its removal.

Organic matter content of a clay soil is a measure of decomposable matter in a typical clay soil. Table 1 also revealed the percentage organic matter content of natural, Zn^{2+} and Fe^{3+} modified Ire-Ekiti soil; the results showed that pH and modification of clay soil did not affect its organic matter content

4.2 Chemical composition
The chemical compositions of the natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay soil were determined by x-ray fluorescence spectroscopy (Table 1). It was revealed that natural Ire-Ekiti clay soil was a typical alumina silicate mineral with SiO_2/Al_2O_3 ratio 2.60. Slightly difference ratios of alumina silicate values (2.00 and 1.6) were obtained for Zn^{2+} and Fe^{3+} modified Ire-Ekiti clay soil. Modifications of the clay did not affect aluminosilicate ratio but also concentrations of other chemical composition varied extensively. However, the metallic oxides reported in this work, makes Ire-Ekiti clay soil a potential substrate for the de-fluoridation of water. This is because active cationic sites are provided the presence of these oxides on the clay for possible chemisorptions. Sepehr *et al.* [13] reported that modification of natural clay had effect on its chemical composition.

4.3 Batch Adsorption Experiments
The equilibrium adsorption time was determined by evaluating the rate of adsorption of F^- onto the surfaces of natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay soil at different time ranging from 0-35 min, using 2 g adsorbent at 200 rpm for 60 min (Fig. 1). As observed in Fig. 1, fluoride uptake by natural and modified Ire-Ekiti clay soil increased from initial values; natural (15.6%), Zn^{2+} modified (16.2%) and Fe^{3+} modified (26.2%) at 5 min up to about; natural (34.8%), Zn^{2+} modified (36.2%) and Fe^{3+} modified (56.2%) at 25 min. The rate of surface adsorption of F^- by the natural and modified clay decreased from 25 min., showing that the time for equilibrium adsorption of F^- onto both types of clay adsorbent was 25 min. However, the effect of modification of Ire Ekiti clay by Zn^{2+} and Fe^{3+} ion had positive effect on the rate of adsorption, with Fe^{3+} modified Ire-Ekiti clay; optimal adsorption of F^- occurring at 25 min. Researchers have reported that contact time had influence on the rate of adsorption of fluoride on different substrate [14,15,16].

The dosage of adsorbent applied in this study was in the range 0.25-2.5 g, agitated with 10 mg/L F^- for 60 min at 200 rpm. The aim was to determine the equilibrium adsorbent dosage and evaluate the performance of natural and modified Ire-Ekiti clay soil for F^- removal. Figure 2 revealed that F^- removal efficiency increased with mass of adsorbent in natural and modified batch adsorption experiments. For natural and Zn^{2+} modified adsorption, the optimal adsorption 56.9% and 54.9% occurred at dosages of 2.25g and 2.50 g respectively. However, higher concentrations of F^- ions were adsorbed onto the surface of Fe^{3+} modified Ire-Ekiti clay, when compared with natural and Zn^{2+} modified experiments; with optimal adsorption of 65.3% occurring at 2.50 g dosage. Sepehr *et al.* (2014) reported that modifications of natural clay improved the rate of adsorption of fluoride ions. The increased efficiency of

adsorption relative to adsorbent dosage was due to availability of active sites for either physiosorption or chemisorption.

pH plays a significant role in the control of the surface charge of the adsorbent and in the removal of the adsorbate from the solution. As a result of this, its effect on fluoride adsorption by natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay was evaluated (Fig. 3). In all cases, optimal F^- adsorption occurred at pH value of 6. The optimal F^- adsorption at pH 6 were 48.2%, 56.8% and 59.% for natural, Zn^{2+} and Fe^{3+} modified Ire-Ekiti clay soil respectively. However, modification of clay had positive impacts on the adsorption capacity of the substrate. Sepehr *et al.* [13] reported that adsorption is controlled by the combined effect of chemical and electrostatic interactions between oxide surface and the fluoride ions in solution, as well as by the availability of active sites on the oxide surfaces. Conversely, the decrease in fluoride removal under alkaline conditions may be due to the availability of other competing ions, such as hydroxyl ions, competing with available active sites [14].

The efficiency of adsorption of natural and modified Ire-Ekiti clay soil was evaluated at different speed of agitation of between 50-400 rpm, using 2g of adsorbent in each case. Optimal adsorption occurred at 350 rpm. The adsorption of 46.8% occurred for natural, while for Zn^{2+} modified and Fe^{3+} modified; they are 48.8% and 66.2% respectively. It is worthy of note that modifications of natural Ire-Ekiti clay had positive impacts on the efficiency of adsorption with equilibrium adsorption occurring at 350 rpm.

5. CONCLUSION

In the assessment of the use of natural, Zn^{2+} modified and Fe^{3+} modified Ire-Ekiti clay soil for the de-fluoridation of groundwater, the following conclusions were made:

❖ both natural and modified Ire-Ekiti clay showed good performance in the de-fluoridation experiments;

❖ Fe^{3+} modified Ire-Ekiti clay soil showed optimum performance at 25 min contact time at a speed of 350 rpm, with adsorbent dosage of 2.5 g/100mL and pH 6;

❖ There is need to further research in adsorption isotherms, kinetic studies and field water experiment to complement the research on de-fluoridation experiments.

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