

ZIBELINE INTERNATIONAL
PUBLISHING

ISSN: 2521-5035 (Print)

ISSN: 2521-5043 (Online)

CODEN: ESMACU



CrossMark

RESEARCH ARTICLE

GEOCHEMICAL AND MINERALOGICAL CHARACTERIZATION OF SOME CLAY MATERIALS AS FLUORIDE ADSORBENT FROM GROUNDWATER IN GHANA

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ARTICLE DETAILS

Article History:

Received 14 July 2020

Accepted 18 August 2020

Available online 4 September 2020

ABSTRACT

This research conducted in the Upper East Region of Ghana characterizes *Termitaria* and residual clays from Navrongo to establish effective fluoride adsorbent from boreholes in Bongo area. Specific objectives are to determine (1) geochemical and mineralogical compositions of the clays using ICP-MS and X-ray diffraction devices, respectively; (2) fluoride degradation in groundwater using a Batch test (3) water quality after fluoride removal. The Batch test uses 250 ml of groundwater with 2.29 mg/l fluoride and clay masses of 25, 50, 100 and 200 grams to perform within a minimum and varying time of 10 minutes to a maximum of 120 minutes. Results indicate enrichments of major elements in *Termitaria* clay and trace elements in residual clay. Fluoride reduces to 0.778 mg/l and 0.294 mg/l at a mass of 0.8 kg/l over 80 minutes for *Termitaria* and residual clays, respectively. Optimum defluoridation time occurs within an hour in the pH range of 7.83 to 8.04. Quartz-hematite-magnetite-illite-montmorillonite suite occurs in residual clay with defluoridation capacity of 66.25 %, while quartz-illite-montmorillonite suite occurs in *Termitaria* clay with defluoridation capacity of 87.25 %, and constitute the more efficient adsorbent. TDS and conductivity are within WHO standard guidelines, which confirms the clays as non-toxic.

KEYWORDS

Concentration, Fluoridation, *Termitaria*, Residual, Navrongo, Bongo.

1. INTRODUCTION

Fluoride contamination in groundwater is a major concern around the world due to its toxic effects on humans. Developing countries are mostly affected by fluoride toxicity due to the great reliance on groundwater as a source of potable water supply in rural and peri-urban communities such as northern Ghana (Smedley et al., 2007; Salifu et al., 2012). According to a study, about 90% of rural and 25% of urban communities in Ghana depend largely on groundwater for their domestic water needs (Abugri, 2011). These facts, therefore justify the Millennium Development Goals (MDGs 7c) on safe and potable drinking water and reduction in water-related diseases and improve sanitation (UNDP, 2012).

For the course of the MDGs 7c, the government of Ghana in partnership with other stakeholders have invested a lot of human and capital resources into groundwater exploration and development (Salifu et al., 2012). However, the problem of fluoride contamination in groundwater in some parts of rural northern Ghana remains a major impediment to achieving the MDG 7c (Abugri, 2011). In these areas, fluoride is mobilized from fluorite, biotite, topaz, in rocks such as granite, basalt, syenite, and shale through groundwater-rock interaction (Anim-Gyampo et al., 2012; Sunkari et al., 2018).

Safety-wise, a narrow beneficial range for fluoride concentration in drinking water concerning human health exists; this benefits or negative health impact to humans, especially children depend on the concentration and time of continuous uptake. Usually, ingesting small amounts of

Fluoride in water is considered to have a beneficial effect on the rate of occurrence of dental caries; on the contrary, intake of excess fluoride or long periods of exposure may lead to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder (Vinati et al., 2015). Fluorosis is one of the commonest symptoms of high fluoride ingestion manifested by mottling of teeth in mild cases and embrittlement of bones and neurological damage in severe cases. Notably, severe cases due to the effects of excess Fluoride in water occur in areas of Northern Ghana, particularly the Bongo area in the Upper East Region.

The maximum acceptable drinking water guideline value for Fluoride by the World Health Organization is less than 1.5 mg/L (WHO, 2012). Given the health impacts of fluoride, considerable efforts have been made over the years to mitigate the impacts. Some of these efforts led to the discovery of materials and methods such as membrane techniques, Reverse Osmosis and Nano-filtration, Dialysis and electro-dialysis (Feenstra et al., 2007; Gogoi and Baruah, 2008). However, these methods aside their operational complexity and cost, can also sometimes result in secondary pollution due to the generation of toxic sludge (Meenakshi and Maheshwari 2006).

Developing a protocol for fluoride removal from groundwater is an enormous one that cannot be afforded by the local and semi-literate people in northern Ghana (Ayamsega et al., 2008). Some researcher noted that the efficiency of fluoride removal varies according to site-specific environmental conditions that may affect specific generalizations during applications of a method (Meenakshi and Maheshwari, 2006).

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DOI:

10.26480/esmy.02.2020.135.139

These, therefore, require the search for locally available cost-effective materials for effective fluoride removal methods.

Elsewhere, various alternative methods have been developed for smaller communities of about 200 people that can span for 2–3 hours. An example is the Nalgonda technique, which prescribes additions of alum, lime, and bleaching powder to raw water, followed by rapid mixing, flocculation, sedimentation, filtration and disinfection (Meenakshi Maheshwari 2006). In the application of these methods, different types of adsorbents of natural or artificial sources are used. Examples are; alumina, aluminium-calcium-iron-based complexes of oxides/hydroxides/ oxyhydroxides, among others.

However, some researcher explored and experimented with various naturally occurring cost-effective materials such as clays as adsorbents that have a fluoride removal potential in the range of 80- 90% at a pH range of 2-9 (Vinati et al., 2015). On this basis, biologically modified clay from termite mound was identified for use to establish its suitability to remove excess fluoride from groundwater to a suitable level. *Termitaria clay* constitutes a unique, but common micro-landforms that are associated with soils in savanna zones in the tropics (Figure 1).



Figure 1: Termite mound as the source of *Termitaria* clay.

The use of suitable natural materials such as clays as fluoride adsorbents in groundwater is low in Ghana despite the abundance of clay deposits in endemic areas, where the clays can be used in a very sustainable way. The research aimed to establish an effective fluoride adsorbent for fluoridated groundwater using *Termitaria* and residual clays in Ghana. The specific objectives are to determine (1) geochemical and mineralogical compositions of the clays (2) fluoride removal pattern in groundwater, and (3) water quality after the fluoride removal process.

2. MATERIALS AND METHODS

2.1 Study Area

The research area is situated in the Upper East region of Ghana and underlain by the Birimian granitoids with minor pyroclastic and volcanoclastic rocks (Figure 2).

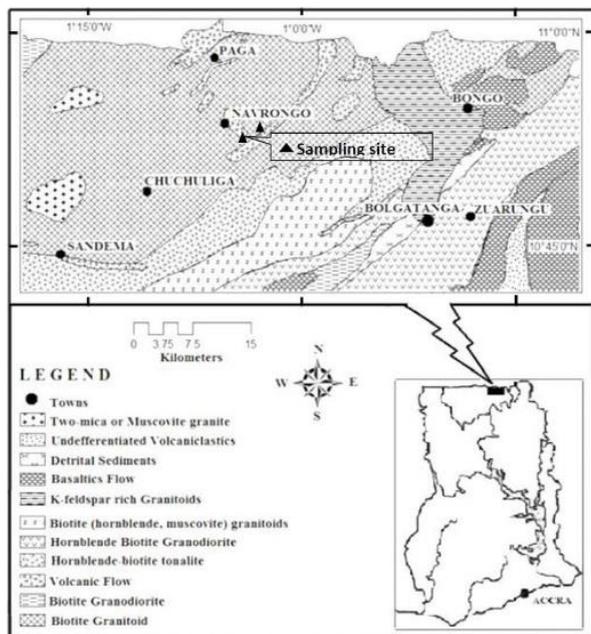


Figure 2: Geological map of the study area (After Foli et al., 2012).

The soils in the area include ochrosols that are often hydromorphic, deeply weathered and heavy to medium in texture and dominated by high clay contents (Bayari et al., 2019). The vegetation is the Sudan savanna type, with wet and dry seasons from May-October and October-April, respectively. Mean annual rainfall is about 700-1200 mm, with annual evaporation range and aridity indexes are 1652-1720 mm and 0.60, respectively.

2.2 Sampling strategy and analytical procedures

A reconnaissance survey and review of the site history as well as location of potential sampling sites and general environmental conditions was carried out. Sampling equipment for digging and collecting samples was composed of stainless steel, clean steel shovel or spade, porcelain zip-lock bag, a geological hammer, mattock, GPS and field notebook, marker and 30 cm ruler. Also, well-cleaned litre jars were used for borehole sampling.

Fresh *Termitaria* clay was sampled from five different termite mounds from two locations with central coordinates as 10°52.17', 001°04.59' and 10°51.52', 001°05.09'. Before the sampling, the termite mounds were damaged for termites to rebuild overnight so that fresh material can be obtained. Samples from both locations were thoroughly mixed. Residual clay samples were also taken at 5 meters away from each sampled *Termitarium* at depths of about 30-35 cm into the saprolite zone (Bayari et al., 2019).

During both sampling episodes, the clay samples were cleaned by removing plant roots and rock debris. About 500 g of the different clay sample types were extracted with a plastic hand trowel and bagged into porcelain bags. At the laboratory, the samples were dried at room temperature for two days and pulverized into powder using laboratory pestle and mortar. Boreholes with elevated concentration of fluoride were identified at Bongo, in the Bongo District in the Upper East Region; and 13 litres of the fluoridated water was sampled and used for the analyses.

2.3 Mineralogical and Geochemical Characterization of clay types

The mineralogical and geochemical assessment was done using the X-Ray Diffraction (XRD). About 100 g aliquots of each of the two types of clay samples were pulverized, packaged and sent to the ALS Geochemical Laboratory, Vancouver Canada for chemical analyses. In all, 51 trace elements were analyzed, using the inductively coupled plasma-mass spectroscopy (ICP-MS). The XRD device was used to analyse about 2 g aliquots of the two kinds of samples for mineralogical composition at the Materials Engineering Department at Kwame Nkrumah University of Science and Technology, Kumasi, Ghana.

2.4 Batch test for fluoride removal from groundwater

A Batch Test was used to test the ability of clay to remove fluoride from water samples, using the SPADNS and Spectrophotometer. The SPADNS colourimetric method relies on the reaction between fluoride and a zirconium-dye lake. Under acidic conditions, fluorides react with zirconium SPADNS solution in equal measure by bleaching of SPADNS reagent to form ZrF_6 . As fluoride increases, the colour of the dye fades and directly proportional to the fluoride concentration. The reaction is directly influenced by the acidity of the reaction mixture, where at high acidity, the reaction can be instantaneous.

The test for fluoride removal was done by progressively adding 5, 25, 50, 100 and 200 grams of the adsorbent for each clay sample using a digital balance into a 500 ml beaker. Each time, 250 ml of the fluoride elevated borehole water was added to each mass of clay and the content shaken/agitated by stirring for set equilibrium at time intervals of 10 minutes, over the range of 10-120 minutes. The mixtures were filtered through 0.15/mm filter paper and the filtrates analyzed for residual fluoride by using fluoride reagent spectrophotometer.

The effect of contact time on fluoride removal was investigated by allowing different but a uniform contact time interval between the sorbent and the raw water. On each occasion, the filtrates were drawn after the regular time interval and analyzed for residual fluoride concentrations. Similarly, to investigate the pH effect, the pH of the filtrate of each contact time was measured. Observation on the effect of adsorbent dose was done by administering the different concentrations of the adsorbent and tested at different contact time interval.

A portion of the filtrate was poured into a cuvet and 0.05 ml of Acid-zirconyl/SPADNS reagent added and shaken well to mix. In the mixture, fluoride ions with red Zirconium dye (SPADNS) solution containing demineralized water and hydrochloric acid in different per cent proportions reacted. The contents of the cuvet were placed in 580 nm

digital spectrophotometer and the absorbance measured. Absorbance values for each mass of clay samples and contact times were fed into a Water Research Institute's Fluoride Absorbance-Concentration Reading Computer programme to estimate the amount of fluoride removed. At the end of the Batch test, water quality parameters such as Total dissolved salt (TDS) and electrical conductivity (EC) were determined

3. RESULTS

3.1 Mineralogical and geochemical characterisation of clays

Results of analyses for major and trace element concentrations in the clays are presented in Tables 1 and 2, respectively.

Table 1: Major elements content in ppm of the clays.

Major Element (ppm)	K	Mg	Na	Ti	Fe	Al	Ca	P
Termitaria Clay	0.1	0.76	0.17	0.09	5.49	4.1	0.7	250
Residual Clay	0.2	0.06	0.05	0.01	19.3	2.71	0.1	130

Table 2: Trace elements content in ppm of the clays.

Trace Element (ppm)	Cu	Ni	Mn	Cr	Co	Zn	As	Sr	Sc	Rb
Termitaria Clay	48	94	1240	137	37.9	50	1.7	72.9	14	10.8
Residual Clay	118	276	4850	344	181	62	981	13	6	6.1

From Table 1, the major elements essential for biological development are Mg, Na, Al, Ca, P, Fe (Mujinya *et al.*, 2013), and are selectively enriched in the *Termitaria* clay (TC) as compared to that of the residual clay (RC). Conversely, trace elements; Cd, Zn, Pb, Cr, Co are highly enriched in the residual clay but depleted in the TC, as presented in Table 2.

XRD scan diagram for the RC and TC are shown in Figures 3 and 4.

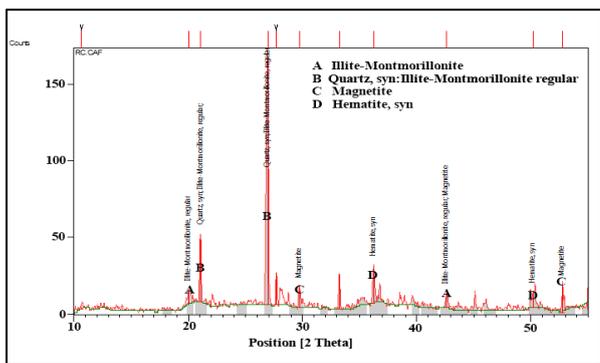


Figure 3: XRD pattern plot of residual clay, showing the various minerals.

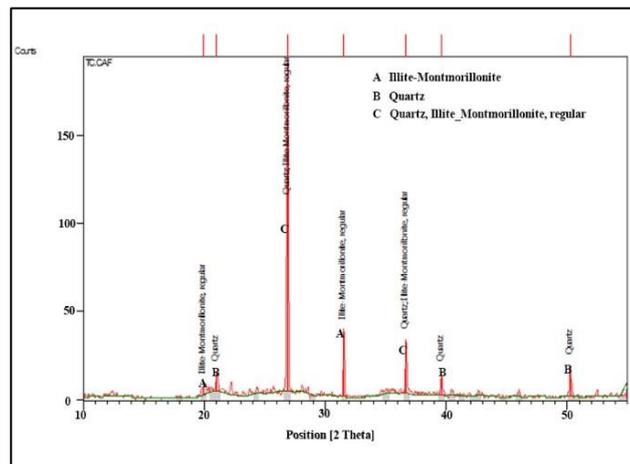


Figure 4: XRD pattern plot of Termitaria clay, showing the various minerals.

In Figure 3, the main minerals phases are quartz (46.27 %), haematite (32.84 %), magnetite (12.69 %), Silicon Oxide (4.48%) and illite-montmorillonite (3.73 %). This composition shows that the adsorbent has a stable mixed sorptive surface of aluminosilicate and high-affinity iron oxide-based surfaces. It is therefore anticipated that the RC material would exhibit high F⁻ adsorption capacity due to the high proportion of iron (hydr)oxide levels (Kaufhold *et al.*, 2010). The high chemical and surface heterogeneity in the RC showed that the adsorbent could exhibit mixed adsorption mechanism. For example, Schoonheydt and Johnston (2006) noted that the structure of the clay plays a key role in determining the charge on the clay surface and type of exchange that can occur with ions in solution.

In Figure 4, analysis of the TC reveals a mineralogical composition phase of illite-montmorillonite (85.67%) and quartz (14.33%); such assemblage has often been described as mix-layered clay by Leroy and Revil (2004). However, there is a high possibility of the presence of other amorphous organic/mineralogical components that are not XRD sensitive. The very chemical nature of adsorbent surface influences the adsorption capacity of a clay mineral, hence a need to delve into the geochemical characteristics of the clays.

3.2 Batch test for fluoride removal from groundwater

The effect of TC and RC dosages on Fluoride removal and pH was compared by varying the mass of both clay samples from 25 g to 200 g as shown in Table 3.

Table 3: Concentration of F⁻ left in solution after treatment of raw water with various doses of Residual Clay and Termitaria Clay at different times.

Time/mins	25g/250mL				50g/250mL				100g/250mL				200g/250mL			
	RC		TC		RC		TC		RC		TC		RC		TC	
	Conc	pH	Conc	pH	Conc	pH	Conc	pH	Conc	pH	Conc	pH	Conc	pH	Conc	pH
0	2.305	7.21	2.288	7.21	2.305	7.21	2.288	7.21	2.305	7.21	2.305	7.21	2.305	7.21	2.305	7.21
10	2.269	7.21	2.088	7.31	2.242	7.17	1.915	7.38	2.205	7.3	2.002	7.36	2.301	7.37	1.278	7.62
20	2.248	7.24	1.964	7.33	2.107	7.22	1.649	7.39	2.088	7.32	1.589	7.38	2.197	7.38	1.019	7.68
30	2.199	7.24	1.781	7.35	1.870	7.25	1.238	7.43	1.785	7.34	1.067	7.39	2.013	7.39	0.905	7.72
40	2.107	7.27	1.534	7.38	1.654	7.26	0.909	7.46	1.487	7.37	0.902	7.43	1.671	7.40	0.753	7.78
50	2.001	7.29	1.079	7.42	1.392	7.27	0.773	7.49	1.002	7.40	0.669	7.48	1.020	7.45	0.588	7.83
60	1.864	7.32	0.956	7.45	0.991	7.33	0.662	7.54	0.883	7.40	0.432	7.65	0.806	7.47	0.363	8.04
70	1.859	7.34	0.921	7.49	0.973	7.39	0.635	7.62	0.87	7.46	0.367	7.67	0.784	7.49	0.296	8.09
80	1.866	7.35	0.903	7.52	0.952	7.37	0.546	7.68	0.869	7.44	0.359	7.71	0.778	7.51	0.294	8.09
90	1.866	7.33	0.886	7.53	0.948	7.38	0.494	7.66	0.866	7.43	0.363	7.76	0.781	7.51	0.297	8.06
100	1.875	7.33	0.882	7.51	0.949	7.35	0.487	7.63	0.866	7.43	0.366	7.75	0.789	7.50	0.303	8.03
120	1.881	7.31	0.885	7.48	0.954	7.34	0.491	7.60	0.872	7.41	0.374	7.71	0.794	7.48	0.319	8.02

From Table 3, the initial fluoride concentration in water (2.305 mg/L) rapidly decreased for each dosage to the acceptable concentration of 1.5 g/mL, except for the 25g RC dosage. Moreover, the adsorbent type and its

dosage have an effect on the time taken for the reaction to cause defluoridation to reach the acceptable limit. The data presented in Table 3 are further illustrated in Figures 5 and 6 for interpretations.

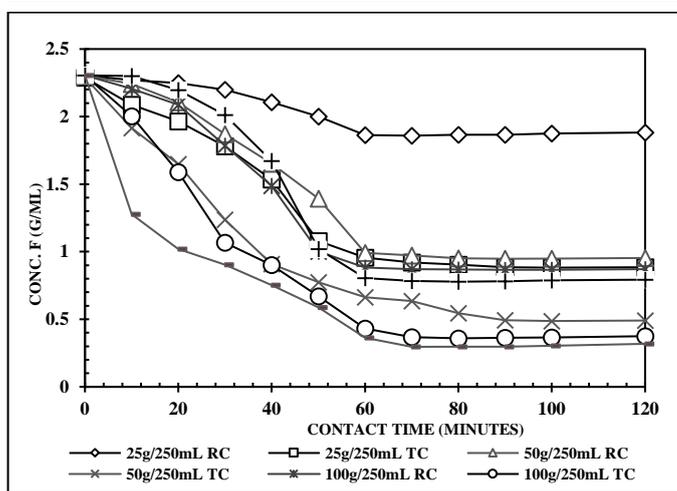


Figure 5: Plot of fluoride concentration left in the groundwater with the time of contacts.

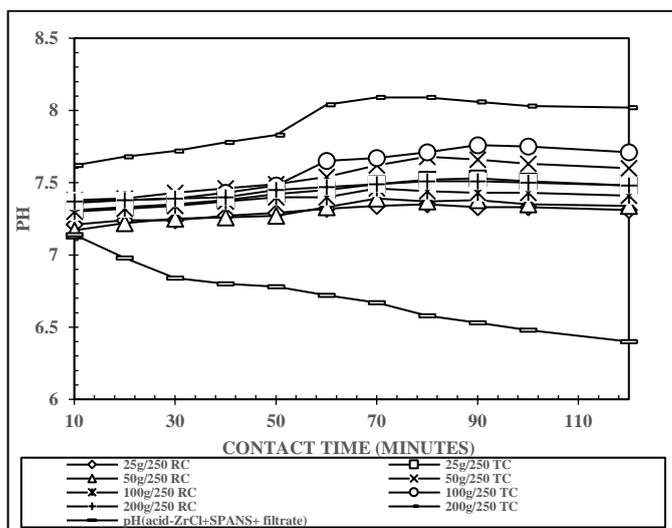


Figure 6: Plot of pH of the raw groundwater after various contact times with the clays.

Observation from Figure 5 shows that, between the reaction time of 10 to 40 minutes, TC dosages of 25, 50, 100 and 200 g had adsorbed fluoride ions that resulted in the reduction of elevated fluoride in the raw water to 1.5 g/mL. Conversely, RC dosages of 50, 100 and 200 g only caused defluoridation of the raw water to the acceptable limit after a reaction time of 40 minutes.

Further from Figure 5, for each adsorbent type and the respective dosage, the defluoridation reaction mechanism reached equilibrium at approximately 60 minutes resulting in the flattening of the plots between 60 to 100 minutes. The above observation might be attributed to the possible agglomeration of the adsorbent caused at a higher adsorbent dose which minimizes its effective surface area for adsorption (Borgohain *et al.*, 2020). However, there is an observed reverse of the reaction mechanism, this is shown by the sudden increase in the concentration of fluoride ions from the 80th minute.

In Figure 6, it can be observed that the reaction mechanism took place at near-neutral to a basic medium. The pH, therefore, plays a critical role in the adsorption mechanism of both adsorbents. All administered adsorbent dosage of 25, 50 and 100 g reacted with the raw water within a steady rise in pH over the first 50 minutes. There is a noticeable sudden jump in pH from 7.45 to 7.65 for the 100 g dose of TC at the 50th to the 60th minute. It is also observed that the pH for the 200 g dose of TC shows some peculiarity; the starting pH is 7.62 to a maximum of 8.09 at 70th minute, at which time where all the pH dosages for both TC and RC begin to steadily drop.

Total Dissolved Solids (TDS) and Electrical Conductivity (EC) were determined to assess the possible dissolution of chemical constituents in the water after the adsorption process to assess the suitability of the water (filtrate) for drinking purposes (Table 4).

Table 4: Water quality parameters.

Parameter/	TDS (mg/l)	Conductivity (mS/cm) 25° C
0	410	684
20	429	715
40	412	692
60	421	700
80	407	677
100	426	709

From Table 4, results show that there was a little dissolution of chemical constituents into the water as the contact time of the clay and water increased. These measurements were found to be generally within the WHO standard guideline for drinking water.

4. DISCUSSION

The effect of different variables (adsorbent dosage, pH and contact time) on the adsorption capacity of both *Termitaria clay* and residual clay proves a better potential application for *Termitaria clay* than the residual clay. The different dosages applied, especially for 50 g, 100 g and 200 g have proved the robustness of the *Termitaria clay* to reduce fluoride ions in raw groundwater. Observation in Figure 5 suggests that the dosage influences the time taken for the reaction to bring about the desired results and the reaching of equilibrium.

It was found that the removal of fluoride ions for *Termitaria clay* dosage of 200 g in 250 mL of the raw contaminated water is optimum at 70 minutes of contact time and the initial Fluoride concentration of 2.305 g/mL was brought lower than the WHO acceptable limit (1.5 g/mL) for fluoride in drinking water. At this dosage and time, equilibrium was approximately reached as the adsorbed Fluoride ions slowly desorbed back into solution.

The chemical nature of the adsorbing surface influences the adsorption capacity of the clay mineral. Thus, the surface chemical characteristics of the adsorbents can be significantly altered by the pH of an adsorption system (Jagtap *et al.*, 2009; Maiti *et al.*, 2011). On this basis, it is observed that the pH readings for the reaction mechanism played a critical role. For example, in Figure 6, the pH readings suggest that basicity of the reaction system favoured the reaction mechanism for optimum results, especially in the case of *Termitaria clay*, where the absorption capacity shot up significantly with a corresponding increase in basicity from 7.83 to 8.04. Further, observations on the uptake of fluoride ions at their optimum pH values indicate that the processes are quite rapid.

On average, more than 60% of the adsorption occurs within the first 60 minutes of the contact of the initial solution with raw clays sorbents (Figure 5). Studies by Hamdi and Srasra (2007) produced similar results. On the other hand, some studies on defluoridation have only achieved optimum absorption at pH 4 (Gogoi and Baruah 2008) and this does not put the filtrate in the condition for any form of domestic use.

The enrichment of Na, Mg, Al and Ca, and the general depletion of trace metals in the *Termitaria clay*, and the converse occurring in the residual clay, explains the high absorptivity of fluoride by the *Termitaria clay*. Generally, fluoride, being a halogen, exist as a diatomic molecule with high ionization energy and high electronegativity and so reacts vigorously with alkali and alkali earth metals such as Na, Mg and Ca. According to Okazaki *et al.* (1985) and Kebede *et al.* (2016), high phosphate content inhibits the uptake of fluoride; however, this did not happen in this research, although phosphate content is higher in the TC than the RC (Table 1). This, therefore, confirms the stronger influence of the metals, particularly Ca over the reactivity of fluoride.

Also, the high amount of Ca in the *Termitaria clay* probably led to the precipitation of fluoride as insoluble calcium fluoride and raised the pH value of the water by the process: $\text{Ca}(\text{OH})_2 + 2\text{F}^- \rightarrow \text{CaF}_2 + 2\text{OH}^-$. It is noted that Mg^{2+} , Ca^{2+} , Na^+ and K^+ are the exchangeable cations present in most clays of a mixed-layer type such as illite-montmorillonite (Vinati *et al.*, 2015); the metals, therefore, play a vital role in the sorption of the fluoride onto the *Termitaria clay* surfaces. The low TDS and EC are due to the high adsorptive property of clays, which made TDS and EC meet the WHO standard guideline for drinking water.

However, from analysis of the XRD, the percentage abundance of the possible minerals that may be suspected to contribute to fluoride removal is illite-montmorillonite forming only 3.73% for Residual clay. By comparing the Residual clay to *Termitaria clay*, the abundance of the illite-montmorillonite mineral phase in the latter was found to be as high as 85.67% is then suspected to be the fluoride removal agent. It is therefore evident to say the illite-montmorillonite is the dominant mineral phase responsible for fluoride removal when both *Termitaria clay* and residual

clay are used as absorbent, with some amount though not so significant from hematite and magnetite in the case of residual clay.

5. CONCLUSION

The present study highlights the significant potential of raw *Termitaria* clay for Fluoride removal from groundwater over the residual clay. For the given initial fluoride concentration, the removal efficiency of the adsorbents; residual and *Termitaria* clay, increased with increasing adsorbent dose and contact time. However, the *Termitaria* clay adsorbent batch-test showed a much rapid defluoridation in the first 40 mins and equilibrium was reached at 60 minutes for all dose amounts over the residual clay. Optimum defluoridation of the raw groundwater with elevated fluoride to a value lower than the WHO standard of 1.5mg/l occurred with the *Termitaria* clay dose of 0.8kg/L within the time interval of 50 to 70 minutes in a pH range of 7.83 to 8.04.

Geochemical and mineralogical characterization suggests that *Termitaria* clay presents both a unique assemblage of minerals and elements which play a critical role in the mechanism of fluoride adsorption. The experimental data suggest that *Termitaria* clay could be efficient, inexpensive, eco-friendly and convenient adsorbents for remediation of fluoride from water over the residual clay.

The water quality parameters: TDS and conductivity of the *Termitaria* clay batch-test filtrate showed that the filtrate (water) was generally within the WHO standard guideline for drinking water, thereby making the water safe for domestic use. Therefore, the reported adsorbent shows a potentially low cost and toxicity with a rapid and exceptionally high adsorption performance that can make it an attractive material for remediation of fluoride from water at the local community level.

ACKNOWLEDGEMENTS

The authors acknowledge the Senior Members of the Department of Geological Engineering (KNUST), Department of Earth and Environmental Science (UDS) and the technicians of the Water Research Institute, Water Quality Laboratory Tamale for their immense assistance during the research.

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