

## Defluoridation of Drinking water by Using Modified and Unmodified Bentonite from Minjingu Mining Site in Tanzania

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**Abstract:** This study aims to assess the fluoride sorption by the use of Bentonite categorized into four groups that is Bentonite (B), activated Bentonite (800°C) (BAA), Bentonite impregnated with iron (BI) and Bentonite impregnated with aluminium (BA). Characterization was done by XRF before and after impregnation, showed that highest percentage composition of SiO<sub>2</sub>, CaO, P<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. XRD revealed higher composition of illite, calcite, quartz and albite. Batch experiments were conducted by using homogeneous mixture of water having 16 mg/L of fluoride measured by fluoride ion selective electrode. All adsorbents were found to be effective on removing fluoride ions from fluoride bearing water with removal efficiency of 83.73% for BAA, 92.70% for BI and 94.98% for BA except Bentonite (B) alone which showed negative result. The optimum pH were found to be 8, 3, 7 and the optimum doses of 9, 8 and 7 g, optimum contact time of 70, 60 and 50 minutes respectively with the batch volume of 50 mL. The adsorption process obeyed Langmuir model for BAA and BI, for BA agreed with Langmuir and Freundlich models. For the kinetics perspective, the fluoride adsorptive reaction followed the pseudo-second order model. Therefore, the activated and impregnated Bentonite is the alternative and cheap adsorbents for water defluoridation.

**Keyword:** Bentonite, Characterization, Fluoride, Impregnation, Sorption.

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Date of Submission: 24-08-2017

Date of acceptance: 05-09-2017

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### I. Introduction

Chemical contamination generally occurs during the water cycle as the infiltrate through the surrounding ground and picks natural contaminants. One of the most well documented naturally occurring contaminants is fluoride which affects drinking water supplies in a number of countries [1]. Fluoride is the most electronegative and reactive element in the periodic table, occurring primarily as the fluoride ion (F<sup>-</sup>). Fluoride is naturally present in all waters, air and food. It enters the food via drinking water [2].

At concentrations of approximately 1 mg/L, fluoride in drinking water can provide significant protection against dental decay and aids in bone development [3]. While at above 1.5 mg/L fluoride is dangerous to human health leading to dental and skeletal fluorosis [4, 5]. Fluorosis is endemic in at least 25 countries around the world, many people are currently afflicted with the diseases [6], but conservative estimates are the tens of millions of people [6]. There is no treatment for fluorosis, which leaves prevention as the only means of controlling the disease worldwide. In Tanzania, people obtain water from various sources including rain, surface waters (lakes, rivers and ponds) and groundwater (boreholes, shallow well, and springs) [7]. Ground water is the main source of water in Tanzanian rural areas especially in Hai District. It is well known that groundwater contains dissolved gases and minerals, including fluoride salts [8].

It is reported in the literature that fluoride concentrations in groundwater from some parts of Tanzania is 17 mg/L (Shinyanga), 21.3 mg/L (Singida), 29 mg/L (Kilimanjaro), 32 mg/L (Arusha) and 46 mg/L (Manyara) [9], while in Hai District it was varied from 8-25 mg/L [7], even though fluoride concentration in Hai District is small compared to the other Districts, but some of the villages in this District have higher fluoride concentration leading to the fluoride related health problems in number of communities in this District. Other reason for selecting this district for the study was the District is nearby Ngurdoto Defluoridation Research Centre (NDRC) in Arusha and made the process of taking water samples easier for analysis. A number of defluoridation methods have been tested at (NDRC) in Arusha and other places. The well-studied defluoridation methods using some of the adsorbent materials include Nalgondatechnology using lime and alum, activated clay, activated alumina and bone char. Each of these defluoridation techniques have one or more weaknesses including the need for high chemical doses, large amounts of sludge, local unavailability in Tanzania, slow and low fluoride removal [9]. Bentonite is adsorbent aluminum phyllosilicate clay consisting mostly of montmorillonite. The bentonite used in this study was calcium bentonite (green) identified by geologists [10].

This study focused on the removal of fluoride by using bentonite, a clay mineral in modified and unmodified form, because this material is inexpensive and available plenty at site so it can be used by both rural and urban communities.

## **II. Materials and Methods**

### **2.1 Chemicals**

Analytical grade reagents NaF, NaOH, HCl, NaCl, CH<sub>3</sub>COOH (glacial), fluoride standard solution, Cyclo hexane diaminetetraacetic acid (CDTA), FeCl<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, tri sodium citrate and distilled water was used in all experiments.

### **2.2 Water sampling**

Water samples were collected from water sources of nine villages that are eight wells and one spring distributed into different wards at Hai District in Kilimanjaro Region of Tanzania by using high-density polyethylene (HDPE) bottles. Before collecting the water samples, the HDPE bottles were washed by distilled water for three times and then by the water to be sampled, then randomly collected samples were mixed together to obtain homogeneous mixture for each village. Finally packed into one liter HDPE and transported to Ngurdoto Defluoridation Research Centre (NDRC) for analysis.

### **2.3 Adsorbent sampling and preparation**

Bentonite was collected at Minjingu mining sites found in Babati District in Manyara Region, Tanzania. It was collected from a large roundish soil dumped as waste, splitted by the use of hammer into small sized particle then packed into plastic bags and transported to Geological Survey of Tanzania (GST) laboratory, grinded by the use of grinder mills machines (MBX5) and sieved into small sized particle by the use of sieve machines (MTM Series) and packed into plastic seal poly bags ready for further analysis.

### **2.4 Categorization of Bentonite**

Bentonite was categorized into different adsorbents, Bentonite alone (B), Bentonite impregnated with iron (BI) in different ratios, Bentonite impregnated with aluminium (BA) in different ratios and thermally activated Bentonite at 800<sup>0</sup>C (BAA) by using muffle furnace (Nabertherm, Germany) in 2 h.

### **2.5 Characterization of Bentonite.**

The elemental composition of adsorbents B, BI and BA were carried out using XRF Spectrometer (MINI PAL 4) connected to the desktop computer (HP LI 710). The samples were thoroughly grinded into fine powder, then 4.9 g of B were mixed with 0.1 g of iron and aluminum separately to make 5 g for the BI and BA and 5 g of an impregnated B were placed into small plastic cup covered with plastic at the bottom, finally the cup were introduced into XRF spectrometer for the analysis and determined the elemental composition in percentage for all adsorbents.

X-Ray Diffractometric (XRD) analysis for the phase composition present in bentonite was conducted by using XRD (D2-PHASER, BRUKER, GERMANY) directly connected to the screen. In a typical procedure, bentonite were grinded into powder and small sized particle, packed into an aluminium holder, which was then placed in goniometer and bombarded with X-rays generated from cobalt tubes. The XRD was operated at 32 kV, 33 mA and 2 $\theta$  range from 10<sup>o</sup>-70<sup>o</sup>, the results were displayed on the screen.

### **2.6 Preparation of TISAB II**

The total ionic strength adjustment buffer (TISAB II) was prepared by taking 57 ml of glacial acetic acid, 58 g of sodium chloride, 4 g of Cyclo hexane Diamine Tetraacetic Acid (CDTA), and 0.5 g of sodium citrate were added to 500 mL distilled water and allowed to dissolve, then the pH was adjusted to 5.3 by using well prepared 1M NaOH and 1M HCl transferred into one liter volumetric flask filled with distilled water to reach the mark.

### **2.7 Water analysis**

Fluoride ions present in water samples was measured by a potentiometer connected by ion selective electrode (Orion 4 Star, India) and display the number directly on the screen. Before measuring fluoride concentration in water samples each time calibration was done in order to obtain required slope and comparing it with theoretical values. Equal volumes (5mL) of water sample and TISAB II mixed and placed into 50 mL plastic beaker and the mixture was stirred by a speed of 360 rpm for one minute by using magnetic stirrer. In all experiments the same amount of sample was used and the experiments were done in triplicate.

### 2.8 Preliminary test

Preliminary test was carried at the beginning of the experiments to check the adsorption performance of all the adsorbents. 50 mL of the solution having initial fluoride concentration from the source was transferred into small plastic bottle, 5 g of B, BAA heated from 100°C-900°C, and BI (4:1g) adsorbent was added independently to the bottles containing water, then magnetic pellet was placed into bottle for stirring and rotated at a speed of 360 rpm. A filtrate of 5 mL were drawn at different interval of time (0.5, 1, 2, 3, 4, 5, 8, 12 and 24 h) and mixed with 5 ml of TISAB II, and then fluoride concentration was determined. After preliminary test, impregnation test were conducted for both BI and BA, the ratios tested were 4:1g, 6:1 g and 8.9: 0.1g.

### 2.9 Batch adsorption experiments

All batch experiments were conducted by using 50 mL of aqueous solution containing fluoride ion to which a weighed amount of BAA, BI, and BA were added into three small plastic bottles separately. The mixtures were shaken by the use of stirrer at room temperature and the speed of 360 rpm. A sample were periodically taken out from each bottle and filtered by the use of Whatman filter paper number 1. Fluoride ion concentrations in water were analyzed using fluoride ion selective electrode.

### 3. Optimization of different parameters

The effects of various parameters on percentage of adsorption were observed by varying contact time, initial concentration, pH of solution and adsorbent dosage. The percentage adsorption of fluoride (%) at any instant of time and deflouridation capacity was determined by equations 1 and 2.

$$\% \text{ Adsorption} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$\text{Deflouridation capacities, } q_e \left( \frac{\text{mg}}{\text{g}} \text{ F}^- \right) = \frac{(C_0 - C_t)}{m} \times v \quad (2)$$

Where,  $C_0$  = Initial F<sup>-</sup> concentration,  $C_t$  = Residual fluoride concentration at time t, m = Mass of adsorbent and V = Volume of the solution used in the batch.

## III. Results and discussion

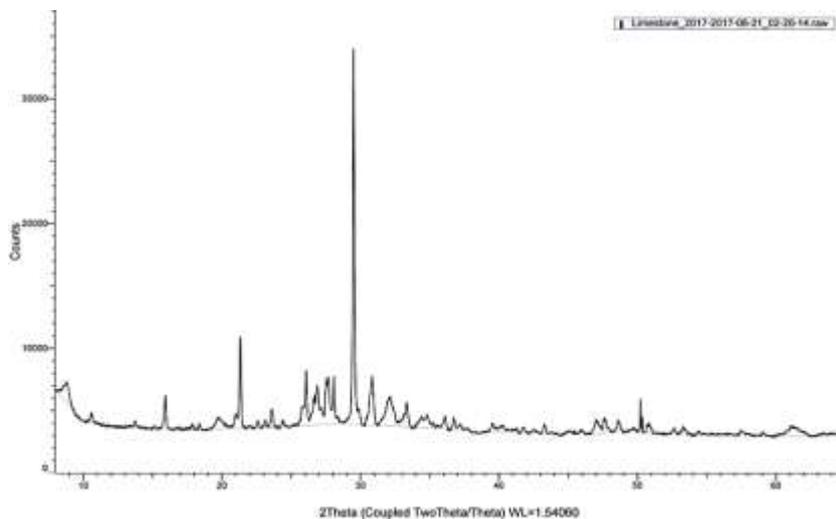
### 3.1 Characterization of the adsorbents

The pattern of adsorption of fluoride by the bentonite adsorbent is attributed due to the presence of silicon, calcium, phosphorus, iron, and aluminium in the form of oxide which is the good adsorbent [11]. Before impregnation bentonite have higher percentage of 37.4 % SiO<sub>2</sub> followed by 20.3% CaO, 9.2% P<sub>2</sub>O<sub>5</sub>, 8.6% Fe<sub>2</sub>O<sub>3</sub>, 8.3% Al<sub>2</sub>O<sub>3</sub>, 0.7% TiO<sub>2</sub>, 0.4% SO<sub>3</sub>, 0.3% SrO and 0.2% MnO. After impregnation, bentonite mixed with iron showed high composition of 49.65% Fe<sub>2</sub>O<sub>3</sub> and lower composition of 19.9 % SiO<sub>2</sub>, 10.5% CaO, and 4.1% Al<sub>2</sub>O<sub>3</sub> (Table 1). Impregnation with aluminium showed high composition of 17% Al<sub>2</sub>O<sub>3</sub>, 41.4% CaO, 15.1 % Fe<sub>2</sub>O<sub>3</sub> and 5.1% K<sub>2</sub>O and emerging of some new elemental oxide like SO<sub>3</sub>, SrO and MnO [12]. All of the above elemental oxide which showed higher percentage of its composition is the good adsorbents. Fluoride was not detected in XRF Spectrometer (Mini Pal 4) because its atomic weight is below 11.

**Table1:** XRF analysis results showing elemental composition in bentonite before and after impregnation.

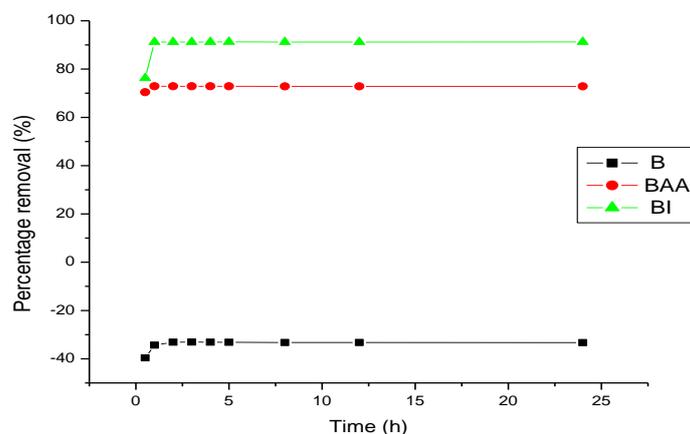
| Before impregnation            |                    | After impregnation             |                    |       |
|--------------------------------|--------------------|--------------------------------|--------------------|-------|
| Composition                    | Adsorbent type (%) | Composition                    | Adsorbent type (%) |       |
|                                | B                  |                                | BI                 | BA    |
| SiO <sub>2</sub>               | 37.4               | Fe <sub>2</sub> O <sub>3</sub> | 38.30              | 15.10 |
| CaO                            | 20.3               | SiO <sub>2</sub>               | 15.00              | 23.00 |
| P <sub>2</sub> O <sub>5</sub>  | 9.22               | CaO                            | 10.50              | 41.4  |
| Fe <sub>2</sub> O <sub>3</sub> | 8.62               | Al <sub>2</sub> O <sub>3</sub> | 4.10               | 17.00 |
| Al <sub>2</sub> O <sub>3</sub> | 8.30               | K <sub>2</sub> O               | 4.11               | 5.12  |
| MgO                            | 5.52               | P <sub>2</sub> O <sub>5</sub>  | 2.80               | 5.20  |
| K <sub>2</sub> O               | 4.01               | TiO <sub>2</sub>               | 0.94               | 1.55  |
| Na <sub>2</sub> O              | 2.28               | CuO                            | 0.67               | 0.819 |
| CuO                            | 1.17               | SO <sub>3</sub>                | 0.67               | 0.83  |
| TiO <sub>2</sub>               | 0.74               | SrO                            | 0.31               | 0.96  |
| SO <sub>3</sub>                | 0.44               | MnO                            | 0.25               | 0.32  |
| SrO                            | 0.28               | V <sub>2</sub> O <sub>5</sub>  | 0.055              | 0.06  |
| MnO                            | 0.22               | ZnO                            | 0.046              | 0.05  |
|                                |                    | ZrO <sub>2</sub>               | 0.043              | 0.06  |
|                                |                    | NiO                            | 0.02               | 0.02  |
|                                |                    | BaO                            | ND                 | 0.60  |
|                                |                    | Cl                             | ND                 | ND    |

The X-Ray Diffractograms of bentonite revealed poor crystalline minerals due to overlapping of peaks in diffractograms and their percentage composition. The diffractogram of bentonite revealed, presence of illite ( $(K,H_3O)(Al,Mg,Fe)_2(SiAl)_4O_{10}[(OH)_2(H_2O)]$ ), calcite ( $CaCO_3$ ) and albite ( $NaAlSi_3O_8$ ) in higher composition and pyrite ( $FeS$ ), and chlorite in lower composition [11]. The XRD diffractogram of Bentonite was shown in Fig .1.



**Figure 1:** X-Ray Diffractogram of bentonite alone.

Preliminary test results showed in Fig. 2, revealed that the Bentonite alone as an adsorbent tend to add fluoride in water by -33.10% and raise up within two hour, because of fluoroapatite ( $Ca_{10}PO_4)_6F_2$ ) present on it when contact with water release fluoride in water and raised it, then from there up to 24hour remain constant after attaining an equilibrium [11]. The activated bentonite removed fluoride by 72.90% which was good because heating increased number of pores for fluoride ions binding on it and the bentonite coalesced with iron in the ratio of 4:1g within the time of 2 h showed good response for fluoride removal by 91.25% and remain constant because the amount of iron added increased the naturally occurring iron which is good adsorbent. Therefore, out of three adsorbents two were selected (BAA and BI) for further experiment and BA was added as another adsorbent.



**Figure 2:** Preliminary test of bentonite (bentonite alone, bentonite activated at 800°C and bentonite mixed with iron (dose=5 g, speed of stirring=360 mg/L, initial fluoride concentration=16 mg/L).

### 3.2 Optimization of factors affecting fluoride adsorption

The parameters such as contact time, initial fluoride concentration, pH and adsorbent dosage which affect the removal of fluoride ions were optimized by varying each parameter at a time keeping the remaining parameters constant. The results were presented below:

### 3.2.1 Effect of contact time

To describe the effect of contact time, the batch adsorption procedure were used and residual fluoride concentrations were measured for different contact time of adsorption, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 minutes based on preliminary test in order to investigate the effect of contact time within 2 h. The effect of contact time on fluoride adsorption efficiency was shown in Fig.3. The studied three adsorbents showed good percentage of adsorption which is above 50 % but the better percentage of adsorption (94.30 %) has been shown by bentonite mixed with aluminium with the shortest time of 50 minutes and above this time of adsorption remained constant followed by bentonite mixed with iron that had 91.80 % of adsorption with the time of 60 minutes as a shortest time then remain constant up to 2 hrs, lastly activated bentonite showed 74.15% of adsorption within 70 minutes and again remain constant for the 2 hrs. From the data above it seems each adsorbent behave differently on adsorption depending on number of active sites for the fluoride ions binding on the surface of the adsorbent and its composition before attaining an equilibrium, the number of active sites in bentonite mixed with aluminium was highly occupied with in a shortest time followed by bentonite mixed with iron and activated bentonite.

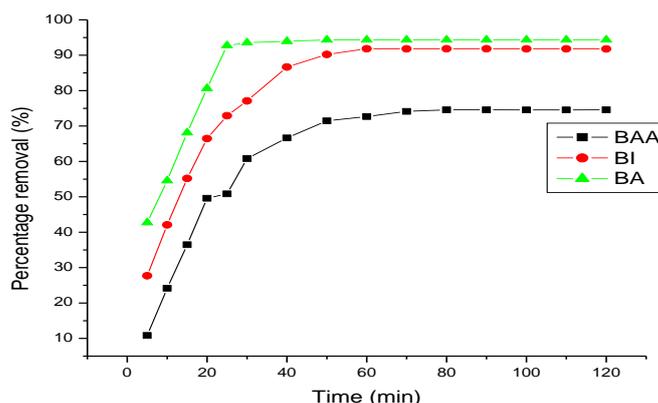


Figure 3: Percentage removal of fluoride by using three adsorbents versus time (initial fluoride ion concentration in water=16 mg/L, dose=9 g, pH of water=7.6, Speed of stirring =360 rpm)

### 3.2.2 Effect of initial fluoride concentration

The effect of initial fluoride concentrations on the adsorption of fluoride was studied by varying the initial fluoride concentrations of 8, 12, 16, 20, 24 mg/L and keeping the other parameters constant. As shown in Fig.4, at lower fluoride concentration maximum adsorption occurred for all adsorbents. This is due to the intensive utilization of all active sites at the surface of adsorbent, and as initial concentration increased it seems percentage of adsorption tend to decrease gradually this is because all active sites have already occupied and for the incoming fluoride ions from water was repelled by repulsive forces [13]. Therefore, it is very important to determine initial fluoride concentration at the beginning of any adsorption experiment because parameter like pH, contact time and doses depend much on initial concentration of fluoride in water.

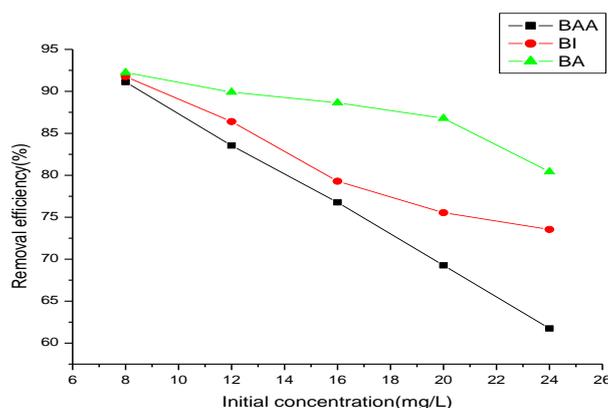
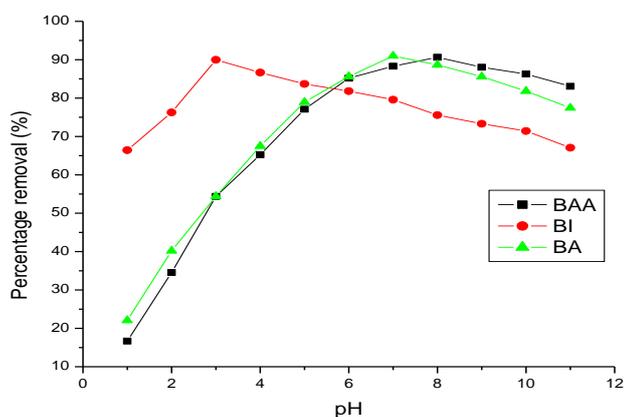


Figure 4: Removal efficiency (%) versus initial fluoride concentration (mg/L) for BAA, BI and BA (contact time=70, 60, 50 minutes respectively for BAA, BI and BA, pH of water=7.6, speed of stirring=360 rpm)

### 3.2.3 Effect of pH

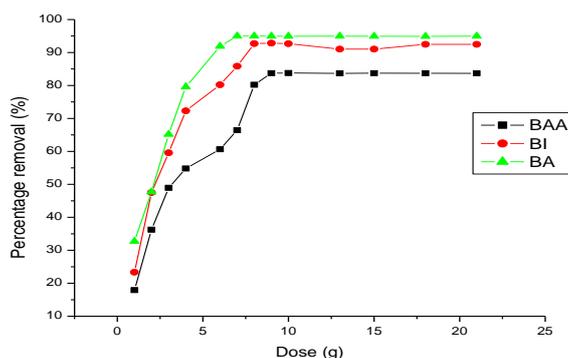
One of the important parameter for adsorption of fluoride is pH which can be acidic, neutral and basic. Fig.5 showed the trend for fluoride removal under different condition of pH. Activatedbentoniteshowed maximum adsorption of fluoride occurred slightly under basic condition with the percentage adsorption of 90.63%.Under this condition, the oxides of iron, aluminium and silicon provide more positive charge for the anion of fluoride to bind on it hence, maximum adsorption appeared.When the pH increased to more basic condition the percentage of adsorption decreased slowly because no more positive charge was produced for binding with fluoride ions [13]. For the bentonite mixed with iron their percentage of adsorption was 89.80% under highly acidic medium because on additionof iron to bentonite raised acidic condition and provide more positive charge for the fluoride ions to bind on it. The bentonite impregnated with aluminium revealed maximum adsorption of fluoride onto its surface compared to the above adsorbent with 90.98% under neutral condition because aluminium which is amphoteric in nature provided this situation to bentonite and raised positivecharge of aluminium ion for fluoride binding.



**Figure 5:** Percentage removal (%) versus pH for the adsorbents BAA, BI and BA (Initial Fluoride ion concentration in water=16 mg/L, pH of water=7.6, contact time=70, 60, 50 minutes respectively for BAA, BI and BA, speed of stirring =360 rpm).

### 3.2.4 Effect of adsorbent dosage

It was clearly shown in Fig. 6 for all three adsorbents as the adsorbent dose increases also percentage for the removal of fluoride ions increases until each adsorbent reaches equilibrium and remained constant up to 21 g [14]. This means that initially as dose increases, availability of fluoride ions binding sites also increases until each adsorbent reaches their saturation in different doses. Bentonite impregnated with aluminium showed maximum percentage for the removal of fluoride that is 94.98% with the dose of 9 g, this is because the addition of aluminium raised its composition and increased active sites for the fluoride binding of fluoride ions, followed by bentonite impregnated by iron with 92.70% of fluoride removal with a dose of 8 g, the iron added increases the number of active sites for the fluoride binding but their extent cannot be compared to aluminium and lastly activated bentonite with a dose of 7 g, 83.73% of fluoride removed, this means that activation increased number of vacant sites for the fluoride ion to bind on it and gave good percentage of adsorption.



**Figure 6:** Percentage removal (%) versus dose(s) for the adsorbents BAA, BI and BA (Initial fluoride ion concentration in water=16 mg/L, pH=8, 3 and 7 respectively for BAA, BI and BA, speed of stirring =360 rpm)

### 3.3 Application to real water samples

The efficiency of BAA, BI and BA adsorbents on removing fluoride was tested on real water samples under optimized conditions. The average concentrations of fluoride in all the water samples collected in nine water sources at Hai District was observed to be 16 mg/L which is above required level by WHO and local standard's, this concentration was reduced to 0.80 mg/L after treatment with bentonite categorized into three groups mentioned earlier, out of three adsorbent, BI and BA was able to reduce fluoride concentration below 1.5 mg/L.

### 3.4 Adsorption isotherms

The process of adsorption is usually studied through graphs known as adsorption isotherms. It is the graph between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature [15]. Adsorption isotherms were drawn by studying the adsorption behaviors of BAA, BI, and BA with the prepared concentrations of 5, 10, 15, 20 and 25 mg/L for the sodium fluoride, mixed with the optimized doses of 9, 8 and 7 g respectively. Langmuir isotherm is the model explaining the estimation of maximum adsorption capacity corresponding to complete monolayer coverage [16]. The linear Langmuir equation is given in Equation 3.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_a q_m C_e} \quad (3)$$

Where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is the amount of ion adsorbed (mg/g),  $q_m$  is  $q_e$  for a complete monolayer (mg/g),  $K_a$  is adsorption equilibrium constant. The plot of reciprocal of specific sorption ( $1/q_e$ ) against the reciprocal of the equilibrium concentration ( $1/C_e$ ) for F<sup>-</sup> ions was shown in Fig.7 a, b and c.

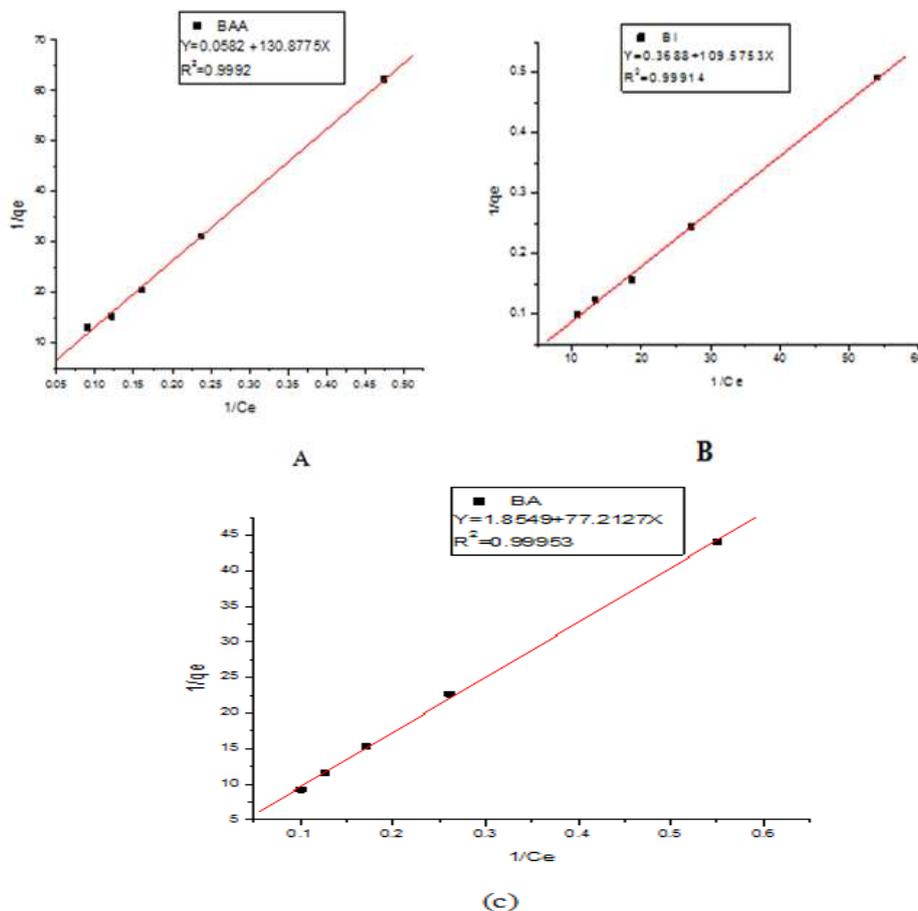


Figure 7: Linear Langmuir adsorption isotherm for (a) BAA (b) BI (c) BA (optimized dose=9, 8 and 7 g, optimized contact time =70,60 and 50 minutes, optimized pH= 8, 3 and 7 respectively)

Freundlich isotherm assumes unlimited sorption sites which correlated with better heterogeneous surface of the adsorbent media. The Freundlich equation represented as linearized form in Equation 4 [17].

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (4)$$

Where  $q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent, mg/g,  $C_e$  is the equilibrium adsorbate concentration in solution in mg/L,  $k_f$  and  $1/n$  are the Freundlich constants. From the experimental data, the Freundlich parameters along with correlation coefficients were obtained by plotting  $\log q_e$  vs  $\log C_e$  shown in Fig. 8 a, b, and c. The constant value of adsorption isotherm obtained from the slope and intercept of the plot of each isotherm [15].

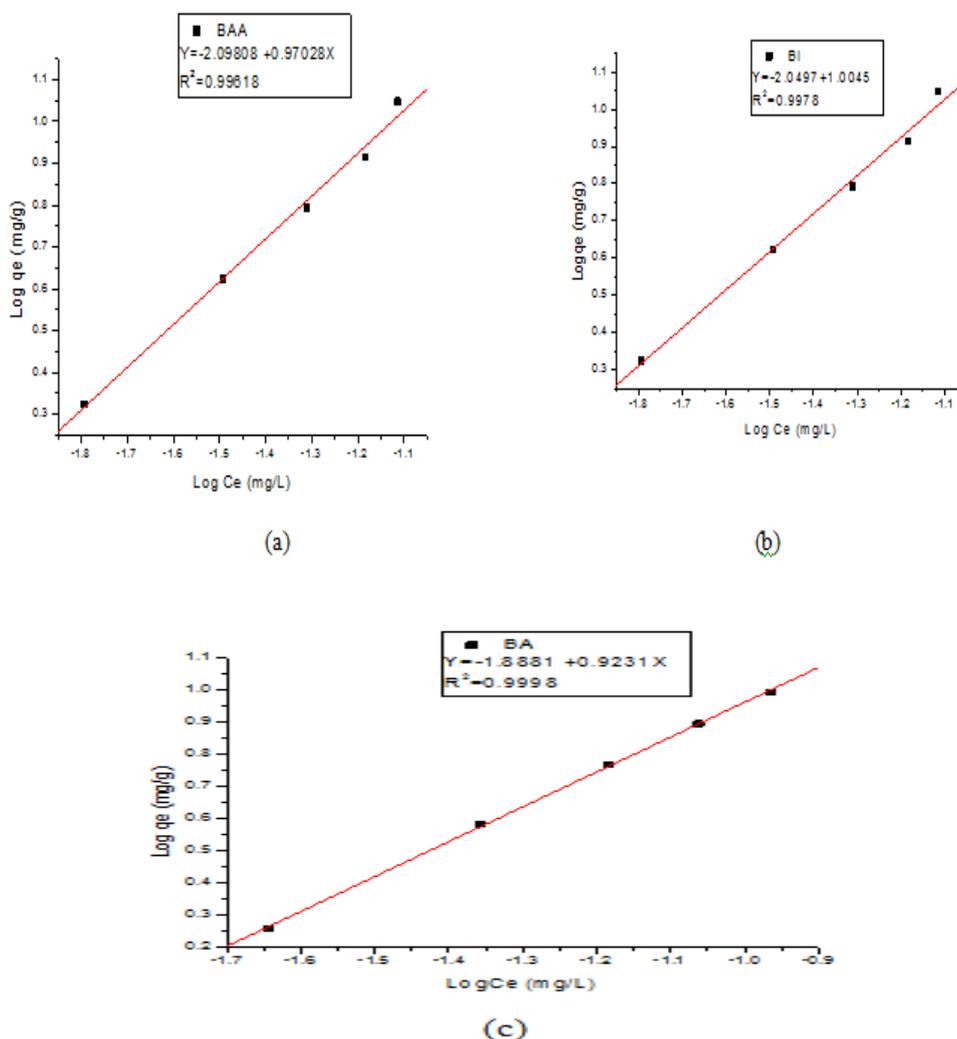


Figure 8: Freundlich adsorption isotherms for (a) BAA (b) BI (c) BA (optimized dose=9, 8 and 7 g, optimized contact time =70,60 and 50 minutes, optimized pH= 8,3 and 7 respectively)

Table 2(a): Langmuir isotherm parameters

| Adsorbent | Equation                         | $q_m$ (mg/g) | $K_a$ (L/mg)         | $R^2$  |
|-----------|----------------------------------|--------------|----------------------|--------|
| BAA       | $C_e/q_e = 130.8775C_e + 0.0582$ | 0.00764      | $2.2490 \times 10^3$ | 0.9992 |
| BI        | $C_e/q_e = 109.5753C_e + 0.3688$ | 0.0091       | $2.9797 \times 10^2$ | 0.9991 |
| BA        | $C_e/q_e = 77.2127C_e + 1.8549$  | 0.0130       | $4.1470 \times 10^1$ | 0.9995 |

Table 2(b): Freundlich isotherm parameters

| Adsorbent | Equation                        | $k_f$  | $1/n$  | $R^2$  |
|-----------|---------------------------------|--------|--------|--------|
| BAA       | $\log q_e = 0.9703C_e - 2.0981$ | 0.0038 | 0.9703 | 0.9962 |
| BI        | $\log q_e = 1.0045C_e - 2.0497$ | 0.0037 | 1.0045 | 0.9978 |
| BA        | $\log q_e = 0.9231C_e - 1.8887$ | 0.0051 | 0.9231 | 0.9998 |

Table 2 (a) and (b) showed that correlation coefficient of both Freundlich and Langmuir model are greater than 0.8 means that all points its fitted to the straight line or close to it but the good fitting was shown by BA for Freundlich and for the Langmuir were BAA, BI and BA.

### 3.5 Adsorption kinetics

The kinetic data are obtained from the sorption experiment and fitted into pseudo-second order, to show the mechanisms of adsorption and potential rate controlling steps [18]. The kinetics of the adsorption of fluoride has been conducted for initial fluoride concentration of 16, 20, and 24 mg/L prepared by the use of sodium fluoride, matched with the corresponding adsorbent dose of 8, 10 and 12 g respectively.

#### 3.5.1 Pseudo first order

The pseudo-first order rate model is used as a rate equation for assigning the adsorption of an adsorbate onto adsorbent.  $q_e$  and  $k_1$  values obtained from the graph of  $\log(q_e - q_t)$  versus  $t$  if it is straight line and it is represented by Equation (5) [19].

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (5)$$

The plot of  $\log(q_e - q_t)$  versus  $t$  were shown in Fig. 9a, b and c.

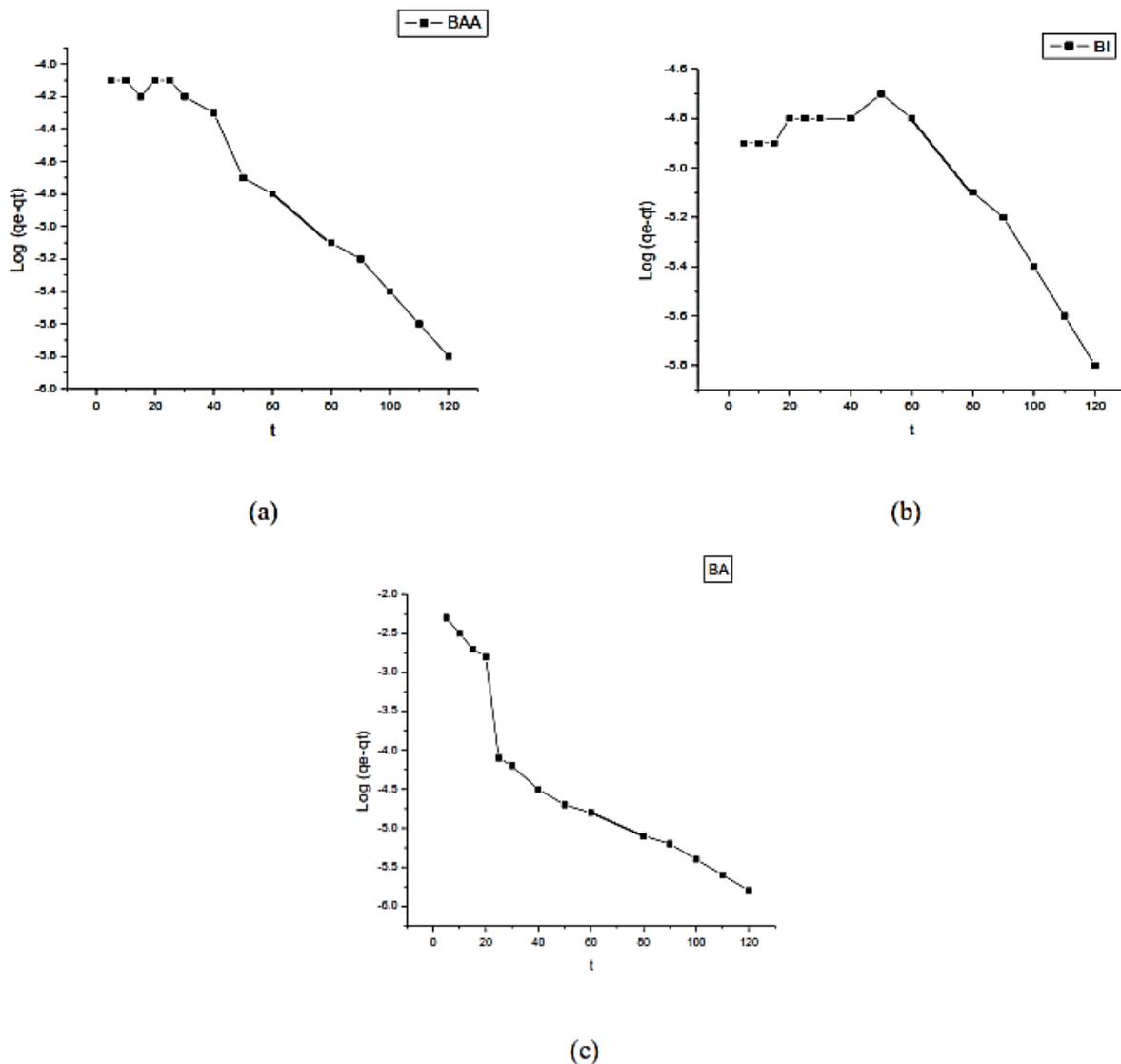


Figure 9: Pseudo first order plot for the removal of fluoride by (a) BAA (b) BA and (c) BI (dose=8,10, and 12g, initial concentration= 16, 20 and 24 mg/L, optimized contact time=70,60 and 50 minutes, optimized pH= 8,3 and 7 respectively)

### 3.5.2 Pseudo Second Order

Pseudo-second order is the kinetic expression for describing the adsorption of fluoride ions onto the adsorbent also is useful for determining  $q_e$  values and  $k_2$  from the graph of  $t/q_t$  versus  $t$ , it is represented by equation (6)[19].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The plot of  $\frac{t}{q_t}$  versus  $t$  is shown in Fig. 10a, b and c.

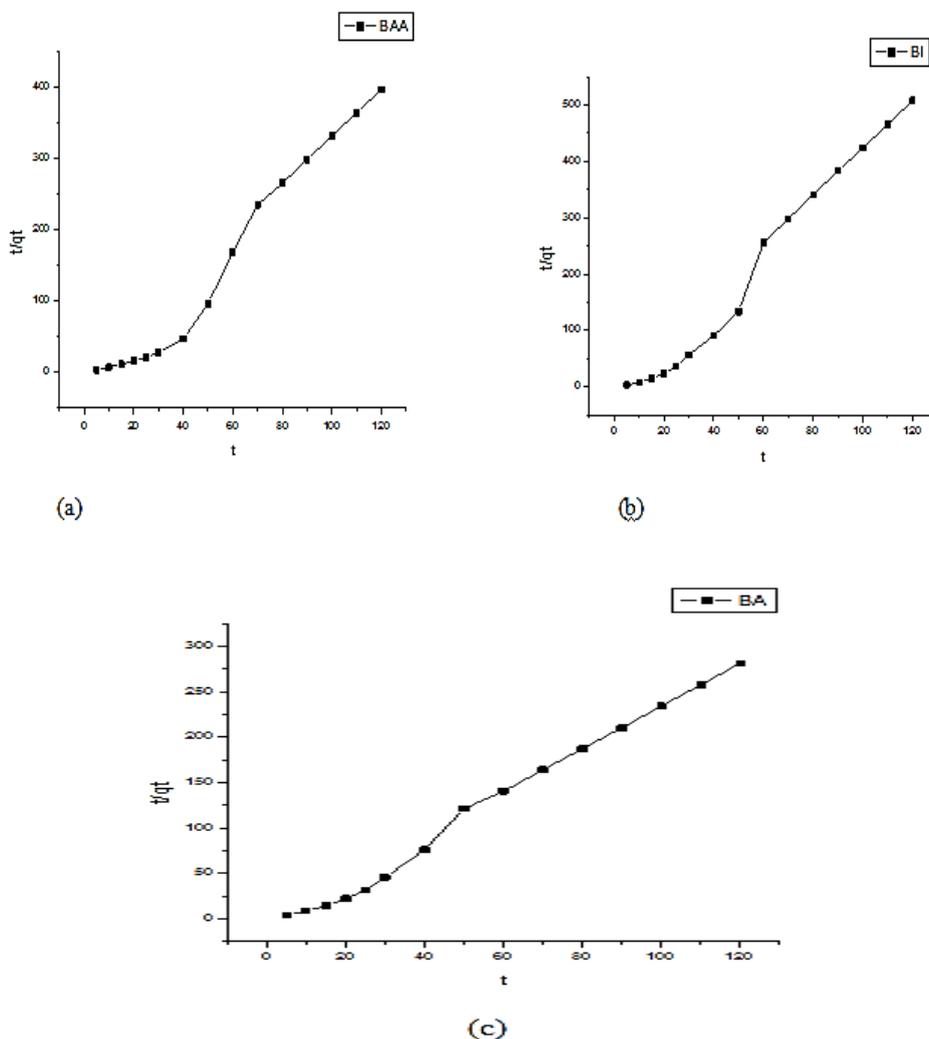


Figure 10: Pseudo second order plot for the removal of fluoride by (a) BAA (b) BA and (c) BI (dose=8,10 and12g, initial concentration= 16, 20 and 24 mg/L, optimized contact time=70, 60 and 50 minutes, optimized pH= 8, 3 and 7 respectively).

Based on the results in Figure 9 and 10, it can be concluded that, since Figure 10 showed good fitting for linearity[20]. It is an indication that the reaction follows pseudo-second order reaction.

### IV. Conclusion

XRF analysis showed that elemental composition in bentonite differ before and after impregnation, impregnation gave the best result in adsorption of fluoride and XRD result showed poor crystalline structure in bentonite. Optimization of different parameter like contact time, pH, adsorbent dose and initial concentration was investigated for the removal of fluoride ions by using bentonite adsorbent categorized into BAA, BI and BA. All of these parameters were observed to be very important on adsorption but adsorbent dose was most important with maximum percentage removal of 94.98%. The average concentrations of fluoride in all the water samples collected in nine water sources at Hai District was observed to be 16 mg/L which is above required level by WHO and local standard's, this concentration was reduced to 0.80 mg/L after treatment with

bentonite categorized into three groups BAA, BI and BA. Out of three adsorbents, BI and BA were able to reduce fluoride concentration below 1.5 mg/L. The adsorption process obeyed Langmuir adsorption model for BAA, BI and BA. But in the case of BA, agreed with both Langmuir and Freundlich models indicating that monolayer and multilayer adsorption occurred in the surface of the adsorbent. The adsorption process followed pseudo second order reaction. Activated Bentonite and impregnated Bentonite are more effective for fluoride removal and can be used by the community especially in rural and urban areas.

## V. Acknowledgements

The authors thank Ngurdoto Defluoridation Research Centre (NDRC) at Arusha for providing chemicals, apparatus and equipments used for conducting the experiments. The special thanks also to Geological Survey of Tanzania for XRF analysis and Twiga Cement Company in Dar es Salaam for XRD analysis.

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Idd Ally Hussein and Vegi Maheswara Rao “Defluoridation of Drinking water by Using  
Modified and Unmodified Bentonite from Minjingu Mining Site in Tanzania.” *International  
Journal of Engineering Science Invention (IJESI)*, vol. 6, no. 9, 2017, pp. 46–56.