

## Remediation of Fluoride Laden Water by Sorption using Kenyan Kisii Soapstone and Calcium Bentonite

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### Abstract

**Background:** The aim of this study was to evaluate the adsorption potential of natural and locally available soapstone and Calcium bentonite clay for fluoride removal from aqueous solution and to determine the optimum conditions for use. Adsorption potential was anchored on the availability of hydroxyl and aluminum ions inherent in both minerals which have been established to have ability for fluoride adsorption in aqueous solutions. Adsorption potential was investigated using batch equilibrium experiments.

**Materials and Methods;** Mineralogical characterizations were done using X-ray fluorescence spectroscopy. Fluoride ion selective electrode was used in determination of fluoride content in aqueous solution. Optimization studies on initial pH of the solution, contact time, initial fluoride concentration, adsorbent dose, and heat pretreatment of the adsorbent were done in batch adsorption experiments at room temperature.

**Results:** It was observed that calcium bentonite exhibited better adsorption capacity of 0.21 mg/g while soapstone had 0.08 mg/g at a contact time of 45 min and 5 min respectively. The optimum pH for both adsorbents was established at 3.6. The experimental data for bentonite fitted well with Langmuir isotherm indicating a monolayer adsorption while for Soapstone fitted better into Freundlich adsorption, indicating multilayer adsorption with heterogeneous energetic distribution of active sites.

**Conclusion:** Based on these findings, the two adsorbents can be fitted into household defluoridation apparatus for domestic remediation of fluoride contaminated water.

**Keyword:** Adsorption, adsorbent, defluoridation, fluorides, soapstone, bentonite, clay

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### I. Introduction

Availability of adequate water, suitable for domestic use, is affected by the inherent components of the natural water sources. Although anthropogenic activities may also introduce fluorides (F<sup>-</sup>) into water bodies (Khati, et al., 2015), along the Great Rift Valley some rocks introduce fluorides through leaching into the waters in quantities that make the water unsuitable for human consumption (Edmunds, et al., 2013). Fluorides though important for reducing dental carries, when consumed at elevated levels may cause many health problems including dental and crippling skeletal fluorosis (WHO, 2004) and its accumulation in the bones over many years causes stiffness and joint pain, changes to bone structure and calcification of ligaments (UN, 2006). World Health Organisation (WHO) classifies F<sup>-</sup> as a major water pollutant, and has set the maximum permissible limit of F<sup>-</sup> in drinking water is 1.5 mg/L.

In Kenya, the National Standards Body also regulates supply of bottled drinking water ensuring compliance to the same limits. The presence of higher than allowable F<sup>-</sup> levels in natural water used for drinking has led to a lot of studies on how to lower their levels. Various methods have been applied, including physicochemical and biological methods in the remediation of F<sup>-</sup> laden water (Loganathan, et al., 2013). Many physicochemical methods are based on membrane separation techniques which can be divided into microfiltration (MF), ultrafiltration (UF), Nano filtration (NF), and reverse osmosis (RO), blending, precipitation, coagulation, electrocoagulation, ion exchange, electrochemical methods and adsorption techniques. Adsorption techniques have great advantage and are considered more attractive due to their ease of use, their effectiveness and simplicity of design. Some adsorbents have been observed as being capable of removing fluorides from water only at a low concentration of 2 mg/L, while others are effective only at extremely low pH levels and may thus not be effective in natural conditions limiting their applicability (Ravindranath, et al., 2015). Despite availability of a good variety of low-cost adsorbents and with reasonable effectiveness, the adsorbents for reducing fluoride concentration levels to the accepted levels have not been exhaustively explored (Ayoob, et al., 2006). Adsorption of fluorides theoretically proceeds in three

essential steps; diffusion or transport of fluoride ions to the external surface of the adsorbent, adsorption of the ions on to the solid adsorbent surface and finally ions exchanging with the structural elements inside adsorbent particles or the adsorbed fluoride ions being transferred to the internal surfaces for porous materials (Sanghratna, et al., 2015). Both Calcium bentonite (Ca-bent) and soapstone have characteristics that can allow adsorption of the fluoride minerals by ion exchange (with OH<sup>-</sup>) and adsorption (through Al<sup>3+</sup>) onto the surface and may thus offer a bigger advantage (Medellin-Castillo et al., 2014; Vardhan et al., 2011).

## **II. Materials and Methods**

### ***Chemicals and reagents***

This study used 100.0 mg L<sup>-1</sup> of ammonium fluoride solution having 99.5% purity with expanded uncertainty of ±0.4 mg L<sup>-1</sup>, analytical grade sodium chloride crystals (NaCl, 99.5% purity), 0.1 M sodium hydroxide (NaOH) of 99.5% purity with expanded uncertainty of ±0.005 mg L<sup>-1</sup> and 99.5% pure citric acid crystals and Total Ionic Strength Adjustment Buffer II (TISAB II). These reagents were obtained from Romil Pure Chemistry<sup>®</sup>, United Kingdom.

### ***Preparation of fluoride solution***

From the 100 mg L<sup>-1</sup> F<sup>-</sup> standard solution, further dilutions were made using a class A volumetric flask. Total Ionic Strength Adjustment Buffer II (TISAB II) was used with each test to maintain the ionic strength and pH and to decomplex any Metal-F complexes that may occur in the course of the experiment or that may be inherent to the measurements (Ionode, 2019). The adsorption experiments were performed at temperatures of 25±1 °C.

### ***Preparation of adsorbents***

Ca-bent originally from Mount Kenya area in Kenya was received in fine powder form and thus did not require any further preparation to increase its surface area. Soapstone samples obtained from Tabaka area of Kisii County in Kenya were crushed in the form obtained from the quarries using a Retsch<sup>®</sup> sample mill which had a maximum speed of 1200 revolutions per minute and was able to reduce the required sample quantity for each batch experiment to powder form in less than 30 seconds. No further sample preparation was done.

### ***Instrumentation***

The two adsorbents were subjected to XRF (X-ray fluorescence) analysis using the handheld S1-Titan model of Bruker instruments. F<sup>-</sup> concentration was measured by the potentiometric method using EDT directION DR359TX - Ion Concentration Meter with a fluoride-specific ion electrode. When determining the effect of pH on adsorption of F<sup>-</sup>, a Hanna HI98191, Portable pH meter was used.

### ***XRF characterization***

Powdered samples of soapstone and Ca-bent were placed into 30 mm open-ended XRF. The cups were then sealed with a 3.0-µm prolene X-ray film. The appropriate XRF mode was selected from the instrument control panel. The XRF rays were directed onto the samples passing through the X-ray film. The mode selected took several readings and returned the average reading.

### ***Optimization studies***

Known quantities of adsorbents were added to the prepared synthetic fluoride solutions and the reaction mixtures continuously agitated in an orbital shaker at 150 revolutions per minute. At the end of each experiment, the solutions were filtered into a vacuum flask by vacuum filtration through Whatman No. 42 filter paper for F<sup>-</sup> analysis.

To determine the influence of contact time on fluoride removal, experiments were carried out at constant concentration and volume of the adsorbate solution and constant weight of adsorbent while varying the agitation time. To study the influence of adsorbent dosage experiments were performed by changing the amount of adsorbent in the 50 ml solution of ammonium fluoride. The influence of preheat treatment of the adsorbents on fluoride adsorption was investigated by conditioning the adsorbents at temperatures of 100°C, 210°C, 300°C and 500°C for two hours each then cooling to room temperature while the fluoride concentration and dosage of the adsorbent for all these batches were kept constant. Batch experiments were also conducted to study the effects of Chlorides ions by varying the concentration while maintaining the initial fluoride concentration. The effect of initial adsorbate concentration was also carried out by varying the concentrations of the adsorbate and maintaining the other parameters constant.

**Fluoride Removal Calculation**

Amount of the adsorbed F<sup>-</sup>, Q<sub>e</sub> (mg/g), was calculated according to Equation 1:

$$Q_e = (C_0 - C_e) / W \times V \dots\dots\dots(1)$$

where,

Q<sub>e</sub> is the adsorption capacity (mg/g) of the adsorbent at equilibrium; C<sub>0</sub>, C<sub>e</sub> are initial and equilibrium concentrations of F<sup>-</sup> (mg/L) in aqueous solution, respectively; V is the volume of the aqueous solution (L) and W is the mass (g) of adsorbent used in the experiments.

The percent removal %R, at equilibrium, was calculated by using Equation 2:

$$(\%R) = (C_0 - C_e) / C_0 \times 100 \dots\dots\dots(2)$$

**III. Results and Discussion**

**Elemental analysis**

When elemental analysis was carried out to find the chemical composition of the Soapstone and Ca-bent, the analysis revealed that silica (SiO<sub>2</sub>) followed by alumina (Al<sub>2</sub>O<sub>3</sub>) were the main components as shown in Tables 1 and 2 respectively.

**Table No. 1.** XRF compositional analysis of soapstone

Element	%m/m
<b>Silica as SiO<sub>2</sub></b>	<b>50.74</b>
<b>Aluminum as Al<sub>2</sub>O<sub>3</sub></b>	<b>34.74</b>
<b>Titanium as TiO</b>	<b>3.6</b>
<b>Potassium as K<sub>2</sub>O</b>	<b>2.17</b>
<b>Calcium Oxides as CaO</b>	<b>0.96</b>
<b>Phosphorus as P<sub>2</sub>O<sub>5</sub></b>	<b>0.86</b>
<b>Iron as Fe<sub>2</sub>O<sub>3</sub></b>	<b>0.35</b>
<b>Sulphur as S</b>	<b>0.13</b>
<b>Barium as Ba</b>	<b>0.09</b>
<b>Tin as Sn</b>	<b>0.07</b>
<b>Rubidium as Rb</b>	<b>0.04</b>
<b>Manganese as MnO<sub>3</sub></b>	<b>0.01</b>
<b>Chromium as Cr<sub>2</sub>O<sub>3</sub></b>	<b>0.01</b>

**Table No. 2.** XRF compositional analysis of Ca- bent

Element	%m/m
<b>Silica as SiO<sub>2</sub></b>	<b>63.17</b>
<b>Aluminum as Al<sub>2</sub>O<sub>3</sub></b>	<b>18.44</b>
<b>Iron as Fe<sub>2</sub>O<sub>3</sub></b>	<b>8.04</b>
<b>Potassium as K<sub>2</sub>O</b>	<b>7.3</b>
<b>Calcium Oxides as CaO</b>	<b>1.06</b>
<b>Phosphorus as P<sub>2</sub>O<sub>5</sub></b>	<b>0.84</b>
<b>Titanium as TiO</b>	<b>0.33</b>
<b>Zirconium as Zr</b>	<b>0.23</b>
<b>Manganese as MnO<sub>3</sub></b>	<b>0.16</b>
<b>Sulphur as S</b>	<b>0.12</b>
<b>Barium as Ba</b>	<b>0.08</b>

Zinc as Zn

0.02

The results show that in Ca-bent, the element with the highest content by mass was silica having 63.17%, followed by Aluminum at 18.44% and then Iron at 8.04%. These results compare well with the results from a study on Characterization and Qualitative Analysis of Some Nigerian Clay, where sample 1 had Silica value of 63.35%, followed by Aluminum at 22.42% and then Iron at 6.109% (Folorunso, et al., 2014).

### Optimization of Experiments Results

#### Effect of pH

In order to determine the resulting effect of change in the pH of the solutions in the removal of fluorides in water, the pH values of the water samples were varied from 1.5 to 11.6, and the solutions subjected to both soapstone and Ca-bent defluoridation tests. The pH was adjusted accordingly using 0.1M Citric acid 0.1M NaOH. Figure 1 shows the influence of pH on fluoride removal.

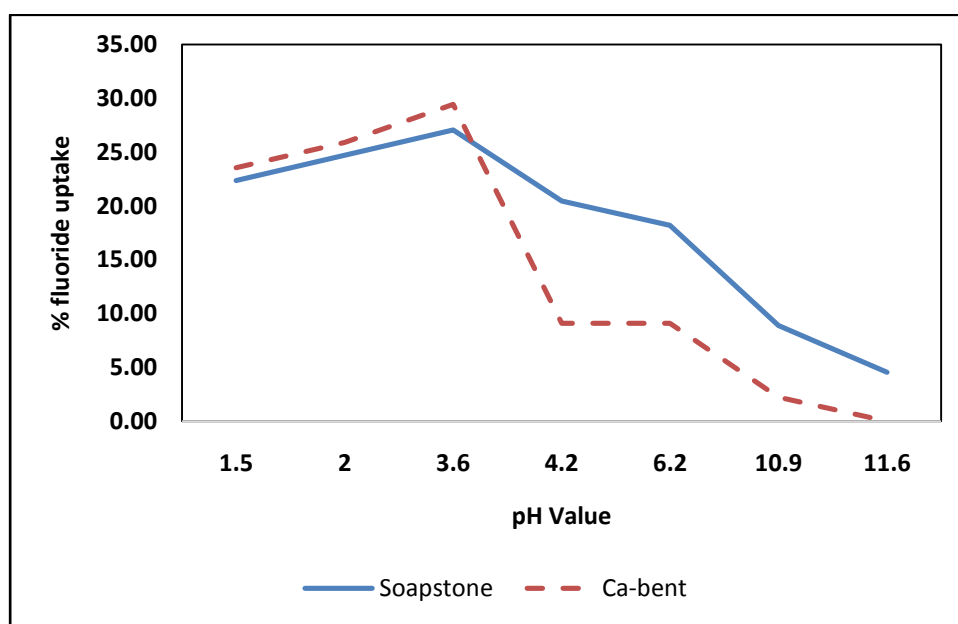


Figure 1. Effect of pH on uptake of F<sup>-</sup>

Fluoride adsorption onto the surface of both soapstone and Ca-bent adsorbents was analysed. The contact time applied for Soapstone was 5 minutes while that of Ca-bentonite was 30 minutes. It was observed that adsorption in both cases was dependent on the pH of the fluoridated water. pH effect examined in the range of 1.5 to 11.6 indicated a peak adsorption at around 3.6 for both adsorbates. This observation tends to agree that a comparatively higher level of adsorption of fluorides from water usually occurs at pH values of 3.6 since the solution's pH values can affect the surface properties of adsorbents (Collivignarelli, et al., 2020). The relatively high adsorption at low pH may be since the two adsorbents consist of a mixture of several oxides that tend to develop charge on the surface in a humid environment (Assaoui, et al., 2020). As the pH lowers and the environment becomes more acidic, the negative charges developed on the surface of the adsorbents are neutralised resulting in the further adsorption of the negatively charged fluoride ions. The graph clearly illustrates this phenomenon. As the pH reduces from the basic of 11.6 through neutral to acidity, more adsorption takes place for both adsorbents. Similar to these results, a study for evaluation of Bentonite/Chitosan beads for adsorption of fluoride from aqueous solution demonstrated that lower pH values favoured fluoride adsorption (Zhang, et al., 2013).

#### Effect of Contact Time

The effect of contact time was investigated by varying the contact time at intervals from 5 minutes, 10 minutes, 15 minutes, 30 minutes, and 60 minutes. Variation of contact time allows for determination of the ideal time required for the anion to be adsorbed onto the adsorbate sites and reach saturation.

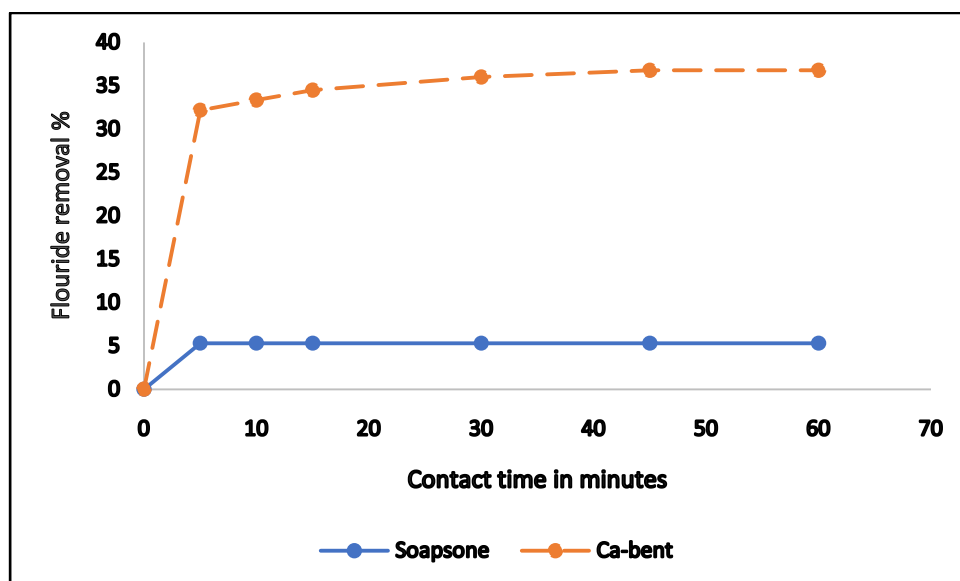


Figure 2. Effect of Contact time on adsorption

The results obtained showed that after 5 minutes of contact time adsorption on the surface of soapstone was at its optimum since the amount of Fluoride remained constant from that point onwards as illustrated in Figure 2.

On the other hand, for Ca-bent clay, 45 minutes of contact time was found to offer the optimum period of adsorption since the amount of Fluoride reached its peak at that point as illustrated in the Figure 2. From the illustration above, the rate of fluoride removal rose very fast and subsequently slowed. This can be attributed to the fact that initially there were several adsorption sites on the surface of the adsorbent available for immediate adsorption and as the sites became fewer the probability of adsorption decreased. Similar pattern of adsorption was reported in the study of adsorption of fluoride from water by  $Al^{3+}$  and  $Fe^{3+}$  pretreated natural Iranian zeolites by Rahmani, et al (2010).

#### Effect of initial $F^-$ concentration

The effect of initial concentration on the extent of removal of the fluoride was studied by varying the concentrations from 0.5 to 10 mg/L, while keeping other parameters constant at their respective optimum. The adsorbents' dose was held constant at 0.75g. The graph below (Figure 3.) illustrates the relationship.

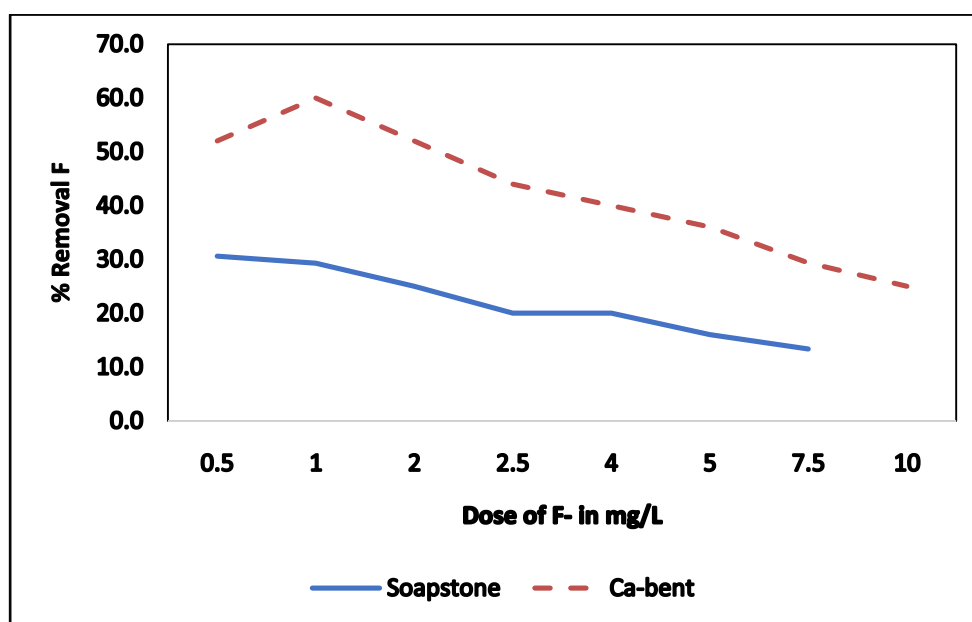


Figure 3. Effect of initial  $F^-$  concentration

Increasing the adsorbate dose provides the system with constant supply of the  $F^-$ , the adsorbent to adsorbate ratio reduces leading to saturation of adsorption sites lowering the % removal (Yu et al., 2003). as can be seen from Figure 3. The slight initial increase may be attributed to more exposed active sites on Ca-bent as compared to soapstone that has some adsorption sites internal to its structure and only available at the edges of the silica sheet (Zhang, et al., 2013). After saturation they both show a similar downward trend.

**Effect of adsorbent dose on adsorption of  $F^-$**

To determine the effect of increasing the adsorbent dose on defluoridation, the two adsorbents were added in different quantities as shown in the subsequent subheadings.

**Effect of soapstone dose on adsorption of  $F^-$**

The amount of soapstone added to 50ml of 10mg/L of synthetic fluoridated water, was as follows; 0.1 g, 0.5g, 1.0g 2.0g, 4.0g 6.0g and 8.0g.

With the increase of adsorbent, there was an increase in the amount of fluorides adsorbed. This could be attributed to the fact that the increased dosage of the adsorbent is accompanied by more adsorption sites. However, at a dosage of 4 grams it was observed that there was an onset of decline in the rate of adsorption, and this was taken as the ideal adsorption weight. The illustration is on Figure 4.

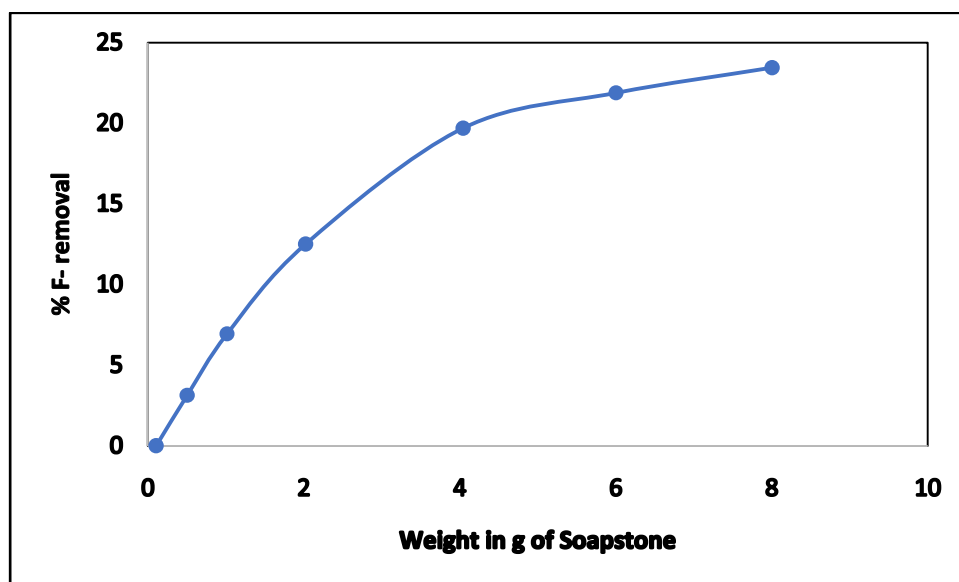


Figure 4. Effect of soapstone dose

**Effect of ca-bent dose on adsorption of  $F^-$**

Similarly, investigation on the effect of increasing the Ca-bentonite adsorbent dose was done. The amount of bentonite added to 50ml of 10mg/L of synthetic fluoride ion solution was in increments of 0.1g, 0.25g, 0.5g 0.75g, 1.0g, 1.50g and 3.0 g. It is noticed from the graph in Figure 5. That the optimum weight of the adsorbent is 0.75g. This infers that the amount of the adsorbate adsorbed per unit mass of adsorbent has a limit with the adsorbent dosage due to the matter rate transfer at the surface of the adsorbents (Daouda, et al., 2019) The illustration is as depicted in the graph (figure 5) below.

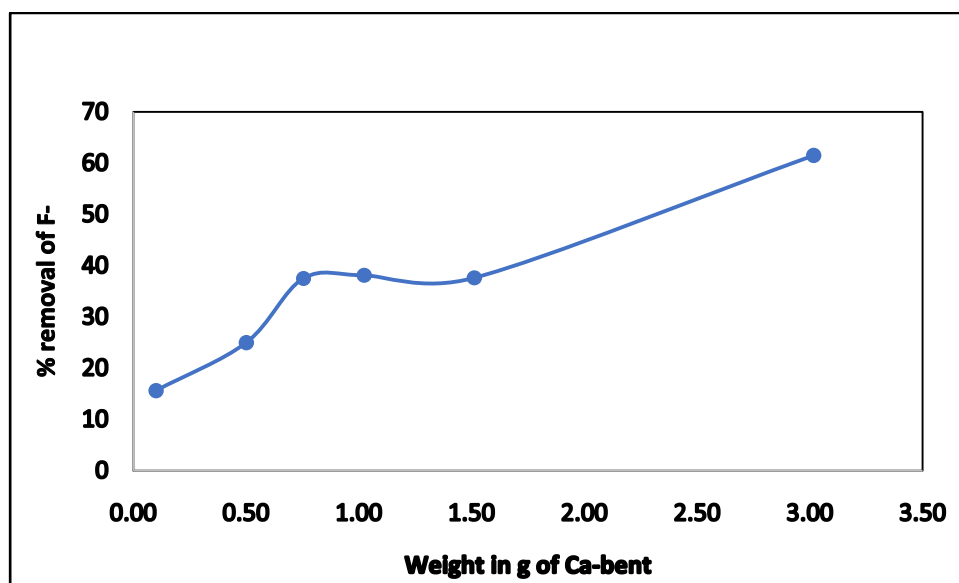


Figure 5. Effect of Ca-bent adsorbent dose

The experimental conditions for both adsorbents were held constant except for the adsorbent dose. As in the case of soapstone, in Ca-bent, initial increase of adsorbate resulted in increased adsorption and the initial rate of adsorption reached a peak at 0.75g after which it plateaued (Figure 5) and then started rising again after with adsorbent dose of 1.51g from 37.625% to 61.5% at 3.02g of the clay. The ideal weights of adsorbents for the subsequent studies were thus taken as 4.0g and 0.75g for soapstone and Ca-bent respectively. Similar results were obtained in research (Kanaujia, et al., 2015; Daouda, et al., 2019) which found that increasing adsorbent dosage increased the fluoride uptake, and thereafter the relative adsorption of fluoride reduced with an increase in the adsorbent dosage.

#### Effect of chlorides as coexisting anions

Competing co-ions such as chloride in natural groundwater, and the selectivity of the adsorbent used may influence the process of defluoridation (Marzbani, 2013). To determine the effect of chlorides (Cl<sup>-</sup>) in the adsorption of fluorides from water, a solution of 10ppm of fluoridated water was constituted together with different concentrations of sodium chloride to make 2.5ppm, 5.0ppm and 7.5ppm of Cl<sup>-</sup> separately. These three Cl<sup>-</sup> concentrations having 10ppm of F<sup>-</sup> ions were then subjected to adsorption studies using optimum weights of 0.75g of Ca-bentonite and 4.0g of soapstone for the optimum period obtained in the optimization experiments. The graph below illustrates the relationship of with two adsorbents.

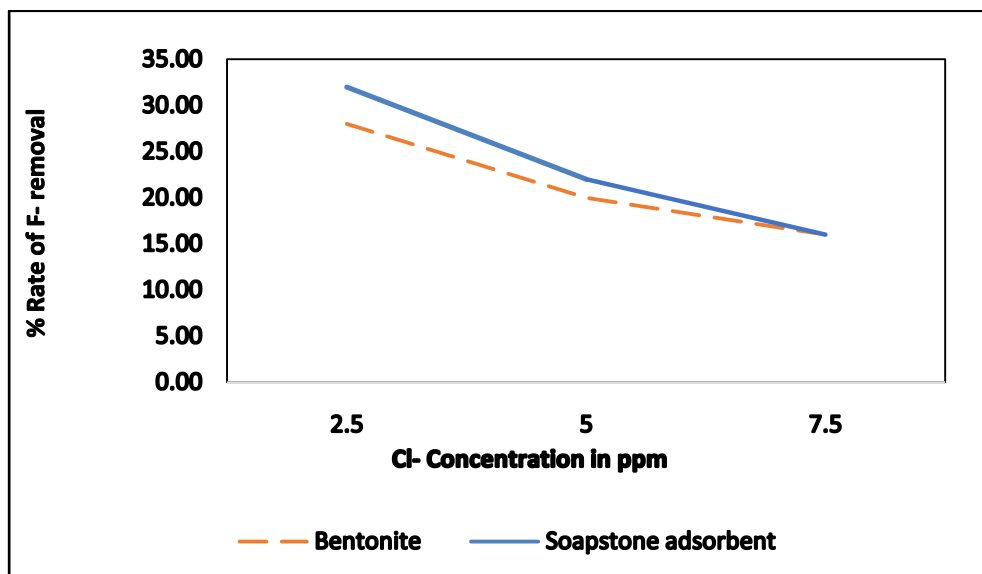


Figure 6. Effect of Cl<sup>-</sup> concentration on adsorption of F<sup>-</sup>

Figure 6 shows that with increase in Cl<sup>-</sup> ions, there is a corresponding decrease in uptake of the fluorides by the two adsorbents. This indicates that there is competition for adsorption sites by the two anions. Water treatment with chlorine prior to removal of F<sup>-</sup> by adsorption method may therefore have a negative effect on the efficiency of fluoride adsorption using the two adsorbents. It has been observed that some anions are capable of intensifying coulombic repulsion forces and thus offer competition with fluoride for the active sites, lowering adsorption. However, the multivalent compared to monovalent anions are adsorbed more easily (Nabizadeh, et al., 2015).

#### Effect of preheat treatment of the adsorbent

Heat has been used to optimize adsorbent and improve their adsorption efficiency by altering the surface chemistry, exposing the adsorption sites by improving the porosity and oxidation (Sáenz-Alanís, et al., 2017). The reverse is also possible leading to collapse in the structure and dihydroxylation of the adsorbates thus reduction in adsorption (Stagnaro, et al., 2012).

The adsorbents were heated in an oven and muffle furnace to temperatures ranging from 100°C to 500°C. This was done to determine if the chemistry of the adsorbents would be improved by the heat treatment and thus optimize their defluoridation ability. The graph below (Figure 7.) depicts the behavior of the adsorbents when they were subjected to defluoridation studies.

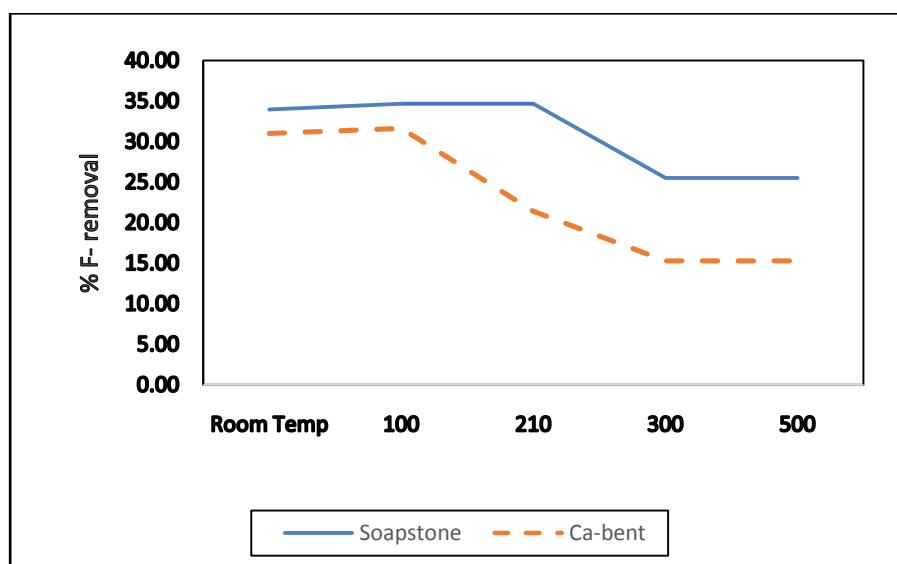


Figure 7. Effect of heat treatment of adsorbents on adsorption of F<sup>-</sup> ions

Ca-bentonite was preheated for 2 hours at 100°C and then allowed to cool to room temperature. It was noted that there was a slight improvement in the uptake of fluorides. A similar effect was observed on soapstone when it was preheated at 100°C to 210°C for 2 hours and then cooled. This can be attributed to the fact that moisture in the adsorbents was reduced and thus the net weight of the adsorbents increased, increasing the comparative % F<sup>-</sup> uptake. Upon further preheat treatment of both adsorbents to temperatures of up to 300 °C and subsequent cooling to room temperature, their fluoride uptake ability was reduced. In similar experiments that were carried out to determine the effect of heating SiO<sub>2</sub>, TiO<sub>2</sub> and their composites on adsorption of Cd<sup>2+</sup>, observations indicated that the Brunauer, Emmett and Teller (BET) surface area of all the adsorbents increased with heat pretreatment from 105°C to 299°C and decreased upon further heat treatment (Waseem, et al., 2017). The change in adsorption would be due to the distortion of the adsorption sites by extreme heat. An experiment that was done to determine the influence of Ca-bent treated to temperatures ranging from room temperature to 750°C on the adsorption of Pb, Cd and Zn in an aqueous solution also indicated a decrease in adsorption with increased heat treatment (Stagnaro, et al., 2012).

#### Removal capacity

The experimental results were treated to Langmuir and Freundlich isotherms. The removal capacity of



Ca-bent was found to be 0.21mg/g while that of soapstone 0.08mg/g. The Langmuir isotherm for Ca-bent had a correlation coefficient  $R^2$  value of 0.977 while the Freundlich isotherm  $R^2$  value was 0.9405. As for Soapstone, the  $R^2$  for Langmuir isotherm was 0.9671 and Freundlich gave a value of 0.9767. The applicability of the isotherm equation is compared by judging the correlation coefficients,  $R^2$  where Langmuir adsorption presumes a homogeneous site of adsorbent while Freundlich presumably takes place on a heterogeneous surface of adsorbent with irregular release of heat of adsorption about the adsorbent surface (Daouda, et al., 2019). From these observations it is noted that Ca-bent fitted better with Langmuir model suggesting a monolayer type of adsorption while soapstone fitted well with the Freundlich model suggesting a heterogeneous surface adsorption.

#### IV. Conclusion

Results from this study of defluoridation of drinking water with a naturally occurring and available soapstone and Ca-bent clay in Kenya, demonstrated that the efficiency of adsorption process using Ca-bent and Soapstone adsorbents depends on the pH (optimum of 3.6) of the medium, concentration of medium and time of contact (5 min for soapstone and 45 minutes for Ca-bent), adsorbent dose and competing ions present in the water. Heat pretreatment of the adsorbents have no substantive benefit in adsorption properties of the two adsorbents. Ca-bent was found to be a better adsorbent for F removal in aqueous solutions at the experimental conditions assessed having an adsorption capacity of 0.21mg/g while that of soapstone was 0.08mg/g. Kinetic studies of the two minerals revealed that Ca-Bent adsorption favoured the Langmuir isotherm model of adsorption, while Soapstone was more inclined towards the Freundlich adsorption model. Both materials demonstrated that they could reduce fluorides in ground water to the WHO acceptable levels. We recommend that further experiments with other competing ions be investigated as the information may also help in determining dual or multiple purpose use in contaminated water remediation.

#### Acknowledgment

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