

## **Effect of Essential Mineral Ions from Aqueous Media on Adsorption of Fluoride by Bone Char**

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**Abstract:** Leaching of fluoride, a toxic element, from industrial wastes and fluoride minerals like fluorspar (CaF<sub>2</sub>) into ground water may cause significant contamination, which may require major treatment before use as drinking water. The present study described the removal of F<sup>-</sup> on bone char in batch studies as a function of co-existing mineral ions phosphate, carbonate, sulphate, chloride, sodium, magnesium, etc. present in drinking water (surface and groundwater), at constant temperature conditions and without pH adjustments. Fourier transform infrared spectra of bone char before and after adsorption demonstrated that *ca-PO<sub>4</sub><sup>3-</sup>* and *ca-OH* functional groups played an important role for F<sup>-</sup> removal, and the mechanism was complex where both ion-exchange and electrostatic ion-binding between the active positive sites of calcium in the bone char and fluoride ions. This led to an increase in pH of the water during the sorption of fluoride. The results suggest that bone char can be used effectively the removal of F<sup>-</sup> ions from groundwater utilized as drinking water.

**Keywords:** Defluoridation, fluorosis, fluoroapatite, hydroxyapatite.

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### **I. Introduction**

Fluoride is a persistent and non-biodegradable pollutant that accumulates in soils, water, plants and in humans.[1,2] The level of fluoride ion (F<sup>-</sup>) in water bodies is of great environmental concern worldwide because when coupled with the risk of fluorosis associated with using such water for human consumption can cause large scale health problems.[3,4] Diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder can attack the human body on excessive intake of fluoride.[5] In addition, excess fluorides can cause dental fluorosis if it is above 2 mg/L while at higher fluoride concentration (>4 mg/L) dental fluorosis progresses to incurable crippling skeletal fluorosis.[6] High levels of fluoride (≥30 mg/L) in ground water have been reported in many countries in the Rift valley such as Kenya, Tanzania and Turkey, as well as India, China and parts of South Africa[4] and may result from high fluoride containing effluents from industries or dissolution of fluoride minerals like fluorspar (CaF<sub>2</sub>) and fluorapatite ]to acceptable limits. The World Health Organization (WHO) optimum value of fluoride in drinking water lies between 1–1.5 mg/L and is considered beneficial to health.[7,8]

Various methods to remove fluoride from fluoride-rich industrial wastewaters, drinking and groundwater have been reported and include: sedimentation with calcium and aluminium salts, ion-exchange, reverse osmosis, electro-dialysis and membrane processes.[8,3,9] Among the different types of adsorbents, bone char is considered as a potential adsorbent for defluoridation of drinking water because it is relatively inexpensive. Also, it is made from spent bone, can be manufactured in sufficient amounts and quality, and can be recycled through a simple thermal process at 200 °C.[10] Bone char consists mainly of hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] and calcite (CaCO<sub>3</sub>).[11]

Recently the use of bone char has been postulated in water treatment,[12] mainly to retain fluoride as has been reported in our laboratory, thus performing an effective way of recycling this waste material.[13,14] Chemisorptions and ion-exchange between the fluoride ions in solution and the phosphate and carbonate of the apatite seem to be the main operating mechanism of fluoride removal from the aqueous media. [3] After the ion-exchange monolayer, the adsorption process may be extended further due to the attraction of anions and cations,[15] a process that is somewhat concentration, pH and temperature dependent. Studies by Bjovatt et al [16] have shown a significant decrease in calcium concentration and an increase in concentration of chromium, while a report by the European Commission showed that bicarbonate and sulphate content had little or no effect on defluoridation by alumina adsorbent, even for water with very high sulphate concentration.[17] Other results have also revealed that bicarbonate was released from the bone char while the carbonate was adsorbed on the bone char.[18] In addition; physico-sorption, solution pH as well as temperature are known to influence such processes due to adsorption itself, ion speciation and dehydration that occur on increasing temperatures.[19]

The mechanism of fluoride adsorption on bone char, However, has not been fully elucidated, and little attention has been paid to the effects of major co-existing mineral ions in aqueous media like Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> on fluoride removal potential of bone char. The objective of this study was, therefore, to

evaluate the fluoride removal potential of bone char in the presence of co-existing mineral ions phosphate, carbonate, sulphate, chloride, sodium, magnesium, etc. present in drinking water (surface and groundwater), without pH adjustments and at constant temperature conditions during the adsorption process. The interactions of the bone char surface and the fluoride ions in solution were studied in order to gain a better understanding of the adsorption and desorption mechanisms of fluoride on the bone char.

## **II. Experimental**

### **Preparation of bone char**

The bone char with particle sizes between 0.6–2.0 mm in diameter (Filter medium used in community and households) were obtained from the Water Quality Department of the Catholic Diocese of Nakuru, Kenya. The adsorbent was rinsed with distilled water to remove suspended impurities as well as soluble salts such as NaCl. This was followed by drying process at 105 °C for 24 h. Finally the dried samples were kept in a desiccator for use as biosorbent.

### **Water samples**

Natural water from the local sources of drinking water: ground water, spring water, well water and tap water in the study area (Njoro and Lanet areas of Nakuru County in the Rift Valley of Kenya), were collected, filtered to remove any suspended impurities (Whatman No. 4 filters) and stored in polyethylene bags in a refrigerator. Ground water sources, mainly boreholes, have been recognized as the greatest threat (source) of fluoride in drinking water, with reported fluoride levels in the tens range (up to 50 mg/l) in Nakuru area.[20]

### **Instruments and apparatus**

The chemical and physical properties of the bone char were tested (Ca, Pb, Cd, Fe, Mg, Al, Na content detected by Inductive Coupled Plasma-Optical Emission Spectrophotometry (ICP-OES) Sequential Analyzer (model: Perkin Elmer 5300 DV spectrometer, fitted with auto-sampler: model AS-93 plus): argon gas flow rate, 1.5 mL/min; pump flow rate, 1.5 mL/min and plasma radio frequency, 1300 watts. Surface property of bone char was confirmed by high-resolution transmission electron microscopy (HRTEM): JOEL-2010F at 200 kV and 0.2 nm microscope resolution; IR spectra were recorded on a Perkin-Elmer, FITR, Model RXI spectrometer. The pH of the water samples at the beginning and the end of the experiment were measured by using Hanna Instruments model: pH 211 digital pH meter. The pH meter was calibrated using buffers of pH 4.0, 7.0 and 10.0 (Merck, UK) prior to the measurements. Determination of fluoride in water solutions was carried out by potentiometric procedure described by Orion Research Incorporation, Beverly, Massachusetts, USA (1999), using fluoride ion selective electrode Thermo Orion Ion Analyzer Model 3405 (Jenway of Fsted, Dunmow, UK.). The method allowed the determination of fluoride concentrations in the range 0.1 to 5.0 mg/L. This method required calibration curves prepared with standard solutions of fluoride (NaF, analytical grade).

### **Analytical techniques**

The concentration of metal ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ ) in water samples were measured by atomic absorption spectrophotometer, AAS (Thermo Jarrell Ash S11-Waltham, MA, USA). The concentrations of Na and K in the water samples were determined using Corning Flame Photometer Model 410 (Corning Science Products of Halstead, Essex, England). The concentrations of  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  in drinking water samples were determined by standard procedures using UV-Vis spectrophotometer, Nova spec II Model 80-2088-64 (Pharmacia Biotech, Cambridge, UK). The concentrations of bicarbonate, carbonate and chloride in the water were determined using the methods recommended by Association of Official Analytical Chemists (official method No. 920.94, 1995).

### **ICP-OES analysis**

The bone char sample solution for elemental analysis was prepared by digesting 1.0 g of bone char, under reflux, in a mixture of 6.0 mL  $\text{HNO}_3$ , 2.0 mL  $\text{HClO}_4$  and 4.0 mL  $\text{H}_2\text{O}_2$ , for 6 h to obtain a clear solution. The contents were transferred into a 25 mL standard flask and diluted to the mark using distilled water. The samples were prepared in triplicate. The digests were analysed for Ca, Pb, Cd, Fe, Mg, Si and Na on ICP-OES sequential analyser, using external multi-element standard in the range 10–50 mg/L.

### **Batch sorption experiment**

Column operations of fixed bed column systems containing bone char prepared out of animal bones were conducted in this study to evaluate fluoride removal through adsorption on the bone char. A series of experimental columns consisting of 500 mL volume separating funnels containing 300 mL bed volume of bone char were assembled as shown in Fig. 1. Sufficient distilled water was then added such that the water completely covered the bone char. The mixture was left to stand for 30 minutes before being drained off

completely. The isothermal adsorption experimental equilibration data were then obtained as follows: a 500 mL portion each of natural drinking water samples of known initial concentration of fluoride was added to the 300 mL bed volume bone char. The solution remained in contact with the bone char at room temperature ( $25 \pm 1$  °C) for 30 minutes, while the initial pH of the natural water samples was in the range 6.36–8.14. This procedure was adopted to simulate the domestic one recommended by the Catholic dioceses of Nakuru, Kenya, to ensure equilibration is attained. All the water was finally drained off into plastic bottles after filtering off any solids. The fluoride ions concentration of the supernatant was determined using fluoride ions selective electrode. The percent removal (%) of ions was calculated using the following equation:

$$\text{Removal efficiency (\%)} = 100(C_i - C_f)/C_i \quad (1)$$

The initial and final concentrations of the metal ions— $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ , in the water samples and their effluents (filtrate) were measured by AAS and Photometric methods, respectively. Finally, the initial and final content of fluoride and: bicarbonate, carbonate, chloride, sulphate and phosphate in the water samples and their effluents after equilibration, were determined using the methods already mentioned. Each experiment was conducted three times and average values are reported. Control experiments, performed without addition of bone char, confirmed that adsorption of fluoride on the walls of the separating funnels and Erlenmeyer flasks were negligible. All the sorption tests were in triplicate and the reported data are mean values with standard error values ranging from 1.5 to 4.0%.

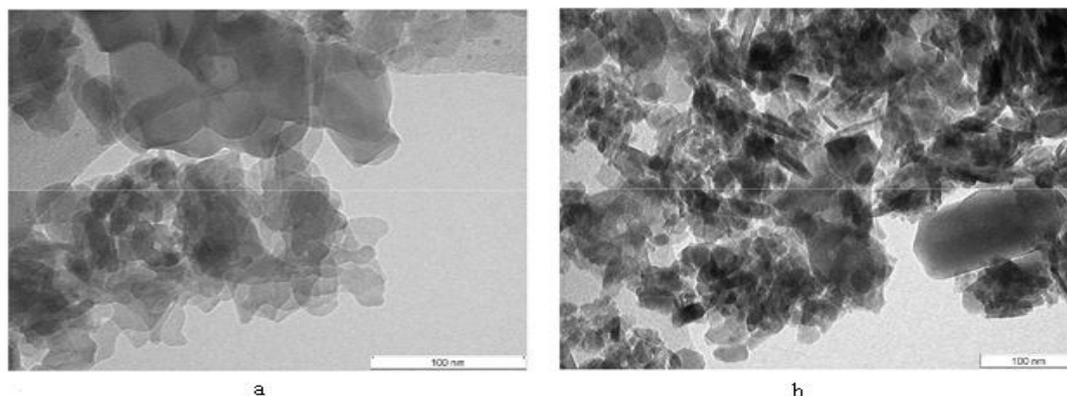


**Figure 1:** The defluoridation units

### III. Results And Discussion

#### Characterisation of bone char before and after sorption of Fluoride

The surface and morphology of size distribution of the bone char particles were observed by means of a high-resolution transmission electron microscope (HRTEM). The morphology of the bone char particles before and after  $\text{F}^-$  adsorption is shown in Fig. 2a and Fig. 2b. It is seen that the particles presented a fractured, porous and irregular surface, indicative of a high surface area and high adsorptive capacity. After adsorption of fluoride ions the sorbent seems denser with fewer pores presumably due to replacement by fluoride ions.



**Figure 2:** HRTEM micrograph of bone char (a) before and (b) after fluoride adsorption

The elemental composition of the bone char was determined by means of the ICP-OES and the data obtained are presented in TABLE 1.

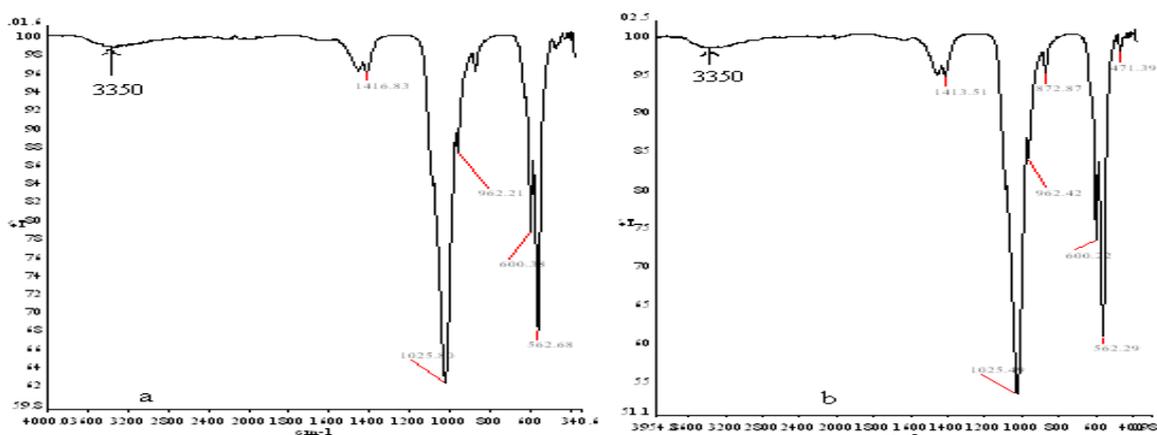
The results revealed that the bone char was composed of Ca, C, Si, Al, Mg and Na, which indicates that it is mainly composed of calcium hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>], carbon, calcite (CaCO<sub>3</sub>) and calcium sulphate and their weight percentages could be in the ranges 70-76, 9-11, 7-9, and 0.0-0.2%, respectively.[18,21]

**Table 1: Chemical properties of bone char**

Items	Limits (wt %)
Phosphorous	0.05
Ca	17.63
Mg	0.41
Iron-Fe <sub>2</sub> O <sub>3</sub>	0.045
Na	0.18
Cd	<0.1

**FTIR analysis**

The IR analysis is important in order to identify characteristic functional groups on the surface of the adsorbent that are responsible for adsorption of fluoride ions.[22] The FTIR spectra (KBr, 4,000–300 cm<sup>-1</sup>) of the bone char before and after fluoride adsorption are shown in Fig. 3a and Fig. 3b. The results show the presence of characteristic strong bands of phosphate, -PO<sub>4</sub><sup>3-</sup> group (ν<sub>stretching mode</sub>, 962 cm<sup>-1</sup> and ν<sub>vibrational mode</sub>, 1,023 cm<sup>-1</sup>); sharp peaks at 563 cm<sup>-1</sup> assigned to bending mode of phosphate (Ca<sup>2+</sup>) and 600 cm<sup>-1</sup> for presence of -OH group (Ca<sup>2+</sup>); the absorption peaks at 1,416–1,460 cm<sup>-1</sup> and 872 cm<sup>-1</sup> indicate vibration mode of carbonate groups.[23] These results are similar to the FTIR reported for camel bone char.[11] Swine bone adsorbent,[24] and fish bone.[25] The results suggest that fluoride interacts with metal oxides as well as -OH groups present on the surface of the bone char.



**Figure 3:** FTIR Spectrum of the bone char sample (a) before and (b) after fluoride sorption

**Removal of Fluoride from drinking water as well as ground water**

All the experimental conditions for the adsorption of fluoride from the actual drinking water sources obtained from Lanet and Njoro areas of Nakuru County, Kenya, are given in TABLE 2. The initial fluoride concentrations of all the water samples were between 1.58–5.89 mg/L. These concentrations were well above 1.5 mg/L that is the guideline value recommended by the World Health Organization.[26] As such, these water sources may be deemed as unsuitable for domestic consumption since they have high fluoride concentration. This problem is bound to be exacerbated by the need to drink more water, especially in hot months due to heat. As a consequence, in hot climates, where water intake is higher, the fluoride concentration guideline value should be even lower.

Although pH has no direct effect on the human health, pH value of 7.0 is considered as best and ideal for all biochemical reactions, while acidic water (low pH) can leach metals (e.g. lead, copper, zinc, etc.) from plumping systems that can cause health problems. In the present study, the initial pH values of the water samples varied in a narrow range of 6.36 and 8.13 as observed in TABLE 2. These results are within the permissible limits of pH lying between 6.5 and 8.5 recommended by the U.S. environmental Protection Agency (EPA) for surface and ground water systems.

**Table 2: Experimental conditions and Results for Fluoride adsorption from drinking water (Borehole water, spring/well water and tap water) on bone char at 25 °C**

Water Source	Fluoride (mg/L)		pH of water		Percent Removal
	Initial	Final	Initial	Final	
<b>Boreholes</b> (150–200 m)					
Njoro area					
St. Joseph	3.12	0.18	6.36	8.65	95.8
Ngondu	5.89	0.16	8.12	8.62	97.3
Egerton	4.96	0.16	8.13	8.56	97.3
Lanet area					
BH1	3.12	0.17	7.00	8.61	95.6
BH2	4.49	0.21	7.48	8.70	95.4
<b>Spring water</b>					
Cold spring	2.96	0.17	6.83	8.41	94.3
Hot spring	5.12	0.17	7.46	8.48	96.8
<b>Well water (18 m)</b>					
Belbur	1.58	0.20	7.12	8.47	87.6
<b>Tap water</b> blend of river and ground water-Egerton	4.19	0.17	8.00	8.21	95.9

It is clearly seen that the pH of the drinking water samples increased as the fluoride adsorption progressed during the 30 minutes equilibration period. The final pH values of the natural drinking water ranged between 8.21 and 8.70 during the defluoridation process. This indicates that H<sup>+</sup> ions were adsorbed on the bone char within the initial pH values of 6.36 to 8.13, resulting in the observed increase in pH values. From previous studies, the zero point charge (ZPC) of bone char occurs at pH 7.9–8.4.[15,18] The surface is positively charged when the solution pH is below the point of zero charge. Therefore, the surface of the bone char used in our study is positively charged since the water solution pH values are either below or within the reported PZC values.

As expected, the fluoride ions were attracted to the positively charged surface of the bone char, caused by the protonation of the hydroxyapatite hydroxyl groups. This led to enhanced accumulation of the fluoride ions onto the surface. The final concentrations of fluoride were between 0.16 and 0.21 mg/L from raw water sources having an average fluoride concentration of 3.94 mg/L. Thus, the fixed bed system produced defluoridated water with an average residual fluoride content of 0.18 mg/L, which is well below the 1–1.5 mg/L guideline limit recommended by the World Health Organization. In other words, the fixed bed column of bone char can be efficiently applied for removal of fluoride from water solutions with initial concentrations higher than or equal to 6 mg/L. Our results agree well with those reported by Badillo-Almaraz et al.[27] which showed that the best pH range for fluoride adsorption on hydroxyapatite is 7.0–7.5, when the mineral adsorbs 19 mg fluoride per 1 g solid.

In the 30 minutes, the rate of fluoride uptake was high enough, removing total mean percentages of 87.6, 94.5, 95.9, 96.8, 95.5 and 96.8% for well, cold spring and hot spring water, and Lanet and Njoro area ground water, respectively. This can be explained by recalling that the bone char composition includes 70–76% calcium phosphate, 6–9% calcium carbonate, 8–11% carbon and so on. The high removal efficiency of bone char may be attributed to an effect on mineral components other than carbon, because anions are known not to adsorb to activated carbon.[18] Our results compare favourably to a value of <0.8 mg/L of fluoride in effluent obtained in a study using a fixed bed of 1 T/h, in Northeast China, where the content of fluoride was 4 mg/L in ground water.[8] What is more, due to the high affinity of the bone char for the fluoride ions, it is evident that it is not worthwhile to continue the adsorption beyond 30 minutes.

### Effect of anions in drinking water on fluoride adsorption onto bone char

TABLES 3 and 4 summarise the data obtained before and after the progress of fluoride adsorption from drinking water. The average concentrations of phosphate, sulphate, carbonate, hydrogen carbonate, and chloride anions in the actual drinking water were 2.0, 17.1, 10.7, 296.7 and 410.1 mg/L, respectively. Phosphate and sulphate anions were not significantly adsorbed onto the bone char as their concentrations increased over time, whereas chloride, hydrogen carbonate and carbonate anions were somewhat adsorbed on the bone char. The concentration of phosphate and sulphate in the drinking water increased to reach mean concentration values of 88.8 to 100% PO<sub>4</sub><sup>3-</sup> and 14.8 to 82.5% SO<sub>4</sub><sup>2-</sup>, respectively, while those of chloride, hydrogen carbonate and carbonate decreased from mean values of 410.1, 296.7 and 10.7 to an average value of 334.2, 223.7 and 10.9 mg/L (n = 6 averaged values for CO<sub>3</sub><sup>2-</sup>), respectively.

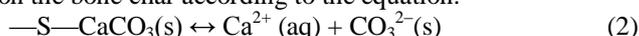
The results revealed that phosphate and sulphate ions were released from the bone char, but the chloride, hydrogen carbonate and carbonate anions were adsorbed onto the bone char. It was further observed that if the concentrations of phosphate and sulphate anions are high (>80 mg/L for PO<sub>4</sub><sup>3-</sup>; >50 mg/L for SO<sub>4</sub><sup>2-</sup>) in the drinking water, both anions adsorb onto the bone char. The solubility product of calcium phosphate,

calcium sulphate and calcium fluoride are  $1.0 \times 10^{-26}$ ,  $7.1 \times 10^{-5}$  and  $1.5 \times 10^{-10}$  at 25 °C,[28] respectively, which shows that calcium fluoride is the more stable compared with calcium phosphate but less stable than calcium sulphate present in the bone char.

**Table 3: Effect of monovalent anions in drinking water (Borehole water, spring/well water and tap water) on fluoride sorption on bone char at 25 °C**

Water source	Cl <sup>-</sup> mg/L		Percent Adsorbed	HCO <sup>-</sup> mg/L		Percent Adsorbed	CO <sub>3</sub> <sup>2-</sup> mg/L		Percent Adsorbed
	Initial	Final		Initial	Final		Initial	Final	
St Joseph	266.0	207.7	21.9	280.0	246.3	12.0	5.0	11.0	Released (54.5%)
Ngonda	166.0	131.7	20.7	265.0	229.8	13.3	11.0	9.0	18.2
Egerton	159.0	126.3	20.6	266.0	225.2	15.3	14.0	9.5	32.1
BH1	213.0	193.7	9.1	303.0	220.8	27.1	4.0	8.0	Released (50%)
BH2	140.0	97.2	30.6	375.0	278.0	25.9	12.0	11.3	5.8
Cold spring	282.0	241.3	14.4	268.0	210.2	21.6	17.0	10.0	41.2
Hot spring	302.0	277.3	8.2	257.0	222.8	13.3	14.0	13.8	1.4
Well (Belbur)	2024.0	1598.3	21.0	382.0	161.2	57.8	7.0	7.8	Released (10.3%)
Tap water	139.0	134.3	3.4	274.0	218.8	20.1	12.0	11.8	1.7

When the concentration of carbonate anions was less than 10 mg/L in the drinking water, the carbonate ion was also released from the bone char. This occurred because of the dissolution of calcite ( $K_{sp}CaCO_3 = 4.5 \times 10^{-9}$ )[28] present on the bone char according to the equation:



This reaction may also be responsible for the observed increase in the pH of the drinking water during the defluoridation process. Guedes et al.[21] reported that about 4% of calcium carbonate dissolution released  $4 \times 10^{-4}$  M CO<sub>3</sub><sup>2-</sup> in solution from a solid-liquid concentration of 10 mg/L. Thus, depending on the total phosphate, sulphate and carbonate concentrations and solution pH, solid phosphates, sulphates and carbonates can be formed in solution and hence, adsorb on the bone char.

**Table 4: Effect of sulphate and phosphates in drinking water (Borehole water spring/well water and tap water) on fluoride sorption on bone char at 25 °C**

Water source	SO <sub>4</sub> <sup>2-</sup> mg/L		Percent Released	PO <sub>4</sub> <sup>3-</sup> mg/L		Percent Released
	Initial	Final		Initial	Final	
St Joseph	4.6	7.2	36.1	87.9	60.9	Adsorbed (30.7%)
Ngonda	11.5	15.2	24.3	4.1	91.5	95.5
Egerton	14.0	17.3	19.1	6.8	60.8	88.8
BH1	15.3	19.1	19.9	1.4	69.2	98.0
BH2	12.9	37.6	65.7	1.7	84.2	98.0
Cold spring	2.5	14.3	82.5	<LOD	48.0	~100.0
Hot spring	20.0	27.4	27.0	<LOD	48.6	~100.0
Well (Belbur)	56.6	25.3	Adsorbed (55.3%)	<LOD	29.2	~100.0
Tap water	16.1	18.9	14.8	2.1	59.8	96.4

Nevertheless, the order of affinity of the anions for the adsorbent was:



This is associated with the size of the ion, surface charges on the bone char which become more negative at high pH, and differential pore development on the heterogeneous adsorbent (Fig. 2). This trend follows that that was reported by Johnston and Heijnen[29] for adsorption of anions on activated alumina in the pH range of 5.5–8.5 given below:



Exception is that sulphate and phosphate anions leached from the bone char. This may be attributed to dissolution of calcium phosphate (apatite) and calcium sulphate (anhydrite) in the bone char to release SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> anions. Studies have shown that the phosphate in bone char was exchanged for a fluoride ion in tandem calcium phosphate changed to calcium fluoride.[12] This led to an increase in concentration of phosphate ions on adsorption of fluoride ion onto the bone char.

In view of that, the effect of competing ions on adsorption of fluoride onto the bone char was statistically significant for the anions: hydrogen carbonate, chloride and carbonate, as a result of “salting out” effect since at observed high concentrations (TABLE 3), chloride, hydrogen carbonate and carbonate ions are extensively hydrated in water solution. This reduces the number of water molecules available for dissociation of fluoride ions causing the amount of fluoride ions in water to decrease, leading to the increase in the rate of fluoride uptake of between 87.6 and 97.3% by the bone char.

**Effect of metal ions on adsorption of fluoride onto bone char**

The presence of cations, in particular Ca<sup>2+</sup> and Mg<sup>2+</sup>, in drinking water can promote defluoridation to some degree by aiding transfer of the ions to the surface of bone char via precipitation. The Na<sup>+</sup>, K<sup>+</sup>, and Fe<sup>2+</sup> ions were absorbed by bone char while Mg<sup>2+</sup> was released into the water solution as summarised in TABLE 5. The presence of Fe<sup>2+</sup> in water had little effect, if any, on the adsorption of fluoride on the bone char as the percentage adsorption was between 0.0 and 70.8%, with about 50% of iron remaining unadsorbed. The amount of dissolved Mg<sup>2+</sup> ion was in the range 0.39–6.25 mg/L. The concentration of Mg<sup>2+</sup> ion released (percent released 30.8–100%) increased with the adsorption of fluoride ion onto the bone char (percent adsorbed 87.6–97.3%). This indicated that magnesium ions leached from the bone char. By the principle of electro-neutrality, Mg<sup>2+</sup> ions were required to balance the charges on released the PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> ions in water solution.

**Table 5: Effect of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, \*\*Ca<sup>2+</sup> and Fe<sup>2+</sup> ions in drinking water (borehole water spring/well water and tap water) on sorption of fluoride on bone char at 25 °C**

Source	Na <sup>+</sup> mg/L		Adsorbed (%)	K <sup>+</sup> mg/L		Adsorbed (%)	Mg <sup>2+</sup> mg/L		Released (%)	Fe <sup>2+</sup> mg/L		Adsorbed (%)
	Initial	Final		Initial	Final		Initial	Final		Initial	Final	
St Joseph	125.0	51.0	59.2	14.0	9.7	30.7	0.89	5.97	85.1	4.00	1.17	70.8
Ngonda	104.0	81.3	21.8	9.0	7.5	16.7	<LOD	0.83	≈100.0	4.33	2.00	50.8
Egerton	104.0	82.0	21.2	15.0	9.9	34.0	0.02	0.35	94.3	0.84	0.33	60.7
BH1	90.0	65.8	26.9	18.0	12.2	32.2	0.95	2.27	58.1	0.33	0.33	0.0
BH2	84.0	58.5	30.4	22.0	15.8	28.2	0.26	0.57	54.4	0.33	0.33	0.0
Cold spring	79.0	93.7	Re <sup>*</sup> 15.7%	20.0	14.8	26.0	0.08	6.25	98.7	1.00	0.78	22.0
Hot spring	135.0	15.0	88.9	22.0	15.0	31.8	0.07	5.68	98.8	0.67	0.67	0.0
Well (Belbur)	115.0	59.5	48.3	63.0	25.5	59.5	0.27	0.39	30.8	0.33	0.33	0.0
Tap water	110.0	44.7	59.4	22.0	14.3	35.0	0.05	4.83	99.0	0.30	0.29	3.3

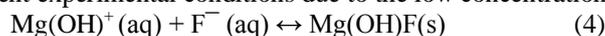
\*\*Ca<sup>2+</sup> = concentration of Ca<sup>2+</sup> ions in solution before and after fluoride adsorption was below detection limit and insignificant; Re\* = Percentage of Na<sup>+</sup> released.

Generally, the multivalent metal ions like Mg<sup>2+</sup> and Fe<sup>2+/3+</sup> have high affinities for anions such as CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> than for monovalent anions. Scott et al.[30] observed that the amount of fluoride removed is a function of the initial fluoride concentration and the amount of magnesium removed, and the relationship is shown by following equation:

$$F_r = F_i - (0.07 \times F_i \times \sqrt{Mg}) \quad (3)$$

where, F<sub>r</sub> and F<sub>i</sub> are residual and initial fluoride concentrations, Mg is concentration of magnesium removed, all expressed in mg/L.

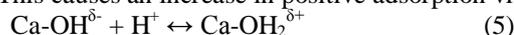
In their case, fluoride was removed by adsorption on the precipitated magnesium hydroxide after liming and at pH 9.0. While in our case the concentration of Ca<sup>2+</sup> ion in drinking water was negligible (TABLE 5) and the pH was < 9.0 and would not aid flocculation. Hence, there was no precipitation, if at all, of Mg(OH)<sub>2</sub>. Medellin-Castillo et al.,[18] reported that the hydroxyl anion did not competitively interfere with fluoride adsorption on bone char at initial pH of 8.41 for a concentration of 4.02 mg/L of fluoride in drinking water. Similarly, from our results, it would be reasonable to conclude that, under the experimental conditions, the hydroxyl ion did not interference with fluoride adsorption. Again, by the principle of ionic activity product, it could also be expected that MgF<sub>2</sub> will only precipitate when the concentration of Mg<sup>2+</sup> and F<sup>-</sup> in water exceeds the solubility product of F<sup>-</sup> (K<sub>sp</sub>MgF<sub>2</sub> = 7.4 x 10<sup>-11</sup>).[28] However, the following reaction is not possible under the current experimental conditions due to the low concentration of the hydrolysis product, Mg(OH)<sup>+</sup>:



These results suggest that fluoride removal by bone char is not limited to surface adsorption or precipitation alone, but also could occur by slow diffusion of the fluoride ions into the intra-particle pores of the adsorbent.[31,32]

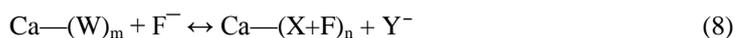
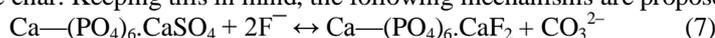
**Mechanisms of fluoride sorption**

It was found that the bone char had a significant ion exchange capacity for fluoride (TABLE 2). As already mentioned, the surface of the bone char is positively charged since the pH of the water is below the ZPC values. This causes an increase in positive adsorption via the reactions:[32]

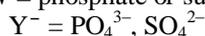


Thus, considering bone char adsorption mechanism, it is inferred that the active sites of calcium on the bone char surface can bind fluoride. The combined effect of chemical and electrostatic attraction between the bone surface sites and the fluoride ions are therefore responsible for adsorption of fluoride on adsorbent. However, because bone char is acid soluble, the operating pH of the drinking water in the range 6.8–8.13 was optimum for observed high fluoride removal capacity (TABLE 2) while at the same time minimising media loss.

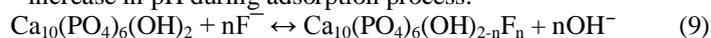
Secondly, the bone char also reacted with the fluoride ion by ion-exchange adsorption mechanism between the fluoride in solution and the carbonate (calcite), hydroxylapatite and calcium sulphate (anhydrite) comprising the bone char. Keeping this in mind, the following mechanisms are proposed:



where, W = phosphate or sulphate



At pH >6, fluoride ion is pre-dominantly adsorbed by the following mechanism, which was supported by the increase in pH during adsorption process:



These mechanisms are supported by the increase in concentrations of phosphate, sulphate, hydroxyl groups and to some extent carbonate ions, on adsorption of fluoride ion onto the bone char. This demonstrates that the phosphate, sulphate, hydroxyl and carbonate in the bone char were exchanged for a fluoride to form calcium fluoride product.

Studies have also shown that in the temperature range: [12] 283–315 K, the content of fluoride adsorbed increased with the increase in temperature indicating the endothermic nature of adsorption of fluoride onto the bone char. So, at 25 °C used in this study, the phosphate, sulphate, hydroxyl and carbonate in the bone char consumed heat energy when exchanging with the fluoride ions, showing that ion-exchange plays a vital role during the adsorption of fluoride onto the bone char. The interference of competing anions,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  as well as presence of  $\text{Mg}^{2+}$  ion in drinking water was less important on the removal of fluoride through adsorption on the bone char. None interference is supported by lack of formation of observable precipitates due to  $\text{CaF}_2$  and  $\text{Mg}(\text{OH})\text{F}$  in the water solutions.

#### IV. Conclusion

Bone char has high affinity for fluoride. The fixed bed system of 300mL bed volume of bone char produced treated water with an average of 0.17 mg/L of fluoride after equilibration for 30 minutes; which was less than the potable water quality standard for fluoride of 1.5 mg/L. The raw drinking water had fluoride content of between 1.58 and 5.89 mg/L. The removal of fluoride may be attributed to two processes, first, electrostatic ion-binding between the active positive sites of calcium in the bone char and fluoride ions, which led to an increase in pH of the water during the sorption of fluoride; and ion-exchange mechanism between calcium phosphate and calcium sulphate and fluoride ions. Moreover, high concentrations of chloride, hydrogen carbonate and carbonate anions in drinking water enhanced adsorption of fluoride onto the bone char due to “salting out” effect. However, the magnesium ion released into the water was not adsorbed or precipitated, but may only have adhered to the surface of the bone char through electrostatic attractions to the negatively charged surface at the final pH of  $\geq 8.0$  ( $\text{pH}_{\text{PZC}} = 7.9-8.4$ ). From the economic point of view, it is fair to conclude that bone char exhibits efficient fluoride removal capacity in ground water and could be a helpful solution for rural impoverished areas since it is inexpensive and locally available.

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