ASSESSMENT OF FLUORIDE LEVELS IN DIFFERENT WATER SOURCES IN LOWLAND AREAS OF BOMET COUNTY, KENYA AND REMEDIATION WITH *MORINGA OLEIFERA* SEEDS

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ABSTRACT

The use of water with high fluoride concentration poses a health threat to millions of people around the world. The objectives of the study were to assess the levels of fluoride in the water sources in the lowland areas of Bomet County and remediation with *moringa oleifera* seed extract. Water samples were colllected in dry season in the month of January 2012 and rainy season in the month of April 2011 from different water sources. The samples were therefore analysed for pH, TDS, conductivity, Na^+, K^+, Mg^{2+}, Ca^{2+} , F^- and HCO_3^-. The results showed the variations of the analysed parameters in water samples as follows: F^- 0.2-6.07 mg/L, K^+ 2.0-38.4 mg/L, Na 8.0-432.5 mg/L, Ca^{2+} 2.5-23.54 mg/L, Mg^{2+} 0.05-14.4 mg/L pH 5.7- 9.1, EC 0.09-2.01 mS/cm, TDS 42-1316 mg/L. *Moringa oleifera* powder was also studied as an alternative adsorbent for removal of fluoride from aqueous solution. Sorption parameters such as pH, contact time, adsorption kinetics, initial ions concentration and adsorption capacity. The results showed that the optimum pH for biosorption of fluoride was 6.0. Contact time for fluoride was observed to occur after 120 min. Biosorption kinetic data fitted well with pseudo-second-order kinetic model (R^2 , 0.9805). The biosorption isotherms for the biosorbent fitted better with the Langmuir isotherm model than Freundlich isotherm model. In conclusion, the study revealed that *Moringa oleifera* seed powder is an efficient biosorbent for removal of fluoride from aqueous solution.

Keyword: Fluoride; defluoridation, Bomet County, biosorption and *Moringa oleifera*.

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INTRODUCTION AND LITERATURE REVIEW

Water is one of the elements that is essential for sustenance of all forms of life and is available in abundance in nature covering approximately three quarters of the surface of the earth A large proportion of people in developing countries lack access to safe drinking water. Major substances that are found to contaminate water are fluorides, heavy metals and organic waste. The presence of fluorides in high concentration tends to pose health risks such as dental fluorosis, skeletal fluorosis and in high concentrations crippling (Kloos *et al.*, 1999). According to WHO, 1.1 billion people in developing countries lack access to safe water for drinking, personal hygiene and domestic use (WHO, 2004). In Kenya most of the population continues to fetch water from rivers, wells, streams and water pans without any form of treatment. Continued consumption of water with fluoride levels above 1.5 mg/L can result in fluoride related diseases such as dental and skeletal fluorosis. Therefore, there is need to control intake of fluorides. In order to remove excess fluoride in water, it is essential to determine and monitor the causal factors of enrichment of fluoride concentration in water (Ahmed *et al.*, 2003). The removal of fluoriode from potable water has seen many attempts over the years, using a wide variety of material giving various efficiencies.

Defluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes (Bulusu,1979). The most commonly used methods are Nalgonda technique, where alum is mixed with lime at the ratio 700/300 mg/L, was tested at a research station in Arusha, Tanzania and reduced fluoride concentration from 21 to 5 mg/L at pH 6.9 (Bregnhoj,1990). The bone char method has not been accepted by some communities and use of natural plat materials have been tried such as Moringa Oleifera and rice husks (Vardhan *et al.*, 2011). Studies conducted in India, have further demonstrated Moringa oleifera seeds have remarkable defluoridation efficiency, even better than that of activated alumina (Subramanian *et al.*, 1992, Ranjan *et al.*, 2009). Desirable characteristics of defluoridation processes include cost effectiveness, easiness to be operated (by local population), independent of influences of such factors as fluoride concentration, pH (acidity/alkalinity) and temperature, no effect on taste of water, and not requiring the inclusion of other undesirable substances (e.g.. aluminum) for treatment of water (Hardman *et al.*, 2005).

The water sources in Rift valley are contaminated with fluoride and fluoride concentration tends to vary. In this study, the level of fluoride in different water systems in the lowland areas of Bomet County, Kenya were assessed. Several documented studies have been done in the central part of Kenyan Rift Valley such as Nakuru (Mavura *et al*., 2003; Naslund *et al*., 2005; Nair *et al*., 1984; Njenga 2004), Elementaita (Kahama *et al*., 1997) and Baringo (Naslund *et al*., 2005; Mutonga *et al*., 2006). Further the use of moringa oleifera to clean fluorides in water was also done.

MATERIALS AND METHODS

Study area

The study area is in the lowland area of Bomet County, which covers part of Bomet district and sotik district. It is situated in Rift Valley region (southern part). The area is defined by coordinates, longitude 35^0 12 00 E and latitude 00^0 56 00 S. It covers an area of about 1884 km^2. This lowland area is partly Semi Arid. There are no major boreholes and the main source of drinking water are water pans, few springs, wells and river water.

Instrumentation

Conductivity, total dissolved solids and temperature were measured using a digital potable TDS meter, fitted with temperature probe (TDS meter 4076,Jenway, UK). A portable digital meter was used to measure pH during sampling. Potassium and sodium ions were measured using Corning Flame Photometer model 410 from science products of Halstead, Essex, England. Magnesium and calcium was determined using atomic absorption spectrophotometer S11 (Thermo Jarrell Ash, 1978). The fluoride meter used was an ion selective combination Electrode, model: Thermo ORION, 96-09 manufactured by Orion Research, inc. of Beverly Mass, USA.

Reagents

Orion reagents, TISAB (total ionic strength adjustment buffer) and fluoride standards were used for fluoride analysis. Analytical grade salts were used to prepare the stock solutions of 1000 ppm of sodium, potassuim, calcium and magnesium. Distilled water was used in all solutions prepared. Analytical grade hydrochloric acid (37%) from ReAgent Chemical services (UK) was used. The acetate buffer was prepared using sodium acetate and acetic acid from Sigma –

Aldrich (USA). The pH values were adjusted using sodium hydroxide pellets (purity 98%) and nitric acid (65%) both from ReAgent Chemical services (UK).

Sample collection

30 water samples were collected from rivers, water pans, springs and boreholes within the study area. Water samples were collected during the rainy (April- 2011) and 28 samples in dry season (January-2012) in the same sampling points. Clean 500 mL plastic bottles were rinsed several times with distilled water and twice with water which were being sampled. Samples were transported to Egerton university laboratory and kept refridgerated at 4^0 C awaiting analysis.

Determination of K^+, Na^+, Ca^{+2}, Mg^{+2} ions and HCO_3^-

Analysis of K, Na, Ca and Mg working standards and samples were carried out using flame atomic absorption spectrophotometer and atomic absorption spectrometer. Analysis of bicarbonates was done by using AOAC official method 920.124, titrimetric method.

Determination fluoride by standard addition method

Fluoride analysis was carried out using fluoride meter an Ion- Selective Combination Electrode, model: Thermo ORION, 96-09. 50 mL of the water samples and 5 mL of the TISAB III were measured into a 150 mL plastic beaker and stirred thoroughly. The electrode were rinsed with distilled water, blot dried, and placed into sample in a beaker. When a stable reading was displayed, the pontential (E_1) in millivolts were recorded. 10.0 ML of a 8.0 ppm fluoride standard solution were pipetted into the beaker and again stirred thoroughly. When a stable reading was displayed, the new pontential (E_2) were recorded. The first reading (E_1) were subtracted from the second(E_2) to find change in pontential, ΔE**.** The concentration of fluoride in the sample was calculated as follows;

$$Csample = QCstandard$$

Where, $Csample$ = sample concentration

$Cstandard$ =Standard concentration

$$Q = P \,/\, [(1 + P)10^{\Delta E/S}] - 1$$

$\Delta E = E_2 - E_1$

S = slope of the electrode **Hint:** obtained from manual instructions.

P = Volume of standard /volume of sample

Preparation of *Moringa Oleifera* seeds powder

Dried *Moringa Oleifera* pods were obtained from a local vendor in Nairobi. They were shelled and kernels dried in sunlight, they were then kept in an oven at 50 °C for 24 hrs. The seeds were grounded into powder and then sieved, using a sieve with an aperture of 0.5 mm to obtain almost uniform particle size. About 50 g of crushed *moringa oleifera seed* were fed to a lab-scale Soxhlet extractor fitted with a 1 L round-bottom flask and a condenser to remove oil. The extraction was executed for 6 hours with 350 mL of hexane as solvent. Seed cake obtain was then dried and used for Biosorption studies.

Fig. 1 *Moringa oleifera* pods and seeds

Optimization of pH

Batch biosorption experiments were conducted on model solutions of fluoride to determine the optimum pH for fluoride uptake by *moringa oleifera* seed extract. Fluoride stock solution was diluted to 200 µg/mL using 0.1 M acetate buffer solution and divided into 50 mL batches. Batches were adjusted to pH values of 2.0, 3.0, 4.0, 5.0, 5.5, 6.0 ,7.0 and 8.0 using sodium hydroxide and nitric acid. One batch was equilibrated with 2.0 g of ground *moringa oleifera* seed extract for two hours. The solution was filtered through a 0.45 µm filter membrane and the fluoride ion concentration in the filtrate determined by fluoride ion selective electrode. All experiments were done in triplicate.

Optimization of contact time

Stock solution (1000 µg/mL) of fluoride was diluted with acetate buffer to obtain 500 mL solutions of 10 mg/L of fluoride. The pH of the solution was adjusted to the optimum value of 6.0. 2.0 g of dried and ground *moringa oleifera* seed extract was added to 500 mL of each solution and stirred continuously with a magnetic stirrer at 300 revolutions per minute (rpm). 10 mL portions of this solution were withdrawn at 0, 10, 15, 20, 25, 30, 40, 50, 60, 75, 90, 105, 120 and 140 minutes. Each portion was immediately filtered through a 0.45 µm membrane filter after being withdrawn and the residual fluoride ion concentration in the filtrate determined by ion selective electrode. All experiments were done in triplicate. A plot of percentage fluoride ion removal against time was used to determine the contact time for the adsorption process.

Effect of Initial Fluoride Concentration

The initial concentration which gives rise to the highest fluoride uptake was investigated. The effect of initial fluoride concentration on the fluoride removal efficiency of the *moringa oleifera* seed extract was tested for 5, 10, 15 and 20 mg of fluoride/L of solution. Each of the Solutions were equilibrated with 2.0 g of dried and ground *moringa oleifera* seed extract at optimum pH 6.0 for two hours with stirring at 300 rpm. After equilibration, each solution was filtered through a 0.45 µm membrane filter and the residual fluoride ion concentration in the filtrate determined by fluoride ion selective electrode. The data was fitted to both Freundlich and Langmuir adsorption isotherms and the adsorption capacity calculated from the linearized Langmuir isotherm. A plot of equilibrium metal uptake (mg/g) against initial fluoride ion concentration was done to determine the optimum initial fluoride concentration. The fluoride concentration retained in the adsorbent phase, *q*e (mg/g), was calculated according to :

$$qe = \frac{CO - Ce}{W} \times V \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$\%REMOVAL = \frac{CO - Ce}{C_o} \times 100\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where *q*e is the amount of fluoride adsorbed (mg/g); *C*o and *C*e are the initial and residual concentration of fluoride in solution at equilibrium (mg/L), respectively; *V* is the volume of aqueous solution (L) and *W* is the dry weight of the ardsorbent (g).

RESULTS AND DISCUSSION

Physico-chemical parameters

For 30 samples of water collected in rainy season, 17 (56.7 %) samples had fluoride levels above WHO maximum permissible limits (1.5 mg/L). Nine samples (30.0.%) were below the minimum level (1.0 mg/L) and the rest were within permissible levels. Metal ions analysed have the following ranges: Na^+ ,7.0-432.5 mg/L, K^+ 2.0-38.4 mg/ L, Ca^{+2}, 0.19-20.7 mg/L and Mg^{+2} 0.05-9.28 mg/L. The levels of anions ranged as follows: HCO_3^- : 51.85-527.65 mg/L , F^- , 0.24 mg/L- 6.95 mg/L in differrent water sources . Electrical conductivity ranged from 0.09-2.01 mS/cm, TDS 46-1316 mg/L and pH 5.7-9.1. 28 samples were collected in the dry season (January-2012) and 18, (64.3 %) samples had fluoride levels above WHO maximum permissible limits (1.5 mg/L). 10 samples (35.7%) were below the minimum level (1.0 mg/L). The levels of fluoride ranged from 0.23-6.03 mg/L. Metal ions analysed had the following ranges : Na^+ ,13.98-167.33 mg/L, K,$^+$ 7.42-42.51 mg/ L, Ca^{+2}, 2.50-23.54 mg/L and Mg^{+2}, 1.26- 6.19 mg/L. The levels of HCO_3^- range from 45.78 to 317.06 mg/L. TDS ranged from 86.80-684.42 mg/L, Electrical conductivity 0.10±0.01-0.97±0.19 mS/cm and pH 7.04-7.85. Mean concentrations of all physico-chemical parameters fall within WHO acceptable levels for drinking water except fluoride in some water sources. The fluoride contents in rivers (0.38±0.09) are very low, due to dilution effects caused by precipitation. It is almost the same concentration of about 1.0 mg/L, that can be measured in spring (0.83±0.00)and shallow wells(0.73±0.10). The fluoride level in the boreholes (4.37±0.50 mg/L) and water pans (2.74±0.30 mg/L) are above the WHO maximum permissible level of 1.5 mg/L. High level of fluoride in boreholes is atributed to presence of volcanic rocks and long contact times due to slow movement of water in bedrocks. Variation of fluoride from one source to another is attributed to the irregular distribution of fluoride bearing minerals in the soils and bedrocks. High fluoride is associated with the distribution of volcanic rock occurring in the rift area of kenya. Volcanic rock is kown to be rich in fluoride, particularly in form of fluospar, CaF_2 (Nyamweru, 1980).

The bicarbonate and sodium content was found to be high during both seasons. In the study area high fluoride water is generally associated with high bicarbonates values and low calcium and magnesium contents. The combination of fluoride and sodium forms water-soluble salt. The content of fluoride ion increases relatively because of increase of 90p;sodium in groundwater, the opportunity for sedimentation of calcium fluoride (CaF2) is greatly decreased (Gupta *et al.*, 2005).

Seasonal Variation Of Fluoride

The seasonal variation indicates fluoride levels are high in rainy seasons when compared to dry seasons**.** The variation in fluoride levels is minimal due the fact that the dry spell was so short in that year.

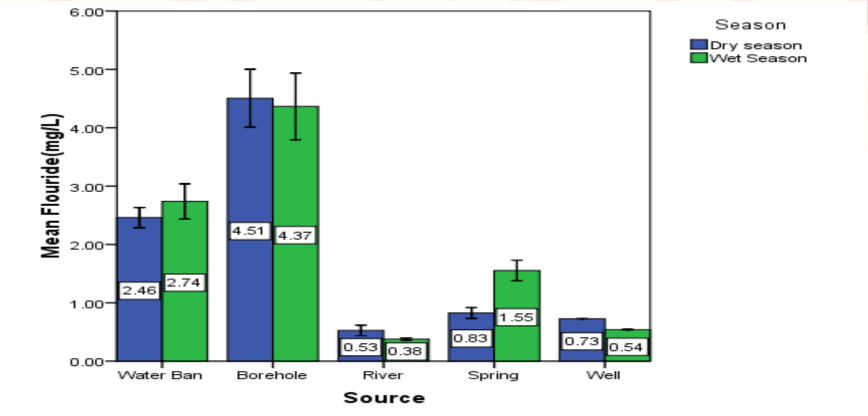

Figure 2: Seasonal variation of fluoride in different water sources in the study area.

Comparing mean fluoride concentrations in the different sources, fluoride levels in dry season are higher than rainy season. Mean concentration of fluoride ions varied from 0.38 to 4.37 mg/L and 0.53 to 4.51 mg/L in wet and dry season respectively. Minimum fluoride concentration observed during wet could be due to the availability of large volume of water leading to dilution of chemicals present. High concentration during dry season could be due to depletion of water leading to the concentration effect. The concentration levels of fluoride ions in boreholes and water pans in both seasons were above the limit set by WHO for fluoride in drinking water (1.5mg/l). This could be attributed to weathering and leaching of bedrock with a high fluoride content. Same results were reported by Ombaka O. *et al.*, 2013 and Okoo J.A. *et al.*, 2007. Fluoride ranges for rainy and dry seasons were almost similar. This implied that people in high fluoride areas were exposed to high fluoride water throughout the seasons.

Cleaning of fluoride in water by *Moringa Oleifera* seeds extract

Fluoride removal by coagulation with *moringa oleifera* seeds was investigated in part of this study. Model fluoride solutions of 10 mg/L, was subjected to a coagulation process with aqueous extracts of *moringa oleifera* seed extract at room temperature for all sorption studies. The coagulation process with 2.0 g/l of *moringa oleifera* seed extract, were able to remove fluoride of initial concentration of 10.0 mg/L by 81.7 % in the treated water, making it posssible for rural communities without any water treatment to use this water.

Biosorption studies

Biosorption studies involved the optimization of pH, contact time and adsorption capacity of fluoride. Mechanism of adsorption depends on the physical and or chemical characteristics of adsorbent.

Optimization of pH

The effects of pH is considered in the sorption process because it may affect both the properties of the adsorbent and the composition of the solution . It is also important due to the ionisatin of surface functional groups and composition of solutions. The residual fluoride concentrations after batch equilibration with *moringa oleifera seed extract* at various pH values were determined. The lower concentration of fluoride observed in the filtrates were due to removal of fluoride by biosorption. Removal of Fluoride by *moringa oleifera seed extract* increased from

15.5% to 81.9% as pH was increased from 2 to 6. From pH 7 to 8 the Fluoride removal decreased from 80.9% to 78.9%.

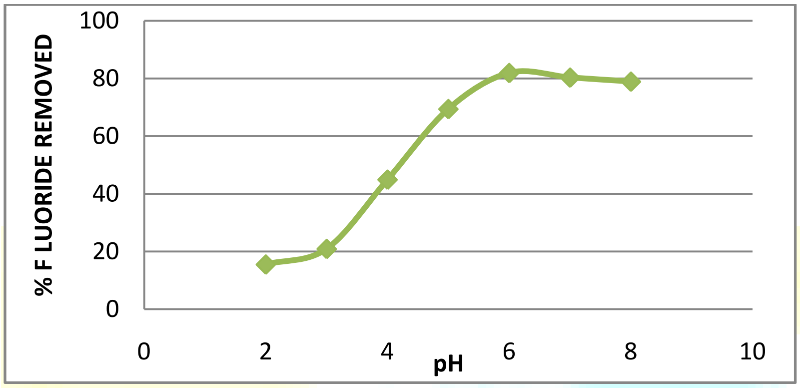

Figure 3: Percentage of fluoride removal at different pH values.

At low pH value below 4, H^+ ions reacts with fluoride ion to forms hydrofluoric acid which implies a decrease in the concentration of fluoride ions in solution reducing fluoride biosorption. As solution pH rises, the functional groups become negatively charged, inhibiting fluoride biosorption by this material, and the curve starts to drop. This behavior may me explained because when the pH of the solution increases to 8, the number of positively charged sorbent sites decreased and the number of –OH groups increased. Therefore, the positive sites of the sorbent and the presence of –OH groups are likely responsible for the low sorption at pH values higher than 8. Based on these facts, it can be deemed that the optimum pH values for fluoride biosorption is 6.0.

Effect of Contact Time

The minimum time required for quantitative uptake of fluoride ions from solution was determined by following concentration of model solutions over a 150-minute time interval at room temperature. The changes in concentration are shown in figure 5. Effect of contact time on the fluoride removal efficiency was studied using the mean residual fluoride concentration results obtained from 2.0 g/L *moringa oleifera* seed extract applied, to remove fluoride ion from water sample of initial fluoride concentration of 10.0 mg/L at pH 6.0. Fluoride removal efficiency increased from 34.2 % to 81.7 % as the contact time between the fluoride and *moringa oleifera* seed extract increased from 15 to 150 minutes. Rapid increase in the percent of fluoride removal, 74.9 % was observed within the first 60 minutes. The efficiency of fluoride removal was almost negligible for the rest of the remaining minutes.

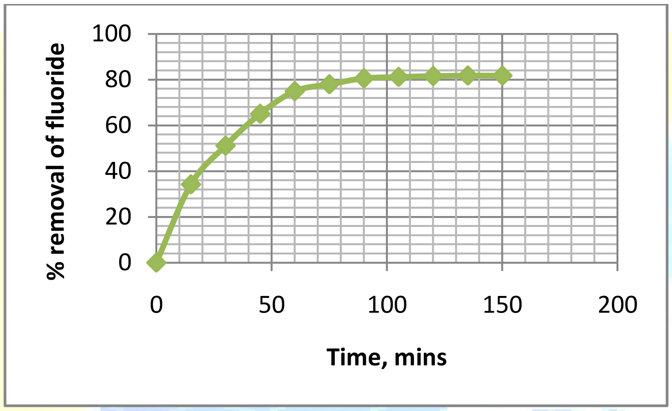

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Figure 4: Percentage fluoride removal by biosorption at different contact times.

After 120 mins, further increase in the contact time did not remarkably increase the uptake of fluoride due to deposition of fluoride ions on the available binding sites of the *moringa oleifera* seed extract, where it has attained equilibrium. This observation can be explained as, initially the binding sites were open and fluoride ions interacted easily with the sites. The concentraion differnce between bulk solution and the solid liquid phase interface was initially higher, which leads to higher rates of adsorption as observed in first 60 minutes. The fluoride removal efficiency decreased for the rest of remaining time due to saturation of binding sites.

Optimum dose

Optimum dose of the *moringa oleifera* seed extract on the removal of fluoride from water was analyzed using the results obtained from the measurements of the residual fluoride concentration using initial concentration of 10 .0 Mg/L of fluoride, at pH 6.0 and contact time of 105 min for 0.5, 1.0, 2.0, 3.0 and 4.0 g/L of the doses of the *moringa oleifera* seed extract.

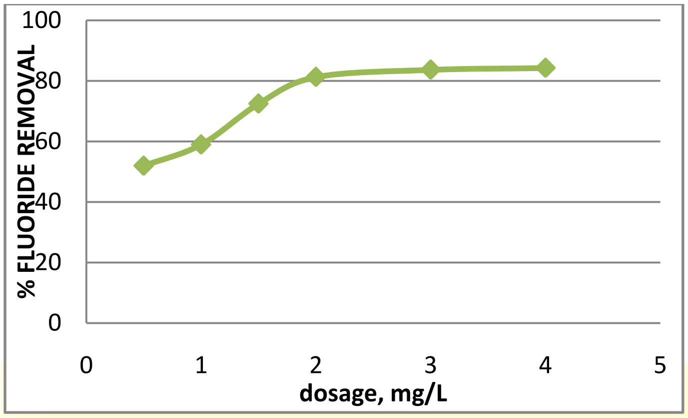


Figure 5: % fluoride removal by biosorption at different at different doses of *moringa oleifera* seed extract.

It is observed that fluoride removal increases with an increase in the amount of ardsorbent. For all the triplicate experiments, initial fluoride concentration was fixed at 10.0 g/l , at 6.0 pH and a contact time of 2 hours.

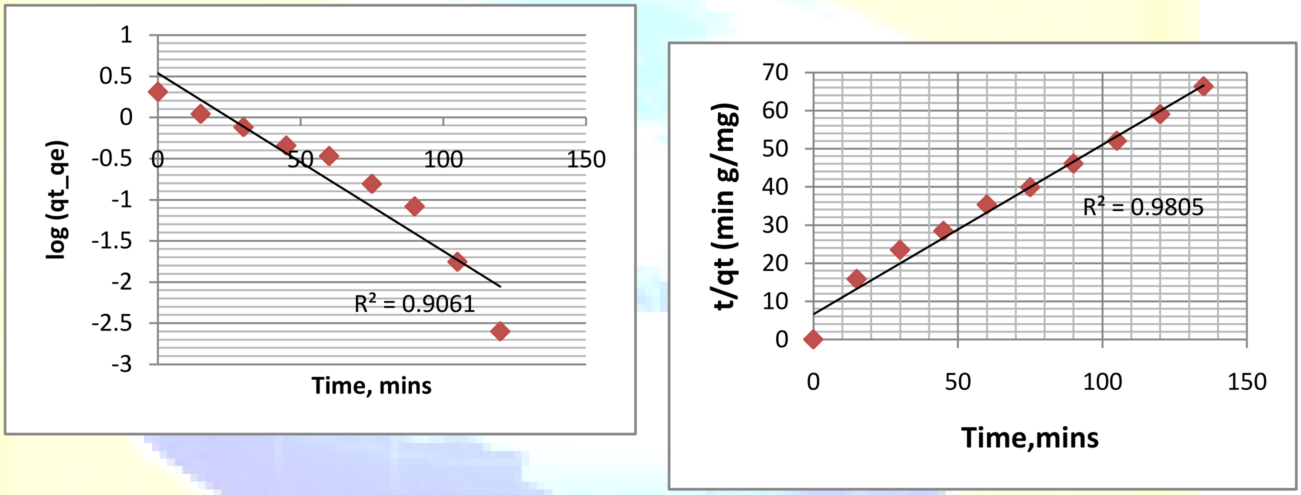
Other defluoridation studies using bioadsorbents prepared from the leaves of neem (*Azadirachta indica*), pipal (*Ficus religiosa*) and khair (*Acacia catechu willd*) trees (Jamode *et al.*, 2004); 20% Lanthanum – modified chitosan (Kambel *et al.*, 2007) and nano – scale aluminum oxide hydroxide (Wang *et al.*, 2009) also revealed similar results on the effect of the dose applied. The increased in fluoride removal efficiency of the adsorbents with increasing dose might be due to the increase in enhanced active binding sites available for fluoride uptake (Tembhurkar and Dongre, 2006; Kambel *et al.*, 2007; Wang *et al.*, 2009).

Order of reaction

The variation of fluoride ion concentration with time during the adsorption process was used to follow the kinetics of the adsorption until equilibrium was achieved. The mass q_t of fluoride adsorbed after time t is related to the equilibrium fluoride uptake q_e by the integrated first and second order equations:

$$k_1 t = \ln q_e - \ln(q_e - q_t) \quad \text{and} \quad \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^{2}}$$

respectively, where k_1 and k_2 are the first and second order rate constants. A plot of $\ln(q_e - q_t)$ against time (minutes) was used for the first order linearity test, while a plot of $\frac{t}{q_t}$ (min g/mg) against time (minutes) was used for the second order linearity test and the calculation of q_e, which is the fluoride uptake in milligrams per gram of biosorbent at equilibrium. The order of reaction for fluoride was deduced from the linearity of the respective plots. Figure (7) give the slopes and the R^2 values from which q_e and the linear correlation coefficients may be obtained.



(a) **(b)**

Figure 6. First (a) and second (b) order linearity test for fluoride adsorption on *moringa oleifera* seed extract

The second order plot for fluoride has higher R^2 value than the corresponding first order plot as shown in figure 6 above. Since the correlation co-efficient (R^2) is 0.9805 and the experimental fluoride uptake at equilbrium value 2.045 mg/g is consistent with calculated one, the adsorption system studied could well be explained by pseudo-second-order kinetic model at all time intervals than the pseudo first- order kinetic model (R2= 0.972).

Table1. Kinetic parameters for fluoride adsorption on *moringa oleifera* seed extract

First order	Second order	

	Initial concentration, (mg/L)	Calculated fluoride uptake at equilbrium q_e, (mg/g)	R^2	Calculated fluoride uptake at equilbrium q_e, (mg/g)	R^2	Experimental fluoride uptake at equilbrium q_e, (mg/g)
Fluoride	10.0	2.9614	0.9061	2.2665	0.9805	2.045

The process is therefore second order for fluoride. The low R^2 value obtained for first order indicate that sorption is not occurring exclusively onto one site per ion. In second order mechanism, the overall rate of F^- sorption process appear to be controlled by the chemical process, through sharing of electrons between biosorbent and sorbate.

Adsorption capacity and optimum initial fluoride ion concentration

The equilibrium concentrations C_e of fluoride in the filtrates were determined by fluoride- ion selective electrode and reported in Table 8 together with the corresponding initial concentrations, C_i and the calculated fluoride uptake at equilibrium, q_e. The data was fitted to the linearized Freundlich and Langmuir isotherms represented by the equations

$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$ and $\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}}$, respectively, where q_{max} is the adsorption capacity, b is a Langmuir constant, K_F and n are Freundlich constants. Linear regression coefficients (R^2) were used to deduce the isotherm which best fitted the data. **Table 2.** Equilibrium concentrations C_e (μg/mL) and fluoride uptake q_e (mg/g) at equilibrium

Fluoride concentration, C_i (mg/L)	5.0	10.0	15	20
C_e	0.34±0.02	1.92±0.04	6.830±.01	11.02±0.04
q_e	1.165	2.02	2.0425	2.245

The adsorption capacity q_{max} was obtained as the reciprocal of slope of the linearized Langmuir plot $\frac{C_e}{q_e}$ against the equilibrium concentration C_e, and the Langmuir constant b from the y – intercept .

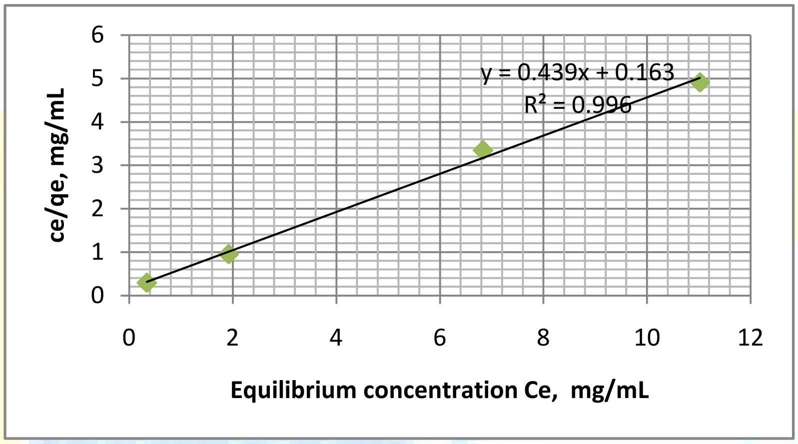


Figure 7. Linearized Langmuir plot for fluoride.

The adsorption capacity of was *moringa oleifera* seed extract found to be 2.2748 mg/g for fluoride (Table 3). These results show that the adsorption capacity for fluoride compare well with those of other biosorbents in literature.

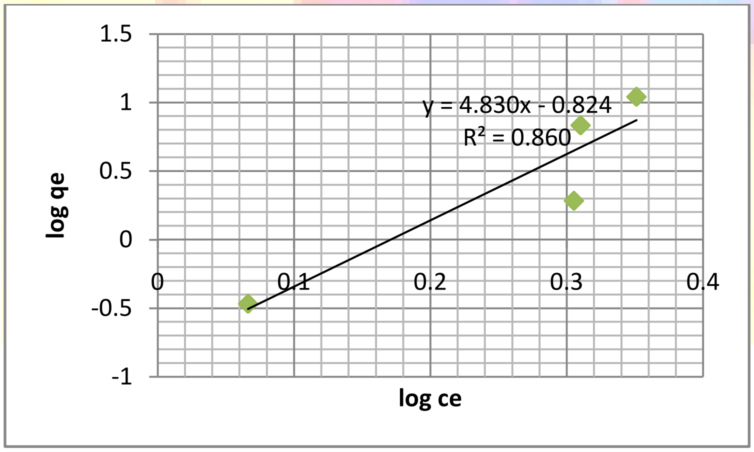


Figure 8. Linearized Freundlich plot for fluoride.

It is evident from a comparison of the values of coefficient of correlation (R^2) that the equilibrium adsorption of Fluoride on to follow *moringa oleifera* seed extract s Langmuir adsorption isotherm model which reflects apparent monolayer adsorption on a more or less homogeneous surface of uniform energy levels. The same results have been obtained by use of other biosorbents in literature, Vivek and Karthikeyan (2011) Valencia-Leal *et al.*, 2012 and Pandey *et al.*, 2012.

Table 3. Calculated adsorption isotherm parameters for metal adsorption

	Langmuir parameters			Freundlich parameters		
	R	b (L/mg)	q_{max} (mg/g)	R	K_F	n
F^-	0.9967	2.690	2.2748	0.8606	0.496	0.207

According to Freundlich model the parameter k_F should have values lying in the range of 1 to10 for classification as favorable adsorption (Sujana et al., 2009). K_F (0.1496) and n (0.207) were calculated from the slopes of the Freundlich plots. According to Kadirvelu and Na-masivayam (2000), n values between 1 and 10 represent beneficial adsorption. The magnitude of K_F and n shows easy separation of fluoride. The value of n, which is related to the distribution of bonded ions on the sorbent surface, is indicating that adsorption of fluoride is unfavorable. A smaller value of nF indicates a weaker bond between adsorbate and adsorbent and also it indicates the adsorbent surface to be of heterogeneous nature. The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL, which is defined as

$$RL = 1/(1 + bCo)$$

where b is the Langmuir constant and Co is the initial concentration of fluoride. The RL value 0.0358 obtained indicates the shape of isotherm. According to McKay *et al.* (1982), RL values between 0 and 1 indicate favourable adsorption. The value of RL in this study lies within the stated range, meaning the adsorption was favourable.

Conclusion

The level of fluoride concentration was found to be more than WHO value of 1.5 in all the boreholes sampled (mean of 4.51 mg/L in dry season and 4.37 mg/L in wet season), water pans had a mean level of 2.46 mg/L in dry season and 2.74 mg/L in wet season of while rivers had 0.53 mg/L in dry and 0.38 mg/L in wet seasons. Springs had fluoride levels of 0.83 mg/L in dry and in wet 1.55 mg/L ,while shallow wells showed a level of 0.73 mg/L in dry and in wet 0.54 mg/L. From the results rivers, springs and wells are safe to use unlike other sources.

Crushed *moringa oleifera* seed extract had higher fluoride reduction efficiency from 10.0 mg/L to 1.83 mg/L. In order to mitigate the debilitating effects of dental fluorosis in the area low cost defluoridation methods should be introduced for example use of *moringa oleifera* seed extract. The biosorption and biomonitoring study conducted in this work provides significant information regarding suitability of *moringa oleifera* seed extract as a biosorbent for the fluoride. Adsorption parameters were determined. The best pH for adsorption for fluoride was found to be 6.0 at optimum contact time of 120 minutes using optimum dosage of 2.0 g/L of *moringa oleifera* seed extract. In general, it can be concluded that *moringa oleifera* seed extract have good properties for the sorption of fluoride from aqueous solutions. The pseudo-second order model describes the fluoride sorption kinetic using *moringa oleifera* seed extract . The Langmuir model best describes the isotherm's experimental data, which may indicate that the sorption mechanism of fluoride ions on *moringa oleifera* seed extract is chemisorption on a homogeneous material.

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