ASSESSMENT OF FLUORIDE LEVELS IN DIFFERENT WATER SOURCES IN LOWER REGION OF BOMET COUNTY, KENYA AND REMEDIATION USING *MORINGA OLEIFERA* SEED CAKE

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other University

Signature___________________________________ Date____________________

Chelangat Bornes Mosonik

This thesis has been submitted for examination with our approval as university supervisors.

Signature___________________________________ Date______________________

Prof. W.J Mavura,
JKUAT, Kenya

Signature___________________________________ Date______________________

Dr. Jackson Kiptoo,
JKUAT, Kenya

DEDICATION

This work is dedicated to my husband and my children.

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LIST OF ABBREVIATIONS/ ACRONYMS

AAS	Atomic Absorption Spectroscopy
CCEFW	Consultative committee on excess fluoride in water
CDN	Catholic Diocese of Nakuru
ICPS	International Programme on Chemical Safety
ISE	Ionic Selective Electrode
KEBS	Kenya Bureau of Standards
TISAB	Total Ionic Strength Adjustment Buffer
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WQA	Water Quality Authority

ABSTRACT

The use of water with high fluoride concentration poses a health threat to millions of people around the world, therefore there is need to determine the levels of fluoride in water for domestic use and to find ways of removing these ions from water.

The objectives of the study were to assess the levels of fluoride in the water sources in the lower region of Bomet County and to determine remediation effectiveness of *moringa oleifera* seed cake. Water samples were collected in wet season in the month of April 2011 and dry season in the month of January 2012 from different water sources. The samples were analyzed for pH, Total dissolved solids, conductivity, Na^+, K^+, Mg^{2+}, Ca^{2+}, F^- and HCO_3^-. Ion selective electrode method, Thermo-Orion 96-09 model was used for the fluoride determination in the laboratory. Flame photometer was used for analysis of Na^+ and K^+ ions and Flame atomic absorption spectrometry was for Mg^{2+} and Ca^{2+} respectively. Bicarbonates were analyzed by standard method 920.194 (titration) approved by the Association of Official Analytical Chemists (AOAC). Data obtained was subjected to Microsoft Excel and analysis of variance. For both dry and wet seasons, mean concentrations for all selected physico-chemical parameters were within the KEBS and WHO permissible limits except for fluorides in some sources (borehole and water pan water) were found to be above 1.5 mg/L permissible limit. *Moringa oleifera* seed cake was studied as an alternative adsorbent for removal of fluoride from aqueous solution. 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 and therefore adsorption is limited to the formation of a monolayer. In conclusion, the study revealed that *Moringa oleifera* seed powder is an efficient biosorbent for removal of fluoride from aqueous solution.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 Background Information

Water is one of the essential substances for sustenance of all forms of life and is available in abundance in nature covering approximately three quarters of the surface of the earth. The quality of waters is one of the most important criteria that determine its usefulness for a specific need and as such not all the water are fit for drinking. Consequently, large proportion of people in developing countries lack access to safe drinking water (UNICEF, 2009). Major substances that are found to contaminate water are fluorides, heavy fluorides and organic waste. The presence of fluorides in high concentration tends to pose health risks (Kloos *et al.*, 1999). The dental and skeletal fluorosis is irreversible and no treatment exists. The only remedy is prevention by keeping fluoride intake within the safe limits [Teutli-Sequeira *et al*., 2012 and Sujana *et al.,* 2009). Fluoride is a persistent and non-degradable poison that accumulates in soil, plants, wild life and in humans. Fluoride can be enriched in natural waters by geological processes. Besides, there can also be contributions from industries. High fluoride containing wastewaters are generated by thermal power plants, rubber, fertilizer and semiconductor manufacturing, glass and ceramic production and electroplating industries. According to the World Health Organization guidelines and recommendations in the areas with a warm climate, the optimal fluoride concentration in drinking water should remain below 1 mg/L, while in cooler climates it could go up to 1.2 mg/L (Jiménez-Becerril *et al.*, 2012).

Drinking water is often the main source of fluoride intake by humans, especially in areas where fluoride concentration in groundwater and/or surface water are high (Jeffery *et al*., 1998; Edmunds *et al*., 2005; Tekle *et al*., 2006). In some areas, foodstuffs and / or indoor air pollution due to the burning of coal may make significant contributions to the daily intake of fluorides (Nielson *et al*., 2002). Low concentration of fluoride (about 1.0 mg/L) in food and drinking water can prevent dental carries; however uptake of high amounts causes severe diseases in teeth and bones (Shomar et al., 2004; Fung *et al*., 1999). A study carried out to determine the levels of fluoride in foods indicate that food categories with the highest mean fluoride levels were fish (2.118 mg/L), beverages (1.148 mg/L), soups (0.606 mg/L) and tea (4.97 mg/L) (Agency for Toxic Substances and Disease Registry, 2001). Studies in Kenya have established that a greater population in most parts of Rift Valley in the country is susceptible to fluorosis due to exposure to great proportion of fluoride in drinking water (Gikunju *et al.*, 2002) and other beverages such as raw vegetables juices (Njenga *et al.*, 2005) and also in milk (Kahama *et al.*, 1997). Food samples were analyzed for fluorides in Elementaita in Kenya showed cow's milk with fluoride range of 0.05-0.22 μg/mL; vegetables ranged from 7.9-59.3 μg/mL and drinking water from boreholes ranged from 0.2-20.9 μg/mL (Kahama, *et al.*, 1997). Samples collected in 18 sources in Njoro Division, Nakuru District showed fluoride level ranging from 0.78 mg/L river water to 11.0 mg/L borehole water (Mavura *et al.*, 2003). Fluoride mapping from KEBS 2010 report shows that the areas with at least 50% of boreholes with fluorides levels of greater than 1.5 mg/L include Baringo, Kajiado, Kericho, Laikipia, Nairobi, Nakuru, Narok, and Thika. Whereas these areas are known to have water with high levels of fluorides, there are pockets of water with less than 1.5 mg/L. Although considerable research has been conducted on some parts of Rift valley, there is not much research done in the southern Rift valley such as Bomet and Trasmara to mention but a few, in spite of the fact that there is fluorosis which is an indicator of fluoride presence in these areas

Adsorption is the most popular new method for treatment of fluoride polluted water. However, commercial adsorbents are expensive and require frequent regeneration, which limits application of the technology in most developing countries (Haron & Yunus, 2001). Thus, more affordable and easy-to-use defluoridating media is desired. This research assessed water quality with focus on the fluoride concentration in various water systems in the lower areas of the Bomet County, in Southern Rift valley, Kenya and the effectiveness of *moringa oleifera* seed cake as a biosorbent.

1.2 Distribution of fluoride

Geographical belts of high fluoride concentrations in groundwater extend from Syria through Jordan, Egypt, Libya, Algeria, Morocco and the Rift Valley of Western Africa through the Sudan and Kenya. Another belt stretches from Turkey through Iraq, Iran and Afghanistan to India, northern Thailand and China (WHO, 1986) as show in Figure 1.1.

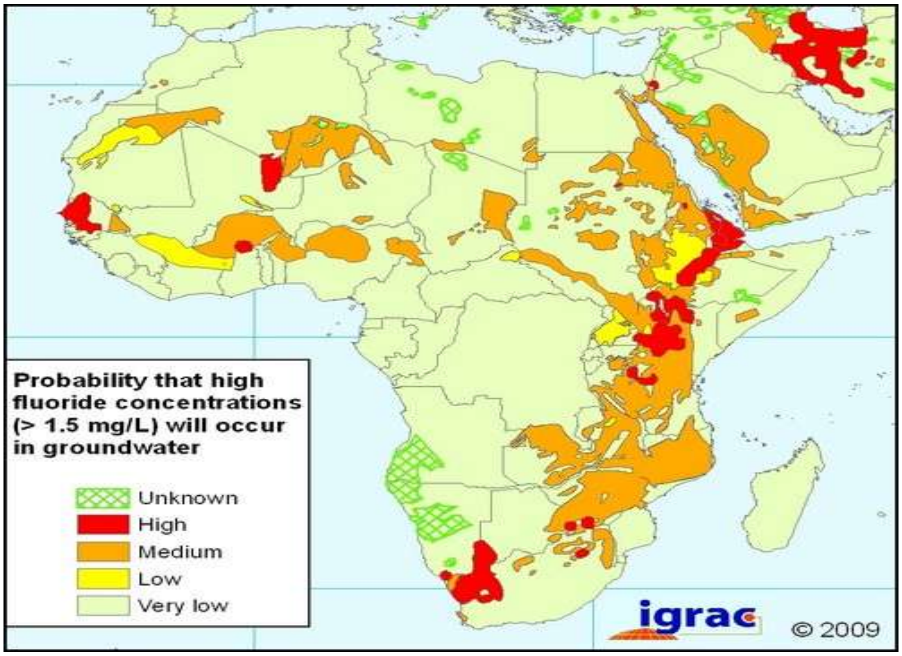

Figure 1.1: Probability of occurrence of excessive concentrations of fluoride in ground water sources in Africa.

High concentrations of flouride in groundwater are found in many countries around the world, notably in Africa, Asia and USA as reported by Czarnowski, (1996) and Azbar (2000). The most severe problems associated with high flouride in waters occur in China (Wang, 2002), India (Agarwal, 2003) and Rift Valley countries in Africa (Du Plessis, 1995).

Groundwater with high fluoride contents have been studied in detail in Africa, in particular Kenya and Tanzania (Moges, 1996; Chernet 2000; Mjengera, 2002; Moturi, 2002). High fluoride groundwater is also found in the East Upper Region of Ghana (Apambire, 1997).The concentration of fluoride is between 0.11 and 4.60 mg/L. The hydrogeology and hydrochemistry of ground waters of Senegal has been thoroughly studied by Travi (1988). In France two major basins; Aquitan Basin and Parisian Basin, have fluoride concentrations between 0.6 mg/L and 4.2 mg/L.

Fluoride is found in all natural waters at varying concentrations. Sea water typically contains about 1.0 mg/L, while rivers and lakes generally exhibit concentrations of less than 0.5 mg/L. In groundwater however, low and high concentration of fluorides can occur, depending on the nature of the rocks and the occurrence of fluoride- bearing rocks (WHO, 2006). Many of the lakes of the Rift Valley especially the soda lakes, have extremely high fluoride concentration; 1,640 mg/L and 2,800 mg/L in the Kenyan lakes Elementaita and Nakuru, respectively (Nair *et al.*,1984), and up to 690 mg/L in the Tanzanian Momella soda lakes. In Kenya, detailed survey of fluoride in groundwater was undertaken by Nair *et al*., (1984). Out of over 1,000 groundwater samples sampled nationally, 61% exceeded the 1.0 mg/L level, almost 20% exceeded 5.0 mg/L and 12% exceeded 8.0 mg/L. The volcanic areas of the Nairobi, Rift valley and central provinces had the highest concentration, with maximum groundwater fluoride concentration reaching 30.0-50.0 mg/L. Most of the sampled wells and boreholes were providing drinking water and the prevalence of dental fluorosis in the most affected areas was observed to be very high (Manji & Kapila, 1986).

It has been found that fluoride concentration in discharge areas are higher than in recharge areas, with a trend of fluoride enrichment along the direction of flow. These features have been attributed to the smaller quantities of dissolved solids in the recharge areas (Gaciri & Davies, 1993). Volcanism is an important factor determining content of the natural waters (Gaciri & Davies, 1993).

1.3 Occurrence of fluorides

Fluoride naturally occurring in water can be above, at, or below recommended levels. Rivers and lakes generally contain fluoride levels less than 0.5 mg/L, but groundwater, particularly in volcanic or mountainous areas, can contain as much as 50 mg/L (Fawell *et. al.*, 2006). Higher concentrations of fluorine are found in alkaline volcanic, hydrothermal, sedimentary, and other rocks derived from highly evolved magmas and hydrothermal solutions, and this fluorine dissolves into nearby water as fluoride. In most drinking waters, over 95% of total fluoride is the fluoride ion, with the magnesium–fluoride complex being the next most common. Because fluoride levels in water are usually controlled by the solubility of fluorite (CaF_2), high natural fluoride levels are associated with calcium-deficient, alkaline, and soft waters (Ozsvath, 2009). Anthropogenic sources also contribute to presence of fluorides in drinking water. The anthropogenic sources include fluorine bearing fertilizers, pesticides or disinfectants used in agriculture (Mwende, E., 2000). Fluoride in water is derived from rock minerals whereas other sources such as air and anthropogenic activities constitute a relatively small proportion (Lahermo *et al.*, 1991).

Fluoride is commonly associated with volcanic activity and fumarolic gases. Thermal waters especially those of high pH, are also rich in Fluorides (Edmunds & Smelley, 1996). Minerals that contain fluorides include cryolite and rock phosphates. Cryolite is used for the production of Aluminum (Murray, 1986) and as pesticide (USEPA, 1996). Other minerals like Fluorspar, Fluormica, tremolite, villuanite, epidote, fluorapatite and certain varieties of mica contribute fluoride (Raju *et al*., 2009).

1.3.1 Occurrence of fluoride in Kenya

About 41% of Kenyans lack clean drinking water (UNICEF Kenya country programme, 2009-2013). The highest natural fluoride concentration ever found in water (2,800 mg/L) was recorded in Lake Nakuru in the Rift .valley in Kenya (Nair *et al*., 1984; IPCS, 2003). High groundwater fluoride concentrations are associated with volcanic rocks, granites and salt deposits of marine origin. The type of rock formation in areas with high fluoride concentrations are mostly volcanic and lower part of Great Rift Valley which is fluoride rich fall under this area. Fluoride occurs in combined form in minerals such as fluorspar, cryolite and fluorapatite. Water passing through these minerals may register high fluoride concentration (up to 180 mg/L), signifying that the leaching of the rift valley volcanic soil exhibit high alkalinity (pH >7) and are high in Potassium, Sodium and bicarbonate as well as chloride and fluoride (Gaciri & Davis, 1993). Most of the studies carried out in Kenyan Rift Valley shows that high concentrations of fluorides are found in Nakuru (Gikunju *et al*., 2002; Naslund *et al*., 2005; Nair et al., 1984), Gilgil and Elementaita (Wambu *et al*., 2011; Kahama *et al*., 1997) and Koibatek-Baringo area (Naslund *et al*., 2005; CCEFW, 2010), which are fluorspar deposits regions.

1.4 Factors affecting the natural fluoride concentrations

Fluoride contamination of water is a function of many factors such as geology, climatic conditions, pH, contact time with aquifers and chemical composition of groundwater (Chandra *et al*., 1981; Largent, 1961).

1.4.1 Geology

During weathering and circulation of water in rocks and soils, fluorine can be leached out and dissolved in groundwater and thermal gases. The fluoride content of groundwater varies greatly depending on the geological settings and type of rocks. Therefore, fluoride problems tend to occur in places where these minerals are most abundant in the host rocks. Soils dominated by clay minerals have high sorption capacity and frequently serve as natural geochemical barriers preventing pollutants from reaching groundwater (Subba & Rao, 2003). Fluorides are adsorbed on clay minerals where ion exchange takes place.

Igneous and volcanic rocks have a fluorine concentration from 0.1-1.0 mg/g (Frencken *et al*., 1992). In general fluorine accumulates during magmatic crystallization and differentiation processes of the magma. Consequently, the residual magma is often enriched in fluorine. Groundwater from crystalline rocks, especially alkaline granites are particularly sensitive to relative high fluoride concentrations. Such rocks are found especially in Precambrian basement areas. The fluorine, which cannot be incorporated in crystalline phase during crystallization and differentiation of magmas, will be accumulated in hydrothermal solutions. These fluids may form hydrothermal fluorite deposits and veins. Fluoride transport in these aqueous solutions is controlled mainly by the solubility of CaF_2 (Allmann *et al*., 1974). Further, of the volcanic series, the alkaline volcanoes, typical of a continental rift (East Africa), hot spot, continental margin (Andes) or island arc (Japan), produce relative fluorine rich lava. (Rosi *et al*., 2003).

Sedimentary rocks have a fluorine concentration in the range of 0.2-1.0 mg/g limestone (Frencken *et al*., 1992). In carbonate sedimentary rocks, the fluorine is present as fluorite. Clastic sediments have higher fluoride concentrations as the fluorine is concentrated in micas and illites in the clay fractions. High concentrations may also be found in sedimentary phosphate beds (shark teeth) or volcanic ash layers (Frencken *et al*., 1992).

Metamorphic rocks have a fluorine concentration from 0.1-5.0 mg/g. In these rocks the original minerals are enriched with fluorine by metasomatic processes (Frencken *et al*., 1992). Bedrock mineralogy is in general, a primary factor for variations in fluoride content of groundwater (Chae *et al*., 2007). Besides geological changes, this results in changes in recharge composition and mixing. Several chemical processes have been identified as being important in controlling the major ion chemistry. Other existing minerals in the subsurface and other major and minor ionic constituents of groundwater may affect the dissolution characteristics of minerals, such as CaF_2 (Rao, 1997).

1.4.2 Contact time

The ultimate concentration of fluoride in groundwater largely depends on reaction times with aquifer minerals. High fluoride concentrations can be built up in groundwater which has long residence times in the aquifers. Such ground waters are usually associated with deep aquifer systems and a slow groundwater movement (Brunt *et al*., 2004).

Shallow aquifers which contain recently infiltrated rainwater usually have low fluoride. Exceptions can occur in shallow aquifers situated in active volcanic areas affected by hydrothermal alteration. Under such conditions, the solubility of fluoride increases with increasing temperature and fluoride may be added by dissolution of Hydrogen Fluoride gas (Frencken *et al*., 1992).

1.4.3 Climate

Arid regions are prone to high fluoride concentrations. Here, groundwater flow is slow and the reaction times with rocks are therefore long. The fluoride contents of water may increase during evaporation if solution remains in equilibrium with calcite and alkalinity is greater than hardness. Dissolution of evaporative salts deposited in arid zone may be an important source of fluoride. Fluoride increase is less pronounced in humid tropics because of high rainfall inputs and their diluting effect on the groundwater chemical composition (Frencken *et al*., 1992).

1.4.4 Chemical composition of groundwater

High-fluoride ground waters are mainly associated with a sodium-bicarbonate water type and relatively low calcium and magnesium concentrations. Such water types usually have high pH values (Brunt *et al*., 2004). Study conducted in Kendu Bay, Kenya shows that pH has significant control of fluoride (Okoo, 2007).

Information on chemical composition of groundwater can be used as an indicator of potential fluoride problems. The formation of fluoride rich waters is described by Frencken *et al*., (1992). Variation in fluoride distribution can also be related to changes in calcium concentration resulting from dissolution of calcium minerals and mixing with the waters of different chemical composition originated from variable hydrological environment across the rift valley (Ayenew, 2007).

1.5 Health effects of fluoride

Fluoride substitutes the carbonate component in teeth and bones, therefore the building of calogen is hindered which destroys the teeth and bone apatite. A concentration in drinking water above 1.5 mg/L causes dental fluorosis (WHO, 1984). Prolonged intake of water with fluoride content of 3 to 6 mg/L causes skeletal fluorosis, if these concentrations are exceeded, crippling skeletal fluorosis occur (Kloos *et al*.,1999). All enamel surfaces are affected and present a corroded-like appearance (Figure 1.2).

Figure 1.2: Inhabitant of study area with dental fluorosis

Normally, the degree of fluorosis depends on the amount of exposure up to the age of 8 to 10 years. Due to isomorphic substitution, fluoride mainly get deposited in joints of the neck, knee, pelvis and bony outgrowth may occur, vertebrae may fuse together and a victim may be crippled (Meenakshi & Maheshwari, 2006; WHO, 2002; Fawell *et al*., 2006). These negative health effects of fluoride are permanent and irreversible (Rajagopal & Tobin, 1991). In China alone, more than 10 million people are estimated to suffer from skeletal fluorosis (WQA 2006). As intake of amounts of fluoride leads to severe health problems, WHO has set the maximum concentration of fluorides for drinking water to be 1.5 mg/L and EPA to be 2.0 mg/L (WHO 1984).

1.6. Defluoridation

Continued consumption of water with fluoride levels above 1.5 mg/L can result in fluoride related diseases such as fluorosis. Therefore, there is dire 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 fluoride from poTable 4.4.water has seen many attempts over the years, using a wide variety of materials giving various efficiencies. Defluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes (Bulusu, 1979). Adsorption is the most popular method for treatment of fluoride polluted water. However, commercial adsorbents which are expensive and require frequent regeneration, limits application of the technology in most developing countries (Haron & Yunus, 2001).Thus, more affordable and easy-to-use defluoridating media is therefore desired. The most commonly used method is Nalgonda technique, where alum is mixed with lime at the ratio 700/300 mg/L, it was a test at a research station in Arusha, Tanzania and reduced fluoride concentration from 21 to 5 mg/L at pH 6.9 (Bregnhoj,1995). Clays, ion exchange resins, activated carbons, sulphonated coals, magnesium compounds, serpentine, iron and aluminium salts have also been applied (Bulusu, 1979). The use of cartridge filter which is packed with bone char has been found to have, efficiency of about 99.5% (Mavura *et al*., 2004). The bone char method has not been accepted by some communities and use of natural plant materials have been tried such as *Moringa Oleifera* seeds and rice husks (Vivek *et al*., 2011). *Moringa oleifera* seed consists chemical compounds like 4-(4'-*O*-acetyl-a-L-rhamnopyranosyloxy)benzyl isothiocyanate,4-(a-rhamnopyranosyloxy)benzy isothiocyanate, niazimicin, pterygospermin, benzylisothiocyanate, and 4-(a-L-rhamnopyranosyloxy)benzyl glucosinolate and several studies reported on the performance of *Moringa oleifera* seeds as a primary coagulant, coagulant aid and conjunctive with alum (Jed & Fahey, 2005). Studies conducted in India, have further demonstrated *Moringa oleifera* seeds to 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).

1.7 Kinetics of fluoride adsorption

The dependence of a chemical reaction on initial reactant concentration can be shown by a rate equation. The rate equation once integrated gives expressions for the variation of concentration of a reactant with time. The order of reaction is deduced from the integrated rate equation. For instance, the first order rate equation for fluoride adsorption on fluoride is;

$$\frac{\partial q_t}{\partial t} = k_1(q_e - q_t) \qquad \text{……………………………..………..........................} \ (1)$$

Where q_t and q_e are the masses of fluoride adsorbed by the *moringa oleifera* seed cake in (mg/g) at any time *t* and at equilibrium, respectively k_1 is the rate constant for the adsorption. On integration, equation 1 gives the solution;

$$k_1 t = \ln q_e - \ln(q_e - q_t) \ \text{…………………………….....................} \ (2)$$

The straight-line plot of ln (q_e – q_t**)** against t gives ln (q_e) as slope and intercept equal to k1/2.303. Hence the amount of solute sorbed per gram of sorbent at equilibrium (qe) and the first-order sorption rate constant (k1) can be evaluated from the slope and the intercept. If plotting ln (q_e – q_t**)** against t gives a straight line with a correlation coefficient (R^2 value) tending to unity then the experimental data agrees with first order kinetics and the reaction is first order. The second order rate differential equation can be represented as;

$$\frac{\partial q_t}{\partial t} = k_2(q_e - q_t)^2 \qquad \text{……...…………………...................................} \ (3)$$

Where k_2 is the second order rate constant, q_e and q_t are as defined above. Upon integration, equation 3 gives the solution;

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e{}^2} \qquad \text{………..............………………………………} \ (4)$$

Equation 4 predicts that for a second order process plotting t/q_t against *t* should give a straight line from which the rate constant k_2 and the fluoride uptake at equilibrium q_e, can be calculated from intercept. From the R^2 values for the first and second order plots, it is possible to deduce the order of reaction. The curve with the higher value of R^2 tending to unity, corresponds to the order of the reaction.

1.7.1 Calculations

A plot of equilibrium fluoride 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 :

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

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

Where qe is the amount of fluoride adsorbed (mg/g); Co and Ce are the initial and residual concentration of fluoride in solution at equilibrium (mg/L), respectively; V is the volume of aqueous solution in litres and W is the dry weight of the adsorbent (g).

1.8 Adsorption Isotherms

An adsorption isotherm is an equation that describes how the amount of a substance adsorbed onto a surface depends on its concentration (if in a solution), or its pressure (if a gas) at a constant temperature. Adsorption isotherms focus mainly on systems where the adsorbate particles are mostly concentrated on the surface of an adsorbent. The adsorption isotherms considered are Langmuir and Freundlich Isotherm.

1.8.1 Langmuir Isotherm

The Langmuir isotherm has been widely used to describe and determine the adsorption capacity q_{max} of fluoride ions during biosorption processes. The Langmuir adsorption isotherm is useful in quantifying and contrasting the performance of different biosorbents. In its formulation, binding to the surface is primarily by physical forces mainly electrostatic and implicit in its derivation is the assumption that all sites possess equal affinity for the adsorbate. It has been used to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase. One of the simplest representations of the adsorption phenomenon calls for the migration to and the occupation of a surface site, S, on the adsorbent by an adsorbate, A.

This can be represented by an equilibrium reaction as follows:

$$S + A \rightleftharpoons SA \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

Where SA is the adsorbed complex. Surface species concentration may be expressed in molarity of solution, per gram of solid, per unit area of solid surface or per mole of solid. Assuming that all surface sites have the same affinity for the solute A, a mass action law can be written as;

$$K_{ads} = \frac{[SA]}{[S][A]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

where K_{ads} is the equilibrium constant for the adsorption process, [S], [SA] and [A] refer to molar concentrations. The total concentration of surface sites S_T, is given by;

$$[S_T] = [S] + [SA] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Combining equations 2 and 3 gives

Defining the surface concentration as Γ, we have

$$\Gamma = \frac{[SA]}{mass\ of\ adsorbent} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5)}$$

Where Γ is the surface concentration of the adsorbate whose limiting value Γ_{max}, is given by

$$\Gamma_{max} = \frac{[S_T]}{mass\ of\ adsorbent} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

The surface concentration of an adsorbate can be expressed as,

$$\Gamma = \Gamma_{max}\left(\frac{K_{ads}[A]}{1 + K_{ads}[A]}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(7)}$$

Equation (7) is the general form of the Langmuir equation. Compliance to the Langmuir isotherm theory requires that (1) adsorption is limited to the formation of a monolayer, or the number of adsorbed species, [SA], does not exceed the total surface sites [ST]; and (2) all surface sites have equal affinity for the adsorbate. This means that the [SA]: [ST] ratio does not affect the energy of adsorption (Davis *et al.*, 2003). At least one of these conditions is implicitly not met in the case of biosorption (Stumm & Morgan, 1996). Previously it has seen that there is more than one type of functional group contributing to the biosorption process, each of which has a different affinity for absorbing fluoride. Furthermore, the one-to-one stoichiometry is also not complied with, since ion-exchange has been shown to be a dominant mechanism, and typically approximately one proton is released upon the binding of one monovalent ion. Despite this fact, the Langmuir equation is frequently used to fit experimental data. In this case, the following form of the Langmuir equation (7) above is traditionally applied:

$$q = q_{\max}\left(\frac{bC_e}{1+bC_e}\right), \quad \text{………………………......................………} (8)$$

Where q, q_{max}, C_e and b is the fluoride uptake at any time (in milligrams of fluoride per gram of biosorbent), the maximum fluoride uptake, the final equilibrium concentration of the fluoride in solution and the Langmuir empirical constant, respectively.

Experimental results can most easily be compared with the Langmuir theory if equation (8) above is expressed in its linear form as follows;

$$\frac{C_e}{q} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad \text{………………..................................…} (9)$$

If the experimental data agrees with the theory, a plot of C_e/q versus C_e yields a straight line. From this curve the adsorption capacity q_{max} and the Langmuir constant b can be obtained.

1.8.2 Freundlich Isotherm

The Freundlich isotherm (Freundlich, 1907) was originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation. In this model, the energy of a fluoride ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. The Freundlich equation takes the form:

$$q_e = K_F\left(C_e\right)^{1/n} \quad \text{...} (10)$$

where q_e and C_e is the mass of solute adsorbed per gram of the adsorbent and the solute concentration at equilibrium respectively. K_F and n are empirical constants characteristic of the system and are indicators of the adsorption capacity and intensity, respectively. Large values of K_F and n indicate high adsorption capacity and intensity, respectively. This equation is most conveniently used in its linearized form namely;

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad \dots\dots\dots\dots \quad (11)$$

Experimental results agree with the Freundlich isotherm if a plot of ln q_e versus ln C_e yields a straight line. The Freundlich constants K_F and $1/n$ can be calculated from the linear plot as intercept and slope respectively .

1.9 Conceptual Framework

The fluorides from the sources listed in Figure 4. 3 below get into the food chain through crops growing on such a soil contaminated with fluorides. The fluorides may adversely affect the soil eco-system safety, not only agricultural products and water quality, but also the human health and animals.

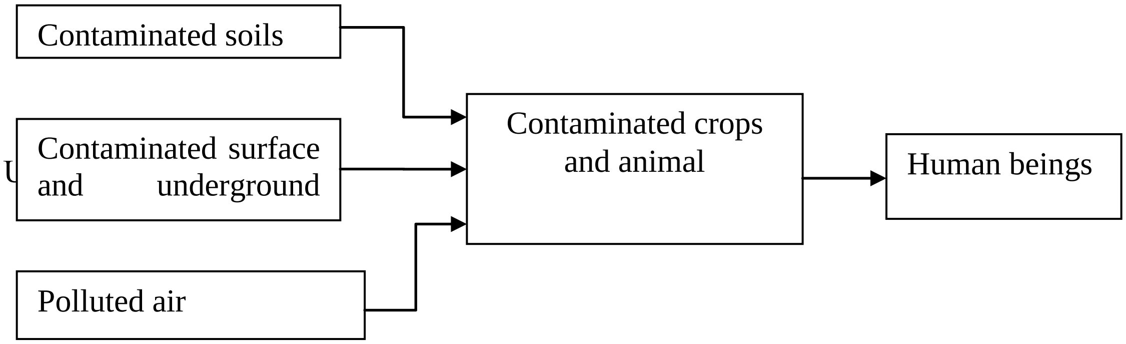

Figure 1.3: Conceptual framework

1.10 Statement of the problem

The geology of Kenya makes it one of the countries in the world where fluoride occurs in highest concentration, not only mineral rocks and soil but also in surface and ground water (Nair et al., 1984). Fluoride is found more frequently in different sources of water, with higher concentration found in ground water due to presence of fluoride bearing mineral rocks (WHO, 2002).

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. This water sources particularly 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 lower areas of Bomet County, Kenya will be assessed. There is no systematic and scientific investigation conducted on fluorides in the area before. 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) but no documented studies have been carried out in this lower area of Bomet County, which falls under Rift Valley.

Biosorption is a new technology that provides an effective, low cost and environmentally friendly means of removing fluoride pollutants from water. Moringa oleifera is a promising biosorbent for this purpose. The use of the seeds of Moringa oleifera for the removal of fluoride from water has been suggested by researchers as an alternative (Kloos and Haimanot, 1999), but it was not properly addressed as far as the application of seeds of moringa oleifera seed cake is concerned. The use of sophisticated technologies and different chemicals for coagulation are difficult and inappropriate in the context of developing countries (Schulz and Okun, 1984). Compounds of Aluminum that have been used as a coagulant and defluoridation substance have a negative impact on the environment and human health as well as they are not much more accessible and affordable for developing countries (Miller et al., 1984). The use of natural purifying agents is therefore of practical importance.

1.11 Justification of study

The use of water with high fluoride concentration poses a health threat to millions of people around the world. Drinking water is often the main source of fluoride intake by humans, especially in areas where fluoride concentrations of groundwater or surface water are high. During formative stages (up to eight years of age), fluoride ingested is distributed throughout the body and retained in bones and teeth (WHO, 1984). As a result people develop brown to black teeth and weak bones which fracture easily; a condition known has dental and skeletal fluorosis respectively (Mkawale, 2011). In more severe cases, the skeletal fluorosis affects limb bones making them brittle and weak resulting in ricketed legs. Excess fluoride in water has been linked to hip fracture from studies conducted in UK (Hiller et al., 2000) and the US (Jacobsen, 1993). Therefore there is need to know the quality of water used for drinking and other domestic chores in order to avoid exposure to fluorides. Communities in rural areas use water from natural sources without treatment, and water quality monitoring is not possible because many rural areas are relatively inaccessible. Thus, especially in recent studies, it has been proposed that more fluoride surveys should be conducted to establish the risk posed by increasing fluoride exposure in certain communities (Gikunju et al., 2002).

The use of moringa oleifera seed cake powder for the removal of fluoride in contaminated water is a healthy and cost-effective venture due to the biodegradability and lower cost of the moringa oleifera seed cake. Reverse osmosis is even more costly. Precipitation is inefficient at low ion concentrations and generates toxic sludge which is difficult to dispose off. Moringa oleifera seed cake also reduces turbidity of water, which is also another benefit. Moringa oleifera is a plant which is drought resistant and grows well in tropical and sub-tropical regions in altitude ranging from 0-2000 metres above sea level and rainfall ranging from 250-3000 mm and therefore can be grown well in Bomet County. In addition, other parts of the plant like leaves can be used as vegetables, roots and barks as herbal medicine. Moringa oleifera seed cake powde are safer and more cost effective than their competitors. The adsorption capacity for moringa oleifera seed cake is good and takes place at pH values which are near that of pure water hence easy to achieve. The biosorption process is fairly rapid, with contact times of about one hour for most biosorbents. Biosorption is therefore a potential solution to fluoride contamination.

1.12 Hypothesis

There is no significant difference in fluoride concentration level in water sources in lower region of Bomet County. Moringa oleifera seed cake does not remove fluorides in contaminated water.

1.13 Objectives

1.13.1 General objective

The broad objective of the study was to assess the levels of fluoride in the water sources in the lower region of Bomet County and remediation using moringa oleifera seed powder.

1.13.2 Specific objectives

(i) To determine selected physico-chemical water quality parameters such as pH, conductivity, temperature, total dissolved solids, Na^+, K^+, $Mg^{2+,}$ $Ca^{2+,}$ and HCO_3^-.

(ii) To determine the levels of fluoride in water samples from different water sources in lower areas of Bomet County.

(iii) To investigate the potential of moringa oleifera seed cake remediation of fluorides in water samples.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Study area

The study area figure 2.1 is in the lower part of Bomet County, which covers Bomet Sub-County and part of Sotik Sub-County. The area is generally flat and its altitude lies between 1689 m and 1962m.

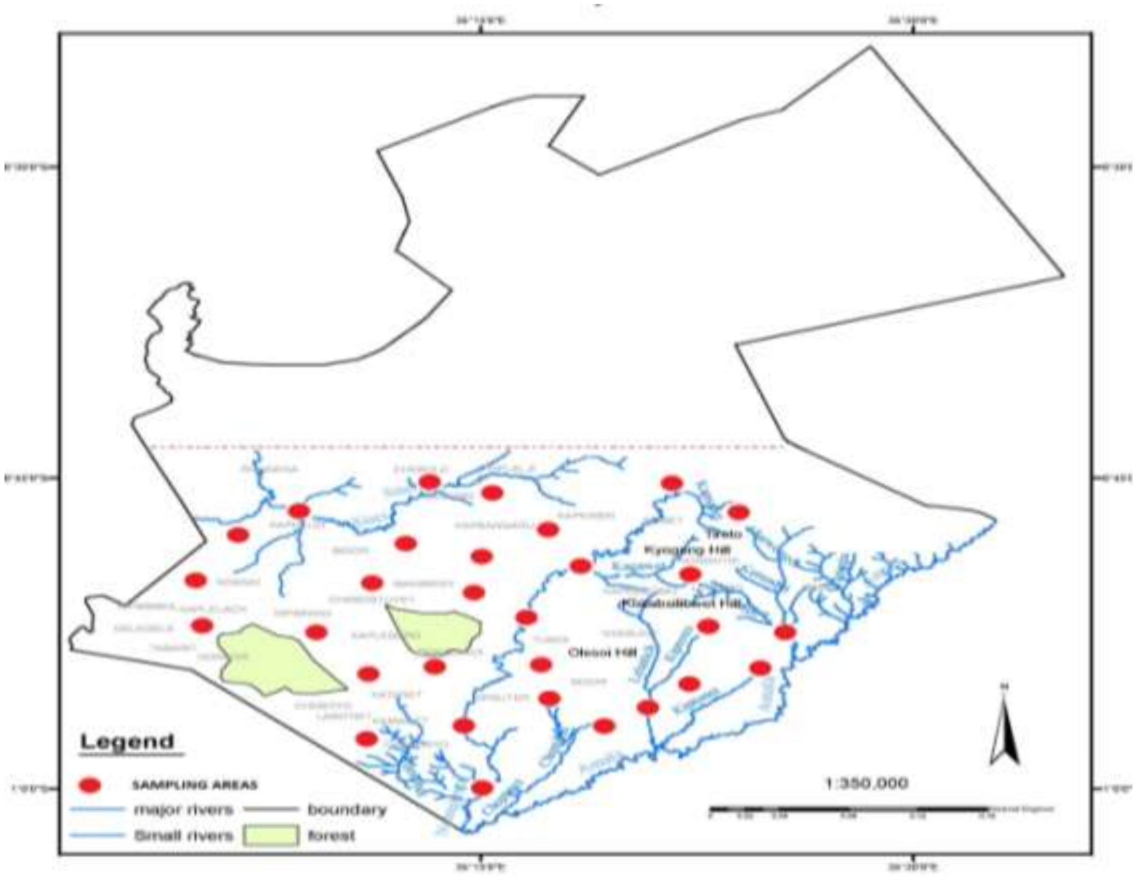

Figure 2.1: Study area sites in Bomet County. Source: Adapted from GOK, 2015

The area is defined by coordinates, longitude 350 12 00 E and latitude 000 56 00 S. It covers an area of about 1,100 km^2. The main source of drinking water in the study area is water pans. Rivers, bore holes, springs and wells are very few. The population of the study area is approximately 331,122 according to 2009 census.

2.2 Instrumentation

Conductivity, total dissolved solids and temperature were measured using a digital portable total dissolved solids meter, fitted with temperature probe (Total dissolved solids meter 4076, Jenway, UK). A portable digital pH 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 were determined using Flame 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.

2.3 Reagents

Orion reagents, TISAB III (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, potassium, 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).

2.4 Sample collection

Water samples were collected from rivers, water pans, springs and boreholes within the study areas by stratified random sampling. During the rainy season (April- 2011), 30 Water samples were collected 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.

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

Analysis of bicarbonates was done by using AOAC official method 920.124, titrimetric method. Analysis of K, Na, Ca and Mg working standards and samples were carried out using flame photometer and atomic absorption spectrophotometer (AAS) respectively. The calibration curves of respective metals were used to calculate concentration for AAS and flame photometer. The instrumental condition are given in 2.1

Table 2.1: Instrumental conditions for the AAS in the determination of Ca^{2+} and Mg^{2+} ions

Metal	**Wavelength (nm)**	**Slit width(nm)**
Calcium	422.70	1.0
Magnesium	285.20	1.0

2.6 Determination fluoride by standard addition method

2.6.1 Determination of electrode slope

50 mL of distilled water and 10 mL of the TISAB III were measured into a 150 mL plastic beaker, 1 mL of 100 ppm fluoride stock solution was added and mixture stirred thoroughly. The electrode were rinsed with distilled water, blot dried, and placed into sample in a beaker. When a stable 4.4.reading was displayed, the pontential (E_1) in millivolts were recorded. 10.0 ML of a 100 ppm fluoride standard solution were pipetted into the beaker and again stirred thoroughly. When a stable 4.4.reading was displayed, the new pontential (E_2) were recorded. The first reading (E_1) was subtracted from the second (E_2) to find change in pontential, ΔE which is the slope of the electrode, S of the instrument**.** (Thermo Orion 96-09 model)

2.6.2 Determination of fluoride concentration in water samples

Fluoride analysis was carried out using fluoride meter an Ion- Selective Combination Electrode, model: Thermo ORION, 96-09. 50 mL of the water sample 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 mixture in a beaker. When a stable 4.4.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 4.4.reading was displayed, the new potential (E_2) were recorded. The first reading (E_1) was subtracted from the second (E_2) to find change in pontential, ΔE**.** The concentration of fluoride in the samples were calculated as follows;

$Csample = QCstandard$ (Thermo-Orion 96-06 instructional manual)

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

P = Volume of standard /volume of sample

2.7 Preparation of *Moringa Oleifera* seed cake 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 ^{o}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. 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.

Figure 2.2: Moringa oleifera pods and seeds

2.7 Optimum dosage

Experiments were conducted on model solutions of fluoride to determine effect of dose of the *moringa oleifera* seed cake on the removal of fluoride from water. 200 mL of solution with initial fluoride concentration of 10mg/L of fluoride, at pH 6.0 and contact time of 120 minutes was equilibrated with for 0.5 g/L of *moringa oleifera* seed cake and stirred continuously with a magnetic stirrer at 300 revolutions per minute (rpm). 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. The same procedure was repeated for 1.0, 1.5, 2.0, 3.0 and 4.0 g/L.

2.8 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 cake. Fluoride Stock solution, 1000 ppm was diluted using 0.1 M acetate buffer solution to obtain 10 mg/L of flouride solution and divided into 200mL 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 cake 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.

2.9 Optimization of contact time

Stock solution (1000 ppm) of fluoride was diluted with 0.1M 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 cake 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.

2.10 Optimum dosage

Experiments were conducted on model solutions of fluoride to determine effect of dose of the *moringa oleifera* seed extract on the removal of fluoride from water.100 mL of solution with initial fluoride concentration of 10mg/L of fluoride, at pH 6.0 and contact time of 120 minutes was equilibrated with for 0.5 g of *moringa oleifera* seed extract and stirred continuously with a magnetic stirrer at 300 revolutions per minute (rpm). 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. The same procedure was repeated for 1.0, 1.5, 2.0, 3.0 and 4.0 g.

2.11 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 cake was tested for 5, 10, 15 and 20 mg/L of solution. Each of the solutions was equilibrated with 2.0 g of dried and ground *moringa oleifera* seed cake 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.

2.12 Statistical Analysis

2.12.1 Linear Regression

Calibration graphs were plotted using the absorbance values of the standards. Graphs of absorbance versus concentration were drawn using Microsoft Excel and regression equations of $y = bx + a$ obtained where b was the slope of the line and a was its intercept on the y axis. The Correlation Coefficient (R) was obtained. Concentrations of the test samples were determined by interpolation. The concentration (x-value) corresponding to any measured absorbance (y-value) was calculated using both the determined slope and intercept of the regression line.

2.12.2 Analysis of Variance (ANOVA)

ANOVA tests were conducted for the concentrations of fluoride and other selected ions in different water samples from different water sources using statistical analysis systems. A one way analysis of variance (SNK-test) was used to find out if there was a significant difference between the sample means. Where significant differences ($p = 0.05$) between the sample means was detected least significant difference was calculated (Miller & Miller, 1988).

2.12.3 Spearman Rank Correlation Coefficient

A non-parametric measure of association between two variables x and y, is denoted by r_s

$$r_s = \frac{1 - 6\sum d2}{n(n2 - 1)}$$

The values of r_s ranged from -1 to +1. A value of +1 or -1 indicated perfect association between x and y, the plus sign occurring for identical rankings and the minus sign occurring for reverse rankings. When r_s was close to zero, we concluded that the variables were uncorrelated.

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 Physico-chemical parameters

Variation in concentrations of selected physico-chemical parameters for 30 water samples from different water sources in wet season is shown in appendix 8. For 30 samples of water collected in rainy season (April, 2011), 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. Mean concentrations of selected physic-chemical parameters for wet season are shown in Table 3.1 below.

Table 3.1: Mean concentrations of selected physico-chemical parameters for wet season.

Parameter	**Water Pan mean±SE**	**Borehole mean±SE**	**River mean±SE**	**Spring mean±SE**	**Well mean±SE**	**p-value**
pH	7.43±0.19	7.85±0.24	7.04±0.10	7.36±0.09	7.70±0.06	0.082
Electrical conductivity (S/cm)	0.21±0.02	0.97±0.19	0.10±0.01	0.28±0.03	0.28±0.01	<0.0001
Total dissolved solids (mg/L)	114.40±8.60	642.75±118.72	50.47±4.38	142.56±17.84	183.00±0.00	<0.0001
Temp(degree Celcius)	23.51±0.53	20.38±0.54	18.75±0.55	21.43±0.29	19.80±0.06	<0.0001
Sodium(mg/L)	10.12±0.46	190.50±44.61	11.64±0.93	160.49±134.95	31.40±0.70	0.492
Potassium(mg/L)	10.16±0.91	30.95±1.72	4.18±0.23	10.66±1.61	13.40±0.06	<0.0001
Calcium(mg/L)	4.74±1.30	7.97±2.27	0.64±0.21	1.90±0.28	0.78±0.01	0.002
Magnesium(mg/L)	2.21±0.25	3.67±0.9	0.27±0.02	1.68±0.31	0.85±0.01	<0.0001
Flouride(mg/L)	2.74±0.30	4.37±0.57	0.38±0.02	1.55±0.18	0.54±0.01	<0.0001
Hydrogen Carbonates(mg/L)	120.07±8.41	618.33±90.52	69.54±3.66	111.02±8.74	70.15±0.00	<0.0001

Mean concentrations for selected Physical parameters analyzed are as follows: Electrical conductivity, 0.10±0.01-0.97±0.19 mS/cm, total dissolved solids 50.47±4.38-642.75±118.72 mg/L and pH 7.04±0.10-7.85±0.24 in different water sources (Table 4.1).

The levels of alkali and alkaline earth metals; potassium (K), sodium (Na), magnesium (Mg) and calcium (Ca) were determined in water samples from different water sources from Bomet County. The samples were analysed in triplicates for all metals. Flame photometer and AAS was used respctively. The calibration curve of calcium shown in Figure 3. 1 below is a representation of the calibration curves of potassium, sodium and magnesium are given in appendix 1 to 3. The calibration curves of respective metals were used to calculate concentration for flame photometer and AAS.

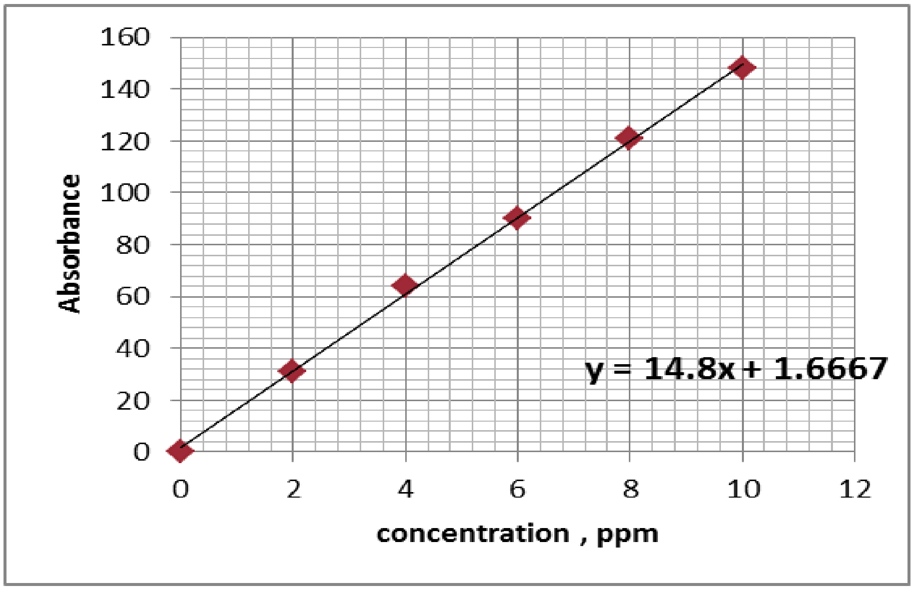

Figure 3.1: Calibration curve for calcium

Mean concentrations for selected chemical parameters analyzed have the following ranges: Na^+ , 10.12±0.46-190.50±44.61 mg/L, K^+ 4.18±0.23-30.95±1.72 mg/ L, Ca^{+2}, 0.64±0.21-7.97±2.27 mg/L, Mg^{+2} 0.27±0.02-3.67±0.9 mg/L, HCO_3^- 69.54±3.66-618.33±90.52 mg/L, F^-, 0.38±0.02-4.37±0.57 mg/L. Mean concentrations of all physico-chemical parameters in wet season fall within WHO and KEBS acceptable levels (appendix 10) for drinking water except fluoride in some water sources. There was Significance difference in the mean concentration of selected parameters in different water sources, $p < 0.05$, except for sodium and pH, $p > 0.05$. The difference could be due to type and composition of bed rock and anthropogenic sources for example fertilizers and pesticides as reported by Mwende, 2000. Mean fluoride concentration in the boreholes and water pans was higher than WHO permissible limits, 1.5 mg/L (WHO, 1984). The mean Fluoride level (0.38±0.09) in river water in this study was fairly low in wet season Table 3.1. This could be attributed to dilution effects caused by large volumes of water, (Frencken *et al.*, 1992). In order for rivers to attain high levels of fluoride, special conditions must be present which usually do not occur on the surface but only in the ground. Ordinarily, a long contact time between water and fluoride-bearing minerals is needed, and therefore river waters are not expected to be high in fluoride, (Gikuju *et al.*, 2002). The abundance of fluoride in rift valley groundwater is due to the weathering of alkaline volcanic rocks rich in fluorides, (Apambire, 1997).

For 28 samples collected in the dry season (January-2012) showed that 18 (64.3 %) samples had fluoride levels above WHO maximum permissible limits (1.5 mg/L) and 10 samples (35.7%) were below the minimum level (1.0 mg/L) as shown in appendix 9. Mean concentrations of selected physico-chemical parameters for dry season are given in Table 3.2.

Table 3.2 Mean concentrations of selected physico-chemical parameters for dry season in various water sources in study area.

Parameter	Water Ban mean±SE	Borehole mean±SE	River mean±SE	Spring mean±SE	Well mean±SE	p-value
pH	6.52±0.05	6.69±0.22	6.47±0.04	5.89±0.03	6.20±0.01	<0.0001
Electrical conductivity (S/cm)	0.24±0.02	1.02±0.18	0.22±0.05	0.24±0.03	0.43±0.00	<0.0001
Total dissolved solids(mg/L)	125.55±5.45	684.42±119.93	86.80±7.30	152.14±18.69	283.00±2.89	<0.0001
Temp(degree Celcius)	25.85±0.51	22.75±0.54	19.74±0.82	22.82±0.59	18.30±0.06	<0.0001
Sodium(mg/L)	13.98±1.52	167.33±31.62	14.80±1.46	30.79±3.89	36.80±0.06	<0.0001
Potassium (mg/L)	18.98±1.19	42.51±1.30	7.42±0.37	15.31±2.33	20.07±0.03	<0.0001
Calcium(mg/L)	7.66±0.71	23.54±3.16	2.50±0.27	7.06±1.28	12.03±0.03	<0.0001
Magnesium (mg/L)	2.26±0.10	6.19±1.50	1.26±0.16	2.12±0.34	4.16±0.00	<0.0001
Flouride(mg/L)	2.46±0.17	4.51±0.50	0.53±0.09	0.83±0.09	0.73±0.00	<0.0001
Hydrogen Carbonates (mg/L)	78.27±4.39	317.06±63.64	49.73±3.02	76.74±8.57	45.78±0.00	<0.0001

The Mean concentrations of selected physico-chemical parameters for dry season in various water sources had the following range: Total dissolved solids ranged from 86.80±7.30 - 684.42±119.93 mg/L, Electrical conductivity 0.22±0.05 - 1.02±0.18 S/cm and pH 5.89±0.03 - 6.69±0.22. F^-, 0.53±0.09-4.51±0.50 mg/L, Na^+, 13.98±1.52-167.33±31.62 mg/L, K,$^+$ 7.42±0.37-7.42±0.37 mg/ L, Ca^{+2}, 2.50±0.27-23.54±3.16 mg/L and Mg^{+2}, 1.26±0.16 - 6.19±1.50 mg/L. The levels of HCO_3^- range from 45.78±0.00 - 317.06±63.64 mg/L.

The fluoride level in the boreholes (4.51±0.50 mg/L) was above the WHO maximum permissible level of 1.5 mg/L. Similar results on groundwater were obtained by Gikunju *et al.* 2002. High level of fluoride in boreholes is attributed to presence of volcanic rocks and long contact times due to slow movement of water in bedrocks during dry spells. 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 known to be rich in fluoride, particularly in form of fluorspar, CaF_2 (Nyamweru, 1980). Surface water from springs, shallow wells and rivers had fluoride levels below minimum permissible limits of 1.0 mg/L except in water pans (2.46±0.17 mg/L). High level of fluoride in water pans could be attributed to anthropogenic sources, such as fertilizers, herbicides and pesticides (Mwende, 2000).

pH is a numerical expression that indicates the degree to which water is acidic or alkaline. It causes chemical reactions such as solubility and metal toxicity depending on its concentrations. It did not vary significantly in the seasons i.e., the results were uniform throughout this study, with minor seasonal differences (Table 3.2 and 3). The changes in pH may occur due to agricultural and domestic waste. All values lied within the tolerance limit. The lower pH value tends to make water corrosive and higher pH provides taste complaint and negative impact on skin and eyes (Rao& Rao, 2010).

The bicarbonate and sodium content was found to be high as given in Table 3.2 and 3 but not exceeding the maximum limits. In the study area, high fluoride water could be generally associated with high sodium- 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 sodium in groundwater, the opportunity for sedimentation of calcium fluoride (CaF_2) is greatly decreased (Gupta *et al.,* 2005).

3.2 Seasonal variation of fluoride

Fluoride ions have dual significance in water supplies. High concentration of fluoride ion cause dental fluorosis. At the same time a concentration less than 0.8 mg/l results in dental carries. Hence it is essential to maintain the fluoride ion concentration between 0.8 to 1.0 mg/l in drinking water (WHO, 2002). Seasonal variation of fluoride in different water sources in the study area are given in Figure 3.2 below.

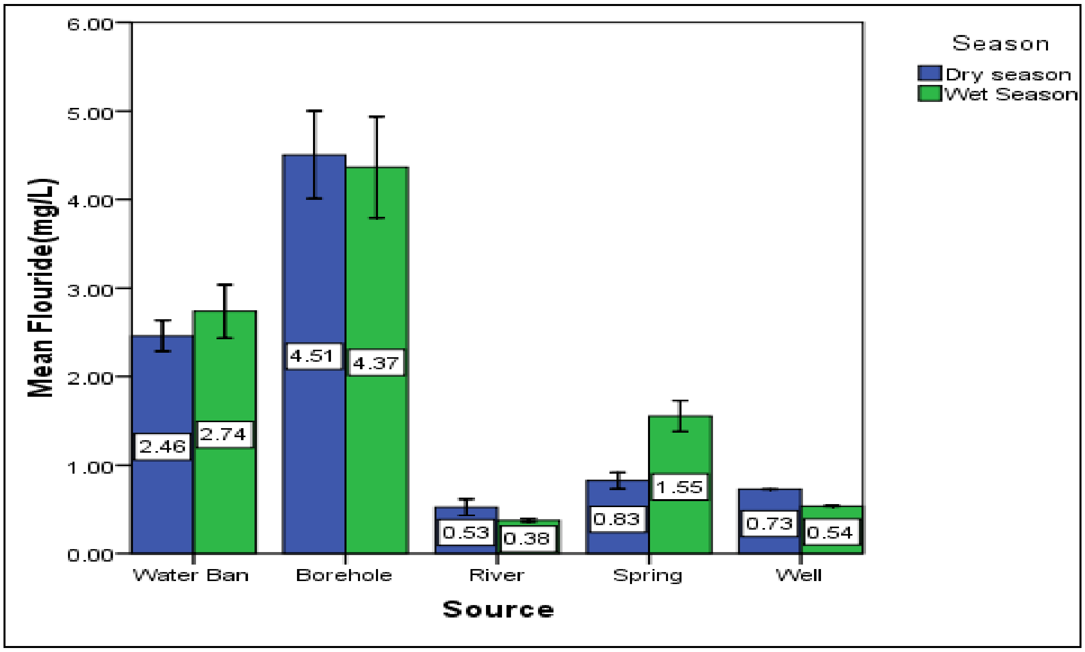

Figure 3. 2: Seasonal variation of fluoride in different water sources in the study area.

Mean concentration of fluoride ions in different water sources varied from 0.38 to 4.37 mg/L and 0.53 to 4.51 mg/L in wet and dry season respectively, Figure 4.2. The concentration levels of fluoride ions in boreholes and water pans in both seasons, (appendix 8 and 9) were above the limit set by WHO for fluoride in drinking water (1.5 mg/l). Fluoride level was found to be highest in a water pan at Kamotyo in Chebunyo location, (5.23 mg/L and 6.95 in dry and wet seasons respectively). The inhabitants that use water from this water pan were found to have severe dental fluorosis. This could be attributed to the nature of soil and human activities such as use of pesticides. The levels fluoride in Itembe borehole (6.1 mg/L in dry and 5.97 mg/L in wet) was found to be highest. This could be attributed to weathering and leaching of bedrock with high fluoride content.

The seasonal variation indicates fluoride levels are high in rainy seasons for the water pans and springs when compared to dry seasons while fluoride levels in boreholes, shallow wells and rivers showed higher concentration in dry season compared to wet season. Minimum fluoride concentration observed during wet season for shallow wells, boreholes and river water could be due to the availability of large volumes of water leading to dilution of chemicals present. High concentration during dry season in water pans and springs 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 (1.5 mg/l). This could be attributed to weathering and leaching of bedrock with high fluoride content. Same results were reported by Ombaka O. *et al.*, 2013 and Okoo J.A. *et al*., 2007. Generally, the seasonal variation in fluoride levels is minimal due the fact that the dry spell was so short in that year, (January, 2012). Seasonal variations of selected physico-chemical parameters at 95 % confidence level were determined and the results obtained are given in Table 3.3.

Table 3.3: Seasonal variation of physio-chemical parameters

Parameter	**Dry season mean±SE**	**Wet Season mean±SE**	**t calculated**	**df**	**tcritical**
pH	6.36±0.05	7.41±0.08	11.03	138	1.977
Electrical conductivity (mS)	0.35±0.04	0.32±0.04	0.529	169	1.974
Total dissolved solids(mg/L)	210.74±27.67	187.36±26.20	0.614	169	1.974
Temp(degree Celcius)	23.29±0.39	21.49±0.30	3.66	156	1.975
Sodium(mg/L)	41.05±7.28	82.66±42.62	0.946	169	1.974
Potassium(mg/L)	19.40±1.37	12.26±1.06	4.121	156	1.975
Calcium(mg/L)	9.01±0.92	3.46±0.60	5.059	169	1.974
Magnesium(mg/L)	2.68±0.29	1.87±0.21	2.289	168	1.974
Flouride(mg/L)	1.94±0.18	2.11±0.19	0.672	169	1.974
Hydrogen Carbonates(mg/L)	109.45±15.66	175.55±23.00	2.375	138	1.977

Fluoride ranges for rainy and dry seasons were almost similar. Fluoride, student t-test calculated 0.672 is less than t-test critical, 1.977 at 5 % confidence level as shown in Table 3.3. This means that there was no significant difference in mean fluoride concentration in the two seasons at 5 % confidence level. Therefore people in high fluoride areas were exposed to high fluoride water throughout the seasons. Other Parameters which did not show a significant variation between the seasons (independent t-test, (5% confidence level) include electrical conductivity, total dissolved solids and Na^{+} while Mg^{+2}, Ca^{+2}, pH, temperature and K^{+} showed significant variation, t-test calculated is greater than t-test critical Table 3.3 at 5% confidence level.

3.3 Correlation of fluoride with selected physiochemical parameters

Fluoride ion concentrations in natural water have been found to depend on a number of factors. These include pH, solubility of fluoride bearing minerals, anion exchange capacity of aquifer materials (OH^{-} or F^{-}), type of geological formations traversed by water and contact time of water with certain geological formations as was found out by Apambire, *et al.* 1997. To examine the relationship of fluoride with other parameters, the data obtained was subjected to correlation analysis using the Pearson moment correlation coefficient technique as is found in the Statistics for Physical and Social Sciences (SPSS 11) software package and the results is shown in Table 3.4 below.

Table 3.4: Correlation for physio-chemical parameters.

	pH	EC (mS)	TDS (mg/L)	Temp	Na	K	Ca	Mg	F-	HCO3-
pH	1.00	**.282**	**.280**	-0.047	**0.190**	-0.037	-0.099	-0.005	0.116	0.**296**
EC(mS)		1.000	**.969**	0.030	**0.242**	**0.664**	**.482**	**.342**	**0.434**	**0.702**
TDS (mg/L)			1.000	0.015	**0.252**	**0.717**	**.498**	**.383**	**0.446**	**0.703**
Temp (degree Celsius)				1.000	-0.015	**0.163**	**.331**	**.265**	0.133	-0.110
Sodium (mg/L)					1.000	**0.168**	0.048	0.062	**0.373**	0.**188**
Potassium (mg/L)						1.000	**0.600**	**0.545**	**0.539**	**0.575**
Calcium(mg/L)							1.000	**0.772**	0.075	**0.189**
Magnesium (mg/L)								1.000	0.142	**0.231**
Flouride(mg/L)									1.000	**0.523**
Hydrogen Carbonates (mg/L)										1.000

Pearson correlation coefficients that are in bold are the ones that show a significant correlation ($p<0.05$ at 95% confidence level).

Total Dissolved Solids showed good correlation (R2, 0.446) with fluoride concentration compared to other physical parameters studied. Electrical Conductivity also had good correlation (R2, 0.434) followed by temperature (R2, 0.133) and pH (R2, 0.11). The main ions contributing total dissolved solids are bicarbonates, fluorides, sodium, potassium, calcium and magnesium (EPA, 1976). Magnesium ($R^{2,}$ 0.142) and calcium (R^2, 0.075) ions showed poor positive correlation with fluoride compared to other chemical parameters (Na^+, 0.373, K^+, 0.539 and HCO_3^-, 0.523). Similar observation was found by (Mavura & Tiffani B. (2003)) and Handa (1995) that there is poor correlation between Ca, Mg and F^-. The phenomenon of decrease in Ca and Mg concentration contributing to higher fluoride concentration may be attributed to calcium complexing effect. Fluoride complexes are formed more readily in mineralized water than in dilute water, (Allmann *et al*., 1974). Correlation coefficient (Pearson correlation coefficient) showed positive correlation between pH and electrical conductivity, total dissolved solids, Na^+, F-, and HCO_3^-. ($p<0.05$). Positive correlation between pH and Fluoride has also been established by Handa, 1975; Edmunds, 1994, Gaciri & Davies, 1994; Rao *et al.,* 2002 and Fordyce *et al.*, 2007. Negative correlation was found between pH and temperature, potassium, calcium and magnesium.

3.4 Removal of fluoride from water by *Moringa oleifera* seed cake

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

3.5 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.

3.6 Optimization of pH

The effect of pH is considered in the adsorption process because it may affect both the properties of the adsorbent and the composition of the solution. It is also important due to the ionization of surface functional groups and composition of solutions. The residual fluoride concentrations after batch equilibration with *moringa oleifera* seed cake at various pH values were determined, appendix 5.

The lower concentration of fluoride observed in the filtrates were due to removal of fluoride by biosorption. Removal of Fluoride by *moringa oleifera* seed cake 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% as shown in Figure 3. 3 below.

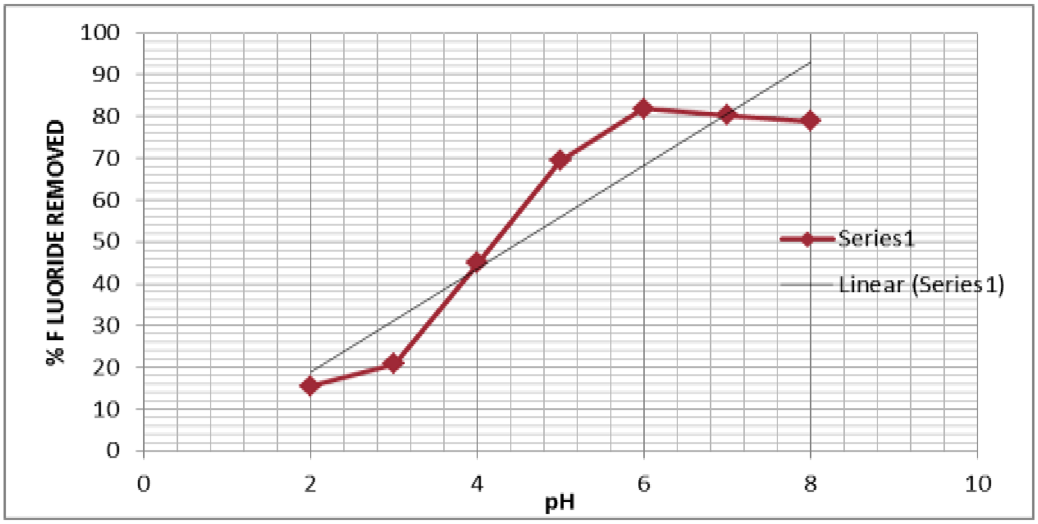

Figure 3.3: Fluoride removal at different pH values.

At low pH value below 4, H^+ ions react with fluoride ion to form hydrofluoric acid which implies a decrease in the concentration of fluoride ions in solution reducing fluoride biosorption This behavior may be 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 value for fluoride biosorption is 6.0.

3.7 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, appendix 7. The changes in fluoride concentration are shown in Figure 3. 4. 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 cake applied, to remove fluoride ion from water sample of initial fluoride concentration of 10.0 mg/L at pH 6.0.

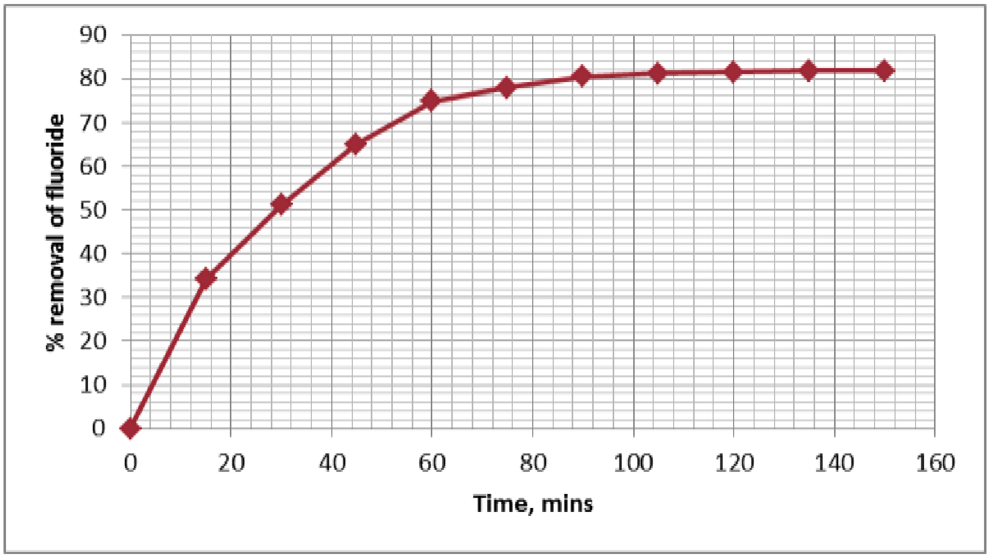

Figure 3.4: Percentage fluoride removal by biosorption at different contact times.

Fluoride removal efficiency increased from 34.2 % to 81.7 % as the contact time between the fluoride and *moringa oleifera* seed cake 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.

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 cake, 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 concentration difference 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 may be due to saturation of binding sites.

3.8 Optimum dose

Optimum dose of the *moringa oleifera* seed cake 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 120 min for 0.5, 1.0, 2.0, 3.0 and 4.0 g/L of the doses of the *moringa oleifera* seed cake (Appendix 6).

Results for adsorption of fluoride at different doses of *moringa oleifera* seed cake are given in the Figure 3. 5 below.

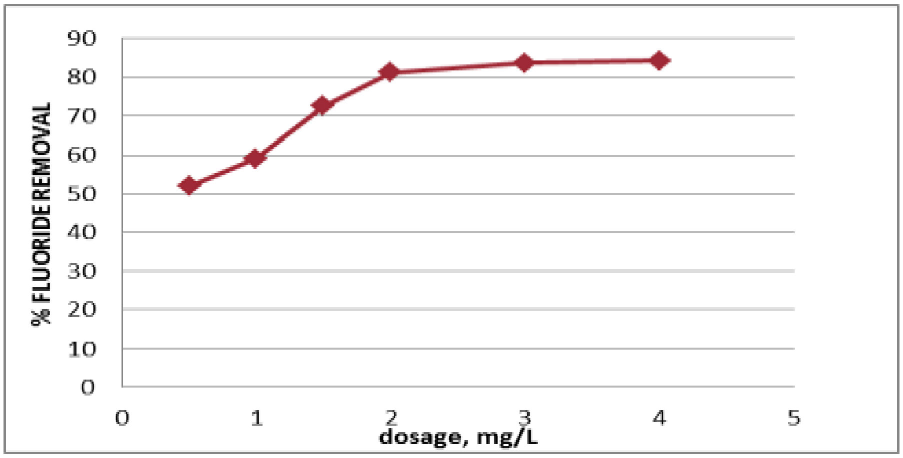

Figure . 3.5: Fluoride removal by biosorption at different doses of moringa oleifera seed cake.

It is observed that fluoride removal increases with an increase in the amount of adsorbent. 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 wild*) 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 increase 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 & Dongre, 2006; Kambel *et al*., 2007; Wang *et al*., 2009).

3.9 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 (2) and (4). A plot of $\ln(q_e - q_t)$ against time (minutes) was used for the first order linearity test Figure 3. 10 , while a plot of t/q_t (min g/mg) against time (minutes) was used for the second order linearity test Figure 3. 6 and the calculation of q_e, which is the fluoride uptake in milligrams per gram of biosorbent at equilibrium**.**

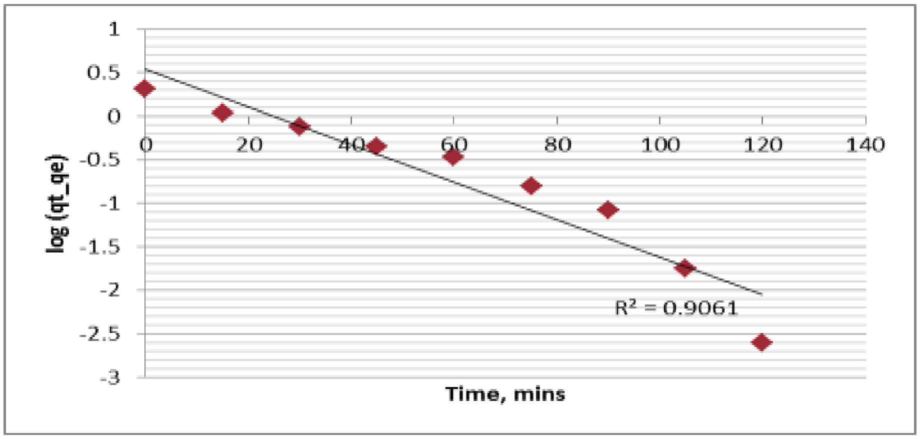

Figure 3.6: First order linearity test for fluoride adsorption on *moringa oleifera* seed cake

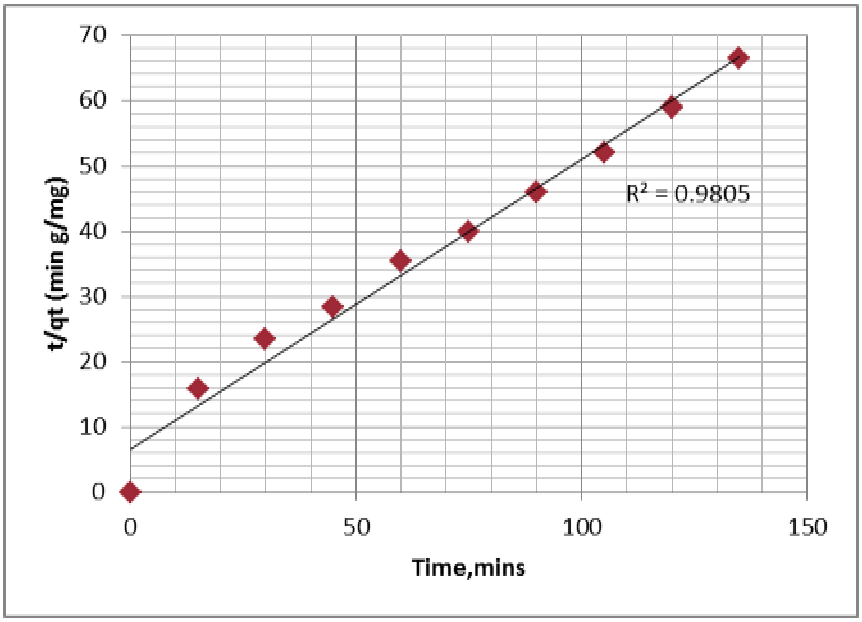

Figure 3.7: Second order linearity test for fluoride adsorption on *moringa oleifera* seed cake

The order of reaction for fluoride was deduced from the linearity of the respective plots, Figure 3.5 and Figure 3.6. The slopes and the R^2 values from which q_e and the linear correlation coefficients are obtained from Figure 3.5 and 3. 6. The second order plot for fluoride, Figure 3.6 has higher R^2 value than the corresponding first order plot, Figure 3. 10 as shown above. Since the correlation co-efficient (R^2) is 0.9805 for first order and the experimental fluoride uptake at equilibrium value 2.045 mg/g is consistent with calculated one (Table 3.5), 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 (R^2= 0.9061).

Table 3. 5: Kinetic parameters for fluoride adsorption on *moringa oleifera* seed cake

First order				Second order		
	Initial concentration, (mg/L)	Calculated fluoride uptake at equilibrium q_e, (mg/g)	R^2	Calculated fluoride uptake at equilibrium q_e, (mg/g)	R^2	Experimental fluoride uptake at equilibrium 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 indicates that sorption is not occurring exclusively onto one site per ion. In second order mechanism, the overall rate of fluoride sorption process appears to be controlled by the chemical process, through sharing of electrons between biosorbent and sorbate.

3.10 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 appendix 4 together with the corresponding initial concentrations, C_i and the calculated fluoride uptake at equilibrium, $q_{e.}$ The data was fitted to the linearized Langmuir and Freundlich isotherms represented by the equations (9) and (11).

Linear regression coefficients (R^2) were used to deduce the isotherm which best fitted the data. Equilibrium concentrations C_e (µg/mL) and fluoride uptake q_e (mg/g) at equilibrium obtained are as shown in Figure 3. 8 below. 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 as in Figure 3.8 below.

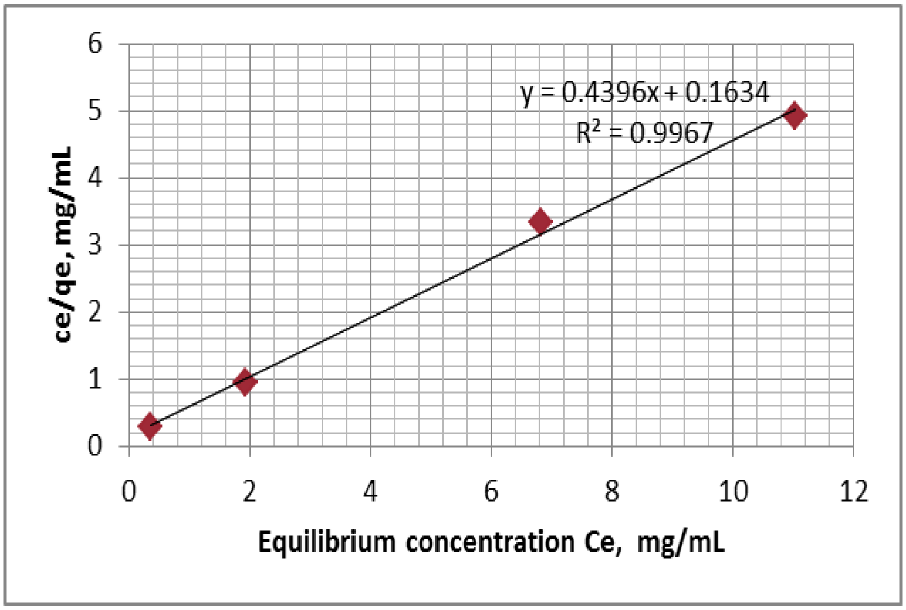

Figure. 3.8: Linearized Langmuir plot for fluoride.

The adsorption capacity, q_{max} of *moringa oleifera* seed cake was found to be 2.2748 mg/g for fluoride (Table 3.6).

Table 3.6: Calculated adsorption isotherm parameters for fluoride adsorption

	Langmuir parameters			Freundlich parameters		
	R^2	*b* (L/mg)	q_{max} (mg/g)	R^2	K_F	1/n
F^-	0.9967	2.690	2.2748	0.8606	0.496	0.207

The magnitude of the Freundlich constants was used to asses the adsorption intensity. Freundlich constants were obtained from a plot of lnq_e against lnC_e in which n is the reciprocal of the slope and lnK_F is the y – intercept. Figure 3.9 shows the linearized Freundlich plot for fluoride. The Langmuir and Freundlich constants obtained from Figure 3.7 and 3.8 are reported in Table 3.6

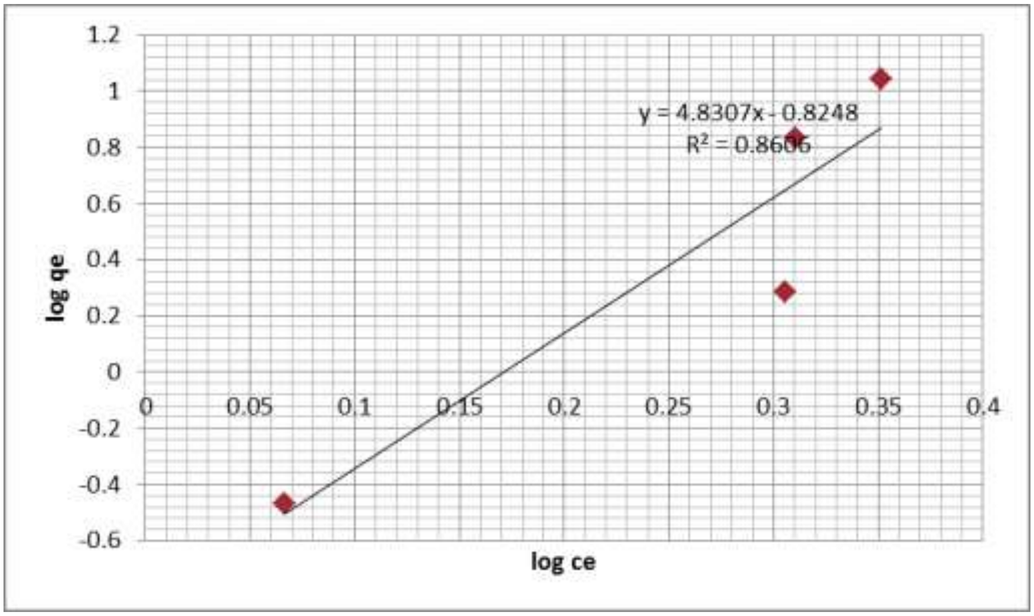

Figure 3. 9: Linearized Freundlich plot for fluoride.

It is evident from a comparison of the values of coefficient of correlation (R^2) Table 3.6, that the equilibrium adsorption of Fluoride onto *moringa oleifera* seed cakes follows 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, Hugo *et al*., 2013 and Pandey *et al.*, 2012.

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 (0.496) 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 n 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.

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

1. The seasonal variation for selected physico-chemical parameters for rainy season **(**Electrical conductivity, 0.10±0.01-0.97±0.19 mS/cm, Total dissolved solids, 50.47±4.38-642.75±118.72 mg/L and pH 7.04±0.10-7.85±0.24, Na^+, 10.12±0.46-190.50±44.61 mg/L, K^+ 4.18±0.23-30.95±1.72 mg/ L, Ca^{+2}, 0.64±0.21- 7.97±2.27 mg/L, Mg^{+2} 0.27±0.02-3.67±0.9 mg/L, HCO_3^-, 69.54±3.66-618.33±90.52 mg/L, F^-, 0.38±0.02-4.37±0.57 mg/L) and dry season (Total dissolved solids, 86.80±7.30 - 684.42±119.93 mg/L, Electrical conductivity 0.22±0.05 - 1.02±0.18 S/cm and pH 5.89±0.03 - 6.69±0.22 F^-, 0.53±0.09-4.51±0.50 mg/L, Na^+, 13.98±1.52-167.33±31.62 mg/L, $K,^+$ 7.42±0.37-7.42±0.37 mg/ L, Ca^{+2}, 2.50±0.27-23.54±3.16 mg/L and Mg^{+2}, 1.26±0.16 - 6.19±1.50 mg/L) were minimal. The mean concentrations of all selected parameters in different water sources were within KEBS and WHO permissible limits except for fluorides.
2. Fluoride levels in all borehole water sampled (4.51 mg/L in dry season and 4.37 mg/L in wet season) and water pans water (2.46 mg/L in dry season and 2.74 mg/L in wet season) was found to be higher than KEBS and WHO permissible limits. River water (0.53 mg/L and 0.38 mg/L in dry and wet seasons respectively), Spring water levels (0.83 mg/L in dry and in wet 1.55 mg/L) and shallow wells showed a level of (0.73 mg/L in dry and in wet 0.54 mg/L) contain fluoride levels below 1.5 mg/L. Therefore safe for domestic use throughout the year.
3. Crushed moringa oleifera seed cake showed high fluoride reduction efficiency from 10.0 mg/L to 1.83 mg/L (81.7 %). The biosorption studies conducted in this work provides significant information regarding suitability of moringa oleifera seed cake as a biosorbent for the fluoride. The pseudo-second order model describes the fluoride sorption kinetic using *moringa oleifera* seed cake. The Langmuir model best describes the experimental data, which may indicate that the sorption mechanism of fluoride ions on *moringa oleifera* seed cake is chemisorption on a homogeneous monolayer material.

4.2 Recommendations

1 Since spring, river and shallow wells water conatain fluoride levels below 1.5 mg/L should be used.Over 50 % of the inhabitants in the area use water pan water, which contains high levels of fluoride, thereby posing a serious risk of fluorosis. Therefore it is recommended that clean alternative sources should be used such as harvesting of rainwater.

2 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 cake.

3 Furthermore, this project recommends *moringa oleifera* plant to be used in defluoridation of water polluted with fluorides. This research has shown that plant seed cakes absorb fluorides from water. *Moringa oleifera* seeds being such a promising biosorbent able to grow in most climatic zones should be cultivated in this study area and the residents educated on its use in water treatment.

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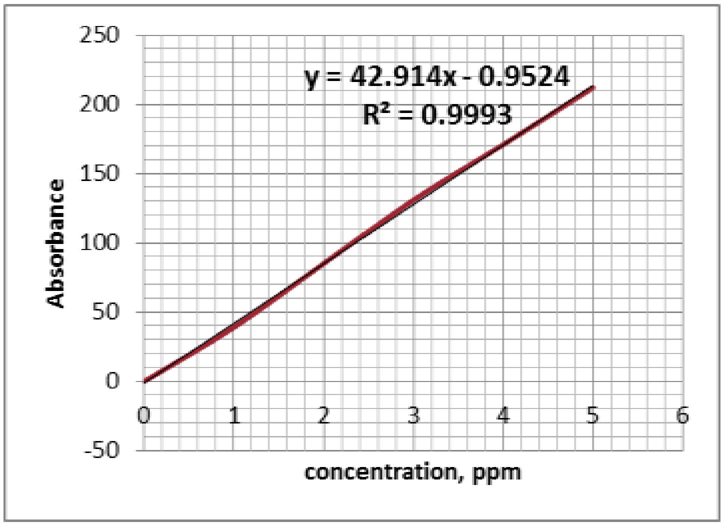
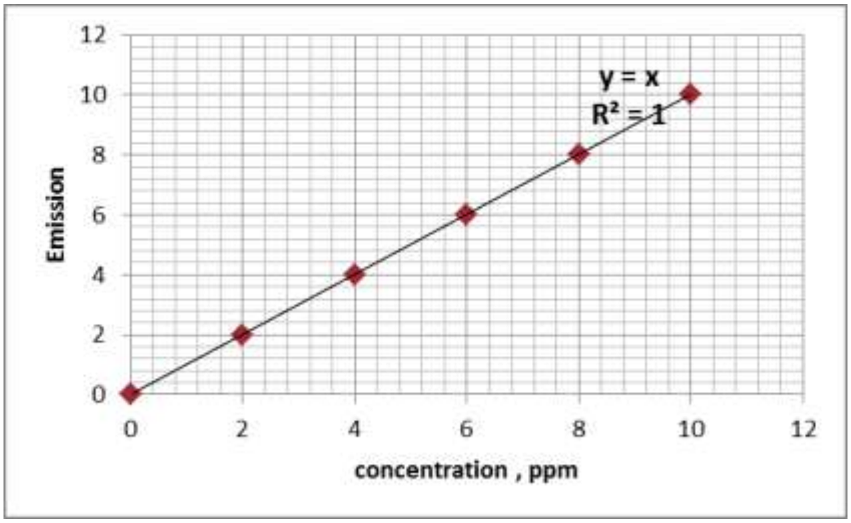
APPENDICES

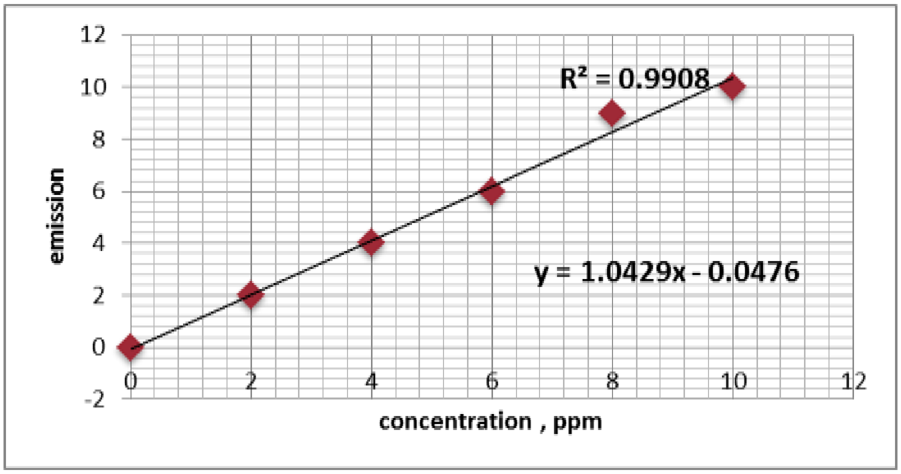
Appendix 1: Calibration magnesium



Appendix 2: calibration curve for sodium



Appendix 3. calibration curve for potassium



Appendix 4 :calculation of Langmuir and Fruendlich parameters

initial F	Ce	qe	ce/qe	log Ce	log qe
5	0.34±0.02	1.165	0.2918	-0.4685	0.0663
10	1.92±0.04	2.02	0.9505	0.2833	0.3053
15	6.83±0.03	2.0425	3.3439	0.834	0.3102
20	11.02±0.01	2.245	4.9087	1.0422	0.3512

Appendix 5. Percentage fluoride removal by biosorption at different pH values

pH	2	3	4	5	6	7	8
Residual fluoride (Mg/L)	8.45±0.04	7.91±0.02	5.51±0.02	3.06±0.03	1.83±0.01	1.91±0.00	2.11±0.03
Fluoride removed (%)	15.5	20.9	44.9	69.4	81.9	80.9	78.9

Appendix 6: Fluoride removal by biosorption at different doses of *moringa oleifera* seed cake.

Dose (g/L)	0.5	1.0	1.5	2	3	4
Residual fluoride(g/L)	4.8±0.01	4.1±0.03	2.75±0.01	2.23±0.01	1.68±0.00	1.57±0.02
% fluoride removal	52.0	59.0	72.5	81.3	83.7	84.5

Appendix 7. Percentage fluoride removal by biosorption at different contact times.

Contact time, (mins)	**0**	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**	**135**	**150**
Residual fluoride, (mg/l)	10.0 ±0.01	6.58 ±0.03	4.89 ±0.02	3.50 ±0.04	2.51 ±0	2.21 ±0.01	1.95 ±0.02	1.89±0.01	1.85 ±0	1.83 ±0.01	1.83 ±0.03
Fluoride removed, (%)	0	34.2	51.1	65	74.9	77.9	80.5	81.1	81.5	81.7	81.7

Appendix 8: Physio-chemical parameters of water sampled in wet season

Sampling Site	**pH**	**EC (mS)**	**TDS (mg/L)**	**Temp. (°C)**	**Na^+(mg/L)**	**K^+ (mg/L)**	**Ca^{2+} (mg/L)**	**Mg^{2+} (mg/L)**	**HCO_3^-**	**F^- (mg/L)**
kapkures WB	6.6	0.17	107	19	10	17.3	1.4	1.33	115.9	1.78
ItembeBH	7.5	0.76	502	19.7	173.1	33.6	1.94	0.94	527.65	6.1
SACCO BH	7.2	0.68	443	19	120.3	28.8	3.96	1.77	454.45	6.07
St. marys p. well	7.6	0.29	183	19.9	32.2	13.5	0.77	0.86	70.15	0.53
Nyangores R. BOMET	6.4	0.09	40	16.7	8	3.9	0.25	0.21	57.95	0.26
Gagawet R.	6.8	0.16	84	17.3	18.1	5.8	0.38	0.42	94.55	0.35
Sugumerica S	7.4	0.1	54	18.8	7.5	6.8	0.21	0.05	61	1.44
Nyangores R. SIGOR	7.5	0.09	43	21.5	8	3.9	0.32	0.24	57.95	0.44
Marangetit S.	7.3	0.58	373	22	85.5	31.7	3.95	4.49	198.25	1.47
Sigor S.	7.5	0.2	126	19.9	35.7	8.7	2.48	0.2	115.9	2.71
Nyangores R.Kaboson	7.1	0.1	42	20	9	3.9	0.24	0.25	64.05	0.45
Kamotyo WB	7.5	0.34	200	23.6	13.5	14.4	25	4.22	198.25	6.95
Chebunyo WB1	8.6	0.2	101	24	10.5	10.6	4.09	2.06	128.1	2.66
Chebunyo WB2	5.9	0.33	195	23.1	8.9	17.3	1.43	3.63	210.45	3.08
Chebunyo WB3	5.7	0.23	132	27.4	7.5	3.9	6.3	1.65	112.85	2.74
Chebunyo WB4	8.3	0.21	109	26	8	9.6	4.48	1.82	85.4	3.83
Seron BH	9.1	2.01	1316	21.3	432.5	38.4	5.32	2.69	1128.5	4.3
Chesambai S	8.1	0.32	201	22.9	36.69	15.4	2.8	2.8	122	1.17
Aonet S1	8	0.2	122	22.8	25.6	6.8	2.38	3.44	115.9	0.24
Aonet S2	7.7	0.24	132	23.4	7.5	2	0.19	0.12	57.95	0.35
Ngurwo S.	7.3	0.2	111	20.3	13	8.7	3.8	2.9	137.25	1.2
Kaplomboi catholic BH.	8.1	0.5	317	22.8	36.2	24	20.7	9.28	362.95	1.78
Kaplomboi S.	7.5	0.17	82	22.3	15	3.9	0.42	0.51	51.85	2.71
Ndanai WB1	7.8	0.15	92	24.9	15.5	4.8	0.51	4.8	103.7	0.88

Ndanai WB2	8.2	0.14	70	27	7	3.9	3.1	1.04	91.5	1.27
Ndanai S.	6.7	0.15	78	20.6	7.5	10.6	0.9	0.76	137.25	2.61
Ndanai WB3	8.1	0.13	63	20.7	11	11.6	1.1	1.05	85.4	2.23
Tembwo WB	7.7	0.14	74	20.4	8.67	9	0.45	0.61	69.3	1.98
Sisei R.	7.2	0.09	46	17.2	12	3.9	1	0.2	73.2	0.38

Appendix 9: Physio-chemical parameters of water sampled in dry season

sampling site	**pH**	**EC (mS)**	**TDS (mg/L)**	**Temp. (^{0} C)**	**Na$^+$(mg/L)**	**K$^+$ (mg/L)**	**Ca2$^+$ (mg/L)**	**Mg2$^+$ (mg/L)**	**F-**	**HCO 3-**
kapkures WB	**6.75**	**0.16**	**105**	**20.1**	**8.59**	**20**	**3.9**	**2.42**	**1.79**	**95.21**
Itembe BH	**6.35**	**0.75**	**503**	**20.1**	**178**	**45**	**7.5**	**1.76**	**5.97**	**367.6**
Sacco BH	**6.27**	**0.68**	**472**	**22.2**	**118**	**35**	**21**	**2.65**	**6.03**	**598.34**
St. Mary Primary well	**6.21**	**0.43**	**288**	**18.4**	**36.9**	**20**	**12**	**4.17**	**0.73**	**45.78**
Nyangores R 1 Bomet	**6.5**	**0.1**	**56**	**18.8**	**8.69**	**6**	**1.9**	**0.93**	**0.28**	**38.9**
Gagawet R.	**6.32**	**0.16**	**98**	**17.3**	**22.5**	**9**	**1.1**	**0.92**	**1.17**	**63.27**
Sugumerica S.	**5.76**	**0.12**	**76**	**20.2**	**9.19**	**6**	**2.1**	**0.99**	**0.76**	**81.71**
Nyangores R 2 at Sigor	**6.4**	**0.11**	**65**	**22.8**	**11.2**	**6**	**3.2**	**0.97**	**0.25**	**52.29**
Marangetit S.	**5.93**	**0.44**	**302**	**21.8**	**67**	**15**	**14**	**4.42**	**1.27**	**75.95**
Sigor S.	**6.06**	**0.17**	**105**	**20.4**	**33.9**	**6**	**0.7**	**0.25**	**1.42**	**125.1**
Nyangores R3 kaboson	**6.53**	**0.17**	**113**	**23.7**	**11.7**	**7**	**2.3**	**1**	**0.38**	**40.43**
Kamotyo WB	**6.32**	**0.25**	**154**	**26.7**	**10.2**	**20**	**7.7**	**3.31**	**5.23**	**112.56**
Chebunyo WB 1	**6.41**	**0.2**	**120**	**26.6**	**8.69**	**8**	**17**	**2.22**	**2.83**	**107.4**
Chebunyo WB 2	**6.28**	**0.26**	**167**	**21.1**	**21.5**	**15**	**6.6**	**2.57**	**2.19**	**83.21**
Chebunyo WB 3	**6.42**	**0.17**	**103**	**25.8**	**6.22**	**35**	**8.1**	**1.56**	**3.18**	**61.54**
Chebunyo WB 4	**6.52**	**0.2**	**124**	**28.5**	**5.23**	**15**	**13**	**2.06**	**2.04**	**54.87**
Seron BH	**7.91**	**2.05**	**1376**	**24.5**	**331**	**45**	**32**	**5.99**	**3.99**	**111.14**
Chesambai S.	**5.8**	**0.41**	**265**	**27.8**	**40.8**	**35**	**14**	**3.62**	**1.09**	**113.81**
Aonet S1	**Not done**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
Aonet S2	**6.09**	**0.25**	**154**	**24.9**	**29.5**	**13**	**11**	**3.34**	**0.53**	**34.67**
Ngurwo s	**not done**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
Kaplomboi catholic BH	**6.2**	**0.6**	**410**	**24.4**	**45.3**	**45**	**34**	**14.4**	**2.04**	**294.21**
Kaplomboi S.	**5.78**	**0.15**	**93**	**23.4**	**19.6**	**6**	**1.5**	**1.14**	**0.48**	**47.82**

Ndanai WB1	**6.53**	**0.15**	**85**	**26.7**	**5.73**	**20**	**1.9**	**1.79**	**1.93**	**75.45**
Ndanai WB2	**6.72**	**0.25**	**153**	**29.4**	**33.4**	**15**	**5**	**2.36**	**2.27**	**69.01**
Ndanai S.	**5.71**	**0.16**	**95**	**21.1**	**17.6**	**20**	**2.7**	**1.06**	**0.23**	**58.21**
Ndanai WB3	**6.8**	**0.23**	**152**	**28.9**	**14.1**	**25**	**8.1**	**2.99**	**1.87**	**78.90**
Ndanai WB4S	**6.7**	**0.18**	**102**	**26.4**	**16.8**	**19**	**7.2**	**1.56**	**1.69**	**79.21**
Tembwo WB	**6.1**	**0.13**	**91**	**24.6**	**23.5**	**17**	**5.9**	**1.93**	**2.07**	**43.78**
Sisei R.	**6.58**	**0.17**	**117**	**16.2**	**20.1**	**9**	**4**	**2.47**	**0.57**	**53.76**

Appendix 10. KEBS and WHO maximum permissible limits

Parameters	**KEBS**	**WHO**
pH	**6.5-8.5**	**6.5-8.5**
Electrical conductivity, *u*S/cm	**2500**	**1000**
Total Dissolved Solids, mg/L	**1500**	**1500**
Sodium, mg/L	**200**	**200**
Potassium, mg/L	**50**	**50**
Calcium, mg/L	**100**	**200**
Magnesium, mg/L	**100**	**150**
Hydrogen Carbonates, mg/L	**Not available**	**-**
Fluoride, mg/L	**1.5**	**1.5**

Adapted from: WHO, 2006 and KEBS, (1996) KS 05-459