UNIVERSITY OF NAIROBI

Department of Civil and Construction Engineering

Evaluation of Bone Char Defluoridation of Water using Adsorption Isotherms and the Bed Depth Service Time (BDST) Model

Bertha Naliaka

Research Thesis Submitted in Partial Fulfillment for the Requirements for the Award of the Degree of Master of Science in Civil Engineering (Environmental Health Engineering) of the University of Nairobi

2016

DECLARATION

This research thesis is my work and has not been presented in any other university.

Signature …… Date …….

Bertha Naliaka

This research project is presented for examination with my approval as university supervisor**.**

Signature…..**.....**Date ……..

Dr. Peter K. Ndiba

Senior Lecturer

Department of Civil and Construction Engineering

This research project is presented for examination with my approval as the Chairman, Department of Civil and Construction Engineering**.**

Signature…..**.....**Date ……..

Dr. S.W Mumenya

Chairman, Department of Civil and Construction Engineering

ABSTRACT

Sustained intake of elevated fluoride concentrations cause dental or skeletal fluorosis, a chronic disease manifested by mottling of teeth in mild cases and softening of bones and neurological damage in severe cases. Excessive and undesirable levels of fluoride in drinking water supplies are a major problem in the Rift Valley of Kenya. Fluoride concentrations range from 5 to 15 mg/L as compared to the WHO maximum permissible levels of 1.5 mg/L in drinking water. Current methods of fluoride removal from water include adsorption onto activated alumina, bone char and clay, precipitation with lime, dolomite and aluminum sulphate, ion exchange, and membrane processes such as reverse osmosis, electrodialysis and nano filtration. Most of these methods are expensive and technically non-feasible for rural communities in Kenya. This study evaluated the efficacy of locally available bone char in removal of fluoride from water. The bone char reduced fluoride concentration from 8.1 mg/L to within WASREB threshold of 3 mg/L for exceptionally high concentration of fluoride in 50 minutes and to within the WHO limit concentration of 1.5 mg/L in 2 hours. Fluoride removal was analyzed using adsorption isotherms; namely, Freundlich and Langmuir isotherms. Adsorption of fluoride on to bone char conforms to Freundlich Isotherm but not to Langmuir Isotherm indicating that the bone char media is not a homogenous media. Freundlich adsorbate capacity, K_f, increased with media size from 3.95×10^{-3} to 1.75×10^{-2} (L/g) for fine and medium size media, respectively, but adsorption intensity, 1/n, decreased from 1.657 to 1.043, which may explain the lack of significant difference between the fine and medium size media. To predict the fluoride breakthrough in a bone char fixed-bed system, fluoride removal was modeled using the bed depth service time (BDST) model with bed capacity, No, of 79, 411 and 1269 mg/cm^3 and adsorption rate constant, K, of0.139, 0.017 and 0.005 (cm^3/mg-hr) for 80, 60 and 40 ml/L flowrates respectively. The study recommended further work on optimization of the continuous process with other adsorption configurations such as up flow fixed and moving bed.

DEDICATION

I dedicate this work to my Late Grandfather Patrick Wekesa Waswa-Omukwangwa.

ACKNOWLEDGEMENT

This research thesis would not have been possible without the guidance and the help of several individuals.

First, my profound gratitude goes to my supervisor Dr. Peter K. Ndiba of the Department of Civil Engineering for his scholarly advice, encouragement and guidance without which this study would not have been possible. The study would also not have been successful without the valuable input of my course lecturers who taught me in class in the Department of Civil and Construction Engineering, University of Nairobi.

I also express my heartfelt gratitude to Naivasha Water and Sanitation Company managing director Eng. Gichana and the Technical Manager Douglas for providing samples from their facilities, I would not forget University of Nairobi Environmental Laboratory technicians Mr. Kaunda, Ms Nyawira and Ms. Muriithi who guided through the experimental work. I also acknowledge my course mates especially group members with whom we shared ideas in carrying out our group assignments. Finally, my appreciation goes to my family and friends for their support and encouragement. May all Honor and Glory be to God.

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

ABBREVIATIONS AND ACRONYMS

a	Slope of BDST plot (h cm^{-1})
b	Intercept on the ordinate of BDST plot (h)
B	Langmuir constant (mg/g)
C	Liquid phase sorbate concentration in equilibrium (mg/L)
C_b	Breakthrough fluoride concentration (mg/L)
C_e	Equilibrium solute concentration (mg/L)
C_o	Column influent or initial fluoride concentration (mg/L)
C_t	Column effluent fluoride concentration at time t (mg/L)
D	Packed-bed column depth (cm)
D_{min}	Minimum bed depth sufficient to prevent the effluent concentration to exceed the desired breakthrough concentration at zero time (cm)
De	Effective diffusion coefficient (cm^2 s^{-1})
ε	Bed porosity (dimensionless)
K	Freundlich constant (L/g), (dimensionless)
K	Adsorption rate constant (L mg^{-1} h^{-1})
k_b	Measure of affinity of adsorbate for adsorbent
K_d	The linear distribution coefficient (cm s^{-1})
K_F	Adsorption capacity (mg/g) based on Freundlich isotherm
m	Mass of adsorbent in column (g)
n	a measure of how affinity for the adsorbate changes with changes in adsorption density.
N_o	Average adsorption capacity per volume of bed (mg cm^{-3})
q_o	Maximum solid phase concentration of the solute (mg/g)
q	Amount of solute adsorbed per unit weight of material (mg/g)
q_m	Maximum adsorption capacity (mg/g)
Q	solid phase sorbate concentration in equilibrium (mg/g);
Q_v	Volumetric flow rate (mL min^{-1})
Q_vC_o	The influent flow of solute in the column (mg/min);
Q_vC_t	The effluent flow of solute leaving the column (mg/min);
T_b	The service time at breakthrough point (h)
V	Throughput volume (mL)
v	Linear flow rate through the bed (cm h^{-1})
V_a	Bulk volume (L)
V_b	Volume of water treated at breakthrough (L)
V_p	Porous volume (L)
x	Liquid retention time (min)
y	Adsorbent exhaustion rate (g/L)
α	Minimum liquid retention time (min)
β	Minimum adsorbent exhaustion rate (g/L)
ρ_s	Density of the solid phase (g cm^{-3})

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Many regions in Kenya have elevated fluoride concentration in water. While water from saline lakes has been known to have the highest fluoride concentration, ground water sources, mainly boreholes, are recognized as the greatest source of fluoride in drinking water. Manji et al. (1984) found fluoride levels of 2,800 mg/L in Lake Nakuru and tens of mg/Lin boreholes in the Nakuru area. Furthermore, boreholes fluoride mapping show widespread fluoride distribution in Kenya with a large section of Nairobi, parts of Rift Valley and Central Kenya having ground water with fluoride levels of up to 50 mg/L.

High intakes of fluoride ion through food or water cause a disfigurement of teeth known as dental fluorosis or mottled enamel. Ingestion of fluoride in excess of 3 mg/1 over a long period can also result in fluoride osteoschlerosis, the hardening of bones (Linsman and MacMurray, 1943). There is evidence (e.g. Harmon and Kalichman, 1965) that osteoschlerosis may give rise to anemia and subsequent kidney damage. The World Health Organization (WHO) recommends a general standard for concentration of fluoride in water, which ranges from 0.5 to 1.5 mg/L. In Kenya, the Water Services Regulatory Board (WASREB) Drinking Water Quality and Effluent Monitoring Guidelines (WASREB, 2015) states that local and climatic conditions necessitate adaptation of fluoride concentration in excess of 1.5 mg/L fluoride and that in exceptional cases, concentration of 3 mg/L can be acceptable.

Areas with elevated fluoride concentration water often lack alternative sources of non-fluoridated water. At the same time, most defluoridation processes are expensive. Communities from areas with high fluoride concentration are exposed to the adverse effects of its long-term consumption. Preventive measures are thus required to reduce fluoride concentration in drinking water

to the acceptable levels of less than 1.5 mg/L. Most people affected by fluoride contamination in the Rift Valley are in small and poor communities that rely on underground water as a source of drinking water. Therefore, there is need of a method for removal of fluoride from water that is cheap, simple to use and adaptable to either household or village scale. One such method involves the use of bone char, a material that can be produced locally by charring or burning animal bones. This research applies adsorption isotherms and bed depth-service time model to study removal of fluoride from water by bone char.

1.2 Problem Statement

High fluoride concentration in drinking water is causes widespread health problems to many residents in the Rift Valley region of Kenya that encompass dental and skeletal fluorosis (Kaseva, 2006). The excessive fluoride in groundwater is a serious water quality problem. The WHO and national standard (ES 261:2001) permit only up to 1.5 mg/L of fluoride whereas the concentration of fluoride in groundwater in the Rift Valley Region is much higher. Use of bone char provides a potential method of fluoride removal through adsorption. Therefore, there is need to study the removal of fluoride by bone char.

1.3 The Objectives of the Research

The overall objective of this study was to determine the efficacy of using bone char to remove fluoride from drinking water.

The specific objectives are:

1. Evaluate bone char removal of fluoride from water with time and size of media.

2. Establish adsorption isotherms for fluoride removal by bone char.
3. Evaluate the use of bed depth-service time (BDST) model in predicting the service time.

1.4 Scope of Study

This study covered investigation of the efficacy of bone char for the removal of fluoride from water. Adsorption isotherms were investigated using batch processes. The service time was studied using bed depth-service time (BDST) model of continuous flow packed bed column.

CHAPTER TWO

LITERATURE REVIEW

2.1 Sources and Standards of Fluoride in Drinking Water

Groundwater plays an important role in supply of drinking-water to rural communities where surface water of acceptable quality is not available. The use of groundwater is usually preferable to that of surface water because well managed groundwater resources are less vulnerable to contamination than surface water and usually require less treatment (Tsai *et al.,* 2001). High fluoride content in the groundwater is caused by fluoride bearing minerals in the rocks and soils. The problem of elevated concentrations of fluoride in natural water, especially groundwater, is severe and widespread in the Rift Valley region of Kenya (Gimba *et al.,* 2004).

Fluoride is a constituent of igneous and sedimentary rocks with an average of 290 ppm in the 16 km deep earth's crust. It is contained in varying amounts in the following minerals: fluorite (fluorspar), apatite, cryolite, biotite, muscovite, hornblende, topaz, phlogophite, lepidolite, and zinnwaldite (Otero, *et al.,* 2003). The natural weathering and dissolution of such minerals is the primary natural source of fluoride in the aqueous environment. However, not all of the fluoride in drinking waters is of natural origin. Phosphate rock processing plants have wastewaters with very high fluoride concentrations. The nature and location of these discharges are such that underground as well as surface waters can be affected (Itodo, 2010). Fluoride can also get into drinking water supplies through the application of fluoride containing phosphate fertilizers to agricultural land (Cheremisinoff, 2002).

2.2 Standards for Fluoride in Drinking Water

The World Health Organization (WHO) recommends a general standard for concentration of fluoride in water, which ranges from 0.5 to 1.5 mg/L. In Kenya, the Water Services Regulatory Board Drinking Water Quality and Effluent Monitoring Guidelines (WASREB, 2015) states that local and

climatic conditions necessitate adaptation of fluoride concentration in excess of 1.5 mg/L fluoride and that in exceptional cases, concentration of 3 mg/L can be acceptable.

2.3 Removal of Fluoride from Water

Defluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes. One of the well-known defluoridation methods is 'Nalgonda Technique,' which was developed by National Environmental Engineering Research Institute of Nagpur, India (Bulusu, et al., 2008). The method is a precipitation processes employing alum followed by sedimentation and/or filtration. The method involves the addition of lime or sodium carbonate, aluminum sulphate (alum) or aluminum chloride and bleaching powder in sequence. The contents are mixed for a brief period and after sedimentation, fluoride free supernatant is removed for supply whereas the chemical sludge is withdrawn and disposed of.

Chemical precipitation methods, employing soluble metal salts are associated with certain problems which render them less attractive for field application. Adsorption and ion exchange processes appear to be a better alternative for field application (Harmon & Kalichman, 1965). Adsorption onto activated carbon, activated alumina, bone char or ion exchange resins has been investigated (Abram, 1973).

Activated carbon prepared from various raw materials exhibits good fluoride uptake capacity (McKay et al., 1984). However, the adsorption process is highly pH dependent being highly effective at pH less than 3.0 and non-effective at pH 7.0. Capacity of fluoride removal with activated alumina increased directly with fluoride concentration and inversely with pH of the water (Bailey, 1972). Low cost materials like serpentine are effective in reducing fluoride concentration from 6.5 to 1.0 mg/L but are of limited scope (Kulkarni and Nawlakhe, 2008). Activated alumina coated silica gel, activated saw dust, activated coconut shell carbon, coffee husk, bone charcoal, and

activated soil sorbent, are some of the different materials investigated for adsorptive removal of fluoride from water (Christian *et al.,* 2005)

2.4 Activated Carbons

Activated carbon is a high porosity, high surface area material manufactured by carbonization and activation of carbonaceous materials that finds extensive use in the adsorption of pollutants from gaseous and liquid streams (Itodo, 2010). It has an amorphous nature in which a high degree of porosity is developed by manufacturing process and treatment (Abram, 1973). The high degree of porosity and surface area makes activated carbon the most versatile absorbent for removal of organic solids. The intrinsic properties of activated carbon are dependent on the raw material source (Tsai et al., 2001). Activated carbon with high specific surface area and pore volumes can be prepared from a variety of carbonaceous material such as coal, coconut shell, wood, agricultural wastes and industrial wastes. In industrial practices, coal and coconut shell are the two main sources for the production of activated carbon. Other materials like lignite, petroleum, coke, saw dust, peat, fruit pits nut shell and animal bones maybe used. The source materials will be bone char raw material based on the need for developing low cost absorbent.

Itodo (2010) has shown that the source materials used to prepare activated carbon have significance effect on its pore structure, surface texture, resistance to fragmentation, and adsorption capacity. For rural water supplies, it is necessary to use source materials, which are economical and readily available for the manufacture of activated carbon. However, the properties of the finished material are governed not only by the raw material used but also by the method of activation.

2.5 Bone Char

Bone char was one of the earliest media suggested for fluoride removal from water (HWTFR, 2011). It was not widely implemented due to the unpleasant taste of treated water, high cost and unavailability. However, in 1988 the

WHO proclaimed bone char to be an applicable technology for developing countries.

Bone char is a blackish porous granular media capable of absorbing a range of contaminants (Catholic Diocese of Nakuru and Müller, 2006). The bone char grains are packed in a vessel such as a bucket, drum or column and water passed through it.

Bone char, is made from animal bones that are charred (burnt) and crushed. Proper preparation of the bone char is essential to ensure good fluoride removal and to avoid unpleasant taste, color and odor in the treated water. Decades ago, bone char was industrially produced and widely available, but the supply is now limited (Harmon and Kalichman, 1965). However, communities can produce bone char grains locally.

2.5.1 Fluoride Removal Capacity

The major components of bone char are calcium phosphate, activated carbon and calcium carbonate (Bailey, 1972). Fluoride is removed from water through a process based on ion exchange. When raw water containing fluoride comes into contact with bone char, the fluoride ion exchange places with the carbonate ion in the bone char, and the fluoride becomes "attached" to the bone char.

Bone char has high fluoride removal efficiency; with a fluoride adsorption capacity of unto 2 mg fluoride per gram of bone char (Albertus, 2000). Bone char can also absorb a wide range of other contaminants.

2.5.2 Bone Char Production

The steps for preparing bone char include charring, crushing, sieving, washing and drying. Bone char from any animal needs to be carbonized at a temperature of 400 to 500 ºC with a controlled air supply. The charred bones are then crushed either manually or by using a crushing machine. Particles between 0.5 and 4 mm can be used as media. If bone char is not prepared

properly, it may result in low defluoridation capacity and/or lower water quality.

The colour of the charred bone is a simple way to determine its quality (Jacobsen and Dahi, 1997). The colour generally indicates the following bone char qualities.

i. Grey-brownish: High fluoride removal capacity

ii. Black: Still contains organic impurities causing odour and colour

iii. White: Limited fluoride removal capacity

2.5.3 Bone Char Filters

For households and small communities, bone char media can be used in different kinds of filters, which can be single, or combined (Figures 2.1 and 2.2). For a drum or 20 liters bucket, a tap is fixed at the bottom connected to an outlet pipe. A perforated plate can be placed on the surface of the media to avoid disturbance during addition of raw water. The water level in the filter should not drop below the top of the media because the adsorption capacity of the bone char will decrease when left dry. The water should be in contact with the bone char for a minimum of 20 minutes. For new filters or after changing the media, the first few filter volumes of treated water should be discarded due to high turbidity and color (Catholic Diocese of Nakuru and Müller, 2006).

2.5.4 Media Regeneration

Bone char media needs to be renewed or regenerated periodically. Regeneration can be done using caustic soda (NaOH). The fluoride concentration in the treated water needs to be measured periodically to know when to replace or regenerate the media. However, an estimation of the lifespan of the media can be made based on the fluoride concentration of the source water; the volume of water filtered each day and the adsorption capacity of the bone char

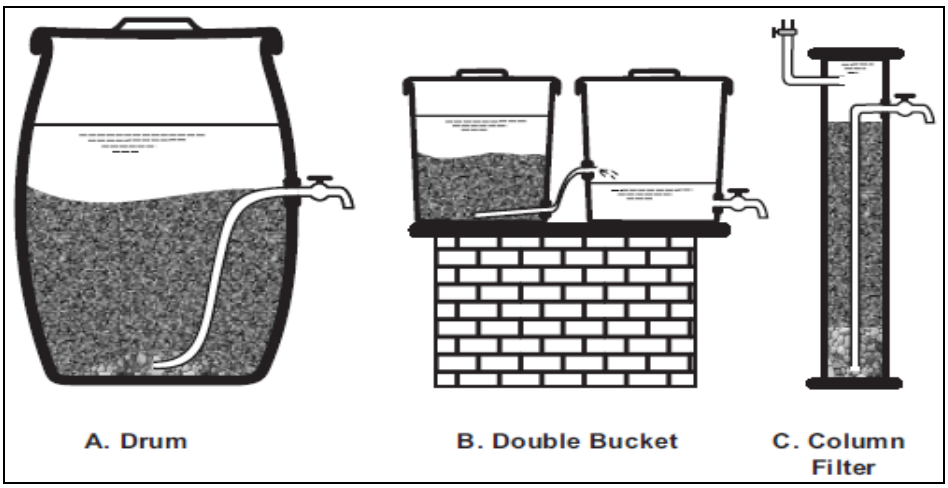

Figure 2.1: Three Common Households Defluoridation Units (WHO, 2004)

Figure 2. 2: Single and Combined Bone Char Filter (Eawag, 2006)

2.6 Fluoride Analysis

The available analytical methods for fluoride determination include (Clesceri et al., 1998):

1) Ion chromatography(IC): laboratory test.
2) Ion selective electrode (pH meter): field and laboratory test
3) Colorimetry:
    i. Complexone Method1(EPA 340.3, Standard Methods 4500F-E): laboratory test
    ii. Complexone Method 2(EPA340.3, Standard Methods 4500F-E): field and laboratory test
    iii. SPANDNS Method (Standard Methods 4500F-D): laboratory test

The ion chromatography or the ion selective electrodes method measures the fluoride activity using a fluoride selective membrane, usually Lanthanum Fluoride crystal. The process is however sensitive to solution pH. At low pH, fluoride can form hydrofluoric acid which lowers the measurement. At high pH, hydroxide can also respond to the ion-selective electrode increasing the measurement. To stabilize the solution pH, a total ionic strength adjustment buffer (TISAB) solution is typically added to the sample, adjusting the solution pH to an optimum value of 5.0 to 5.5.

The electrode method is simplest method of fluoride measurement. It requires use of a special electrode and an expanded-scale pH meter. The colorimetric methods involve breaching of a preformed color by the fluoride ion. This preformed color is the result of the action between the zirconium ion and either alizarin dye or SPADNS dye. The intensity of the color formed is reduced if the amount of zirconium present decreases. Fluoride ions combine with zirconium ions to form a stable complex ion, ZrF2-6, and the intensity of color decreases accordingly. The breaching action is a function of the fluoride ion concentration and is directly proportional to it. Comparisons can then be made visually or photometrically (Sawyer et al, 2003). The SPADNS method

is preferred due to the less time required to get the results as opposed to the alizarin dye procedure.

2.7 The Adsorption Process

Adsorption is the process by which ions or molecules present in phase tend to condense and concentrate on the surface of another phase (Sawyer, 2003). Adsorption of contaminants onto activated carbon is frequently used for purification of the air or water. The material being concentrated is the adsorbate and the adsorbing solid is termed the adsorbent. There are three types of adsorptions; namely, physical, chemical and exchange adsorption. Physical adsorption is relatively non-specific and is due to the operation of weak forces of attraction or van der Waals' forces between molecules. The adsorbed molecule is not affixed to a particular site on the solid surface but is free to move about over the surface. In addition, the adsorbed material may condense and form several superimposed layers on the surface of the adsorbent. Physical adsorption is generally readily reversible.

Chemical adsorption, also referred to as chemisorption, is the result of much stronger forces, comparable with those leading to the formation of chemical compounds. Normally, the adsorbed material forms a layer over the surface, which is only one molecule thick, and for which molecules are not free to move from one surface site to another. When the monomolecular layer covers the surface of the adsorbent, the adsorption capacity is essentially exhausted. Chemical adsorption is seldom reversible; the adsorbent must generally be heated to remove the adsorbed materials.

Exchange adsorption is characterized by electrical attraction between the adsorbate and the surface and involves ion exchange process. The ions of a substance concentrate at the surface as a result of electrostatic attraction to sites of opposite charge on the surface. In general, ions with greater charge, such as trivalent ions are attracted more strongly toward a site of opposite charge than are molecules with lesser charge, such as monovalent ions. The smaller the hydrated radius of the ions the greater the attraction.

Because, adsorption is a surface phenomenon; the rate and extent of adsorption are functions of the surface area of solids used. Activated carbon is used extensively for adsorptive purposes because of its tremendous surface area in relation to mass.

2.7.1 Adsorption Isotherms

An adsorption isotherm is a quantitative relationship describing the equilibrium between the concentration of adsorbate in solution C (mass/volume) and its sorbed concentration q (mass adsorbate/mass adsorbent). The term isotherm is used to signify that the relationship is for a given temperature.

Adsorption isotherms are based on data that are specific for each system; therefore, an isotherm must be determined for every application. An adsorption isotherm besides showing the course taken by the system in a concise form provides a measure of the economic feasibility of the adsorbent for commercial application (Chilton et al., 2002). Major factors in determining the shape of an isotherm include:

i. Numbers of compound in the solution;
ii. Relative adsorption abilities of the compound;
iii. Initial concentration of the solution;
iv. Degree of competition among solutes for adsorption sites;
v. Characteristics of the generated adsorbent.

The analysis of the isotherm data by fitting to different isotherm models is an important step to finding a model for design purposes (Tien, 1994). Adsorption isotherm can be generated based on numerous theoretical explanations. Four commonly used isotherms are linear, Langmuir, Freundlich and BET. The isotherm that may be used for a particular case is dependent on the factors listed above. The linear isotherm is a limited special case of the Freundlich isotherm. It mainly describes sorption of organic chemicals in the natural environment. BET Isotherm was developed by Brunauer, Emmett, and Teller as an extension of the Langmuir isotherm to account for multilayer

adsorption (adsorption of multiple layers of adsorbate). This model assumes that a number of layers of adsorbate accumulate at the surface and that the Langmuir isotherm applies to each layer. It is somewhat more complex than the Langmuir isotherm. The main and well known isotherm models for surface coverage studies are Langmuir and Freundlich isotherm models.

Langmuir isotherm assumes that a single adsorbate binds to a single site on the adsorbent and that all surface sites on the adsorbent have the same affinity for the adsorbate. Surface complexation theory can be used to develop the Langmuir isotherm given below (Benjamin, 2002):

$$q = q_m \frac{k_b c}{1 + k_b c}$$ ---------- Equation 2.1

Where q = sorbed concentration (mass adsorbate/mass adsorbent) (sometimes referred to as adsorption density) (mg/g)

q_m = maximum capacity of adsorbent for adsorbate (mass adsorbate/mass adsorbent)

C = aqueous concentration of adsorbate (mass/volume) (mg/L)

k_b = measure of affinity of adsorbate for adsorbent

As C gets larger, adsorption sites become filled-up and q approaches q_m. Evaluation of the coefficients q_m and k_b can be obtained using the linearised form of Equation 2.1 as shown below:

$$\frac{1}{q} = \frac{1}{q_m k_b}\left(\frac{1}{C}\right) + \frac{1}{q_m}$$ ---------- Equation 2.2

The Langmuir isotherm can be modified to account for competitive adsorption by more than one adsorbate and for adsorbents that have sites with different affinities for a given adsorbate.

The Freundlich isotherm can be derived from Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the

Langmuir isotherm (Benjamin, 2002). Freundlich isotherm assumes adsorption phenomenon can be expressed in exponential form as follows:

$$q = kc^{1/n}$$ ---------- Equation 2.3

Where

Q= solid phase sorbate concentration in equilibrium (mg/g);

C = liquid phase sorbate concentration in equilibrium (mg/L);

K = Freundlich constant (L/g), a measure of the capacity of the adsorbate (mass adsorbate/ mass adsorbent);

n = a measure of how affinity for the adsorbate changes with changes in adsorption density.

When n=1, the Freundlich isotherm becomes a linear isotherm and indicates that all sites on the adsorbent have equal affinity for the adsorbate(s). Values of n>1 indicate that affinities decrease with increasing adsorption density. The term, 1/n, is the heterogeneity factor to be determined from a plot of log C *Vs* log q. Evaluation of the coefficients K and n can be accomplished using linearized form of above equation as follows:

$$\log q = \log k + \frac{1}{n}\log c$$ ---------- Equation 2.4

Evaluation of coefficients for both Langmuir and Freundlich isotherms can be conducted using the same experimental data (Sawyer et al., 2003). Typically, different masses of adsorbent are added to a solution containing the adsorbate(s) of interest. These solutions are mixed and allowed to come to equilibrium. The concentration of adsorbate(s) remaining is measured. By knowing the initial concentration, the mass of adsorbate removed per mass of adsorbent, can be calculated. Equations 2.2 and 2.3 can then be used to determine values of q_m, K_b, K and n using techniques such as least squares

linear regression. Statistical analysis of these regressions should allow determination of which isotherm works best for a given situation.

2.7.2 Fixed-Bed Design Models

Batch adsorption models are simple and useful for design of batch treatment units. For continuous flow systems, fixed-bed models are necessary. A commonly used mathematical model for flow and reaction in porous materials is the one dimensional advection dispersion equation (Equation 2.5) that assumes linear sorption isotherm of the solute onto the solid surface (Damte, 2006).

$$\frac{\partial C}{\partial t} = De\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial X} - \rho_S\frac{1-\varepsilon}{\varepsilon}k_d\frac{\partial C}{\partial t} \quad \text{---------- Equation 2.5}$$

Where

C = the concentration of the solute;

De = effective diffusion coefficient;

ρs = the density of the solid phase;

ε = the porosity of the bed;

q = mass of solute sorbed per unit of sorbent;

v_x = average linear velocity of pore fluid in the x direction; and

K_d = the linear distribution coefficient.

The main objective of the above model is to predict the breakthrough curve. However, to apply the model it is necessary to have physical and kinetic parameters. The parameters can be obtained either from batch adsorption studies or literature. Additionally, the models require the solution of a number of non-linear partial differential equations, which include physical as well as kinetic parameters. These equations can be solved only by numerical methods that are time consuming and tedious (Liljana, 2001). Therefore, there is need to seek other simplified models to design a fixed-bed adsorption column. The operation of fixed-bed adsorption column is commonly expressed in terms of mass balance as shown below.

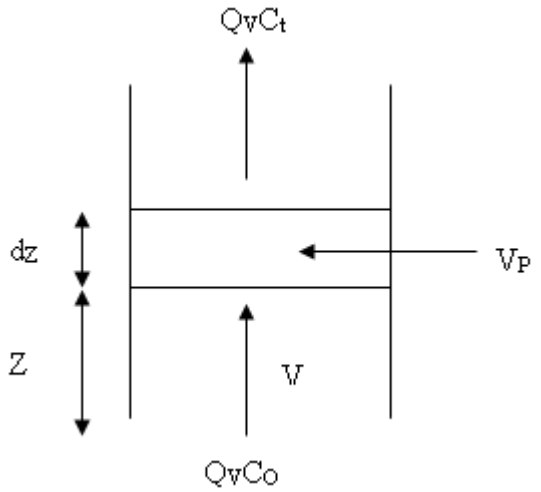

Figure 2.3: Mass balance in a fixed-bed column element (Damte, 2006)

For this system, the mass balance can be expressed follows.

$$Q_v \quad C_t = Q_V \quad C_t + V_p \frac{dC}{dt} + m\frac{dq}{dt}$$ ----------Equation 2.6

Where

Q_v = the volumetric flow of the solution in the column (L min^{-1});

C_o, C_t, = the influent and effluent solute concentrations (mg/L), respectively;

Q_vC_o = the influent flow of solute in the column (mg/min);

Q_vC_t = the effluent flow of solute leaving the column ($mgmin^{-1}$);

V_p = the pore volume (L);

$$V_P = \frac{1}{1-\varepsilon}(V_a)$$ ---------- Equation 2.7

Where

Va = bulk volume and ε the porosity,

$V_P\left(\frac{dC}{dt}\right)$ = flow rate through the bed depth column (mg/min)

$m\left(\frac{dq}{dt}\right)$ = amount of solute adsorbed onto adsorbent (mg/min)

m = mass of adsorbent and

$\frac{dq}{dt}$ = the adsorption rate.

From mass balance of a fixed-bed reactor, the determining factors of the balance for a given bed depth of the column are the linear flow rate v, the initial solute concentration c, the adsorption potential and the pore volume even though the later parameter may be neglected. To optimize the adsorption process in a packed-bed column, it is necessary to examine these parameters and to estimate their influence (Christian et al., 2005). By varying the above process parameters, the optimum conditions for the column operation can be predicted through different design methods. There are a number of simple design models available which are based upon general assumptions. These models include the bed depth service time (BDST), the empty bed residence time (EBRT), and Thomas model. The applicability of simplified models for the removal of organic solutes by activated carbon has been studied extensively while modeling fluoride adsorption with (BDST) model has been applied successfully for activated alumina (Ghorai and Pant, 2005).

2.7.3 Bed Depth Service Time (BDST) Design Model

In a fixed-bed system, the main design criterion is to predict how long the adsorbent material will be able to sustain removal of a specified amount of solute from solution before requiring regeneration. This period is known as the service time of the bed (Liljana et al., 2001). The BDST model describes a relation between the service time of a packed column and the depth of packed bed column. The original work on the BDST model was carried out by Bohart and Adams (1920) on the adsorption in a dynamic system of the chlorine onto activated charcoal and by Thomas (1944) on the adsorption of the ions by zeolites. The model was found to follow Equation 2.8.

$$\ln\left[\frac{C_o}{C_b} - \quad 1\right] = \ln\left(e^{k(N_0/V)D} - 1\right) - K C_O T_b \quad \text{---------- Equation 2.8}$$

In this relation $e^{kN_o/V)D} \rangle\rangle 1$, thus,

$$\ln\left(\left(KN0/V_o\right)^D - 1\right) \equiv \frac{K N_0}{V} D$$ ---------- Equation 2.9

Consequently, Hutchins (1973) proposed the following linear relation between the column bed depth (D) and the service time (T_b):

$$T_b = \frac{N_o}{C_o V} D - \frac{1}{kC_0} \ln\left(\frac{C_o}{C_b} - 1\right)$$ ---------- Equation 2.10

Where T_b is the service time at breakthrough point (h), N_o is the bed capacity ($mg \cdot cm^{-3}$), D the packed-bed column depth (cm), V is the linear flow rate through the bed ($cm\ h^{-1}$), C_o and C_b are the influent and the breakthrough fluoride concentration (mg/L), respectively, and K is the adsorption rate constant ($L\ mg^{-1}\ h^{-1}$).

The equation of a straight line on BDST curve is expressed in the form:

$$y = ax + b$$ ---------- Equation 2.11

Where

y = service time,

x = bed depth,

a = slope (No/C_oV)

b = ordinate intercept ($-\{1/KC_o[\ln (C_o/C_b - 1)]\}$,)

The numerical value, a, the intercept, b, adsorptive capacity of the system, N_o, and the rate constant, K, can be evaluated from the slope and intercept of a straight line plotted as the service time, T_b, against the bed depth from experimental data. The minimum bed depth (D_{min}) which represents the theoretical depth of adsorbent able to prevent the adsorbent concentration from exceeding C_b is obtained when $T_b = 0$ and, therefore, according to Equation 2.8,

$$D\min = \frac{V}{K N_o} \ln\left(\frac{C_o}{C_b} - 1\right)$$ ---------- Equation 2.12

The slope of the line presented by y = ax + b can be used to predict the performance of the bed, if there is change in the initial solute concentration C_{o1} to a new C_{o2}. Hutchins (1973) proposed that the new slope a_2 and new intercept b_2 can be estimated by Equations 2.13 and 2.14, respectively:

$$a_2 = a_1 \frac{C_{01}}{C_{02}} \quad \text{---------- Equation 2.13}$$

$$b_2 = b_1 \frac{C_{01}}{C_{02}} \frac{\ln\left[\left(C_{01}/C_b\right) - 1\right]}{\ln\left[\left(C_{01}/C_b\right) - 1\right]} \quad \text{---------- Equation 2.14}$$

McKay et al. (1984) suggests that if design data are required for a change in volumetric flow rate of solute to the same adsorption system, the new slope with the intercept remaining unchanged can be written as:

$$a_2 = a_1 \frac{Q_1}{Q_2} = a_1 \frac{v_1}{v_2} \quad \text{---------- Equation 2.15}$$

CHAPTER THREE

METHODOLOGY

3.1 Introduction

To meet the objectives of the study, experimental work was carried out on groundwater from Naivasha in the Rift Valley of Kenya to evaluate removal of fluoride from water using bone char (Figure 3.1). Naivasha Town is situated on Lake Naivasha about 100 km North West of the capital city, Nairobi. Batch tests were carried out area to establish isotherms of fluoride adsorption on bone char. Dynamic column tests were carried out to evaluate applicability of bed depth service time (BDST) model for the design of adsorption systems for fluoride removal with bone char.

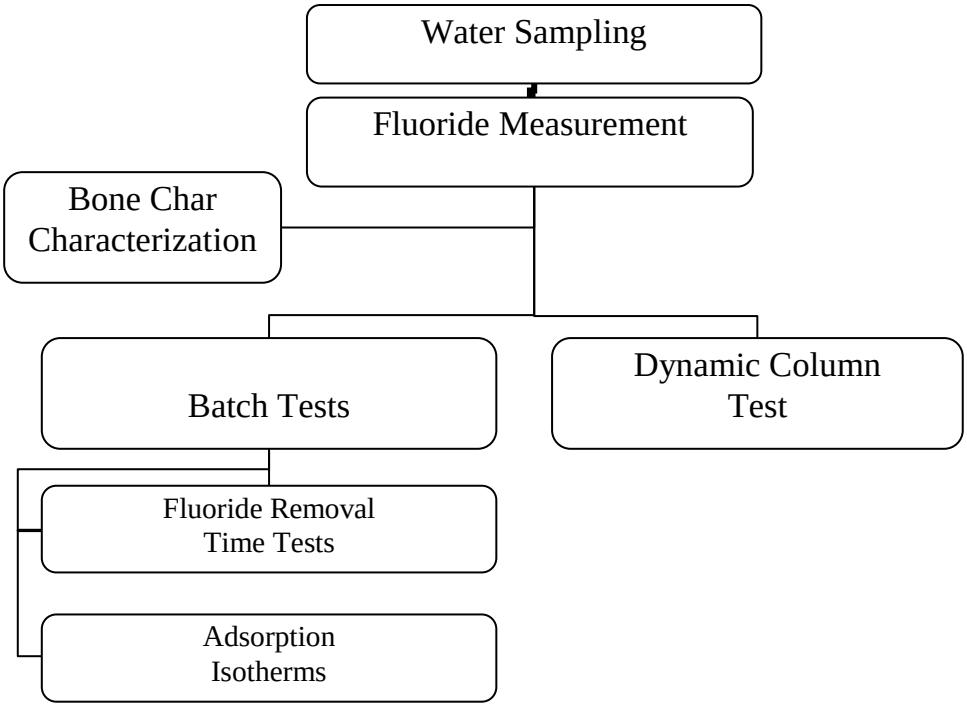

Figure 3.1: Flow Diagram of Methodology

3.2 Water Sampling

Water samples were obtained from five boreholes that supply water to Naivasha Water and Sanitation Company of Naivasha in Nakuru County, Kenya. The samples were placed in 20-liter containers at the point of collection and taken to the laboratory. The samples were analyzed to obtain their initial fluoride concentration.

3.3 Bone Char Sourcing and Characterization

Bone char was obtained from Catholic Diocese of Nakuru. The char is prepared by charring animal bones to carbonize at a temperature of 400 to 500 ^{o}C with a controlled air supply. The charred bones are then crushed, sieved, washed and dried.

Particles between 0.5 and 4 mm were used as the adsorption media. The density of the bone char was determined by packing the media in a column of known mass and volume and measuring the change in mass. The colour of the charred bone was used as a simple way to determine its quality (e.g. Jacobsen and Dahi, 1997).

3.3.1 Fluoride Measurements

Fluoride analysis was carried out using H196739 Fluoride High Range fluoride meter. To obtain the initial fluoride concentration of the water samples, 10 ml of sample was first placed in each of two sample cells. 10 ml of distilled water was placed in one sample cell to act as blank. To the other sample cell, 2 ml of fluoride high range H1 93739B reagent was added. The blank sample was placed in the fluoride meter and used to calibrate the meter to zero. The second sample cell was then placed in the meter and the fluoride concentrations measured.

3.3.2 Batch Test for Fluoride Removal Time Tests

The rate of fluoride removal was evaluated using batch tests of fluoride water in contact with bone char. The residual fluoride concentrations were measured at various contact periods.

Fluoride water 200 ml was placed in 400 ml Erlenmeyer flasks and the initial concentration of fluoride, C_i, measured. 20 g of activated bone char was weighed out on glazed paper and added to the fluoride water in the flasks. Because the adsorption process is also a function of time, the bone char was placed in the flasks at the same time, to provide the same contact period in each flask. The flasks were labeled and fitted with stoppers and then placed on a six paddle stirrer jar test apparatus from Phipps & Birds Stiffer 7790 - 402. The contents were stirred at 10 rpm for 3 hours. Samples were taken at 30 minute intervals. The final concentration after adsorption of fluoride, C_e, in each of the flasks was determined. The test temperature was 25+ 2 ^oC.

3.3.3 Adsorption Isotherms Batch Tests

Adsorption isotherms for fluoride removal by bone char were studied on water from Naivasha Booster Pump Borehole with an initial fluoride concentration of 7.3 mg/L. Batch tests were carried out using varying doses of bone char. The experimental set up was similar to that of fluoride removal time tests; however, five bone char doses: 5, 10, 20 and 30 g in 200 mL equivalent to 25, 50, 100 and 150 g/L, were used. Tests were carried out for 60 minutes contact time while stirring at 10 rpm for fine and medium grain size. To test the effect of pH changes on the isotherms, a buffered solution was tested for the medium size media. The experiments were carried out at 25 ± 2^oC.

3.3.4 Column Dynamics Tests

Batch adsorption studies only may not be directly applied for field applications in the treatment of water especially for continuous flow systems (Musapatika, 2010). Therefore, it is necessary to complement batch

equilibrium and kinetic tests with dynamic column studies to determine system parameters including particle size requirements and contact time. By determining the process parameters, the optimum conditions for the column operation can be predicted through bed depth service time (BDST) model.

Fixed bed column experiments were conducted at room temperature using a laboratory scale glass column of 5.5 cm diameter and 35 cm length (Plate 3.1 and Figure 3.1). The samples were run through defluoridation apparatus containing bone char. Defluoridation runs were conducted for flow rates of 40, 60 and 80 mL min^{-1} equivalent to 1.01, 1.52 and 2.02 m/h, respectively. In a similar study on fluoride adsorption onto granular aluminum hydroxide, Damte (2006) used 2.3 cm diameter columns and flow rates of 12, 23 and 40 mL min^{-1} equivalent to 1.73, 3.32 and 5.77 m/h, respectively. Comparatively, rapid sand filters in water treatment works operate at 4 - 6 m/h.

The concentration of fluoride, C_{i0}, in each flask was measured. The column was run in a down flow mode, which ensured that the bed remained packed and stable during the entire operation, thereby resulting in maximum contact between the adsorbent and the adsorbate. The column was packed with a known mass of bone char to obtain a particular bed depth. This mass was computed from the density obtained from bone char characterization. A glass wool plug slotted in with 50 mm layer of aggregate particles was placed at the bottom to support the bone char bed and another glass wool plug slotted in with 50 mm layer of aggregate particles was also provided on top of the bed to prevent floating up of the adsorbent particles. The presence of air pockets within the packed bone char column would cause channeling of the influent water and lower the adsorption efficiency of the bed (Ko *et al*., 2000). Therefore, the bone char packed column was fully wetted by filling with distilled water before starting the tests.

In each experimental run, influent water was fed at a preset volumetric flow rate, pH and initial concentration. The flow rate was measured at the exit of the column at regular intervals of 30 min by collecting samples of solution for

a known period (e.g. Kumar and Chakraborty, 2009). The fluoride concentration was measured using the fluoride meter at various times intervals. Sampling was carried out at three depths; namely 10, 20 and 30 cm over a period of 8 hours.

Plate 3.1: Experimental set up for Fixed Bed Adsorption Column Studies

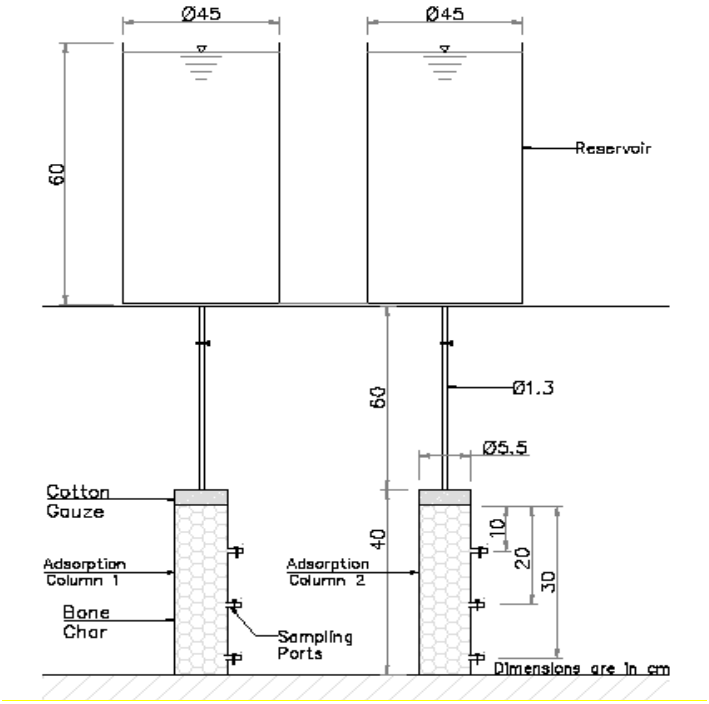

Figure 3.2: Schematic drawing of the column test apparatus

CHAPTER FOUR

RESULTS AND DISCUSSION

The overall objective of this study was to evaluate the efficacy of using bone char to remove fluoride from drinking water. The study covered measurement of fluoride concentration in water, bone char characterization, fluoride removal with time tests, batch tests for equilibrium isotherms and fixed bed service time tests. This chapter presents the results and discussions.

4.1 Concentration of Fluoride in Naivasha Town Borehole Water

The pH and fluoride concentration of the water samples obtained from five boreholes that supply Naivasha Town are shown in Table 4.1. Fluoride concentrations in four of the boreholes were above 6.5 mg/L while that for Karati Boreholes was 2.3 mg/L. These fluoride concentration exceeded the World Health Organization recommended concentration of 1.5 mg/L. They also exceeded WASREB acceptable limit for exceptional cases (WASREB, 2015) mg/L with exception of that for Karati Borehole. Accordingly, there is need for removal of fluoride from the water to achieve drinking water standards.

Table 4.1: pH and Fluoride Concentrations in Naivasha Borehole Water

Sample	Sampling Point	pH	Fluoride Concentration (mg/L)
1	Booster pump	7.6	8.1
2	Waterworks	8.1	6.8
3	Police Line	7.8	8.8
4	Karati	7.7	2.3
5	Karangita Pump	7.8	6.7

4.2 Bone Char Characteristics

The size, grade, color and density of bone char obtained from Catholic Diocese of Nakuru are presented in Table 4.2. The bulk density of bar char ranged from 700 to 800 units. Therefore, the bone char is a lightweight material compared to the commonly used filter sand, which has a density of 1,400 kg/m^3. The course and fine sized media were brownish gray while the medium size was gray (Plate 4.1). The colour of the media indicated high removal capacity and that the media was unlikely to cause odour and colour (e.g. Jacobsen and Dahi, 1997).

Table 4.2: Characterization of Bone Char

Size (mm)	Grade	Color	Bulk Density (kg/m^3)
0.63 mm <	Fine	Brownish Gray	700 - 800
0.63-2 mm	Medium	Gray	700 - 800
> 2-4 mm	Coarse	Brownish Gray	700 - 800

Plate 4.1: Graded Bone Char; from left, Course, Medium and Fine Sizes

4.3 Fluoride Removal - Time Tests

Bone char removal of fluoride from water was evaluated for different contact times using batch tests. Variation of fluoride concentrations with contact time is presented in Table 4.3 for fine and medium sized media and illustrated in Figure 4.1. The bone char reduced fluoride concentration from 8.1 mg/L to within the WHO limit concentration of 1.5 mg/L in 120 minutes (2 hours).

The WASREB threshold of 3 mg/L for exceptional cases in areas with high concentration of fluoride was achieved within a contact time of 50 minutes.

Table 4.3: Fluoride Concentration at Varying Contact Time

Time(min)	Fluoride Concentration (mg/L)	
	Fine media (< 0.63mm) pH 7.62	Medium Size Media (0.63-2 mm) pH 7
0	8.1	8.1
30	3.8	3.2
60	2.4	2.5
90	1.9	1.9
120	1.5	1.5
150	1.3	1.4
180	0.9	1.2

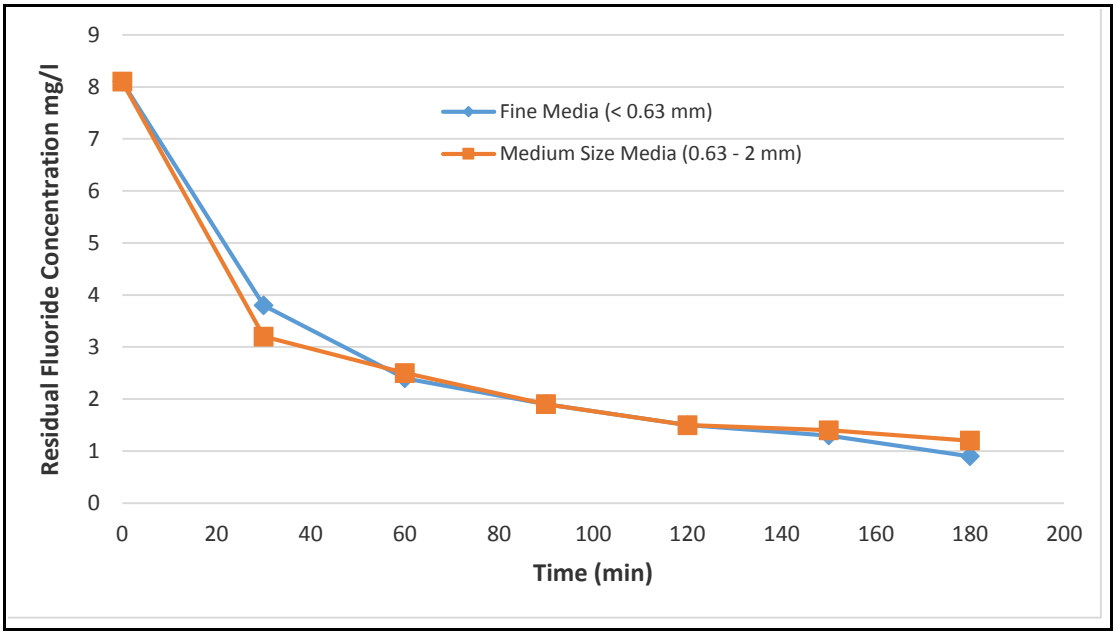

Figure 4.1 Fluoride Concentration at Varying Contact Time

The removal efficiency (RE %) of fluoride in the Naivasha boreholes water was calculated for each contact time sampling using Equation 4.1.

$$RE(\%) = \left(C_O - C_e\right) C_O \; x100 \quad \text{---------- Equation 4.1}$$

The plot of removal efficiency against time (Figure 4.2) show that the bone char achieved 50 to 60% fluoride removal within the first 30 minutes and 85 to 90% removal within 180 minutes.

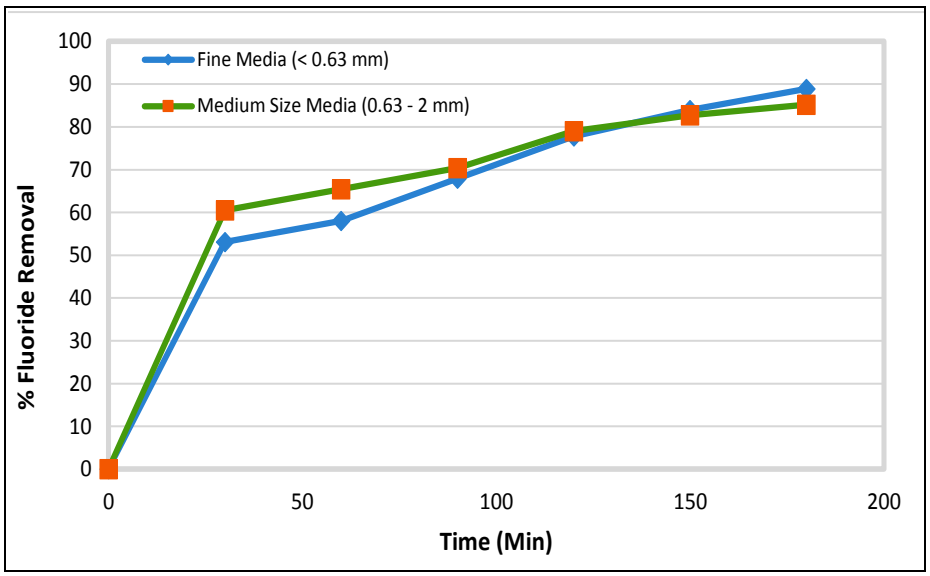

Figure 4.2: Fluoride Removal Efficiency

The paired t-test of the medium and fine media resulted in the two-tailed p value of 0.8968, which exceeded 0.05, indicating that the difference between the two media was not statistically significant.

While it would be expected that the presence of large number of smaller particles would provide a larger surface area for sorption system for fluoride ion removal, the difference between removals by the two media sizes was not significant. On the contrary, the medium size media was more efficient than the fine media, for the most part. A plausible explanation is that fine and medium size aggregate were of different structures; for example, may have originated from different bone types. Consequently, the surface area was not

differentiated by the size of the particles. Alternatively, the bone char could have such an open structure that the range of particles sizes tested did not affect the available surface area.

4.4 Adsorption Isotherms

Adsorption isotherms tests for fluoride removal by bone char were carried out using batch tests for bone char dosages ranging from 5 to 30 g in 200 mL of (25 – 150 mg/L), initial fluoride concentration of 7.3 mg/L and contact time of 60 minutes. The test conducted using the jar test apparatus at 10 rpm for fine and medium size media. To evaluate the effect of pH, tests were also carried out on buffered solution for the medium size media. The equilibrium concentrations are presented in Table 4.4.

Table 4.4: Fluoride Removal for varying Fine and Medium Grain Size Bone Char Dosage at 60 Minutes Contact Time

Mass in 200 mL of water (g)	Co (mg/L)	C (mg/L)
Fine Media (< 0.63 mm)		
5	7.3	5.4
10	7.3	5.0
20	7.3	3.5
30	7.3	3.4
Medium Size Media (0.63 – 2 mm)		
5	7.3	4.6
10	7.3	4.0
20	7.3	3.0
30	7.3	1.8
Medium Media Buffered (0.63 – 2 mm)		
5	7.3	5.2
10	7.3	3.7
20	7.3	2.9
30	7.3	2.4

The mass of fluoride adsorbed at equilibrium, q was calculated from the mass balance equation expressed in Equation 4.2 (Table 4.5)

$$q = (C_0 - C_e)V/M$$ ---------- Equation 4.2.

Where;

q = amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

C_o = initial fluoride concentrations (mg/L)

C_e = final fluoride concentrations (mg/L)

V = volume of fluoride solution (mL)

M = mass of the catalyzed bone char sorbent (g)

Table 4.5: Computation of Sorbate Concentration for Bone Char Dosages at 60 Minutes Contact Time

Mass of media in 200 mL of water (g)	**C (mg/L)**	**q (mg/g)**
Fine Media		
5	5.4	0.076
10	5.0	0.046
20	3.5	0.038
30	3.4	0.026
Medium Media		
5	4.6	0.108
10	4.0	0.066
20	3.0	0.043
30	1.8	0.037
Medium Media Buffered		
5	5.2	0.108
10	3.7	0.066
20	2.9	0.043
30	2.4	0.037

These data was fit into Langmuir and Freundlich isotherms in the following subsections.

4.4.1 Langmuir Isotherm Analysis

Langmuir isotherm assumes that a single adsorbate binds to a single site on the adsorbent and that all surface sites on the adsorbent have the same affinity for the adsorbate. The isotherm is developed from surface complexation theory as follows (Benjamin, 2002):

$$q = q_m \frac{k_b c}{1 + k_b c}$$ ---------- Equation 4.3

Where q = sorbed concentration or adsorption density (mass adsorbate /mass adsorbent), mg/g)

q_m = maximum capacity of adsorbent for adsorbate (mass adsorbate /mass adsorbent)

C = aqueous concentration of adsorbate (mass/volume) (mg/L)

k_b = measure of affinity of adsorbate for adsorbent

As C gets larger, adsorption sites become filled-up and the sorbate concentration q approaches the maximum concentration, q_m. Therefore, a plot of q against C should show a saturation curve. When the sorbate concentrations were plotted against aqueous concentration of fluoride, straight line graphs and not saturation curves were obtained (Figure 4.3); therefore, it was concluded that fluoride adsorption on bone char does not follow the Langmuir Isotherm, which indicates that the media is not homogeneous.

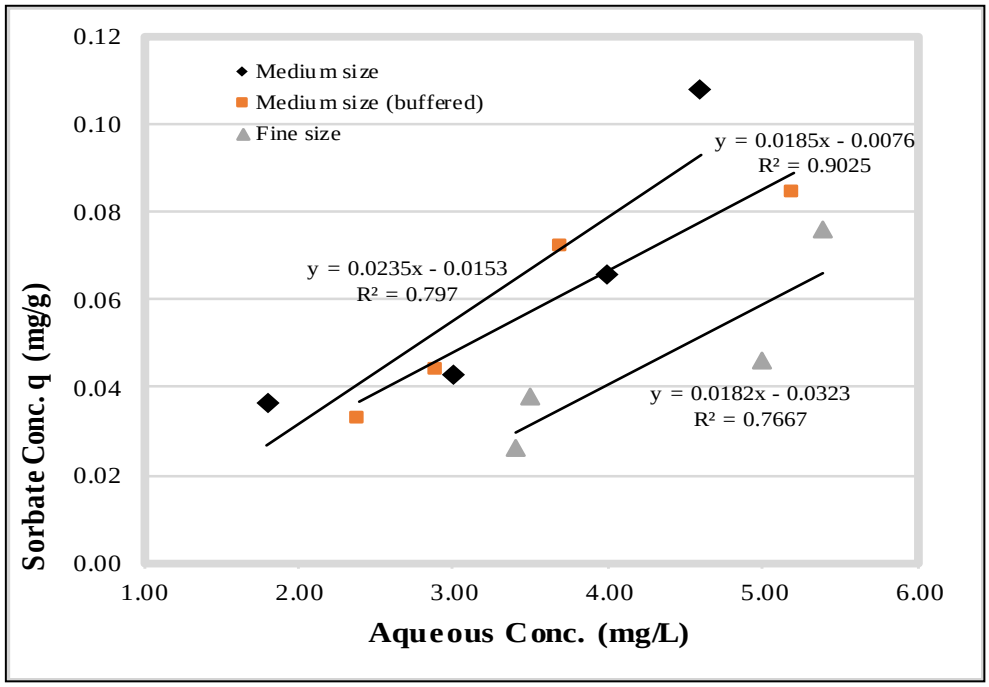

Figure 4.3: Fluoride Sorbate Concentration against Aqueous Concentration

4.4.2 Freundlich Isotherm Relationship

Freundlich isotherm expresses adsorption phenomenon in exponential form as follows:

$$q = k_f c^{1/n}$$ ---------- Equation 4.4

Where

Q= solid phase sorbate concentration in equilibrium (mg/g);

C = liquid phase sorbate concentration in equilibrium (mg/L);

k_f = Freundlich constant (L/g), a measure of the capacity of the adsorbate (mass adsorbate/ mass adsorbent);

n = Adsorption intensity, a measure of how affinity for the adsorbate changes with changes in adsorption density.

When n = 1, the Freundlich isotherm becomes a linear isotherm and indicates that all sites on the adsorbent have equal affinity for the adsorbate(s). Values

of n>1 indicate that affinities decrease with increasing adsorption density. The term, 1/n, is the heterogeneity factor to be determined from a plot of log C *Vs* log q. The logarithmic form of the Freundlich isotherm is given as:

$$\log q_e = \log k_f + \frac{1}{n}\log c \text{ ---------- Equation 4.5}$$

Where:

q_e = Solid phase adsorbate concentration in equilibrium (mg/g);

c = Liquid phase adsorbate concentration in equilibrium (mg/L);

k_f = Freundlich constant (L/g), a measure of the capacity of the adsorbate (mass adsorbate/ mass adsorbent);

n = a measure of how affinity for the adsorbate changes with changes in adsorption density.

Table 4.6: Fluoride Removal Results for Bone Char Dosage, 7.3 mg/L Initial Fluoride Concentration and 60 Minutes Contact Time

Mass of Media in 200 mL of water (g)	C (mg/L)	q (mg/g)	Log q	Log c
Fine Media				
5	5.4	0.076	-1.112	0.732
10	5.0	0.046	-1.337	0.699
20	3.5	0.038	-1.420	0.544
30	3.4	0.026	-1.585	0.531
Medium Media				
5	4.6	0.108	-0.967	0.663
10	4.0	0.066	-1.180	0.602
20	3.0	0.043	-1.367	0.477
30	1.8	0.037	-1.436	0.255
Medium Media Buffered				
5	5.2	0.084	-1.076	0.716
10	3.7	0.072	-1.143	0.568
20	2.9	0.044	-1.357	0.462
30	2.4	0.033	-1.486	0.380

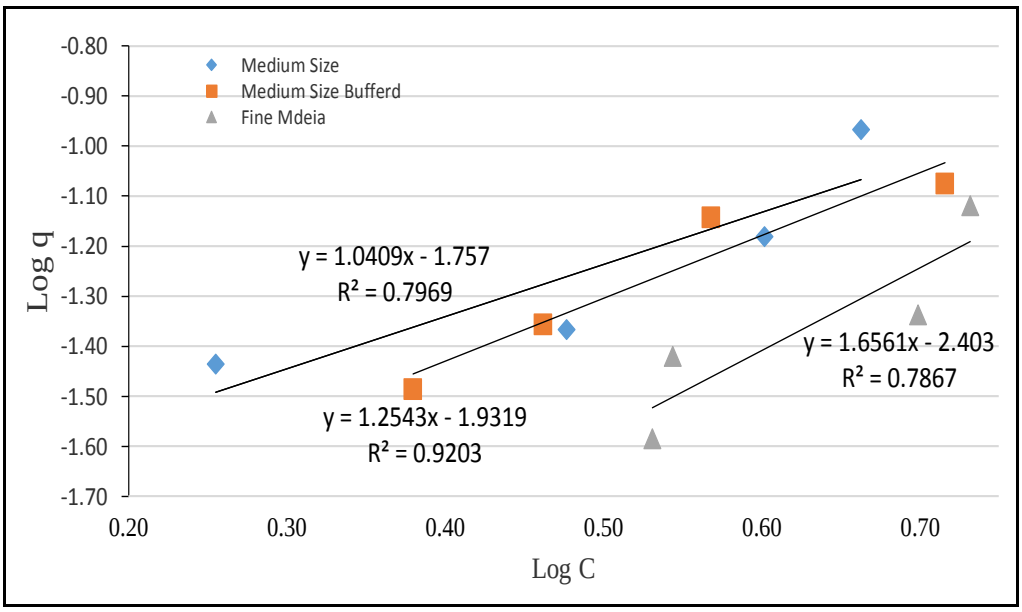

Figure 4.4: Freundlich Isotherm Adsorptions

Plots of log q_e against log C gave a straight line graph indicating that fluoride adsorption to bone char does conforms to Freundlich Isotherm. The values of the sorption capacities and coefficients of correlation (r^2) computed from linearized Freundlich adsorption isotherm equations are given in Table 4.7.

Table 4.7 Bone char Sorption Capacities and Coefficient of Correlation (r^2) for Freundlich Isothermal Equilibrium Models

	Media		
	Fine	**Medium size**	**Medium size (Buffered)**
k_f	3.95×10^{-3}	1.75×10^{-2}	1.17×10^{-2}
1/n	1.657	1.043	1.255
R^2	0.79	0.80	0.92

The k_f value is a rough indicator of adsorption capacity; it increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The 1/n is the adsorption intensity. The numerical value of 1/n is a useful index of adsorption

efficiency and is related to the energy of adsorption. The results show that the fine size and buffered medium size bone char had a higher adsorption intensity of 1.657, than the medium size bone char intensity of 1.04 to 1.26. However, they had lower adsorption capacity than the medium size media, 0.00395 L/g as compared to 0.0117 to 0.0175 L/g for medium size. Buffering the solution increased the adsorption intensity but reduced the adsorption capacity indicating that the adsorption was pH dependent. The opposing parameters may explain why the fine media did not show significantly different adsorption in the fluoride removal tests, despite its larger surface area. It confirms that the coarse and fine media had other differences besides size, which could be a result of originating from different bones or parts of bones.

4.5 Bed Depth Service Time Model

4.5.1 Results of Bed Depth Service Time

Breakthrough curves were obtained using a single column with ports at depths of 10, 20 and 30 mm. Continuous down flow rates of 40, 60 and 80 ml/minute were used. The fluoride concentration of the influent was 8.1 mg/L and the pH 7.6.

Break-through curves were obtained by plotting the ratio of residual fluoride concentration to initial concentration with bed depths for flow rates of 40, 60 and 80 ml/minute. Straight line graphs with correlation coefficients of over 0.9 were obtained for flows with higher flow rates and of below 0.6 for lower flow rates and the different media depth tested (Figure 4.5 - 4.7).

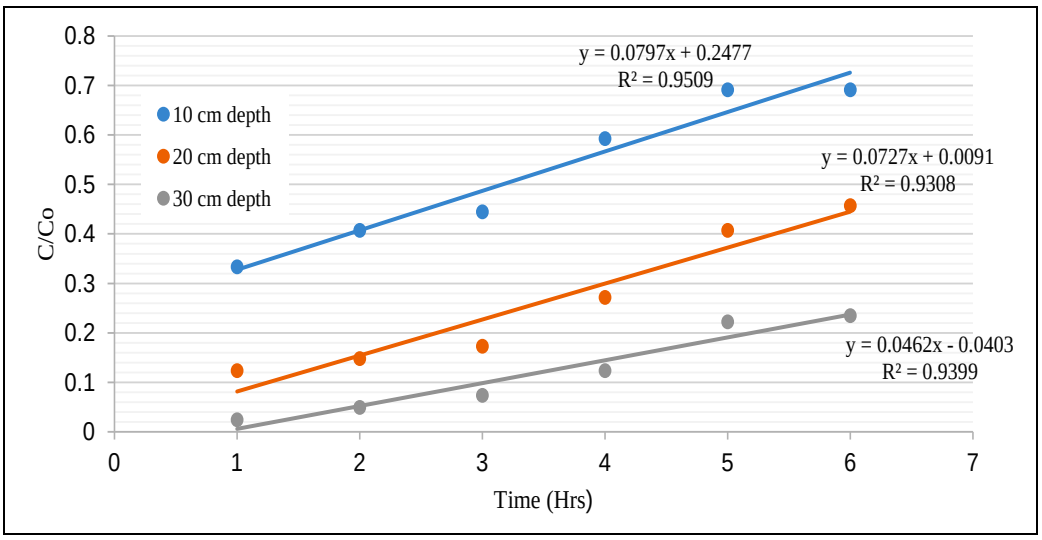

Figure 4.5: Break through curves at 80 ml/min flow rate

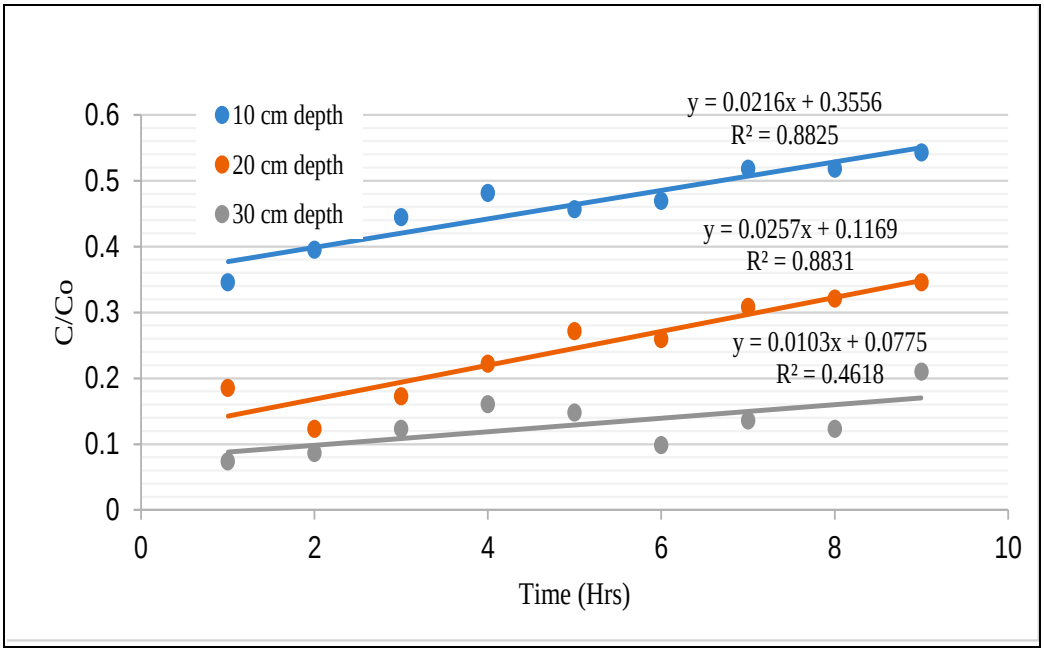

Figure 4.6: Break through curves at 60 ml/min Flow rate

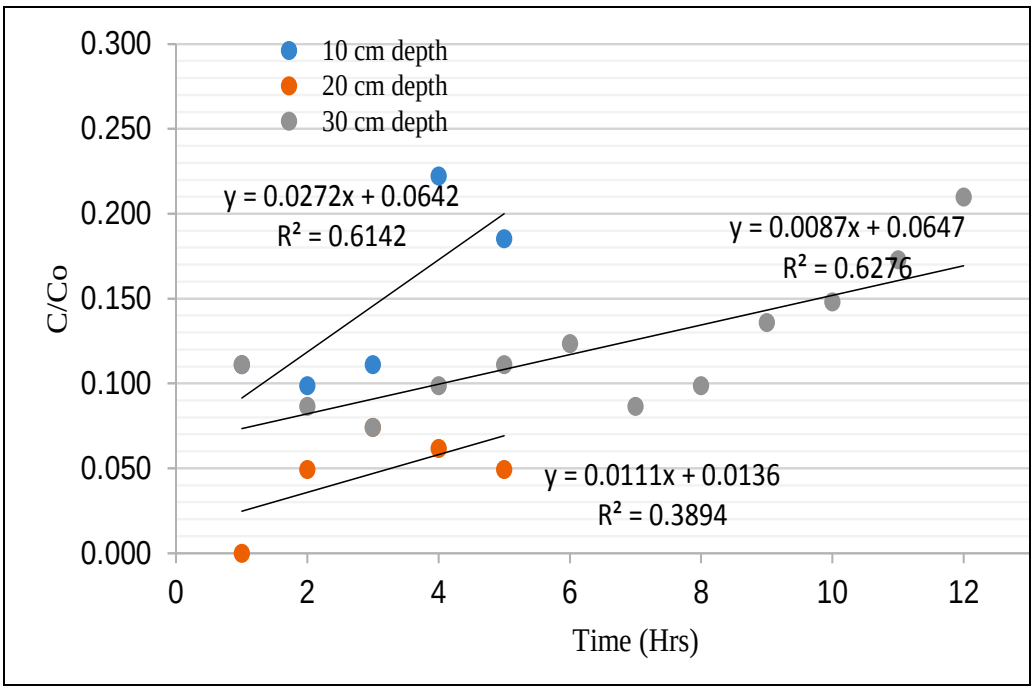

Figure 4.7: Break through curves at 40 ml/min Flow rate

4.5.2 Computation of service Time

The term 'service time' for a defluoridation column is used to refer to the time to breakthrough point. For defluoridation of drinking water, breakthrough point may be taken as the point where the effluent fluoride concentration reaches the drinking water limits. The WHO limit for Fluoride is 1.5 mg/L; WASREB allows 3 mg/L for exceptional cases. Because the fluoride concentration in Naivasha borehole water may be considered exceptional, the less stringent WASREB value of 3 mg/L was adopted for analysis. The corresponding ratio of residual fluoride concentration to initial concentration (C_b/C_o) at breakthrough point for the two standards for the initial 8.1 mg F^-/l is computed as 0.370.

The service time corresponding to the three test bed depths was obtained using the line of best fit. The results are presented in Figure 4.8.

Table 4.8: Service Time at Different Flow Rates and Bed Depths

Bed Depth (cm)	Service Time (Hr)		
	80 ml/min	60 ml/min	40 ml/min
10	1.54	0.68	11.26
20	4.97	9.86	35.13
30	8.89	28.43	32.14

4.5.3 Computation of Column Design Parameters

To compute column design parameters, the service time was plotted against bed depth (Figure 4. 8); straight line were obtained indicating that the service was proportional to the bed depth consistent with the BDST model by Bohart and Adams (1920) (Eq. 4.5).

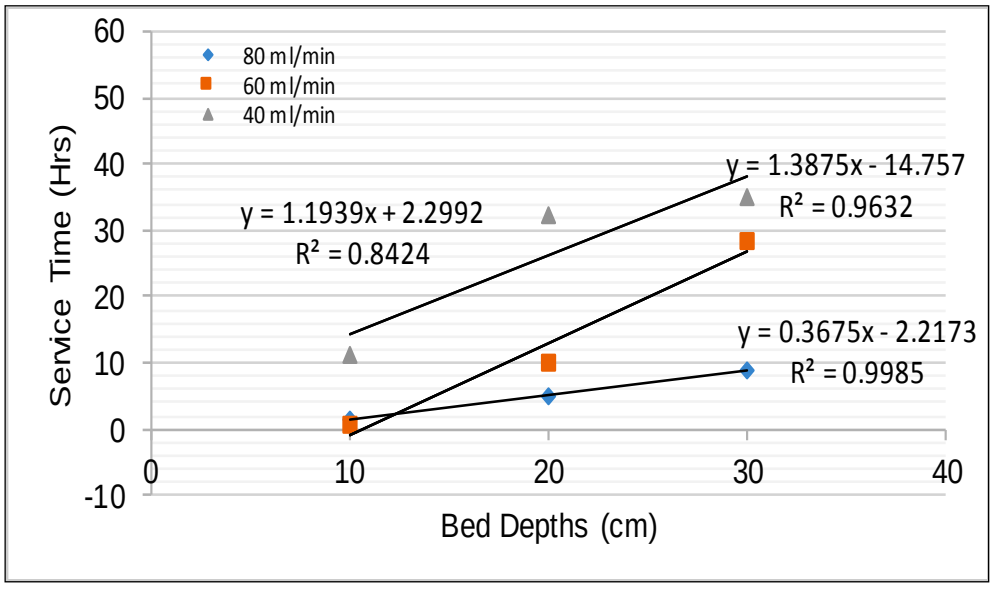

Figure 4.8: Variation of Service Time with Bed Depth

The column design parameters were obtained using the straight line equations BDST model (Eq. 4.5) (Bohart and Adams, 1920).

$$T_b = \frac{N_o}{C_o V} D - \frac{1}{KC_o} \ln\left(\frac{C_o}{C_b} - 1\right)$$ ---------- Equation 4.5

Where

T_b is the service time at breakthrough point (h),

N_o is the bed capacity (mg·cm^{-3}),

D the packed-bed column depth (cm),

V is the linear flow rate through the bed (cm h^{-1}),

C_o and C_b are the influent and the breakthrough fluoride concentration (mg/L), respectively, and

K is the adsorption rate constant (L mg^{-1} h^{-1}).

The equation of a straight line on BDST curve may be expressed in the form:

$$y = ax + b$$ ---------- Equation 4.6

Where

y = service time,

x = bed depth,

a = slope (= No/C_oV)

b = ordinate intercept (-{1/KC_o[ln (C_o /C_b–1)]},)

The adsorptive capacity of the system, N_o, and the rate constant, K, were evaluated from the slope 'a' and intercept 'b' of the straight line service time, T_b, against the bed depth plot. Column design parameters were calculated from Figure 4.7 and are presented in Table 4.9.

Table 4.9. BDST Parameters for different Flow Rates

	Flow Rate (ml/min)		
Parameter	80	60	40
K (cc/mg-hr)	0.139	0.017	0.005
N_o (mg/cc)	79	411	1269

4.5.4 General Discussion of Fluoride Removal with Depth of Bed

Contact time is most important parameter in the design of fixed bed adsorption columns. For a given filter area, bed depth, determines contact time and, therefore, is a major design parameter. Breakthrough was considered to have occurred when the effluent fluoride concentration exceeded the WASREB fluoride concentration of 3 mg/L that is acceptable in exceptional cases in Kenya.

Removal of fluoride in the defluoridation column may be viewed in terms of contact time and mass of the adsorbent. Larger media depths have more contact time and larger adsorbent surface area than smaller depths. Similarly, smaller filtration rates would result in longer contact time faster rates resulting in greater fluoride removal as was observed in the fluoride removal time tests (Section 4.3). Therefore, the time needed to reach the breakthrough point is a function of depth and flow rate.

The service time increased with decrease in flow rate from one to 37.9 hours for the 80 and 40 ml/min flow rates, respectively, at a depth of 30 cm. It also increased with depth from 9 hours to 37.9 hours for the 10 and 30 cm depths, respectively, at a flow rate of 40 ml/min. Overall, the service time varied from about one hour for 80 ml/min flow rate to about 35 hours for 40 ml/min flow rate at 30 cm depth. Correlation improved with flow rate probably because it was easier to maintain a steady flow for the higher flow than for the lower flow.

4.5.5 Significance of Study on Fluoride Removal at Household Level

The service time of 37.9 hours at a depth of 30 cm and 40 ml/min flow rates, was equivalent to 14.8 and 63.8 bed volumes respectively. For a 20 cm diameter and 50 cm depth household defluoridation column, the predicted service time at 40 ml/min would be 54 hours, which would produce 218.2 bed volumes equivalent to 1713.6 L of water. This production would be sufficient to supply an estimated daily household demand of 40 L of drinking and

cooking water for 42 days (six weeks). The column would require 12 kg of bone char, which would cost USD 18. This cost would be out of reach for communities that live on less than a dollar per day; therefore, the cost of bone char would require to be subsidized for sustainability.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study characterized bone char and estimated the dynamic capacities and the reaction rates for bone char by nonlinear regression of the batch tests experimental data. The conclusions of the study were:

1. The bone char reduced fluoride concentration from 8.1 mg/L to within WASREB threshold of 3 mg/L for exceptional cases in areas with high concentration of fluoride a contact time of 50 minutes and to within the WHO limit concentration of 1.5 mg/L in 2 hours.

2. Adsorption of Fluoride on to bone char conformed to Freundlich Isotherm but not to Langmuir Isotherm indicating that the bone char media was not a homogenous media.

3. The Freundlich adsorbate capacity, K_f, increased with size from 3.95 x 10^{-3} to 1.75 x 10^{-2} (L/g) for fine and medium sizes, respectively, but adsorption intensity, 1/n, decreased from 1.657 to 1.043, respectively, which may explain the lack of significant difference between the fine and the medium sizes.

4. Fluoride removal in a bone char column can be model with the bed depth service time (BDST) model with bed capacity, No., 79, 411 and 1269 mg/cm^3 and adsorption rate constant, K, 0.139, 0.017 and 0.005 (cm^3/mg-hr) for 80, 60 and 40 ml/L respectively.

5.2 Recommendations

The study recommends further investigations as follows.

1. Verify applicability of the experimental BDST fluoride removal model to large-scale defluoridation units.

2. Carry out further characterization of bone char to determine its heterogeneity.

3. Evaluate other adsorption configurations of the continuous process such as up flow fixed and moving bed for optimization of removal of fluoride

4. Further to the studied BDST model of adsorption columns, investigate the mass transfer model that based on capacity of adsorption zone, to determine its accuracy in describing fluoride removal in the bone char adsorption column.

REFERENCES

Abram, J. (1973). In *Paper and Proceedings of Water Research Association Conference* (pp. 3-5). University of Readings.

Albertus, J. (2000). Bone char quality and defluoridation capacity in contact precipitation. 3rd International Workshop on Fluorosis Prevention and Defluoridation of Water Session 1 . (p.). Epidemiology: 57.

Anderson, R. (1987). *"Practical Statistics for Analytical Chemists,"* . New York, : Van Nostrand Reinhold.

Babaninde. A.A.N. (2002). Pure and Appl. Sci. *5 (i)* , 81 – 85.

Bailey, H. E. (1972). *Effects Of Water Composition On Fluoride Removal* . The University Of Arizona : Graduate College of the Department Of Civil Engineering And Engineering Mechanics

Bansode, R. L., J., M. E., & Portier, J. (2003). Bioresource Tech.

Bohart, G. S., & Adams, E. Q. (1920). Some aspects of the behavior of charcoal with respect to chlorine. J. Chem. Soc.

Caria, M. (2001). *"Measurement Analysis: An Introduction to the statistical Analysis of Laboratory Data in Physics, Chemistry and the Life Sciences,"* . London,: Imperial College Press.

CAWST, C. f. (2011). Household Water Treatment for Fluoride Removal Factsheet: Bone Char Filter. Alberta, Canada: Website:www.cawst.org.

Catholic Diocese of Nakuru, C. D., Müller, K. (2006). Catholic Diocese Of Nakuru's defluoridation experiences on a household scale. Kenya. www.eawag.ch/forschung/qp/wrq/publications/pdfs/household_filters.

Cheremisinoff, P., & F., E. (2002). *Carbon Adsorption Handbook.* Michigan: An Arbor Science Publisher Inc. pp 241 – 279.

Chilton, N., Jack, N., Losso, N., & Wayne, E. A. (2002). *Bioresourse Technology*, 131-135.

Christian, T. V., Henri, F., Catherine, P., & Yuh-Shan, H. (2005). *Removal of lead(II) ions from synthetic and ream effluents using immobilized Pinus Sylvestris sawdust: Adsorption on a fixed bed column.* J. Hazardous Material B.

Christian, T. V., Henri, F., Catherine, P., & Yuh-Shan, H. (2005). Removal of lead(II) ions from synthetic and ream effluents using immobilized Pinus Sylvestris sawdust: Adsorption on a fixed bed column. J. Hazardous Material .

Clesceri, L., A.E.Greenberg, & A.D.Eaton (eds). (1998). *"Standard Methods for The Examination of Water and Wastewater,"* (20th ed.). Washington DC,: American Public Health Association,.

Damte, E. M. (2006). *"Removal Of Fluoride From Water Using Granular Aluminum Hydroxide: Adsorption In A Fixed-Bed Column".* Addis Ababa University: School of Graduate Studies Environmental Science Program.

Dean, H. T., & Elvove, E. (1962). Studies on the Minimal Threshold of the Dental Sign of Chronic Endemic Fluorosis (Mottled Enamel). In *Publication 825* . Fluoride: aliAna Waters, U. S. Dept. of H. E. W., P. H. S.

Eager, J. M. (1962). "Denti de Chiale (Chiale Teeth). "Fluoride Drinking Waters, Publication 8-75.

Ghorai, S., & Pant, K. K. (2005,). Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. Sep. Puri. Technol.

Gimba, C., Ocholi, O., & Nok, A. (2004). Nig Journal of Scientific Research. *4 (2)* , 106 - 110.

Gitahi, C. M. (2012). *Efficacy of Bone Char Defluoridation in Water.* Department of Civil and Construction Engineering, UON.

Graham, R. (1993). *"Data Analysis for the Chemical Sciences: A Guide to Statistical Techniques,"* . New York.: John Wiley & Sons,.

Harmon, J. A., & Kalichman, S. G. (1965). Defluoridation of Water in Southern California. *Jour. Amer. Water Works Assn.,* 57, 245.

Hartman, J. (1947). *Colloid Chemistry,*. Cambridge.: Houghton Mifflin Company,.

Hauge, S., Osterberg, R., Bjorvatn, K. & Selvig, K. 1994 *Defluoridation of drinking water by the use of pottery: effect of firing temperature.* Unpublished report, Artadveien, Bergen, Norway.

Hutchins, R. A. (1973, .). New methods simplifies design of activated carbon systems,. Am. J. Chem.Eng.

HWTFR. (2011). *Household Water Treatment for Fluoride Removal Factsheet: Bone Char Filter.* Calgary, Alberta, Canada: CAWST (Centre for Affordable Water and Sanitation Technology).

Itodo H.U. (2010). Academia Arena. pp. 51-60.

Jacobsen, P., & Dahi, E. (1997). Charcoal Packed Furnace for Low- Tech Charring of Bone. *Proceedings of the 2nd International Workshop on Fluorosis and Defluoridation of Water.* Ethiopia .

Kaseva M. E. (2006) .Optimization of regenerated bone char for fluoride removal *Journal of Water and Health 4 (1)*

Kopecký F., K. P. (1996). *Laboratory manual for physical chemistry,*. Bratislava,: Farmaceutical faculty of Comenius University,.

Liljana, M., Vera, M., & Vladimir, N. (2001). *Adsorption of basic dyes in a fixed-bed column.* Korean J. Chem. Eng.

Linsman, J. F., & MacMurray, C. A. (1943). "Fluorine Osteoschlerosis (From Drinking Water).". Radiology.

Manji.F. (1984). "Dental fluorosis in an area of Kenya with 2ppm fluoride in drinking water". *Journal of Dental Research* , 65(5) 659-62.

McKay, G., Blair, H. S., & Gardner, J. R. (1984,). The adsorption of dyes on to chitin in fixed-bed columns and batch adsorbers. J. Appl. Polym. Sci.

Meier, P., & Zund:, R. (2000). *Stastistical Methods in Analytical Chemistry,* (2nd ed.). New York,: John Wiley & Sons,.

Miller, J., & J.C.Miller. (2000). *"statistics and Chemometrics for Analytical Chemistry,"* (4th ed.). Upper Saddle River, NJ,: Prentice Hall.

Mjengera, H. (1988). *Excess fluoride in potable water in Tanzania and defluoridation technology with emphasize on the use of polyaluminium chloride and magnesite*. Unpublished report, University of Tampere.

Musapatika, E. T. (2010). *Use Of Low Cost Adsorbents To Treat Industrial Wastewater* . Johannesburg: Faculty Of Engineering And The Built Environment; University Of The Witwatersrand.

Okiemen, F., Ojokoh, F., Okiemen, C., & Wuana, R. (2004). Chemelass Journal. 191-196.

Otero, M., Razade, F., Calvo, L., Garcia, A., & Martin-Villacorta. (2003). *Bioresource technology,* , 87 : 221 – 230.

Sawyer, C. N., McCarty, P. L., & Parkin, G. F. (2003). *Chemistry for environmental engineering and science* (5th ed.). New York: McGraw-Hill.

Snoeyink, V., & Jenkins, D. (1980). *'water chemistry,".* New York,: Wiley,.

Steve, K., Erika, T., Reynold, & Paul, A. (1998). Activated carbon. In *Environmental Engineering 2nd Edn.* (pp. p 25, 350, 749). PWS Publishing Co.

Thomas, H. C. (1944). Adsorption of the ions by Zeolites. J. Am. Chem. Soc.

Tien., C. (1994). Adsorption Calculations and Modeling. Boston: Butterworth – Heinemann.

Tsai, W., Chang, C., Wang, Y., Chien, F., & Sun, H. (2001). Bioresource Technology. *78 (2)* , 203-208.

WASREB. (2005). *Drinking Water Quality and Effluent Monitoring Guideline* Water Services Regulatory Board.

Weber, T., & Chakkravorti., k. R. (1974). Pore and solid diffusion models for fixed bed adsorbers, AlChE J.

Weber, W. (1972). *Physiochemical Processes for Water Quality Control.* London. : Wiley Interscience.

WHO. (2004). Guidelines for Drinking Water Quality. Geneva: 3rd Edition.

Woldetsadik, Y. A. (July 2007). *"Fluoride Removal From Water With Aluminum Oxide Hydroxide: A Pilot Study For Household Application."* Addis Ababa University: School of Graduate Studies Environmental Science Program.

APPENDICES

Appendix I: Flow Rates for Medium Grain Size

Table A1:

Flow rate 80 ml/min				Flow rate 60 ml/min				Flow rate 40ml/min			
Time (Hr)	**10 cm**	**20 cm**	**30 cm**	**Time (Hr)**	**10 cm**	**20 cm**	**30 cm**	**Time (Hr)**	**10 cm**	**20 cm**	**30 cm**
1	2.7	1	0.2	1	2.8	1.5	0.6	1	0.9	0	0.9
2	3.3	1.2	0.4	2	3.2	1	0.7	2	0.8	1	0.7
3	3.6	1.4	0.6	3	3.6	1.4	1	3	0.9	0.6	0.6
4	4.8	2.2	1	4	3.9	1.8	1.3	4	1.8	0.5	0.8
5	5.6	3.3	1.8	5	3.7	2.2	1.2	5	1.5	1.1	0.9
6	5.6	3.7	1.9	6	3.8	2.1	0.8	6		0.4	1
				7	4.2	2.5	1.1	7		0.5	0.5
				8	4.2	2.6	1	8		0.9	0.8
				9	4.4	2.8	1.7	9			1.1
								10			1.2
								11			1.4
								12			1.7

Appendix II: Flow Rates for Fine Grain Size

Table A2

Flow rate 80ml/min				**Flow rate 60ml/min**				**Flow rate 40ml/min**			
Time (Hr)	**10 cm**	**20 cm**	**30 cm**	**Time (Hr)**	**10 cm**	**20 cm**	**30 cm**	**Time (Hr)**	**10 cm**	**20 cm**	**30 cm**
1	0.2	0.7	0.9	1	1	0.4	0.9	1	1	1.5	0.9
2	0.7	0.4	0.5	2	1.1	0.5	0.4	2	0.7	0.3	0.6
3	0.3	0.4	0.4	3	1.1	0.5	0.5	3	0.7	0.3	0.4
4	0.5	0.1	0.5	4	1.7	0.4	0.5	4	0.8	1.2	0.9
5	0.3	0.6	0.6	5	2.7	1.3	0.2	5	0.7	0.3	0.9
6	1	0.5	0.7	6	3	0.5	0.1	6	1.2	2	1.5
7	2	1	0.6	7		0.7	1.1	7	0.8	0.7	1
8		0.9	0.3	8		0.8	1.3	8	0.8		
				9		1.2	1.7	9	0.7		
				10		1.6	2				

Appendix III: Paired T-Test for Medium and Fine Media

Table A3

Group	Fine media < 0.63mm,	Medium media0.63-2 mm,
Mean	2.843	2.829
SD	2.503	2.427
SEM	0.946	0.917
N	7	7

Values used in calculation were: T=0.1353; Df = 6 and Standard error of difference = 0.106 with P value calculated as Probability (one tailed): 0.448 and Probability (two tailed): 0.896.