

**Investigation of Household Defluoridation of Water Using Locally
Available Materials as Sorbent Media: A Case of Keren Community
in Eritrea**

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**A thesis submitted in partial fulfillment for the Degree of Master of
Science in Civil Engineering in the Jomo Kenyatta University of
Agriculture and Technology**

2014

DECLARATION

This is my original work and has not been presented for degree consideration/award in this or any other university and all the resource material used for the thesis have been duly acknowledged to the best of my knowledge.

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DEDICATION

I Dedicate This Research Thesis To:

My love Rahwa Zeray for sharing my life and showing love and faith, my future Mellawi Beraki and Nazreth Beraki for always making my life exciting and whose enthusiasm are a source of inspiration to me, my parents and brothers/sisters for their lifelong influences and for providing me courage, strength, support and comfort.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my research supervisors Prof. A. O. Mayabi and Mrs. Beatrice K. Kakoi for their dedicated assistance, invaluable comments, suggestions and constructive criticisms throughout my research work. Prof. A. O. Mayabi deserves additional credit for his usual heartfelt discussion from the beginning of my research proposal and following up of my research work and his rich experiences throughout my research work benefited me a lot.

I am grateful to the National Board of Higher Education (NBHE), Eritrea, who sponsored my study through technical cooperation with African Development Bank, Hamelmalo Agricultural College (HAC) for granting me a study leave and Department of Water, Ministry of Land, Water and Environment for their kind cooperation and material support during the field and laboratory work in Eritrea. Special thanks also go to Mr. Netsereab, Ministry of Agriculture, Elabered, Eritrea, Mr. Efrem, Water Department, Asmara, Eritrea and Mr. Munyi, Civil Engineering Department, JKUAT, Kenya, whose assistance and guidance in water sample collection, adsorbent and Laboratory work were invaluable. I owe the whole Civil Engineering staff for which they were kind and cooperative to me in all aspects of my life during my stay at JKUAT.

I recognize and appreciate the lifelong influences of my parents, my brothers and sisters and my teachers and friends whom their personal sacrifice showed me the way of achieving my goal. I would like also to thank Kahsay Nuguse and Brhan Khair, PhD fellowships, for their encouragement, guidance, friendly approach, and willingness for discussion and help whenever I need them. I deeply thank all who

supported me in every aspect during my study in one or the other way in which their names are not included here.

Special thanks go to my wife Rahwa Zeray and my kids Mellawi and Nazreth, for being patient while I was taking their time. Their trust, endurance and patience are always my motive forces to move toward the end line of my mission in my life. Thanks a lot for being part of me.

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LIST OF ABBREVIATION AND ACRONYMS

ADA	American Dental Association
APHA	American Public Health Association
AWWA	American Water Works Association
a	Langmuir constant
BDST	Bed Depth Service Time
b	Maximum adsorption capacity constant for Langmuir isotherm
C_b	Breakthrough fluoride concentration (mg/l)
C_e	Equilibrium solute concentration (mg/l)
C_o	Initial (influent) fluoride concentration (mg/l)
C_t	Effluent fluoride concentration at time t (mg/l)
CEE	Center for Environmental Education
CaCO₃	Calcium carbonate
conc.	Concentration
D	Daily personal water demand
D₁₀	10% finer
D₃₀	30% finer
D₆₀	60% finer

EBRT/EBCT Empty Bed Residence/Contact Time

EC Electrical Conductivity

EU European Union

F⁻ Fluoride ion

F_t Total fluoride removal during a period

GPS Global Position System

HhDU Household Defluoridation Unit

H_t Total height of the column

H₁ Distance from bottom of the column to the bottom level of the packed media

H₂ Distance from top level of the packed media to the point where tap is fixed

H₃ Distance between the tap & top of the column

h_c Height of the packed column (bed depth)

HCl Hydrochloric acid

HCO₃ Hydro carbonate

K Adsorption rate constant (l/mg/h)

k Adsorption capacity (mg/g) based on Freundlich isotherm

M	Amount of medium (Mass of adsorbent, mg or g)
N	Normality
NaF	Sodium fluoride
NaOH	Sodium hydroxide
N^o	Number of users
N_o	Average adsorption capacity per volume of bed (mg/cm ³)
NTU	Nephelometric Turbidity Units
n	Adsorption equilibrium constant for Freundlich isotherm
OP	Operation Period
OSc	Operational sorption capacity
PVC	Polyvinyl Chloride
ρ_b	Bulk Density of Medium
pH	Acidity or alkalinity on a logarithm scale
Q	Volumetric flow rate (ml/min)
Q_d	Daily water treatment
q	Linear flow rate through the bed (cm/h)
Ø	Diameter (dia)
SG	Specific gravity

T_b	Service time at breakthrough point (h)
TDS	Total dissolved solids
V	Throughput volume (ml)
V_b	Volume of water treated at breakthrough (l)
V_m	Volume of the medium in the filter (l)
V_t	Total volume of water treated in a filter period (l)
UNICEF	United Nation International Children Emergency Fund
USA	United States of America
μS/cm	microseisms per centimeter
WEF	Water Environment Federation
WHO	World Health Organization
X	Adsorption capacity (mg/g)
x	Amount of adsorbate adsorbed (mg or g)

ABSTRACT

Fluoride in water in some parts of Eritrea is above the WHO guideline of 1.5 mg/l. The Keren community suffers dental and skeletal fluorosis as a result of being exposed to water with high fluoride content. A survey of 16 water sources in 13 villages around Keren town in Eritrea was made and 87% of the samples exceeded the guideline, having fluoride levels ranging between 1.40-3.98 mg/l. Therefore, defluoridation is required to make the water safe for drinking. Fluoride sorbent materials namely crushed burnt clay pot, Keren soil, Adigerghish soil and household ash were studied in a batch study for the removal of fluoride from water. At pH of 7, crushed burnt clay pot, Adigerghish and Keren soils had higher removal of fluoride but household ash had optimum fluoride removal at pH of 4. However, the contact time was similar and the equilibrium time was 120 minutes (2 hours). Particle size had no significant effect in the case of crushed burnt clay pot, however, in other three adsorbents, fine particles performed better than coarse ones. In all adsorbents studied, similar increasing trend in adsorption were observed when the initial fluoride concentration was increased. Comparison of the adsorbent materials was made based on the fluoride removal efficiency. The study revealed that crushed burnt clay pot has superior fluoride removal capacity than the other three adsorbents. Its average fluoride removal capacity was about 0.26 mg F⁻/g of the medium compared to the capacity of the other adsorbents which ranged from 0.08-0.1 mg/g for the same mass of 7g. Crushed burnt clay pot is a suitable low cost adsorbent to remove fluoride from water and was thus selected for further defluoridation tests carried out in a mini column unit. The result from the mini column indicated that optimum

removal of fluoride was obtained at a bed depth of 25 cm and a flow rate of 2.5 ml/min, treating 7.3 litres of water meeting the WHO drinking water guidelines. The set-up of the mini column was scaled up to a pilot scale unit. The pilot scale managed to treat 324 litres of water while satisfying the WHO standards of fluoride concentration. The performance of the pilot column agreed with that obtained from the mini column and therefore, can be upgraded for larger application. Moreover, the fixed bed data of the mini column were investigated for simplified fixed bed models (BDST and EBRT) application. The results show that the data could be successfully applied to analyze the column performance and evaluate the model parameters. The BDST model gave a good prediction for the service time when compared to the observed result from the pilot scale experiment and thus could be used in designing and optimizing of fluoride adsorption system onto crushed burnt clay pot.

CHAPTER ONE

1.0. INTRODUCTION

1.1. Background

All people, whatever their stages of development, social and economic conditions have the right to access an adequate supply of safe drinking water. The importance of this has led the WHO to publish guidelines on drinking water quality in 1958 as International Standards for Drinking water (WHO, 1958). Subsequently the guidelines were revised in 1963 and 1971 under the same title (WHO, 1963, 1971). The guidelines provide an assessment of the health risk presented by microorganisms and chemicals in drinking water. It also helps to develop and implement national standards for drinking water quality (WHO, 1993).

Microorganisms or excessive amounts of inorganic components such as fluoride dissolved from rocks in water may affect the quality of water (Riemann and Banks, 2004). It also becomes a challenge for the human welfare, especially for low income developing countries. Fluoride is one of the few chemicals that may be of public concern when present excessively in drinking water. It has detrimental effects on human health in terms of the prevalence of dental caries, skeletal fluorosis and bone fractures (WHO, 2006).

Fluoride commonly occurs in the earth's crust making groundwater more susceptible to contamination (Manahan, 1994). Fluoride at elevated concentration is known to occur in a number of parts of the world and in such circumstances can have adverse impact on public health and wellbeing (UNICEF, 1999). The distribution of fluoride

across the world is presented in Figure 1.1. The colored areas of the map are areas where water has high fluoride levels which could possibly be a source of fluorosis (UNICEF, 1999).

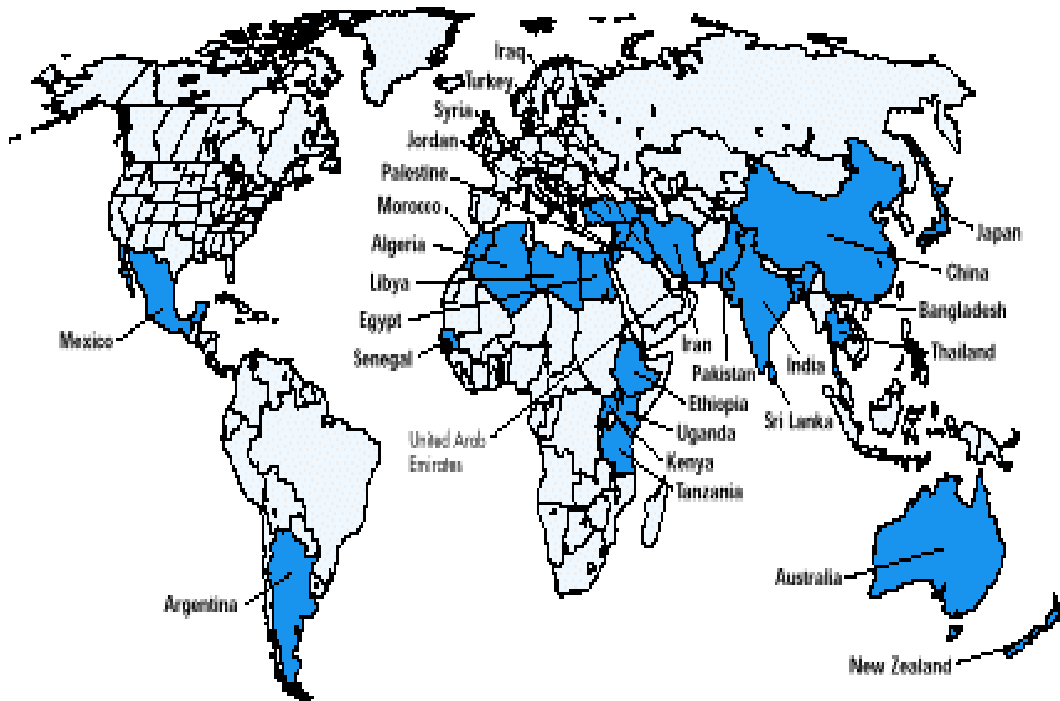


Figure 1.1: Countries with endemic fluorosis due to fluoride in drinking water (Source: UNICEF, 1999)

The part of the East Africa particularly the rift valley is susceptible to fluorosis. This is because most of the fluoride level in drinking water at the Rift valley fails to pass the current European Union (EU) drinking water directives (Reimann et al., 2003) and exceeds the WHO recommendation (WHO, 1984).

Eritrea is situated in the horn of Africa and shares part of the Rift valley. It has a total area of 124320 km² and a population of more than 3.5 million (Srikanth et al., 2002; MLWE, 2007). It is located in arid and semiarid region of Africa, and is not adequately endowed with natural resources including water.

Water is a scarce commodity in rural Eritrea. There are no perennial rivers except Setit River which is shared with Ethiopia. The majority of the population depends on groundwater for their consumption where the fluoride content of the water is high in some places of the country (Srikanth et al., 2002; Estifanos, 2005; Zerai 1996). Fluorosis is a common phenomenon particularly in villages around Keren town and coastal parts of the country where groundwater is used for domestic purposes (Srikanth *et al.*, 2002). However, there is no any method used to remove fluoride from drinking water in the country.

Fluoride removal mechanisms such contact precipitation, membrane techniques and adsorption/ion exchange methods based on addition of chemicals (alkali, chlorine and aluminium sulphate or aluminium) are high in operational and maintenance cost (Dahi et al., 1996; Reardon and Wang, 2000). They are not cost effective for rural communities in developing countries as well (Ghorai and Pant, 2004). It is therefore necessary to search for locally available adsorbent media that suit local conditions for household and community use. However, the physical and chemical characteristics of the adsorbent must be studied as it affects the removal efficacy (Cheremisionoff and Morresi. 1978).

The design of defluoridation units requires a number of information, which could be obtained from series of batch, mini column and pilot plant studies (Ko Chun, 2002). The applicability of simplified fixed bed sign models are extensively studied for the removal of organic solutes by activated carbon. Their applicability to model fluoride adsorption is now emerging. The bed depth service time (BDST) model was applied successfully for the design of fluoride adsorption system onto activated aluminal (Ghorai and Pant, 2005; Eyobel, 2006; Yoseph, 2007; Agegenehu, 2008).

1.2. Statement of the Problem

The rural community around Keren town, Eritrea, has been suffering from dental and skeletal fluorosis as result of consuming water containing excessive fluoride. Despite the prevalence of fluorosis symptoms in those areas, nothing has been done to remove fluoride from the community drinking water supply. No Well-established study has been carried out to know the fluoride content of the groundwater of the community. However, certain literatures have reported fluoride levels of 3.73 mg/l in some of the villages around Keren where fluorosis is salient (Srikanth et al., 2002; Estifanos, 2005). According to those studies, the fluoride level is in excess of the guideline for drinking water given by WHO (WHO, 1984).

However, so far there is no yet even a single means existed to remove the excess fluoride from water in Eritrea. Moreover, in villages around Keren, alternative water sources with low fluoride level are not easily available and hence treatment of fluoride contaminated water is the most reasonable approach to prevent and control dental caries and skeletal fluorosis.

1.3. Objectives of the Study

1.3.1. Main Objective

The main objective of the study is to identify locally available fluoride adsorbent materials and develop water defluoridation unit for household use in rural community in Eritrea.

1.3.2. Specific Objectives

The study was carried out under the following specific objectives:

- i. To characterize drinking water in selected villages and investigate the fluoride content where fluorosis is prevalent.

- ii. To compare the performance of local adsorbents namely fired clay, Keren soil, Adigerghish soil and Household ash for fluoride adsorption and use for household defluoridation.
- iii. To investigate the application of simplified fixed bed design models (bed depth service time (BDST) and empty bed residence time (EBRT)) for the design of fluoride adsorption system for the selected media.
- iv. Design, develop and test a pilot household defluoridation unit.

1.4. Justification of the Study

Generally speaking, much work has not been done to determine the chemical content of groundwater in Eritrea. However, understanding the chemistry of groundwater is important for environmental, economic and social purposes. This is helpful to identify contaminant chemicals and toxic substances and to look for remedial measures to avoid or minimize their impacts on society and the environment.

A study to assess the chemical content of drinking water in general and contaminants such as fluoride, heavy metals and other pollutant in particular is therefore important. This study is thus expected to contribute information on the fluoride levels in the selected villages and may even prompt the government of Eritrea for further assessment of the groundwater.

Water containing high fluoride should not be used for drinking and cooking to avoid health problems. However, alternative water sources with low fluoride content may not be available because the area is located in arid and semiarid region. Therefore defluoridation is needed to render the water potable. In rural community of Eritrea,

however, techniques for removal of fluoride are not yet practiced. This is mainly because of lack of power as well as lack of skilled operators for defluoridation plants.

It is therefore necessary to research on a means to remove excess fluoride using a locally and available material which operate easily and able to reduce fluoride content to an acceptable level for household and community use. This study may further contribute and provide researchers with baseline information for further work and thus fill some of the gaps existing and contribute to the water knowledge of the country. This study was thus based on this core idea.

1.5. Scope and Limitations of the Study

The study is carried out on a case study basis in some of the fluorosis endemic villages in Eritrea. Considering the extent of the area under study, time and budgetary, only 13 villages are covered in this study. However, there could possibly be more villages with a similar fluorosis problem.

Water samples to characterize the study area are sampled during the dry season. However, water sample collection during the rainy season might be required to determine if there could be some changes in the fluoride content of the water. Moreover, synthetic fluoride solution in water is used in all the defluoridation experiments; obtaining water sample from Eritrea was practically impossible due to distance from the study area.

Different potential fluoride adsorbents media could be available locally in a number places of Eritrea. However, in this study, only four locally available adsorbent materials from Keren and its surrounding were tested for defluoridation. There was also a practical limitation to obtain more adsorbent materials.

CHAPTER TWO

2.0. LITERATURE REVIEW

2.1. Importance of Fluoride and its Environmental Occurrence

Fluoride is a naturally occurring compound. The fluoride ion comes from the element fluorine. Fluorine is abundant in the earth crust and is the 13th most natural occurring mineral (Murray, 1986). It occurs only in combination with other elements as a fluoride compound and never exists as a gas in a free state. Fluoride is mainly accumulated in water and soil during weathering processes from fluorine rich minerals, such as fluorospar CaF_2 , cryolite Na_3AlF_6 , and fluoroapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (Murray, 1986). According to Tebutt (1983), the average crustal abundance of fluoride is 300 mg/kg.

Fluoride is commonly associated with volcanic activity and fumarolic gases. Thermal waters especially those of high pH, are believed to be rich in fluoride (Fawell et al., 2006). Moreover, fluoride can be released to the environment from various anthropogenic sources. Discharge of agricultural and industrial products such as glass, electronics, steel, aluminium, pesticide and fertilizer manufacture's (Pietrelli, 2005) are among possible sources of fluoride contamination in water.

It has been reported that there are numerous fluoride belts throughout the world where groundwater contain unsafe levels of fluoride. These belts span over 14 countries in Africa including Eritrea, 8 countries in Asia and 6 countries in America, all having water considered unsafe by the World Health Organization (Tekle-Haimanot, 1995).

It is noted that there are numerous myths and misconception of fluorosis in the community of Keren in Eritrea. They believe occurrence of fluorosis, especially skeletal disorder comes from an evil curse and they assume it is inheritable as well. There is a similar believe in some society for instance in Kenya where it is believed that eating hot potatoes or neglecting to brush teeth would lead to dental fluorosis while skeletal fluorosis is believed to come from carrying a child to field before the age of six months (Muller, 2007). However, this is not true and it is purely a medical condition caused by taking high levels of fluoride in drinking water (WHO, 2006; UNICEF, 1999).

Fluoride intake in humans is necessary as long as it does not exceed safe limits. It has both beneficial and detrimental effects on human health in terms of the prevalence of dental caries, skeletal fluorosis and bone fractures. Studies by WHO indicated that there is a dose response relationship between the concentration of fluoride in drinking water and the prevalence of dental caries (WHO, 2006). According to WHO, maximum allowable limit fluoride uptake in humans is 1.5 mg/l (WHO, 1984); but depending on climatic conditions such as temperature, it may range from 0.5 mg/l-1.0 mg/l (WHO, 1994; Dissanayake, 1991). In his report, Dissanayake (1991) augmented the WHO recommendations and presented typical fluoride concentrations in drinking water and their associated health effects. Table 2.1 shows typical fluoride concentrations with the associated potential health effects arising from consuming excess fluoride as described in Dissanayake (1991).

Table 2.1: Typical fluoride concentration and their potential health effects

F ⁻ conc. (mg/l) in drinking water	Potential health effects
<0.5	Minimal effect in prevention of dental carries
0.5-1.5	Beneficial effects in preventing dental carries
1.5-4	Dental fluorosis
4-10	Dental and skeletal fluorosis
>10	Crippling fluorosis

Source: Dissanayake (1991)

It is well known that our body needs some fluoride at certain levels. The controversial issue, however, is how much fluoride is required for the body to function normally. Some countries, including the United States of America (USA) add fluoride to drinking water. They believe that fluoridation of community water supplies is the single most effective public health measure to prevent dental decay (ADA, 2005). According to this, water fluoridation is practiced to adjust the natural fluoride concentration of fluoride deficient water to the level recommended for optimum dental health.

Despite such controversies, it is believed that high amounts of fluoride intake would result in fluorosis manifested by dental and skeletal deterioration. In worst cases, it results in muscle and ligament damage. The amount of fluoride increases in the bones up to the age of 55 years but children are the ones affected most and those affected remain crippled or deformed for the rest of their lives (WHO, 1984). To minimize the prevalence and severity of tooth decay, the fluoride content in the water must be limited and if possible must be reduced to meet the WHO recommendation.

2.2. Status of Fluoride in Eritrea and its Potential Effects

One of the best known high fluoride belts on land extends along the East African Rift from Eritrea to Malawi and along a belt from Turkey through Iraq, Iran, Afghanistan,

India, northern Thailand, and China. The Americas and Japan have similar belts (WHO 2005; CEE, 2007). Plate 2.1 shows the effect of excess fluoride resulting in dental and skeletal fluorosis in the Rift valley Ethiopia which is likely possible in Eritrea as well.



a. Dental fluorosis



b. Child with skeletal fluorosis



c. Skeletal fluorosis

Plate 2.1: Photos showing dental and skeletal fluorosis

Source: http://www.appropedia.org/Water_Defluoridation

Eritrea is known to be among the most severely fluoride affected countries in the world. Although not much research work has been done to determine the fluoride content of groundwater, there are many places endemic to fluorosis. The studies conducted by Srikanth et al. (2002) and Estifanos (2005) respectively in villages around Keren town Eritrea indicated that fluoride content in groundwater was 3.73 mg/l and 3.27 mg/l. Besides, Zerai (1996) reported fluoride levels in coastal region of Eritrea in the range of 7-17 mg/l which is much higher than the recommended WHO standard for drinking water.

The baseline study carried out by Srikanth et al. (2002) and Estifanos (2005) in rural Eritrea around Keren town to estimate fluoride content in the groundwater is an important one. The study indicated elevated concentration of fluoride in the

groundwater where dental fluorosis is prevalent. The source of fluoride in groundwater in the study area is attributed to geology of the area. The main lithological units recognized in the study area are mica schists and amphibole schists of medium grade and chlorite schists of low grade metamorphism with pegmatite intrusions and aplitic dykes which are likely to contain high fluoride (Srikanth et al., 2002). According to the study, the incidence of dental fluorosis in the affected villages is over 50% in children and about 20% among adults (Srikanth et al., 2002).

2.3. Methods of Fluoride Measurement

The presence of fluoride in water is tasteless, odorless and colorless. Depending on the purpose and accuracy, electron method, colorimetric method, complex-one method and ion chromatography can be used to determine the concentration of fluoride ion. Among the methods suggested for determining fluoride ion in water, the electron and colorimetric (SPADNS) methods are the most satisfactory as they are simple and rapid technique with high accuracy (APHA, AWWA, WEF, 1995).

2.4. Mitigation Options of Fluorosis and Overview of Defluoridation Methods

Defluoridation methods may be grouped based on removal mechanisms. They are contact precipitation, membrane techniques and adsorption/ion exchange methods. Precipitation requires addition of chemicals such as alkali, chlorine and aluminium sulphate or aluminium chloride which lead to the formation of fluoride salts. Precipitation method of fluoride removal like Nalgonda technique (Dahi et al., 1996) and limestone reactor (Reardon and Wang, 2000) are high in operational and maintenance cost. Specific cost estimation of operation and maintenance is difficult as cost varies from place to place because of the variation in cost of labour and material. They also generate large volumes of sludge and may produce undesirable

effects on water quality such as smell and taste (Tembhurkar and Dongre, 2006). Besides, the water may not achieve the desired water quality levels of less than 1.5 mg/l of fluoride.

In recent years a large number of adsorbents have been reported to possess fluoride removal capacity. Some of these materials are however not cost effective while others such as bone char can produce undesirable taste in water and may be of low adsorption capacity if the charring process was not properly carried out (Sajidu et al., 2008).

A wide range of material has been attempted for fluoride uptake. Few are silica gel (Wang et al., 1995), natural soil (Mayabi et al., 2009), zeolites (Mayadevi, 1996), fired clay (Moges et al., 1996; Pranab, 2004), fly ash (Pranab, 2004). However selection is based on removal capacity, design simplicity, local availability of materials and chemicals and user preference.

Most of the adsorbent materials for defluoridation currently available are not cost-effective. They are not either technically feasible in rural areas as well (Ghorai and Pant, 2004). It is therefore necessary to search for locally available defluoridation media that is safe and easy to use at household and community level.

Defluoridation devices should be modest in investment, have low maintenance cost, simple in design and operation at village level and should meet acceptable water quality. Adsorption methods particularly in packed bed are preferred over the other defluoridation methods. This is mainly due to easier operation, no daily sludge encountered, have reasonable running and investment cost, and the exhausted media

can be replaced with virgin one after relatively longer periods of time (Eyobel, 2006). However, not a single method meets the entire requirement. Moreover, materials used as sorbent media may affect water quality parameters such as pH, turbidity, hardness and bacteriological contaminants.

2.5. Defluoridation Using Low Cost Materials

Commercial fluoride removal from water through adsorption, membrane separation, and ion exchange techniques are expensive for developing countries. It is important then to search for low cost defluoridation materials which can be used by communities in developing countries including Eritrea. Fired clay chips and natural soils are among the large number of cost effective adsorbents which have been reported to possess fluoride removal capacity (Mayabi et al., 2009; Mayadevi, 1996; Moges et al., 1996; Pranab, 2004). The materials are also cheap and are locally available in large quantities.

Domestic clay column filters can be constructed by normally packing them using clay chips which can be obtained from waste of brick manufacturing, pottery or tile. The filter is based on up-flow water movement in order to allow for settling of suspended solids within the filter bed. The filter does not have a clean water reservoir and the filtration rate is controlled by slow withdrawal through the tap (Figure 2.2). However, they generally have far lower capacities and treat water far too slowly compared to other adsorption methods such as bone char or activated alumina (K Bjorvatn, 1997; Bjorvatn, 1997). Clay filters have been used with some success in a number of regions, most notably in countries such as Sri Lanka (Fawell et al., 2006). Though there is significant variability in fluoride uptake capacity, they could be potential alternatives in rural areas such as Eritrea.

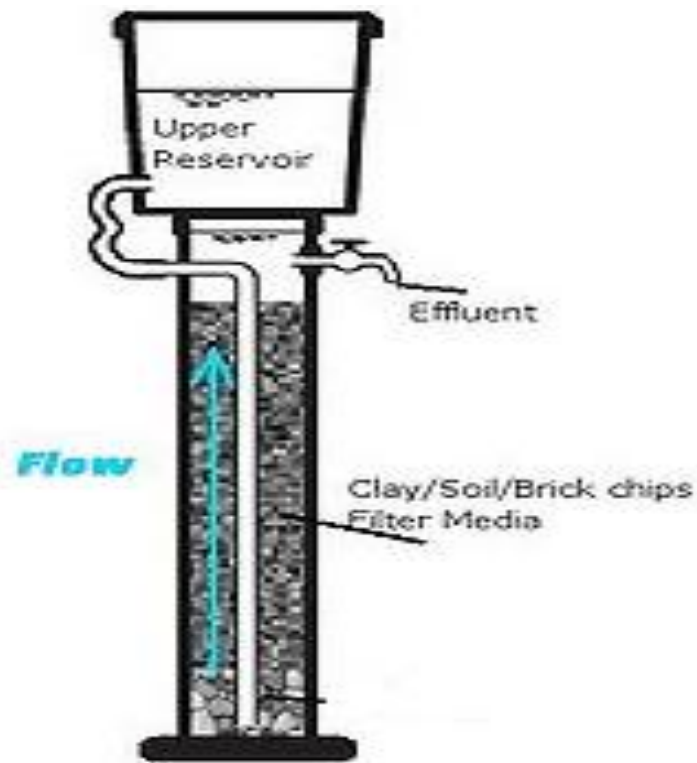


Figure 2.1: Schematic diagram of a Clay/Soil/Brick type filter column for household defluoridation

Source: http://www.appropedia.org/Water_Defluoridation

2.6. Adsorption

Sing et al. (1985) defined adsorption as the enrichment of material or increase in the density of the fluid in the vicinity of an interface with a solid (the adsorbent). Depending on the nature of interactive forces, it may be classified as chemisorption and physisorption. In chemisorption the transfer of electrons is significant and equivalent to the formation of a chemical bond between the sorbate and the solid surface while in physisorption, the interactive forces are relatively weak.

The intermolecular forces involved are of the same kind as those responsible for the imperfection of real gases and the condensation of vapors (Kenny *et al.*, 1993;

Kaneko, 1997). In addition to attractive dispersion forces and short range repulsive forces, the so called van der Waals forces, dipole–dipole, induced dipole–induced dipole and dipole–induced dipole interactions all occur as a result of particular geometric and electronic properties of the adsorbent. When their potential energy is at a minimum, the molecules get adsorbed.

It is widely recognized that sorption processes provide a feasible technique for the removal of pollutants from water and wastewater (McKay, 1995). Of major interest, adsorption process, a surface phenomenon by which a multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds is recognized as the most efficient, promising and widely used fundamental approach in water and wastewater treatment processes (Foo and Hameed, 2009). This mainly hinges on its simplicity, economic viability, technical feasibility and social acceptability (Nouri et al., 2007).

Adsorption proceeds through the following steps: mass transfer, intra-granular diffusion and physical adsorption.

Cheremisionoff and Morresi (1978) stated that adsorption is dependent on:

- a. The physical and chemical characteristics of the adsorbent
- b. The physical and chemical characteristics of the adsorbate
- c. The concentration of the adsorbate
- d. Experimental conditions, such as temperature, pH, air flow velocity and relative humidity.

2.7. Principles of Adsorption System Design

The design of defluoridation units requires a number of information, which could be obtained from series of batch, mini column and pilot plant studies. The latter is time consuming and expensive with regard to the amount of adsorbent and water usage. However, conducting a pilot scale column run is important to predict what would happen in a full scale column when various operating parameters are involved. These parameters include flow rate, feed and product concentration, bed height, particle size, type of adsorbent, pH, temperature and viscosity (Ko Chun, 2002). Indeed, it is difficult to apply small scale laboratory column studies data to design application as operational problems in large scale units could occur due to uneven flow patterns, selective flow paths and uneven packing (Ko Chun, 2002)

2.7.1. Batch Adsorption Models

An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Limousin et al., 2007; Allen et al., 2004). Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with the adsorbate concentration in the bulk solution in a dynamic balance with the interface concentration. Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration (Ncibi, 2008).

Laboratory evaluation of the adsorption isotherm and the adsorption capacity is time consuming and may be affected by toxicity or availability of the adsorbate. For such

difficult cases, a model that can predict the adsorption capacity, making testing unnecessary, would be highly desirable (Ko Chun, 2002).

Over the past years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm) have been formulated in terms of three fundamental approaches (Malek and Farooq, 1996). Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined as being a state of dynamic equilibrium, with both adsorption and desorption rates equal (Langmuir, 1916). Thermodynamics, being a base for the second approach, provides a framework of deriving numerous forms of adsorption isotherm models (De Boer, 1968; Myers and Prausnitz, 1965). Potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve (Dubinin, 1960). However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters (Ruthven, 1984).

The most commonly used equilibrium models to understand adsorption systems are the Freundlich and Langmuir isotherm equation. These models are simple and have ability to describe experimental results in wide range of concentration. Both models can be easily transformed into linear forms to obtain adjustable parameters by graphical means or linear regression analysis (Orhan et al., 1998).

a. Langmuir Isotherm

It is one of the most commonly used isotherms for either gas or liquid adsorption. It was developed in 1918 based on the kinetics of condensation and evaporation of gas molecules at a unit solid surface (Orhan et al., 1998). The Langmuir adsorption isotherm is derived from consideration based upon the following assumptions;

- i. Adsorption is a reversible process.
- ii. The adsorbed layer is made up of a single layer of molecules.
- iii. The adsorbed molecules do not move on the surface of the adsorbent. However, they can be lost back to the solution.
- iv. The enthalpy of adsorption is the same for all molecules independently of how many have been adsorbed.

The Langmuir adsorption isotherm equation is presented in *Equation [2.1]*.

$$\frac{x}{M} = \frac{abCe}{1 + aCe} \quad [2.1]$$

And the linearized form can be represented as:

$$\frac{1}{x/M} = \frac{1+aCe}{abCe} = \frac{1}{b} + \frac{1}{abCe} \quad [2.2]$$

Where x = amount of adsorbate adsorbed (mg or g)

M = mass of adsorbent (mg or g)

Ce = Conc. of adsorbate in the solution, remaining when equilibrium is achieved (mg/l or g/l),

b= the maximum adsorption capacity and is constant

a= the Langmuir constant

If the adsorption can be modelled by Langmuir's isotherm, a plot of $\frac{1}{x/M}$ vs $\frac{1}{C_e}$

yields a straight line with the intercept of $\frac{1}{b}$ and a slope of $\frac{1}{ab}$

b. Freundlich Isotherm

The Freundlich isotherm model describes a multilayer adsorption with the assumption of heterogeneous surface in which the energy, a term in the Langmuir equation varies as a function of the surface coverage (Orhan et al., 1998). The model is presented in Equation [2.3]

$$\frac{x}{M} = kC_e^{1/n} \quad [2.3]$$

The linearize form of the equation can be expressed as:

$$\text{Log}\left(\frac{x}{M}\right) = \text{Log}k + \frac{1}{n}\text{Log}C_e \quad [2.4]$$

Where x = amount of adsorbate adsorbed (mg or g)

M = mass of adsorbent (mg or g)

C_e = Conc. of adsorbate in the solution, remaining when equilibrium is achieved (mg/l or g/l)

k= the measurement of the adsorption capacity (mg/g) based on Freundlich isotherm

n = the adsorption equilibrium constant

Adsorption that follows Freundlich isotherm, when $\text{Log}\left(\frac{x}{M}\right)$ is plotted against

$\text{Log}C_e$, it would have a straight line with $\frac{l}{n}$ as a slope and $\text{Log}k$ as an intercept.

2.7.2. Fixed Bed Continuous Flow Adsorption Models

Batch adsorption models are simple and are useful in designing batch treatment units.

Their application for the design of continuous treatment units is limited. However, there is a commonly used fixed-bed mathematical model for a continuous flow and reaction in porous materials with one dimensional advection-dispersion equation, assumes linear sorption isotherm of the solute onto the solid surface (Zewge, 2001) and is presented in Equation [2.5].

$$\frac{\partial C_t}{\partial t} = D_e \frac{\partial^2 C_t}{\partial x^2} - v_x \frac{\partial C_t}{\partial x} - \rho_s \frac{1-\varepsilon}{\varepsilon} K_d \frac{\partial C_t}{\partial t} \quad [2.5]$$

Where,

C_t = the concentration of the solute at time t ;

D_e = effective diffusion coefficient;

ρ_s = the density of the solid phase;

ε = the porosity of the bed;

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

K_d = the linear distribution coefficient

The above model is helpful to predict the breakthrough curve in a more accurate way. However, it needs to have the physical and kinetic parameters determined that can be obtained from batch adsorption studies or from literature. Moreover, the

model requires the solution of a number of non-linear partial differential equation including physical and kinetic parameters. Solving the equation analytically is tedious and time consuming. Numerical method of solving is the only applicable option (Liljana, 2001).

A simplified model to design a fixed bed adsorption column is therefore needed. There are a number of simple design models available which are based upon general assumption. These include bed depth service time (BDST), empty bed residence time (EBRT), and Thomas model. The applicability of simplified models is extensively studied for the removal of organic solutes by activated carbon and their applicability to model fluoride adsorption is now emerging. It has been indicated by Ghorai and Pant (2005) that the bed depth service time (BDST) model was applied successfully for fluoride adsorption onto activated alumina. Similar studies were carried and the model was found successful for further application (Eyobel, 2006; Yoseph, 2207; Agegenehu, 2008).

2.7.3. Simplified Fixed Bed Design Models

a. Bed Depth Service Time (BDST) Model

One of the most important unit processes in water and wastewater treatment plant is adsorption. However, the design of the adsorption column usually requires information from pilot-plant experiments (Ko Chun, 2002). Adsorbents providing a large surface area, on which the contaminant molecules can adhere, are generally used in beds through which the water and wastewater passes for treatment continuously. The type of adsorbent is usually determined before sizing the column as different kinds of adsorbent will have significant variation in adsorption capacity.

Once the adsorbent has been chosen, the next important aspect of adsorption column design is the sizing of the column.

The column performance is subjected to different operating conditions. However, the adsorption breakthrough curve is used to evaluate the performance of the packed bed. The shape of the breakthrough curve and the time taken for breakthrough are important characteristics for defining the dynamics and operational response of an adsorption column (Aksu and Gonen, 2004). The breakthrough curves are found by plotting throughput volume at any time versus effluent concentration. The packed column design generally follows either scale up or Kinetic approach.

In both of the approaches, a breakthrough curve from a test column, either laboratory or pilot scale, is required. Besides, the column should be as large as possible to minimize side wall effects. The advantage of these approaches is neither of them requires the adsorption to be represented by an isotherm such as the Freundlich equation (Aksu and Gonen, 2004).

In scale up approach, the pilot test column is filled the same adsorbent as to the mini-column to be used in full scale application. In this approach, the linear flow (infiltration) rate and contact time of the mini-column requires to be the same with the full scale application to obtain similar mass transfer characteristics (Eyobel, 2006).

The main design criterion in a fixed bed continuous flow adsorption system is to predict how long the adsorbent material will be able to sustain removing a specified amount of solute from solution before regeneration or replacement is needed. This

period of time is known as the service time of the bed. The BDST model describes a relation between the service time of the column and the depth of packed bed column. Bohart and Adams (1920) developed a relationship between the bed depth, h_c , and the service time, T_b , as presented in Equation [2.6].

$$\ln\left[\frac{C_o}{C_b} - 1\right] = \ln\left\{e^{\left(\frac{KN_o}{v}\right)h_c} - 1\right\} - KC_o T_b \quad [2.6]$$

Where:

T_b = service time at breakthrough point (h)

N_o = the bed capacity (mg/cm³)

h_c = packed-bed column depth (cm)

v = linear flow rate through the bed (cm/h)

C_o = initial influent fluoride concentration (mg/l)

C_b = effluent fluoride concentration at breakthrough (mg/l) and

K = adsorption rate constant (l/mg/h).

Equation [2.6] can also be simplified by the following approximation.

$$\text{Since } e^{\left(\frac{KN_o}{v}\right)h_c} \gg 1, \text{ thus } \ln\left\{e^{\left(\frac{KN_o}{v}\right)h_c} - 1\right\} \cong \frac{KN_o h_c}{v} \quad [2.7]$$

Rearranging and solving equation [2.7] for T_b , Hutchins (1973) has come with the linear relation between the bed depth (h_c) and the service time (T_b) of the form;

$$T_b = \frac{N_o}{C_o v} h_c - \frac{1}{KC_o} \ln\left[\frac{C_o}{C_b} - 1\right] \quad [2.8]$$

Equation [2.8] helps to determine the service time, T_b , of an adsorption bed when the bed depth, h_c , of an adsorbent is given. The service time, T_b , and bed depth, h_c , are correlated with the process parameters such as initial solute concentration, water flow rate and adsorption capacity of the adsorbent.

Equation [2.8] has the form of a straight line and hence the BDST curve could be expressed using the equation of a straight line in the form of:

$$y = ax + b \quad [2.9]$$

Where: y = service time (T_b), x = bed depth (h_c), a = slope, and b = ordinate intercept.

In this case a and b are equivalent to:

$$a = \frac{N_o}{C_o v} \quad [2.10]$$

$$b = -\frac{1}{K C_o} \ln\left[\frac{C_o}{C_b} - 1\right] \quad [2.11]$$

The constants in Equation [2.9], the 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 against the bed depth from experimental data, respectively. However, the BDST model works well if the specific bed adsorption capacity is constant and does not change with time. In practice, the bed adsorption capacity does change with time which makes the prediction to become less accurate, but the extent of change varies from system to system. In order to use the BDST

equation with a more accurate result, the dependence on time of the bed adsorption capacity must be investigated (Agegnehu, 2008).

b. Empty Bed Residence Time (EBRT) Model

Empty bed residence time (EBRT) is the time required for the liquid to fill the column, on the basis that the column contains no adsorbent packing. It is a direct function of liquid flow rate and column bed volume. This EBRT model is sometimes referred to as empty bed contact time (EBCT). It is a design tool used to determine the optimum adsorbent usage in the fixed-bed adsorption column. McKay and Bino (1990) proposed and concluded that the capital and operation costs of the adsorption system for a fixed liquid flow rate, feed concentration and adsorbent characteristics were almost entirely dependent on EBRT and adsorbent exhaustion rate only. This is basically hydraulic retention time and it could be expressed as in Equation [2.12]

$$EBRT = \frac{\text{Bed Volume}}{\text{Volumetric Flow Rate of the Liquid}} \quad [2.12]$$

It is also important to find out the rate of exhaustion of the adsorbent before the time breakthrough occurs. The adsorbent exhaustion rate is the weight of adsorbent used in the column per volume of liquid treated at the breakthrough time and could be represented as in Equation [2.13].

$$\text{Adsorbent Exhaustion Rate} = \frac{\text{Mass of Adsorbent used}}{\text{Volume of Liquid Treated at Breakthrough}} \quad 2.13]$$

The EBRT model uses data which are obtained from the BDST analysis. The service time of the column can be found before breakthrough is reached if the breakthrough percentage is specified. This thus helps to obtain the adsorbent exhaustion rate and

the EBRT at various adsorbent bed heights. When the adsorbent exhaustion rates are plotted against the EBRT values, a single line relating these two variables is obtained and is called the operating line. Ko Chun (2002) stated that the operating line concept can be used to optimize the basic design to achieve the lowest cost or other objectives. It can be predicted that the lower the adsorbent exhaustion rate, the longer the EBRT, the smaller the amount of adsorbent is needed per unit volume of feed treated which implies a lower operating cost.

CHAPTER THREE

3.0. RESEARCH METHODOLOGY

3.1. Study Area Water Characterization

A preliminary field survey to identify fluorosis prevalent areas was conducted and 16 sites (water sources) identified by interviewing the local people, contacting key informants in the area and from personal experiences and observations of the resident's conditions (teeth and leg conditions). Thenceforth, the sites were clearly identified and described (distance from the main road, access of road, direction of their location and their water source for sampling).

Water samples were collected from drinking water wells/boreholes and surface water in each village in 1000ml plastic bottles to characterize the water of the study area. The bottles were first washed thoroughly with dilute hydrochloric acid (HCl) and distilled water before sampling. The samples were kept in a refrigerator to avoid any contamination until physico-chemical analysis was done. The fluoride concentration (mg/l) of each sample was determined in the laboratory of the Ministry of Land, Water and Environment in Eritrea using SPADNS (DR/2000 Spectrometer model) as outlined in the Standard Methods for Examination of Water and Wastewater (APHA, AWWA, WEF, 1995). Moreover, other physico-chemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), Total hardness, hydro-carbonate (HCO_3) of the water were also determined. A summary of methods/materials used in the laboratory of Ministry of Land, Water and Environment in Eritrea for the analysis of physico-chemical parameters to characterize the water in the study area is presented in Table 3.1.

Table 3.1: Summary of Water Parameters and Methods/materials used in Water Resource laboratory, Eritrea

S.No	Water Parameter Tested	Materials/methods
1	pH	Hach pH meter
2	EC	Hach EC electrode meter
3	TDS	Hach TDS electrode meter
4	Total hardness as CaCO ₃	Titrometric (Digital Titrate)
5	HCO ₃	Titrometric (Digital Titrate)
6	Fluoride (F ⁻)	SPADNS (DR/2000 Spectrometer)

3.2. Adsorbent Collection, Preparation and Adsorption Capacity Determination

Soil materials in their pristine state were collected from Keren and Adigerghish where the impact of fluorosis is salient. Stones and gravel were removed manually. A name was assigned for convenience according to the place of origin as Keren and Adigerghish soils. The soil materials are exploited by the community for different purposes for making dish pot, coffee pot, and water pot. For this reason Keren and its surrounding areas are well known for fired clay products in Eritrea.

Fired clay pots were purchased from the market and then crushed manually into grains and sieved. Household ash was also collected from households as a by-product of burned fire wood.

All the adsorbent materials were sun dried, sieved and graded using the US bureau of standards (Noriaki and Kameru, 1988). Particles passing through 2.36 mm and retained in 0.60 mm sieve were selected for defluoridation experiment in the pilot scale experiment. This was to enhance permeability and to decrease to a greater extent the turbidity and color of the water. The physical characteristics (particle size distribution, particle density, bulk density and porosity) were also determined using particle size distribution curve and water displacement method. The photos presented

in Plate 3.1 show the different adsorbent materials collected and tested for defluoridation study.



a. Adigerghish soil b. Burnt clay pot c. Keren soil d. Household ash

Plate 3.1: Photos of adsorbent materials before preparation

Batch adsorption tests were conducted in order to investigate the fluoride adsorption capacities of the different materials collected. This was important to compare and select the material with the highest capacity to remove fluoride and hence to be used in the pilot scale experiment for the development of the household defluoridation unit. The fluoride adsorption capacity of the different materials and their efficiency to take up fluoride from the solution was known by measuring the residual fluoride concentration and was calculated using the equations presented in *equations* [3.1] and [3.2].

$$\% \text{ Adsorption} = \frac{C_o - C_t}{C_o} * 100 \quad [3.1]$$

$$\text{Adsorption capacity, } X, (\text{mg/g}) = \frac{C_o - C_t}{M} * V \quad [3.2]$$

Where: C_o = initial fluoride concentration

C_t = residual fluoride concentration at time t

M = mass of adsorbent

V = volume of the solution used in the batch

X = adsorption capacity (mg of fluoride removed/g of adsorbent used)

3.3. Conducting Defluoridation Experiment

The defluoridation experiment was carried out in the environmental laboratory of Civil Engineering department, JKUAT. Both batch method and continuous flow method of defluoridation experiment were used. In both cases, water quality test such as pH, EC and turbidity were conducted to assess the water quality for drinking purpose.

3.3.1. Batch Adsorption

A series of synthetic standard fluoride solution was prepared by dissolving 221 mg of anhydrous sodium fluoride (NaF) in distilled water. Magnetic stirrer was used to mix the solution and then diluted to 1000 ml. This is equivalent to 100 mg of F⁻ in a litre of distilled water. i.e. to say 100 mg/l of fluoride stock solution. 25 ml of fluoride solution was taken from this fluoride stock using a pipette and diluted to 500 ml distilled water to prepare 5 mg/l F⁻ solution to carry out defluoridation experiment. This was the concentration of fluoride used in all subsequent batch studies throughout the experiment.

In the batch experiment, six beakers containing 500 ml solution at 5 mg/l F⁻ concentration was employed of which one was a control (no adsorbent added). Adsorbents ranging from 3-10 g were added to the fluoride solution in the beakers. The beakers containing the mixture were placed in a jar tester and stirred at an agitation speed of 160 revolutions per minute for 2 hours. This was repeated in all subsequent batch experiments to test the different materials for their optimum capacity and examined the defluoridation performance of available adsorbents (crushed burnt clay pot, household ash, Keren and Adigerghish soil).

After two hours, samples were taken from the each beaker using a pipette of 10 ml. The samples were then filtered using a Whatman[®] filter paper and the fluoride residue in the solution measured by the SPADNS using Hanna HI 83099 model (COD and Multiparameter). The effect of adsorbent dose, particle size, initial fluoride concentration, contact time, and pH (pH was adjusted by 0.1N hydrochloric acid, HCl and 0.1N sodium hydroxide, NaOH) on the removal capacity were evaluated.

Water quality tests such as pH, electrical conductivity (EC) and turbidity was measured to assess if there were undesirable effects after adsorbents were added to the water to remove fluoride. Comparison was made and the better sorbent media to be used for household was selected based on the potential to remove fluoride and other practical considerations.

3.3.2. Fixed Bed Continuous Flow Adsorption Column Test

A defluoridation experiment in the continuous flow mode was carried out using selected material based on the batch defluoridation tests. A mini column experiment was performed before the household defluoridation unit was developed for a pilot test. In this mini column defluoridation experiment, the selected adsorbent material was packed in a column as a defluoridating filter media. Before packing, it was washed with tap water until clear water was obtained to remove any fine particles which could block the adsorption sites and which might create clogging condition and interfere with the flow.

The continuous flow experiment in a down-flow mode was carried out in the mini column to correlate the flow rate and bed depth on the fluoride removal capacity

before up-scaling in to a household system. This was to select the ideal flow rate and bed depth to bring optimum fluoride removal more or less the same value obtained in the batch experiment. The mini column experimental set up used is presented in Figure 3.1.

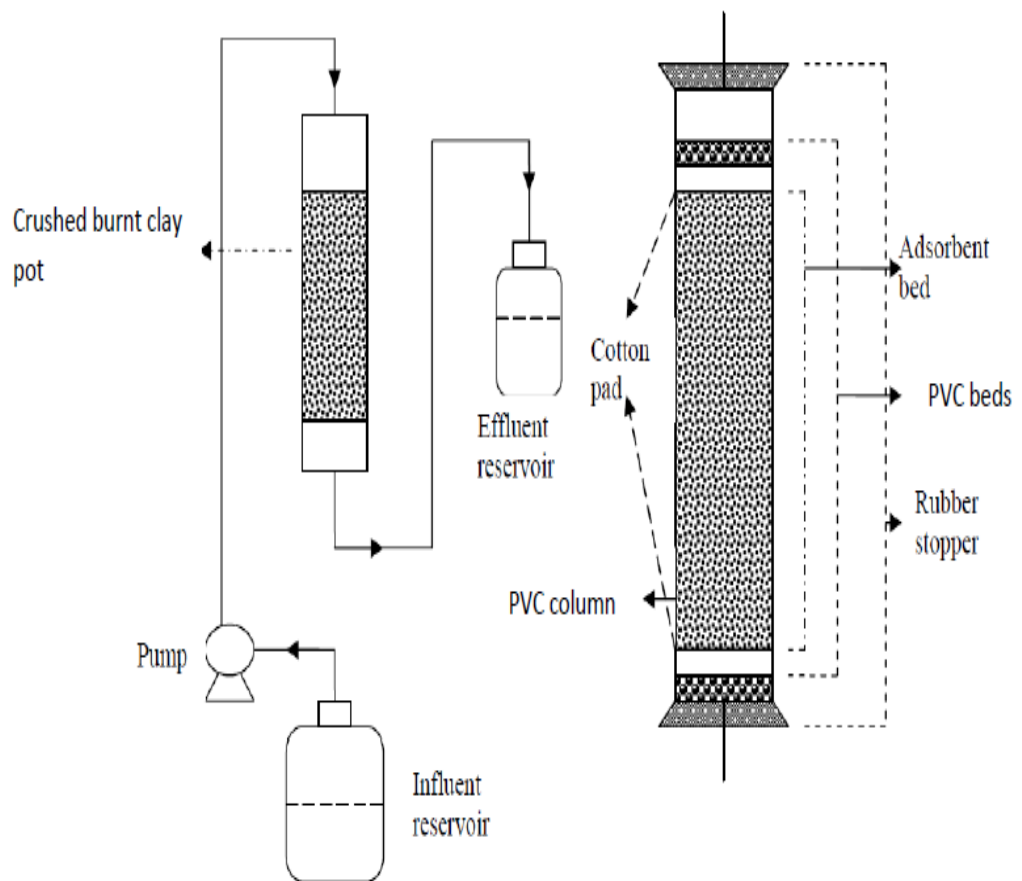


Figure 3.1: Schematic diagram of the Laboratory mini column experimental apparatus.

The bed of the mini column was packed with selected adsorbent media and supported and closed with cotton pad and rubber stopper respectively to prevent flow of adsorbent together with the effluent. Moreover, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particles. The particle size of the medium packed ranged in size from 0.60 to 2.36 mm in diameter.

Water containing 5 mg/l fluoride concentration was pumped in a down flow mode by a peristaltic pump. The pump was used to control the flow rate at 2.5 ml/min, 5 ml/min, 10 ml/min and 15 ml/min in a fixed bed depth of 15 cm, 20 cm and 25 cm and maintained constant during each run.

Samples were withdrawn at the outlet of the mini column at one hour interval using 100 ml measuring cylinder. The fluoride concentration determined and a breakthrough curve generated. The desired breakthrough concentration (C_b) was determined at 30% of the initial concentration (5 mg/l) which was 1.5 mg/l. The experiment was carried out at room temperature (23 ± 1 °C). The pH of the inflow was maintained at 7.10 ± 0.10 throughout the experiment. Table 3.2 shows details of the bed depth and flow rate used in the mini column experiment with their corresponding adsorbent mass.

Table 3.2: Variable bed depth at a fixed flow rate in a fixed bed column for the removal of 5 mg/l of fluoride for selected adsorbent (Internal $\phi=2.3$ cm)

flow rate (Q, ml/l)	Linear flow rate (q, cm/h)	bed depth (hc, cm)	Bed volume (cm ³)	Weight of adsorbent (g)
2.5	36	15	62.35	60
		20	83.13	80
		25	103.91	100
5	72	15	62.35	60
		20	83.13	80
		25	103.91	100
10	144.6	15	62.35	60
		20	83.13	80
		25	103.91	100
15	216.6	15	62.35	60
		20	83.13	80
		25	103.91	100

3.4. Scale up, Design and Construction of Pilot Household defluoridation Unit

The breakthrough curve of the mini-column was studied at different bed depths and flow rates and optimum fluoride removal was obtained. The result of the mini-column that showed optimum adsorption was scaled up for sizing of the pilot household defluoridation unit. The scale up was done, keeping the filtration rate constant. This was to obtain similar mass transfer characteristics in mini and pilot column units.

The Pilot Household Defluoridation Unit was designed on the assumption that 21 litres of water is the daily requirement for cooking and drinking for a family having 5 to 7 (an average of 6) persons each consuming 3-4 (an average 3.5) l/day. The pilot unit was designed for a service time of half month (15 days). Accordingly, the total volume of water to be defluoridated before reaching the breakthrough was assumed at 315 litres. The diameter of the pilot column was selected 10.3 cm diameter as available from the market. From the direct scale-up of the mini-column, the corresponding flow rate of the pilot column was worked out. Table 3.3 shows details of the design parameters associated with the design of the pilot household defluoridation unit used in the pilot scale.

The Pilot Household Defluoridation Unit was constructed with PVC pipes of varying diameters and lengths. The Column was constructed using plumbing materials available in the market. PVC pipe was used as the column bed and PVC female adapters were cemented to each end of the length of PVC column. The feed tank was placed over a wooden support at 90 cm above the ground to provide enough head.

Table 3.3: Design parameters associated with the construction of the pilot column household defluoridation unit.

Given parameters	Description	Unit
D	Daily personal water demand	l/(c d)
V _t	Total volume of water treated	l
N	Number of users	N ^o
OSc	Operational sorption capacity (F ⁻ /Adsorbent)	mg/g
ρb	Bulk Density of Medium (loose)	Kg/l
C _o	Raw water fluoride concentration	mg/l
C _e	Treated water average fluoride concentration	mg/l
q	linear flow rate (as selected from the mini column experiment)	cm/h
Derived parameters		
Q _d =D*N	Daily water treatment	l/d
F _t =V _t *(C _o -C _e)	Total fluoride removal during a period	mg
M=F _t /OSc	Amount of medium required for removal	g
V _m =M/ρb	Volume of the medium in the filter	l
Corresponding dimensions		
Ø	Column (filter) diameter (selected as available)	cm
Q =q* Π*(Ø/2) ²	flow rate	l/h
H _w =Q _d /Q	working hours in a day	h/d
H ₁	Distance from bottom of the column to the bottom level of the packed media	cm
H ₂	Distance from top level of the packed media to the point where tap is fixed	cm
H ₃	Distance between the tap & top of the column	cm
h _c =V _m /(Π*(Ø/2) ²)	Height of packed column	cm
H _t _c	Total height of the column (H ₁ + H ₂ +H ₃ +h _c)	cm

This was connected to the column through PVC tubing. A circular perforated PVC plate with equal diameter to the column was placed at 5 cm above the bottom of the column to support the adsorbent. A PVC tubing (external Ø=2.5 mm) was used to transfer water from the feed tank and passed through the center of the perforated circular plate to the bottom of the column and water was released at this point and

water inside the column flowed upward. The flow rate was adjusted to operate at the designed flow rate and was marked at the control valve and operated under this throughout the run. A 1/2-inch hole was drilled 10cm below the top of the column and a tap fixed to this point to collect the effluent in receiving tank.

Unlike the mini column experiment, a synthetic solution was prepared from tap water for the pilot scale experiment. 221 mg of anhydrous NaF salt was dissolved in a tap water to prepare 100 mg/l F⁻ synthetic solution. In a different container of one liter, 4000 mg/l of total hardness was prepared by dissolving anhydrous dry CaCO₃ salt. The contents of both containers were drained and mixed in a plastic bucket and diluted to 20 litres tap water. This was made to prepare water with characteristic resembling those of the study area. The resulting solution was homogenized before commencement of defluoridation and was used as influent (raw water) for the pilot experiment.

Moreover, unlike in the mini column, an up-flow filter column was used in the pilot experiment so that suspended solids were allowed to settle within the filter bed. This was to reduce the turbidity of the water to a greater extent and to make it fit for drinking. The performance of the household defluoridation unit was monitored at three hour intervals and the operation discontinued when the fluoride level reached 1.5 mg/l. The physico-chemical characteristic of the treated (effluent) water was also measured (pH, EC, turbidity and total hardness). Table 3.4 summarizes the parameters determined and methods/materials used in the pilot scale experiment.

Table 3.4: Summary of parameters determined and Methods/Materials used in Environmental laboratory Civil Engineering Department, JKUAT

S.No	Parameter	Method/Materials
1	pH	Microprocessor pH Meter (pH 211)
2	EC	EC Conductivity Meter
3	Turbidity	Turbidimeter
4	Fluoride (F ⁻)	SPADNS (HI 83099 COD and Multi-parameter Photometer)
5.	Total hardness as CaCO ₃	Titrometric method

3.5. Investigation of BDST and EBRT models and Prediction of Service Time using BDST Model

The fixed bed depth data obtained in section 3.3.2 are used to analyses the simplified fixed bed design models (BDST and EBRT) for the design of fluoride adsorption system onto the selected adsorbent media. The BDST parameters determined from linear regression. The service time of different columns with different operating parameters were predicted by applying the BDST model and comparison made with the observed value from the pilot scale experiment.

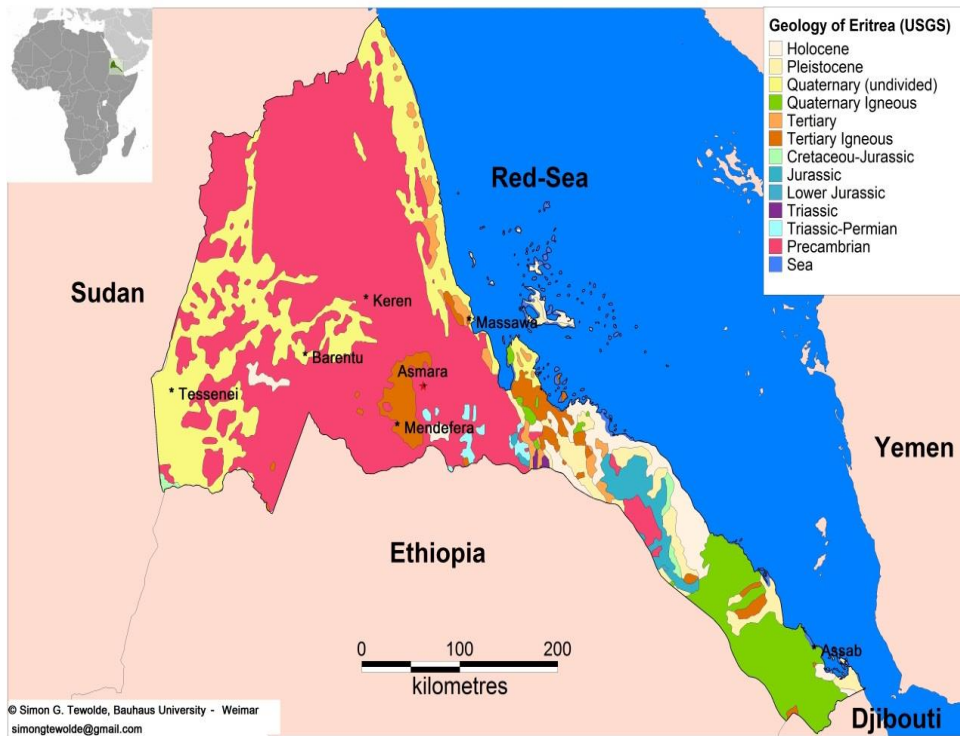
CHAPTER FOUR

4.0. RESULTS AND DISCUSSION

4.1. Study Area and its Geological Characteristics

The study area is located in between the midland to lowland along the river Anseba within Keren town in Eritrea. The geology of the area is underlain by granotoid intrusive which are rich of biotite granite, and granodiorite. According to studies made by Srikanth et al. (2002) the main lithological units recognized in the study area are mica schists and amphibole schists of medium grade and chlorite schists of low grade metamorphism with pegmatite intrusions and aplitic dykes which are likely to contain high fluoride. Moreover, the study concluded that the excess fluoride level in these areas is mainly attributed to the geological activities from the weathered rocks. Figure 4.1a shows the general geological map of Eritrea and the general field data is presented in table 4.1. Figures 4.1b and 4.1c also show the map of Eritrea and the study area in general and the specific villages' in particular as generated from Table 4.1 using GIS.

Geological Map of Eritrea (USGS)

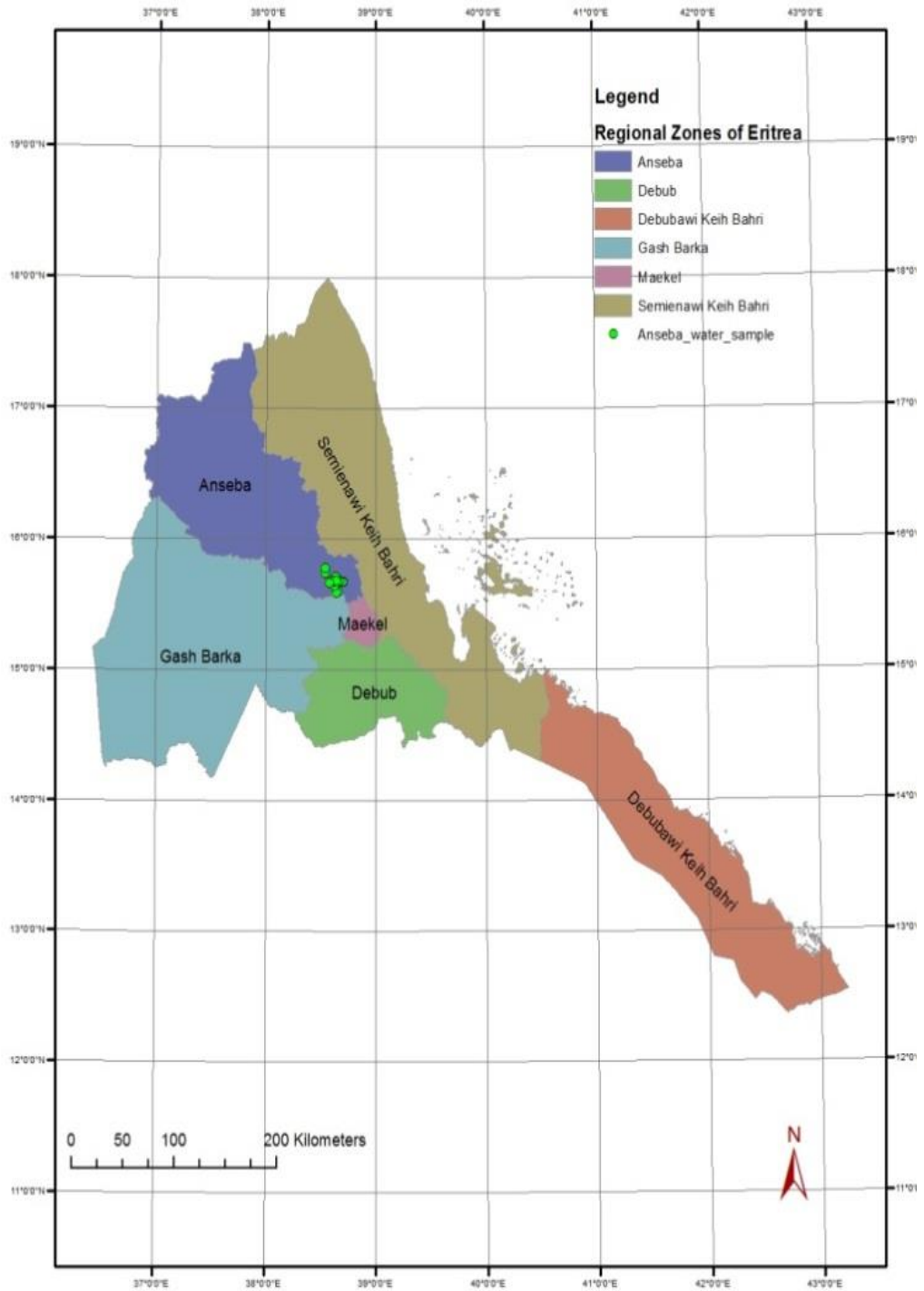


4.1a. Geological Map of Eritrea

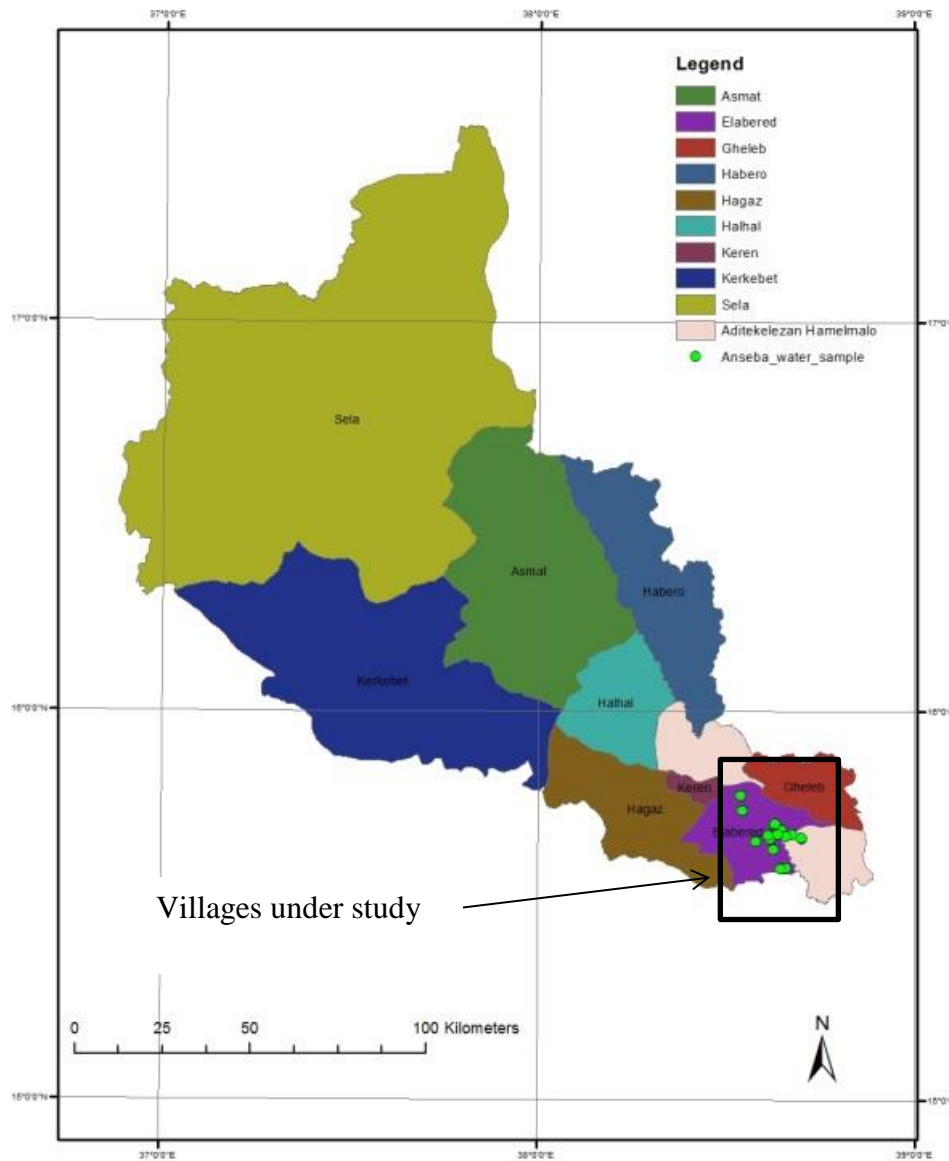
(Source: http://commons.wikimedia.org/wiki/File:Geological_Map_of_Eritrea.jpg)

Table 4.1: Location, source of drinking water and Temperature of selected villages with high fluoride content

Name of Village	Zone	Sub zone	UTM		Elevati on (m)	Average Temp. (°C)	Source of water
Balwa 1	Anseba	Elabered	468104 E	1732669 N	1629	23.8	Spring
Balwa 2	Anseba	Elabered	467704 E	1732868 N	1629	24.5	Hand dug well
Adiberbere	Anseba	Elabered	465240 E	1733983 N	1570	27.4	Hand dug well
Aghelaama	Anseba	Elabered	462315 E	1735215 N	1532	26	Deep well
Harkokia	Anseba	Elabered	463506 E	1733299 N	1848	23.5	Hand dug well
Eden 1	Anseba	Elabered	460199 E	1736655 N	1539	29.9	Hand dug well
Eden 2	Anseba	Elabered	460405 E	1736884 N	1558	32.6	Hand dug well
Halibmentel	Anseba	Elabered	451214 E	1740704 N	1430	27.7	Deep well
Kochie	Anseba	Keren	450702 E	1745056 N	1334	28.5	Spring
Broana	Anseba	Elabered	463531 E	1724382 N	1742	26.1	Hand dug well
Bekoshebnock	Anseba	Aditekelezan	462026 E	1724175 N	1749	28	Hand dug well
Hadush Addi	Anseba	Elabered	460024 E	1729706 N	1686	30.3	Deep well
Gush	Anseba	Elabered	458961 E	1732765 N	1475	26.9	Hand dug well
Gush	Anseba	Elabered	458474 E	1733706 N	1464	25.2	Hand dug well
Adighergish	Anseba	Elabered	461251 E	1733920 N	1487	28.1	Spring
Wasdama	Anseba	Elabered	455009 E	1731920 N	1912	25.1	Hand dug well



4.1b. Map of Eritrea and study area



4.1c. Map of Anseba zone and the specific villages under study

Figure 4.1: Geological and Sampling area location map

4.2. Characteristics of Groundwater in the Study Area

The drinking water from 13 villages around Keren, where mottling of children's teeth and skeletal fluorosis are common were analyzed. The collected water samples were analyzed for fluoride content and other physico-chemical parameters such as

pH, EC, total hardness, HCO₃ and total dissolved salts. Table 4.2 shows the the physico-chemical water characteristics used for drinking.

Table 4.2: The physico-chemical characteristics of drinking water in selected villages

S. No.	Village	EC (µS/cm)	TDS (mg/L)	pH	Total Hardness (mg/L as CaCO ₃)	HCO ₃ (mg/L)	F ⁻ (mg/L)
1	Balwa 1	637	295	7.25	260	317.0	1.40
2	Balwa 2	538	256	7.4.0	240	234.2	3.14
3	Adiberbere	746	357	7.23	240	348.9	2.78
4	Aghelaama	591	282	7.25	196	253.7	1.54
5	Harkokia	631	376	7.30	248	278.1	3.98
6	Eden 1	637	306	7.70	222	253.0	2.88
7	Eden 2	588	287	7.19	220	263.0	3.58
8	Halibmentel	533	317	7.70	240	170.0	1.52
9	Kochie	632	812	7.10	240	224.4	1.46
10	Broana	723	441	7.75	340	370.0	2.88
11	Bekoshebnock	960	675	7.67	480	180.5	3.26
12	Hadush Addi	843	408	7.60	260	317.0	3.74
13	Gush 1	816	608	7.25	248	478.0	3.36
14	Gush 2	678	464	7.30	160	366.0	3.70
15	Adighergish	632	316	7.59	248	195.2	1.78
16	Wasdama	365	174	7.49	100	146.0	1.84
Average values		659	398	7.40	246	275.0	2.70

The fluoride levels in most of the wells analyzed was found to be higher than the 1.5 mg/l WHO guideline for drinking water. The average fluoride concentration of the villages was about 3 mg/l. The typical analysis of the fluoride level in the villages around Keren is presented in Figure. 4.2. In three villages studied, there were two water sources sampled and named for convenience as Balwa 1 and Balwa 2, Eden 1 and Eden 2 and Gush 1 and Gush 2.

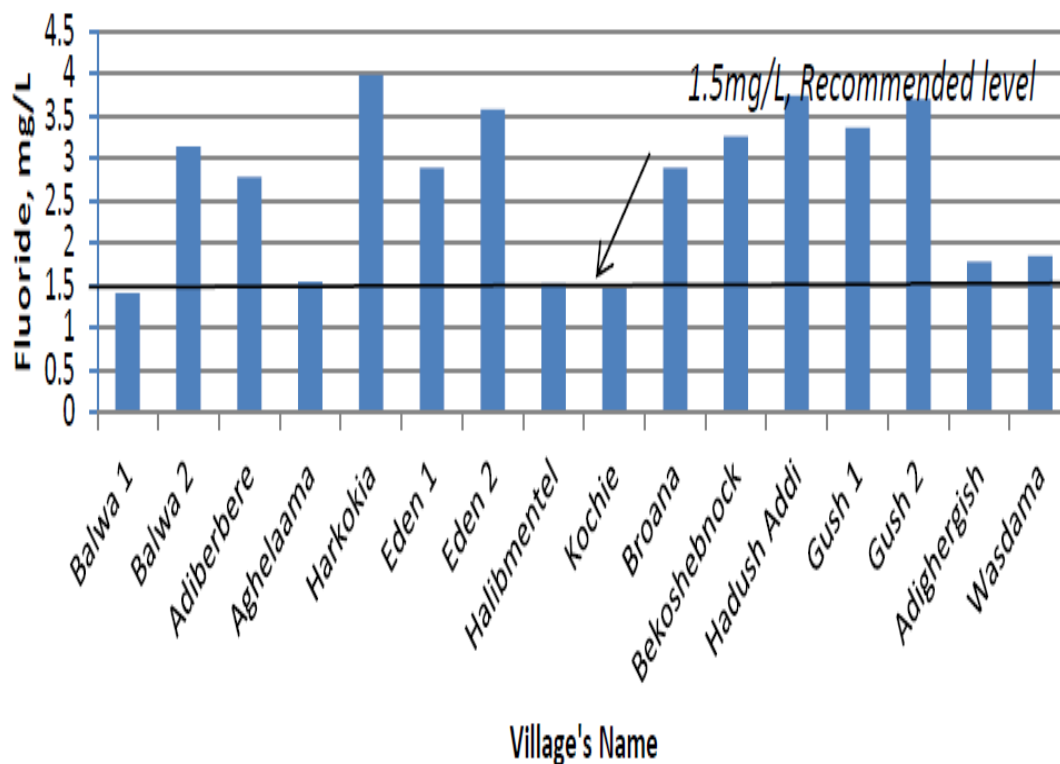


Figure 4.2: Fluoride level in selected villages around Keren town

The preliminary survey in current study showed that 87% of the samples exceeded the WHO guideline. Moreover, the result of the study indicated that, except in two villages, Balwa 1 and Kochie, all water sources in other villages have fluoride levels ranging from 1.52 to 3.98 mg/l, thus exceeding the threshold value of 1.5 mg/l prescribed by WHO (1984). Unpublished report by the Water Resource Department, MLWE (1999), Eritrea, indicated that dental fluorosis is not a wide spread problem in the country. Despite such reports, however, there are certain pockets of the country which they are known to have high levels of fluoride in water. One of the areas with high fluoride content in drinking water is Keren and its surrounding. The results of this study is in agreement with the reports by Srikanth *et al.* (2002); Estifanos (2005); Zerai (1996).

It has also been observed that the rural communities suffer dental and skeletal fluorosis as result of consuming water containing excessive fluoride. A direct relationship between the level of fluoride in drinking water and magnitude and severity of fluorosis is evident as it manifested by mottling of teeth in children and skeletal disorders in adults in those villages. A report by Srikanth *et al.* (2002) also indicated similar trends as 50% children and about 20% adult suffer from fluorosis at various levels. The photos in Plate 4.1 were captured during the preliminary survey confirming wide spread fluorosis in the area.



4.1a. Sample photos for Dental fluorosis at Broana village



4.1b: Sample photos for Dental fluorosis at Harkokia village

Plate 4.1: Sample photos of dental fluorosis in two villages

The region is associated with temperatures of 23.5-32.6 °C throughout the year resulting in high water consumption and increasing susceptibility to fluorosis.

Generally speaking, the rural communities of Eritrea including the villages under study belong to lower economic strata with farming as their main livelihood. Majority also suffer from malnutrition and low dietary calcium and magnesium. Low concentration of calcium and magnesium in groundwater and diet aggravates the fluorosis problem as the fluoride would be retained. Fluoride excretion as calcium fluoride or magnesium fluoride is inhibited from the gastrointestinal track and thus make people endemic to fluorosis (Jolly *et al.* 1971).

It was observed that there were high incidences of skeletal fluorosis and gastrointestinal and other discomforts at villages having fluoride concentrations above 2.75 mg/l. This is in agreement with studies made by Susheela *et al.* (1992) and WHO (2005).

4.3. Factors Affecting Fluoride Adsorption Efficiency

Batch studies were carried out using local materials (crushed burnt clay pot, Keren mud soil, Adigerghish mud soil and Household ash) and the effect of different parameters on fluoride removal capacity studied (Appendices I-V).

4.3.1. Effect of Adsorbent Mass on Fluoride Adsorption Efficiency

The percentage of F⁻ adsorbed for crushed burnt clay pot, Keren soil, Adigerghish soil and Household ash are presented in Figure 4.3. The results indicated that the adsorption capacities of the materials range from about 27.6% for Keren soil to 81.6% for crushed burnt clay pot at 10g adsorbent mass. From the figure, crushed burnt clay pot showed the highest fluoride removal capacity. This is because crushed

burnt clay pot was heat treated and hence adsorbent sites could possibly be activated while Keren and Adigerghish soils were in their pristine state. Hence, the adsorbent sites might not be activated well. Household ash had higher fluoride adsorption efficiency than Keren and Adigerghish soil. It is well documented that fluoride is adsorbed more to clay materials better when it is heat treated up to certain levels. Moreover, fluoride uptake is better in clays containing more Aluminum and Iron oxides and the results show that higher adsorption capacity could be associated with clay samples having higher Aluminum and Iron oxide (Mayabi *et al.*, 2009; Tikariha and Sahu, 2013).

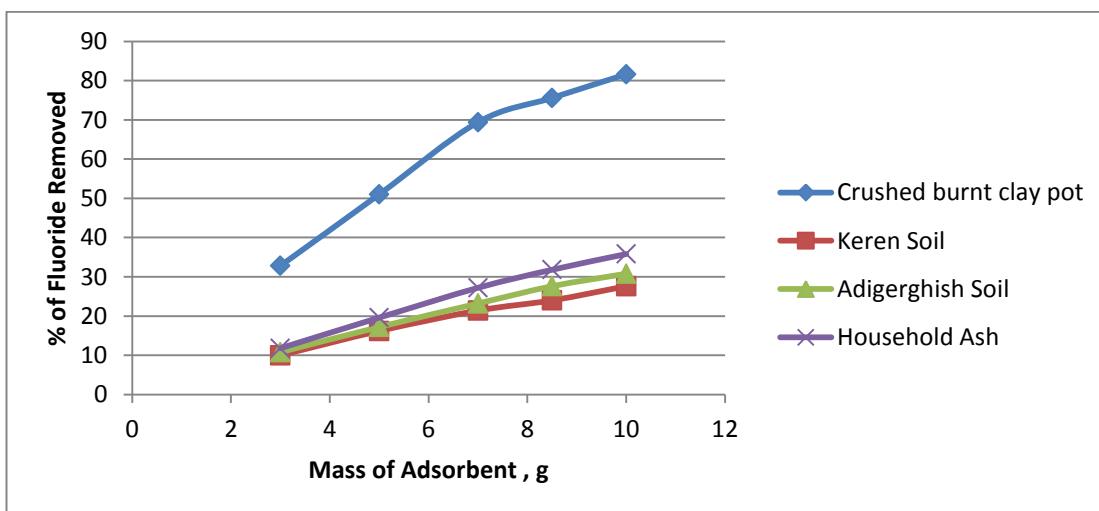


Figure 4.3: Adsorption efficiency of crushed burnt clay pot, Keren soil, Adigerghish soil and household ash for different mass of adsorbent (Initial fluoride conc. =5.0 mg/l)

As indicated in Figure 4.3, it was found that crushed burnt clay pot was found to have better removal efficiency than the other adsorbents. When 7g of it was added to the solution, the fluoride residue was reduced from 5 mg/l to almost 1.5 mg/l and at this level, the adsorption capacity of crushed burnt clay pot was 0.26 mg/g. However, the adsorption capacity of Keren soil, Adigerghish soil and household ash was 0.076

mg/g, 0.083 mg/g and 0.097 mg/g respectively at the same mass of 7g. Hence, more adsorbent mass was required in the three of the adsorbents to bring fluoride to the same level as of 7g crushed burnt clay pot.

Figure 4.4 shows typical analysis of the fluoride residue in solution when different amounts of crushed burnt clay pot doses were added to the solution. The figure shows that at 14 g/l dose, the fluoride residue was approaching the WHO recommendation of 1.5 mg/l fluoride concentration. Moreover, the slope of the curve was falling rapidly before reaching 14 g/l adsorbent dose and it tended to flatten beyond that and the reduction in fluoride level was significantly low to the right. From this, it could be concluded that optimum mass required to bring fluoride level from 5 mg/l to the WHO recommended (1.5 mg/l) is approximately 14 g/l in the case of crushed burnt clay pot. This dose is equivalent to 7g of crushed burnt clay pot. Hence, in subsequent experiments, 7g mass was employed for further testing.

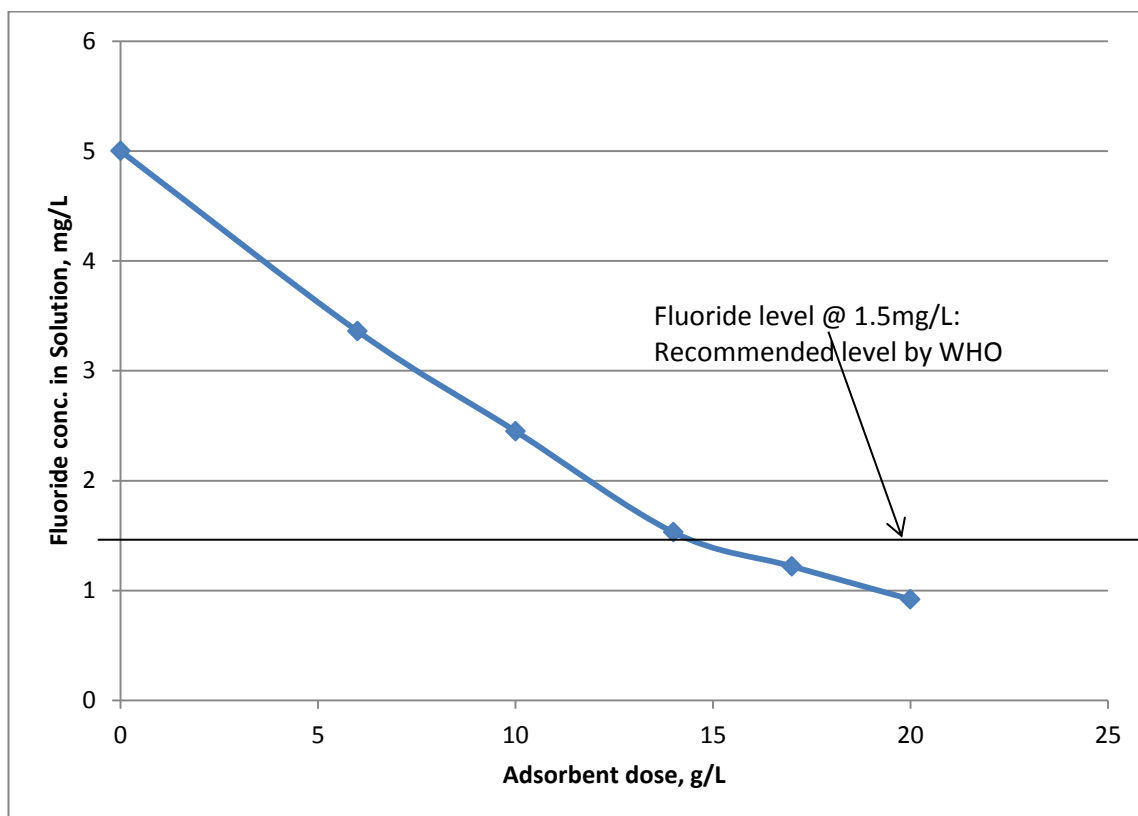


Figure 4.4: Fluoride residue in solution at different doses of crushed burnt clay pot

4.3.2. Effect of Contact Time on Fluoride Removal Efficiency

Investigation on the effect of contact time on the adsorption efficiency was studied.

Typical analyses of the results are indicated in Figure 4.5. The figure shows as the contact time increased, the rate of adsorption of fluoride increased rather rapidly in the first 50 min in the case of crushed burnt clay pot but then gradually approached a more or less constant value denoting attainment of equilibrium. The instantaneous sorption reaction in which fluoride ions adsorbed rapidly onto the surface of crushed burnt clay pot could be due to specific chemical interaction. The affinity and diffusive property could be contributing driving forces as well. However, in three other materials studied, the increase in fluoride removal was gradual. This could be mainly due to the fact that the adsorption sites were less or not well activated.

Nevertheless, an increase in fluoride removal at a retention time greater than 90 minutes (1 and a half hour) was insignificant in all materials. At 120 minutes (two hours) contact time, equilibrium was attained as there was no further adsorption observed to take place. Thus 2 hour contact time was employed in all subsequent studies.

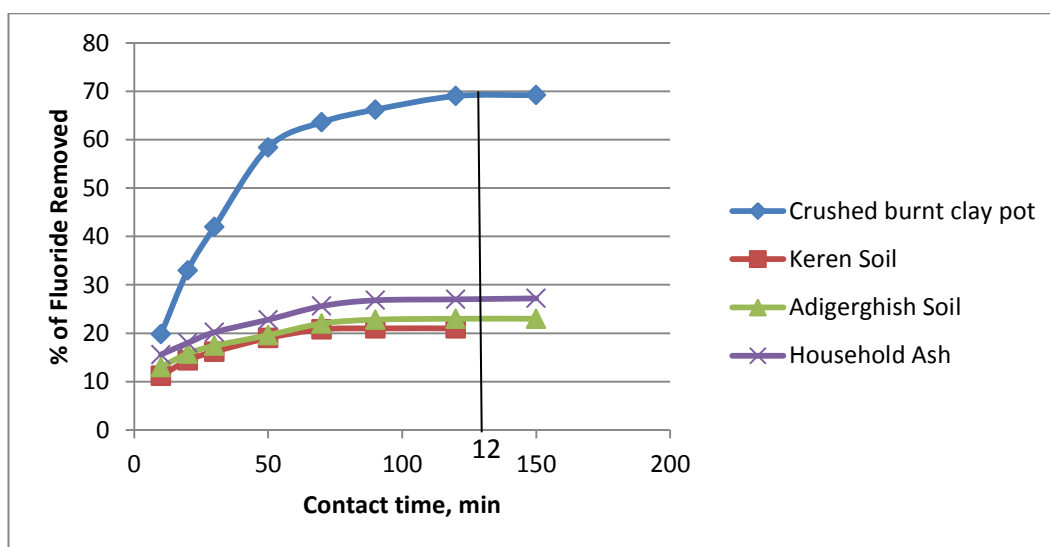


Figure 4.5: Effect of contact time on adsorption efficiency (Initial fluoride conc. =5.0 mg/l and adsorbent mass = 7g).

4.3.3. Effect of pH

Experiments were conducted to assess the effect of pH for the four adsorbent materials. The initial pH of water significantly played a major role affecting fluoride uptake capacity of the adsorbents. Figure 4.6 indicates the effect of pH. The optimum pH was 7 for all the materials except for the household ash. A higher adsorption capacity for household ash was observed at lower pH values, with the optimum pH of 4. The adsorption rapidly declined at pH greater than 7 for crushed burnt clay pot while for Keren and Adigerghish soils the decline was gradual. On the other hand, adsorption for household ash declined rapidly at pH values greater than 4. Decrease in adsorption efficiency might be due to decrease in positive charges of the adsorbent

and increase in competition of F^- . Tikariha and Sahu (2013) and Weber (1972) have made similar observations and the result of the experiment corroborates their observation. Nevertheless, adsorption is not just due to pH dependent but other mechanisms such as ligand exchange and complex-ion formation and precipitation may have played a role. Hence this could affect the performances of the adsorbent to certain levels. This is also was in agreement with the observation made by Mayabi et al. (2009)

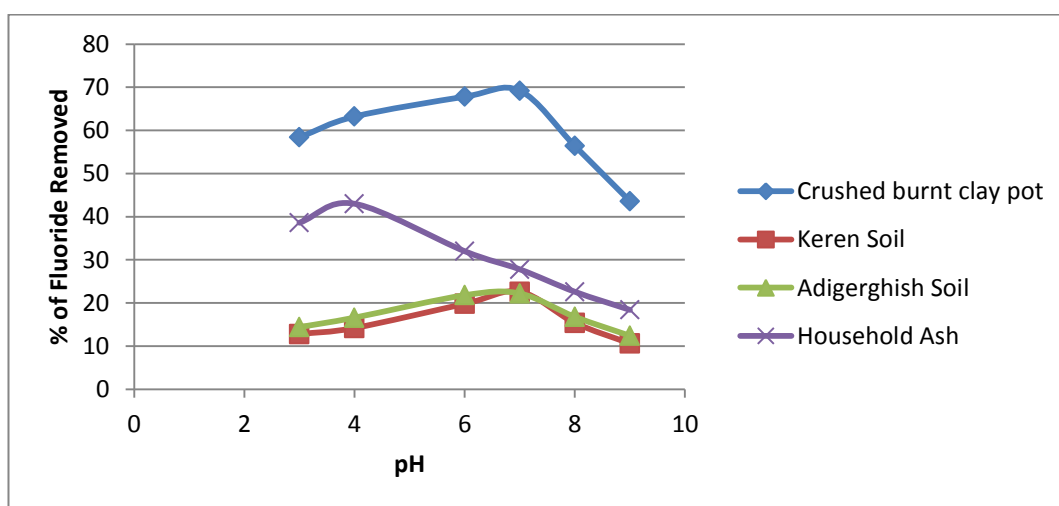


Figure 4.6: Effect of initial pH of raw water on the removal of fluoride (Initial fluoride conc. =5.0 mg/l and adsorbent mass=7g).

4.3.4. Effect of Particle Size

Table 4.3 shows that particle sizes ranging from 1.70 mm to 2.36 mm gave a lower adsorption capacity in the case of Keren and Adigerghish soils and more adsorption capacities was achieved for fine particle size (<0.15mm). However, significant change of adsorption capacity was not observed for crushed burnt clay pot with changing particle size. The table further shows that crushed burnt clay pot remained superior in removal capacity than the others adsorbents. Effect of particle size for

household ash was not studied as household ash particles were very fine during sieve analysis and grading was not possible according to sieve size analysis (0.15-2.36 mm) used in the study as indicated in Table 4.3.

Table 4.3: Effect of particle size on adsorption efficiency (Initial fluoride conc. =5.0 mg/l and adsorbent mass =7g).

Particle size (mm)	% of Fluoride removed		
	Crushed burnt clay pot	Keren Soil	Adigerghish Soil
<0.15	69.6	21.8	23.4
0.15-0.60	69.2	19.4	23.0
0.60-1.20	68.8	18.6	22.2
1.20-1.70	68.2	15.2	18.0
1.70-2.36	65.8	13.2	15.8

4.3.5. Effect of Initial Fluoride Concentration

The experiment indicated that for a given mass of adsorbent, the fluoride removal efficiency increased gradually with increasing initial concentration. Figure 4.7 shows the effect of initial fluoride for all materials, higher removal efficiency was observed for crushed burnt clay pot followed by household ash. Increase in adsorption capacity with increase in initial fluoride concentration could be mainly due to an increase in diffusion of fluoride to adsorption sites. Moreover, utilization of less accessible or less active sites of the adsorbent could occur when there was more fluoride in the solution to be taken up. Thus, this could increase the adsorption efficiency of the adsorbents. In a similar study, Hassen (2007) made similar conclusion on different clay types in Ethiopia.

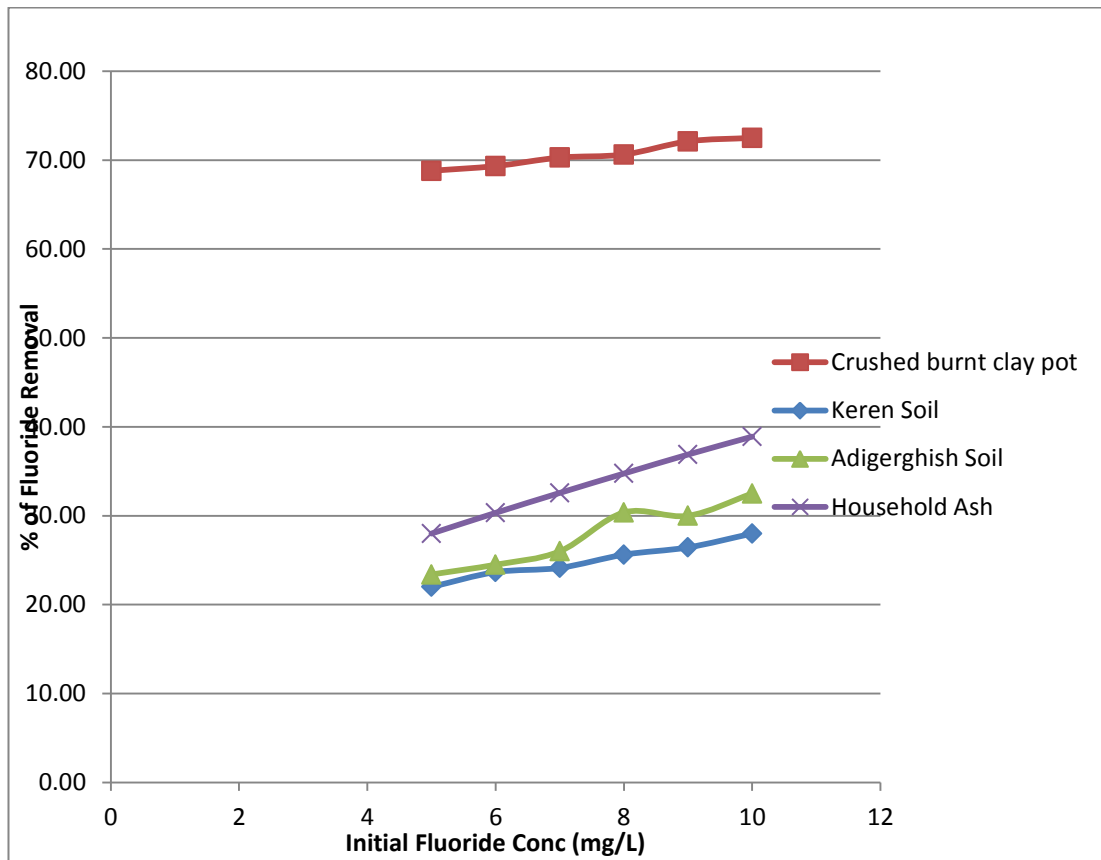


Figure 4.7: Effect of initial fluoride concentration on adsorption efficiency (Adsorbent mass=7g)

4.4. Selection of Adsorbent for the Development of Household Defluoridation Unit

The four local materials that have been studied in batch were compared by noting their adsorption capacities for fluoride uptake. The study indicated that crushed burnt clay pot had the highest removal capacity and hence selected for the development a household defluoridation unit.

Water quality monitoring study was done to assess the effect of adsorbent addition to water for fluoride removal in the batch study. The water quality test was done for all the adsorbent media for selected water quality parameters such F, pH, EC and turbidity results are presented in Table 4.4.

Table 4.4: Effect of adsorbent addition on water quality (adsorbent mass = 10g)

Type of adsorbent	Before adsorbent addition				After adsorbent addition			
	pH	EC, $\mu\text{S/cm}$	Turbidity, NTU	F ⁻ , mg/l	pH	EC, $\mu\text{S/cm}$	Turbidity, NTU	F ⁻ , mg/l
Crushed burnt clay pot	7.15	35	0.3	5	7.25	45	90	0.92
Keren soil	7.10	36	0.2	5	7.28	48	105	3.62
Adigerghish soil	7.20	38	0.1	5	7.23	49	85	3.46
Household ash	7.16	35	0.2	5	11.4	3180	30	3.22

Addition of adsorbents brought some undesirable changes in water quality and created more turbid water in all cases (Table 4.4). Particularly an increase in pH and EC in household ash was noted. However, fluoride levels were reduced to an acceptable level in the case of crushed burnt clay pot only below the WHO recommended value. Keeping other parameters the same for all, if selection of adsorbent was to be made based on the water quality of the effluent, none would be selected unless some other means of improving the water quality was introduced. In spite of this, crushed burnt clay pot showed a better removal capacity for fluoride while EC and pH were within the permissible levels. Nevertheless, turbidity existed in all materials and hence the batch method of water treatment in this case could not be justified as the effluent water quality did not meet the WHO drinking water guidelines.

However, there could be many alternatives which can improve water quality. A number of effective coagulants of plant origin have been identified elsewhere to enhance turbidity removal. Plant materials such as Nirmali, Okra, red bean, sugar and red maize (Gunaratna *et al.*, 2007), Moringa oleifera (Jahn, 1988; Asrafuzzaman

et al., 2011), cactus latifera, and seed powder of *Prosopis juliflora* (Diaz et al., 1999) could remove turbidity and hence improve the water quality. However, in this case, such method was not employed for practical limitations. Although the use of crushed burnt clay pot had created turbid water, this could be avoided by placing a filter media in a fixed bed. Taking all factors into consideration and the superiority of the material to remove fluoride, crushed burnt clay pot was selected for subsequent study for household defluoridation. This is discussed in more detail section 4.8.3.

4.5. Particle Size Analysis of Crushed Burnt Clay pot

Physical characteristics of the crushed burnt clay pot such as effective size, porosity and uniformity coefficient play a major role in design of the defluoridation unit and thus determined. Particles passing through 2.36 mm and retained in 0.60 mm sieve was selected as a filter medium to enhance permeability and decrease turbidity and color.

It was noted in the batch study (section 4.3.4) that the particle size has no significant effect on the removal capacity in the case of crushed burnt clay pot. However, it did affect the water quality as far as turbidity is concerned. Tables 4.5, 4.6 and Figure 4.8 show the particle size distribution and analysis of crushed burnt clay pot.

Particle-size distribution curve (Figure 4.8) was developed from the particle size distribution (Table 4.5) and the effective size of the particles, coefficient of uniformity and Coefficient of Gradation was found from D_{10} , D_{30} and D_{60} of the curve is presented in Figure 4.8.

Table 4.5: Particle size distribution of crushed burnt clay pot

Sieve size (mm)	Weight retained (g)	% Retained	Cumulative % retained	% Finer
2.36	0.00	0	0	100
1.7	2790.00	45	45	55
1.2	2170.00	35	80	20
0.6	1240.00	20	100	0

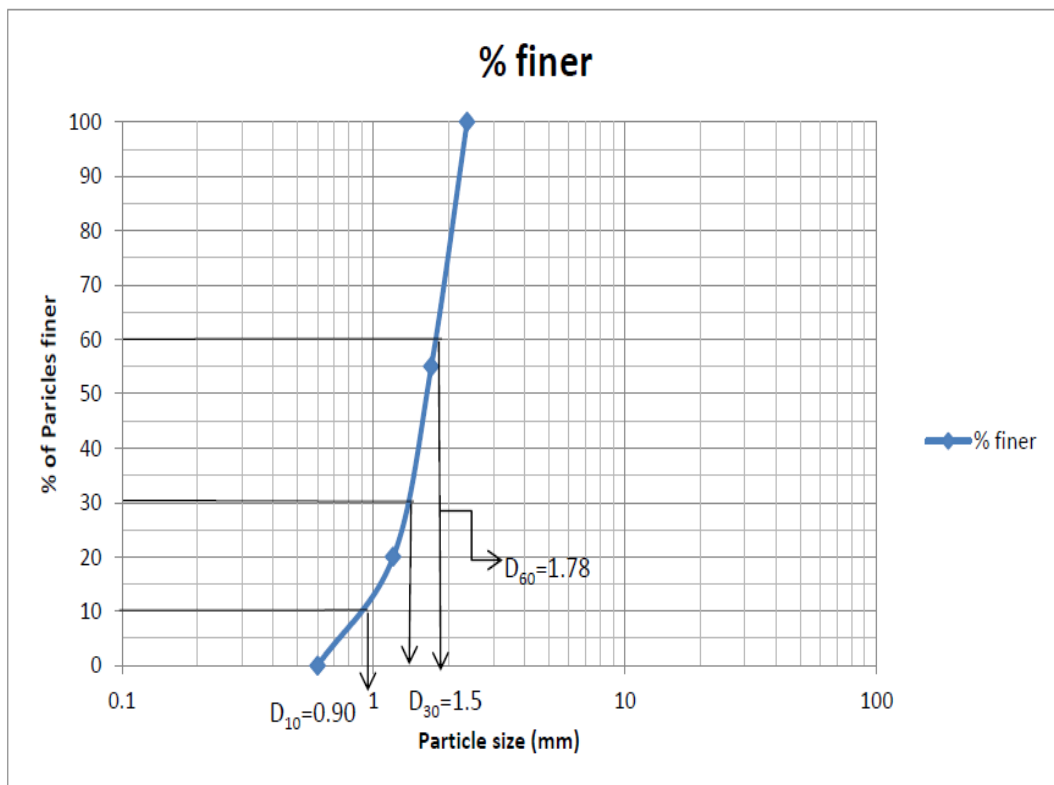


Figure.4.8: Particle Size Distribution Curve of crushed burnt clay pot

From Figure 4.8, it was approximated that $D_{10}=0.90$ mm, $D_{30}=1.50$ mm and $D_{60}=1.78$ mm and the other parameter were determined from the following relationships.

The diameter in the particle-size distribution curve corresponding to 10% finer is defined as the effective size or D_{10} and empirically, D_{10} has been strongly correlated with the permeability of the medium.

Hence, Effective size = D_{10} of the particles = 0.90 mm

The uniformity coefficient (Cu) is given by the relation:

$$Cu = \frac{D_{60}}{D_{10}} = 1.78/0.90 = 1.98$$

Where, D_{60} is the diameter corresponding to 60% finer in the particle size distribution.

The coefficient of gradation (Cc) expressed as;

$$\text{Coefficient of Gradation} = D_{30}^2 / (D_{10} * D_{60}) = 1.50 * 1.50 / (0.90 * 1.78) = 1.40$$

Where, D_{30} is the diameter corresponding to 30% finer in the particle-size distribution.

The particle size distribution curve shows not only the range of particle sizes presented in the medium but also the type of distribution of various size particles. In subsequent Tables 4.6 and 4.7, particle specific gravity, bulk density and porosity of the media were analyzed and determined respectively using a pycnometer or water displacement method. The results indicate that the medium's bulk density lay within the typical mineral soils that have bulk densities that range from 1.0 to 1.6 g/cm³. Moreover, the porosity of the medium was found to be about 52% and hence this was believed to facilitate free-water movement within the medium.

Table 4.6: Particle Specific Gravity Determination of crushed burnt clay pot

Sample No		1	2
Bottle No		138	131
Mass of Bottle	m1 g	53.21	47.16
Mass of Bottle + Dry medium	m2 g	106.45	97.81
Mass of Dry Medium	ms= m2-m1	53.24	50.65
Mass of Bottle + Dry medium + Water	m3 g	180.56	174.38
Mass of Bottle + Water	m4 g	152.74	147.76
Mass of Water replaced	mw=ms-m3+m4	25.42	24.03
Temperature	T °C	23.0	23.0
SG @ T1 °C	Gs(T °C) = ms/mw	2.094	2.108
C1 @ T1 °C	C1	0.999	0.999
SG @ 20 °C	Gs(20 °C) = C1*Gs(T °C)	2.093	2.106
Average Particle Specific Gravity		2.0995 ≈ 2.10	

Table 4.7: Bulk Density and Porosity Determination of crushed burnt clay pot

Sample No		1	2	3
Mass of container	m1 g	42.64	42.63	42.65
Mass of container + Medium	m2 g	208.44	208.25	207.12
Mass of container + water	m3 g	206.35	206.45	206.65
Mass of water	mw=m3-m1	163.71	163.82	164
Mass of Medium	ms=m2-m1	165.8	165.62	164.47
Bulk density of medium(loose)	(m2-m1)/(m3-m1)	1.013	1.011	1.003
Average		1.009 ≈ 1.01		
$Porosity\ of\ Medium = 1 - \frac{Bulk\ Density}{Particle\ Density}$		0.519048 ≈ 0.519 51.9% ≈ 52%		

The general appearance of the crushed burnt clay pot used in the continuous adsorption experiment is as indicated in Plate 4.2



Plate 4.2: Photo of crushed burnt clay pot and its particle size distribution

4.6. Fixed Bed Continuous Flow Adsorption Column Test

The batch method of fluoride removal was found inapplicable for household defluoridation as the water quality was declining and did not meet the standards for drinking water. Therefore, alternative has been sought so that the local adsorbent material could be utilized for fluoride removal without having undesirable effect on the water quality. This was done by selecting particle sizes of the medium and placing them in a filter bed so that particles were allowed to settle within the filter bed. The results of the experiment (raw data) for the continuous flow adsorption in the mini column are presented in Appendices VI-X

In the batch experiment, average fluoride removal capacity of crushed burnt clay pot was found to be 0.26 mg F⁻/g. Taking this in mind, a continuous flow experiment in a down flow mode was carried out in a mini column to help correlate the flow rate and bed depth on the fluoride removal capacity before up scaling to a household system.

4.6. Breakthrough Study of the Mini-Column Test

Crushed burnt clay pot was packed in a mini-column (Plate 4.3) in a fixed-bed depths of 15, 20 and 25 cm and the experiment run in a down flow mode. The typical adsorption of fluoride onto crushed burnt clay pot media are presented in the breakthrough curves (Figures 4.9-4.12). Figures 4.9, 4.110, 4.11 and 4.12 show the effect of bed depth and flow rate on the breakthrough curves of fluoride adsorption onto the crushed burnt clay pot at fixed bed depths of 15, 20, and 25 cm for constant flow rates of 2.5, 5, 10 and 15 ml/min respectively. The breakthrough volume was taken at 30% of the initial fluoride concentration ($C_e/C_o = 0.3$) as indicated by the horizontal line in Figures 4.9-4.12 in which C_o and C_e are raw and treated water average fluoride concentration respectively. The horizontal line (recommend value

by WHO as 1.5 mg/l of fluoride level) crossing each curve in each figure indicates a point where the breakthrough occurred. The breakthrough volume could be obtained by projecting the point of intersection vertically down for a given flow rate. A summary of the results of Figures 4.9-4.12 are presented in Table 4.8.



Plate 4.3: Experimental Photo of the mini column packed with crushed burnt clay pot

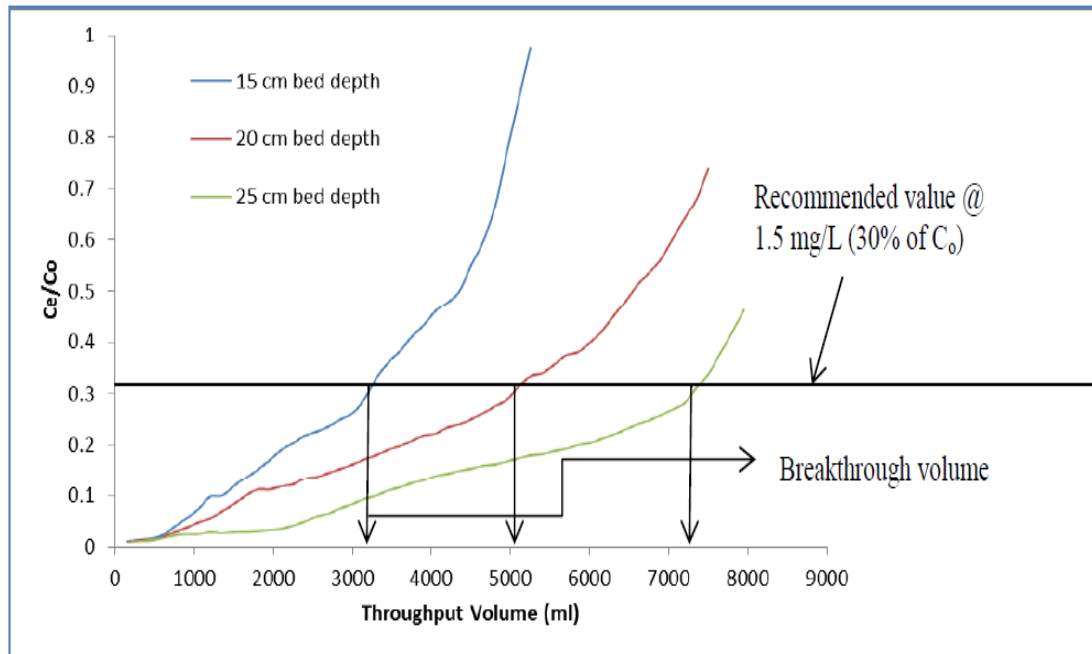


Figure 4.9: Effect of bed depth on breakthrough volume at a constant flow rate of 2.5 ml/min ($C_o = 5$ mg/l).

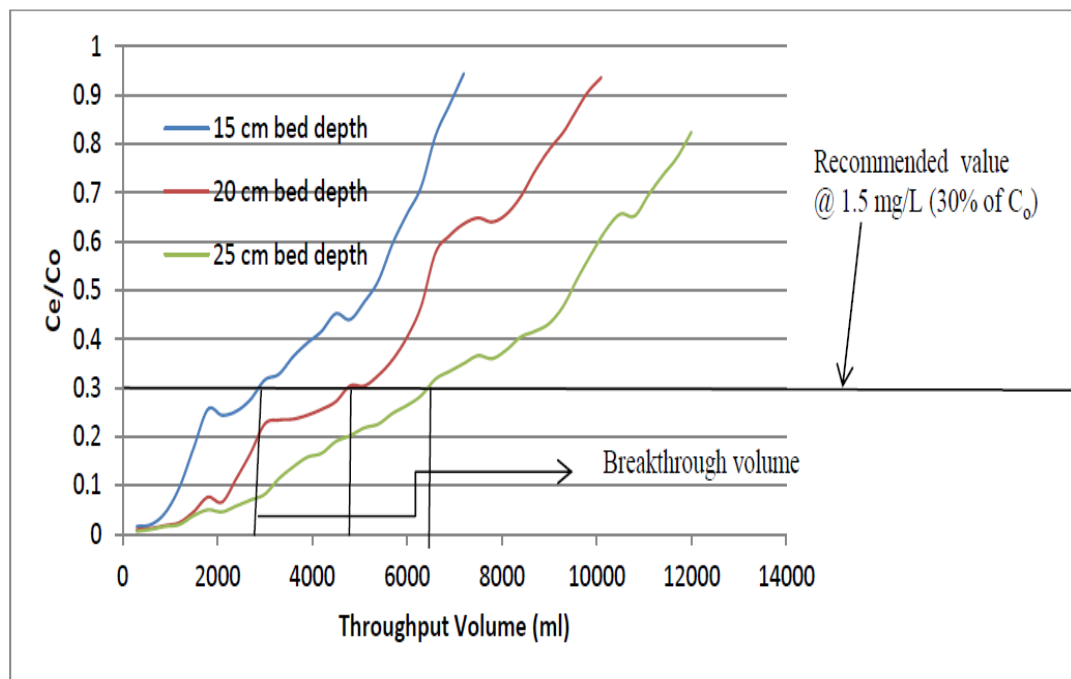


Figure 4.10: Effect of bed depth on breakthrough volume at a constant flow rate of 5 ml/min ($C_o = 5$ mg/l).

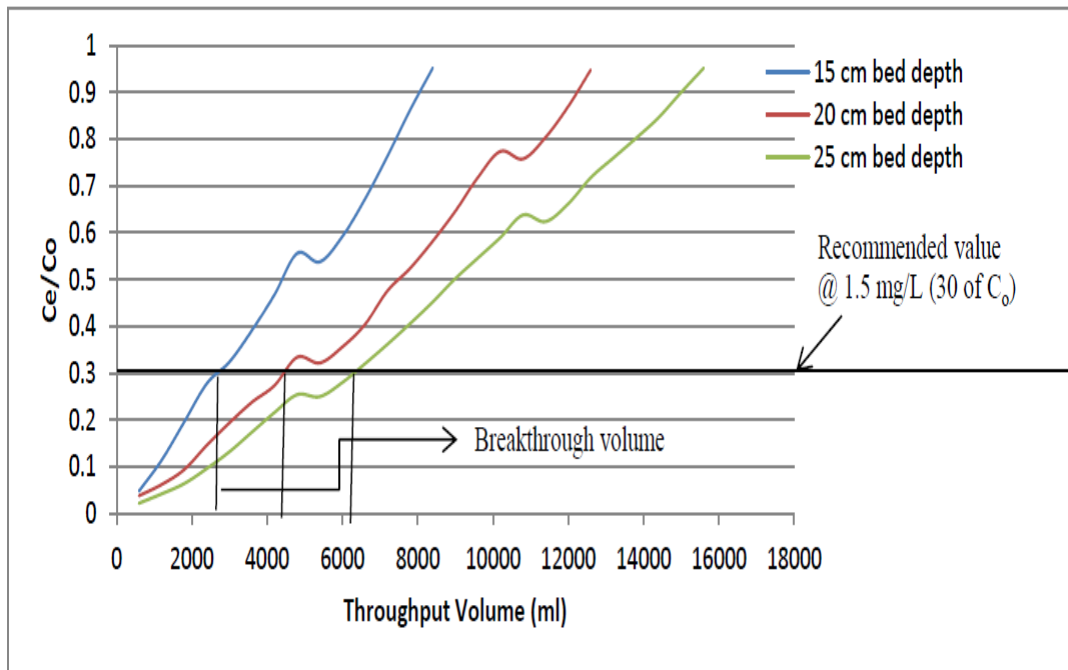


Figure 4.11: Effect of bed depth on breakthrough volume at a constant flow rate of 10 ml/min ($C_o = 5$ mg/l).

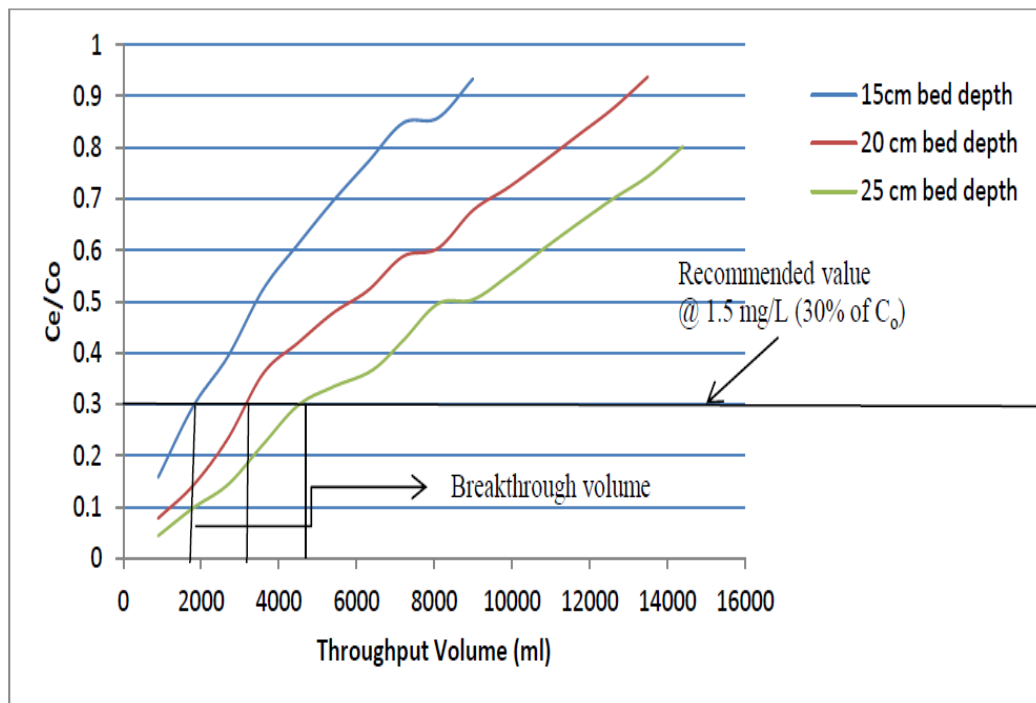


Figure 4.12: Effect of bed depth on breakthrough volume at a constant flow rate of 15 ml/min ($C_o = 5$ mg/l).

As can be seen from Figures 4.9 -4.12, most of the fluoride was initially adsorbed, so the concentration in the effluent was low. However, as the adsorption advanced, the effluent fluoride concentration increased slowly and adsorbent exhausted gradually. Typical analysis on the effect of bed depth and flow rate on the breakthrough curve was carried out. The results indicated that with increasing bed depth from 15 to 25 cm, the breakthrough volume increased from 3.2 to 7.3 litres at a flow rate of 2.5 ml/min. Hence, the breakthrough time increased proportionally from 21.33 to 48.67 hours (Figure 4.9 and Table 4.8). The analysis further shows that the breakthrough time (service time) is directly related to the bed depth of the column as indicated in Table 4.8. This could be associated with an increased in bed depth, increased the adsorbent mass and hence provides greater adsorption sites which led to improve the adsorption performance. Moreover, an increased in bed depth could increase the contact time and hence improved the adsorption capacity.

Similar analysis was carried out on the effect of flow rate. An increase in flow rate from 2.5 to 15 ml/min resulted in a reduction of treated volume of water at the breakthrough associated with a decrease in service time of the bed. Table 4.8 shows that 7.3 litres and 4.5 litres of water were treated at a flow rate of 2.5 ml/min and 15 ml/min respectively at a bed depth of 25 cm at the breakthrough point. It also shows that the breakthrough time was reduced from 48.67 to 5 hours for the same.

However, at 15 cm bed depth, increasing the flow rate from 2.5 to 15 ml/min resulted in a decrease in a treated volume from 3.2 litres to 1.8 litres respectively and consequently the service time of the bed was reduced from 21.33 to 2 hours (Figures 4.9-4.12 and Table 4.8). Hence bed depth and flow rate played a major role in the

adsorption performance and thus the amount of water to be treated varied accordingly. This was mainly due to the decrease in contact time between the fluoride and the adsorbent at higher flow rates and shorter bed depths. Intra-particle diffusion could also control the adsorption rate and hence, an early breakthrough occurred led to a low bed adsorption capacity. This is supported by a study carried by Christian et al. (2005).

On the other hand, when the flow rate was decreased, the contact time in the column was longer, intra-particulate diffusion then became effective. Thus the adsorbate had more time to diffuse in to the particles of the adsorbent and a better adsorption capacity resulted. Depending on flow rate and bed depth used, the service time of the medium varied as indicated in Table 4.8 before reaching the WHO recommendations. Thereafter, regeneration or replacement of the medium would be necessary for the next run.

In an ideal adsorption system, the shape of the breakthrough curve has an S shape profile. The breakthrough curves indicated in Figures 4.10-4.12 show that at lower bed depths, the shape of the curve didn't show the characteristic S shape profile. However, at 25 cm column depth, the shape was approaching S shape curve for a flow rate of 2.5 ml/min (Figure 4.9) and hence an ideal adsorption is said to take place in this case. Further, at 25 cm bed depth and 2.5 ml/min flow rate, the adsorption capacity of the medium was 0.26 mg/g (Table 4.8) which is the same with what was obtained in the batch test. Thus, the mini column with the optimum adsorption and ideal breakthrough curve was selected for scaling up. Furthermore, the analysis showed that the EBRT increased from 24.94 to 41.56 min (Table 4.8)

when the bed depth increased for a 2.5 ml/min flow rate and similar trends were observed with other flow rates.

The mini-column was operated for 6-9 hours and stopped for 15-18 hours and the on-off pump operation continued until the complete exhaustion of the column. In some of the breakthrough profiles illustrated in Figures 4.9-4.12, effluent fluoride concentrations were lower than that prior to shut-down. This could be due to the fact that the on-off-pump cycle allowed fluoride diffusion along the internal pore surfaces and adsorption at binding sites resulting in a decrease in fluoride concentration in the stagnant layer around the particle. Thereafter, when the system was restarted, a higher concentration gradient existed between liquid and solid surface fluoride concentrations. Those observations could lead to a suggestion that fluoride adsorption onto porous adsorbents are limited by intra-particle diffusion. Similar observations were made by Christian et al. (2005), Yoseph (2007) and Ko Chun (2002).

4.6.2 Simplified Fixed Bed Design Models

The bed depth data of the mini column were analyzed for the application of simplified fixed bed models to upgrade and optimize the fixed bed depth. These are Bed Depth Service Time (BDST) and Empty Bed Residence Time (EBRT) which are used to predict, optimize and describe the fixed bed column operation.

a. Bed Depth Service Time (BDST) Model

Table 4.8 shows details of the variable bed depth at a fixed flow rate in a fixed bed column. BDST plots were constructed with data from Table 4.8 by plotting the breakthrough time (T_b) versus the bed depth (h_c). The influent fluoride concentration

(C_0) was 5 mg/L and flow rates of 2.5, 5, 10 and 15 ml/min were used at 30% breakthrough for 15, 20 and 25 cm bed heights. Figure 4.13 shows BDST plots as obtained from the analysis of Table 4.8. The EBRT values in Table 4.8 were determined using *equation* [2.12].

Table 4.8: Variable bed depth at a fixed flow rate in a fixed-bed column for the removal of 5 mg/l of fluoride by crushed burnt clay pot (Internal $\phi=2.3$ cm)

flow rate (ml/min)	bed depth (cm)	Bed vol. (cm ³)	Adsorbent mass (g)	EBRT (min)	V _b (l)	T _b (h)	Adsorbent exhaustion rate (g/l)	Adsorption capacity (mg/g)
2.5	15	62.35	60	24.94	3.20	21.33	18.75	0.19
	20	83.13	80	33.25	5.05	33.67	15.84	0.22
	25	103.91	100	41.56	7.30	48.67	13.70	0.26
5	15	62.35	60	12.47	2.93	9.75	20.48	0.17
	20	83.13	80	16.63	4.80	16.0	16.67	0.21
	25	103.91	100	20.78	6.40	21.17	15.65	0.23
10	15	62.35	60	6.24	2.605	4.33	23.03	0.15
	20	83.13	80	8.31	4.501	7.50	17.77	0.20
	25	103.91	100	10.09	6.15	10.25	16.26	0.21
15	15	62.35	60	4.15	1.80	2.0	33.33	0.11
	20	83.13	80	5.54	3.00	3.33	26.67	0.13
	25	103.91	100	6.93	4.50	5.0	22.22	0.16

The analysis of the BDST graph shows that the BDST curve obtained from straight lines. Hence, the BDST curve could be expressed using equation [2.8] in compliance with Hutchins (1973) approximation. Therefore, applying equation [2.8] and solving the equation, the coefficients N_0 and K of the equation for the four flow rates were calculated and are presented in Table 4.9. The correlation coefficient (R^2) of BDST plots of the fixed bed depth data were more than 0.996 in all four cases and this led to the conclusion that Hutchins (1973) approximation is relevant.

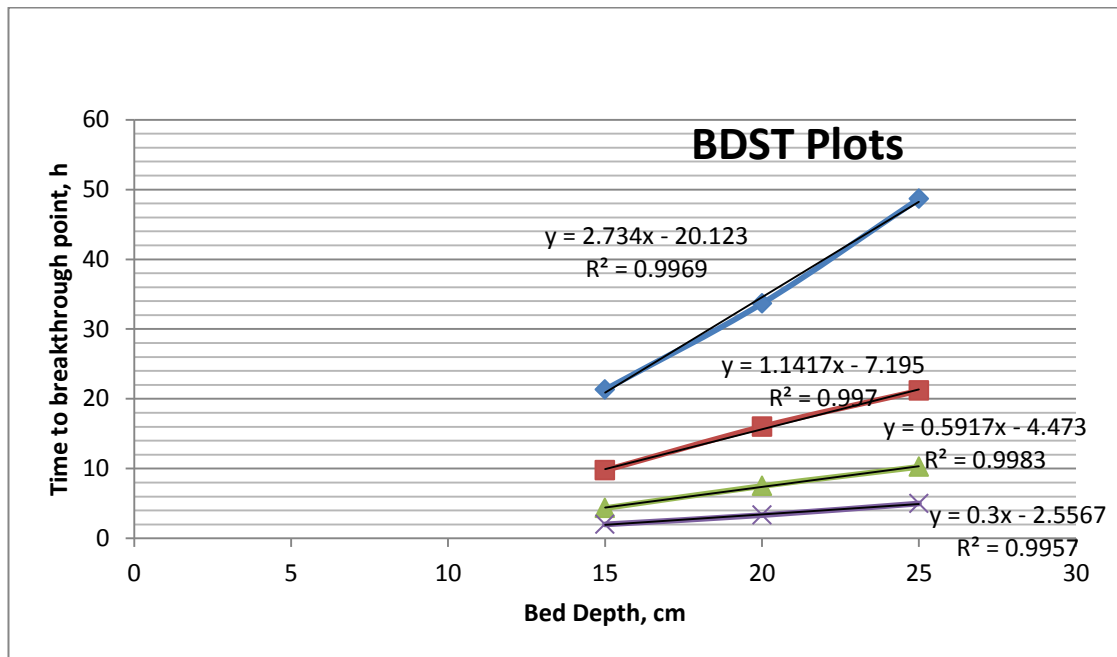


Figure 4.13: BDST plot at 30 % breakthrough in a fixed-bed column at different flow rates: ◆-2.5; ■-5; ▲-10; X-15 ml/min ($C_0 = 5$ mg/l).

Hence, *equation* [2.8] is applicable in the case of crushed fire clay pots, and the BDST model could be applied to predict service time of an adsorption system for a crushed burnt clay pot. Its application to predict the service time was compared with results from the pilot experiment and the results are presented in detail in section 4.8.2.

The adsorption capacity of the medium for 25 cm bed depth at breakthrough was found at each flow and the results are indicated in Table 4.9. The reduction in adsorption capacity of the medium could be associated with a decrease in contact time between the fluoride and the adsorbent at higher flow rates. The adsorption capacity obtained at 2.5 ml/min was almost the same with adsorption capacity obtained in the batch test for the same medium and hence this value was used in the

design of the household defluoridation unit in the continuous adsorption for the pilot scale experiment.

Table 4.9: Constants of BDST curve

Flow rate (Q, ml/min)	Linear flow rate, q (cm/h)	N_0 (mg/cm ³)	K (L/mg/ h) x 10 ⁻³	Adsorption capacity, X (mg/g)
2.5	36	0.493	8.426	0.26
5	72	0.412	23.552	0.22
10	144.6	0.427	37.885	0.21
15	216.6	0.325	66.3	0.16

b. Empty Bed Residence Time (EBRT) Model

From the BDST analysis, data used for the EBRT model was obtained. The breakthrough percentage was specified as before at 30% and hence the service time for the column before breakthrough was found from the mini column experiment. The adsorbent exhaustion rate was found by dividing mass of the adsorbent used by the volume of treated water at breakthrough, V_b . Thus the adsorbent exhaustion rate and the EBRT at various adsorbent bed heights were obtained as presented in Table 4.8. A plot of the adsorbent exhaustion rate versus EBRT was then constructed as shown in Figure 4.14. The figure indicated that the adsorbent exhaustion rate decreased with increasing EBRT. Besides, the figure shows that at lower flow rate, the operating line shifted to the right indicating that it has got higher EBRT.

At lower flow rates, the curves tend to flatten and no significant reduction in adsorbent exhaustion rate was obtained with contact time greater than 15 and 25 min for 5 and 2.5 ml/min flow rates respectively. The corresponding adsorbent exhaustion rate was 18.75 and 16.67 g/l. The figure further shows that the adsorbent dose for the batch system was nearly 14 g/l and this was equivalent to the adsorbent

exhaustion rate of 2.5 ml/min at a bed depth of 25 cm. Hence the same dose of adsorbent could be used to design the HhDU for the pilot study.

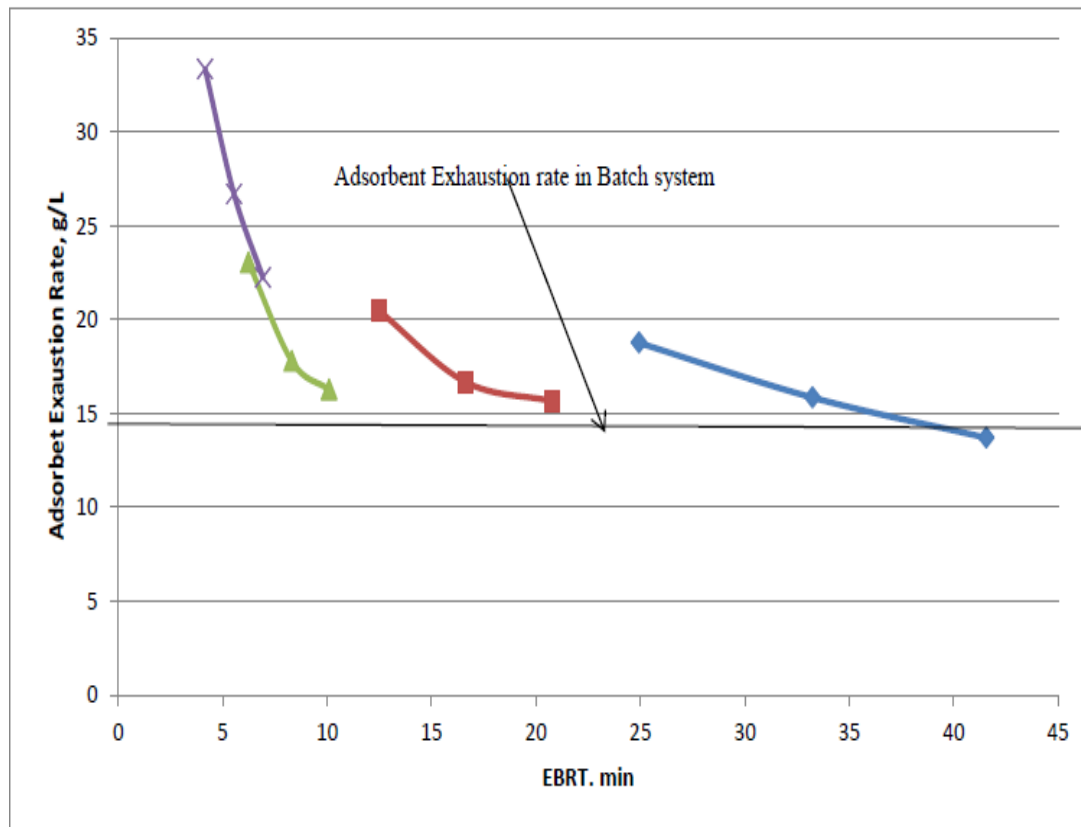


Figure 4.14: Adsorbent exhaustion rate versus EBRT for ◆-2.5; ■-5; ▲-10, X-15 ml/min.

4.7. Design and Construction of Pilot Household Defluoridation Unit (HhDU) for a Pilot Experiment

Table 4.10 shows the details and summary of various parameters with their corresponding values used in the design of the pilot scale unit. The design calculation of the Household Defluoridation Unit was made from the mathematical relationships existing among the parameters and the results are presented in Table 4.10. Design values were selected from practical considerations and from results of the mini column at which ideal adsorption were took place. A daily water demand of 21 litres was assumed and the unit was designed to serve for at least half month (15 days) for

the pilot run before reaching 1.5 mg/l fluoride concentration. Accordingly, in a period of 15 days, 315 litres of water at 5 mg/l fluoride was to reduce to 1.5 mg/l and hence a total of 1102.5 mg of fluoride has to be removed in the operational period. At a sorption capacity of 0.26 mg/g of the medium, the adsorbent mass required was 4240g. For 10.3 cm diameter column selected for the pilot scale unit, the corresponding flow rate from the direct scale up was 50 ml/min (3 l/hour). To accommodate the said mass, 50 cm packed bed depth was required. However, an allowance was made at different sections of the column bringing the total height of the column to 70 cm (Table 4.10).

Moreover, the summary of the scale up ratio of the mini column and pilot column is presented in Table 4.11. The scaling ratio was calculated by dividing corresponding values of the mini-column to the pilot column. A schematic diagram of the pilot scale unit (Plate 4.4) representing the Pilot Household Defluoridation Unit (HhDU) is also described in Figure 4.15.

Table 4.10: Summary of the Design calculation of the Household Defluoridation Unit

Given parameters	Description	Unit	Corresponding value
D	Daily personal water demand	l/(c d)	3-4 (3.5)
N	Number of users	N ^o	5-7 (6)
V _t	Total volume of water to be treated	l	315
OSc	Operational sorption capacity (F ⁻ /Adsorbent)	mg/g	0.26
ρ _b	Bulk Density of Medium (loose)	Kg/l	1.01
Co	Raw water fluoride concentration	mg/l	5
Ce	Treated water average fluoride concentration	mg/l	1.5
q	linear flow rate (selected from the mini column experiment)	cm/h	36
Derived parameters			
Q _d =D*N	Daily water treatment	l/d	21
F _t =V _t *(Co-Ce)	Total fluoride removal during a filter period	mg	1102.5
M=F _t /OSc	Amount of medium required for removal	g	4240
V _m =M/ρ _b	Volume of the medium in the filter	l	4.198
Corresponding dimensions			
Ø	Column diameter (selected as available)	cm	10.30
Q =q* Π*(Ø/2) ²	flow rate	l/h	3.0
H _w =Qd/Q	working hours in a day	h/d	7
h ₁	Distance from bottom of the column to the bottom level of the packed media	cm	5
h ₂	Distance from top level of the packed media to the point where tap is fixed	cm	5
h ₃	Distance between the tap & top of the column	cm	10
h _c =V _m /[Π*(Ø/2) ²]	Height of packed column	cm	50
H _{tc}	Total height of the column (h ₁ + h ₂ +h ₃ +h _c)	cm	70



Plate 4.4: Photo of the Pilot Household Defluoridation Unit

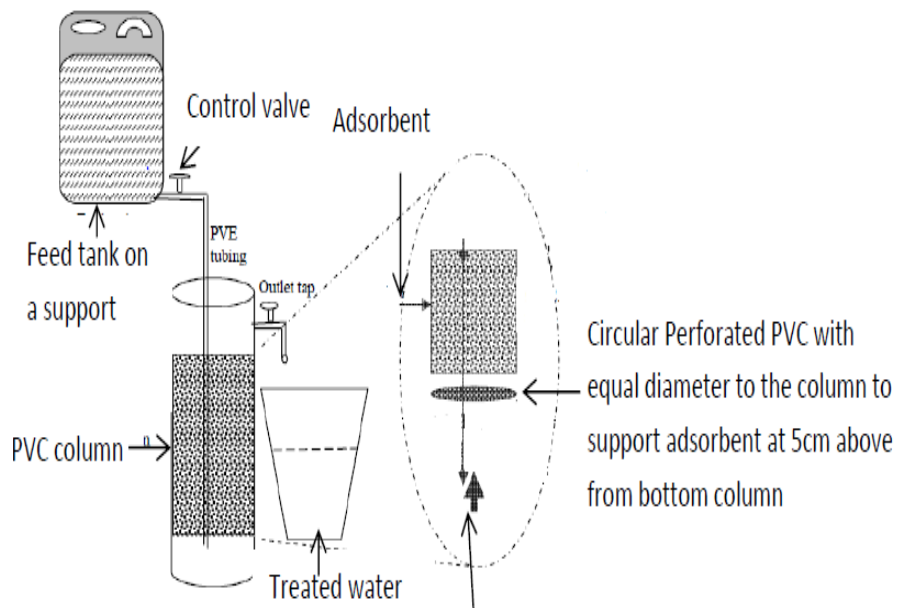


Figure 4.15: Schematic diagram of the Household Defluoridation Unit

Table 4.11: Scale up parameters and Scale up ratios

Geometric Parameters	Mini column	Large column	Scale-up ratio
Cross Sectional Area (cm ²)	4.15	83.32	0.05
Bed volume (cm ³)	103.87	4166.14	0.02
Operating parameters			
Influent fluoride conc. (mg/l)	5	5	1
Linear flow rate (cm/h)	36	36	1
Volumetric flow rate (l/h)	0.15	3	0.05
Mass of adsorbent (g)	100	4240	0.02

4.8. Pilot Scale Experiment

For the designed Pilot Household Defluoridation Unit, a pilot experiment was run to evaluate its performance. The characteristics of the raw water used in the pilot scale experiment are presented in Table 4.12.

Table 4.12: Characteristics of raw water for the pilot experiment

Water Quality Parameters	Corresponding value
F ⁻ (mg/l)	5.0 ± 0.10
pH	7.10 ± 0.10
EC (µS/cm)	200 ± 10
Turbidity (NTU)	0.1 ± 0.01
Total hardness as CaCO ₃ (mg/l)	250 ± 10

4.8.1. Performance of Pilot HhDU

The performance of the Pilot Household Defluoridation Unit (HhDU) was monitored at three hour intervals and operation discontinued when the fluoride level reached 1.5 mg/l. The linear flow (infiltration) rate was fixed the same as in the mini column. The pilot unit was running for 7 hours a day to treat 21 litres of water at a rate of 3 l/h and the Volume of safe water produced determined in each case. Figure 4.16 shows the breakthrough curve where the concentration ratio C_t/C_o is plotted versus treated volume. The total volume of treated water at the breakthrough concentration (C_b) was 324 litres and the corresponding breakthrough time was 108 hours. The value so obtained in the pilot scale unit was sufficient for 15.43 days based on 21

litres daily water demand. The result was in agreement with the design value (Table 4.10) despite there being a slight increase in treated volume by 9 litres more than the anticipated design volume (higher by 2.8% only). This was insignificant increase and the unit could be said to have performed well.

However, when compared to the values obtained from the BDST model, it was slightly lower than the predicted service time by 8% only (Table 4.13), which was not significant. The quantity of water to be defluoridated was calculated using BDST model and was found to be about 350 litres. Uneven flow patterns and selective flow paths through the bed could possibly occur during the operation. Hence, this could be the reasons for the slight underperformance.

Moreover, an increase in the column diameter during the scale up and the presence of different ions in synthetic water as compared to the mini-column might also contribute to the decrease of breakthrough time of the pilot HhDU despite there being an increase of EBCT to lengthen the service time of the bed. Ghorai & Pant (2005) made similar observations.

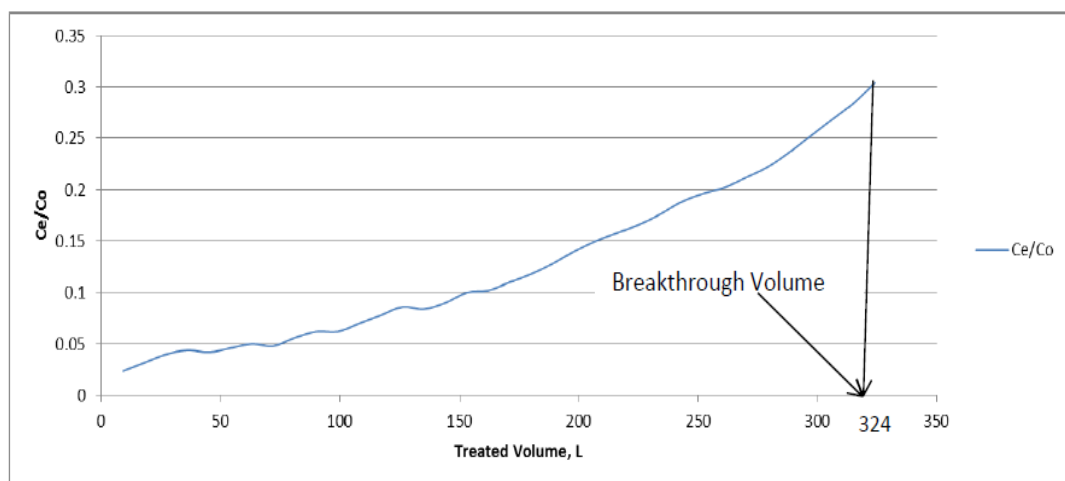


Figure 4.16: Treated Volume of the Pilot column (flow rate=50 ml/min, $C_o = 5$ mg/l, bed depth= 50 cm, packed mass= 4240g).

4.8.2. Treated Water Quality Monitoring of the pilot HhDU

Water quality monitoring was carried out for selected physico-chemical characteristics of the treated water such as pH, turbidity, electrical conductivity and total hardness. The conductivity, turbidity and total hardness of the treated water were slightly higher at the beginning of the test but decreased thereafter. This may be due to the release of fine and unstable soluble particles of the media. However, the effluent pH remained almost constant. Hence, it could be said that there was no much deviation in water quality values from the raw water. Besides, the treated water was colourless and tasteless with no smell observed. This indicates therefore, that crushed burnt clay pot filter was efficient in filtering of the raw water. The up flow column unit had a plug flow pattern, where the lower parts of the packed bed become saturated first. Then the saturation zone moved slowly towards the upper treated water point. Moreover, the up flow arrangement helped suspended particles to settle within the filter bed and thus reduced the turbidity of the water to a greater extent.

Table 4.13 shows water quality parameters for the treated water. The results of the tests indicate that values were within the acceptable range despite slight increments. Hence it can be said that the Pilot Household Defluoridation Unit performed well and the rural community can receive safe water for drinking with fluoride content of less than 1.5 mg/l.

Table 4.13: Physico-chemical analysis of treated water.

Water quality parameter	Range of values	WHO standard	Remark
F (mg/l)	≤1.5	Less than 1.5	Satisfactory
pH	7.0 -7.3	6.5-8.5	Good
EC (μS/cm)	230.57-260.8	Less than 500	Acceptable
Turbidity (NTU)	0.3-1.3	Less than 5	Acceptable
Total hardness as CaCO ₃ (mg/l)	276.4-309.2	-	Acceptable
Taste	Normal	-	Good
Smell	None	-	Good
Colour	Clear	-	Good

4.9. Prediction of Service Time of different HhDU by BDST Model

Earlier, it was discussed that the BDST model could be applied to predict the service time of an adsorption system of fluoride onto crushed burnt clay pot. The BDST constants were used then to predict service time. Table 4.14 presents summary of the results of the predicted service time for different operating parameters for two possible scenarios. The other two scenarios were omitted intentionally as their breakthrough point occurred earlier associated with high flow rates. Calculation was made using *Equation* [2.8] and Table 4.14 was compiled by assuming different operating parameters.

The predicted service time in both scenarios was compared taking a reference operating parameters of the bed depth as 50 cm and initial fluoride concentration (F-) at 5 mg/l as indicated in bold in Table 4.14. This reference values was selected because the pilot study was carried out at that operational conditions and thus making comparison would be easier. The results presented in Table 4.14 indicates that for a similar operating parameters of a fixed bed depth, when the linear flow rate increased from 36 to 72 cm/h for a bed of 50 cm and 5 mg/l F-, the service time could have been 50 h. The corresponding breakthrough volume could have been 300 litres,

which would be 50 litres less than the value that could be obtained in a linear flow rate of 36 cm/h. This is mainly due to the fact that at higher flow rates, the adsorbent material has lower chances to interact with fluoride (lower contact time) resulting in an early breakthrough point. Hence, the service time would be reduced accordingly.

In addition to changing flow rates, when the fluoride concentration in raw water was assumed at 3 mg/l, a service time of 228 h would have been obtained while keeping the bed depth at 50 cm and the linear flow rate at 36 cm/h. This is resulting in a corresponding breakthrough volume of 684 litres. In a similar condition, for a linear flow rate of 72 cm/h, a service time of 95.4 h would have been obtained resulting in a corresponding breakthrough volume of 572 litres. This would be 112 litres less than the value that could be obtained at 36 cm/h for the same parameters.

Similar trends would have been observed when the bed height was increased. For instance an increase in bed depth from 50 to 70 cm, a service time of 171.6 h would have been obtained for a flow rate of 36 cm/h and 5 mg/l F^- resulting in a breakthrough volume of 514 litres. In other words, an increase in bed depth of 40% (50 cm to 70 cm) would have resulted in an increase in service time of 46.9% (Table 4.14).

The villages' water studied had fluoride concentration ranging from 1.40-3.9 mg/l. The average fluoride concentration was almost 3 mg/l. If the BDST model is to be applied for such cases to predict the service time of the bed that would be relevant for such villages (3 mg/l F^-), a unit with a bed depth of 50 cm at a flow rate of 36 cm/h could produce 684 litres safe water before reaching the breakthrough point. This would serve the household for more than a month if 21 litres water is the daily

requirement for cooking and drinking for a family having 5-7 persons each consuming 3-4 l/day. For the same village and same situation, comparatively if the bed depth increases of 40% (50 cm to 70 cm) the service time would have increased by almost one and half times and the household would get safe water (959 litres) for at least 45 days. This would offset the economic cost of the increased column length. For annual use, however, the pilot unit was upgraded and discussed in detail in section 4.10.

Result from the BDST model was compared (Table 4.15) to cross check the validity of the application of the BDST model with result from the observed working column from the pilot scale experiment. The objective was to know what would happen ideally if a practical adsorption was to take place. In the pilot unit, 324 litres of water at breakthrough was treated. However, using BDST model, 350 litres of water could be treated for the same operating parameters. The increase was only 8% higher and thus was not significant.

Practically, intra particle of the adsorbent and external resistance of the column itself could play a major role in the adsorption process along the column. Moreover, a number of factors like irreversibility of the sorption process at high sorbent solid phase loadings, dispersion and uneven flow pattern through the bed might have occurred. This might affect the adsorption process and thus decrease the volume of water that could be treated in reality when compared to results from the BDST model. It was also pointed out by Yoseph (2007), Eyobel (2006) and Agegnehu (2008) that similar observations were made on fluoride removal in a fixed bed with Aluminum Oxide Hydroxide.

Table 4.14: Predicted Service Time of an Adsorption Column using the BDST Model

hc (cm), v (cm/h), Co (mg/l)	Predicted bed service time (h)	Corresponding breakthrough volume, Vb (l)
Scenario 1: No=0.493 mg/cm ³ , K=8.426*10 ⁻³ l/mg/h and flow rate (Qv)=3 l/h (linear flow rate=36 cm/h)		
70, 36, 5	171.6	514
60, 36, 5	144.2	432
50, 36, 5	116.8	350
40, 36, 5	89.5	268
30, 36, 5	62.1	186
70, 36, 4	224.5	673
60, 36, 4	190.26	571
50, 36, 4	156	468
40, 36, 4	121.8	365
30, 36, 4	87.6	263
70, 36, 3	319.6	959
60, 36, 3	273.9	822
50, 36, 3	228	684
40, 36, 3	182.6	547
30, 36, 3	136.9	411
Scenario 2: No=0.412 mg/cm ³ , K=23.552*10 ⁻³ l/mg/h and flow rate (Qv)=6 l/h (linear flow rate=72 cm/h)		
70, 72, 5	72.9	437
60, 72, 5	61.4	368
50, 72, 5	50	300
40, 72, 5	38.6	231
30, 72, 5	27.1	162
70, 72, 4	94.7	568
60, 72, 4	80.4	482
50, 72, 4	66.1	396
40, 72, 4	51.8	310
30, 72, 4	37.5	224
70, 72, 3	133.5	801
60, 72, 3	114.4	686
50, 72, 3	95.4	572
40, 72, 3	76.3	457
30, 72, 3	57.2	343

Besides, the average adsorption capacity and adsorbent exhaustion rate at breakthrough of the media in the pilot experiment was 0.27 mg/g and 13.10 g/L

respectively. However, when the BDST model was applied, the adsorption capacity and adsorbent exhaustion rate at breakthrough point were estimated to be 0.29 mg/g and 12.10 g/l respectively. But the increase was just nominal and the values were still tolerable. Thus when BDST model was applied to predict the service time, the change was not significant to what was observed in the pilot scale experiment. This indicate that the application of simplified fixed bed design models (BDST and EBRT) for fluoride adsorption onto crushed burnt clay pot could be successfully applied for further scale up for the design of larger scale defluoridation unit based on crushed burnt clay pot as a fluoride sorbent media.

Table 4.15: Comparison of predicted and working columns

Parameter	Unit	Calculated/Theoretically value of the HhHU column using BDST model	Working pilot column
Treated water	l	350	324
Adsorption capacity	mg/g	0.29	0.27
Adsorbent exhaustion rate	g/l	12.10	13.10
Influent Fluoride concentration	mg/l	5	5
Effluent fluoride concentration	mg/l	1.50	1.52
Mass of adsorbent	g	4240	4240
Volumetric flow rate	ml/min	50	50
Linear flow rate	cm/h	36	36
Internal Diameter	cm	10.30	10.30
Area	cm ²	83.36	83.36
Bed depth (hc)	cm	50	50
Bed volume	cm ³	4167.82	4167.82
EBCT	min	83.36	83.36

4.10. Upgrading the Pilot HhDU for Annual Use

In the previous section, the design of the Pilot Household Defluoridation Unit using crushed burnt clay pot as sorbent medium in a column type defluoridator was evaluated. The unit was designed to operate for 15 days and to treat 315 litres of

water containing 5mg/l. From typical analysis of the results, the performance of the unit was found appropriate, efficient and hence the set-up can be upgraded for large scale application. Moreover, the treated water quality was monitored and there was no significant increase in the physico-chemical parameters.

The pilot household defluoridation unit was run for an experimental fluoride concentration of 5 mg/l. The design was done for the worst condition (value) which in this case, the maximum fluoride concentration was about 4 mg/l in the villages studied. For safety purpose, the maximum design value of the fluoride was taken 5 mg/l (4 + 25% contingency). The assumption was that if the unit would able to work for the worst condition, it would obviously perform better for values less than the design value. In reality, a larger percentage of the raw water in the study area has fluoride concentration values lower than 5 mg/l. In fact the fluoride concentration is less than 4 mg/l. Thus minor change might be required during the upgrading of the pilot household unit for large application.

However, the performance of the adsorbent media at 3 mg/l fluoride concentration, which was the common concentration in the study area, would remain lower than the experimental value of 5 mg/l fluoride concentration as the adsorption capacity decreased when the fluoride concentration decreased. This is so because at lower fluoride concentration, the diffusion of fluoride onto the adsorbent would be lower. To compromise this, more adsorbents sites must be available to be utilized when the diffusion of fluoride is lower at 3 mg/l. Upgrading the system for 5 mg/l would then help to pack more adsorbent materials than it could be packed for a fluoride concentration of 3 mg/l to reduce to same level of 1.5 mg/l. Hence, it would be

preferable to stick to the experimental fluoride concentration of 5 mg/l for safety purposes in order to provide enough contingency and avoid any unpredictable occurrences.

The advantage of the unit is that the rural community can operate it and adsorbent materials are easily available locally. According to the experimental study carried out, the unit can also reduce fluoride from 5 to 1.5 mg/l from drinking water. If operated under similar condition to the pilot scale unit, there would be no need to monitor continuously. This would be an advantage for the users as frequent checking would not be necessary. The summary of the upgraded HhDU which is supposed to serve on an annual basis is presented in Table 4.16. The linear flow (infiltration) rate in the upgraded unit is maintained the same as the pilot scale unit at 36 cm/h.

From Table 4.16, increasing the diameter of the column by almost 4 fold and the bed height by 60%, the unit can defluoridate about 7665 litres of water, reducing fluoride concentration from 5 mg/l to 1.5 mg/l. This is sufficient for annual use by a family of 5-7 consuming 21 litres of water per day. Thereafter, the unit would require a replacement or regeneration of the material to run for the next service. The flow rate in the upgraded unit would be 45 l/h and hence the time taken to defluoridate 21 litres of water would be almost half an hour (30 minutes). Two working options could be recommended for this. The unit could be operated daily for 30 minutes or it could be operated for 1 hour for one day and the next day would be idle. Depending on the family preferences, this schedule could be adaptable to their situations.

Nevertheless, the design values of the household defluoridation unit in table 4.16 are not exclusive values; as different households could have variable water demand

depending on their family size, while the fluoride content of water also varies from source to source. It does show however, that households could come up with their own unit that suits their needs.

Table 4.16: Projection of design parameters associated with crushed burnt clay pot filter in a large scale for annual use

Given parameters	Parameter Description	Unit	Quantity
D	Daily personal water demand	l/(c d)	3-4 (3.5)
N	Number of users	N ^o	5-7 (6)
V _t	Total volume of water treated	l	7665
OSc	Operational sorption capacity (F ⁻ /Adsorbent)	mg/g	0.26
ρ _b	Bulk Density of Medium (loose)	Kg/l	1.01
Co	Raw water fluoride concentration	mg/l	5
Ce	Treated water average fluoride concentration	mg/l	1.5
q	linear flow rate (as selected from the mini column experiment)	cm/h	36
Derived parameters			
Q _d =D*N	Daily water to be defluoridated	l/d	21
F _t =V _t *(Co-Ce)	Total fluoride removal during a filter period	g	26.83
M=F _t /OSc	Amount of medium required for removal	Kg	103.18
V _m =M/ρ _b	Volume of the medium in the filter	l	102.16
Corresponding dimensions			
∅	Column diameter	cm	40
Q =q* Π*(∅/2) ²	flow rate	l/h	45.0
h ₁	Distance from bottom of the column to the bottom level of the packed media	cm	2
h ₂	Distance from top level of the packed media to the point where tap is fixed	cm	2
h ₃	Distance between the tap & top of the column	cm	2
h _c = V _m /{Πx(∅/2) ² }	Total height of the filter (packed) media	cm	81
H _{tc}	Total height of the column (h ₁ + h ₂ +h ₃ +h)	cm	87

CHAPTER FIVE

5.0. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In the present study, it was found that except in two water sources, all water sources in other fourteen sources registered fluoride levels ranging from 1.50 to 4.0 mg/l, thus exceeding the threshold value of 1.5 mg/l prescribed by WHO. The region is associated with temperatures ranging 23.5-32.6 oC resulting in higher water consumption and hence increasing susceptibility to fluorosis. It has also been observed that those rural communities suffer from skeletal and intestinal disorder as a result of consuming water containing excessive fluoride to certain levels. Therefore, defluoridation is required to make the water safe for drinking.

Defluoridation studies were carried based on four locally available materials. Comparison of the adsorbent materials was made based on the fluoride removal capacity. The study revealed that crushed burnt clay pot has superior capacity to remove fluoride than the other three adsorbents. Its average fluoride removal capacity was about 0.26 mg F/g of the medium. Others ranged from 0.08-0.1 mg/g for the same mass of 7g adsorbent. Crushed burnt clay pot was hence selected to be packed for defluoridation study carried out in a mini column unit to correlate the flow rate and bed depth for a given fluoride concentration of 5 mg/l. The result of the mini column indicated that optimum removal of fluoride was obtained at a bed depth of 25 cm and a flow rate of 2.5 ml/min, treating 7.3 litres of water meeting the WHO guideline for drinking water. The result is in agreement to the results obtained in the

batch study and therefore, crushed burnt clay pot is suitable low cost adsorbent to remove fluoride from water..

The set-up of the mini column unit was scaled up in a pilot household defluoridation unit and its performance was checked against the mini column result. The performance of the pilot column agreed with that obtained from the mini column. The unit managed to defluoridate 324 litres of water containing 5 mg/l of fluoride, satisfying the WHO drinking water guideline. The result of the pilot column was also in agreement with the design value. Hence, the pilot household defluoridation unit could be upgraded for larger application for the adsorption of fluoride onto crushed burnt clay pot.

The fixed bed data of the mini column were investigated for simplified fixed bed models (BDST and EBRT) application. The results show that the data could be successfully applied to analyze the column performance and evaluate the model parameters with a correlation coefficient (R^2) more than 0.996. The BDST model gave a good prediction for the service time when compared to the observed result from the pilot scale experiment and thus could be used in designing and optimizing of fluoride adsorption system onto crushed burnt clay pot.

Last but not least, the study is believed to contribute to the water knowledge of the area, and it will provide researchers and other interested individuals baseline information for further work.

5.2. Recommendations

Eritrea has a number of places which are endemic to fluorosis, yet nothing is done to solve the problem. Therefore, it is recommended that the study must be implemented at ground in order to help the rural community.

For an inclusive and sustainable development to take place, the government of Eritrea must plan to help disadvantaged rural community who can't afford purchasing the defluoridating unit. Governmental and Nongovernmental organization must involve in initiating defluoridation practices and financing the defluoridating unit developed from local sorbent materials to help the rural community as part of extension of humanity.

Training needs to be organized by concerned bodies to bring experts and stakeholders together to develop awareness, share experience and to look forward for implementation. To disseminate the research findings, seminars, workshops and conferences must be organized to share knowledge and experiences with stakeholders and other countries that have already a history of success in defluoridation practices. Moreover, Beneficiaries (rural community) must be trained on how to prepare adsorbents, pack them in column and operate the unit.

The developed HhDU was run using synthetic fluoride solution in water and hence further study could be important to assess its performance using actual water. Besides, the effect of various ions in water must be studied if they have some kind of influence on the performance of the defluoridation unit.

Moreover, there could be different locally available materials which could possibly potential adsorbents for fluoride in Eritrea. Hence, further study must be carried out

to identify and assess them so that rural community would be able to make choices based on their preferences, accessibility and affordability.

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APPENDICES

Appendix I: Effect of Adsorbent mass on fluoride removal (Co=5 mg/l)

Mass of adsorbent (g)	Residual Fluoride in solution (mg/l) at equilibrium			
	Crushed burnt clay pot	Keren Soil	Adigerghish Soil	Household Ash
3	3.36	4.50	4.46	4.41
5	2.45	4.19	4.14	4.02
7	1.53	3.93	3.84	3.64
8.5	1.22	3.80	3.62	3.41
10	0.92	3.62	3.46	3.21

Appendix II: Effect of Contact time on fluoride removal (Mass of adsorbent used=7g, Co=5mg/l)

Contact time (min)	Residual Fluoride in solution (mg/l)			
	Crushed burnt clay pot	Keren Soil	Adigerghish Soil	Household Ash
10	4.01	4.44	4.35	4.22
20	3.35	4.28	4.21	4.10
30	2.90	4.19	4.13	3.99
50	2.08	4.05	4.02	3.86
70	1.82	3.96	3.90	3.72
90	1.69	3.95	3.86	3.66
120	1.55	3.95	3.85	3.65
150	1.54	-	3.85	3.64

Appendix III: Effect of particle size on fluoride removal (Mass of adsorbent used= 7g (14 gram/l, Co=5 mg/l)

Particle size (mm)	Residual Fluoride in solution (mg/l) at equilibrium		
	Crushed burnt clay pot	Keren Soil	Adigerghish Soil
<0.15	1.52	3.91	3.83
0.15-0.60	1.54	4.03	3.85
0.60-1.20	1.56	4.07	3.89
1.20-1.70	1.59	4.24	4.10
1.70-2.36	1.71	4.34	4.21

Appendix IV: Effect of pH on fluoride removal (Mass of adsorbent used= 7g , Co=5 mg/l)

pH	Residual Fluoride in solution (mg/l) at equilibrium			
	Crushed burnt clay pot	Keren Soil	Adigerghish Soil	Household Ash
3.0±0.10	2.08	4.36	4.28	3.07
4.0±0.10	1.84	4.29	4.17	2.85
6.0±0.10	1.61	4.01	3.91	3.40
7.0±0.10	1.54	3.87	3.89	3.61
8.0±0.10	2.18	4.23	4.16	3.87
9.0±0.10	2.82	4.47	4.38	4.08

Appendix V: Effect of initial fluoride concentration on fluoride removal (Mass of adsorbent used= 7g, Co=5 mg/l)

Initial fluoride conc. (mg/L)	Residual Fluoride in solution (mg/l) at equilibrium			
	Crushed burnt clay pot	Keren Soil	Adigerghish Soil	Household Ash
5.0 ± 0.10	1.56	3.90	3.83	3.60
6.0 ± 0.10	1.84	4.58	4.53	4.18
7.0 ± 0.10	2.08	5.31	5.18	4.72
8.0 ± 0.10	2.35	5.95	5.57	5.22
9.0 ± 0.10	2.51	6.62	6.30	5.68
10.0 ± 0.10	2.75	7.20	6.75	6.11

Appendix VI: Raw data of effluent fluoride concentration (mg/l) and treated water (ml) at different Bed-depth (2.3 cm Internal ϕ , Q = 2.5 ml/min, Co = 5 mg/l)

Time (h)	15 cm		20 cm		25 cm	
	F ⁻ conc. (mg/l)	Treated water (ml)	F ⁻ conc. (mg/l)	Treated water (ml)	F ⁻ conc. (mg/l)	Treated water (ml)
1	0.06	149	0.05	148	0.05	147
2	0.07	300	0.07	299	0.06	297
3	0.09	451	0.07	450	0.07	449
4	0.12	599	0.10	599	0.09	599
5	0.20	751	0.15	750	0.12	750
6	0.28	900	0.19	901	0.13	901
7	0.37	1049	0.24	1050	0.13	1050
8	0.49	1200	0.28	1200	0.15	1200
9	0.50	1350	0.35	1350	0.14	1350
10	0.59	1500	0.42	1500	0.15	1500
11	0.68	1651	0.50	1651	0.15	1651
12	0.76	1801	0.56	1801	0.16	1801
13	0.85	1950	0.56	1950	0.17	1950
14	0.95	2100	0.59	2100	0.18	2100
15	1.02	2252	0.61	2252	0.21	2252
16	1.09	2400	0.67	2400	0.25	2400
17	1.13	2550	0.69	2551	0.30	2551
18	1.18	2700	0.73	2700	0.33	2701
19	1.25	2851	0.77	2851	0.38	2850
20	1.31	3000	0.81	3001	0.42	3001
21	1.45	3151	0.86	3150	0.47	3152
21.33	1.51	3200	-	-	-	-
22	1.65	3300	0.90	3300	0.50	3301
23	1.80	3451	0.95	3450	0.55	3450
24	1.91	3600	0.99	3601	0.58	3601
25	2.05	3750	1.04	3750	0.62	3750
26	2.16	3901	1.09	3901	0.65	3901
27	2.30	4049	1.11	4049	0.70	4049
28	2.39	4200	1.17	4201	0.72	4200
29	2.50	4350	1.20	4350	0.75	4349
30	2.75	4500	1.25	4501	0.77	4500
31	2.98	4652	1.31	4652	0.80	4651
32	3.32	4801	1.38	4801	0.81	4800
33	3.85	4950	1.44	4950	0.84	4951
33.67	-	-	1.49	5050	-	-
34	4.36	5101	1.57	5101	0.87	5100
35	4.88	5250	1.67	5250	0.90	5250
36	-	-	1.70	5402	0.91	5401
37	-	-	1.78	5550	0.94	5551

38	-	-	1.87	5701	0.96	5700
39	-	-	1.90	5849	1.00	5850
40	-	-	1.99	6000	1.02	6001
41	-	-	2.10	6151	1.06	6150
42	-	-	2.25	6300	1.10	6301
43	-	-	2.40	6451	1.15	6452
44	-	-	2.56	6601	1.20	6600
45	-	-	2.68	6750	1.24	6750
46	-	-	2.81	6900	1.29	6901
47	-	-	3.01	7051	1.35	7051
48	-	-	3.20	7200	1.41	7201
48.67	-	-	-	-	1.48	7300
49	-	-	3.40	7351	1.56	7351
50	-	-	3.70	7500	1.69	7500
51	-	-	-	-	1.89	7651
52	-	-	-	-	2.09	7799
53	-	-	-	-	2.31	7950

Appendix VII: Raw data of effluent fluoride concentration (mg/l) and treated water (ml) at different Bed-depth for a flow rate of 5 ml/min (2.3 cm Internal ϕ , $C_o = 5$ mg/l)

Time (h)	15 cm		20 cm		25 cm	
	F ⁻ conc. (mg/l)	Treated water (ml)	F ⁻ conc. (mg/l)	Treated water (ml)	F ⁻ conc. (mg/l)	Treated water (ml)
1	0.08	298	0.05	299	0.03	297
2	0.10	601	0.06	600	0.05	599
3	0.22	899	0.09	901	0.08	900
4	0.48	1200	0.12	1199	0.10	1201
5	0.86	1498	0.23	1500	0.19	1499
6	1.18	1802	0.38	1800	0.25	1802
7	1.14	2100	0.33	2101	0.23	2103
8	1.26	2397	0.57	2400	0.29	2401
9	1.38	2699	0.83	2700	0.35	2699
9.75	1.49	2930	-	-	-	-
10	1.58	3000	1.13	3001	0.41	2999
11	1.64	3298	1.17	3301	0.57	3300
12	1.82	3600	1.18	3599	0.69	3600
13	1.96	3899	1.22	3897	0.79	3902
14	2.08	4199	1.28	4200	0.83	4201
15	2.26	4500	1.36	4501	0.95	4499
16	2.20	4798	1.52	4800	1.01	4801
17	2.38	5101	1.56	5101	1.09	5100
18	2.60	5399	1.63	5400	1.13	5400
19	2.98	5699	1.79	5700	1.24	5701
20	3.28	6001	2.02	6002	1.34	6000
21	3.56	6300	2.34	6302	1.45	6300
21.167	-	-	-	-	1.48	6390
22	4.08	6601	2.88	6600	1.59	6602
23	4.40	6900	3.06	6900	1.67	6902
24	4.72	7200	3.18	7198	1.75	7201
25	-	-	3.24	7501	1.83	7500
26	-	-	3.20	7800	1.80	7801
27	-	-	3.28	8100	1.89	8102
28	-	-	3.46	8400	2.02	8398
29	-	-	3.72	8701	2.08	8700
30	-	-	3.94	9001	2.16	9000
31	-	-	4.12	9300	2.34	9301
32	-	-	4.28	9500	2.62	9598
33	-	-	4.52	9801	2.88	9900
34	-	-	4.70	10100	3.12	10201
35	-	-	-	-	3.28	10500
36	-	-	-	-	3.26	10801

37	-	-	-	-	3.48	11100
38	-	-	-	-	3.68	11401
39	-	-	-	-	3.86	11698
40	-	-	-	-	4.12	12000
41	-	-	-	-	4.36	15000

Appendix VIII: Raw data of effluent fluoride concentration (mg/l) and treated water (ml) at different Bed-depth for a flow rate of 10 ml/min (2.3 cm Internal ϕ , $C_0 = 5$ mg/l).

Time (h)	15 cm		20 cm		25 cm	
	F ⁻ conc. (mg/l)	Treated water (ml)	F ⁻ conc. (mg/l)	Treated water (ml)	F ⁻ conc. (mg/l)	Treated water (ml)
1	0.24	597	0.19	596	0.11	594
2	0.57	1198	0.31	1197	0.21	1196
3	0.98	1801	0.47	1798	0.32	1797
4	1.39	2401	0.73	2399	0.48	2396
4.33	1.48	2605	-	-	-	-
5	1.62	3000	0.97	3001	0.66	2999
6	1.96	3602	1.19	3599	0.87	3598
7	2.34	4199	1.37	4200	1.08	4198
7.50	-	-	1.51	4501	-	-
8	2.78	4799	1.67	4800	1.27	4799
9	2.69	5400	1.61	5401	1.25	5400
10	2.96	6000	1.78	5999	1.43	6000
10.25	-	-	-	-	1.52	6150
11	3.36	6601	2.02	6600	1.65	6599
12	3.82	7200	2.38	7200	1.81	7201
13	4.31	7798	2.62	7799	2.03	7801
14	4.76	8401	2.91	8400	2.26	8399
15	-	-	3.23	9000	2.51	9000
16	-	-	3.59	9599	2.73	9600
17	-	-	3.87	10199	2.95	10201
18	-	-	3.79	10800	3.19	10799
19	-	-	4.02	11399	3.12	11400
20	-	-	4.35	12000	3.31	12001
21	-	-	4.74	12598	3.59	12602
22	-	-	-	-	3.80	13200
23	-	-	-	-	4.01	13801
24	-	-	-	-	4.23	14399
25	-	-	-	-	4.50	15000
26	-	-	-	-	4.76	15601

Appendix IX: Raw data of effluent fluoride concentration (mg/l) and treated water (ml) at different Bed-depth for a flow rate of 15 ml/min (2.3 cm Internal ϕ , $C_o = 5$ mg/l).

Time (h)	15 cm		20 cm		25 cm	
	F- conc. (mg/l)	Treated water (ml)	F- conc. (mg/l)	Treated water (ml)	F- conc. (mg/l)	Treated water (ml)
1	0.79	899	0.39	897	0.22	897
2	1.48	1800	0.71	1798	0.49	1797
3	1.97	2699	1.27	2698	0.72	2698
3.33	-	-	1.51	3000	-	-
4	2.62	3600	1.80	3601	1.11	3600
5	3.06	4499	2.10	4500	1.49	4500
6	3.48	5401	2.39	5402	1.67	5399
7	3.86	6300	2.61	6299	1.83	6398
8	4.24	7201	2.94	7200	2.12	7199
9	4.29	8099	3.02	8100	2.48	8100
10	4.67	9000	3.39	9001	2.52	9000
11	-	-	3.61	9901	2.75	9902
12	-	-	3.86	10800	3.01	10801
13	-	-	4.12	11701	3.26	11700
14	-	-	4.38	12600	3.50	12599
15	-	-	4.69	13501	3.72	13500
16	-	-	-	-	4.02	14401

Appendix X: Raw data of the pilot scale unit (50 cm column depth, 10.30 cm Internal ϕ , Co=5 mg/l, Adsorbent mass 4240g)

Service Time (h)	F ⁻ (mg/l)	Volume treated (l)	pH	EC (μ S/cm)	Turbidity (NTU)	Total hardness as CaCO ₃ (mg/l)
3	0.12	8.99	7.30	260.78	1.30	309.20
6	0.16	18.0	7.25	255.98	1.16	305.43
9	0.20	27.01	7.20	255.12	1.12	303.50
12	0.22	36.0	7.21	254.23	1.20	301.90
15	0.21	45.01	7.30	253.95	1.10	299.99
18	0.23	54.0	7.25	253.87	0.76	285.60
21	0.25	62.99	7.18	250.91	0.56	280.89
24	0.24	72.01	7.13	249.89	0.45	281.45
27	0.28	81.0	7.19	247.93	0.52	281.0
30	0.31	90.0	7.16	249.23	0.44	279.51
33	0.31	98.99	7.20	248.12	0.39	282.78
36	0.35	107.99	7.16	249.10	0.35	277.46
39	0.39	117.0	7.21	246.75	0.39	280.31
42	0.43	126.01	7.09	249.21	0.58	285.21
45	0.42	135.01	7.12	250.10	0.35	289.50
48	0.45	144.0	7.15	251.32	0.45	286.90
51	0.50	153.0	7.07	251.90	0.39	288..98
54	0.51	162.01	7.14	248.27	0.38	289.10
57	0.55	171.0	7.12	249.51	0.34	285.60
60	0.59	179.99	7.20	248.98	0.31	289.60
63	0.64	189.01	7.23	247.78	0.33	285.21
66	0.70	198.0	7.16	245.86	0.40	285.0
69	0.75	206.99	7.13	243.94	0.39	289.90
72	0.79	216.01	7.22	242.10	0.41	289.70
75	0.83	225.01	7.10	239.71	0.42	286.67
78	0.88	233.99	7.12	240.45	0.45	282.75
81	0.94	243.0	7.15	241.20	0.39	285.70
84	0.98	252.01	7.09	239.50	0.42	289.87
87	1.01	261.01	7.05	236.10	0.41	285.56
90	1.06	269.99	6.99	234.43	0.48	287.24
93	1.11	279.01	7.01	235.83	0.43	280.20
96	1.18	288.01	7.10	238.15	0.42	283.53
99	1.26	297.0	7.11	234.57	0.45	280.20
102	1.34	306.01	7.12	230.99	0.49	278.12
105	1.42	315.01	7.18	231.34	0.41	277.43
108	1.52	324.00	7.13	230.57	0.41	276.40