INVESTIGATING CONTACT PRECIPITATION AS A VIABLE WATER DEFLUORIDATION TECHNIQUE

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A Thesis Submitted to the Graduate School in Partial Fulfillment for the Requirements of the Degree of Master of Science in Chemistry of Egerton University

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DECLARATION AND RECOMMENDATION

DECLARATION

I hereby declare that this thesis is my original work and has not been submitted wholly or in part in any institution of learning for award of any certificate to the best of my knowledge.

Pamela Khamala Okello
SM 11/1583/05

Signature……………………….
Date…………………………….

RECOMMENDATION

We wish to confirm that this thesis was prepared under our supervision and has our approval to be presented for examination as per the Egerton University regulations.

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Date…………………………….

DEDICATION

To my husband Dr. Kennedy Ondede and children: Geoffrey, Hope, Christian and Angie. Thanks a lot for your patience and for believing in me.

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I am very grateful to my supervisors, Prof. W. J. Mavura and Prof. M. S. Ngari who deserve credit for their guidance, supervision and assistance during the entire period of this study. This work would not have been a reality if they had left me on my own. Their contributions, suggestions and positive criticism helped shape the direction and scope of this work. It got so rough at times to the point of giving up but they were patient enough, encouraged me to soldier on and made me believe in myself. I am also very grateful to the DVC (Research and Extension), Egerton University for awarding me a research grant to facilitate my research.

I am greatly indebted to my employer, the Government Chemists Department for giving me study leave to concentrate on my studies and allowing me to use the laboratory facilities during my research. My colleagues at the Government Chemists Department specifically those from the water laboratory deserve mention for their moral support throughout my study.

To my family, especially my husband Dr. Kennedy Ondede, thank you for being there and standing by me throughout the entire period.

ABSTRACT

Fluorosis is a condition caused by excessive intake of fluoride, and is characterized mainly by mottling of teeth. A number of defluoridation techniques have been proposed, studied and even implemented in a number of countries, to varying degrees of success. Among these techniques, contact precipitation, a hybrid technique involving the use of calcium and phosphate compounds together with bone char to effect defluoridation of water has been extensively used. The mechanism of fluoride ion removal by this technique was investigated in this study. The objective was achieved by carrying out four sets of experiments, each done in triplicates. The first set of experiment was aimed at determining the saturation point of a known amount of bone char. The second set was aimed at determining the role and fate of calcium and phosphate compounds in contact precipitation, while the third and fourth sets were aimed at determining the efficacy of natural rock phosphate either as a defluoridation medium or as an alternative additive in contact precipitation respectively. These experiments were set up in similar glass columns. The column effluent in the first three experiments was analysed for calcium, phosphate, fluoride, pH and electrical conductivity. For the fourth set of experiment, only the fluoride levels were determined in the column effluent. The calcium concentrations were obtained volumetrically using EDTA and the phosphate concentrations obtained using the UV spectrophotometer. The amount of fluoride was estimated colorimetrically using acid zirconium – alizarin complex, whereas the pH and conductivity were obtained using the pH meter and conductivity meter respectively. The results obtained were presented in form of tables and graphs and their respective trends studied and discussed. It was found that the defluoridation capacity of bone char was limited to a maximum of 1.99 mg/g, an efficiency of 75.72%, while that of contact precipitation was limited to 2.59 mg/g, an efficiency of 94%. Plain Minjingu rock recorded a maximum defluoridation capacity of 1.0 mg/g, an efficiency of 33.33% while the combined media of Minjingu rock phosphate and saturated bone char recorded a defluoridation capacity of 2.12 mg/g, an efficiency of 70.6%. From the results, it was concluded that fluoride immobilization in contact precipitation involved a series of reactions namely Adsorption, Ion exchange and Co- precipitation.

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CHAPTER ONE

INTRODUCTION

1.1 Background Information

Contact precipitation is a technique of fluoride removal from water by precipitation of fluorapatite, $Ca_{10}(PO_4)_6F_2$, through the addition of calcium and phosphate compounds to fluoride rich water that is in contact with bone char. This technique has been developed further and now incorporates the combined use of calcium phosphate pellets and bone char as the defluoridation medium and has shown considerable potential for removing fluoride over the past few years (Korir *et al.*, 2009). Without contact with the bone char no precipitation would take place, most probably due to the slow kinetics of the reaction. It has been reported that the precipitation of fluorapatite is easily catalyzed in a contact bed of bone char, which also acts as a filter for the precipitate (Dahi, 1997).

Several defluoridation methods have been studied in detail and even reported as appropriate techniques for the removal of excess fluoride in water. These include but not limited to the Nalgonda technique, the use of bone char, the use of activated alumina, the use of activated carbon, aluminium sulphate, solar distillation, electro dialysis and reverse osmosis (Feenstra, *et al.*, 2007). Of all these methods, bone char is the oldest known and most favored defluoridation agent, due to its specific ability to take up fluoride from water as a result of its chemical composition mainly hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. With time however, the bone char becomes saturated with fluoride and no more uptake of fluoride from water is possible (Mavura and Tiffany, 2002). Contact precipitation is an improvement of the bone char technique and is marketed here in Kenya by the Catholic Diocese of Nakuru (Korir *et al.*, 2009).

The main advantage of the contact precipitation technique compared to simple filtration with bone char is that the regeneration process is avoided yet there is an overall increase in the lifespan of the bone char. There is also a marked improvement in the defluoridation capacity of water as noted in bucket experiments, (Dahi, 1998). Other advantages include low operation costs, (Bulusu *et al.*, 1979) and no health risks in case of misuse or over dosage of the chemicals. Several methods of recharging the bone char have been tried including the use of a 1% solution of sodium hydroxide resulting in the formation of hydroxyapatite with the fluoride being removed as sodium fluoride, and regeneration by heating the saturated bone char at 500°C for 2 hours both options having varying degrees of success and limitations (Mcharo, 1986; Kaseva, 2006).

Addition of calcium and phosphate compounds such as calcium chloride and monosodium phosphate to the already saturated bone char medium has been proved to recharge the bone char and lead to a further reduction in the fluoride content of the water, and hence increases the lifespan of the defluoridation process (Dahi, 1996). Studies have come up with varying theories on the mechanism of defluoridation by contact precipitation; for instance, two possibilities as to whether the observed removal was due to a steady state condition or through a non steady state condition have been advanced (Dahi, 1997). In the first case, the removal would likely continue as long as the chemicals were added, the only problem being a decrease in filter permeability. A decrease in filter permeability would mean a reduction in the fluoride removal efficacy due to precipitation of calcium phosphates such as fluorapatite, in the upper parts of the filter bed. In the later case, the bone char would be moving towards its saturation at a higher capacity level, implying that no more hydroxyl exchangeable ions would be available on the bone char for the fluoride ions in water, and therefore would need to be regenerated at final saturation, by addition of calcium and phosphate compounds (Dahi, 1997).

Another possibility was that either the observed removal was a kind of regeneration of the bone char (Maier, 1953) or it was a contact precipitation of the added chemicals along with fluoride from the water. Treatment of saturated bone char in a solution of calcium chloride and sodium dihydrogen-phosphate regenerates the bone char by coating it with a fresh layer of hydroxyapatite. This new hydroxyapatite layer takes longer to saturate, removes more fluoride from water and therefore leads to an increase in the uptake efficiency (Christoffersen *et al.*, 1991). This however, does not explain why the new layer is more efficient compared to the initial layer. It has been suggested that a combination of the precipitation of fluorapatite, $Ca_{10}(PO_4)_6F_2$ and calcium fluoride, CaF_2, was responsible for the further removal of fluoride (Albertus *et al.*,2002). Precipitation of calcium fluoride would occur if there already were precipitated compounds to initiate the process for example bone char, while precipitation of fluorapatite would only occur in contact with the apatite structure in the bone char and was dependent on the pore water velocity and contact time in the filter. Apatite refers to a group of phosphate minerals, usually referring to fluorapatite, chlorapatite and hydroxyl apatite, named for high concentrations of F^-, Cl^-, or OH^- ions, respectively in the crystal. The formula of the admixture of the three most common species is written as $Ca_5(PO_4)_3(F, Cl, OH)$ (Gilinskaya, 1990). All these studies were able to give convincing theories of what could be taking place but they all fell short of explaining the actual chemical processes or mechanisms involved in the contact precipitation process.

1.2 Statement of the Problem

There is an increasing concern worldwide over high levels of fluoride in drinking water and its adverse health effects namely dental and skeletal fluorosis (Fewtrell *et al.*, 2006; WHO, 2010). Contact precipitation as a defluoridation technique is very effective and has been in use for many years in countries like Tanzania, Ethiopia and Kenya. Many researchers have attempted to explain its chemistry with divergent theories (Maier, 1953; Christoffersen *et al.*, 1991; Dahi, 1997; Albertus *et al.*, 2002). To date, the chemistry remains unknown because there have not been thorough and systematic investigations of the technique. This study aims at determining the most probable mechanism for fluoride removal in contact precipitation by conducting a series of experiments including the analysis of calcium, phosphate, fluoride, pH and conductivity of water before, during and after the contact precipitation process. This would help in advancing further improvements on the efficiency of the technique.

1.3 Objectives

1.3.1 Main Objective

To investigate the mechanism of fluoride ion removal from water in contact precipitation.

1.3.2 Specific Objectives

1. To determine the available calcium and phosphate before and after the contact precipitation defluoridation process in water.
2. To determine the catalytic effect of saturated bone char in contact precipitation.
3. To determine the efficacy of natural rock phosphate (Minjingu rock) in extending the lifespan

of saturated bone char as compared to the commercially produced calcium and phosphate compounds.

1.4 Justification

The rapid increase in population and diminishing surface water reserves has led to widespread harnessing of underground water sources. Unfortunately, most of these sources have been found to have high fluoride levels. The high levels of fluoride in drinking water presents a challenge to the water service providers in their quest to provide safe, low fluoride drinking water to the consumers. In cases where alternative sources are not available, defluoridation of water remains the only measure to prevent fluorosis. Most of the available water defluoridation techniques however, have inherent limitations in their application. Bone char use for instance is hampered by an early saturation necessitating the recharging process. The contact precipitation technique solves the saturation problem in bone char use due to its enhanced defluoridation capacity. The findings of this study would be a boost to scientific knowledge in understanding the mechanisms of fluoride ion removal from water in contact precipitation and offer a sustainable option for water defluoridation.

1.5 Expected outputs

1. Knowledge of the chemistry involved in the removal of fluoride from water by contact precipitation.
2. Dissemination of the research findings in scientific fora such as conferences, workshops and symposia and also to government water agencies under the umbrella of the Water Services Regulatory Board (WASREB).
3. Publication of the research findings in peer reviewed scientific journals.
4. Award of Master of Science degree in chemistry.

CHAPTER TWO

LITERATURE REVIEW

2.1 Fluoride element

Fluoride is the most electronegative of all chemical elements and is therefore, never encountered in nature in the elemental form. It is seventeenth in the order of frequency of occurrence of the elements, and represents about 0.06 to 0.09% of the earth's crust. Fluoride is an essential ion for man. It helps in the normal mineralization of bones and formation of dental enamel (Kaseva, 2006).

When fluoride is consumed in inadequate quantities (less than 0.5 mg/L) health problems like dental caries, lack of formation of dental enamel and deficiency of mineralization of bones, especially among children occurs (WHO, 1993). Ingestion of between 1.5 mg/L to 3.0 mg/L causes dental fluorosis characterized by mottling and modification of the dental enamel to produce yellow and brown stains. Long term exposure to levels between 3 mg/L to 6 mg/L results to skeletal fluorosis, characterized by severe pain and stiffness of the backbone as well as pain in joints. Fluoride levels beyond 10 mg/L results in crippling fluorosis characterized by bending of the bones and difficulties in walking (Kaseva, 2006).

High fluoride concentrations exert a negative effect on the course of metabolic processes and an individual may suffer from skeletal fluorosis, dental fluorosis, non skeletal manifestation or a combination of the above (Susheela & Kumar, 1991). The incidence and severity of fluorosis is related to the fluoride content in various components of the environment, *viz*. air, soil and water. Out of these, groundwater is the major contributor to the problem. Fluoride is a typical lithophile element under terrestrial conditions. The bulk of the element is found in the constituents of silicate rocks, where the complex fluorophosphate apatite $Ca_{10}(PO_4)_6F_2$, seems to be one of the major fluoride minerals. Next, with regard to fixation of the bulk of fluoride, come some complex hydroxy-silicates and hydroxy-alumino-silicates, in which the hydroxyl ions (OH^-) may be largely replaced by fluoride (Omueti &Jones, 1977), as is the case in amphiboles and minerals of the mica family (biotite and muscovite). In many rocks, especially in those of late magmatic stages of evolution, the fluoride in such silicates may even greatly exceed the amount fixed in the apatite. Interest in fluoride has greatly increased over a number of years, owing to its importance in the precipitation of fixation of phosphate in minerals like fluorapatite, and to the recognition of pathological conditions in man and animals, described as fluorosis (Agrawal *et al*., 1997).

2.2 Distribution of Fluoride in Soil

Fluoride occurs mainly in the silicate minerals of the earth's crust at a concentration of about 650 mg/L. It is ubiquitous in the environment and is always present in plants, soils, and phosphatic fertilizers. The fluoride concentrations in these materials are on the order of 300 mg/L, 306mg/L, and 312 mg/L for plants, soils, and phosphatic fertilizers, respectively (Sparks, 1995).

Very common soil minerals, such as biotite, muscovite, and hornblende may contain as much as several percent of fluoride and, therefore, would seem to be the main source of fluoride in soils. However, it is believed that micas, apatite, and tourmaline in the parent materials were the original source of fluoride in soils. It appears, therefore, that the fluoride content of soils is largely dependent on the mineralogical composition of the soils inorganic fraction. The total fluoride concentrations in United States soils range from slightly below 100 mg/L to over 1,000 mg/L (Adriano, 1986). For world soils, the median value reported ranged from 200 to 300 mg/L, whereas an average of 430 mg/L was reported for United States surface soils. In general, fluoride was concentrated in colloidal material. Natural fluoride content of soil increases with increasing depth, and only 5% to 10% of the total fluoride content of soil is water-soluble (Adriano, 1986).

Under natural conditions, the concentrations of fluoride in soil solutions are usually below 1 mg/L, but under severely polluted soils by fluoride they may reach levels of about 10 mg/L. In soils in the humid temperate climate, fluoride could be readily lost from minerals in the acid horizons. A substantial amount of this fluoride is retained in subsoil horizons, where it complexes with alumina that is mostly associated with phyllosilicates. The extent of fluoride retention depends on the pH and amount of clay, therefore, the pattern of fluoride distribution with depth follows the clay pattern closely. Fluoride occurs only in trivial amounts in the organic matter fraction of soils (Omueti & Jones, 1977).

Several studies have shown that the solubility of fluoride in soils is highly variable and has the tendency to be higher at acidic and alkaline pH. Fluoride solubility in soil is complex and may be controlled by solid phases even more insoluble than CaF_2. In addition, fluoride solubility may be related to the solubility of alumina or other ionic species with which it forms complexes (Arnesen, 1998). Soils having high pH and low levels of amorphous alumina species, clay, and organic matter generally adsorb little fluoride (Omueti & Jones, 1977). Thus, it appears that the predominant retention mechanism is that of fluoride exchange with the OH^- group of amorphous materials, such as aluminium hydroxides. In this case, fluoride resulting in a simultaneous release of aluminium and iron replaces the crystal lattice group OH^- of clay minerals. Other fluoride retention mechanisms include the binding of fluoride to soil cations (e.g., Ca^{2+}, $A1^{3+}$), or fluoride precipitation as CaF_2, as in calcareous soils (Gupta *et al.*, 1982).

2.3 Geographic Distribution of Fluoride in Water Sources

Generally, fresh water is low in fluoride concentrations. Studies have shown that more than 95% of fresh water sources in the world contain less than 1.5 mg/L fluoride. The problem arises in the last 5% of the water sources, which are distributed all over the world, with dominance in the developing countries (Phantumvanit *et al.*, 1988). Information on fluoride concentrations in drinking water sources has been reported in the form of tables with highest and lowest concentrations in different countries. A general or average fluoride concentration in a country or an area is not useful because concentrations vary even between adjacent sources. Normally, an area is said to have high fluoride concentrations if a number of sources in the area has fluoride concentrations higher than 1.5 mg/L. Most intensive mapping of fluoride concentration in drinking water has been done in the United States of America (USA). High and extremely high concentrations are generally found in states bordering Mexico and around the vertical centerline in the country (Cholak, 1959). Concentrations have been reported at more than 8 mg fluoride per liter in some water supply systems. In the rest of the American continent, Argentina is cited to have high concentrations of fluoride.

In Africa, countries along the Great Rift Valley, *i.e.* Ethiopia, Kenya and Tanzania are probably facing the most severe problems of fluoride in drinking water sources. In the Northern provinces of Tanzania, parts of Nairobi, Central and the Rift Valley provinces of Kenya, concentrations of more than 8 mg/L fluoride are consumed (Bardecki, 1974; Moturi *et al.*, 2002). Intensive mapping of fluoride concentration in drinking water sources in Kenya has not been done extensively to date. A case study of fluoride in groundwater sources for two districts in the Rift-

Valley province of Kenya was done and the data is available in the Geographic Information System (GIS) mapping for groundwater sources (Jorgen & Ingemar, 2005). Most of the studies carried out focus mainly on the effects of fluorosis within a population. In a study on the incidence of dental fluorosis in Kenya, it was found that fluorosis incidences among populations was at 60% in Central Kenya, 45% in Nairobi and Eastern Kenya, 30% in Rift valley, 15% in North Eastern Kenya and Nyanza while Western and Coast provinces recorded a 5% incidence rate (Chibole,1987). In the Ethiopian Rift Valley several villages are supplied with drinking water containing more than 30 mg/L fluoride.

In Asia most attention has been drawn to the fluoride problem in India. A large number of people in various parts of India are hit by high concentrations of fluoride which however, rarely exceeds 10 mg/L fluoride (Handa, 1975; Bulusu *et al.*, 1979). China, Thailand and Japan are equally facing high fluoride concentrations (Cholak, 1959). In Europe and Australia, high fluoride concentrations are found but they seem to be generally scattered. The problem is normally overcome by utilization of alternative water sources (Phantumvanit *et al.*, 1988) .

2.4 Distribution of Fluoride in Groundwater

Fluoride incidence in groundwater is mainly a natural phenomenon, influenced basically by the local and regional geological setting and hydro-geological conditions. The chief source of fluoride in groundwater is the fluoride-bearing minerals in the rocks and soils. The weathering and leaching processes, mainly by moving and percolating water, play an important role in the incidence of fluoride in groundwater (Coetsiers *et al.*, 2008). The various factors that govern the release of fluoride into water, by the fluoride bearing minerals are; the chemical composition of water, the presence and accessibility of fluoride minerals to water and the contact between the source mineral and water. However, the concentration of fluoride in water is mainly restricted by the solubility product of the fluorite, CaF_2 . In Rajasthan, India, occurrences of fluorite and precipitation of calcite ($CaCO_3$) are shown to determine fluoride concentration (Handa, 1975). High fluoride concentrations occur often in areas of former volcanic activity. In Kenya and Tanzania in the volcanic alkaline Rift Valley, fluoride is assumed to originate from dissolution of fluorite, evaporative concentration and hydrothermal activity. Surface water can be further enriched by fluoride containing salts on the ground of mount Meru in northern Tanzania (Nair *et al.,* 1984).

2.5 Human Exposure to Fluoride

2.5.1 Fluoride in Food and Beverages

Fluoride is found in foodstuffs in various concentrations. In vegetables, fluoride concentrations seldom exceed 10 mg/L, even with high concentrations in the ground water (WHO, 1984). Milk typically contains low levels of fluoride for example; human breast milk contains 0.02 mg/L whereas cow's milk contains between 0.02 to 0.05 mg/L. Dried tea leaves contain high levels of fluoride, up to 400 mg/L. Fluoride exposure due to ingestion of tea has been reported to range from 0.04 mg to 2.7 mg per person per day (Pires *et al.,* 1996). In principle, tea made from older tea leaves contain much higher fluoride than that from young tea leaves.

Generally, western style diets appear to contribute only slightly to the total daily fluoride intake. However fluoride contaminated trona ($Na_3H(CO_3)_2.2H_2O$), used to tenderize certain vegetables during the cooking process, has contributed significantly to the prevalence and severity of dental fluorosis in Tanzania**.** Similarly consumption of high fluoride black tea as a beverage and maize polluted by fly ash generated by the burning of high fluoride coal has been noted as a contributor to fluorosis in some Indian regions (Cao *et al.,* 2007). The composition of the diet influences retention of dietary fluoride. High protein diets (western style diets) result in more acidic urine than a vegetarian diet. More acidic urine results in increased retention of fluoride due to decreased renal excretion. At present the effects of vegetarian versus non vegetarian diets on the effects produced by fluoride in different regions of the world are unclear (Cao *et al.,* 2007).

2.5.2 Fluoride in Air

Due to dust, industrial production of phosphate fertilizers, coal ash from burning coal and volcanic activity, fluorides are widely distributed in the atmosphere. However, air is only responsible for a small fraction of the total fluoride exposure. In non industrial areas, the fluoride concentration in air is quite low (0.05 to 1.90 ppm). In areas where fluoride containing coal is burned or phosphate fertilizers are produced and used, the fluoride concentration in air is elevated leading to increased exposure by inhalation (Cao *et al.,* 1997).

2.5.3 Fluoride in Dental Products

A number of products administered to or used by both children and adults to reduce dental decay contain fluoride. These include toothpaste (up to1450 mg/L fluoride), fluoride solutions and gels for topical treatment (ranging from 250 to 24000 mg/L fluoride) and fluoride tablets (0.25, 0.50 or 1.00 mg fluoride per tablet). These products contribute to the total fluoride exposure albeit to different degrees. It is estimated that the swallowing of toothpaste by some children may contribute about 0.50 or 0.75 mg fluoride per child per day (Levy & Guha, 1999).

2.5.4 Fluoride in Drinking Water

Drinking water is by far the largest single contributor to the daily fluoride intake. However as noted above, this is not necessarily true in every case. For a given individual, fluoride exposure in mg per kg of body weight per day *via* drinking water is determined by the fluoride level in the water and the daily water consumption (litres per day), which increases with availability, temperature, humidity, exercise, state of health and is modified by other factors including diet (Fomon *et al.,* 2000). Based on a general estimate by WHO (1993), the daily per capita consumption of fluoride with drinking water could be 60 mg or more assuming a concentration of 30 ppm fluoride in a water source.

2.5.5 Guidelines for Fluoride Intake

In order to avoid the adverse effects of fluorosis, WHO has recommended a maximum concentration of fluoride in drinking water of 1.5 mg/L, based on a total daily intake of less than 4 mg (WHO, 1993). This value has been adopted by various countries as a local standard, though some highly affected developing countries like Tanzania, have adopted less stringent standards because the WHO recommendation would mean closing down most of the water sources in some areas. The maximum allowed limits of fluoride in drinking water in Tanzania is 8 mg/L. This is in spite of the fact that investigations have revealed that 1.5 mg/L fluoride or less in some cases results to unacceptable high degree of fluorosis, especially in hot climates where water consumption is expected to be high (Moturi *et al*., 2002).

2.6 Defluoridation Strategies

Occurrence of fluoride at excess levels in drinking water in developing countries is a serious problem. Its detection demands analytical grade chemicals, laboratory equipment and skills. Similarly, the prevention of fluorosis through management of drinking water is a difficult task, which requires favorable conditions combining knowledge, motivation, prioritization, discipline, technical and organizational support. Many filter media and several water treatment methods are known to remove fluoride from water. However, many initiatives on defluoridation have resulted in frustration and failure (COWI, 1998). Therefore, in any attempt to mitigate fluoride contamination for an affected community, the provision of safe, low fluoride water from alternative sources, either as an alternative or for blending should be investigated as the first option. In cases where alternative sources are not available, defluoridation of water remains the only measure to prevent fluorosis.

2.6.1 Categories of Defluoridation Processes

The common methods used for water defluoridation are categorized according to their working principle thus:

a) Adsorption and Ion Exchange Processes

These involve the passage of water through a contact bed where fluoride is removed by ion exchange or surface reaction with the solid bed matrix. After a period of operation, a saturated column must be refilled or regenerated (Dahi, 1996). Bone char, activated alumina, carbon, clay and synthetic ion exchange resins resemble sorption media used in columns for defluoridation.

b) Precipitation Processes

These involve the addition of chemicals and formation of fluoride precipitates. Among these are precipitations with calcium and aluminum salts. Chemicals must be added daily and in batches. Other precipitation techniques like the Nalgonda technique are used but they produce a certain amount of sludge every day (Bulusu & Nawalakhe, 1990).

c) Membrane Filtration Processes

Reverse osmosis and electrodialysis are two membrane filtration processes used for removal of fluoride. These processes are very efficient, advanced technologically and involve very high costs. They are therefore less suitable for many applications in developing countries (Zakia *et al.*, 2001).

d) Distillation Processes

Distillation units can also be used for treating drinking water. Large scale electrodialysis plants are already used for making drinking water out of brackish water with high fluoride concentrations. The technique is very efficient but involves higher costs and is therefore less suitable for developing countries (Feenstra *et al*., 2007). Other new technologies introduced in recent years include:

e) The Crystalactor or pellet reactor: This is a fluidized – bed type crystallizer where fluoride is removed from water in the form of very pure calcium fluoride pellets. Developed in the Netherlands, the technique is most suited for treating waste waters whose fluoride concentrations exceed 20 mg/L. In case of treating drinking water with similar fluoride concentration and in order to achieve a concentration of less than 1mg/L, a second technique has to be incorporated (Giesen, 1998).

f) Memstill Technology: This technology combines multistage flash and multieffect distillation modes into one membrane module. It is mainly applicable for large scale desalination of sea water (Hanemaaijer *et al*., 2007).

g) The water pyramid solution and the solar dew collector system. These utilize evaporation and condensation principles using solar as the source of energy, to process clean drinking water out of salty or polluted water. The product water quality is constant and similar to that of distilled water (Feenstra *et al*., 2007).

2.7 The History of Bone Char Defluoridation

In the early 1930s, after it became known that fluoride in drinking water was responsible for dental fluorosis, researchers in USA developed methods for removing fluoride from drinking water. Bone char was discovered as a defluoridation agent twice by two individual research teams. Smith & Davey (1939), investigated degreased bone for defluoridation, but recommended calcined bone char because of problems of putrification and difficulties of wetting of degreased bone. Burwell *et al.* (1945) shifted to pyrolysed bone char because of dissatisfaction with the performance of the synthetic apatite. In the rest of the world, little attention was given to bone char until in the 1980s where the Intercountry Centre for Oral Health in Thailand started investigations of the method for use in household and community filters (Phantumvanit *et al.*, 1988). This work from Thailand, motivated similar efforts in other parts of the world especially in Kenya, Tanzania, India and Denmark.

In Kenya and India, bone char defluoridation was first tested in the laboratory in batch and column in the early 1990s (Korir *et al.*, 2009). From 1998, the technique was adopted and widely used by the Catholic Diocese of Nakuru (CDN) to defluoridate water in Nakuru and its environs both at the household and community levels. Further improvements on this technique by CDN over the years has led to the development of a more efficient system that involves the addition of calcium phosphate pellets to the bone char medium to effect defluoridation. The CDN personnel prepare their own media of bone char and calcium phosphate pellets, which they incorporate in household bucket filters and community tanks that they sell at subsidized rates, to families that reside in the high endemic areas (Korir *et al.*, 2009).

2.8 Contact Precipitation for Defluoridation of Water

It is worth noting that, there are many methods for water defluoridation, which have been studied and even reported as appropriate, but none of them has been carried out successfully as a routine in any country in the recent past (Dahi, 1996). This is probably due to the fact that most of the available defluoridation methods do have disadvantages that turn out to be unsustainable under the given socioeconomic conditions. Some of these are; high costs (technologically or price wise), limited efficiency, unnoticeable break down necessitating continuous monitoring of fluoride residual, limited capacity, and deteriorated water quality (Dahi, 1998). Using calcium chloride (CC) and sodium dihydrogenphosphate (MSP) as chemicals in contact precipitation, the following equations illustrate removal.

Dissolution of calcium chloride (CC)

$CaCl_2.2H_2O_{(S)} \rightarrow Ca^{2+} + 2Cl^{-} + 2H_2O$……………………………………………..………....i

Dissolution of sodium dihydrogenphosphate (MSP)

$NaH_2PO_4.H_2O_{(S)} \rightarrow PO_4^{3-} + Na^{+} + 2H^{+} + H_2O$…………………..................................ii

Precipitation of calcium fluoride

$Ca^{2+} + 2F^{-} \rightarrow CaF_{2\ (S)}$ ……………………………………………………………....iii

Precipitation of fluorapatite

$10\ Ca^{2+} + 6PO_4^{3-} + 2F^{-} \rightarrow Ca_{10}(PO_4)_6\,F_{2\ (S)}$ …………………………………….…………iv

The basic contact precipitation set up comprises a column, containing a relatively small saturated bone charcoal contact bed. Gravel or coarse grained bone charcoal is used as a supporting medium. Above the bed, a relatively large space is used for mixing the chemicals with the raw water. From the bed the defluoridated water flows continuously by gravity to a shallow but wide clean water tank. One or more clean water taps are fitted at the bottom. The flow from the raw water tank to the clean water tank is constrained by a valve or a narrow tube arrangement to allow for appropriate contact time in the bed. Too short contact time would reduce the removal capacity and increase the escape of chemicals in the treated water. Too long contact time may result in precipitation of calcium phosphates in the upper parts of the filter bed thus reducing removal efficacy. The optimum contact time is not yet known but contact times of 20 to 30 minutes have been shown to give excellent results in defluoridation (Dahi, 1998).

The construction of the contact precipitation plant is simple but the theoretical background for doing this is not. Probably both reactions (iii) and (iv) play important roles but the extent to which each reaction occurs is not well understood. In calcium fluoride precipitation, the Ca: F weight ratio is about 1, equivalent to a CC: F ratio of about 4. In fluorapatite precipitation, the Ca: F ratio is 11 and the PO_4: F ratio is 15, equivalent to a CC: F ratio of about 39 and a MSP: F ratio of about 23. Thus the more fluoride that is precipitated as calcium fluoride rather than as fluorapatite, the lower is the required dosage of chemicals. Calcium fluoride precipitation is probably more dominant with higher raw water fluoride concentration (Dahi, 1998).

Long term operation of the contact precipitation technique in Tanzania where the fluoride concentration is about 10 mg per liter has shown the process functions effectively when the dosage ratios are 30 and 15 for calcium chloride and sodium dihydrogenphosphate respectively. This dosage would ensure at least 65 % precipitation of fluorapatite and a surplus of calcium for precipitation of the residual fluoride as calcium fluoride. Over dosage is of no economic or health significance and lower dosage levels may be recommended on a trial- and - error basis (Dahi, 1998). The process seems to be promising because it implies,

a) Relatively low daily working load.
b) High reliability without need of surveillance of flow or effluent concentration.
c) High removal efficiency, even in case of high raw water concentrations.
d) No health risks in case of misuse or over dosage of chemicals.

The challenge nevertheless, in the implementation of this technique remains to be at least two sided: motivation of users and availability of the chemicals at user points (Korir *et al.,* 2009).

2.9 Natural Rock Phosphate

Natural Rock Phosphate (Minjingu Rock Phosphate) has been used for years to maintain the optimum soil phosphorus levels. It is known to have a high phosphate content ranging between 28 – 32 % (Obaga *et al.*, 2005). The phosphate is released from the rock as a result of the various chemical reactions it has with the soil constituents, favoured by acidic pH (Kanabo & Gilkes, 1987). Minjingu or natural rock phosphate is natural, environmentally friendly, cheap and easily available, and is therefore used as a cheap source of phosphate fertilizer. Furthermore, it is very valuable for producers of specialty crops that may not be fertilized with chemically treated materials.

The chemical composition of natural rock phosphate according to Obaga *et al*., (2005) is Calcium (39.9%), Phosphorus (16.53%), Potassium (0.18%) and Iron (0.52%). Due to the high percentage of calcium phosphate in natural rock phosphates, a possibility exists of it being a suitable substitute for the commercial calcium and phosphate compounds in the contact precipitation process.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Preliminary Preparations

Ready to use Bone char (grain size ranging between 2.0 – 2.8 mm) and calcium phosphate pellets were bought from the manufacturer, the Catholic Diocese of Nakuru. Natural Rock Phosphate was bought from a fertilizer manufacturing company in Nairobi, the Minjingu Phosphate Fertilizer Co. Ltd. All the chemicals used for analysis were of analytical grade. The apparatus were washed with soap and water then rinsed with distilled water followed by acetone. They were allowed to drip dry before use. A stock solution having a fluoride concentration of 100 mg/L was prepared, and diluted further to make a fluoride solution of concentration 10 mg/L for use as influent water into the experimental columns.

a). Preparation of standard fluoride solution (100 mg/L)

A known weight (0.2210 g) of analytical reagent grade anhydrous sodium fluoride was dissolved in distilled water and diluted to the 1 L mark in a calibrated flask. The resultant solution was then stored in a polyethylene container.

1 mL= 100 µg fluoride

b). Preparation of fluoride standard solution (10mg/L)

100 mL of the 100 µg/L standard fluoride solution was pipetted into a 1 L calibrated flask and made upto the mark with distilled water. The resultant solution was stored in a polyethylene bottle.

1mL =10 µg fluoride

c). Preparation of ethylene diammine tetraacetate disodium salt (EDTA) for calcium determination

0.02 N EDTA solution was prepared directly from an ampoule and standardized by titration with standard calcium chloride solution to give 1ml EDTA = 1mg $CaCO_3$.

d). Preparation of calcium hardness buffer solution

40 g borax was dissolved in 800ml distilled water and kept aside as solution A. Solution B was prepared by dissolving 10g NaOH together with 5g sodium sulphide in 100 ml distilled water. Both solutions A and B were then mixed on cooling and diluted to 1 L mark to make the calcium hardness buffer solution.

The pH and conductivity meters were conditioned for use with buffer solutions of pH value 4.0, 7.0 and 9.0 (prepared by dissolving respective pH tablets in 100ml distilled water) and distilled water respectively. Standard solutions for the analysis of phosphate were prepared according to standards methods of water and waste water analysis, from stock solution and the respective calibration graph drawn (APHA, 1995). The fluoride standards and acid zirconium –alizarin solution for the analysis of fluoride were prepared according to standard methods of water and waste water analysis (APHA, 1995).

3.1.1 Sampling and Experimental Procedure

The experimental set up and analysis was done in the Government Chemists Department laboratories in Nairobi. Four sets of experiments each done in triplicate, were carried out using similar glass columns with an internal diameter of 8 cm and a length of 50 cm. Each of the glass columns contained different defluoridation media. Before the onset of each experiment, plain distilled water was used to set the baselines for the amounts of fluoride, calcium, total phosphates, pH and conductivities of the defluoridation media. The values obtained were recorded in the first row of each table of results. A water influent containing 10 mg/L fluoride was passed though each set of the columns. Aliquot samples of 300ml were withdrawn at 30 minute intervals from the columns, and the levels of fluoride, calcium, phosphate, pH and conductivity in each aliquot determined.

Ten grams of plain bone char was used as the defluoridation media in the first experiment. Experiment two incorporated the use of 10 g of saturated bone char and 10 g of calcium phosphate pellets as the media for defluoridation. Experiment three was set up using 10 g of ground Minjingu rock alone as the defluoridation media. Experiment four used 10 g of ground Minjingu rock with 10 g of saturated bone char as the defluoridation media.

Fluoride concentration in effluent water was determined colorimetrically using the zirconium – alizarin complex technique following a procedure laid out in the Standard Methods of Water and Waste Water analysis (APHA, 1995). Calcium levels were determined volumetrically by use of EDTA, according to Standard Methods of Water and Waste Water Analysis. Phosphate levels were determined colorimetrically (ascorbic acid method) using a UV spectrophotometer, according to Standard Methods of Water and Waste Water Analysis. The solution pH and conductivities were determined electrometrically using the pH meter and conductivity meter respectively.

3.2 Determination of the Saturation Point of a Given Amount of Bone Char

The initial calcium, phosphate and fluoride concentration, the pH and conductivity of 10 g bone char washed with 2 litres of distilled water was found to be constant at 10 mg/L, 5.999 mg/L, 0.5 mg/L, pH 8.721 and conductivity 37.4 µs/cm respectively after three and six hours. An influent of 10 mg/L fluoride rich water was introduced into the column containing 10 g bone char alone. The results as shown in Table 1, in chapter four were obtained when 300 mL aliquots of effluent were sampled out of the columns at 30 minute intervals and the respective concentrations of calcium, phosphate, fluoride, the pH value and conductivities of the samples determined. A graph showing the fluoride concentration in effluent with volume as a factor of time was plotted. The trend of the curve was studied and possible conclusions were made on any observations noted. The calcium: phosphate ratio, the defluoridation capacity and the percentage removal efficiency of the bone char at each interval was calculated using the general formulae (Kaseva, 2006) below;

$$DC_{FC} = \frac{S_o - S_t}{X_{fc}}$$

Where;

DC_{FC} = Defluoridation capacity mg/g

S_o= Initial fluoride mg/l

S_t = Concentration after contact time mg/l

X_{fc} = Defluoridation media g/l

and

$$Q_t = \frac{S_o - S_t}{S_o} \times 100$$

Where,

Q_t = Percentage removal efficiency

S_o = Initial fluoride mg/l

S_t = Concentration after contact time mg/l

3.3 Determination of the Role of Calcium and Phosphate Compounds in Contact Precipitation

The initial calcium, phosphate and fluoride concentration, the pH and conductivity of 10 g calcium phosphate pellets was found to be constant at 30 mg/L, 18.82 mg/L, and 1 mg/L respectively, pH 9.114 and conductivity 56.4 µs/cm.

After equilibration with saturated bone char medium, the available calcium, phosphate and fluoride concentration, the pH and conductivity of column effluent were determined and the results recorded as shown in Table 2, in chapter four.

The reintroduction of fluoride rich water into the set up was done soon after. After allowing a contact time of 30 minutes, the effluent fluoride, calcium and phosphate concentrations, the pH and conductivities were monitored with time during the defluoridation process at pre- set intervals. A concentration – volume graph of the process was plotted. Analysis of this graph by comparison to the one in the experiment using bone char alone was done and possible conclusions on the observed trends were made. At saturation point, the amount of the precipitated fluoride in contact precipitation was calculated from the additive model (Dahi, 1996) below:

$$MF^{-}_{\text{Precipitated}} = MF^{-}_{\text{Total removed}} - MF^{-}_{\text{Adsorbed on bone char}}$$

The calcium: phosphate ratio, the removal efficiency and the defluoridation capacity of contact precipitation at each interval was calculated accordingly and recorded in table 2, in chapter four.

3.4 Determination of the Efficacy of Plain Natural Rock Phosphate (Minjingu) in Defluoridation

The initial calcium, phosphate and fluoride concentration, the pH and conductivity of 10 g ground natural rock water was found to be constant at 50 mg/L, 24.96 mg/L and 20 mg/L respectively, pH 9.051 and conductivity 182.2 µs/cm. Fluoride rich water of concentration 10 mg/L was introduced into the set up. At 30 minute intervals, the available calcium, phosphate and fluoride concentration, the pH and conductivity of an aliquot of the column effluent was determined and the results recorded as shown in Table 3, in chapter four. The calcium: phosphate ratio, the removal efficiency and the defluoridation capacity of contact precipitation at each interval was also calculated and recorded in the same table.

A concentration - volume graph of the process was plotted.

3.5 Determination of the Efficacy of Natural Rock Phosphate in Contact Precipitation

Ten grams of ground natural rock phosphate was added to an equal weight of saturated bone char in a column. Fluoride rich water with a concentration of 10 mg/L was introduced into the column set - up. After equilibration, only the fluoride levels in aliquot samples withdrawn from the column at 30 minute intervals were monitored. The defluoridation capacity and removal efficiency of the media was subsequently calculated and the results recorded as shown in Table 4, in chapter four.

A concentration – volume graph of the defluoridation process was plotted. Analysis of this graph by comparison to the one in the contact precipitation experiment above was done and conclusions on the observed trends drawn.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Defluoridation Using Bone Char

The results presented in Table 1 show the variations of different parameters in the column effluent during the defluoridation of water using bone char.

Table 1: Defluoridation of water using bone char.

Volume (l)	F^- conc. mg/L	Ca^{2+} conc. mg/L	PO_4^{3-} conc. mg/L	pH	Conductivity µs/cm	Ca/P Ratio	Removal efficiency (%)	Defluoridation capacity of media mg F^-/g
0.000	0.500 ± 0.002	10.000 ± 1.732	5.999 ± 0.005	8.721 ± 0.004	37.400 ± 0.153	1.6669	-	-
0.300	4.650 ± 0.002	0.971 ± 0.035	0.580 ± 0.009	7.648 ± 0.037	60.800 ± 0.132	1.6741	55.710	1.463
0.600	4.020 ± 0.009	1.624 ± 0.009	0.892 ± 0.006	7.816 ± 0.005	117.20 ± 0.087	1.8206	61.710	1.620
0.900	3.650 ± 0.087	0.813 ± 0.003	0.513 ± 0.001	8.024 ± 0.021	52.300 ± 0.100	1.5848	65.240	1.713
1.200	3.310 ± 0.002	0.373 ± 0.019	0.221 ± 0.003	7.37 ± 0.017	101.40 ± 0.002	1.6878	68.480	1.798
1.500	3.110 ± 0.002	0.290 ± 0.004	0.264 ± 0.002	8.384 ± 0.007	95.600 ± 0.003	1.0985	70.380	1.848
1.800	3.120 ± 0.021	1.181 ± 0.010	0.610 ± 0.002	8.241 ± 0.003	62.700 ± 0.046	1.9361	70.290	1.845
2.100	2.790 ± 0.008	0.432 ± 0.005	0.596 ± 0.003	8.609 ± 0.008	60.800 ± 0.009	0.7248	73.430	1.928
2.400	2.590 ± 0.002	0.182 ± 0.011	0.323 ± 0.002	8.136 ± 0.010	54.900 ± 0.102	0.5635	75.330	1.978
2.700	2.560 ± 0.009	0.134 ± 0.005	0.082 ± 0.003	8.169 ± 0.096	46.500 ± 0.008	1.6342	75.620	1.985

3.000	2.540 ± 0.001	0.080 ± 0.056	0.291 ± 0.006	8.581 ± 0.042	39.300 ± 0.026	0.2749	75.810	1.990
3.300	2.540 ± 0.002	0.081 ± 0.020	0.244 ± 0.010	8.042 ± 0.014	49.200 ± 0.009	0.3320	75.810	1.990
3.600	2.560 ± 0.007	0.043 ± 0.003	0.028 ± 0.007	8.165 ± 0.003	44.300 ± 0.026	1.5479	75.620	1.985

The figure below shows the change in the fluoride concentration of the column effluent with volume observed at preset intervals of time during the defluoridation process with bone char.

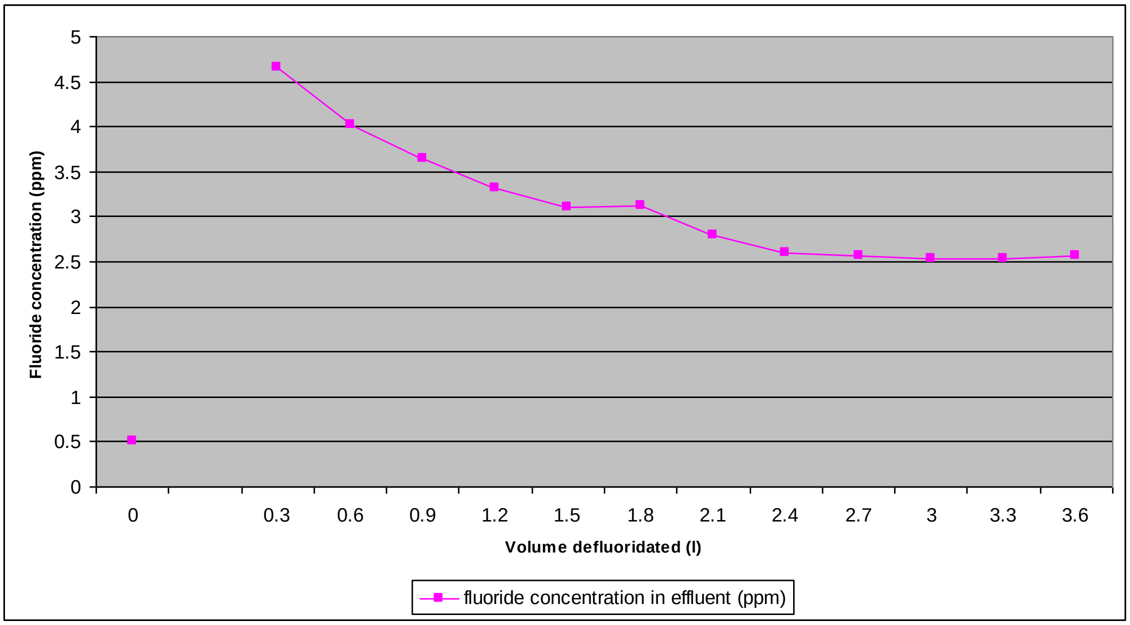

Figure 1: Determination of saturation point of bone char by fluoride.

Initially, the fluoride levels in plain distilled water that was allowed six hours contact with bone char was found to be 0.5 mg/L. When fluoride rich water (10 mg/L) was introduced into the column and sufficient contact time (30 minutes) allowed (Dahi, 1998), an initial high concentration of fluoride was evident in the effluent which decreased steadily with time. The curve leveled off at a fluoride level of 2.56 mg/L to imply that the defluoridation media was saturated with fluoride. The total volume of defluoridated water at saturation was found to be 2.7 liters. The amount of fluoride taken up by 10 g of bone at saturation was calculated using the formula;

Amount taken up = Volume at saturation (L) x (Conc. initial - Conc. at saturation time t) mg/L
Hence 2.7L x (10 - 2.56) mg/L = 20.088 mg.

This meant that one gram of bone char defluoridated approximately 2.09 mg of fluoride. This is very close to findings by Mwaniki and Nagelkerke (1990) who reported that uptake of fluoride was limited to 2 mg of fluoride per gram of bone char (specifically grey bone char), heated to 450^{o}C.

For an adsorbent like bone char, the surface area, surface chemistry, pore and particle size distribution are major factors that would affect fluoride adsorption. The adsorptive capacity is proportional to surface area although not all surface area is accessible to the adsorbate (fluoride).The effective surface area available to a given adsorbate is determined by the pore size distribution, and therefore, smaller particle size results in larger surface area per gram of adsorbent available to the adsorbate. The calculated defluoridation capacity of bone char in this experiment was shown to increase steadily and then level off at a value of 1.99 mg/g (Table 1) at the same volume where the efficiency of the bone char was leveling off. This implies that the maximum defluoridation capacity of bone char is 1.99 mg/g (Figure 2 below) in agreement with the calculated values above.

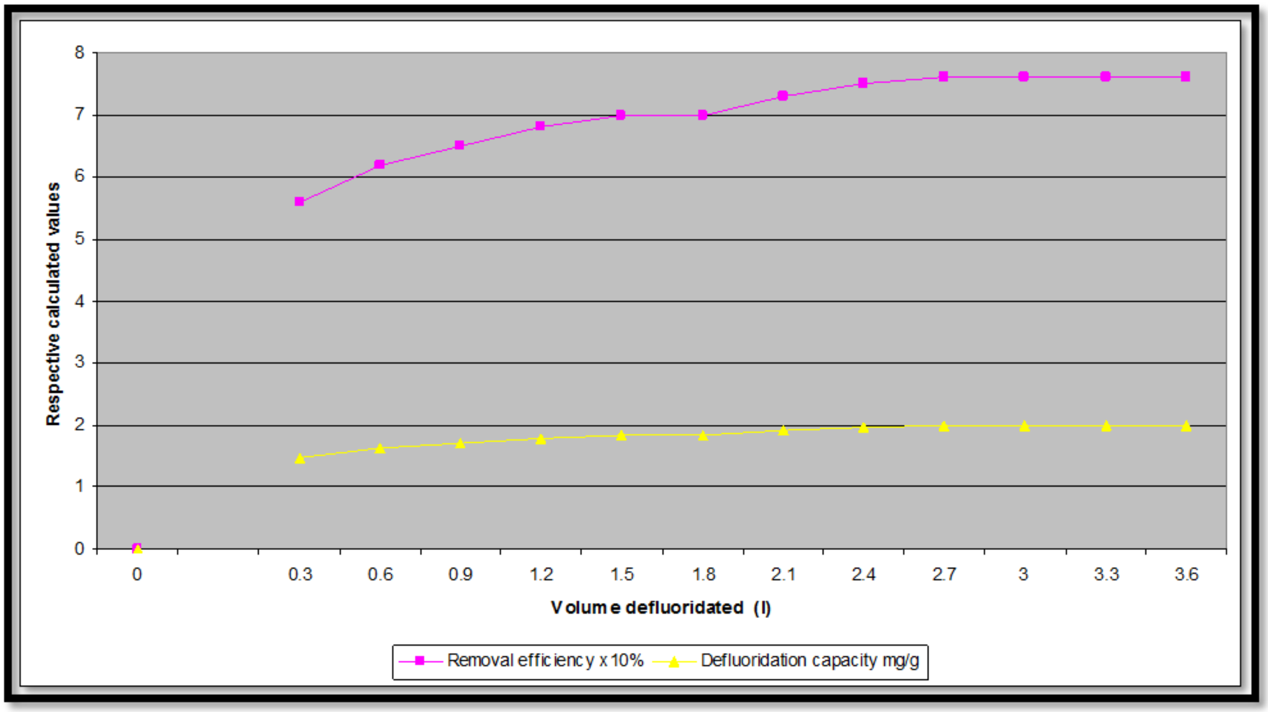

Figure 2: Relationship between removal efficiency and defluoridation capacity of bone char

From Table 1 above, it is evident that the removal efficiency of bone char increased with the amount of defluoridated water. However, the value of the removal efficiency oscillates at values between 75.62% and 75.81%, at the same volume where the fluoride concentration in effluent water was also leveling off with a concentration of 2.54 mg/L. This comes to an average efficiency of 75.72% for the bone char media.

The initial amount of available calcium and phosphate was noted to have reduced when fluoride rich water was introduced into the column (Table 1 and Figure 3). During defluoridation, the calcium and phosphate levels decreased further and at the point of saturation, the levels were very low, less than 1% of the initial levels of each remained. Both the calcium and phosphate curves exhibited a similar trend. This suggests that the calcium and phosphate ions were taking part in the defluoridation process during the formation of fluorapatite.

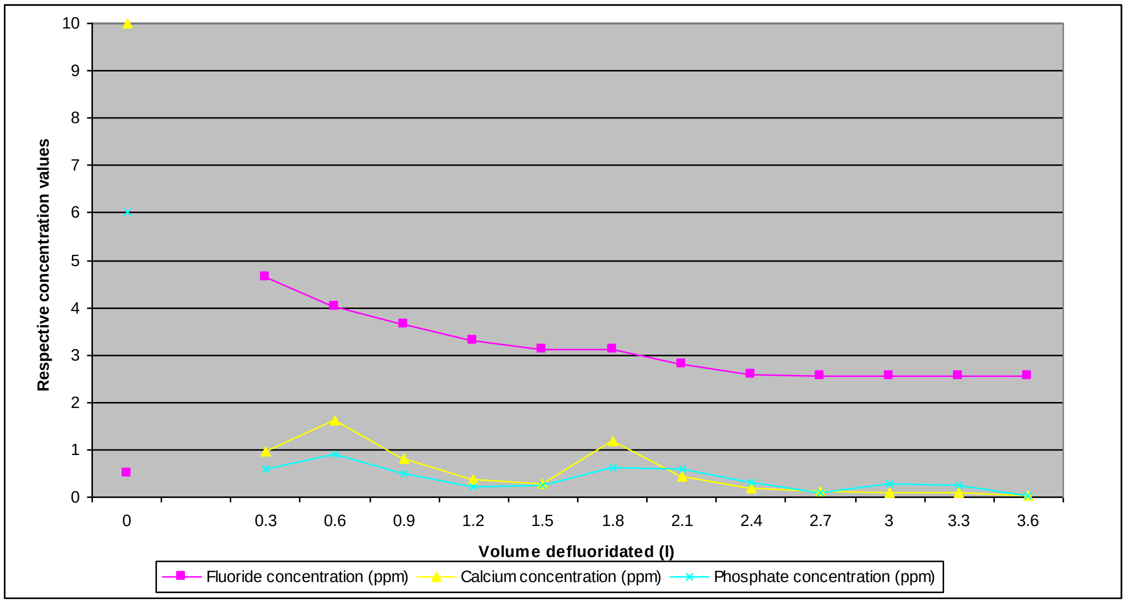

Figure 3: Relationship between fluoride, calcium and phosphate ions during defluoridation using bone char.

Going by its chemical formula, the Ca:P ratio in pure hydroxyapatite is calculated to be 1.67. Initially, in this experiment, this ratio was almost constant implying that the fluoride immobilizing reactions taking place were apatitic (not changing the Ca:P ratio in bone char or water). However, summarily, this ratio was noted to increase at some few instances and to decrease at most instances during defluoridation with the bone char. The fact that the ratio was not constant pointed to some reactions taking place either involving calcium or phosphate or both at the same time.

The Ca: P ratio is lowered when higher amounts of fluoride are adsorbed implying an increase in calcium involvement during the reaction. It is suggested that this could be due to the simultaneous adsorption of fluoride to the bone char and calcium to other vacant sites or desorption of phosphate as HPO_4^{2-} , thereby maintaining electro neutrality (Henrik, 1995).

During defluoridation of water with bone char, it is proposed that there is an exchange of the fluoride ions from water with the hydroxyl ions from the hydroxyapatite (HAP) to form a more stable complex known as fluorapatite (FAP);

$HAP + F^{-} \rightarrow FAP + OH^{-}$

However, this does not take place in a one step process. According to (Christoffersen, 1984), it is proposed that fluoride is adsorbed to bone char in vacant sites, systematically through a series of the followig steps;

(i) External diffusion or dispersion of fluoride to the particle surface,

(ii) Particle diffusion in particle pores and then,

(iii) Ion exchange hence OH-AP + $F^{-} \rightarrow$ FAP + OH^{-}

In this study, the pH of the solution was noted not to change much, remaining within a range of 7.370 and 8.721. Ion exchange would therefore be ruled out. It was suggested that the bone char surface released OH^{-} when in contact water, irrespective of the presence of fluoride (Henrik, 1995). Fluoride therefore is adsorbed to bone char without being coupled to the release of OH^{-}.

Literature search points to another reaction, recrystallization, which takes place during defluoridation with bone char. This is the process where hydroxyapatite (HAP) or bone mineral dissolves and precipitates with fluoride as fluorapatite (FAP). In studies by Henrik, (1995) and Christoffersen et al., (1984), it was concluded that at pH range 7 - 8.5, recrystallization was an important part of fluoride uptake. The solubility of HAP was highest within this pH range making more calcium and phosphate available for reaction with fluoride. However it was a slower reaction than adsorption. The shape of the fluoride curve (Figure 1) points to this, where saturation is seen to have set in initially (adsorption sites full) and then defluoridation continues further (after recrystallization) to a point of final saturation, thus;

$2Ca(HPO_4).2H_2O \rightarrow 2Ca^{2+} + 2HPO_4^{2-} + 2H_2O$………………..Dissolution of HAP

$10Ca^{2+} + 6PO_4^{3-} + 2F^{-} \rightarrow Ca_{10}(PO_4)_6.F_2$………………………..Precipitation of FAP

4.2 Defluoridation using Saturated Bone Char with Calcium Phosphate Pellets (Contact Precipitation).

The initial calcium, phosphate and fluoride concentration, the pH and conductivity of 10 g calcium phosphate pellets was found to be constant at 30 mg/L, 18.82 mg/L, and 1 mg/L respectively, pH 9.114 and conductivity 56.4µs.

Table 2: Defluoridation of water by contact precipitation

Volume (l)	F^- conc. (mg/L)	Ca^{2+} conc. (mg/L)	PO_4^{3-} conc. (mg/L)	pH	Conductivity (µs/cm)	Ca:P ratio	Removal efficiency (%)	Defluoridation capacity of pellets (mg/g)
0.000 (at equilibrium with distilled water in bone char column)	0.140 ± 0.002	3.280 ± 0.002	2.219 ± 0.138	9.004 ± 0.002	115.60 ± 0.192	1.4781	-	-
3.900	2.410 ± 0.198	0.106 ± 0.014	0.058 ± 0.013	8.729 ± 0.076	82.500 ± 0.025	1.8276	78.090	2.148
4.200	1.740 ± 0.048	0.083 ± 0.025	0.050 ± 0.002	8.741 ± 0.071	69.600 ± 0.017	1.6734	84.180	2.315
4.500	1.680 ± 0.050	0.069 ± 0.003	0.071 ± 0.003	8.650 ± 0.022	60.200 ± 0.087	0.9664	84.700	2.330
4.800	1.530 ± 0.028	0.048 ± 0.001	0.030 ± 0.001	8.732 ± 0.002	63.000 ± 2.309	1.6000	86.090	2.368
5.100	1.280 ± 0.002	0.022 ± 0.005	0.012 ± 0.002	9.011 ± 0.001	58.400 ± 0.002	1.6296	88.360	2.430
5.400	0.980 ± 0.004	0.017 ± 0.001	0.010 ± 0.001	8.920 ± 0.003	63.700 ± 0.002	1.7000	91.090	2.505
5.700	0.860 ± 0.002	0.013 ± 0.004	0.008 ± 0.002	8.731 ± 0.004	61.300 ± 0.004	1.6667	92.180	2.535
6.000	0.840 ± 0.002	0.009 ± 0.003	0.007 ± 0.001	7.993 ± 0.006	56.500 ± 0.036	1.3235	92.360	2.540

6.300	0.750 ± 0.010	0.012 ± 0.001	0.007 ± 0.001	7.982 ± 0.080	52.900 ± 0.010	1.6667	93.180	2.563
6.600	0.740 ± 0.004	0.004 ± 0.002	0.003 ± 0.002	8.810 ± 0.002	53.500 ± 0.020	1.600	93.270	2.565
6.900	0.680 ± 0.053	nil	Nil	8.714 ± 0.005	48.600 ± 0.016	nil	93.820	2.580
7.200	0.630 ± 0.010	nil	Nil	7.955 ± 0.010	43.700 ± 0.020	nil	94.270	2.593
7.500	0.630 ± 0.017	nil	Nil	8.870 ± 0.010	59.800 ± 0.010	nil	94.270	2.593
7.800	0.640 ± 0.020	nil	Nil	8.076 ± 0.001	54.200 ± 0.173	nil	94.180	2.590

A larger volume of fluoride rich water was defluoridated by the same amount of enriched bone char. Since volume defluoridated is a factor of time in these experiments, it follows that immobilization of fluoride is also dependent on time and hence more fluoride is immobilized with time. The concentration curve for fluoride leveled off at 0.63 ppm with the total volume of effluent at 7.2 L. The total fluoride taken by the combined media was given by the formula;
Volume at saturation (L) x (Conc. initial - Conc. at saturation time t) mg/L
Hence,
7.2 L x (10-0.63) mg/l = 67.464 mg.

The amount precipitated as a result of enriching the media with the pellets was calculated from the additive model below;
Amount F^{-} (precipitated) = Amount F^{-} (total) removed – Amount F^{-} (taken up by bone)
Hence;
67.464 mg – 20.088 mg = 47.376 mg F^{-} precipitated.

On introduction of calcium phosphate pellets to the saturated bone char column followed by equilibration with distilled water, the initial concentrations of calcium, phosphate and fluoride in the calcium phosphate pellets were reduced. On the contrary, the conductivity of the column effluent increased considerably (Table 2). This points to some ionic activity in the column.

Looking at the general trend of the defluoridation process (Figure 4), it was noted that after the introduction of calcium phosphate pellets to the saturated bone char medium, the fluoride curve dropped sharply initially from a level of 2.41 mg/L to 1.74 mg/L (indicative of a 27.80% difference in concentration reduction), then almost leveled off before another gradual drop from 1.28 mg/L to 0.98 mg/L (indicative of a 23.43% difference in concentration reduction) and finally gradually leveling off to signify saturation at 0.63 mg/L. The distinct change in the reaction order noted from the shape of the curve (Figure 4) suggests that more than one reaction is involved in fluoride immobilization in contact precipitation.

Addition of calcium phosphate pellets into the column introduced more solutes to the system in the form of calcium and phosphate. Theory dictates that in a multisolute system, the adsorptive capacity of the adsorbent is a function of the initial concentration of the adsorbate (Chin H. *et al.*, 1996). It is therefore expected that due to competitive adsorption phenomena, the adsorbent performance would be adversely affected. This was not the case with this experiment as the fluoride defluoridation capacity of the media and its efficiency actually improved.

The initial available calcium, phosphate and fluoride in the pellets were significantly reduced during the equilibration period with plain distilled water from levels of 30 mg/L, 18.82 mg/L and 1 mg/L for calcium, phosphate and fluoride to 3.28 mg/L, 2.219 mg/L and 0.140 mg/L respectively. The reduction in the calcium, phosphate and fluoride concentrations could imply that during equilibration, some Ca^{2+} could have been retained up on some existent vacant sites on the bone char since bone char is known to be calcium deficient. Electro neutrality is assumed to be maintained by subsequent desorption of HPO_4^{2-}. For this to hold true however, one would expect an increase in the PO_4^{3-} ions in solution which was not the case with this experiment.

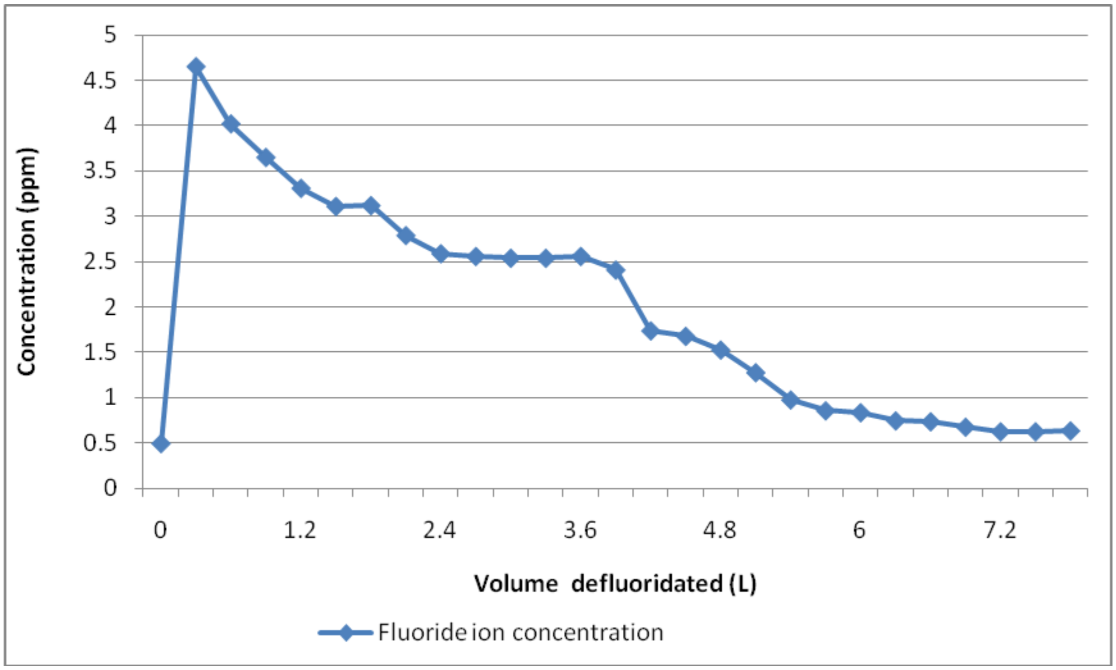

Figure 4: The general trend of defluoridation using bone char followed by contact precipitation.

The theoretically desorbed HPO_4^{2-} could have been utilized in the formation of fluorapatite, explaining the reduction of fluoride levels at equilibrium. Alternatively, the reduction in the levels could be attributed to the precipitation of CaF_2 and fluorapatite, suggesting a possible recharging of the bone char. The reduction of fluoride levels could also imply a preferential uptake of fluoride on to the recharged strong binding sites on the adsorbent surface (saturated bone char).There was a slight decrease in the solution pH at equilibrium. Three possible reactions involved could be,

$Ca^{2+} + 2F^{-} \rightarrow CaF_{2\,(S)}$

$Ca_3(PO_4)_2 + 2H_2O + 2F^{-} \rightarrow Ca_3PO_4.(HF_2)(OH)_2 + PO_4^{3-} + H^{+}$

$10\ Ca^{2+} + 6PO_4^{3-} + 2F^{-} \rightarrow Ca_{10}(PO_4)_6\,F_{2\,(S)}$

All these reactions are possible because there is the presence of an already saturated bone char media acting as a nucleating surface, while forming a fresh layer of hydroxyapatite.

On re-introduction of fluoride rich water into the set up, a gradual decrease in both calcium and phosphate ions to undetectable levels at saturation point was noted (Figure 5). These ions definitely take part in fluoride immobilization in contact precipitation.

In a report by Albertus *et al*. (2002), it was suggested that removal of fluoride was due to a combination of the precipitation of fluorapatite and calcium fluoride, only that precipitation of calcium fluoride depended on the presence of saturated bone char to initiate the process while that of fluorapatite occurred within the apatite structure of the bone char, and depended on the pore water velocity and contact time in the filter. Addition of the pellets to saturated bone char medium however, resulted in high concentrations of calcium and phosphate making the solution to be highly supersaturated with respect to fluorapatite.

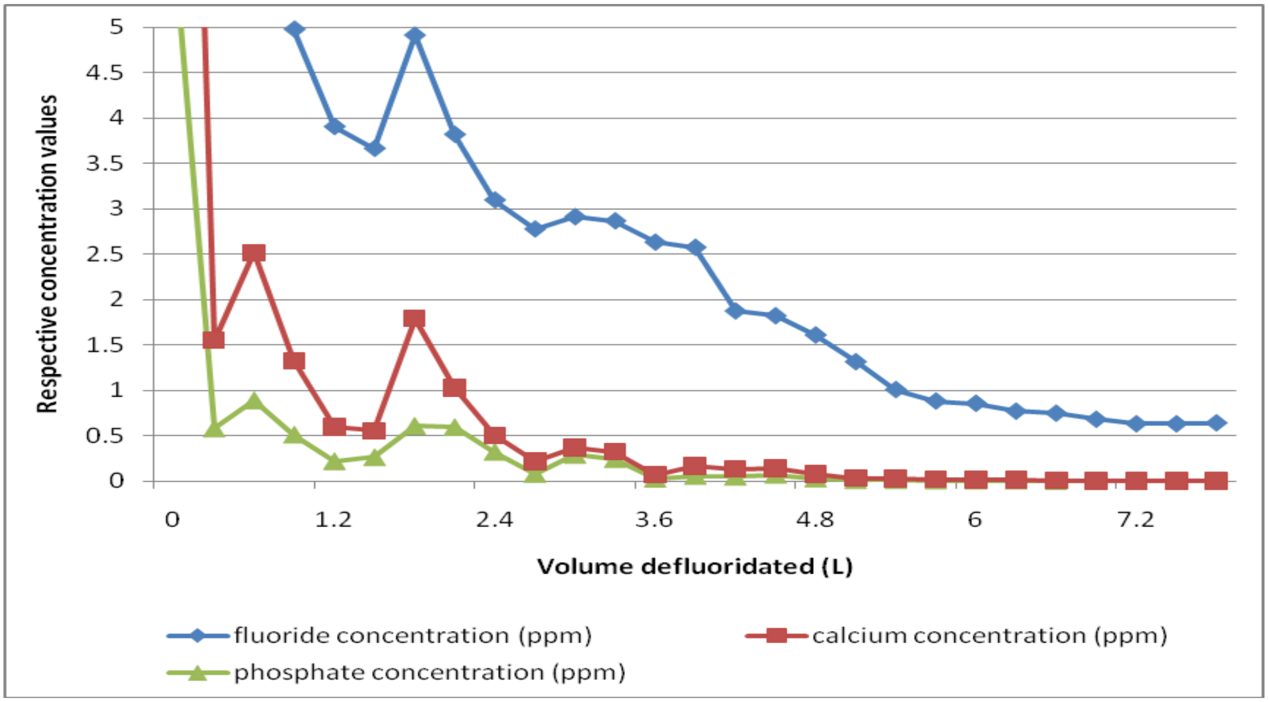

Figure 5: Relationship between fluoride, calcium and phosphate ions during defluoridation.

Consequently, the precipitation of fluorapatite in a kind of heterogeneous crystal growth phenomenon was enabled as a result of the adjacent water being rich with the precipitated components. This led to a tenfold increase in the removal of fluoride from the water. The shape of the graphs (Figure 5) suggests an adsorption isotherm describing the thermodynamics of the whole adsorption process.

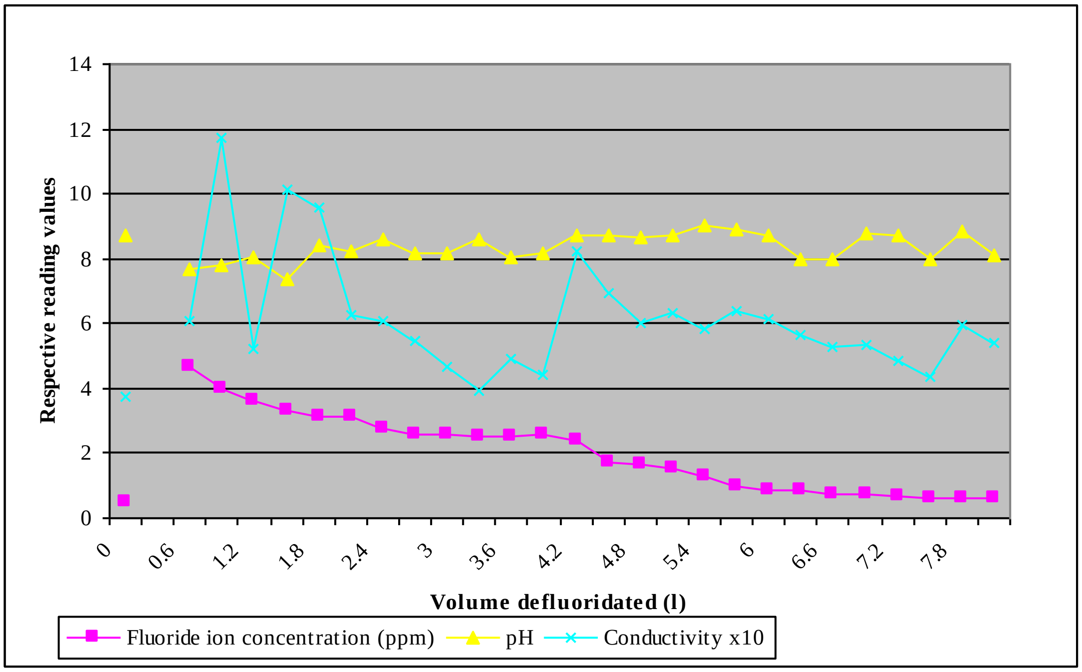

Figure 6 a: Relationship between fluoride ion concentration, pH and conductivity during defluoridation

The effluent pH remained within a narrow range, but generally showed an upward trend during the defluoridation process. The change in solution pH notwithstanding, defluoridation was noted to continue. The possible reactions indicating the different rates of fluoride uptake at different pH ranges and hence the shape of the defluoridation curve could be;

At about neutral pH (pH = 7.6 -8.5)

$Ca_3 (PO_4)_2 + 2H_2O + 4F^- \rightarrow Ca_3PO_4.(HF_2)_2(OH) + PO_4^{3-} + OH^-$

At alkaline pH (pH = 8.5 -9.5)

$Ca_3(PO_4)_2 + 2H_2O + 2F^- \rightarrow Ca_3PO_4.(HF_2)(OH)_2 + PO_4^{3-} + H^+$

These equations point to an ion exchange mechanism. The conductivity showed marked fluctuation (Figure 6a). This could be indicative of several ions interacting during the defluoridation process and not just confined to OH^- alone. Ion exchange of fluoride with OH^- and carbonates could be an appropriate reason. The exact form of the carbonates present in the crystal lattice of bone mineral (CO_2, HCO_3^-, CO_3^{2-}) is not clear from the literature, but it has been suggested that the carbonate present in bone mineral exchanges with fluoride, during experiments with enamel and bone (Neuman *et al.*,1950, McCann and Bullock,1955). The resultant rise in effluent pH could however account for ion exchange of fluoride with OH^-. The efficiency of the defluoridation process was shown to have improved to about 94% as shown in Figure 6 b after addition of calcium phosphate pellets.

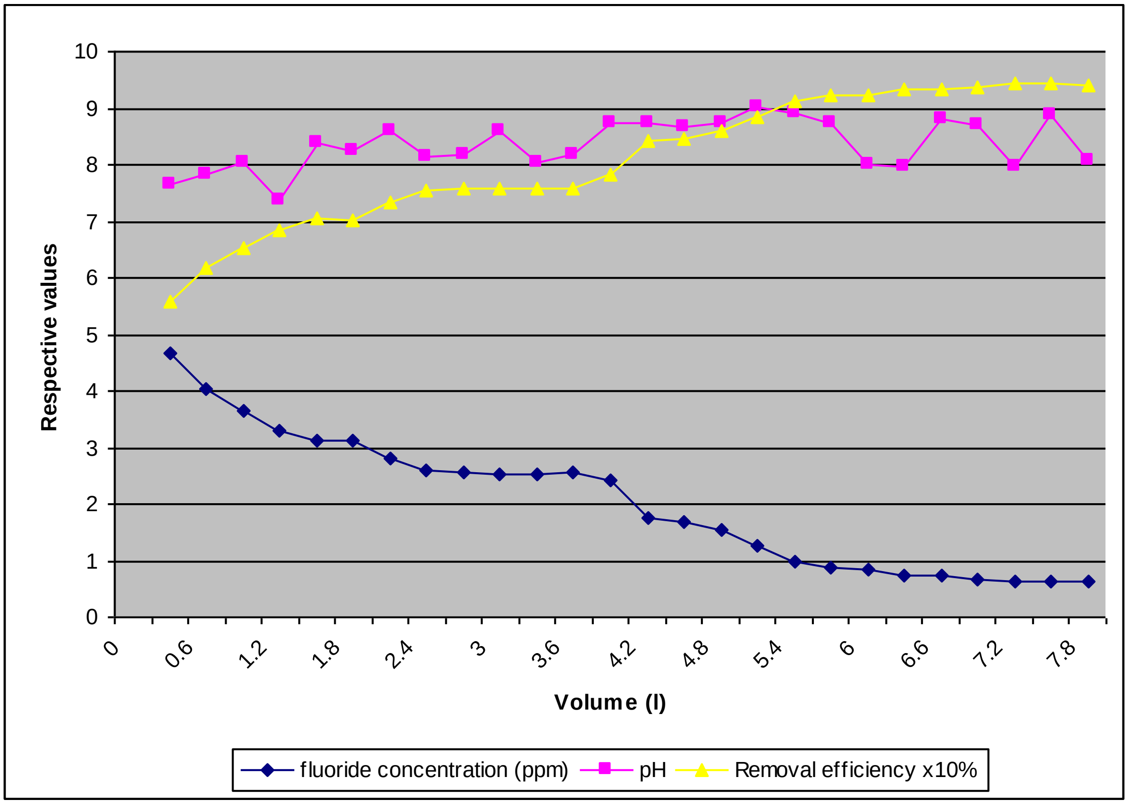

Figure 6 b: Relationship between pH, fluoride concentration and removal efficiency during defluoridation.

The efficiency curve leveled off at 94% indicating a capacity of 2.593 mg/g. This implies that the enriched media has a maximum defluoridation capacity of 2.593mg/g (Table 2). There was a negative correlation between the fluoride concentration of the column effluent and the removal efficiency of the defluoridation system.

4.3 Defluoridation with Plain Natural Rock Phosphate:

The initial calcium, phosphate, fluoride and conductivity of 10 g of Natural Rock Phosphate washed with 2 litres plain distilled water was found to be constant at 50 mg/L, 24.96 mg/L, 20 mg/L and 182.2 µs/cm respectively. On introduction of a 10 mg/L fluoride solution into the column, there was a fluctuating upward trend in the effluent fluoride concentration levels against a subtle defluoridation capacity curve whose maximum was found to be 1 mg/g. This point of maximum defluoridation capacity corresponded with the point of maximum fluoride removal on the fluoride defluoridation curve.

The calcium and phosphate levels were noted to increase with the effluent volume during the experiment suggesting a possibility of leaching of the rock. The fluoride levels in the effluent was also noted to increase with time over four hours, and then remained constant at 20 mg/L. This was indicative of the presence of fluoride in Minjingu/Natural rock phosphate that easily leached out.

The results presented in Table 3 and Figure 7 show the variations of different parameters in the column effluent before and during the defluoridation of water using plain natural rack phosphate.

Table 3: Defluoridation of water using plain Natural Rock Phosphate.

Volume (l)	Fluoride conc. (mg/L)	Calcium conc. (mg/L)	Phosphate conc. (mg/L)	Conductivity (µs/cm)	Ca:P ratio	Removal efficiency (%)	Defluoridation capacity (mg/g)
0	20.0 ± 2.600	50.00 ± 1.732	24.96 ± 0.018	182.2 ± 0.346	2.0034	-	-
0.3	26.0 ± 0.854	42.86 ± 0.009	26.33 ± 0.285	150.1 ± 1.646	1.628	13.33	0.4
0.6	25.0 ±	63.49 ±	34.28 ±	117.3 ±	1.852	16.66	0.5

	0.200	0.009	0.117	0.889			
0.9	20.0 ± 0.100	60.27 ± 0.081	42.41 ± 0.183	75.1 ± 1.004	1.4209	33.33	1.0
1.2	25.0 ± 1.206	51.42 ± 0.011	52.58 ± 0.103	68.2 ± 0.200	0.9779	16.66	0.5
1.5	25.0 ± 0.600	55.3 ± 0.664	53.07 ± 0.097	79.6 ± 0.872	1.042	16.66	0.5
1.8	28.0 ± 0.100	54.28 ± 0.196	44.023 ± 0.003	81.2 ± 1.058	1.2329	6.66	0.2
2.1	22.0 ± 1.804	67.11 ± 0.005	40.33 ± 0.120	93.5 ± 1.803	1.6640	26.66	0.8
2.4	22.5 ± I.000	51.25 ± 0.025	33.497 ± 0.300	103.6 ± 0.872	1.5673	25.00	0.75
2.7	20.0 ± 0.872	46.1 ± 0.042	69.77 ± 0.017	88.2 ± 0.200	0.6607	33.33	1.0
3.0	20.3 ± 0.889	52.31 ± 0.010	68.08 ± 0.173	87.1 ± 0.100	0.7684	32.33	0.97
3.3	20.3 ± 0.058	54.14 ± 0.066	65.051 ± 0.103	76.7 ± 0.265	0.8322	32.33	0.97

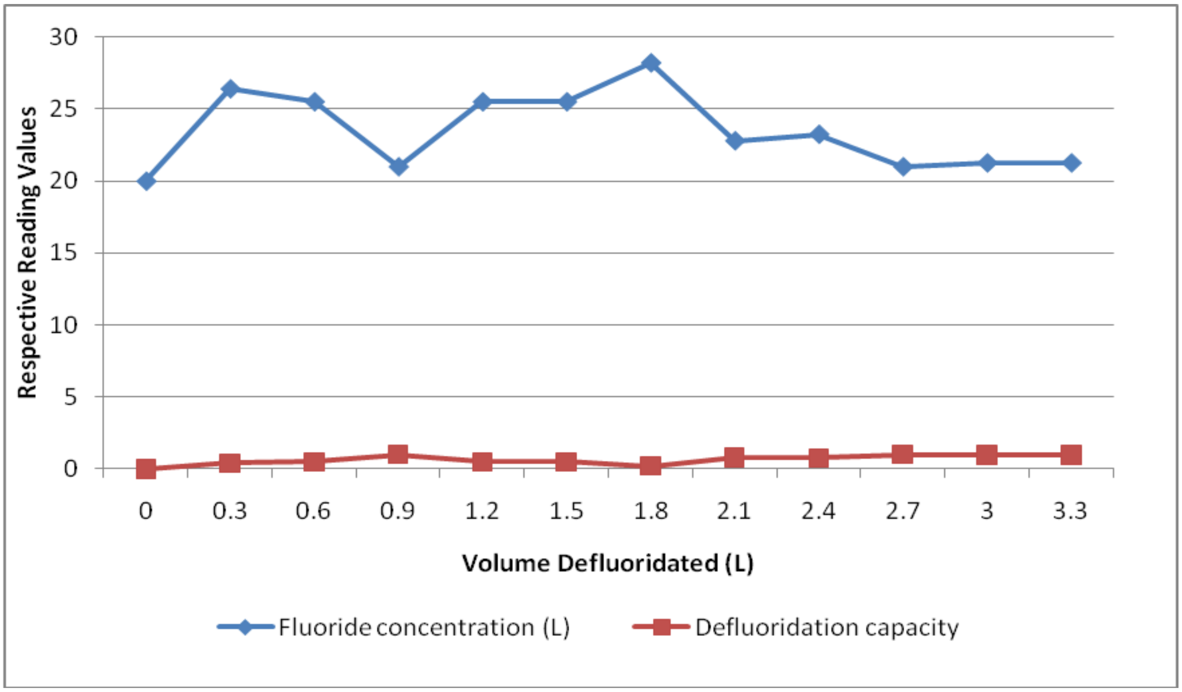

Figure 7: Defluoridation using plain Natural Rock Phosphate.

4.4 Defluoridation using Saturated Bone Char with Natural Rock Phosphate:

The results presented in Table 4 and Figure 8 show the variations of fluoride in the column effluent before and during the defluoridation of water using saturated bone char with Natural Rock Phosphate**.**

Table 4: Defluoridation of water using saturated Bone Char with Natural Rock Phosphate

Volume (l)	F^- concentration mg/L	Defluoridation capacity mg/g	Removal efficiency %
0	20.00 ± 1.000	-	-
0.300	17.57 ± 0.095	1.230	41.430
0.600	14.390 ± 0.017	1.561	52.030
0.900	11.980 ± 0.002	1.802	60.070
1.200	8.820 ± 0.017	2.118	70.600

1.500	9.940 ± 0.004	2.006	66.870
1.800	11.530 ± 0.003	1.847	61.570

On introduction of a 10 mg/L fluoride rich water solution into the column of saturated bone char with Natural Rock Phosphate, there was a gradual drop in the fluoride concentration from 20 mg/L to 8.82 mg/L in the first four 300ml effluent aliquots withdrawn from the column in a span of 2 hours.

A gradual increase in fluoride concentration was noted subsequently (Figure 8).The defluoridation capacity during the experiment ranged between 1.230 and 2.118 mg/g. The sharp reduction in the fluoride levels in column effluent could be due to the presence of calcium and phosphate ions that leach into solution from Minjingu Rock Phosphate that recharged the saturated bone char to some extent. Due to the presence of saturated bone char, precipitation of fluoride with the calcium and phosphate to CaF_2 and fluorapatite was enabled. The efficiency of defluoridation using the combined media of Minjingu Rock Phosphate and saturated bone char was noted to improve from a maximum of 33.3% (plain Minjingu Rock Phosphate) to a maximum of 70.6% (combined media).This efficiency is comparable to that of bone char.

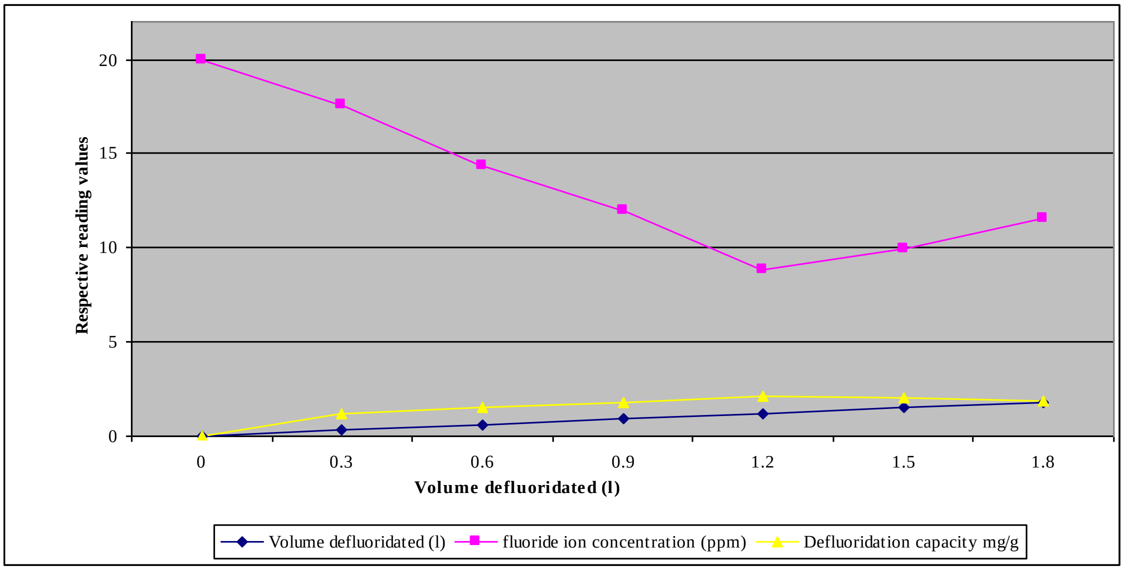

Figure 8: Defluoridation using saturated bone char with Minjingu rock Phosphate .

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The acceptable fluoride level in drinking water in Kenya is 1.5mg/L (WHO, 1993). This study has shown that the contact precipitation technique is capable of reducing the excess fluoride in water to fall within these acceptable levels. The defluoridation capacity of contact precipitation was found to be 2.59 mg/g with an efficiency of 94%. Plain Minjingu rock phosphate was found to have a defluoridation capacity of 1.0 mg/g and efficiency of 33.33% while the combined media of Minjingu rock phosphate and saturated bone char was found to have a defluoridation capacity of 2.12 mg/g with an efficiency of 70.6%.

Based on the observed trends of fluoride, calcium, phosphate, conductivity and pH in the experiments, we can infer that;

i). The main processes in the immobilization of fluoride on bone char are:

a). A relatively fast adsorption of fluoride, where electro neutrality is maintained by release of phosphate and adsorption of calcium and

b). Dissolution of bone mineral accompanied by precipitation of fluorapatite (recrystallization).

ii). Both calcium and phosphate ions introduced as calcium phosphate pellets into a saturated bed of bone char take part in the contact precipitation defluoridation process with the bone char acting as a nucleating surface for the reactions. It is proposed that fluoride immobilization in contact precipitation is as a result of a series of reactions namely; adsorption, ion exchange and co- precipitation as fluorapatite crystal growth.

iii). It is possible to defluoridate water using Minjingu rock (natural rock phosphate) as a substitute to the commercial calcium phosphate pellets in contact precipitation. The reactions involved could most probably be ion exchange and co-precipitation.

These conclusions are formed on the basis and strength of the observed trends of the measured parameters. However, in the absence of instrumentations like X-ray diffraction, it was not possible to determine the exact products and intermediate products during the various reactions.

The identity of such products would give us evidence of the mechanisms of the reactions taking place.

5.2 Recommendations

On a policy level, the fluoride issue in water should be taken seriously as a matter of national concern with the option of defluoridating the waters using an efficient, safe and affordable water defluoridation technique , the contact precipitation technique , especially in high endemic rural areas. Residents of these areas should be sensitized on the adverse irreversible health effects of consuming elevated levels of fluoride in their drinking water and to be encouraged to use non - fluoridated toothpastes instead of the traditional fluoridated toothpastes in the market today.

From the findings of the study, it is suggested that;

i). Further investigations including the X-ray diffraction analysis of the defluoridation media be carried out to pinpoint the products formed during the different stages of defluoridation. This will help identify the sequence of the reactions taking place during defluoridation. These studies should also incorporate the adsorption thermodynamics and reaction kinetic studies in order to identify the adsorption isotherms of each of the defluoridation media.

ii). Further research on the nature of natural rock phosphate (Minjingu rock), its constituents, adsorption characteristics and conditions under which it could best work should be done.

iii).The trends of calcium, phosphate, pH and conductivity during the defluoridation of water using saturated bone char and natural rock phosphate (Minjingu rock) as defluoridation media should be investigated in more detail.

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APPENDICES

APPENDIX 1: RAW DATA

Table A1: Triplicate results of defluoridation of water using bone char

Volume (l)	F^- conc. Ppm	Ca^{2+} conc. mg/L	PO_4^{3-} conc. mg/L	pH	Conductivity µs/cm	Ca/P Ratio	Removal efficiency %	Defluoridation capacity of media mg F^-/g
Plain distilled H_2O in.	0.498 0.502 0.500	11.000 11.000 8.000	5.997 6.001 6.006	8.718 8.720 8.725	37.200 37.500 37.300	1.6669	-	-
0.300	4.651 4.651 4.648	1.010 0.942 0.961	0.570 0.588 0.582	7.680 7.656 7.608	60.850 60.650 60.900	1.6741	55.710	1.463
0.600	4.028 4.010 4.022	1.628 1.614 1.630	0.897 0.885 0.894	7.818 7.820 7.810	117.250 117.100 117.250	1.8206	61.710	1.620
0.900	3.690 3.710 3.550	0.810 0.816 0.813	0.513 0.514 0.512	8.040 8.032 8.000	52.300 52.200 52.400	1.5848	65.240	1.713
1.200	3.308 3.310 3.312	0.376 0.353 0.390	0.222 0.223 0.218	7.360 7.390 7.360	101.398 101.402 101.400	1.6878	68.480	1.798
1.500	3.112 3.108 3.110	0.290 0.294 0.286	0.266 0.263 0.263	8.380 8.392 8.380	95.604 95.60 95. 590	1.0985	70.380	1.848
1.800	3.100 3.141 3.119	1.190 1.183 1.170	0.612 0.610 0.608	8.244 8.241 8.238	62.650 62.740 62.710	1.9361	70.290	1.845
2.100	2.782 2.790 2.798	0.436 0.426 0.434	0.597 0.593 0.598	8.611 8.616 8.600	60.805 60.790 60.805	0.7248	73.430	1.928

2.400	2.588	0.190	0.321	8.142	54.796	0.5635	75.330	1.978
	2.590	0.170	0.324	8.141	54.904			
	2.592	0.186	0.324	8.125	55.000			
2.700	2.550	0.132	0.080	8.260	46.505	1.6342	75.620	1.985
	2.564	0.130	0.085	8.178	46.491			
	2.566	0.140	0.081	8.069	46.504			
3.000	2.540	0.131	0.292	8.621	39.310	0.2749	75.810	1.990
	2.542	0.020	0.296	8.601	39.270			
	2.540	0.089	0.285	8.540	39.320			
3.300	2.542	0.060	0.245	8.042	49.190	0.3320	75.810	1.990
	2.538	0.083	0.226	8.052	49.206			
	2.542	0.100	0.241	8.024	49.204			
3.600	2.566	0.044	0.022	8.165	44.270	1.5479	75.620	1.985
	2.551	0.045	0.036	8.168	44.320			
	2.563	0.040	0.026	8.162	44.310			

Table A2 : Triplicate results of defluoridation of water by contact precipitation

Volume (l)	F^- conc.mg/L	Ca^{2+} conc.mg/L	PO_4^{3-} conc.mg/L	pH	Conductivity µs/cm	Ca/P ratio	Removal efficiency %	Defluoridation capacity of pellets mg/g
Plain distilled H2O through combined media	0.139 0.142 0.139	3.280 3.277 3.281	2.053 2.328 2.176	9.002 9.006 9.004	115.82 115.47 115.51	1.4781	-	-
3.900	2.631 2.250 2.349	0.097 0.099 0.122	0.046 0.071 0.057	8.802 8.734 8.651	82.483 82.527 82.483	1.8276	78.090	2.148
4.200	1.771 1.764 1.685	0.097 0.098 0.054	0.048 0.052 0.050	8.867 8.810 8.726	69.615 69.581 69.604	1.6734	84.180	2.315
4.500	1.721 1.694 1.625	0.068 0.072 0.067	0.070 0.069 0.074	8.640 8.635 8.675	60.300 60.150 60.150	0.9664	84.700	2.330
4.800	1.552 1.498 1.540	0.048 0.046 0.047	0.029 0.030 0.031	8.732 8.734 8.730	64.250 64.480 60.370	1.6000	86.090	2.368
5.100	1.280 1.278 1.282	0.028 0.020 0.018	0.010 0.012 0.014	9.011 9.010 9.012	58.402 58.400 58.398	1.6296	88.360	2.430
5.400	0.984 0.977 0.979	0.017 0.018 0.016	0.011 0.009 0.010	8.921 8.917 8.922	63.702 63.701 63.699	1.7000	91.090	2.505
5.700	0.860 0.858	0.009 0.016	0.006 0.008	8.728 8.735	61.304 61.299	1.6667	92.180	2.535

	0.862	0.014	0.010	8.730	61.297			
6.000	0.840 0.838 0.842	0.008 0.012 0.007	0.006 0.008 0.007	7.998 7.995 7.986	56.460 56.510 56.530	1.3235	92.360	2.540
6.300	0.753 0.758 0.739	0.013 0.011 0.012	0.006 0.008 0.007	8.050 8.002 7.894	52.900 52.890 52.910	1.6667	93.180	2.563
6.600	0.742 0.735 0.743	0.006 0.003 0.003	0.005 0.002 0.002	8.810 8.808 8.812	53.520 53.500 53.480	1.600	93.270	2.565
6.900	0.740 0.660 0.640	nil	nil	8.719 8.709 8.715	48.615 48.602 48.583	nil	93.820	2.580
7.200	0.640 0.620 0.630	nil	nil	7.955 7.965 7.945	43.720 43.680 43.700	nil	94.270	2.593
7.500	0.650 0.620 0.620	nil	nil	8.860 8.880 8.870	59.810 59.790 59.800	nil	94.270	2.593
7.800	0.660 0.640 0.620	nil	nil	8.077 8.076 8.075	54.400 54.100 54.100	nil	94.180	2.590

TableA3: Triplicate results of defluoridation of water using plain Minjingu rock.

Volume (l)	Fluoride conc. (mg/L)	Calcium conc.mg/L	Phosphate conc. (mg/L)	Conductivity µs/cm	Ca/P ratio	Removal efficiency %	Defluoridation capacity mg/g
0	21.40 17.00 21.60	7.000 4.000 4.000	2.492 2.480 2.516	181.800 182.400 182.400	2.0034	-	-
0.3	24.10 25.80 25.10	4.276 4.290 4.292	2.666 2.333 2.900	151.10 148.20 151.00	1.628	13.33	0.4
0.6	24.80 25.20 25.00	6.359 6.345 6.343	3.456 3.528 3.300	116.60 118.30 117.00	1.852	16.66	0.5
0.9	20.10 19.90 20.00	6.134 6.020 5.977	4.400 4.041 4.282	75.40 73.98 75.92	1.4209	33.33	1.0
1.2	23.80 25.20 26.20	5.144 5.152 5.130	5.158 5.216 5.358	68.00 68.20 68.40	0.9779	16.66	0.5
1.5	24.40 25.00 25.60	5.59 5.57 4.43	5.314 5.400 5.207	78.60 80.20 80.00	1.042	16.66	0.5
1.8	27.90 28.10 28.00	5.228 5.620 5.428	4.402 4.405 4.400	81.60 80.00 82.00	1.2329	6.66	0.2

2.1	23.80 22.20 20.20	6.712 6.715 6.706	4.066 3.900 4.133	94.00 91.50 95.00	1.6640	26.66	0.8
2.4	21.5 23.5 22.5	5.125 5.150 5.100	3.649 3.049 3.351	104.2 102.6 104.0	1.5673	25	0.75
2.7	19.40 21.00 19.60	4.63 4.57 4.65	7.000 6.971 6.970	88.4 88.0 88.2	0.6607	33.33	1.0
3.0	20.00 19.60 21.30	5.230 5.241 5.222	6.700 6.716 7.008	87.1 87.0 87.2	0.7684	32.33	0.97
3.3	20.30 20.40 20.40	5.444 5.338 5.460	6.510 6.605 6.400	76.5 76.6 77.0	0.8322	32.33	0.97

Table A4: Triplicate results of defluoridation of water using Minjingu rock with saturated bone char.

Volume (l)	F - concentration mg/L	Defluoridation capacity mg/g	Removal efficiency %	Defluoridation capacity mg/g
0	19.000 21.000 20.000	-	-	-
0.300	17.470 17.660 17.580	1.230	41.430	1.230
0.600	14.370	1.561	52.030	1.561

	14.400 14.400			
0.900	11.978 11.982 11.980	1.802	60.070	1.802
1.200	8.840 8.810 8.810	2.118	70.600	2.118
1.500	9.943 9.935 9.942	2.006	66.870	2.006
1.800	11.530 11.533 11.527	1.847	61.570	1.847