# **UNIVERSITY OF NAIROBI**



# DEPT. OF CIVIL ENGINEERING

# RESEARCH THESIS ON: <sup>\*</sup> REMOVAL OF FLUORIDE FROM WATER BY USING A NATURAL LOCAL MATERIAL - CHOKAA

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^okaa

Removal of fluoride from water by using a natural local material'

### Declaration

This thesis is my original work and has not been submitted for a degree in  $^{11}$ 

Ruth S. T. Adora Candidate

Date

2004

^jty supervisor This thesis has been submitted for examination with my approval as  $\textsc{Univ}^{\wedge}$ 

## Dedication

To my son Paul Masiga Wandera who will forever remain close to my heart.

### Acknowledgement

I wish to acknowledge the participation of various people without whom this research would not have been a success.

First I thank my supervisor Prof. B. N. K. Njoroge who has shown me his support through keen supervision and constructive criticism which I needed in order to present work that can be appreciated. I would also like to acknowledge the fact that he read my work in good time.

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Thanks a lot!

....

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### Abstract

This research investigated the potential for the removal of fluoride from water by use of a natural local material - chokaa. The material investigated is mined from quarries in Muranga, Kenya and is locally referred to as "chokaa" (Swahili for chalk). A number of methods have been investigated at the experimental level, of their potential to remove fluoride in Kenyan water. These include bone charcoal, charcoal from coffee husks, clay and activated alumina. These methods have been found to be either too costly or simply inappropriate for the Kenyan situation. Removal of excess fluoride is the only major form of treatment required for groundwater in several areas of the country; it is with the desire to develop a cheap and effective de-fluoridation technique, that the need to investigate a locally available material's potential seems necessary.

Batch experiments were carried out to determine various parameters like the optimal mass of chokaa required, the equilibrium time, effect of sorbent particle size, nature and rate of the sorption process, and the effect of pH and temperature. It was found that chokaa removed at least 70% of the fluoride ion in water at a pH of between 6.8 -7, temperature 25°C, and equilibrium time of one hour, for an original fluoride concentration of 25ppm. The optimal mass for 50ml fluoride ion solution was lOg. The equilibrium data fitted the Freundlich adsorption model.

Bench scale column studies were also carried out. The column dimensions were height, 25.2cm diameter, 3.4cm and operated at 49.5cm head of water. The initial fluoride concentration was 9.5ppm and water flow rate of 4ml/min. The effluent fluoride concentration from the treated water was 1.3ppm. The column treated 220ml of water before regeneration, it was regenerated and operated again. After regeneration, 9.5ppm fluoride ion concentration was reduced to 1.5ppm at a flow rate of 3.5ml/min. The flow in the column was between 0.264 m/hr and 0.033m/hr which is comparable to a slow sand filter (0.02 - 0.2m/hr for 1000 - 2000m<sup>2</sup> bed). The bed volume for the column was 229cm<sup>3</sup> and treated 220ml volume of water before the filter was regenerated. After regeneration the bed volume treatment was 209ml.

The mass of fluoride ions sorbed per unit mass of chokaa,  $Q_e$ , for column studies was O.Olmg/g while for batch studies, it was 0.096mg/g.-this shows that the fluoride removal for batch was better, however a batch setup is not ideal for industrial scale application. The use of chokaa was found to be an effective method of removing fluoride from Kenyan water. However it's regeneration cost was about Kshs. 72 per litre of water which appears rather expensive. The cost could reduce if treatment is on a large scale.

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#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 BACKGROUND INFORMATION

Kenya has both surface and groundwater sources. These sources are however limited in terms of quantity and quality and in many cases they are situated far from the high demand points as in the case of Nairobi and Mombasa where water has to be piped from as far as 100km away (Survey of Kenya, 1970).

Ground water quantity in Kenya is also limited. In some areas of the country where yielding aquifers are found, the presence of undesirable or harmful chemicals in excessive concentrations has prevented the use of ground water. Out of about 6000 bore-holes that have so far been drilled in Kenya, over half have had to be abandoned due to very low yields or the presence of excessive chemicals, the most common ones being fluorides and chlorides (Gitonga, 1985).

In Kenya, the only form of treatment done on ground water is chlorination for urban water supplies and no treatment is usually done for rural water supplies from bore-holes. The most pressing factor at present in the rural areas is provision of sufficient water. In poor communities like those found in many parts of Kenya, emphasis cannot be laid on water treatment while the people cannot afford the raw water in the first place. Removal of excess fluoride is the only major form of treatment required for groundwater in several areas of the country. It is with the development of a cheap effective defluoridation technique, that the quality and quantity will be fulfilled by groundwater in these areas (Gitonga, 1985).

There are huge financial burdens on individual patients who require remedial treatment for unsightly fluorosed teeth. Cosmetic veneers provide an extremely lucrative spin-off for the privatised dental profession. Charges may range from Kshs. 20,000 to Kshs. 60,000 per tooth and repeat treatments are required every five or six years throughout the victim's life. People who cannot afford cosmetic veneers, professional bleaching or micro-abrasive treatment have no option but to live with their fluoride-damaged leeth and the attendant social stigma and psychological trauma.

### **\ I** THE FLUORIDE ION

The fluoride ion is the ionic form of fluorine. Fluorine is a greenish diatomic gas and is the most chemically reactive of all elements, a fact, which for a long time hindered its isolation. It is also the most electronegative of all elements. There is no evidence that a positive oxidation state of fluorine exists and the ionic form of fluorine is invariably F". Covalent fluorides of many elements however exist.

The very reactive nature of fluoride means that it does not exist in uncombined form in nature. It is usually found in combined form as fluorides and is thirteenth in order of abundance of elements in the earth's crust. While very reactive itself, fluorine compounds found in nature are usually only very slightly soluble.

COMPOUND	SOLUBILITY (moles/litre)
Calcium Fluoride (Fluorspar) CaF2	2*10" <sup>4</sup>
Magnesium Fluoride	2* 10 <sup>,,J</sup>
Fluorapatite	1*10"'

Table 1 are examples of fluoride compounds and their solubility in water.

It is when the fluoride compounds dissolve in water, albeit sparingly, that the fluoride ion is released into the water and is usually found in very small concentrations seldom exceeding 50ppm, except in lakes where there is continuos evaporation which makes their waters more concentrated in minerals than ground water. The presence of fluorides is however not restricted to water only and appreciable concentrations are found in foods and beverages like tea (Fluoride Research Society, 1985).

It is mainly from these sources; water, food and beverages that fluoride both as the simple fluoride ion and in several other complex ions, e.g. CaF, MgF, etc. finds its way into the human body. (Fluoride Research Society, 1985; Gitonga, 1985; Fair et al, 1968; WHO, 1970)

### **1.3 PROBLEMS OF FLUORIDE IN DRINKING WATER**

In the 1980s, a Finland study by the Fluoride Research Society revealed that osteoporosis (a condition of weakened bones) sufferers' had extremely high levels of fluoride in their bones, according to the Irish independent newspaper. Finland banned fluoridation because of the study. Holland banned it after medical practitioners revealed that it causes reversible neuromuscular and gastrointestinal harm to some people (Fluoride Research Society, 1985).

Fluoridation may cause a rare bone cancer, called osteosarcoma, in young males. Osteosarcoma has increased dramatically among boys aged 9 to 19 in fluoridated areas of America, but not in non-fluoridated areas (Colquhoun 1990). The New Jersey Department of Health reported Osteosarcoma rates three to seven times higher in the states fluoridated areas than non-fluoridated ones.

Even more chilling, was the evidence from China that children with dental fluorosis had on average lower intelligence scores (Colquhoun 1990).

A 30- year study of 400,000 children in India showed that tooth decay increased as fluoride intake increased. Tooth decay therefore resulted from a deficiency of calcium and an excess of fluoride. (Cameron Woodworth, 2000)

Based on a report form Capital News Service, December 2001, Washington had ensured that fluoride levels in water systems statewide follow Center for Disease Control and Prevention guidelines of one part per million (lppm). Too much fluoride can lead to a cosmetic dental condition called fluorosis, which causes tooth discoloration.

Groups like the Pure Water Committee cite research that suggests that fluoride can lead to far more dangerous conditions than brown teeth: it's toxic, carcinogenic, it's not medicinal, and it's toxic runoff when in surface water. (Carolyn Taschner, 2001)

Environmental Protection Agency (EPA) scientists have taken a strong stand against fluoride. Fluoride is not an essential nutrient. It has never received "Federal Drug Administration (FDA) Approval". In fact it is listed as an "unapproved new drug" by the FDA and as a "contaminant" by the EPA. Although calcium fluoride can occur naturally, the type of fluoride (sodium) added to municipal water is a hazardous waste by-product. (Greens, 2002)

Fluoride was used historically as an excellent rat poison. According to Robert Carleton, former scientist with the EPA, fluoride is more toxic than lead but not quite as toxic as arsenic. It's a waste product of many heavy industries - derived from the production of pesticides, fertilizers, aluminium, iron, steel, copper, lead, uranium, brick, cement and glass, among others. Because of these characteristics, companies would normally have to pay high fees to dispose of fluoride. Instead they sell it to water districts. " In other words," says EPA scientist William Hirzy, "fluoride

that otherwise would be an air and water pollutant is no longer a pollutant as long as it's poured into your reservoir. The solution to pollution is dilution and in this case, the dilution is drinking water..."

The National Institute of Dental Research (NIDR) of the US Public Health Service (USPHS) conducted a massive, two year multi-million dollar study. The results of this study, reported in May 1989, American Laboratory Magazine, indicate that fluoride had no effect on reducing tooth decay therefore it should not be used (<u>http://www.all-natural.com/fleffect.html</u>).

In 1977, congress mandated the National Toxicology program (NTP) study of the carcinogenity of fluoride. After 12 years of extensive research and testing, on January 22, 1990, the NTP reported that fluoridated animals (rats) developed bone cancers (osteosarcoma) which fluoride-free rats did not contract. The dosage of fluoride which revealed this carcinogenic hazard was consistent with the Federal Register's Guidelines (Principle 3, page 45508) which are a necessary and valid method of discovering possible carcinogenic hazards in humans, (http://www.all-natural.com/fleffect.html)

An extensive study by Burke and Yiamouiannis at the National Cancer Institute produced a chart which illustrated dramatic increase in cancer in cities which fluoridated their drinking water. (<u>http://www.all-natural.com/fleffect.html</u>)

Many nations question the safety of fluoride. It has been banned or discontinued in 21 European countries (Greens, 2002).

Fluoride has been banned in many European countries because of possible health hazards. The FDA's decision also was spurred by the growing number of cases of dental fluorosis - an unsightly and permanent discoloration of teeth. The Wall Street journal reports that 22% of American children now have the condition, which occurs in young children under six who have consumed too much fluoride.

In 1999, a union of 1200 scientists, doctors and lawyers who work for the EPA announced their opposition to water fluoridation (i.e. fluoride being added into water) because of a growing body of evidence that indicates " a casual link between Fluoride and cancer, genetic damage and neurological impairment.

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Based on scientific literature, the EPA unions opposition to water fluoridation has grown. These hazards include acute toxic hazard, such as to people with impaired kidney function, as well as chronic toxic hazards of gene mutations, cancer, reproductive effects, neurotoxicity, bone pathology and dental fluorosis.

In 1990, the first study by Fluoride Research Society suggesting a link between fluoridated water and hip fractures in the elderly was published. Hip fracture rates have increased dramatically, independently of the increasing age of populations, Dr. John Colquhoun, the former principal dental officer for Auckland, New Zealand's largest cities writes. "Seven other studies have now reported to this association between low water fluoride levels and hip fractures." "But in addition to these epidemiological studies," he added, "clinical trials have demonstrated that when fluoride is used in an attempt to treat osteoporosis (in the belief it strengthened bones), it actually caused more hip fractures. That is when fluoride accumulates in the bones and weakens them."(Cameron,2002)

Mwangaza, an NGO in Tanzania has also identified problems specific to certain villages and has created "special projects" for these villages. The villages of Minjingu, Vilima Vitatu, Mwada and Masakta have naturally ocurring fluoride in their groundwater, which causes bone deformities in growing children. Together with an Environmental Peace Corp Volunteer, Mwangaza Tanzania built a 4000-liter rainwater-harvesting tank at the Minjingive Primary School. The tank serves as an example to villagers of a cost-effective way to collect water to mix with fluoride-contaminated water to decrease the overall consumption of fluoride. Mwangaza Tanzania is working with Farm Africa to initiate the construction of additional water tanks, (http://www.mwangaza.org/what.html)

### **1.4 FLUORIDE IN KENYAN WATER**

In Kenya, dental fluorosis is mostly observed in Central Province and some parts of Rift valley. From results examined by Williamson, 1953 on bore-hole water, fluoride concentrations were divided into the following ranges: 0 - 0.9 mg/1, 1 - 5.9 mg/1, 6 mg/1 and over and plotted a map of Kenya showing the spatial distribution of fluorides. In total, Williamson was able to show about 200 points on his map. These spread over all the country of about 570,000 km<sup>2</sup> but were very few points indeed, and no definite conclusions'could be made regarding the distribution of fluorides in the whole country (Gitonga, 1985).

McCall (1957) investigated the occurrence of fluorides in groundwater in Nakuru area. Apart from McCall a few other geologists described the distribution of fluorides in the different localities

whose geology they were studying. These included Baker (1958), Bristow (1964), Cavearts (1964), Gentle (1965), Thompson (1963), etc. These studies were however not limited to fluoride alone and did not therefore give essential details about their occurrence.

The second notable attempt to study the occurrence of fluorides nationwide was probably by jtilham and Macky (1971). These two researchers unfortunately did not try to describe special distribution of fluorides in the country since their interest was mainly on the geochemical and ecological significance of fluoride.

Studies carried out by International Organisations on water resources in Kenya all mentioned the fluoride problem. Among these were "Ground Water Resources in Kenya, WHO, 1973"; "Ground Water Survey, Nairobi Area, SWECO 1975"; etc.

In all the above studies, all the researchers indicated that the ground water in this country was found to have very high fluoride concentrations in general, 6mg/l (Gitonga, 1985).

The occurrence of contaminant levels of fluoride in groundwater is widespread in Kiambu, Northern parts of Machakos, Nairobi, Kajiado and Nakuru districts of Kenya. In addition pockets of high - fluoridated areas are found several other parts of the country.

Rivers do not normally contain contaminant levels of fluoride. Saline lakes in Kenya contain extremely high levels of fluoride but these lakes are not important sources of domestic water.

Several forms of treatment have been used in removal of fluoride among them are adsorption techniques using activated alumina, synthetic zeolites, lime, defluoron - 1 and 2, magnesia, sepentine, Tricalcium phosphate, florex, clay, bone charcoal and charcoal from coffee husks. These methods were either inappropriate or too costly for the Kenyan situation.

Ion - exchange resins were uneconomical to use and imparted a taste to the treated water. Treatment by distillation proved very expensive for Kenya. Treatment by electrodialysis was expensive and complicated for Kenya

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Chokaa is a natural material locally available and it was found to remove ammonia from waste water (Mwamachi, 1999) and iron and manganese from bore-hole water (Kituku, 2004). It therefore became an important material to investigate in the removal of fluoride from water.

### J 5 RESEARCH OBJECTIVES

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The objectives of the research were to:

- 1) Investigate the potential of local chokaa in removing fluoride in water.
- 2) To investigate the mechanisms of adsorption of the chokaa with fluoride.

### CHAPTER 2

#### LITERATURE REVIEW

#### 2.1 CHEMISTRY OF FLUORIDE

Fluorine is an element and a highly reactive pale yellow gas. Fluoride is a negative ion (technically called ionic fluoride) and combines with a positive ion called cation, by sharing an electron that generally produces a very stable molecule. There are two forms that the fluoride ion can take. One is as an inorganic chemical and the other an organic chemical that combines the fluoride ion with the carbon ion in some manner. The inorganic form is what is used in water fluoridation and is the one studies seek to remove. The organic form is what is commonly used in the production of pesticides, nerve gas and many other organic compounds. The organic form has no effect on dental caries (Thomas, 2001).

The fluoride ion as one of the four halogens can form various inorganic compounds (or chemicals) like calcium fluoride, sodium fluoride, aluminium fluoride, potassium fluoride, magnesium fluoride, etc, all of which are not poisonous to humans, animals or plants depending on the concentration. The solubility of any of the inorganic fluoride compounds varies widely. The solubility of calcium fluoride is 8ppm while the solubility of sodium fluoride is 18000ppm. Most (but not all) drinking waters have calcium in them and thus when the fluoride level reaches about 8ppm, calcium fluoride starts precipitating out. Lead fluoride has a solubility of about 1ppm thus its very insoluble.

The ionic fluoride is like free fluoride ions but in chemical terms they are really not free, but ionized. This is very confusing because it means that in a liquid solution the ionic bond has been broken. The ionic bond is a chemical bond characteristic of salts and is formed by the transfer of one or more electrons from one atom to another. This breakup is called disassociation. There are always equal numbers of each ion. If the water evaporates or is somehow reduced, the ions will start combining again (precipitating out) and fall out of solution.

The fluoride in the water is just fluoride (in the ionic form). Incidentally, tests that are taken to measure the concentration of fluoride in the water only measure the inorganic form of fluoride.

### **2 2 DE-FLUORIDATION TECHNIQUES**

### 2 2.1 Treatment with Activated Alumina

There are several forms of activated alumina but basically it is a substance whose main component is aluminium oxide, which is an amphoteric compound. This method has been exhaustively investigated and has also been widely used in water de-fluoridation plants in developed countries. The first person to carry out some investigation on activated alumina was probably Boruff in 1934. He recommended the use of a filter bed consisting of granular activated alumina, which on exhaustion could be regenerated with 2% sodium hydroxide solution, followed by neutralization with dilute hydrochloric acid. Different researchers found different removal capacities and different de-fluoridation costs. The main reasons for these differences were:

- a) Fluoride removal capacity depends on the pH of the feed-Water. It has now been established that the optimum pH is between 5.0 and 6.5. Some investigators ignored this aspect and hence obtained varying results.
- b) Activated alumina is not specific for F" and its adsorption capacity is therefore influenced by competing ions.
- c) The regeneration process and history affects the performance of the medium.
- d) System operations such as flow rate also affect its performance.

Under the widely varying conditions used by the different researchers, fluoride removal capacities ranging from about IOOOg of F" per nr of medium (Maier) to about 9600g/nr (Wu) have been reported.

De-fluoridation with activated alumina has been fairly well tested in pilot plants and actual defluoridation plants. The longest running treatment plant based on activated alumina was probably that built at Bartlett Texas USA in 1952. However this plant was abandoned in 1977 (Clifford, 1978). It was not however clear whether the plant was abandoned due to operation and maintenance costs or technical problems or a combination of both. A similar plant built at Elsinor, California in 1960 had to be abandoned after only a few years of operation mainly due to alumina cementation » problems. Another plant at Lake Tamarisk, California was built in 1970, another at Vail, Arizona

was built in 1973 and several other plants thay be in existence.

This method is fairly<sup>^</sup>complex for a developing country like Kenya. It is not suited to individual household units and fairly large communities can only afford the initial installation. It requires thoroughly trained personnel conversant with not only water quality requirements but also with

good knowledge of chemistry, record keeping, equipment servicing and above all be dependable and conscientious.

Rubel and Woosley (1978) estimated that the operation and maintenance cost for de-fluoridating  $lm^3$  of water with an initial fluoride concentration not exceeding 9ppm was in the range of 30 to 70 Kenya cents (July 1985 exchange rates). Taking into consideration inflation and the high cost of the alumina in Kenya (which has to be imported) the cost would be at least 5 times the estimate given by Rubel.

#### 2.2.2 Treatment with Alum and Lime (Nalgonda Technique)

Alum or filter alum is the most common name for aluminium sulphate AL2{S04}3.14H20 while lime (slaked) the common name for calcium hydroxide suspension and solution in water Ca{OH}2. These two substances have been used in the coagulation process in water treatment for a long time. However the first serious investigation on the performance of these substances in water defluoridation was probably that done in 1974 by Nawlakhe, Bulusu and their co-researchers working at the central Public Health Engineering Research Institute at Nehru Marg, India. These researchers extended their laboratory work to the field and pilot plant studies in the Nalgonda district of India hence the name Nalgonda Technique.

It was found that the amounts of chemicals required for effective defluoridation were extremely high compared to those required for conventional water treatment plants. A study of alum usage in existing water treatment in Kenya revealed that the range is about 30mg/l for fairly clear water to about 350mg/l for extremely turbid waters. On the other hand it was found that it requires about 400mg/l of alum and about 200mg/l of lime to reduce fluoride level from 7.4ppm to lppm. For fluoride levels above lOppm it was found difficult to reduce them to lppm.

It was also found that when large doses of alum were added to water, the alkalinity was reduced resulting in the depression of pH. Aluminium is amphoteric and in order to facilitate proper formation of the hydroxide floe, it is necessary to add artificial alkalinity to buffer the water. The best way of doing this is by adding calcium hydroxide. Apart from providing artificial alkalinity, the slaked lime forms excellent nuclei for particle agglomeration, which enhances flocculation and hence improves overall precipitation. However it was found from the experiments performed that when large doses of alum were added to water, very large doses of slaked lime were required for effective buffering. In some cases it was found that buffering the water samples was not practical since this required extremely large doses of lime. In all cases it was found that the concentration of

lime that proved effective was much higher than the 1:25 of the concentration of alum. This was the ratio recommended by researchers in India. The adverse effects on treated water included:

- a) Excessive aluminium residuals which may cause Alzheimers disease and dialysis encephalopathy in humans. Davison et al.(1970) found that kidney patients suffered dialysis dementia when the dialysis fluid contained about 80mg/l aluminium ions. Removal of aluminium from the fluid prior to dialysis decreased the symptoms. Elhot and MacDougal introduced literature on aluminium toxicity syndrome that related aluminium to anaemia, encaphalopathy and cardiotoxicity. Only a maximum of 0.1mg/l of aluminium ions is safe for drinking water.
- b) Excessive sulphate levels i.e. above 400mg/l may cause gastrointestinal irritation especially when magnesium and sodium are present. At much higher levels, sulphates may cause diarrhea. The highest desirable level of sulphate in drinking water is 200mg/l while the maximum permissible level is 400mg/l (W.H.O. guidelines on drinking water, 1972). In many of the cases the sulphate level exceeded 200mg/l while in a few it exceeded 400mg/l.
- c) Introduced turbidity into the water which implied that the water needed to be filtered, another shortcoming of the method if its to be used as a household de-fluoridation technique. The highest desirable level of turbidity is 5 F.T.U. while the maximum allowable level is 25 F.T.U. In a good number of cases the turbidity was above 5F.T.U. and the water appeared milky particularly in those cases where flocculation had not taken place properly.
- d) Large proportion of the water ended up as sludge and thus increased the running costs for the method.

#### 2.2.3 Treatment with Alum

Boruff et al (1934) carried out investigations on the removal of fluorides from water by chemical treatment with alum. The fluoride waters used in the tests that were carried out were prepared by treating University of Illinois water supply with various amounts of sodium fluoride. Alum doses were added to 2 - 3 liters containers' having stock water containing various quantities of fluorides. Mixing was carried out for a time of ^minutes by a mechanical stirrer and the mixture was permitted to stand foiM8 - 24 hours; before filtering off the floe. The samples were then tested for pH and fluoride levels.

From the results of the above experiments, it was concluded that:

- a) Good mixing and flocculation were necessary for the maximum removal of fluorides using alum.
- b) The dose of alum used increased as the level of fluoride was increased.
- c) The dose of alum that was used in the removal of fluoride was a little more than that which was used in turbidity removal.

d) pH was an influential parameter on the removal of fluoride with some advantage on pH 6.7. Two years later, after Boruff, et. Al. (1936) carried out studies on the removal of fluoride from drinking waters in the state of Iowa. They used Aluminium Sulphate,  $A12(S0_4)14H_20$ . Experiments were carried out on continuous flow process at a flow rate of 4.541/min. The fluoride level was lowered fromlOmg/1 to 1.5mg/l. It was however found out that doses of alum required for this removal were very high.

Since it was considered that the Nalgonda technique was improvement of this method, no further consideration was given to the development of this technique for the Kenyan situation.(Gitonga, 1985)

### 2.2.4 Treatment with synthetic zeolites

In 1934, Boruff carried experiments using zeolites. He made a contact filter of 55mm glass tube into which were added 490g of synthetic zeolite. Through this filter stock water containing 5mg/l of fluoride ions was passed through at a rate of 51/s, until the whole bed was exhausted. The regeneration process was then carried out using sodium chloride, and then treated with 2% sodium hydroxide for 30minutes. The bed was washed with water until it was free of alkali. From the results of the above experiment, he found that:

a) 4 - 6 liters of effluent had fluoride level of 0.9mg/l.

b) 11-14 liters of effluent had fluoride level of 2.5mg/l.

From the few results available, it was concluded that this method had poor capacity for F~ removal and was expensive. It therefore had poor potential for further development.

### 2.2.5 Chemical treatment with Lime

In the spring of 1935, incident to the routine examination of raw and treated water supplies, Scott noted that the fluoride concentration in the effluents from lime softening plants showed a substantial reduction as compared to the fluorides in the raw water. No reduction was however noted in zeolite softened water. With a view to verify the above observations, Scott et al.(1935) carried out tests using natural water with and without the addition of graded quantities of sodium fluoride. The tests revealed a reduction of fluoride level by lime treatment and that the degree of reduction was a function of removal of magnesium. As a result of the above tests Scott et al.(1935) derived a formula relating to fluoride and magnesium removal. The relationship that was derived was according to the authors, varied between initial fluoride concentration of 1.5 - 3.5mg/l.

Y = F - (0.07F.X)

Where

Y = residential fluoride mg/1

F = Initial Fluoride mg/1

X = Magnesium removal mg/1

Scott et al. (1935) found that magnesium played a vital role in reduction of fluoride. They found that 51 mg/1 magnesium had to be removed to reduce fluoride level from 2mg/l to lmg/1. Thus it was found necessary to add 15mg/l magnesium or 152mg/l magnesium sulphate. In general this process required the addition of large quantities of chemicals in order to remove an acceptable amount of fluorides. Due to this disadvantage, this method of fluoride removal by lime treatment was only used in cases where the water had a high magnesium hardness and needed softening.

Since the water that requires defluoridation is not normally found to require softening here in Kenya, it was concluded that this method had little potential for further development (Gitonga, 1985).

### 2.2.6 Treatment with Defluoron - 1

Bhakuni. (1966) prepared a sulphonated saw dust which is simply called Defluoron - 1. Carbon from the saw dust had been found to remove fluoride. With the view to verify that sulphonated saw dust could be more efficient, Bhakuni prepared 20 - 40 mesh saw dust with sulphuric acid. The excess acid was washed and the sulphonated product was soaked in an alum solution for two hours and finally it was washed to remove the excess alum. The bulk density of the prepared medium was found to be around 620g/l.

Laboratory tests were then carried out using the medium. The stock water that was used was of fluoride level 4.5mg/l, the flow rate Of the continuous flow process was 0.481/min and pH of effluent was 6.6. From the above experiments the volume that was treated up to breakthrough of lmg/1 was 81iters.

This method was found to have poor fluoride removal capacity and to be relatively expensive. The medium was found to have poor hydraulic properties and to suffer from heavy attrition losses. This method was therefore not considered further.

#### 2.2.7 Treatment with Defluoron - 2

After the discouraging results obtained with defluoron - 1, Indian researchers at CPHERI developed another medium in 1968 which they called defluoron - 2. This medium is simply sulphonated coal. This medium was subjected to laboratory and field testing. In the laboratory studies, test water containing 5 - 6mg/l of fluoride ions and with alkalinities of 140 - 168mg/l was passed through a 100mm diameter column. It was found that the average fluoride content of the effluent was 1.15mg/l fluoride ions.

In the field studies, two plants each with an output of 91m<sup>3</sup> of water per regeneration were built in Nalgonda and Hyderabad, India. After extensive testing particularly at the plant in Hyderabad, several problems have been identified with this technique. After four years of continuous operation the plant in Hyderabad showed formation of white deposits over the medium. This reduced the defluoridation capacity by about 60%. The volume of the medium had swollen by about 40%. It showed on analysis that carbonates, fluorides, sulphates, aluminium, calcium, magnesium and iron had accumulated in the medium. Bulusu and his coresearchers estimated in 1979 that the cost of defluoridating water containing between 3 -10mg/l of fluoride ions would cost an equivalent of Kshs. 0.50 - 2.50 per m<sup>3</sup> of water, the cost being highly dependant on the alkalinity of the raw water. Considering inflation and the fact that most of the materials would have to be imported in Kenya, the cost of defluoridating water using this method would be at least 3 times that estimated by Bulusu and his coresearchers. It was observed that even in India where this technique has undergone substantial testing, it has not given very promising results. It was thus also eliminated from further consideration.

#### 2.2.8 Treatment with Magnesia

This technique was tried by researchers in India who prepared magnesium hydroxide by reacting a magnesium salt with calcium hydroxide. The precipitate was filtered, washed and dried. The dried product was calcined at 1000°C for 3 hours to obtain magnesia (MgO). Jar tests were then carried out on water with a fluoride content of lOppm. It was found that doses of 100, 250, 500, 1500 mg/1 were required to give fluoride residuals of 9.5, 8.9, 8.4 and 1.0mg/l

respectively. The pH of the treated water was found to be above 9.0 in all cases thus rendering pH adjustment necessary.

Thergaonkar and Nawlakhe (1970) estimated that the operation cost using this technique was about Kshs. 1.50 per nr of treated water around 1970. The cost at present would be more than five times this figure.

It was apparent after reviewing this method that it was both expensive and complicated to warrant further consideration as a method that could be developed for Kenya.

#### 2.2.9 Treatment with Serpentine

Serpentine is a mineral found in Andra Pradesh province in India and whose composition closely corresponds to the formula Mg<sub>6</sub>Si40io(CH).

After extensive laboratory tests were carried out on this technique in India, it was found out that while it had some ability to remove fluoride from water, the technique would be expensive (about 10 times that of Magnesia!).

### 2.2.10 Treatment with Tricalcium Phosphate

Adler et al (1938) prepared synthetic tricalcium phosphate and carried out pilot plant experiments with it. They passed stock water solution of 30mg/l fluoride ions through the bed until it was exhausted. The regeneration of the bed was done using sodium hydroxide solution, followed by dilute hydrochloric acid wash. The results of the above experiment showed that:

- a) fluoride concentration was reduced from 30 mg/l to 0.3 mg/l on volume of 3 liters.
- b) The exchange capacity of the bed was found to be 240 530g fluoride per cycle.

However, this method was found to be both expensive and complicated.

#### 2.2.11 Treatment with Florex

Florex is the trade name for a mixture of tricalcium phosphate and hydroxy-apatite. This medium was tested in USA but found unsuitable due to high cost, attrition losses and complexity of operation.

### 2.2.12 Treatment with ion - exchange resfns

Strong base exchange resins remove fluorides. Usually the proportional quantity of fluorides as compared to other anions is very small, and the effective capacity of such resins works out to be quite low. There are no known commercial anion exchange resins which are selective for fluoride only.

Some inorganic ion exchangers e.g. complex metal chloride silicate, formed from barium or ferric chloride with silicic acid, also exchange fluoride for chloride. Cation exchange resins impregnated with alum solution have been found to act as de-fluoridation agents. Experiments were carried out by Bhakuni (1966) where the following resins were used.

- i) Polyanion exchange resin (NCL)
- ii) TulsionA-27
- iii) Deacedite, F-F-IP
- iv) Lewatit, mitt-59
- v) Amberlite, IRA-400

Glass columns of 22mm diameter were filled with 6mm diameter resins and a flow rate of 0.491/min was used. The treated water was collected in one litre containers and the columns were regenerated using 0.16kg of sodium chloride. The results of the above experiments showed that:

- a) The resins lost their fluoride removal capacity on prolonged use and a total replacement was found essential.
- b) A layer of white deposits developed over the resin beds attributing to the drop in the removal capacity.
- c) Anion-exchange resins were found to be of relatively low removal capacity of fluorides, and hence were not economical. They imparted a taste to the treated water, making it unacceptable to the consumers.

### 2.2.13 Treatment by distillation process

Distillation process uses a lot of energy. The high capital and running costs of desalination plants can be justified when complete purification of water is required. However a solar unit uses energy from the sun and this makes it less costly. Fluoride laden water is added to a storage reservoir, which is covered with a glass roof, and water evaporated from the reservoir condenses on the roof and is collected. The distilled water should be free of impurities. This is obviously an expensive method for Kenya or any developing country.

#### 2.2.14 Treatment by electrodialysis

Treatment by electrodialysis method is still in the experimental stage. It is thought to have an advantage over the ion-exchange, since it can be carried out without regeneration. Skripach, (1970) carried out experiments using the method for removal of fluoride and other ions from industrial waste water. The study was carried out in a five chamber filter press type electrodialyzer provided

with cationite and anionite membranes based on k4-2 and EDE-10P resins respectively. The cathode was platinum and the anode was titanium. At the end of the process, water was tested for fluoride. The fluoride level was found to drop from 700mg/l to 1.4mg/l. this method would however be expensive and complicated.

#### 2.2.15 Treatment with clay

Clay was found to have relatively little fluoride removal capacity. Even for this relatively little removal capacity a contact time in excess of two days was found to be necessary. When tested on continuous flow basis clay gave even poorer fluoride removal capacity. Crushing clay and thus increasing the surface area improved the fluoride removal capacity. It was not possible to find a satisfactory regeneration method of clay.

### 2.2.16 Treatment with bone charcoal

Fresh bone charcoal was found to be able to reduce fluoride concentration from about 17ppm in borehole water to about 3ppm with a contact time of about 17 minutes. The fluoride removal capacity was found to be about 300mgF per kg of bone. This capacity is increased considerably by regenerating the bone. It was found that the capacity of the bone fell slightly on regeneration. It was however estimated that it should be possible to regenerate the bone about 5 times.

This method was simple except for regeneration. Without regeneration, it would become prohibitively expensive. Bones are locally available and hence would not require any foreign exchange to purchase. However the cost of de-fluoridation was relatively high compared with normal water treatment for example in 1985, the cost of reducing F" from 15ppm to lppm was Kshs 10.50 per m<sup>3</sup> of water (Gitonga, 1985). There is no telling how much this has skyrocketed 20 years later given the present prevailing economic conditions.

#### 2.2.17 Treatment with charcoal from coffee husks

The fluoride removal capacity of charcoal made from coffee husks was found to be too small to allow this kind of method to be of practical use, the charcoal gave capacities comparable to wood charcoal which was tested in Phase I of the study. Not only was coffee charcoal unable to reduce the fluoride concentration to acceptable levels but the removal capacity was found to be too low to warrant further consideration (Gitonga, 1985).

#### 2.3 SUMMARY

presented under section 2.2, various methods have been investigated on their potential to remove fluoride from water. Many of these methods have been found either to be inappropriate due to technological limitations or too costly to be effective in the removal of fluoride.

Recent research/studies on removal of ammonia from waste water by using chokaa (Mwamachi, 1999) and removal of iron and manganese from bore-hole water by using the same material (Kituku,2004) have shown the potential of the locally available material.

The principle mechanisms portrayed in both cases of chokaa application were ion-exchange and adsorption. In this case, chokaa is being investigated for its potential to remove fluoride from water thus the two mechanisms; adsorption and ion-exchange are reviewed in Section 2.4.

### 2.4 THEORY OF ADSORPTION

The process in which chemicals become associated with solid phases is generally referred to as sorption. This phase transfer process may involve interacting either vapor molecules or dissolved molecules with adjacent solid phases (Schwarzenbach, 1993).

A solid surface in contact with a solution tends to accumulate a surface layer of solute molecules because of the imbalance of surface forces. The solute molecules are called the sorbate and the solid is called the sorbent. If the bonds that form between the sorbate and the sorbent are very strong, the process is almost always irreversible and chemical ac/sorption or chemisorption is said to have occurred. On the other hand, if the bonds that are formed are very weak, as is characteristic of van der Waals forces, physical adsorption is said to have occurred (Metcalf and Eddy, Inc., 1979).

### 2.4.1 Adsorption Forces and Mechanisms.

Adsorption from solution at the solid-liquid interface is a complex and imperfectly understood t phenomenon. Before any adsorption studied are discussed, it is imperative to have an understanding of the physiochemical forces and mechanisms thought to be responsible for the adsorption of ions and molecules. These physiochemical forces can be broken into eight categories as listed below (Reinbold et al., 1979; Griffin and Roy, 1985).

### 4 1.1 London-van der Waals.

These are attractive forces arising from momentary dipoles about atoms or molecules caused by small perturbations of electronic motions. These dipoles induce small dipoles in neighboring atoms of opposite sign. Although the momentary dipoles and the induced dipoles are constantly changing position and sign, the net result is a weak attraction (4 to 8 kJ/mol for small molecules and atoms ). These forces are important in adsorption of organics and are generally attributed to the non-ideal behavior in gases. They also have been partially treated by quantum mechanical perturbation theory, which uses polarizabilities, ionization potentials, and the magnetic susceptibilities of the interacting atoms to explain various phenomena such as adsorption.

#### 2.4.1.2 Coloumbic-electrostatic-chemical.

An electrostatic force results from a charged surface due to isormorphous substitution in the mineral lattice (permanent charge) or protonation of surface oxygen and OH groups (pH-dependent charge) and an oppositely charged species, which maintains the electroneutrality of the surface. In layer silicates, substitution of octahedrally or tetrahedrally coordinated cations by cations of lower valence results in a net negative charge. This excess charge can bring about the formation of a diffuse layer of positively charged atoms or molecules about the colloid; the density of this layer is greater at the surface, and then decreases exponentially to the level of the bulk solution. This type of reaction is important in adsorption of organic ions and ionized organic molecules.

#### 2.4.1.3 Hydrogen Bonding.

A hydrogen atom is bonded to two or more other atoms; the "bond" is generally conceived as an induced dipole phenomenon. No universal agreement has been reached on the best description of the hydrogen bond (Huheey, .1978), but it may be considered as the asymmetric electronic distribution of the Is electron of the hydrogen atom by very electronegative atoms (e.g, F,0,S,C1). Hydrogen bonding is probably more than simply an exaggerated dipole-dipole or ion-dipole **it** interaction, since these concepts do not account for molecular geometry in some cases (Huheey, 1978; Cotton and Wilkinson, 1980). In reality, hydrogen bonds may be delocalized covalent bonds, ^e., resonance bonds or multiple-center bonds (Huheey, 1978). The energy of this attraction ranges from 8 to 42 kJ/mol.

'>4.1.4 Ligand exchange-anion penetration-coordination.

IVlany atoms or molecules form coordinated complexes with ligands that range in complexity from simple linear molecules to extensive chelate complexes. These complexes may in turn be bonded to surfaces by hydrogen bonding or by polyvalent cation bridges linking the complex to a charged surface. The possible geometrical arrangements of coordinated complexes bonded to mineral faces are diverse. The bonded coordinated complexes may be displaced by other coordinated complexes that better satisfy electroneutrality requirements (i.e., are stronger complexing agents while being constrained by steric limitations. The energy of ligand exchange reactions with inorganic ions ranges from 8 to 60 kJ/mol.

2.4.1.5 Chemisorption.

In this adsorption process an actual chemical bond, usually covalent, is formed between the molecule and surface atoms. A molecule undergoing chemisorption may lose its identity as the atoms are rearranged forming new compounds at the demand of the unsatisfied valences of the surface atoms. The enthalpy of chemisorption ( $\sim$ AH >29 kJ/mol) is much greater than physical adsorption. The basis of much catalytic activity at surfaces is chemisorption, which may organize molecules into forms that readily undergo reactions. Chemisorption and physical adsorption are often difficult to distinguish from one another because a chemisorbed layer may have a physically adsorbed layer upon it. Moreover, some ligand exchange reactions are chemisorption processes.

2.4.1.6 Dipole-dipole or orientation energy.

This interaction results from the attraction of a permanent dipole for another permanent dipole. The resulting energy of attraction is less than 8 kJ/mol.

2.4.1.7 Induction or dipole-induced dipole.

This type of interaction results from the attraction of an induced dipole brought about by either (1) a permanent dipole or (2) a charged site or species. The energy of attraction is less than 8 kJ/mol, but this force often adds to coloumbic interactions.

? 4.1.8 Hydrophobic effect.

The exact nature of this adsorption mechanism is uncertain. Some investigators believe that hydrophobic adsorption is primarily an entropically driven mechanism brought about by the destruction of the physical cavity occupied by the solute in the solvent, and from the partial loss of structured water molecules about the solute, ordered by van der Waals forces (Hovath et al., 1976; Sinanoglu and Abdulnur, 1965). Other researchers feel that the hydrophobic effect is the result of simple partitioning. Non polar organic solutes tend to migrate from the aqueuos phase to hydrophobic surfaces on the adsorbent (Dzombak and Luthy, 1984; Chiou et al., 1983; Griffin and Roy, 1985).

### 2.4.2 Adsorption models

When assessing the equilibrium proportion of a particular chemical's presence in association with solids for any particular volume of an aquatic environment, one must consider how the total sorbate concentration associated with the sorbent,  $q_e$  (mol.kg<sup>1</sup>), depends on the total chemical concentration in the solution,  $C_e$  (mol.L<sup>1</sup>). Such a relationship is commonly referred to as a sorption isotherm. The term isotherm is used to indicate that one is considering sorption at a constant temperature. Depending on the dominating mechanism(s), sorption isotherms may exhibit different shapes. Experimentally determined isotherms can commonly be fit with a relationship of the form

### *q*< = *kc*;

...

This equation is known as the Freundlich isotherm model; K is referred to as the Freundlich constant; and n is a measure of the non-linearity involved.



Fig. 2.1 Three types of observed relationships between concentrations of a chemical in sorbed state,  $q_e$ , and the dissolved state,  $C_e$ .

From the above equation, three types of curves can be drawn. Case I in Fig.2.1 (n < 1) reflects the situation in which at higher and higher sorbate concentrations, it becomes more and more difficult to sorb additional molecules due to saturation of the adsorbing surface or active sites. Case II (n = 1) reflects those situations in which the attractiveness of the solid for the sorbate remains the same for all levels of C<sub>e</sub>. This is the so-called linear isotherm case. Case III (n > 1) describes a contrasting situation in which previously sorbed molecules lead to a modification of the surface which favours further sorption. Such effects have been seen for surface active compounds like alkyl benzene sulphonates, where the sorbent becomes coated with the sorbate and increasingly exhibits a non polar nature.

Another model commonly used to describe sorption phenomena is the Langmuir isotherm model. This model takes the form of Case I in Fig. 2-2 and can be viewed as a special case of the Freundlich isotherm. The Langmuir equation is based on an equilibrium between condensation and evaporation of adsorbed molecules, considering a monomolecular adsorption layer:

$$q_e = \frac{abC_e}{abc_e}$$

This can be expressed in linear form as

$$He$$
 b ab  $C_e$ 

where,

٠

= amount adsorbed to form a complete monolayer on the surface and a = constant which increases with increasing molecular size.

Since most wastewaters contain more than one substance, which will be adsorbed, direct application of Langmuir equation is not possible. Morris and Weber have developed relationships from the Langmuir equation for competitive adsorption of two substances (Morris and Weber, 1964):

$$U \qquad \frac{a_A b_{a_A} c_{eA}}{1 + a_A C_{eA} + a_B C_{eA}}$$

$$\frac{Cl}{B^{b}B^{C}cB}$$

$$l + a_{A}C_{eA} + a_{B}C_{eB}$$

More complex relationships could similarly be developed for multicomponent mixtures. It should be noted that although the equilibrium capacity for each individual substance adsorbed in a mixture is less than that of the substance alone, the combined adsorption is greater than that of the individuals alone. In industrial application of activated carbon, contact times of less than one hour are usually used. Equilibrium is probably closely realized when high carbon dosages are employed, since the rate of adsorption increases with carbon dosage.

2.4.3 Influence of Molecular Structure and other Factors on Adsorbability

Most wastewaters are highly complex and vary widely in the adsorbability of the compounds present. Molecular structure, solubility, etc., all affect the adsorbability. These effects are shown in Table 2.1 and are based on adsorption on carbon (Eckenfelder Jr, 2000).

fable 2.1 Influence of molecular structure and other factors on adsorbability.

1 An increasing solubility of the solute in the liquid carrier decreases its adsorbability.

2. Branched chains are usually more adsorbable than straight chains. An increasing length of the chain decreases solubility.

3. Substituent groups affect adsorbability:

Hydroxyl	Generally reduces adsorbability. Extent of decrease depends on
	structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many
	amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule. Glyoxylic acid more
	adsorbable than acetic but similar increase does not occur when
	introduced into higher fatty acids.
Double bonds	Variable effects as with carbonyl.
Halogens	Variable effects.
Sulphonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.

4. Generally, strong ionized solutions are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are in general preferentially adsorbed.

5. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.

6. Unless the screening action of the sorbent pores intervenes, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.

7. Molecules with low polarity are more sorbable than highly polar ones.

### 2 5 **KINETICS OF THE ADSORPTION PROCESS**

The pseudo-first order rate equation of the Lagergen has long been widely applied. Boyd et  $_{aj}$  (1947) developed a rate equation, which considered rates of ion-exchange adsorption in the exchange adsorption of ions from aqueous solutions by organic zeolites.

In the cases of diffusion through a boundary liquid film and adsorption kinetics as a chemical phenomenon, the authors concluded that a mass action rate equation for adsorption kinetics as a chemical phenomenon and a diffusion equation for diffusion through a boundary liquid film are the same as the pseudo-first order rate equation of Lagergen.

They also concluded that if film diffusion is rate controlling, the constant of the equation will vary inversely with the particle size and the film thickness; if the exchange is chemically rate controlled, the constant of the equation will be independent of particle diameter and flow rate and will depend only on the concentration of the ions in solution and the temperature.

(Y.S. Ho, G. Mackay, 1999)

A kinetic model for sorption analysis is the pseudo first order rate expression of Lagergren in the form:

Integrating this for the boundary conditions t = 0 to t = t and  $q_t = 0$  to  $q_t = q_t$ , Equation (1) may be rearranged for linearized data plotting as shown by Equation (2):

 $Log(q, -q_t) = log(q, ) - k_{s1}t/2.303$  (2)

Where

 $K_{s}$  is the rate constant of first order sorption (1/min),

 $qi = q_e$  is the amount of solute sorbed at equilibrium (mg/g),

qt = q is the amount of solute sorbed on the surface of the sorbent at any time t (mg/g). (Y.S. Ho, G. Mackay, 1999)

### 2.6 Theory of Ion Exchangie.

Ion exchange refers to the process by which ions of a given species are displaced from an insoluble exchange material by-ions of a different species in solution. Ion exchange can be used for the removal of undesirable or recovery of useful anions and cations from a wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Ion exchange also takes place in

living materials because cell walls, cell membranes, and other physiological structures have charges.

An ion exchange resin is a natural or synthetic material with electrically charged sites at which one ion may replace another. Natural soils contain solids with charged sites that exchange ions, and certain minerals called zeolites have exhibited remarkable ion exchange properties. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerization of organic compounds into a porous three-dimensional structure. The degree of cross-linking between organic chains determines the internal pore structure, with higher cross-link density giving smaller pore sizes. From a kinetic viewpoint, a low degree of cross-linking would enhance diffusion of ions through larger pores. However, physical strength decreases and swelling in water increases as cross-link density is lowered. The functional ionic groups are usually introduced by reacting the polymeric matrix with a chemical compound containing the desired group. Exchange capacity is determined by the number of functional groups per unit mass of resin.

2.6.1 Types of Ion Exchange Resins.

Basically, there are two types of ion exchange resins: cationic and anionic. Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions. Cation exchange resins have acidic functional groups, such as sulphonic, whereas anion exchange resins contain basic functional groups, such as amine. Ion exchange resins are often classified by the nature of the functional group as strong-acid, weak-acid, strong-base, and weak-base. The strength of the acidic or basic character depends upon the degree of ionization of the functional groups, as with soluble acids or bases. Thus, a resin with sulphonic acid groups would act as a strong-acid cation exchange resins are listed below:

2.6.1.1 Strong-Acid Cation Resins.

Strong-acid resins are so named because tlieir chemical behaviour is similar to that of a strong acid. The resins are highly ionized in both the acid  $(R-SO_3H)$  and salt  $(R-SO_3Na)$  form.

2 6.1-2 Weak-Acid Cation Resins.

In a weak-acid resin, the ionizable group is a carboxylic acid (-COOH) as opposed to the sulphonic acid group (SO<sub>3</sub>H) used in strong acid resins. These resins behave like weak organic acids that are weakly dissociated.

2.6.1.3 Strong-Base Anion Resins.

Like strong-acid resins, strong base resins are highly ionized and can be used over entire pH range. These resins are used in the hydroxide (OH) form for water deionization.

2.6.1.4 Weak-Base Anion Resins.

Weak-base anion resins are like weak-acid resins, in that the degree of ionization is strongly influenced by pH.

2.6.1.5 Heavy-Metal Selective Chelating Resins.

Chelating resins behave like weak acid cation resins but exhibit a high degree of selectivity for heavy metal cations. Chelating resins tend to form stable complexes with the heavy metals. In fact the functional group used in these resins is an EDTA compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

2.6.2 Ion Exchange Reactions (Kinetics).

The ion exchange reactions that occur depend upon chemical equilibria situations in which one ion will selectively replace another on the ionized exchange site. Cation exchange on the sodium cycle can be illustrated by the following reaction:

 $^{\mathbf{N}}\mathbf{a}_{2}\mathbf{.R}$  +  $\mathbf{Ca}^{2+}$   $\leq$   $\geq$   $\mathbf{Ca.R}$  +  $\mathbf{2Na}^{+}$
volumer R represents the exchange resin. When all the exchange sites have been substantially replaced with calcium, passing a concentrated solution of sodium ions through the bed can regenerate the resin. This reverses the equilibrium and replaces the calcium with sodium.

A 10% brine solution is usually used for regeneration:

 $_{2}Na^{+}$  + Ca.R Na<sub>2</sub>.R + Ca<sup>2+</sup>

Similar reactions occur for cation exchange on the hydrogen cycle:

 $\mathbf{C}\mathbf{a}^{2+}$  + H<sub>2</sub>.R <sup>4</sup> • Ca.R + 2H<sup>+</sup>

Regeneration with 2 to 10% H2SO4 yields:

**Ca.R** + 2H<sup>+</sup> <sup>4</sup> • H<sub>2</sub>.R + Ca<sup>2+</sup>

Anion exchange similarly replaces anions with hydroxyl ions:

 $so_4^2$  + R.(OH)<sub>2</sub> R.SO4 + 20H

Regeneration with 5 to 10% sodium hydroxide will renew the exchange sites:

$$R.SO4 + 20H$$
  $R.(OH)_2 + SO4^{20}$ 

In addition to the factors of concentration, the nature of the exchanger, and the exchanging ions, such factors as temperature and particle size of the exchanger are also of considerable importance to the kinetics of ion exchange. The degree of ion exchange depends on several factors:

- The size and valence (charge) of the ions entering into the exchange.
- The concentration of ions in the water or solution.
- The nature (both physical and chemical) of the ion exchange substance.
- The temperature.

2 6.3 Ion Exchange Capacity.

The performance and economics of ion exchange are related to the capacity of the resin to exchange ions and to the quantity of regenerant required. The total capacity of the ion exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of milliequivalents per dry gram of resin or in terms of milliequivalents of wet resin. In some cases capacity has been expressed as kilograms of CaCC<sup>^</sup> per unit of bed volume or as mass of ions per unit volume of bed. In like manner, the quantity of ions to be removed from the wastewater is expressed as equivalents per liter of wastewater to be treated (Eckenfelder Jr, 2000).

In a fixed-bed exchanger, there is a relationship between the operating capacity of the bed and the quantity of regenerant employed. Resin utilization is defined as the ratio of the quantity of ions removed during treatment to the total quantity of ions that could be removed at 100 percent efficiency. The regenerant efficiency is the quantity of ions removed from the resin compared to the quantity of ions present in the volume of regenerant used. The resin utilization will increase as the regenerant efficiency decreases (Eckenfelder Jr, 2000).

### 2.7 NATURAL ZEOLITES

#### 2.7.1 Occurence

They are crystalline aluminosilicates with base- exchange and molecular sieve properties, having three-dimensional, micro-porous lattice framework structures of tetrahedral oxide units. They are also compounds isomorphous to crystalline aluminosilicates wherein the aluminium and silicon atoms in the framework are partly or wholly replaced by atoms of other elements, e.g. gallium, germanium, phosphorus or boron (IPC<sup>7</sup>, 2001).

Zeolites are naturally formed by the hydrothermal alteration of suitable precursors e.g. volcanic glass, clay minerals, vitric tuffs, or biogenic silica. The process is usually accomplished in the presence of water with a high pH. Zeolite formation occurs in nature over a wide range of circumstances. These include lakes, soils, the sea bed, in hot springs or deep underground. The final Product depends on the prevailing ambient conditions e.g. of pressure and temperature.

The nomenclature of zeolites is rather haphazard. Natural zeolites such as sodalite, faujasite, and  $_{nl}$  ordernite, were named by the mineralogists who first described them (Berkout, 2001).

### 7 7.2 Properties of zeolites

### Molecular Sieve effects

Zeolites have the ability to act as molecular sieves, which perhaps is their most unique feature. Within the supercages guest molecules can reside. The strictly defined, uniform shape and size of these cages make sure only molecules of a certain size or smaller can penetrate within the zeolite and adsorb there. This property allows for the very efficient use of zeolites in separation processes. Other materials such as alumina, carbon or porous glass have molecular sieve properties as well, but none so versatile as zeolites have. The main reason for this is the poor pore size distribution in these other materials.

### Water Sorption/Desorption

Water molecules in the zeolite channels are bonded by forces of dipole interactions from cations forming their close surrounds. This water is lost relatively easily often without any change in the 3 - D structure of the zeolite; which has now room to host other molecules.

### Si/Al ratio

This is the measure of the amount of silicon in relation to that of aluminium in the zeolite sample. This ratio determines the zeolite framework which influences most, if not all the zeolite properties. The number of cations present in a zeolite is defined by the Si/Al ratio, because only an  $(AIO^{-1})$  unit needs a charge balancing cation. Al-O-Al bonds are not formed because this would lead to a disadvantageously close proximity of negative charges: therefore the Si/Al ratio must be 1 or greater. If its closer to 1, the framework structure has a rather high net charge, there are many counter ions present, and the zeolite is highly hydrophilic. On the other hand, a very high Si/Al ratio renders a strongly hydrophobic zeolite, with barely counter ions at all. Obviously this also means that a zeolite with a«high Si/Al ratio has rather few ion exchange sites. The Si/Al ratio also determines the window sizes in the zeolite structure. The unit cell dimensions decrease upon increase of the Si/Al ratio, because the Si-0 bond is shorter than the Al-0 bond (1.62A and 1.75 A,

respectively), which leads to the smaller dimensions of the cages and sometimes to subtle **differences** in behavior.

### Ion Exchange

The presence of trivalent aluminium ions gives rise to surplus of negative charge hence the need for counter ions. The number of counter ions present in the unit cell thus depends on the Si/Al ratio. In natural zeolites the most common counter ions are Na<sup>+</sup> and Ca<sup>2+</sup>. These counter ions reside within the 3-D network. They are easily traded in for other ions by ion exchange. Through ion exchange, other metal ions can be introduced and this might influence the supercage size, thereby modifying the molecular sieving or catalytic properties of the zeolite, or promote intersystem crossing.

### Adsorption

Zeolites are able to adsorb other molecules because of the charge imbalance arising from the presence of trivalent aluminium ions in their structures. Adsorption of molecules within the zeolite is influenced by the polarity or electrical field strength within the zeolite. This depends on, among other things, the net charge of the framework (defined by Si/Al ratio), the size and shape of the supercage, the presence of other adsorbed molecules, and the number and size of the counter ions.

### Catalytic properties

Due to the high net charge on zeolite mineral surfaces, they are able to take part in catalytic reactions through the formation of intermediary surface complexes.

### 2.7.3 Uses of zeolite

Zeolites can be used in construction either as a source of dimension stone or as a pozzolanic raw material. They also have a wide range of uses due to their special properties of ion exchange, water and gas adsorption and as catalysts. Of particular importance to developing countries are the many ways in which zeolites can be utilized in agriculture and environmental clean up and protection measures (Parham 1984; Mumpton 1985);\*

### 2-7.4 Natural zeolite as ion exchange resin and adsorbent

Zeolite is a form of ion exchange material, which acts like an insoluble salt, acid or base. One ion is fixed and the other is free. The mobile ions can be exchanged under suitable conditions for others of

the same polarity. If the mobile ion is electropositive the zeolite is cationic, and if negative it is anionic. Zeolites are known to have special properties of ion exchange, water and gas adsorption. It vvorks by a combination of ion exchange and adsorption. If the concentration of counter ions in the solution is low, ion exchange takes place, but with higher concentration of counter ions, adsorption takes place (S.E. Jorgensen; 1974). The structure of zeolite contains channels of defined sizes which are occupied by cations and water molecules and also additional anions. The selective ability to exchange depends on the diameter of the channels and that of intruding ions.

### **CHAPTER 3**

### **RESEARCH METHODOLOGY**

### **31** SOURCE OF MATERIAL

The sorbent being investigated was a natural material mined from quarries in Muranga, Kenya and is locally referred to as "chokaa" (swahili for chalk). It was bought at the Gikomba market where it was sold in small lumps retailing at Kshs 2 each. Its principal users are expectant mothers who chew it.

The department of Mines and Geology of the Ministry of Environment Natural Resources and Wildlife identified it as a Volcanic tuff. Tuff is just a name for rock that was once loose pyroclastic material. It could have been fine ash or coarse cinders but once it cements together (by natural weathering processes) it is called tuff (Scott Rowland, 2003). The Department of Mines and Geology also determined it's chemical composition. The sample was found to be rich in Na<sup>+</sup>, K<sup>+</sup>, and Fe<sup>"</sup>, suggesting the chemical name Hydrated Ferrous Sodium Potassium Aluminosilicate.

### 3.2 SORBENT - CHOKAA TREATMENT

- The lumps were pulverized into smaller particles.
- The pulverized material was placed in an oven at 103°C for 24 hours to drive off moisture. This was then sieved into different particle size ranges (0.3-0.6mm, 0.6-1.2mm, 1.2-2.4mm).
- Each sieved fraction was washed thoroughly with distilled water to remove foreign impurities and the finer particles e.g. dust.
- Washed particles of the material were placed in an oven at 103°C for 12 hours after which they were cooled in a dessicator to room temperature. The fractions were then stored in airtight bottles ready for use.

### **3.3 SORBATE - FLUORIDE PREPARATION**

Stock solution of sodium fluoride  $100 \pm 0.5$  ppm as F was prepared.

On dilution with distilled water the solution showed fluoride activities at  $25 \pm 0.5$  °C as shown in Table 3.1.

Dilution	Fluoride concentration in	Fluoride activity in ppm F"
	ppm F"	
None	100	82.2
1:5	20	19.0
"HT"	10	9.71
1:50	2	1.98
1:100	1	0.991

fable 3.1 Fluoride activity in ppm F" per Fluoride concentration

For fluoride concentration above 20ppm the fluoride activity was less as shown in the table above therefore the experiments were confined within the range 1-20ppm.

### **3.4 THE FLUORIDE METER**

The fluoride meter was an Orion model 94-09 fluoride and model 96-09 combination fluoride electrodes which had the following specifications:

- a) Concentration range saturated solutions to  $10^{10}M$  (0.02ppm)
- b) pH range pH 5-7 at 10"<sup>6</sup>M (O.Olppm F") to pH 11 at 10<sup>-1</sup>M (1900ppm F")
- c) Temperature range 0 to 80°C continuous use, 80 to 100°C intermittent use
- d) Electrode resistance 150 200 Kilo ohms
- e) Reproducibility  $\pm 2\%$
- f) Minimum sample size 3ml in a 50ml beaker
- g) Size Electrode Length: 13.9cm (3cm cap), Body diameter: 1.2cm, Cap diameter: 1.6cm, Cable length: 100cm.

The required solutions for this model were:

- a) Distilled water to prepare all solutions and standards
- b) Standard solutions lOOppm fluoride standard was used
- c) Electrode filling solutions model -.94-09 with model 90-01 reference electrode where equitransferen^filling solution was used.
- d) Combination filling fluoride solution, Total Ionic Strength Adjustor (TISAB) to provide constant background ionic strength, de-complex fluoride and adjust solution pH. TISABII was used whereby 50ml TISABII was added to each 50ml sample or standard.

,roducibility of the instrument is limited by factors such as temperature fluctuations, drift and noise- Within the electrode's operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements reproducible to  $\pm 2\%$  can be obtained. (Orion, 1991)

### **35 EXPERIMENTAL PROCEDURE**

<sub>a</sub>) Fluoride at varying concentrations, (2,5,10,15,20,25,30,35ppm) was used in all plastic volumetric flasks.

b) Distilled water and tap water were used for dilution.

c) The fluoride solution was mixed with ehokaa of varying masses, (5,7.5,10,15g) and shaken at different time intervals (15,30,60,120min).

d) The liquid part was removed by decantation.

e) Using the fluoride meter, and the Filtrate, the concentration of fluoride ions before and after adding ehokaa was determined.

f) Different particle sizes of ehokaa, (0.3-0.6mm, 0.6-1.2mm, 1.2-2.4mm) were used to determine the most effective particle size.

### 3.6 TRIAL SORPTION STUDIES

These were carried out in order to determine the equilibrium time and to investigate the nature and rate of the sorption process.

Plastic conical flasks of 250ml capacity were used in the trial sorption equilibrium experiments. Water samples (50ml) with known fluoride concentration were introduced into the flasks. Carefully weighed amounts of sorbent materials were added into the flasks which were then stoppered and shaken at 100 r.p.m on an electric shaker for a prescribed length of time. The samples were then filtered and analyzed for residual fluoride concentration. (APHA-AWWA-WCPF, 1975)

### 3.7 DETERMINATION OF OPTIMAL DOSE

In order to determine the optimal dose of the sorbent to be used in subsequent experiments, 50ml of different fluoride concentration were shaken with varying amounts of sorbent of particle sizes 0.3 - 0.6mm, 0.6 - 1.2mm, 1.2 - 2.4mm for prescribed lengths of time. The mass of sorbent used was 5g, <sup>7</sup>-%10g and 15g. All subsequent experiments were carried out using the optimal mass of sorbent.

### **3 g** BATCH ADSORPTION ISOTHERMS

After establishment of the optimal conditions, batch experiments were conducted for the development of adsorption isotherms, a maximum of three samples per measurement was used. For all the different particle size ranges, the equilibrium time was determined. Experiments were carried out for fluoride ion concentrations of 2, 5, 10, 15, 20, 25, 30, and 35mg/l in each case. The 50ml of sample was taken and shaken with the optimal mass of sorbent in tightly stoppered conical flasks of 250ml capacity.

For investigations into the effect of temperature and pH, 0.3 - 0.6mm, 0.6 - 1.2mm, 1.2 - 2.4mm particle size ranges were used. The pH range investigated was between 6-7. The experiments into the effect of temperature were carried out in a temperature controlled fridge chamber and at room temperature (14 °C and 25°C respectively).

### **3.9 CONTROL EXPERIMENTS**

These were carried out using either distilled water or tap water mixed with fluoride solution as the blanks.

Tap water has natural ions and the aim of the control experiments with tap water was to investigate the influence of natural ions.

#### 3.10 COLUMN STUDIES

The schematic setup for column study is as shown in Fig 3.1. The column used was of transparent glass-like plastic material and was 3.4cm diameter, 25.2cm long and at a water head of 49.5cm. The column was operated at 4ml/min. The operation of the column was stopped after the flow rate reduced to 0.5ml/min.

The objective of the column experimental work was to study the effect of process parameters such as raw water inlet concentration compared to outlet concentration and possibility of regeneration after chokaa has been completely exhausted. Samples of the outlet bulk solution were collected after a fixed time interval and examined for the F" concentration. Exhausted chokaa was regenerated *insitu* using carbonate/acid treatment.

To regenerate, ehokaa was first rinsed with O.lNsodium carbonate solution; then with dilute hydrochloric acid (0.1N); and finally with distilled water twice. After being air died, the material was ready for reuse.(Xanxin, 1999; Subhashini et al, 2001).



Schematic diagram of experimental set-up for column study. (Source :Subhashini et.al., 2001)

Column height = 25.2cm, Column diameter = 3.4cm, Head = 49.5cm, Column Bed Area = 9.079cm<sup>2</sup>, Volume = 228.796 cm<sup>3</sup>

Fig 3.1 Schematic diagram of experimental set-up for column study.

### **CHAPTER 4**

### **RESULTS AND DISCUSSION**

### <sub>4</sub>J CHEMICAL ANALYSIS

The chemical analysis of chokaa was done and the results are as shown in Table 4.1. This was according to the analysis carried out at the mines and Geological Department, Ministry of Environment and Natural Resources. The sample is rich in  $Na^+$ ,  $K^+$ , and  $Fe^{2+}$ , suggesting the chemical name Hydrated Ferrous Sodium Potassium Aluminosilicate.

Table 4.1 Chemical analysis results of chokaa

CONSTITUENT	% BY WEIGHT
Si0 <sub>2</sub>	57.47
AI2O3	12.30
CaO	0.74
(MgO	0.42
Na <sub>2</sub> 0	3.10
K <sub>2</sub> O	2.60
Ti0 <sub>2</sub>	1.05
MnO	0.13
$Fe_2O_3$	7.70
LOI	5.8

LOI is Loss On Ignition

Si/Al ratio = 4.12

(Ministry of Environment and Natural Resources - Mines and Geological Department) (Adapted from Mwamachi,2004)

### 4.2 PHYSICAL AND CHEMICAL PROPERTIES OF CHOKAA

Some physical and chemical properties of chokaa were tested. These included color, specific gravity, hardness and pH. The results are shown in Table 4.2.

Table 4.2 Physical and chemical properties of chokaa

Color	Creamish white - whitish grey
Specific gravity	2.2-2.4
Hardness	Relatively soft
Suspension pH	6.2

### 4.3 Cationic Exchange Capacity (CEC) of chokaa

The cation exchange capacity of chokaa was measured and the results are as shown in Table 4.3. The test was done at the University of Nairobi, Kabete campus, Department of Soil Science.

Table 4.3 The CEC of chokaa

	cmol/kg					
Sample	Κ	Na	Ca	Mg	CEC	
description						
Chokaa	0.8	3.33	5.35	6.33	16.40	

Any element with a positive charge is called a cation and in this case it refers to the basic cations potassium  $(K^{+1})$ , sodium  $(Na'^{1})$ , calcium  $(Ca^{2})$ , magnesium  $(Mg^{42})$  and the acidic cations, Hydrogen  $(H^{+1})$  and aluminium  $(Al^{+3})$ . The amount of these positively charged cations a sample can hold is described as the CEC and is expressed in centimoles per kilogram of chokaa as shown above.

The percent base saturation tells what percent of the exchange sites are occupied by the basic cations in our case, the percent base saturation is as follows:

0.8+3.33+5.35+6.33= 15.81 cmol/kg

i

Percent base saturation = (15.81/16.4)\* 100 = 96.4%

The acidity is the amount of the total CEC occupied by the acidic cations ( $H^{+1}$  and Al). In our <sup>ca</sup>se; only 3.6% of the ions are acidic? This is equivalent to 0.59cmol/kg of acidic ions.

<sup>1</sup> is therefore the high presence of cations^vhich makes it possible for fluoride removal from <sup>so</sup>lution. (Lippert 200 V)

### 4 4 DETERMINATION OF OPTIMAL MASS

fable 4.4 shows the results obtained in determination of optimal mass of chokaa.

-phis was done by shaking 50ml of 20mg/l fluoride solution in tap water for one hour with different masses of sorbent of varying particle sizes. Two samples were used in this experiment. This was a consequence of the limited resources at the time but under normal circumstances, three samples would be used.

#### Table 4.4 Data on optimal mass of chokaa

TARTICLE	Fluoride removal capacity (%) for different masses				
SIZE (mm)	5g	7.5g	lOg	15g	
0.3 - 0.6mm	67.9	70.8	77.7	77.5	
0.6 - 1.2mm	65.6	68.5	74.2	73.9	
1.2 - 2.4 m m	59.2	67.3	68.9	68.8	

From Table 4.4, the highest achievable fluoride removal of 77% occurred at lOg and 15g. However, lOg was selected for subsequent experiments.

### 4.5 DETERMINATION OF EQUILIBRIUM TIME

Table 4.5 shows the results obtained in determination of equilibrium time where 50ml of 20mg/l fluoride solution in tap water were shaken at varying times with lOg mass of sorbent of different particle sizes. Two samples were used in this experiment and the table shows the average obtained from the results.

Ta	ble	4.5	Data	on	equi	li	brium	time
----	-----	-----	------	----	------	----	-------	------

PARTICLE SIZE (mm)	Fluoride removal capacity (%) for varying times				
	15min	Two hours			
0.3 - 0.6mm	60	68.6	77.7	77.2	
0.6- 1.2mm	52.9	70.6	74.2	74	
1.2 - 2.4mm	52	56.6	68.9	68.2	

From Table 4.5, the highest achievable fluoride removal of 77% occurred after one hour and two hours. Hence one hour is considered the equilibrium time for the conditions investigated.

### 4.6 KINETICS OF EQUILIBRIUM

Tables 4.6 and 4.7 contain data used for the determination of the order of reaction, 50ml samples <sup>w</sup>ere drawn after15, 20, 30, 60, and 120mins

to determine the percent removal after each of these <sup>tlf</sup>nes and hence the removal mechanism. Three samples were used in this experiment and the

averages obtained. The experimental conditions were lOg of sorbent particle size 0.3 - 0.6mm in contact with 50ml solutions of 20 mg/1 fluoride ions in tap water. After 15minutes, 60% of the fluoride had been removed from solution. This was indeed a very fast reaction. After 45 minutes, only 16% was removed. The results therefore show that the reaction takes place in two stages. Stage one is a fast reaction followed by stage two which is a slow reaction. The fast reaction could be due to the easily accessible sites for adsorption which might be on the particle surface. The slow stage is due to the longer time the fluoride ions take to access the active sites in the pores of the chokaa. Thus the second stage being diffusion controlled. This is confirmed by the Lagergren plot in fig 4.1.

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F sorbed,X (nig)	Amount sorbed per unit weight, qe	Removal efficiency %
15	50	35	14	1.05	0.105	60
20	50	35	12	1.15	0.115	65.7
30	50	35	11	1.2	0.12	68.6
60	50	35	8.2	1.34	0.134	76.6
120	50	35	8.1	1.345	0.135	76.9

Table 4.6 Fluoride removal as a function of time

Table 4.7 Data for Lagergen plot

Time	(Time) <sup>172</sup>	Cc	qi	qt	(qi - q <sub>t</sub> )	Log(q,-q <sub>t</sub> )
(min)	$(min)^{,/2}$	(mg/1)	(mg/g)	(mg/g)	(mg/g)	Logio
15	3.87	14	0.14	0.105	0.035	-1.46
20	4.47	12	0.14	0.115	0.025	-1.6
30	5.48	11	0.14	0.12	0.02	-1.7
60	7.75	8.2	0.14	0.134	0.006	-2.22
[Tier	10.95	8.1	0.14	0.135	0.005	-2.3

...



Fig 4.1 Lagergren plot (25±°C) for removal of fluoride ions by chokaa)

The possibility that the diffusion of sorbate ions from solution into the pores of the sorbent is the rate controlling step and was investigated by determining the relative sorption rate or intra particle diffusion constant. The relative sorption rate, described by coefficient,  $k_p$ , is obtained by plotting the

amount of sorbed solute per unit weight of sorbent, q, against the square root of time t " (Morris and Weber, 1963).

The Lagergren plot in fig 4.1 is a straight line fit which shows that the reaction rate is diffusion controlled.

### 4.7 EFFECT OF SORBENT DOSAGE

Table 4.8 shows the effect of increasing the mass of chokaa on sorption.

The particle size ranges were 0.3mm - 0.6mm at 25°C, contact time, one hour in 25mg/l fluoride.

Table 4.8 The % sorption of fluoride ions from solution vs sorbent dosage in tap water.

MASS g, PER 50ML F	% SORPTION
5	67.9
7.5	70.8
10	77.7
on	77.5



Plot of % sorption of Fluoride ions vs sorbent dosage

Fig 4.2 Plot of % sorption of fluoride ions from solution vs sorbent dosage

The results show that lOg and 15g mass of sorbent was the optimum chokaa dose for the fluoride concentration of 25mg/l and for particle size 0.3-0.6mm.

At lOg and 15g the percent sorption was constant because there was not enough fluoride under the prevailing conditions. The lOg mass was the maximum mass of chokaa that was required for 50ml of fluoride solution anything beyond it showed no change in sorption, hence its choice. It was observed that the other particle sizes showed the same characteristic.

### 4.8 EFFECT OF SORBENT PARTICLE SIZE

Table 4.9 and Figure 4.3 show the effect of sorbent particle size on fluoride removal for lOg of sorbent (50ml solutions) in 20mg/l fluoride ions in tap water shaken for one hour at 25°C and pH range 6-7

PARTICLE SIZE (mm)	TIME (mins)	% REMOVAL
ТВ-6	15	60
	20	65.7
	30	68.6
	60	76.6
	120	76.9
1)^1.2	15	52.9
	20	56.6
	30	70.6
	60	74
	120	74.3
"IX-2.4	15	52
	20	53.1
	30	56.6
	60	67.7
	120	68
	1	1

•fable 4.9 Fluoride removal as a function of time for different sorbent particle sizes.

## plot of % removal vs time for different particle size ranges of chokaa



Fig 4.3 Plot of percentage removal versus time for different particle size ranges of chokaa

From the plot it is observed that there w^s not much difference in mass of fluoride removal in differing particle sizejanges. However, 0.3 - 0.6 mm size showed the highest percent removal of 76% after one hour whereas 0.6-1.2mm had 74% removal and 1.2-2.4mm had 70% removal.

pslotably, the size of the particle has effect on adsorptive capacity as expressed by total surface area.  $j_t$  is well known that smaller particles of a given mass of ehokaa would have a greater surface area than larger particles.

The observed results may not have shown much difference probably because there was not much difference in the attractiveness between 0.3-0.6mm and 0.6-1.2mm particle sizes, i.e. there was no remarkable difference in their surface areas.

The postulated mechanism of association between fluoride ions and ehokaa was that there was net positive charge in the ehokaa due to presence of unbalanced ions, aluminium and silicon. Thus an attractive force between the negatively charged fluoride and the net positive charge. When the charge is balanced then maximum adsorption is attained.

### 4.9 SORPTION EQUILIBRIUM ISOTHERMS

Equilibrium studies were carried out for different particle size ranges on distilled water and tap water. The results are attached in the appendix. Langmuir isotherm model and Freundlich model were both evaluated and the best fitting model used. Table 4.10 and Fig 4.4 show results of the isotherm equilibrium studies on different particle size ranges where lOg of sorbent were shaken for one hour in 50ml solutions of varying concentrations (2mg/l - 35mg/l)of fluoride ions in tap water at 25°C and pH range 6-7. The single measurements for Table 4.10 were done instead of duplicate measurements due to limited resources.

particfe size ranges	Initial	Equilibrium	Amount sorbed, Q.
	concentation, C <sub>0</sub>	concentration, C <sub>c</sub>	(mg/g)
	(mg/1)	(mg/1)	
'oX-0.6mm	2	0.8	0.006
	5	1.2	0.019
	10	2.2	0.039
	17	2.5	0.0725
	35	8.2	0.134
0.6 -1.2mm	2	1.4	0.003
	5	2.3	0.0135
	10	3.1	0.0345
	17	4.2	0.064
	35	9.2	0.129
1.2 - 2.4 mm	2	1.6	0.002
	5	2.5	0.0125
	10	4.2	0.029
	17	5.2	0.059
	35	11	0.12

### fable 4.10 Results of equilibrium studies on different particle size ranges



isothermal plots for different size ranges



Fig 4.4 Isothermal plots for different particle size ranges.

The empirical coefficients in the Freundlich equation were obtained by plotting  $lnQ_e$  versus  $lnC_c$  or  $Q_e$  versus  $C_e$ .

Experimental data are often plotted in this manner as a convenient way of determining whether removal of materials from solution is accomplished by adsorption, and also as a means of evaluating the constants.

The Langmuir isotherm is used to describe single layer adsorption and its linear transformation can be written as follows:

 $1/q_e = 1/a + 1/abC_e$ 

Selection of an appropriate adsorption rjiodel is made by fitting the adsorption isotherms to experimental data. v

The Freundlich adsorption isotherm is an empirical expression and it has proved useful under widely varying conditions as would be predicted.

fable 4.11 shows the Freundlich and Langmuir parameters and why Freundlich was best fitting niodel for all particle size ranges.

"particle	Freundlich model parameters			Langmuir model parameters			
sizes							
	1/n	k	$R^2$	а	b	$R^2$	
"0>0.6mm	0.7249	0.114	0.8361	-0.02	-0.4	0.8725	
1x6^1-2 mm	2.01	3.16* 10" <sup>J</sup>	0.9128	-0.01	-0.2	0.8655	
75-2.4mm	2.0661	1.58*10" <sup>J</sup>	0.9242	-0.005	-0.22	0.8252	

fable 4.11 Freundlich and Langmuir model parameters

The Langmuir model shows negative coefficients 'a' and 'b\ However negative coefficients have no meaning therefore the Langmuir isotherm is inappropriate. (Tchbanoglous, 1987)

The Freundlich model has a good fit and hence it was appropriate. However in studies carried out by Mwamachi, 2004 in the removal of ammonia, Langmuir model showed the best fit. This may have been due to a difference in medium of adsorption. Ammonium ions are positively charged whereas the fluoride ions are negatively charged. The postulated mechanism of association between fluoride ions and chokaa is that there is net positive charge in the chokaa due to presence of unbalanced ions, aluminium and silicon. Thus an attractive force between the negatively charged fluoride and the net positive charge. When the charge is balanced then maximum adsorption should be attained. Langmuir model would still be the postulated mechanism of adsorption between the fluoride and the chokaa action sites.

### 4.10 EFFECT OF TEMPERATURE

Table 4.12 and Fig 4.5 show the effect of temperature on amount sorbed by 0.6 -1.2 particle size ranges at 14°C and 25°C. The sorbent was shaken for one hour with 50ml solutions of varying concentrations of fluoride ions in tap water.

-j-able 4.12 The Effect of temperature on amount sorbed by 0.6 -12mm particle sizes at 14°C and  $25^{\circ}$ C

	Temperature °C										
1	4°C	2	5°C								
Equilibrium	Amount	Equilibrium	Amount								
cone. Ce	sorbed, Q <sub>e</sub>	conc. C <sub>e</sub>	sorbed, Q <sub>e</sub>								
(ing/il	(mg/g)	(mg/1)	(mg/g)								
1.8	0.001	1.4	0.003								
4.2	0.004	2.3	0.0135								
6.3	0.0185	3.1	0.0345								
I 7 H	0.049	4.2	0.064								
22	0.065	9.2	0.129								



Fig 4.5 Isothermal plots to show the effect of temperature on sorption

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The effect of temperature on equilibrium was carried out at 14°C and at room temperature,  $25\pm$ °C. The results presented in Fig 4.5, suggest that the sorption of fluoride ions on chokaa is endothermic. The rate and extent of sorption increased v^ith temperature appreciably. This was similar to studies

done by Mwamachi, 2004, whereby removal of ammonium ions by chokaa showed an endothermic process as well.

The direction and magnitude of the temperature dependency will depend on the specific solutesorbent system. An early paper by Jurinak and Bauer (1956) reported that the sorption of zinc by calcite was exothermic; the amount of zinc sorbed decreased with increasing temperature. In  $_{c0}$ ntrast, Kuo and Mikkesen (1979) studied the sorption of zinc by soils at temperatures ranging from 10°C to 35°C and found that zinc sorbed endothermically; increased sorption was associated with higher temperatures.

Sorption at the solid-liquid interface tends to occur when the attractive forces between the surface <sup>a</sup>nd ionic solutes are greater than those between solutes and the solvent (Zottlemeyer and Micale, 1971). The sorption of an ionic or polar solute is often the result of a thermodynamically favorable change in the enthalpy (AH) (Hasset et al, 1981) or sometimes of a favorable change in the entropy (A S) of the system in which the -T AS term of the Gibbs-Helmholtz equation compensates for the positive value of AH (Thomas, 1961) where T is the temperature of the system. Thus the sorption behavior of ionic or polar solutes will probably show some temperature dependency.

### 4.11 COLUMN STUDIES

Bench scale column studies were done to determine the flow rates and removal efficiency of fluoride. These were done as a way of assessing the possible application of chokaa in a water treatment process. Influent concentration used was 9.5mg/l at an initial flow rate of 4ml/min. Table 4.13 shows the removal efficiency of the fluoride ion by chokaa.

Sample	Original F" conc. (ppm)	Final F conc. (ppm)	Fluoride Removal	Volume of Sample (ml)	Time (min)	Flow Rate (ml/min)
			%			
1	9.5	1.3	86.3	80	20	4
2	9.5	1.4	85.3	65	30	2.2
3	9.5	1.42	85.1	45	45	1
4	9.5	1.45	84.7	30	60	0.5

Table 4.13 Fluoride solution passed through a 'fresh' column of chokaa

Samples of the filtrate were collected after 20, 30, 45 and 60min respectively and the fluoride concentration was measured after each time interval. The flow rate decreased from 4ml/min to 0.5ml/min after 60min. The fluoride concentration was reduced from 9.5ppm to at least 1.3ppm as shown in Table 4.13.

The flow rate (0.033 - 0.26 m/hr) through the column is comparable to the one for a slow sand filter  $(0.02 - 0.2 \text{m/hr} \text{ for } 1000 - 2000 \text{m}^2 \text{ bed}).$ 

A bed volume of 229cm<sup>3</sup> and mass 170g treated 220ml of water from 9.5ppm to 1.45ppm after 60 minutes.

The mass of Fluoride ions sorbed per unit mass of ehokaa,  $Q_c$  for column studies was O.Olmg/g while for batch studies was 0.096mg/g this shows that the fluoride removal for batch was better. Assuming the amount adsorbed,  $Q_e$  was constant, and the fluoride concentration at the start was 5mg/l, then the bed volume treatment would be as high as 418ml compared to 220ml for 9.5mg/l. This means that the column could work better at lower fluoride concentration.

### 4.12 REGENERATION OF CHOKAA

Chokaa after the initial operation was regenerated by first rinsing with 0.1N Sodium Carbonate solution; then with dilute hydrochloric acid (0.1N); and finally with distilled water twice. After being air dried, the material was ready for reuse.

After regeneration the column was operated again, Table 4.14 shows results of column operation after the regeneration.

The volume of treated water collected was 209ml still less than the bed volume.

The total cost of regeneration was about Kshs. 14.75 for 209ml of treated water. A half a kilogram of sodium carbonate costs Kshs 240, the cost of amount used was Kshs 5.10. Two and a half litres of conc. hydrochloric acid costs Kshs 2900, the cost of the amount used was Kshs 9.65. This cost translates to Kshs 72 per litre of treated water.

Compared to the methods discussed in Section 2.2 this method of fluoride removal is cheaper.

After one hour the flow rate was quite small, hence after chokaa was regenerated the flow rate increased thus showing that the column could be used for a longer time.

Table 4.14 shows the removal efficiency of a regenerated column after 9.5ppm of fluoride ions were passed through at different time intervals.

Sample	Original F"	Final F conc.	Fluoride	Volume of	Time (min)	Flow Rate
	conc. (ppm)	(ppm)	Removal	Sample (ml)		(ml/min)
			%			
1	9.5	1.5	84.2	70	20	3.5
2	9.5	1.52	84	60	30	2
3	9.5	1.46	54.6	39	45	0.87
4	9.5	1.47	"84.5	40	60	0.67

Table 4.14 Column operation after regeneration of chokaa

### 4 J3 EXPERIMENTAL ERRORS

The sources of errors in this study could arise from errors in measurements of various ehokaa masses. This type of error would not be significant because the amounts of ehokaa used were high (5-15g). An error of say O.lg is only about 2% for 5g and 0.7% for 15g which is rather ^significant. The other major error could have been in determination of fluoride concentration. The fluoride instrument was accurate and had good precision.

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### **CHAPTER 5**

### CONCLUSIONS AND RECOMMENDATIONS

### 5j CONCLUSION

fhe objectives of the proposed research were to investigate the potential of a locally available material chokaa in removing fluoride from water and to investigate the mechanisms of adsorption of the chokaa with fluoride.

From the results the conclusions derived are:

- Chokaa had the potential to remove at least 70% of fluoride ion concentration in water at a pH between 6-7, Temperature 25°C, and equilibrium time one hour for 25ppm fluoride ion concentration in batch studies.
- 2. The optimal mass for 50ml fluoride ion solution was lOg for batch experiments.
- 3. Small particle size 0.3 0.6mm range, a temperature of 25°C and a pH of 6 -7, favor the fluoride ions sorbed in batch.
- 4. The equilibrium data isotherms for batch fitted the Freundlich adsorption model.
- 5. Bench scale column studies (25.2cm high column with a diameter of 3.4cm and 49.5cm head) reduced 9.5ppm fluoride ion concentration to 1.3ppm at a flow rate of 4ml/min. After regeneration, 9.5ppm fluoride ion concentration was reduced to 1.5ppm at a flow rate of 3.5ml/min. The mass of chokaa used was 170g.
- The flow in the column was between 0.264 m/hr and 0.033m/hr which is comparable to a slow sand filter (0.02 0.2m/hr for 1000 2000m<sup>2</sup> bed).
- 7. The mass of fluoride ions sorbed per unit mass of chokaa, Q<sub>e</sub>, for column studies was 0.01 mg/g while for batch studies was 0.096mg/g this showed that the fluoride removal for batch was better, however a batch setup is not ideal for industrial scale application, a column is more conventional.
- 8. The cost of regeneration of chokaa was about Kshs. 72 per litre of treated water which is rather high. This cost could reduce if treatment is on a large scale.

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### RECOMMENDATIONS

flowing the results of this research, the following were the recommendations made:

- j Pilot column studies should be carried out in order to investigate the effects of flow rate and inlet F" concentration on the column performance for F" adsorption.
- i Break through column studies are essential in order to establish the best column conditions like size, flow rates, etc.
- 3. Experiments to determine the best inlet fluoride concentration that gives the highest bed volume treatment are essential.

### APPENDIXES

### APPENDIX A: OPTIMAL DOSE RESULTS

### appendix A1

**5Qnil** of 25mg/l fluoride solution in distilled water shaken for one hour with **5g** of sorbent of varying particle sizes. (Control)

particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc.	mg/1	conc. mg/1				
	1	2	1	2	1	2	Av.
0.3 - 0.6mm	25	25	1.8	1.6	92.8	93.6	93.2
0.6- 1.2 mm	25	25	2.1	2.0	91.6	92	91.8
1.2-2.4 mm	25	25	2.3	2.2	90.8	91.2	91

### Appendix A2

50ml of 20mg/l fluoride solution in tap water shaken for one hour with 5g of sorbent of varying particle sizes

Particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc. 1	mg/1	conc. mg/1				
Samples	1	2	1	2	1	2	Av.
0.3 - 0.6mm	35	35	11.2	11.3	68	67.7	67.9
0.6-1.2 mm	35	35	12	12.1	65.7	65.4	65.6
1-2 - 2.4 mm	35	35	14.2	14.4	59.4	58.9	59.2



### appendix A3

# ^pil\_pf25mg/l fluoride solution in distilled water shaken for one hour with 7.5g of sorbent of particle sizes (Control)

particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc. 1	mg/1	conc. mg/1				
	1	2	1	2	1	2	Av.
~03- 0.6mm	25	25	1.3	1.2	94.8	95.2	95
"(X6 - 1.2 mm	25	25	1.55	1.4	93.8	94.4	94.1
1.2 - 2.4 mm	25	25	1.6	1.7	93.6	93.2	93.4

### Appendix A4

50ml of 20mg/l fluoride solution in tap water shaken for one hour with 7.5g of sorbent of varying particle sizes

Particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc. 1	mg/1	conc. mg/1				
	1	2	1	2	1	2	Av.
0.3 - 0.6mm	35	35	10.2	10.3	70.9	70.6	70.8
0.6- 1.2 mm	35	35	11	11.1	68.6	68.3	68.5
1.2-2.4 mm	35	35	11.5	11.4 '	67.1	67.4	67.3

### appendix A5

^0ril\_of 25mg/l fluoride solution in distilled water shaken for one hour with lOg of sorbent of varying particle sizes (control)

particle size	Original		Final		Fluoride removal		
	Fluoride		fluoride		%		
	conc. 1	mg/1	conc. mg/1				
	1	2	1	2	1	2	Av.
0.6mm	25	25	0.7	0.6	97.2	97.6	97.4
~(16 - 1.2 mm	25	25	0.85	0.83	96.6	96.7	96.7
~ <i>l2</i> - 2.4 mm	25	25	1.1	1.2	95.6	95.2	95.4

### Appendix A6

50ml of 20mg/l fluoride solution in tap water shaken for one hour with 10u of sorbent of varying particle sizes

Particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc.	mg/1	conc. mg/1				
Samples	1	2	1	2	1	2	Av.
0.3-0.6mm	35	35	8	7.6	77.1	78.3	77.7
0.6- 1.2 mm	35	35	9.1	9.0	74	74.3	74.2
1.2-2.4 mm	35	35	11	10.8.	68.6	69.1	68.9

### appendix A7

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^nml of 25 mg/l fluoride solution in distilled water shaken for one hour with  $15_g$  of sorbent of varying particle sizes (control)

<sup>r</sup> particle size	Original		Final		Fluoride removal		
	Fluoride		fluoride		%		
	conc. 1	mg/1	conc. mg/1				
	1	2	1	2	1	2	Av.
"OJ - 0.6mm	25	25	0.72	0.71	97.1	97.2	97.2
- 1 -2 mm	25	25	0.9	0.8	96.4	97	96.7
1.2-2.4 mm	25	25	1.3	1.1	94.8	95.6	95.2

### Appendix A8

50ml of 20mg/l fluoride solution in tap water

for one hour with 15g of Sorbent of varying

particle sizes

Particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc. 1	mg/1	conc. mg/1				
Samples	1	2	1	2	1	2	Av.
0.3 - 0.6mm	35	35	8.1	7.7	76.9	78	77.5
0.6 - 1.2 mm	35	35	9.2	9.1	73.7	74	73.9
1.2-2.4 mm	35	35	11	10.9	68.6	68.9	68.8

The highest achievable Fluoride removal is 97% and 77% respectively therefore the optimal mass i **IOg.** 

The tap water used was bore-hole water with fluoride concentration of 15ppm.

### **APPENDIX B: EQUILIBRIUM TIME RESULTS**

### \ppendix B1

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sOml of 25mg/l fluoride solution in distilled water shaken for **one hour** with lOg of sorbent of varying particle sizes (control)

"particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc. 1	mg/1	conc. mg/1				
	1	2	1	2	1	2	Av.
0.3 - 0.6mm	25	25	0.76	0.77	96.7	96.9	96.8
0.6 - 1.2 mm	25	25	0.9	0.89	96.4	96.4	96.4
1.2-2.4 mm	25	25	0.95	0.96	96.2	96.2	96.2

### Appendix B2

50ml of 25mg/l fluoride solution in distilled water shaken for **two hours** with lOg of sorbent of varying particle sizes (control)

Particle size	Original		Final o	conc.	Fluoride removal		
	conc. mg/1		mg/1		%		
	1	2	1	2	1	2	Av.
0.3 - 0.6mm	25	25	0.85	0.86	96.6	96.6	96.6
0.6 - 1.2 mm	25	25	0.8	0.83 .	96.8	96.7	96.8
1.2-2.4 mm	25	25	0.9	0.89	96.4	96.4	96.4

### appendix B3

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tfjri<u>l of 20mg/l fluoride solution in tap water shaken for **one hour** with lOg of sorbent of varying Part<u>icle sizes</u></u>

particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc. mg/1		conc. mg/1				
	1	2	1	2	1	2	Av.
"OJ - 0.6mm	35	35	8	7.6	77.1	78.3	77.7
"0^6-1.2 mm	35	35	9.1	9.0	74	74.3	74.2
1.2-2.4 mm	35	35	11	10.8	68.6	69.1	68.9

### Appendix B4

50ml of 20mg/l fluoride solution in tap water shaken for **two hours** with lOg of sorbent of varying particle sizes

Particle size	Original		Final		Fluoride removal		
	Fluoride		Fluoride		%		
	conc. 1	mg/1	conc. mg/1				
Samples	1	2	1	2	1	2	Av.
0.3 - 0.6mm	35	35	8.2	7.8	76.6	77.7	77.2
0.6 - 1.2 mm	35	35	9.2	9	73.7	74.2	74
1.2-2.4 mm	35	35	11.3	11	67.7	68.6	68.2

The highest achievable Fluoride removal of 97% and 77% respectively, obtained after 1 hour, hence the equilibrium time.

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### APPENDIX C: RATE (KINETIC) STUDIES (Temp. 25±1°C)

### appendix CI (control)

Fluoride removal as a function of time ( lg of sorbent particle size 0.6 - 1.2 mm in contact with ^Onil solutions of 25mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original cone, (mg/1)	Final conc., Ce, (mg/1)	Amount of F" sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	25	15	0.5	0.5	40
20	50	25	13	0.6	0.6	48
30	50	25	12	0.65	0.65	52
60	50	25	7.2	0.89	0.89	71.2
120	50	25	7.1	0.895	0.895	71.6

### Appendix C2 (control)

Fluoride removal as a function of time (2.5 g of sorbent particle size 0.6 - 1.2 mm in contact with 50ml solutions of 25mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F sorbed, X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	25	14	0.55	0.22	44
20	50	25	13	0.6	0.24	48
30	50	25	12	0.65	0.26	52
60	50	25	7.0	0.9	0.36	72
120	50	25	6.92	0.904	0.362	72.32

### appendix C3 (control)

pluoride removal as a function of time (5.0 g of sorbent particle size 0.6 - 1.2 mm in contact with ^Oml solutions of 25mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	25	6.8	0.91	0.182	72.8
20	50	25	6.6	0.92	0.184	73.6
30	50	25	5.3	0.985	0.197	78.8
60	50	25	5.0	1.0	0.2	80.0
120	50	25	4.8	1.01	0.202	80.8

### Appendix C4

Fluoride removal as a function of time (5.0 g of sorbent particle size 0.6 - 1.2 mm in contact with 50ml solutions of 20mg/l fluoride ions in tap water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F" sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	35	18.6	0.82	0.164	46.9
20	50	35	15.4	0.98	0.196	56
30	50	35	13.2	1.09	0.218	62.3
60	50	35	11.3	1.19	0.237	67.7
120	50	35	11.2	1.19	0.238	68



### appendix C5 (control)

pluoride removal as a function of time (7.5g of sorbent particle size 0.6 - 1.2 mm in contact with ^Onil solutions of 25mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original eonc. (nig/I)	Final conc., Ce, (mg/1)	Amount of F sorbed,X (nig)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency
15	50	25	4.82	1.009	0.135	80.72
20	50	25	3.8	1.06	0.14	84.8
30	50	25	3.2	1.09	0.145	87.2
60	50	25	3.0	1.1	0.147	88
120	50	25	2.9	1.105	0.147	88.4

### Appendix C6 (control)

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Fluoride removal as a function of time (lOg of sorbent particle size 0.6 - 1.2 mm in contact with 50ml solutions of 25mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final cone., Ce, (mg/1)	Amount of F sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	25	2	1.15	0.115	92
20	50	25	1.8	1.16	0.116	92.8
30	50	25	1.6	1.17	0.117	93.6
60	50	25	1.2	1.19	0.119	95.2
120	50	25	1.2	1.19	0.119	95.2
## appendix C7

# fluoride removal as a function of time (10g of sorbent particle size 0.6 - 1.2 mm in contact with ^Qml solutions of 20mg/l fluoride ions in tap water)

Time (min)	Volume of sample (ml)	Original conc. (mg/I)	Final conc., Ce, (mg/1)	Amount of F sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	35	16.5	0.925	0.0925	52.9
20	50	35	15.2	0.99	0.099	56.6
30	50	35	10.3	1.235	0.1235	70.6
60	50	35	9.1	1.295	0.1295	74
120	50	35	9	1.3	0.13	74.3

# Appendix C8 (control)

Fluoride removal as a function of time (10<sup>^</sup> of sorbent particle size 1.2 - 2.4mm in contact with 50ml solutions of 25mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1	Final conc., Ce, (mg/1)	Amount of F" sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	25	3.8	1.06	0.106	84.8
20	50	25	3.5	1.075	0.1075	86
30	50	25	3.2	1.09	0.109	87.2
60	50	25	2.98	1.101	0.1101	88.08
120	50	25	2.88	1.106	0.1106	88.48

#### appendix Cll

# fluoride removal as a function of time (lOg of sorbent particle size 1.2 - 2.4mm in contact with SOml solutions of 20mg/l fluoride ions in tap water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1	Final conc., Ce, (mg/1)	Amount of F sorbed,X (nig)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	35	16.8	0.91	0.091	52
20	50	35	16.4	0.93	0.093	53.1
30	50	35	15.2	0.99	0.099	56.6
60	50	35	11.3	1.185	0.1185	67.7
120	50	35	11.2	1.19	0.119	68

## Appendix CIO (control)

Fluoride removal as a function of time (lOg of sorbent particle size0.3 - 0.6mm in contact with 50ml solutions of 25mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F" sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	25	0.98	1.201	0.1201	96.08
20	50	25	0.92	1.204	0.1204	96.32
30	50	25	0.90	1.205	0.1205	96.4
60	50	25	0.88 '	1.206	0.1206	96.48
120	50	25	0.87	1.207	0.1207	96.52

## appendix C11

cluoride removal as a function of time (lOg of sorbent particle size0.3 - 0.6mm in contact with 50ml solutions of 20 mg/1 fluoride ions in tap water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	35	14	1.05	0.105	60
20	50	35	12	1.15	0.115	65.7
IW	50	35	11	1.2	0.12	68.6
60	50	35	8.2	1.34	0.134	76.6
120	50	35	8.1	1.345	0.135	76.9

## Appendix C12 (control)

Fluoride removal as a function of time (lOg of sorbent particle size 0.6 - 1.2 mm in contact with 50ml solutions of 10mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F" sorbed,X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	10	4.6	0.27	0.027	54
20	50	10	3.5	0.325	0.0325	65
30	50	10	2.6	0.37	0.037	74
60	50	10	2	0.4	0.04	80
120	50	10	1.88	0.406	0.0406	81.2

## appendix Cll

fluoride removal as a function of time (lOg of sorbent particle size 0.6 - 1.2 mm in contact with 50ml solutions of 2mg/l fluoride ions in tap water)

^fTme (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F"sorbed,X (nig)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	17	8	0.45	0.045	52.9
fyT	50	17	6.7	0.515	0.052	60.6
30	50	17	6.2	0.54	0.054	63.5
60	50	17	4.2	0.64	0.064	75.3
120	50	17	4.1	0.645	0.0645	75.9

## Appendix C14 (control)

Fluoride removal as a function of time (lOg of sorbent particle size 0.6 - 1.2 mm in contact with 50ml solutions of 40mg/l fluoride ions in distilled water)

Time (min)	Volume of sample (ml)	Original conc. (mg/1)	Final conc., Ce, (mg/1)	Amount of F" sorbed, X (mg)	Amount sorbed per unit weight, qe (mg/g)	Removal efficiency %
15	50	40	10.2	1.49	0.149	74.5
20	50	40	9.7	1.515	0.1515	75.75
30	50	40	9.0	1.55	0.155	77.5
60	50	40	8.3	1.585	0.1585	79.25
120	50	40	8.28	1.586	0.1586	79.3

## APPENDIX D: EQUILIBRIUM STUDIES (Temp. 25±1°C).

# \ppendix D1

Initial cone. Co (mg/1)	Vol. of sample (ml)	Final conc. Ce (mg/1)	Amt. sorbed, Qe (mg/g)	Ce/qe (g/I)	Log qe Log io	Log Ce Log io	Removal %
2	50	0.6	0.007	85.7	-2.15	-0.22	70
5	50	1.8	0.016	112.5	-1.796	0.255	64
10	50	2.0	0.04	50	-1.398	0.301	80
15	50	2.3	0.0635	36.22	-1.197	0.362	84
20	50	2.4	0.088	27.27	-1.056	0.380	88
25	50	2.5	0.1125	22.22	-0.949	0.398	90
30	50	5	0.125	40	-0.903	0.699	83.33
35	50	6	0.145	41.38	-0.839	0.778	82.86

Equilibrium studies on particle size 0.3 - 0.6mm (lOg of sorbent shaken for one hour with 50ml colutions of varying concentrations of Fluoride ions in, distilled water). (Control)

# Appendix D2

Equilibrium studies on particle size 0.3 - 0.6mm (10g of sorbent shaken for one hour with 50ml solutions of varying concentrations of Fluoride ions in tap water).

Initial conc. Co (mg/1)	Vol. of sample (ml)	Final conc. Ce (mg/1)	Amt. sorbed, Qe (mg/g)	<b>Ce/qe</b> (g/1)	Log qe Log 10	Log Ce Log ,o	Removal %
2	50	0.8	0.006	133.33	-2.22	-0.097	60
5	50	1.2	0.019	63.16	-1.72	-0.079	76
10	50	2.2	0.039	56.41	-1.4	0.34	78
17	50	2.5	0.0725	34.48	-1.14	0.398	85.3
Hn	50	8.2	0.134	61.19	-0.87	0.914	76.6

## \ppendix D3

Equilibrium studies on particle size 0.6- 1.2mm (10g of sorbent shaken for one hour with 50ml solutions of varying concentrations of Fluoride ions in distilled water). (Control)

Initial cone. Co (mg/1)	Vol. of sample (ml)	Final conc. Ce (mg/1)	Amt. sorbed, Qe (mg/g)	Ce/qe (g/1)	Log qe Log io	Log Ce Log ,o	Removal %
2	50	0.9	0.0055	163.64	-2.26	-0.045	55
5	50	2.2	0.014	157.14	-1.85	0.34	56
10	50	2.6	0.037	70.27	-1.43	0.41	74
15	50	3.0	0.06	50	-1.22	0.48	80
20	50	2.9	0.086	33.72	-1.07	0.46	85.5
*25~~	50	3.2	0.109	29.36	-0.96	0.51	87.2
	50	7	0.115	60.87	-0.94	0.85	76.7
[35	50	8	0.135	59.26	-0.87	0.90	77.1

#### Appendix D4

Equilibrium studies on particle size 0.6- 1.2mm (lOg of sorbent shaken for one hour with 50ml solutions of varying concentrations of Fluoride ions in tap water).

Initial conc. Co (mg/1)	Vol. of sample (ml)	Final conc. Ce (mg/1)	Amt. sorbed, Qe (mg/g)	Ce/qe (g/1)	Log qe Log io	Log Ce Log ,o	Removal %
2	50	1.4	0.003	466.67	-2.52	0.146	30
5	50	2.3	0.0135	170.37	-1.87	0.362	54
10	50	3.1	0.0345	89.86	-1.46	0.491	69
17	50	4.2	0.064	65.63	-1.19	0.623	75.3
35	50	9.2	0.129	71.32	-0.89	0.964	73.7

#### Appendix D5

jquilibrium studies on particle size 1.2- 2.4mm (lOg of sorbent shaken for one hour with 50ml solutions of varying concentrations of Fluoride ions in distilled water)(control)

Initial conc. Co (mg/1)	Vol. of sample (ml)	Final conc. Ce	Amt. sorbed,	<b>Ce/qe</b> (g/1)	Log qe Log io	Log Ce Log ,o	Removal %
		(mg/1)	(mg/g)				
2	50	1.2	0.004	300	-2.4	0.079	40
5	50	2.4	0.013	184.62	-1.89	0.38	52
10	50	2.8	0.036	77.78	-1.44	0.45	72
15	50	3.2	0.059	54.24	-1.23	0.51	78.7
20	50	3.6	0.082	43.9	-1.09	0.56	82
25	50	3.8	0.106	35.85	-0.97	0.58	84.8
30	50	9	0.105	85.71	-0.98	0.95	70
35	50	10	0.125	80	-0.90	1	71.4

# Appendix D6

Equilibrium studies on particle size 1.2- 2.4mm (lOg of sorbent shaken for one hour with 50ml solutions of varying concentrations of Fluoride ions in tap water).

Initial conc. Co (mg/1)	Vol. of sample (ml)	Final conc. Ce (mg/1)	Amt. sorbed, Qe (mg/g)	Ce/qe (g/D	Log qe Log io	Log Ce Log io	Removal %
2	50	1.6	0.002	800	-2.7	0.2	20
5	50	2.5	0.0125	200	-1.9	0.4	50
10	50	4.2	0.029	144.8	-1.54	0.6	58
17	50	5.2	0.059	288.1	-1.23	0.7	69.4
35	50	11	0.12	291.7	-0.92	1.04	68.6

# APPENDIX E: EFFECT OF TEMPERATURE (14°C)

## Appendix El

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Equilibrium studies on particle size 0.6 - 1.2mm at 14<sup>U</sup>C (TOg of sorbent shaken for one hour with 50ml solutions of varying concentrations of Fluoride ions in distilled water)(control)

Initial	Vol. of	Final	Amt.	Ce/qe	Log qe	Log Ce	Removal
cone. Co	sample	conc.	sorbed,	(g/1)	Log 10	Log 10	70
(mg/1)	(ml)	Ce	Qe				
		(mg/1)	(mg/g)				
2	50	1.5	0.0025	600	-2.6	0.18	25
5	50	3.8	0.006	633.33	-2.22	0.58	24
10	50	5	0.025	200	-1.60	0.7	50
15	50	6.4	0.043	148.84	-1.37	0.81	57.33
120	50	7	0.065	107.69	-1.19	0.85	65
25	50	7.5	0.088	85.22	-1.06	0.88	70
30	50	15	0.075	200	-1.12	1.18	50
35	50	20	0.075	266.67	-1.12	1.30	42.86

#### Appendix E2

Equilibrium studies on particle size 0.6 - 1.2mm at 14°C (lQg of sorbent shaken for one hour with 50ml solutions of varying concentrations of Fluoride ions in tap water).

Initial conc. Co	Vol. of sample	Final conc.	Amt. sorbed,	Ce/qe (g/1)	Log qe Log io	Log Ce Log ,0	Removal %
(mg/1)	(ml)	Ce	Qe	<i>w</i>			
		(mg/1)	(mg/g)				
2	50	1.8	0.001	1800	-3	0.26	10
5	50	4.2	0.004	1050	-2.4	0.62	16
10	50	6.3	0.0185	340.54	-1.73	0.8	37
17	50	7.2	0.049	146.94	-1.3	0.86	57.6
35	50	22	0.065	338.46	-1.19	1.34	37.1

## APPENDIX F: EFFECT OF SOLUTION pH (Temp 22°C)

# Appendix F1

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Equilibrium studies onlOg of sorbent shaken for one hour with 50ml solutions of 20mg/l respectively of Fluoride ions in distilled water at monitored pH). (Control)

'article sizes	Vol. Of sample (ml)	рН	Equilib. PH	Original conc. (mg/1)	Final conc. Ce (mg/1)	Amt. Sorbed, qe (mg/g)	Removal %
(.3-0.6mm	50	5	5.35	20	0.6	0.097	97
[6-1.2mm	50	5	5.35	20	0.83	0.096	95.85
1.2-2.4mm	50	5	5.35	20	1.2	0.094	94

## Appendix F2

Equilibrium studies on lOg of sorbent shaken for one hour with 50ml solutions of 20mg/l respectively of Fluoride ions in tap water at monitored pH).

Particle sizes	Vol. Of sample (ml)	РН	Equilib. PH	Original conc. (mg/1)	Final conc. Ce (mg/1)	Amt. Sorbed, qe (mg/g)	Removal %
0.3-0.6mm	50	6.8	5.35	35	8.2	0.134	76.6
0.6-1.2mm	50	6.7	5.35	35	9.2	0.129	73.7
1.2-2.4mm	50	6.7	5.35	35	11	0.12	68.6

## Appendix F3

Equilibrium studies onlOg of sorbent shaken for one hour with 50ml solutions of 2mg/l respectively of Fluoride ions in distilled water at monitored pH). (Control)

particle sizes	Vol. Of sample (ml)	рН	Equilib. pH	Original conc. (mg/1)	Final conc. Ce (mg/1)	Amt. Sorbed, qe (mg/g)	Removal %
(.3-0.6mm	50	4.9	5.35	2	0.5	0.0075	75
1.6-1.2mm	50	4.9	5.35	2	0.9	0.0055	55
1.2-2.4mm	50	4.9	5.35	2	1.3	0.0035	35

## Appendix F4

Equilibrium studies onlOg of sorbent shaken for one hour with 50ml solutions of 2mg/l respectively of Fluoride ions in tap water at monitored pH).

Particle sizes	Vol. Of sample (ml)	рН	Equilib. PH	Original conc. (mg/1)	Final conc. Ce (mg/1)	Amt. Sorbed, qe (mg/g)	Removal %
, 0.3-0. <b>6mm</b>	50	6.9	5.35	17	4	0.065	76.4
0.6-1.2mm	50	7.2	5.35	17	4.2	0.064	75.3
1.2-2.4 <b>mm</b>	50	7.0	5.35	17	5.2	0.059	69.4

## APPENDIX G: COLUMN STUDY RESULTS

# **APPENDIX G1**

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	1	1	i	1	1	
Sample	Original F"	Final F'conc.	Fluoride	Volume of	Time (min)	Flow Rate
	conc. (ppm)	(ppm)	Removal	Sample (ml)		(ml/min)
			%			
i	9.5	1.3	86.3	80	20	4
2	9.5	1.4	85.3	65	30	2.2
3	9.5	1.42	85.1	45	45	1
	9.5	1.45	84.7	30	60	0.5

Fluoride solution passed through a 'fresh<sup>7</sup> column of ehokaa

## **APPENDIX G2**

Fluoride solution passed through a regenerated column of ehokaa

Sample	Original F" conc. (ppm)	Final F'conc. (ppm)	Fluoride Removal %	Volume of Sample (ml)	Time (min)	Flow Rate (ml/min)
1	9.5	1.5	84.2	70	20	3.5
2	9.5	1.52	84	60	30	2
3	9.5	1.46	84.6	39	45	0.87
4	9.5	1.47	84.5	40	60	0.67

## **APPENDIX G3**

The CEC of ehokaa was found to be as follows:

	Cmol/kg						
Sample	Κ	Na	Ca	Mg	CEC		
description							
Chokaa	0.8	3.33	5.35	6.33	16.40		

Source: University of Nairobi, Kabete campus, Department of Soil Science

## COLUMN DIMENSIONS

Head = 49.5cm Column Height = 25.2cm Column diameter = 3.4cm

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