



**UNIVERSITY OF NAIROBI**  
**Department of Civil Engineering**

**The potential of Zeolitic Volcanic Tuff to  
remove manganese and iron from water.**

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Reg. No : **F56/7287/2001**

Supervisor: **Professor B.N.K Njoroge**.

A thesis submitted in partial fulfillment for the award of Master of  
Science in Civil Engineering.



*November, 2004.*

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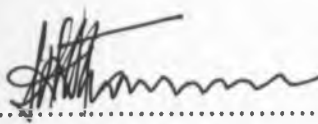
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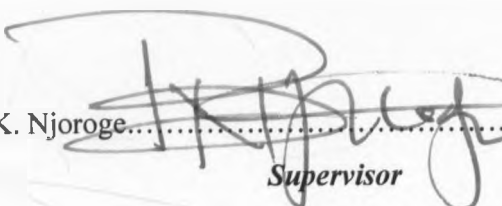
A thesis submitted in partial fulfillment for the award of Master of Science in Civil Engineering.

### Declaration.

This Thesis is my original work and has not been submitted for a degree in any other University.

G.N.Kituku..........Date 24th November, 2004.  
*Candidate*

This thesis has been submitted for examination with my approval as University supervisor.

Professor.B.N.K. Njoroge..........Date November 24, 2004  
*Supervisor*

## **Dedication.**

To my wife Francisca, son Judah and Mum. Their unfaltering patience and encouragement formed the impetus to the successful completion of this research work.

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## ABSTRACT

The study investigated the potential of zeolitic volcanic tuff (chokaa) to remove iron and manganese from water. A series of batch experiments were conducted to ascertain this potential. Iron removal was favoured by small particle sizes of sorbent, high temperature and low pH.

Batch studies carried out at low pH, using sorbent particles of size 0.3mm- 0.6mm indicated that about 93% of the iron was removed from the solution. On the other hand, manganese removal was favoured by small particle size of the sorbent and high pH. Batch studies carried out at a pH of 9 using sorbent particle size of 0.3mm- 0.6mm indicated that over 75% of the manganese was removed from the solution.

Further study showed that the two cations can be removed at normal operating condition of neutral pH, but the sample had to be treated first with potassium permanganate before passing it through a column.

Results from column studies carried out at a pH of 7.35, which was the normal pH of the sample and initial iron concentration of 3.7mg/l, and initial manganese concentration of 0.6mg/l, indicated that up to around 98 bed volumes, the percentage removal for iron and manganese were 92% and 87% respectively.

The cost associated with removal of iron and manganese ions from water using a column packed with zeolitic volcanic tuff is reasonably low and the system practically viable.

Sorption kinetic studies strongly indicated that the sorption process was governed by intra- particle diffusion.

## Table of Contents.

<b>CHAPTER 1.0: INTRODUCTION.....</b>	<b>1</b>
1.1 GENERAL BACKGROUND RESEARCH.....	1
1.2 IRON AND MANGANESE PROBLEMS IN WATER.....	3
1.2.1 Iron bacteria.....	3
1.2.2 Health effects.....	4
1.3. STUDY OBJECTIVES.....	4
<b>CHAPTER 2.0: LITERATURE REVIEW. ....</b>	<b>5</b>
2.1 AQUEOUS CHEMISTRY OF IRON AND MANGANESE.....	5
2.2 MEASUREMENT OF IRON AND MANGANESE CONCENTRATION IN WATER.....	7
2.2.1 Colourimetric methods.....	7
2.2.2 Instrumental methods.....	7
2.3 METHODS OF REMOVING IRON AND MANGANESE FROM WATER.....	8
2.3.1 Polyphosphate treatment.....	8
2.3.2 Ion exchange.....	8
2.3.3 Oxidising filter.....	9
2.3.4 Chemical oxidation followed by filtration.....	9
2.3.5 Aeration followed by filtration.....	10
2.3.6 Catalytic carbon.....	10
2.3.7 Multistage treatment.....	11
2.4 NATURAL ZEOLITES.....	11
2.4.1 Introduction.....	11
2.4.2 Properties of zeolites.....	11
2.5 USES OF ZEOLITES.....	13
2.5.1 Natural zeolite as ion exchange resin and adsorbent.....	13
2.5.2 Sorption of $Fe^{2+}$ and $Mn^{2+}$ .....	14
2.6. ION EXCHANGE AND ADSORPTION.....	14
2.6.1 Theory of ion exchange.....	14
2.6.2 Types of ion exchange resins.....	14
2.7 ION EXCHANGE REACTIONS.....	16
2.7.1 Ion exchange capacity.....	17
2.8 THEORY OF ADSORPTION.....	17
2.8.1 Adsorption forces and mechanism.....	18
2.8.2 Adsorption Models.....	20
<b>CHAPTER 3.0: INDUSTRIAL APPLICATIONS FOR ZEOLITES.....</b>	<b>22</b>
3.1 METAL REMOVAL FROM RAW WATER.....	22
3.1.1 Sewage and waste water treatment.....	23
3.1.2 Radioactive waste treatment.....	23
3.1.3 Sorbent barriers for radioactive waste.....	23
3.1.4 Pollution control.....	24
3.1.5 Aquaculture.....	24
3.1.6 Phytoremediation.....	24
3.1.7 Other uses.....	24
3.1.8 Modified natural zeolites.....	24
3.2 IRON AND MANGANESE REMOVAL FROM WATER USING NATURAL ZEOLITE.....	25

<b>CHAPTER 4.0: MATERIALS AND RESEARCH METHODOLOGY.....</b>	<b>26</b>
4.1 INTRODUCTION .....	26
4.2 MATERIALS AND EQUIPMENTS.....	26
4.2.1 The source of Iron and Manganese .....	26
4.2.3 Reagents and equipment .....	27
4.3 EXPERIMENTAL PROCEDURES.....	28
4.3.1 Determination of iron concentration (procedure).....	28
4.3.2 Trial Studies.....	28
4.3.3 Equilibrium studies.....	29
4.3.4 Column Studies .....	29
4.3.5 Control Experiments.....	31
4.3.6 X- Ray Diffraction test for the sorbent.....	31
<b>CHAPTER 5.0: RESULTS AND DISCUSSION.....</b>	<b>33</b>
5.1 EFFECT OF THE SORBENT PROPERTIES ON THE SORPTION PROCESS.....	33
5.2 CATION EXCHANGE CAPACITY (CEC) FOR THE SORBENT.....	34
5.3 EFFECT OF ZEOLITE DOSAGE ON MANGANESE AND IRON REMOVAL..	36
5.4 EFFECTS OF CHOKAA PARTICLE SIZE ON REMOVAL IRON AND MANGANESE FROM WATER.....	40
5.5 KINETICS OF THE SORPTION PROCESS.....	43
5.6 SORPTION RATES OF IRON AND MANGANESE IONS ON CHOKAA SORBENT.....	51
5.7 EFFECT OF TEMPARATURE ON EQUILBRIUM OF IRON REMOVAL.....	53
5.8 EFFECT OF SOLUTION pH ON REMOVAL OF IRON AND MANGANESE FROM WATER. ....	54
5.9 COLUMN STUDIES.....	57
5.9.1 Dosing the sample with Potassium Permanganate before passing it through a chokaa column. ....	57
5.9.2 Regeneration of chokaa.....	57
<b>CHAPTER 6.0: CONCLUSIONS AND RECOMMENDATIONS.....</b>	<b>60</b>
6.1 CONCLUSIONS.....	60
6.2 RECOMMENDATIONS .....	60
APPENDIX 1.0 RESULTS OF THE EFFECTS OF TEMPERATURE ON IRON REMOVAL.....	61
APPENDIX 2.0 RESULTS OF THE EFFECT OF DOSING THE SAMPLE WITH POTASSIUM PERMANGANATE BEFORE PASSING IT THROUGH A CHOKAA COLUMN.....	62
APPENDIX 3.0 APPROXIMATE COST OF TREATING ALLIANCE GIRLS WATER PER DAY.....	63
BIBLIOGRAPHY.....	64



# CHAPTER 1.0: INTRODUCTION.

## 1.1 General Background Research

Iron and manganese are metallic elements that are found in the earth's crust. When ground water percolates through soil and rock, minerals containing iron and manganese are sometimes dissolved by water. Corroding iron and/or galvanized steel pipes could be a source of iron in household water. The actual concentration of iron species in water depends on its pH, dissolved oxygen content, carbonate and bicarbonate ion concentrations, sulphur containing iron and phosphate ion concentrations (Barnes, 1983). Iron in water can exist in two forms:

Ferrous iron ( $\text{Fe}^{2+}$ ) - This form creates a clear solution when it is dissolved in water and as a result is often referred to as clear water iron.

Ferric iron ( $\text{Fe}^{3+}$ ) - This is formed when ferrous iron is oxidized and is insoluble in water. During the oxidation process, ferrous iron which is colourless changes to white, then yellow and finally to reddish brown (colloidal iron).

Manganese on the other hand is less common than iron and occurs in rocks and minerals as oxides and carbonates. Manganese ion in aqueous solution behaves in a similar manner to iron, the reduced manganous ions ( $\text{Mn}^{2+}$ ) tending to be soluble, while the oxidized manganic oxide ions ( $\text{Mn}^{4+}$ ) is insoluble as manganic oxide ( $\text{MnO}_2$ ). Manganese normally forms a black residue. Generally, water that is oxygenated will have low levels of dissolved iron and manganese because oxygen will react with both iron and manganese to form precipitates, which will settle down. Surface water and shallow wells usually have enough dissolved oxygen to precipitate the iron and manganese and thus have low iron and manganese ion content.

Iron and manganese are most likely to be trapped within the suspended organic matter in the water. Iron and manganese carbonates are relatively soluble in water that has low amount of dissolved oxygen. However, if iron is associated with sulphur as iron sulphide rather than iron carbonate, dissolved iron remains low. Iron and manganese problems are most likely to develop in water from wells with high carbonate content and low amount of dissolved oxygen. Deep wells and boreholes in limestone

formation regions will definitely have iron and manganese problems as the amount of dissolved oxygen decreases with depth ( Barnes and Wilson, 1983).

In most waters the concentration of iron and manganese varies between 0.075 to 5mg/l and 0.01 to 0.75mg/l respectively [Stumm and Morgan, 1981].

The problem of iron and manganese in groundwater in Kenya is common especially in the region of Central province. However, there is limited data on this problem, because ground water is under-exploited in this country. The International Standards for drinking water specify a concentration of 0.3ppm as the maximum acceptable and 1.0ppm as the maximum allowable for iron concentration in water [WHO]. Manganese is more troublesome and the limits are more stringent at 0.1ppm and 0.5ppm respectively [WHO]. Water to be used in textile dyeing, beverage and white paper industries should contain less than 0.05ppm iron and manganese [Cox,1994].

A research carried out in 1982 to determine the quality of groundwater for an area of 800km<sup>2</sup> to the immediate north of Nairobi conservation area, which is mainly in Kiambu and Thika districts, central province, established that 21 out of 47 bore holes gave water whose iron concentration was above WHO guidelines [0.3ppm] [Maina, 1982]. This means that about 45% of the bore holes produced water which had iron problem. .

Thus iron appears to be a problem encountered in ground water in central province. The research focuses on the methods to lower the high levels of iron and manganese in water used at the Alliance Girls High School, Kikuyu.

Alliance Girls High School was started in 1948 and has been one of the best girls schools in Kenya today. The total population of the school is about 1260 persons which includes 760 students, 100 teaching and non teaching staff, and 400 dependants to both teaching and non teaching staff. All this people use water from a 140 metre deep borehole, but unfortunately this water has high levels of iron and, manganese concentrations. This can be attributed to high incidence of iron problem in underground water in central province. The iron and manganese concentrations in the borehole water were 3.70mg/l and 0.60mg/l respectively, which are much higher than WHO guidelines.

The main effects of this problem is corrosion of water pipes and staining of sinks and other fixtures. Existing water treatment plant consists of one large tank and two small tanks. Lime is used in both tanks to reduce the concentrations of iron and manganese, but this is not an effective method.

## **1.2 Iron and Manganese problems in water.**

The presence of iron and manganese in water is objectionable owing to the production of discolouration, turbidity, deposit and taste of the water. Ferruginous waters have an astringent, metallic or bitter taste, and by combination of the iron with tannin impart an ink colour to beverages such as tea and coffee. It is also objectionable for laundry purposes and gives rise to “iron-moulding” of linen and other fabrics being washed. For many industrial purposes such as paper making, dyeing, photographic film manufacture and ice making, the water must be entirely free from iron and manganese. Staining of household utensils and problems of scaling in boilers are also associated with iron and manganese (Taylor, 1958).

### **1.2.1 Iron bacteria**

Presence of iron and organic matter in water leads to formation of iron bacteria. Iron bacteria in water is indicated by appearance of slimy, white, dirty grey, ochre-or brown coloured streamers or deposit. Iron bacteria may be defined as bacteria-like organisms characterized by deposition of ferric hydroxide in morphologically distinct way; the chlamydo bacteria as sheaths and the gallionella as stalks. When manganese is present together with iron, the colour of the bacteria is black rather than brown. Chlorination can be used to control the growth of the bacteria (<http://www.cowhatcom.was.us/health/drinkwa/ironman.htm>)

The growth of iron bacteria in a water supply results to deterioration in water quality, blocking of sand filters, pumps, interference with the flow of water in water mains made of iron and may result to destruction of the pipe materials. Increased energy cost like pumping water through constricted pipes, heating water with heating rods coated with iron and cost of replacing damaged equipments can adversely affect the operation of any water supply project (Taylor, 1958).

### **1.2.2 Health effects**

Iron and manganese are primarily nuisance elements and are not known to cause any health problems at low concentrations. Their concentrations in water are regulated by secondary drinking water standards. Secondary standards apply to drinking water contaminants that affect the aesthetic quality of water. Iron in water can increase the hazard of pathogenic organisms, since many of these organisms require iron for growth (<http://www.cowhatcom.was.us/health/drinkwa/ironman.htm>).

### **1.3. Study Objectives**

The objective of this research is to investigate the iron and manganese problem of Alliance Girls High School borehole water and to propose a method of how the problem can be addressed. More specifically the objectives of the study are: -

- 1: To investigate the potential of naturally occurring chokaa to remove iron and manganese from the borehole water.
- 2: To investigate an appropriate method that can be applied in the iron and manganese removal at Alliance Girls High School borehole water.

## CHAPTER 2.0: LITERATURE REVIEW.

### 2.1 Aqueous Chemistry of Iron and Manganese

Many deep wells and boreholes in the cretaceous water bearing formations such as the chalk and green sand yield slightly ferruginous waters which require treatment to render them suitable for public supply purpose [Taylor, 1958]. Manganese usually in smaller amounts may accompany iron in water. Iron is usually dissolved in the form of ferrous bicarbonate, but, in some instances, mostly ground or surface waters, it may be found as higher oxides in complex combinations. The exposure of water to air results in the oxidation of soluble ferrous bicarbonate to insoluble or colloidal ferric hydroxide. The water thus becomes opalescent and discoloured, and a deposit finally forms which undergoes further oxidation. The reaction can be represented as:-



Iron and manganese are both transition elements. Whereas the properties of other elements in a period show a more or less steady gradation the properties of transition elements are generally similar [Heys, 1975]. Manganese is in group 7B in the Periodic Table and has three stable oxidation states i.e. 2, 4 and 7 and has five electrons in its 'd' orbital. On the other hand iron is in group 8B and has two stable oxidation states i.e. 2 and 3 and has six electrons in its 'd' orbital [Darret, 1993].

Iron exists in soils and minerals mainly as insoluble ferric oxide. Under reducing (anaerobic) conditions ferric oxide is reduced to ferrous iron, which is soluble in water. Manganese exists in the soil principally as manganese dioxide, which is very insoluble in water. Under reducing (anaerobic) conditions, the manganese dioxide is reduced to manganese oxide which is soluble in water.

Evidence to indicate that iron and manganese gain entrance to water supplies through changes produced in environmental conditions as a result of biological reactions can be explained as follows:-

- ◆ Groundwaters that contain appreciable amounts of iron or manganese or both are always devoid of dissolved oxygen and are high in carbon dioxide content. The

high carbon dioxide content indicates that bacterial oxidation of organic matter has been extensive, and the absence of dissolved oxygen shows that anaerobic conditions were developed.

- ◆ Wells producing good quality water, low in iron and manganese for many years have been known to produce poor quality water when organic wastes have been discharged on the soil around or near the well, thereby creating anaerobic conditions in the soil.
- ◆ The iron and manganese problem in impounded surface supplies has been correlated with reservoirs that stratify, but occurs only in those in which anaerobic conditions develop beneath [Sawyer,1967].

In aqueous state, a complex of Fe(II) is more stable than that of Mn(II) and in addition ferrous ions hydrolyses more readily than manganous ions [Stumm and Morgan, 1981]. The rate of oxygenation of Fe(II) in solutions of  $\text{pH} \geq 5$  is first order with respect to the concentration of both Fe(II) and  $\text{O}_2$  and second order with respect to  $\text{OH}^-$  ion. On the other hand the reaction of manganous ions with oxygen is considerably slower than the equivalent reaction with ferrous ions and the course of reaction is slower and requires a higher pH value to achieve significant rates of reaction [Barnes,1983]. The reaction is more complex because the reaction is auto catalytic, that is, it goes faster as the reaction proceeds, unlike the majority of reactions which are fastest initially when there is a high concentration of reactants. This phenomenon is explained by the reaction generating its own catalyst. Therefore the reaction is continually generating more manganic ions. Manganic oxide has high adsorptive capacity for manganous ions; for example at pH of 8, approximately 0.8moles of manganous ions are adsorbed per mole of manganic oxide. This high uptake rate explains the use of potassium permanganate in the treatment of high manganese content waters [Barnes,1983]. The final product of oxidation of manganous ions will be a mixture of manganic oxide ( $\text{MnO}_2$ ) and the adsorption complex ( $\text{Mn.MnO}_2$ ). These products are non-stoichiometric and their relative proportions in the solid phase depend strongly on the pH [Stumm and Morgan; 1981].

## **2.2 Measurement of iron and manganese concentration in water.**

### **2.2.1 Colourimetric methods.**

Colour is a sensation resulting from a perception of visible radiation over a wide range of wavelength. There are two methods of measuring colour; visual and instrumental. In visual method, the colour intensity of the sample is compared with that of a series of standard solutions or permanent glass standards to obtain a colour match. This method is not accurate and is useful only when the object is to assess the aesthetic quality of water.

### **2.2.2 Instrumental methods.**

Instrumental methods are more objective and provide accurate and precise measurements. Since the introduction of atomic absorption instruments, the analytical scope of atomic Absorption spectroscopy technique has been extended to cover many elements. This technique relies on the fact that the depth of colour (absorbance) is governed by the concentration of a material in solution [Lamount, 1981].

One such instrument that relies on the principle of colour absorbance is AAS Varian techron spectra A-10.

This instrument has a detection limit of 0.005mg/l at a wavelength of 248.3nm for iron and 0.003mg/l at a wavelength 279.5nm for manganese, and uses acetylene and oxygen gas. The WHO guidelines for iron and manganese are 0.3 ppm and 0.1 ppm respectively, thus the method is suitable as the detection limits are way below the guideline concentrations.

The principle of operation of A.A.S Varion techron spectra A-10 is as follows:- The sample is sucked in by a nebulizer which conveys it to the flame where it is vaporized into atoms. Each element has a specific spectra AA hollow cathode lamp, which is fitted into the instrument if desired to determine the concentration of that element in a solution. The lamp emits a characteristic radiation towards the flame and in the process, the vaporized atoms absorb some of it. The absorbance is proportional to the concentration of element ions in the solution. The instrument has an inbuilt

microcomputer processor, which automatically converts the absorbance into concentration and records it on the screen.

## **2.3 Methods of removing iron and manganese from water**

Iron and manganese can be removed from water in a number of ways. Principal among them include: Polyphosphate treatment, ion exchange, oxidizing filter, chemical oxidation followed by filtration, aeration followed by filtration and catalytic carbon [<http://www.ian.unl.edu/pups/water/g1280.htm>; Gloyna and Eckenfelder, 1970].

### **2.3.1 Polyphosphate treatment**

Polyphosphates react with dissolved iron and manganese by trapping them in a complex molecule that is soluble in water. As a result the iron and manganese are not available to react with oxygen and precipitate. Polyphosphates are not stable at high temperatures and if water is treated prior to heating, the polyphosphates will release iron and manganese on heating. The released iron and manganese will react with oxygen to form a precipitate. Depending on the type of the polyphosphate used, water with 1 to 3 ppm of iron can be adequately treated using this method. However, polyphosphate dosages should be limited to less than 10 ppm, because excess phosphorous may stimulate bacteria slime growth in the distribution system. Sodium hexametaphosphate is commonly used to stabilize iron and manganese in water [<http://www.ext.vt.edu/pubs/housing/356-478/356-478.htm>; O'Connor, 1971].

### **2.3.2 Ion exchange**

Soluble iron and manganese can be exchanged for sodium on an exchange resin or zeolite. This process of iron and manganese removal is analogous to ion exchange that removes hardness from water. Iron and manganese are removed during normal operation of water softening, and are later removed from the exchange medium along with calcium and magnesium during regeneration and back washing. One of the disadvantages of depending on ion exchange for iron and manganese removal is precipitation by oxygen. Some of the precipitates becomes tightly bound by plugging pores and blocking exchange sites [Bowers, 1971]. If iron bacteria is present, the problem is even worse, and it is advisable to filter out suspended iron and manganese



before water enters the softener. Some water softeners may pose a health concern for people on sodium-restricted diets. This method is suitable for low levels of dissolved iron and manganese, which do not exceed 5ppm.

[<http://www.extension.umn.edu/extpubs/h20qual/watsys/ae1030w.htm>]

### **2.3.3 Oxidising filter**

An oxidizing filter treatment method is an option for moderate levels of dissolved iron and manganese at combined concentrations up to 15ppm. The filter material is usually natural manganese green sand or manufactured zeolite coated with manganese oxide which adsorbs dissolved iron and manganese. Synthetic zeolite requires less (back-wash)water and softens the water as it removes iron and manganese. The system must be selected and operated based on the amount of dissolved oxygen. When used properly, manganese green sand can remove up to 99% of the iron, manganese and hydrogen sulphide in water. The main draw back associated with this method is filter clogging [<http://www.ext.edu/pubs/housing/356-478/356-478.htm>].

### **2.3.4 Chemical oxidation followed by filtration**

High levels of dissolved or oxidised iron and manganese greater than 10ppm can be treated by chemical oxidation using oxidising agents such as chlorine, potassium permanganate, Ozone and hydrogen peroxide followed by a sand trap filter to remove the precipitated material. This treatment is particularly valuable when iron is combined with organic matter or when iron bacteria is present.

The ideal pH range for iron oxidation by chlorine is between 6.5 and 7.5, however chlorination is not the method of choice for high manganese levels since a pH greater than 9.5 is required for complete oxidation. Generally most oxidising media are able to remove iron from water in which concentration does not exceed 10-15ppm and the pH is 7-8.5 [<http://www.ian.unl.edu/pubs/water/g1280.htm>; Eckenfelder Jnr, 1970].

Manganese oxidation with ozone requires 2-5times ozone to the manganese content and further- more ozone is highly reactive, unstable and short-lived besides being very expensive. Oxidation with chlorine dioxide requires 3 – 10 times chlorine dioxide to manganese content and with potassium permanganate it is 1-4 times

potassium permanganate to manganese content. For this reason potassium permanganate is often used to supplement the other processes [Barnes, 1983].

Potassium permanganate provides much more effective oxidation of iron and manganese than does chlorine and the reaction is independent of pH of the water provided that it is above 7. The potassium permanganate dose required may be determined as that needed to produce a faint pink colour in the treated water prior to filtration. Usually the dose required for iron removal is about two thirds the content of iron in the raw water, and for manganese removal about twice the content of manganese. The dose is not critical, any excess will be removed in the filters or contact beds [Cox, 1994]. The removal of iron and manganese on continuously regenerated green sand filters is practiced and reportedly successful. Aeration is avoided as potassium permanganate is continuously added to the raw water prior to passage through a bed of green sand [O'Connor; 1971].

### **2.3.5 Aeration followed by filtration**

An effective aeration system will remove up to 25ppm of dissolved iron. Removal of manganese is slower because greater quantities of oxygen are required to convert manganese from dissolved state to a solid state. Aeration is not recommended for water containing iron and manganese complexes or iron and manganese bacteria, both of which may clog the filter. The most important maintenance step involved in operation is periodic back washing of the filter

[<http://www.ext.vt.edu/pubs/houseing/356-478.htm>; Eckenfelder, Jr. 1970].

### **2.3.6 Catalytic carbon**

This is a relatively new treatment technology that converts soluble iron to insoluble iron in the presence of dissolved oxygen. Essentially, catalytic carbon is activated carbon with modified carbon surface that promotes oxidation on contact. This makes pre-treating water for filtration less complicated. After oxidation, iron particles will settle out of the water and mechanically filtered by activated carbon. This method is not generally recommended for water with soluble iron levels greater than 1.0 ppm. [<http://www.cce.cornel.edu/factsheets/wq-fact-sheets/fact6.htm>].

### **2.3.7 Multistage treatment**

If water has high levels of iron and manganese both in dissolved and in solid state, a multistage treatment operation is necessary. The water will be chlorinated to oxidize dissolved iron and kill iron bacteria, and filtered through a mechanical device to remove particles. This can be followed by activated carbon filtration to remove excess chlorine and a water softener for hardness control as well as removal of any residual, dissolved iron or manganese

[<http://www.ian.unl.unl.edu/pubs/water/g1280.htm>]

## **2.4 Natural Zeolites**

### **2.4.1 Introduction**

Natural zeolites are volcanic minerals with unique characteristics. When volcanoes spewed their ash on ancient lakes a few thousand millennia ago, the resulting chemical reaction of the ash and alkaline water altered the ash into various forms of zeolite crystals [<http://www.markw.com/zeolite.htm>]. Their chemical structure classified them as hydrated aluminosilicate, comprised of hydrogen, oxygen, aluminium and silicon arranged in an interconnecting lattice structure. They are all secondary minerals, occurring most commonly in cavities and veins in basic igneous rocks as basalt, diabase, etc. The three main zeolite deposits are:

- Saline, alkaline lake deposits
- Ground water percolation deposits
- Burial metamorphic deposits.

Approximately 40 natural zeolites have been identified over the past 200 years, the most common of which are analcine, chabazite, clinoptilite, erionite, ferrierite, heulandite, laumontite, mordenite and phillipsite. Zeolites are commercially valuable because of their unique ion exchange, molecular sieving and catalytic properties [Virta, 1998].

### **2.4.2 Properties of zeolites**

Natural zeolites are composed of mainly aluminium, silicon oxide, calcium oxide, sodium oxide and water of crystallization. Other compounds include: potassium

oxide, magnesium oxide, titanium oxide, barium, etc. The arrangement of these elements in a zeolite crystal gives rise to a honey comb framework with consistent diameter connecting channels that vary in size from 2.5 to 5.0 angstroms, depending on the types of zeolite mineral. The crystalline pores are so small, such that only one gram of material has an equivalent surface area of  $40\text{m}^2$ . This unique structure makes zeolites different from other aluminosilicates (kaoline, bantonite, etc) due to the following special properties [<http://www.s-s-m.com/industrial.htm>].

- **Gas adsorption:** The ability to selectively adsorb molecules of gases and vapours.
- **Water absorption/desorption:** The ability to reversibly absorb/desorb water without any chemical or physical change in the zeolite matrix.
- **Ion exchange:** The ability to exchange inherent cations for other cation on a basis of ion selectivity. This substitution of ion enables zeolites to selectively adsorb certain harmful or unwanted elements from soil, water and air. A classic example is the removal of calcium from hard water. Recent studies have shown that zeolites also have a strong affinity for certain harmful heavy metals such as lead and chromium [<http://www.markw.com/zeolite.htm>].
- **The Si/Al ratio:** This ratio determines the zeolite framework which influences most zeolite properties. It varies between (1.1 to 6.1). A zeolite with low Si/Al ratio is highly hydrophilic while a zeolite with high Si/Al ratio is highly hydrophobic.

**Other properties include:**

- **Density:** ranges from 2000 to  $2400\text{kg/m}^3$ .
- **Hardness:** ranges from 3.5 to 5.5 units of hardness on (Moh's scale)
- They are brittle and undergoes cleavage
- **Colour:** depends on composition; common colours include; white, grey, yellow, brown and red.
- They are moderately resistance to mechanical attrition [ Dana; 1954].
- Very high surface area per given weight

The chemical properties of zeolite include;

- Reaction with acids
- High capacity for regeneration

- Radiation stability
- Hydrophilic in nature

[<http://www.s-s-m.com/industrial.htm>]

## **2.5 Uses of Zeolites**

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, 1989, Mumpton 1985]

### **2.5.1 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 works 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 [Jorgensen, 1974]. The structure of zeolite contain channels of defined sizes which are occupied by cations and water molecules and also by additional anions. The selective ability to exchange depends on the diameter of the channels and that of intruding ions.

Separating actions resulting from this is termed as ion sieve separation. Molecular sieve action is also possible and depends upon the relationship between channel diameter and molecular size [Higham, 1959].

## 2.5.2 Sorption of $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$

Sorption reportedly plays a significant role in the removal of iron and manganese from solution. Precipitates of hydrous oxides of  $\text{Fe}^{3+}$  and manganese dioxide both have high sorption capacities for  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  [O'Connor, 1971].

This phenomenon may account for the removal of iron and manganese on contact filters as well as within filters where the filter medium is coated with precipitates. Zeolites and other materials treated with solution of  $\text{Mn}^{2+}$  becomes coated with  $\text{MnO}_2$ .

This coating is then capable of sorbing  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ . Periodically as the sorption capacity is exhausted the sorbed  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , can be oxidized by application of Potassium Permanganate [AWWA, 1971].

## 2.6. Ion Exchange and Adsorption

### 2.6.1 Theory of ion exchange

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 removal of undesirable or recovery of useful anions and cations from water. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Ion exchange also takes place in living material 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 solids with charged sites that exchange ions and certain materials 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 water are synthetic resins [<http://www.rpi.edu/dept/chem-eng/Bioyech-Environ//ONEX/resins.htm>].

### 2.6.2 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 acid, 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 group, as with soluble acids or bases. Thus, a resin with sulphonic acid groups would act as a strong-acid cation exchange resin. The various types of ion exchange resins are listed below [Nordell, 1961].

**(i) Strong –acid cation resins**

Strong-acid resins are so named because their chemical behaviour is similar to that of a strong-acid. The resins are highly ionized in both the acid (R-SO<sub>3</sub>H) and salt (R-SO<sub>3</sub>Na) form, over the entire pH range.

**(ii) 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.

**(iii) 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 hydroxide (OH<sup>-</sup>) form for water deionization, and will remove both strongly ionized acids and weakly ionized acids.

**(iv) Weak-base anion resins**

Weak-base anion resins are like weak-acid resins in that the degree of ionization is strongly influenced by pH, and will only remove strongly ionized acids [Nordell, 1961].

**(v) 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. The functional group used in these resins is an EDTA compound. The resin structure in the sodium form is expressed as R-EDTA-Na.

## 2.7 Ion Exchange Reactions.

The Ion exchange reactions that occur depends upon chemical equilibrium situation in which one ion will selectively replace another on the ionized exchange site. Cation on the sodium cycle can be written as:



Where R represents the exchange resin. This is the reaction that takes place during water softening operation. When all the exchange sites have been substantially replaced with calcium, the resin can be regenerated by passing a concentrated solution of sodium ions through the bed.

During iron removal from water the following reaction takes place.



Similar reaction occur for cation exchange on the hydrogen cycle:



Regeneration with 2 to 10 percent  $\text{H}_2\text{SO}_4$  Yields.



Anion exchange similarly replaces anions with hydroxyl ion



Regeneration with 5 to 10 percent sodium hydroxide will renew the exchange sites.



In addition to the factors of concentration, the nature of the exchanger, and 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 ion 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

[Nordell, 1961; Bowers, 1971].

### **2.7.1 Ion exchange capacity**

The performance and economics of ion exchange are related to the capacity of 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 for some unit weight or 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 kg of  $\text{CaCO}_3$  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 waste water is expressed as equivalent per litre of water to be treated. 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 the ions removed during treatment to the total quantity of ions that could be removed at 100% 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 [ Bowers, 1971; Eckenfelder, Jr 2000].

## **2.8 Theory of Adsorption**

Adsorption is a combination of physical and chemical processes in which a substance accumulates on a solid surface (Mihelcic et al.,1997). As molecules strike repeatedly upon a solid surface and linger for a time, a higher concentration of molecules develops at the surface than in the bulk phase. This phenomenon is called adsorption (Boer, 1953).

Chemical adsorption results in the formation of a mono-molecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules.

Physical adsorption results from molecular condensation in the capillaries of the solid. An adsorbed molecule is at lower energy state than a free molecule, and the difference in the two states is called the heat of adsorption (Boer, 1953). The rate at which molecules are adsorbed is equal to the rate at which the molecule leave the solid surface (desorption) at dynamic equilibrium (Boer, 1953). There is rapid formation of an equilibrium interfacial concentration, followed by slow diffusion of the solute molecules within the capillary of the sorbent particle.

Adsorption can also be explained in terms of ion exchange model. Free metal ions are adsorbed when surface protons are displaced. The adsorption reaction is brought about by reaction between metal ions and their hydroxo species with the formation of surface complexes (Ahrland et al., 1960; Dugger et al., 1964). Adsorption phenomenon is applicable both in gas phase and liquid phase. Ion exchange is basically an adsorption process in liquid phase. The Freundlich and Langmuir adsorption models can also be used to describe ion exchange process in liquid phase.

### **2.8.1 Adsorption forces and mechanism**

Adsorption from solution at the solid liquid interphase is a complex and imperfect understood phenomenon. Before any adsorption studies are discussed it is imperative to have understanding of the physiochemical forces and mechanisms thought to be responsible for the adsorption of ions and molecules. This physiochemical forces can be broken into several categories: -

#### **(i) London Van-der-Waals Forces**

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 neighbouring atoms of opposite sign. Although the momentary dipoles and the induced dipoles are constantly changing positions and sign, the net result is a weak attraction (4 to 8Kj/mol for small molecules and atoms). These forces are important in adsorption of organics and are generally attributed to the non ideal behaviour 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 [Mihelcic et al., 1997].

#### **(ii) Coulumb-Electrostratic Force**

An electrostatic force results from a charged surface due to isomorphous substitution in the mineral lattice. In silicates substitution of octahedrally co-ordinated cation by cation 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 bulk solution [Mehelcic et al., 1997].

#### **(iii) Hydrogen Bonding**

This is a charge transfer which arises from partial orbital overlap of electron rich and electron poor molecules. Electron rich molecules include compounds like alkanes, aromatics, alcohols, e.t.c, while electron acceptors include compounds like trinitro benzene and weakly acidic hydrogen.

In reality, hydrogen bonds may be delocalized covalent bonds i.e. resonance bonds or multiple center bonds [Huhyeey, 1978].

#### **(iv) Ligand exchange**

Many atoms or molecules form co-ordinated complexes with ligands that range in complexity from simple linear molecules to extensive chelate complexes. The bonded co-ordinated complexes may be displaced by other co-ordinated complexes that better satisfy electroneutrality requirements.

#### **(v) 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 physical cavity occupied by the solute in the solvent and from the partial loss of structured water molecule about the solute ordered by Van-der Waal forces [Cowan and White, 1958].

**(vi) Dipole – Dipole Induction**

This results from the attraction of an induced dipole brought about by either a permanent dipole or a charged site of species. The energy of attraction is less than 8Kj/mol, but this force often adds to coulomb interactions [Mihelcic et al., 1997].

**(vii) 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 identity or the atoms are rearranged forming new compounds at the demand of the unsatisfied valences of the surface atoms.

The enthalpy of chemisorption is much greater than physical adsorption. Most catalytic activity at the surface is chemisorption. Chemisorption and physical adsorption are often difficult to distinguish from one another because a chemisorbed layer may have a physically adsorbed layer upon it [Hoffmann, 1988].

**2.8.2 Adsorption Models**

An adsorption isotherm is a plot of the equilibrium amount of solute taken up per unit weight of adsorbent versus the concentration of solute in the moving phase at constant temperature [ Andelman 1971].

The common classical adsorption models for isothermal conditions are the Langmuir, Freundlich and Brunauer, Emmelt and Teller (BET).

**(i) Freundlich Models.**

This is an empirical model which is valid for heterogeneous monolayer coverage (Hand, 1997). The isotherm equation can be expressed as,

$$q_e = KC_e^{1/n} \tag{2.1}$$

Where;

$q_e$  = Mass of sorbate sorbed per gram of sorbent

$C_e$  = Concentration remaining in solution.

K and n are experimentally determined parameters [Varsaraj et al., 1992].

### (ii) Langmuir Model.

The Langmuir model is based on equilibrium between condensation and evaporation of adsorbed molecules, considering a mono molecular adsorption layer.

$$q_e = \frac{abC_e}{1 + aC_e} \quad 2.2$$

This can be expressed in linear form as:

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{abC_e} \quad 2.3$$

Where;

b = Amount adsorbed to form a complete mono-layer on the surface.

a = Constant which increases with increasing molecular size.

$C_e$  = Concentration remaining in solution.

### (iii) BET Model

Brunaur, Emmett and Teller (BET) developed several models for gas adsorption on Solids. The models are valid for multiple layers of adsorption(condensation) on homogeneous surfaces (Hand, 1997).

#### Assumptions underlying BET model

- Gas adsorbs on a flat, uniform surface of the solid with a uniform heat of adsorption due to Van der Waals forces between the gas and the solid.
- There is no lateral interaction between the adsorbed molecules.
- The adsorption of the second and subsequent layers occurs with heat of adsorption equal to the heat of liquefaction of the gas (Swinkels,1999).

The single – solute BET isotherm is expressed as:

$$q_e = \frac{abC_e}{(1-C_e) [1+(a+1)C_e]} \quad 2.4$$

where a and b are analogous to the parameters for Langmuir model

The BET simplifies to Langmuir model when  $a > 100$  and  $C_e < 0.01$

(Varsaraj et al., 1992).

# CHAPTER 3.0: INDUSTRIAL APPLICATIONS FOR ZEOLITES.

## 3.1 Metal removal from raw water.

Zeolites are highly selective scavengers of a variety of metal cations that can be removed from liquid effluents through the process of ion-exchange/adsorption or molecular sieving. These cations include lead, silver, cadmium, cobalt, zinc, copper, mercury, magnesium, manganese, iron, aluminium, chromium and others [http://www.s-s-m/industrial.htm].

Clinoptilolite water polishing treatment systems are applicable in industries such as mining, electroplating and electronics.

The removal of iron and manganese from water using zeolite is analogous to ion exchange process that removes hardness from water (http://www.extension.umn.edu.extpubs/h2oqual/wtasys/ae1030w.htm).

The process can be represented by the equations below:-

Removal stage:



(Nordell, 1961)

This example assumes a sodium zeolite for simplicity.

The removal of iron and manganese on continuously regenerated green sand filters is practiced and reportedly successful. Aeration is avoided as potassium permanganate is continuously added to the raw water prior to passage through a bed of zeolite (green sand) exchange medium. The permanganate oxidizes the iron and manganese so that the exchange medium becomes coated with the oxidation products. The hydrous oxides of iron and manganese deposited on the exchange medium have a large sorption capacity for  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  and this capacity makes it possible to operate the filter on an intermittent basis regenerating with permanganate after the exchange capacity is exhausted [O'Connor 1971].

Research carried out to investigate the possibility of iron and manganese removal from underground water using natural zeolite at Ann. West University in Romania by Burtica and Gand Poda in 1994, produced positive results

[<http://www.ichmt.org/abstracts/MFTP-2000/abstracts/47.pdf>]

Use of ion exchange for iron and manganese removal from water has been reported [Alzentzer, 1963].

The advantage of using ion exchange methods are:-

- Small capital investments than in coagulation-filtration process.
- Higher flow rates and small plant equipment.
- Simple operation.

The obvious drawback to ion exchange is non selective removal of other ions which rapidly increases the operation cost.

### **3.1.1 Sewage and waste water treatment**

Ammonia removal is a major concern in treatment of municipal wastewater. Ammonia levels in municipal wastewater can be reduced to 10-15 ppm through traditional primary and secondary treatment facilities. Final circulation in the tertiary treatment stage is accomplished with polishing filters containing clinoptilolite, a popular form of natural zeolite [<http://www.s.s-m.com/industrial.htm>].

### **3.1.2 Radioactive waste treatment**

Process effluents bearing radioactive isolopes can be treated through columns with natural zeolites. The zeolites selectively removes cesium and short term isotopes through the process of ion exchange. Effluent liquids are purified to acceptable limits for discharge as the radioactive isotopes are held within the zeolite cage structure. One outstanding example of this application is the British Nuclear Fuels Ltd at Sellified, England [<http://www.s-s-m.com/industdrial.htm>]

### **3.1.3 Sorbent barriers for radioactive waste.**

Permeable barriers incorporate sorbent materials, including zeolite, to selectively contain contaminants that are percolating from shallow land burial sites of low level radioactive waste. The zeolites are combined with clays and other materials that retard the migration of leachate for a period long enough to allow exchange and/or decay of radioactive ions [<http://www.s-sm.com/industrial.htm>].

### **3.1.4 Pollution control**

Natural zeolites are adsorbent of choice for many cost effective air pollution control technologies treating the hazardous air pollutants (HAP) and listed volatile organic compounds (VOC). Zeolites contain very small internal pores from 3 to 5 angstroms and therefore are highly selective adsorbent of gas-phase molecules and elements. Many of the identified indoor air pollutants, including formaldehyde, chloroform, ammonia and carbon monoxide, are in a size range that is most effectively sieved by zeolite [<http://www.s-sm.com/industrial.htm>].

### **3.1.5 Aquaculture**

Clinoptilolite is used to control ammonium in filtration systems at many commercial fish farms, in home aquarium products and during fish transportation. The zeolite has the double benefit of performing both chemical filtrations by ion exchange while serving as a biological filtration substrate [<http://www.s-s-m.com/industrial.htm>].

### **3.1.6 Phytoremediation**

Phytoremediation is a process for uptaking heavy metals by certain plant roots and leaves. Natural zeolite can increase the rate of phytoremediation for certain metals and isotopes [<http://www.s-s-m.com/industrial.htm>].

### **3.1.7 Other uses**

These include: - gas purification and separation, heat storage and solar refrigeration, agriculture and fillers in the manufacture of paper, paint and plastics.

### **3.1.8 Modified natural zeolites.**

A variety of products have been formulated where zeolites are palletized and/or activated for utilization in specific applications. Some of these include:-

- Manganese coated zeolites used in home water softening and purification units.
- Air dryers for compressed air brake system.
- Insulated window desiccants
- Genetic packaging and food desiccants.



- Moisture absorbents in refrigeration systems

[<http://www.s-s-m.com/industrial.htm>].

### **3.2 Iron and manganese removal from water using natural zeolite.**

The previous description of natural zeolite, its properties and uses has outlined the tremendous potential of this unique mineral. Natural zeolite are the least known treasures for environmental pollution control. They are cheap and therefore of particular importance to less industrialized countries for use in environmental clean-up and protection measures [Parham 1984, Mumpton 1985].

Natural zeolite is both an ion exchange resin and an adsorbent and removes metals selectively from water

[<http://www.s-s-m.com/industrial.htm>; Higham, 1959].

Use of ion exchange for iron and manganese removal has been reported [Alzenter, 1963].

The removal of iron and manganese from water by zeolitic volcanic tuff is probably through adsorption/ion exchange. This kind of adsorption is mainly due to surface complex formation and/or ion exchange. The free metal ions are adsorbed when surface protons are displaced.

# CHAPTER 4.0: MATERIALS AND RESEARCH METHODOLOGY.

## 4.1 Introduction

Experiments were conducted to investigate the potential of a naturally occurring chokaa to remove manganese and iron from water. A naturally occurring material mined in Muranga district, Kenya, locally known as chokaa was used in previous studies and found to remove ammonia from water [Mwamachi, 2003]. It was identified as zeolitic volcanic tuff of alkali trachytic origin by full chemical analysis and x-ray diffraction technique. All other experiments on sorption studies, column studies and the effects of pH on the removal of the two cations from water, were conducted at room temperature (Which was found to be fairly constant at  $(25 \pm 1^{\circ}\text{C})$ ) except for the experiment to investigate the effect of temperature on the removal of iron and manganese from water. Trial sorption studies were conducted to determine the optimum dosage of sorbent required. Kinetic studies were conducted and the effects of temperature and pH on the removal of the two cations were investigated.

Column studies were also carried out to investigate the possibility of removing both cations from water in a process which simulates the real water treatment process. In this process the water had to be treated first using potassium permanganate before passing it through an adsorption column packed with chokaa. Various relationships between various parameters involved were drawn and the results of these are discussed in the preceding chapters.

## 4.2 Materials and Equipments

### 4.2.1 The source of Iron and Manganese.

Bore-hole water from Alliance Girls High School was used. The initial iron and manganese concentration was determined using atomic absorption spectrometer. This was found to be  $3.7\text{mg/l} \pm 0.01$  and  $0.6\text{mg/l} \pm 0.006$  for iron and manganese, respectively. The sample was collected before it entered into their treatment plant. This was done using 10 litre jericans, which were tightly corked up after filling up. The first batch of sample was collected in three containers, which were filled at intervals of ten minutes. The samples were immediately transported to the Public

Health Engineering Laboratory, University of Nairobi. Nitric acid was added to the samples to keep  $\text{Fe}^{2+}$  ions solubilised, iron can be converted to insoluble higher state of  $\text{Fe}^{3+}$  under oxidising conditions. Iron ions are mainly solubilised at lower valence of  $\text{Fe}^{2+}$ .

#### 4.2.2 The Sorbent

The chokaa mined from quarries in Murang'a district, Kenya, was bought at Gikomba market where it is normally sold to expectant mothers as an iron supplement. The chokaa lumps, which are relatively soft, were crushed to smaller particles by hammer. It was then graded into three different particle size fractions:- 0.3mm-0.6mm, 0.6mm-1.2mm and 1.2mm-2.4mm. The pulverized material was then placed in an open at 103 degrees celcius for 12 hours after which it was cooled in a dessicator to room temperature. The fractions were then stored in a separate airtight bottles ready for use.

Other sample properties included:-

- pH = 7.35.
- Total hardness = 70mg/l of  $\text{CaCO}_3$ .
- Dissolved oxygen (DO) = 7mg/l.
- Carbon dioxide content = 18 mg/l
- Total Alkalinity / Methyl alkalinity = 161mg/l as  $\text{CaCO}_3$ .

The laboratory sample was prepared by dissolving 1.000g of 99.9% iron metal strip in 20 mls of 1: 1 hydrochloric acid and diluting to 1 litre using di-ionized water to give 1000mg/l of iron. All other solutions of iron were prepared from this standard solution by dilution method.

Similarly a standard solution of 1000mg/l of manganese was prepared and all the other different solutions obtained from it by dilution method.

#### 4.2.3 Reagents and equipment

All the reagents used were of analytical grade. Before each experiment, all glassware were cleaned with detergent mixed with dilute nitric acid and repeatedly rinsed with distilled water followed by drying in an oven. An Atomic Absorption Spectrometer (AAS Varian Techtron Spectra A-10) was used to determine the concentration of iron

and manganese in the sample. An electric shaker was used to shake the samples during the tests.

### **4.3 Experimental Procedures.**

#### **4.3.1 Determination of iron concentration (procedure)**

- The optimum wavelength (248.3nm) for iron was set on the AAS instrument.
- The gas taps were opened, starting with oxygen followed by acetylene and the flame lit using a gas gun. This sequence is important to avoid gas explosion.
- A spectra AA hollow cathode lamp for iron was fitted into the instrument and the absorbance optimized by using a control button.
- The instrument was then calibrated with standard iron solutions and distilled water as a blank for control purposes.
- The nebulizer was then dipped into the sample for concentration reading. Two sets of reading were taken for each sample and the average reading recorded. After every four readings, the concentrations of the standards and the distilled water, were read again for control purposes.

The procedure for determining the concentration of manganese ions in the sample was similar to that for iron. But the instrument was set to a wavelength of 279.5nm and a manganese spectra AA hollow cathode lamp was used.

#### **4.3.2 Trial Studies**

Conical flasks of 250ml capacity were used in the kinetic experiments. Borehole water samples (100ml) of known iron and manganese concentration were poured into the flasks. Carefully weighed amounts of the sorbent material of 1g, 2g, 4g, 6g, 8g, and 10g were added to the flasks which were then tightly stoppered and shaken at 200r.p.m on an electric shaker for 2 hours. 0.6mm-1.2mm particle size was used for this study because it is the median of the three particle sizes. The manganese and iron concentration was then determined by using atomic absorption spectrometer in the supernatant water.

The first step was to determine the optimum sorbent dose. 100ml of the borehole samples were shaken with varying amounts of sorbent of particle size range 0.6-1.2mm for 2 hours. The sorption increased with increased sorbent dosage up to 90%

of the original iron content and remained fairly constant at that value. The corresponding sorbent dosage was 4 grams, and therefore this was adopted as the optimum sorbent dose.

Kinetic experiments were carried out to determine the equilibrium time and to investigate the nature and rate of the sorption process. The contact times used were 10, 20, 40, 80 and 120 minutes. For adsorption dynamics, experiments were carried out for duration of 0.5, 1, 2, 4, 8, 16, 30 and 60 minutes using particle size range 0.3 – 0.6mm. The variables in the kinetic studies included particle size, pH, and temperature.

#### **4.3.3 Equilibrium studies**

After the establishment of the optimal conditions, batch experiments were conducted for equilibrium studies. For all the three different particle size ranges, it was found that equilibrium was established before 2 hours had elapsed. For investigations into the effect of temperature and the experiment to investigate the effect of pH on the removal of the two ions from water a sorbent size of 0.3- 0.6 mm was used.

#### **4.3.4 Column Studies .**

This became necessary, because it was found that the chokaa could only remove iron by adsorption at a pH below 4, unlike the case for manganese which could be removed comfortably at pH of above 7. This was noted when the experiment to investigate the effect of pH on removal of the two cations from water was carried out. This is because the two cations behave differently at similar pH. Column was used instead of a batch test because it would simulate the actual treatment process.

The bore water sample was first treated with potassium permanganate before passing it through a chokaa column. Most of the iron was oxidized by the permanganate and filtered out by the column while manganese was partly oxidized and partly sorbed by the chokaa in column. A flow diagram for a set up of a column study experiment is shown in Figure 4.1.

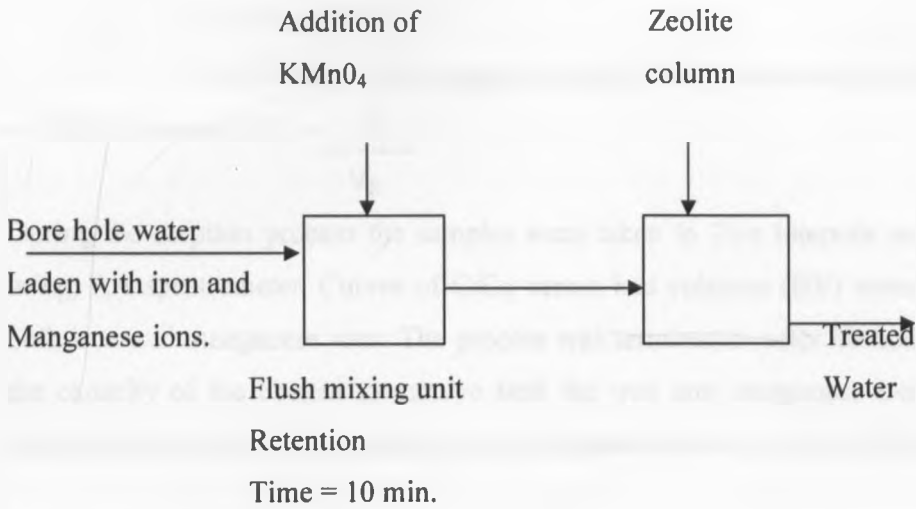


Fig. 4.1 Proposed column treatment set up.

Parameters for the zeolite column used.

- Zeolite size, 0.6 – 1.2mm.( this size was chosen because it compares well with effective size of rapid sand filters i.e. 0.8mm-1.22mm)
- Volume of column,  $V_R = 155.5\text{cm}^3$  .
- EBCT = Empty bed contact time (defined as the time taken by water equivalent to one volume of column to pass through it). The EBCT for this study was taken as 15 minutes because this gave a reasonable volume of water required to run the column per day.
- $Q_f$  = Volume flow rate in the bed.
- $V_R$  = Volume in the column during adsorption process

The column size was 30mm diameter by 220mm height.

$$V_R = \pi/4 \times (30 \times 10^{-3})^2 \times 220 \times 10^{-3} \text{m}^3$$

$$= 1.555 \times 10^{-3} \text{M}^3 = 155.5 \text{cm}^3$$

- $EBCT = \frac{V_R}{Q_F}$

$$\text{Let EBCT} = 15 \text{ min} = \frac{V_R}{Q_F}$$

$$\text{hence } Q_F = \frac{155.5}{15}$$

$$= 10.37 \text{ cm}^3/\text{min.}$$

$$= 14.93 \text{ l/day. This is approximately 96 bed volumes per day.}$$

- $\text{Bed Volumes (BV)} = \frac{V_F}{V_R}$

During the sorption process the samples were taken in 2hrs intervals and analyzed using, AA spectrometer. Curves of C/Co versus bed volumes (BV) were plotted for both iron and manganese ions. The process was terminated after 40 hours, because the capacity of the chokaa to remove both the iron and manganese ions had been exhausted and therefore the column required regeneration to restore its efficacy.

#### 4.3.5 Control Experiments.

For each investigation, 100ml of sorbate without the sorbent were agitated together with the test samples at 200rpm. Iron and manganese concentrations were determined in all cases. This was important for control as everything was subjected to the same environmental conditions.

#### 4.3.6 X- Ray Diffraction test for the sorbent.

This is probably the most important means of identifying minerals in rocks.

The basis of XRD analysis is the diffraction of X-rays passing through a lattice. An X-ray beam is generated by bombarding a metal anode with high-energy electron beam. The angular relationship between the incident X-ray and d-spacing required to produce a diffraction maximum is governed by Bragg's law.

$$n\lambda = 2d \sin\theta$$

where:-

n= Integer

d= d-spacing = distance between two adjacent diffracting crystal planes.

$\lambda$ = wavelength of X-ray

$\theta$ = angle between X-ray and diffracting crystal plane.

XRD analysis relies on the ability to detect diffraction maxima, measure the angular relationship to the crystal and calculate the d-spacing from Bragg's law. Every

mineral has a characteristic series of d-spacing that can be used for identification. Accurate identification of a mineral from an X-ray pattern relies on the matching of more than one peak with quoted values for that mineral. Such matching is increasingly achieved by computer modelling using software packages [ Mathers, et al., 2000]

The XRD equipment used for the chokaa identification did not have the computer modelling software facility for matching the peaks, and therefore matching had to be done manually. In addition the XRD equipment is a mono-minerallic analyzer and volcanic tuffs are known to contain more than one mineral loosely bound together. The XRD results therefore did not give a conclusive identification of the minerals contained in the chokaa, but on further analysis it was identified as volcanic tuff. From the chemical composition results, this kind of tuff can be referred to as a zeolitic volcanic tuff of alkali trachytic origin.

In Italy volcanic tuffs provide an inexhaustible supply of zeolites for industrial use [Sersale, 1972]. Just like natural zeolites, zeolitic volcanic tuffs (chokaa) can be utilized as dessicants, gas adsorbents and cation exchangers [Aillo, et al., 1976; Elia, et al., 1967].

The silicate glasses present in the tuffs have high free energy and very reactive in aqueous conditions and can transform by hydration, solubilization and hydrolysis into clay minerals or zeolites. The most compact tuffs have compressive strength of 30-60kg/cm,<sup>2</sup> which has enabled them to be used for building purposes. In most cases, the tuff is overlain by an amorphous, unwelded product known as pozzolana, which may be considered to be unzeolitized part of the tuff [Di Girolano, 1968].



## CHAPTER 5.0: RESULTS AND DISCUSSION.

### 5.1 Effect of the sorbent properties on the sorption process

The chemical analysis of the (chokaa) sample was done at the Mines and Geological Department Laboratory. The sample was found to be rich in  $\text{Fe}^{3+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ . The results are entered in Table 5.1 below.

**Table 5.1: Chemical analysis of the sample.**

Constituent	% Weight
$\text{SiO}_2$	65.60
$\text{Al}_2\text{O}_3$	12.80
$\text{Fe}_2\text{O}_3$	7.60
CaO	0.47
MgO	0.37
$\text{Na}_2\text{O}$	3.80
$\text{K}_2\text{O}$	3.10
$\text{TiO}_2$	1.67
MnO	0.11
LOI	3.81
<b>Total</b>	<b>99.33</b>

The CEC of the chokaa sample was 16.40 meq/100g.

The average Si/Al mass ratio for the chokaa was 4.54. This means that the chokaa is hydrophilic and has many counterions present. The mineralogical content of the chokaa suggest that sorption of iron and manganese ions could be through a combined mechanism of ion exchange and adsorption on the particles surface.

Surface charge at the phase boundary may be caused by lattice imperfections at the solid surface and by isomorphous replacements within the lattice. If a Si(IV) atom is replaced by Al(III) atom, a negatively charged frame work is established. This is because aluminum has one electron less than silica atom. Similarly if Al(III) atom is replaced by Mg, Fe(II), Zn(II) or Ca atom, a negative charge will result. This negative

charge deficiency is called cation exchange capacity in zeolite (Stumm and Morgan, 1981).

The charge on the silica surface in water can also be explained by the acid base behaviour of the silanol (Si-OH) groups found on the surface of hydrated silica.



This charge depends on the degree of ionization (proton transfer) and pH of the medium. It is positive at low pH values [Stumm and Morgan, 1981].

The zeolite mineral can therefore exhibit both a CEC and an anionic exchange capacity (AEC) at the same time depending on the pH of the media.

The sorption of iron and manganese ions on the chokaa is expected to follow the Langmuir adsorption isotherm if the sorption process proceeds through the mechanisms postulated above. As the manganese and iron ions exchange with counterions present in the chokaa, the amount sorbed asymptotically approaches a constant value set by the total charge density (in this case, the cation exchange capacity of the mineral).

## 5.2 Cation Exchange Capacity (CEC) for the Sorbent.

Cation exchange capacity (CEC) is the sum total of exchangeable cations that a soil, clay, colloid or growth medium can adsorb, and is expressed as milliequivalents per 100g (meq 100g<sup>-1</sup>) or centimoles per kg (cmol kg<sup>-1</sup>)

The cation exchange capacity is important in soils because it causes and corrects soil acidity and basicity besides acting as a mechanism in purifying or altering percolation water by adsorbing toxic cations or the exchange complex.

The seven major cations are: H<sup>+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> with other cations available in smaller amounts. Exchange sites are negatively charged sites on clay complex or colloids. Positively charged cations are attracted onto these exchange sites on the colloid particles and exist in dynamic equilibrium with cations in solution. At low concentrations and ordinary temperatures the affinity of adsorption increases with increasing valency of exchanging cation thus (Na<sup>+</sup> < Ca<sup>2+</sup> < Al<sup>3+</sup> < Th<sup>4+</sup>), but

within the same group the affinity of adsorption increases with increasing atomic number ( $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+$ )

[[www.oceanag.co.zg/articles/ocean/cation%20exchange%20capacity.pdf](http://www.oceanag.co.zg/articles/ocean/cation%20exchange%20capacity.pdf); Ciaccio, 1971]. Typical CEC values for different colloids are shown in Table 5.2 below.

Table 5.2 Typical CEC values for different colloids.

Colloid	CEC meq/100g
Organic matter	200-400
Vermiculite	100-150
Montmorillonite	80-150
Chlorite	10-40
Kaolinite	3-15
Oxides and hydroxides	2-6

Source [Ciaccio, 1971]

The CEC of the sample was carried out at the Department of Soil Science Laboratory Kabete Campus, University of Nairobi. The laboratory uses leaching method for CEC determination. The results are shown in Table 5.3 below.

Table 5.3. Concentration of the major cations in the sample and its CEC value.

Meq/100g					
Sample	K	Na	Ca	Mg	CEC
Volcanic tuff	0.8	3.33	5.35	6.33	16.4

Theoretically the total sum of concentrations of the cations should equal the CEC value. This is not the case because some cations have not been accounted for. Generally if the CEC value is greater than the total sum of the cations, the sample is acidic. This confirms the results in Table 5.4, that the suspension solution had a pH of 6 - 6.5.

Table 5.4. Some Physical properties of the (sorbent) zeolitic volcanic tuff.

Colour	:	Creamish white
Density	:	2000 – 2200kg/m <sup>3</sup>
Hardness	:	3.0 – 5.0 units of hardness (Moh's scale)
Suspension PH	:	6.0 – 6.5

The physical properties of the sorbent (zeolitic volcanic tuff) compares well to that of natural zeolite.

### 5.3 Effect of Zeolite Dosage on manganese and iron removal.

#### (a) Iron removal.

The study was important so as to determine the optimum mass of sorbent. The experimental data is presented in Table 5.5. A pH of 2.5 was chosen because initial preliminary studies indicated that the chokaa can only remove iron ions from water at low pH. The particle size was chosen on the basis that it was the median of the three particle sizes available.

Table 5.5 Effect of mass of chokaa on removal of iron. (*Particle size 0.6-1.2mm, Initial concentration 3.7mg/l and pH =2.5*).

Mass of Chokaa	0	1	2	4	6	8	10
Final Iron Conc, mg/l	3.7	0.78	0.56	0.36	0.38	0.4	0.37
% sorption	0	79	85	90	90	89	90
Specific sorption, mg/g	0	0.292	0.157	0.084	0.055	0.041	0.033

To determine the optimum mass of sorbent for iron removal a graph of percentage sorption of iron versus mass of chokaa shown in Figure 5.1 was plotted.

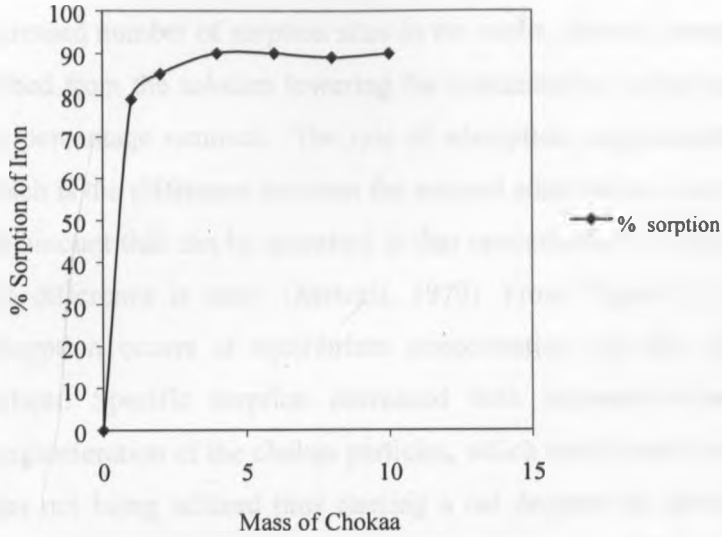


Fig 5.1 Percentage sorption of iron versus chokaa dosage. (Conditions; Initial iron concentration = 3.7mg/l, particle size 0.6 – 1.2mm, pH = 2.5, contact time =2 hrs and volume of sorbate =100ml).

Figure 5.2 shows the specific sorption of iron on chokaa expressed in mg /g.

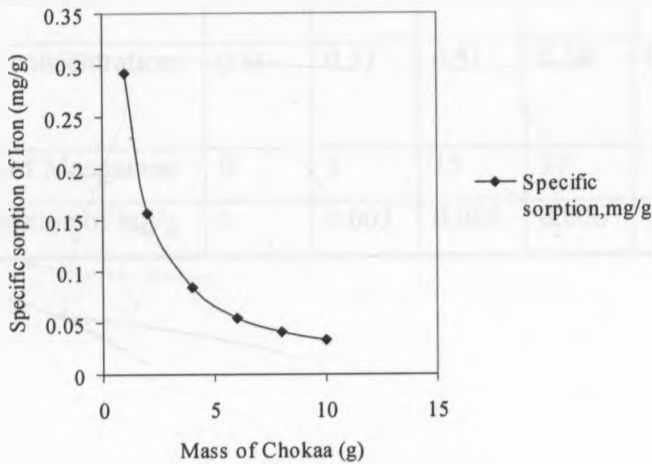


Fig 5.2 Specific sorption versus chokaa dosage. (Conditions; Initial iron concentration = 3.7mg/l, particle size 0.6 – 1.2mm, pH = 2.5, contact time = 2 hrs and volume of sorbate =100ml).

The sorption increased with increased zeolite dosage upto about 90% of iron content and remained fairly constant at that value while the specific sorption capacity decreased with increased zeolite dosage. This can be explained in terms of the increased number of sorption sites as the zeolite dose is increased. More iron ions are sorbed from the solution lowering the concentration in the bulk liquid and increasing the percentage removal. The rate of adsorption is proportional to the driving force, which is the difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At equilibrium concentration, this difference is zero (Metcalf, 1979). From Figures 5.1 and 5.2 the maximum adsorption occurs at equilibrium concentration and this is attained at 4grams of sorbent. Specific sorption decreased with increase in mass of chokaa due to conglomeration of the chokaa particles, which could have resulted to some adsorption sites not being utilized thus causing a net decrease in specific area of sorption. The optimum chokaa dosage was found to be 4grams per 100ml of the sample.

**(b) Manganese removal:**

This experiment was carried out so as to determine the optimum mass of chokaa for manganese removal, and the data is presented in Table 5.6.

Table 5.6 Particle size 0.6 – 1.2mm, initial Manganese concentration 0.6mg/l and a pH of 2.5, volume of sorbate=100mls.

Mass of Zeolite (g)	0	1	2	4	6	8	10
Manganese concentration, mg/l	0.60	0.57	0.51	0.38	0.39	0.39	0.38
% Sorption of Manganese	0	5	15	37	35	35	37
Specific Sorption of mg/g	0	0.003	0.005	0.006	0.004	0.004	0.003

To determine the optimum mass of sorbent for manganese removal, a graph of percentage sorption of manganese versus mass of chokaa was plotted and is shown in Figure 5.3.

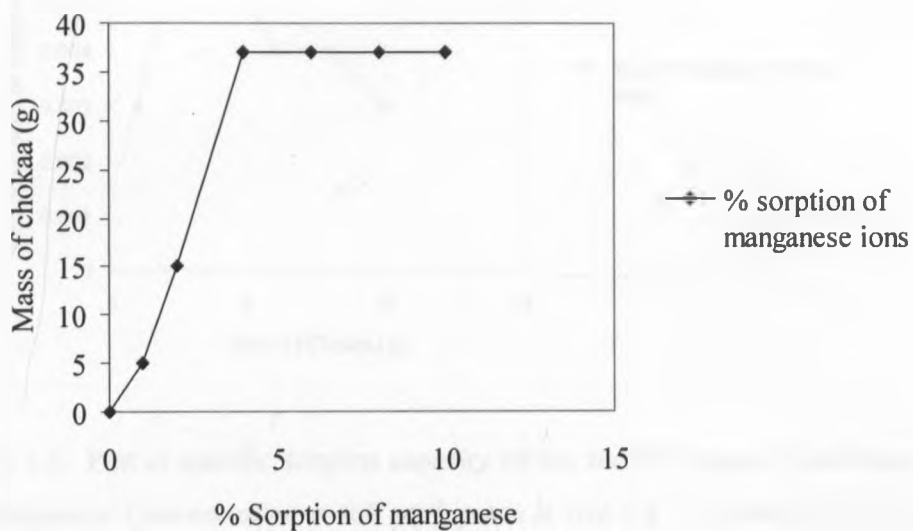


Fig 5.3. Percentage sorption of manganese versus chokaa dosage. (Conditions: Initial Manganese Concentration = 0.6 mg/l, particle size 0.6 – 1.2mm, pH = 2.5, contact time – 2 hrs and sorbate volume=100ml).

Figure 5.4 shows specific sorption of manganese ions expressed in Mg/g.

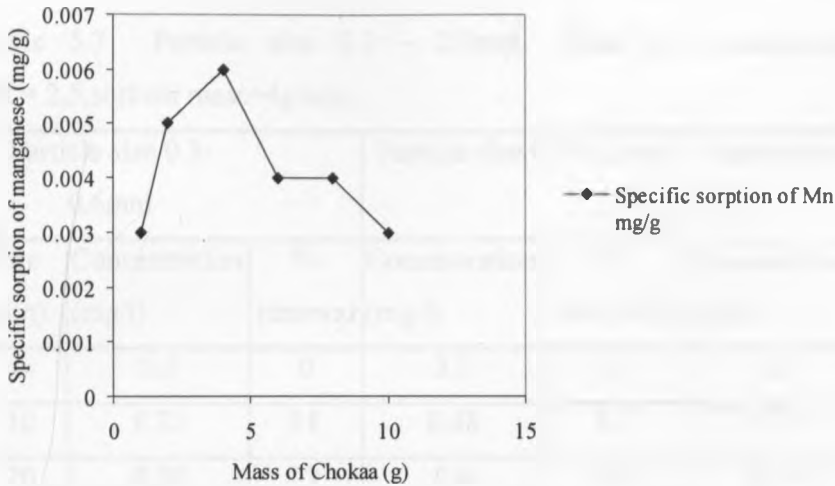


Fig 5.4. Plot of specific sorption capacity versus zeolite dosage. (Conditions: Initial Manganese Concentration = 0.6 mg/l, particle size 0.6 – 1.2mm, pH = 2.5, contact time – 2 hrs and sorbate volume=100ml).

The sorption of manganese ions by zeolite is slower than for iron ions under similar conditions. This is because the two processes are different and their mechanisms of removal are also different. This is explained in section 5.8 of this report. Similarly the optimum dosage for manganese ion removal was found to be 4grams per 100mls of the sample.

## 5.4 Effects of chokaa particle size on removal iron and manganese from water.

### (a) Iron removal

The effect of particle size on iron and manganese removal is represented in Fig. 5.5 and 5.6. These graphs generally show that the sorptive capacity increased with decreased particle size. This can be attributed to large surface area and closer proximity of sorption sites in smaller particle than in larger ones. The size of particle also affects the rate of sorption process and the time to reach equilibrium. Data for the effect of particle size of chokaa on iron removal is presented in Table 5.7. The data generally shows that small particles of chokaa are more effective on removing iron than bigger



particles. The process is also favoured by low pH, however low pH values would require correction for proper usage. This is dealt with in section 5.9 of this report.

Table 5.7 Particle size 0.3 – 2.4mm, initial Iron concentration 3.70mg/l, pH = 2.5,sorbent mass=4grams.

Particle size 0.3-0.6mm			Particle size 0.6-1.2mm		Particle size 1.2-2.4mm	
Time (Min)	Concentration (mg/l)	% removal	Concentration (mg/l)	% removal	Concentration (mg/l)	% removal
0	3.7	0	3.7	0	3.7	0
10	0.32	91	0.48	87	1.11	70
20	0.28	92	0.4	89	0.74	80
40	0.26	93	0.35	90	0.6	84
80	0.26	93	0.33	91	0.52	86
120	0.26	93	0.33	91	0.52	86

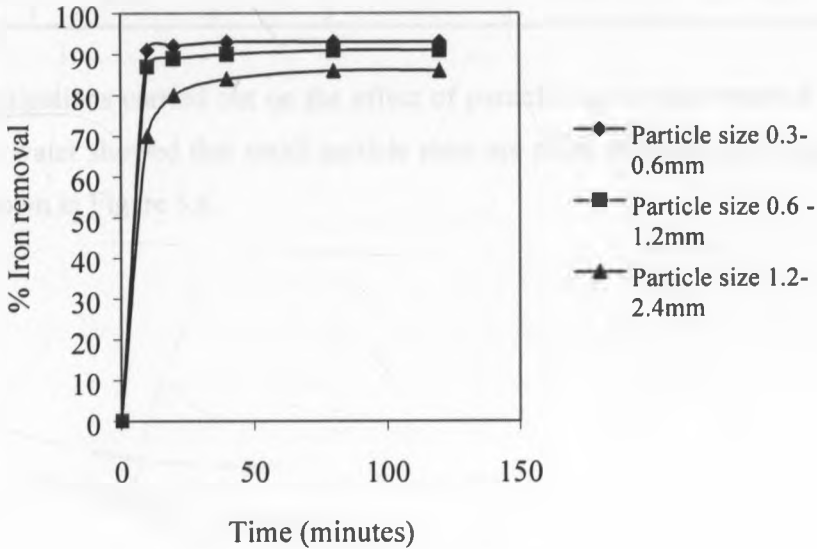


Fig 5.5. Plot of percentage removal of Iron for different particle sizes of chokaa. (Conditions: 4g of zeolite per 100ml solution containing 3.7mg/l of iron at pH = 2.5. sorbate =100ml)

**(b) Manganese removal:**

Data showing the effect of particle size of chokaa on manganese removal is presented in Table 5.8. The data shows that small particles of chokaa are more effective in removing manganese than big particles.

Table 5.8. Particle size versus manganese removal. (*Initial Manganese concentration =0.6mg/l, pH – 2.5, volume of sorbate=100ml. Particle sizes 0.3-0.6mm, 0.6-1.2mm 1.2 – 2.4mm),mass of sorbent=4grams.*)

Particle size 0.3-0.6mm			Particle size 0.6-1.2mm		Particle size 1.2-2.4mm	
Time (Min)	Concentration (mg/l)	% removal	Concentration (mg/l)	% removal	Concentration (mg/l)	% removal
0	0.60	0	0.60	0	0.60	0
10	0.41	32	0.42	30	0.49	18
20	0.39	35	0.40	33	0.47	22
40	0.37	38	0.39	35	0.46	23
80	0.36	40	0.37	38	0.45	25
120	0.36	40	0.37	38	0.45	25

Investigations carried out on the effect of particle size on the removal of manganese from water showed that small particle sizes are more effective than big particle. This is shown in Figure 5.6.

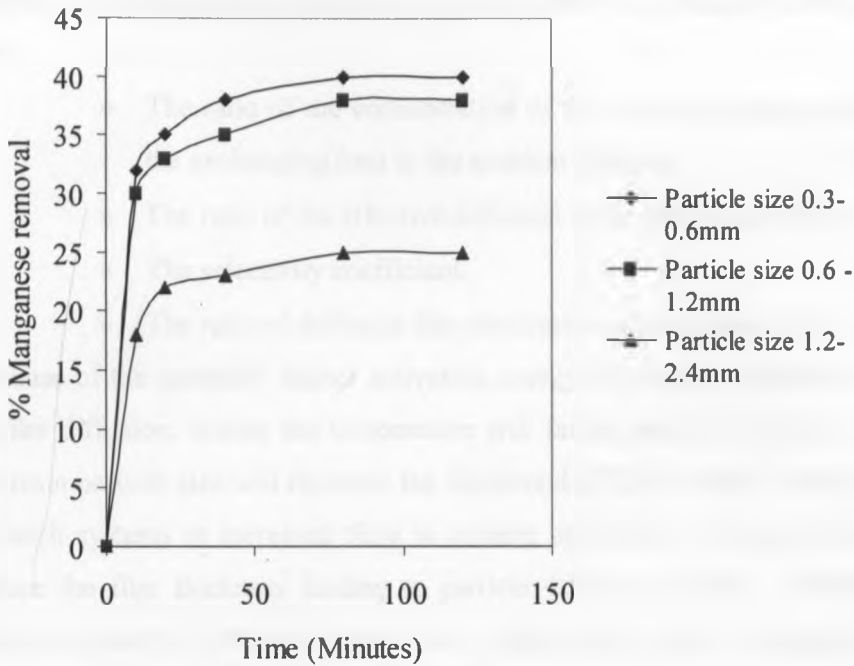


Fig 5.6 Percentage removal of manganese for different particle sizes of chokaa: (Conditions; 4g of chokaa per 100ml solution containing 0.6mg/l of manganese at pH = 2.5)

### 5.5 Kinetics of the sorption process.

Sorption is a time dependent process. Ion exchange is a form of sorption process which is brought about by reaction between metal ions and their hydroxo species with the formation of surface complexes [Ahrlund et al., 1960, Dugger et al., 1964]. Most of ion exchange sites in a typical zeolite/chokaa are located within the matrix or pore structure. Thus, for a typical ion exchange to occur, the ions must pass through the zeolite /chokaa matrix and across a liquid film or a boundary layer at the chokaa – solution interface (Andelman et al., 1971). The rate determining step in the exchange could then be;

- (a) Diffusion in the boundary layer (film diffusion).
- (b) Diffusion in the chokaa phase (particle diffusion).
- (c) Chemical exchange at the exchange sites.

In most cases the chemical exchange is very rapid such that it can not be the rate limiting. The factors that determine whether particle or diffusion will be rate limiting are:-

- The ratio of the concentration of the chokaa exchange sites to that of the exchanging ions in the ambient solution.
- The ratio of the effective diffusion in the chokaa to that in solution.
- The selectivity coefficient.
- The ratio of diffusion film thickness to chokaa bead radius.

Because of the generally higher activation energy for particle diffusion as compared to film diffusion, raising the temperature will favour particle diffusion. Decreasing the resin particle size will decrease the likelihood of film control. Increased agitation in batch systems or increased flow in column operations will create turbulence and reduce the film thickness leading to particle diffusion control. Therefore particle diffusion control is the most likely rate limiting step in this investigation with ion exchange the dominant sorption mechanism.

Kinetic studies on the sorption of iron ions and manganese ions on the chokaa were conducted with particle size range 0.3 – 0.6mm and results are presented in Tables 5.9 and 5.11, respectively. The rate constant for the sorption process at room temperature was determined using Equation 5.1 (Lagergren, 1898).

$$\text{Log}(q_e - q) = \text{Log} q_e - \frac{K_{ad} \cdot T}{2.303} \quad 5.1$$

where,  $q_e$  and  $q$  (both in mg/g) are amounts of sorbate sorbed at equilibrium and at time  $t$ , (min) respectively, and  $K_{ad}(\text{min}^{-1})$  is the rate constant for the sorption process.

Table 5.9 Results of the kinetic studies on the sorption process (*Initial iron concentration*— 3.70 mg/l, *volume of sorbate*=100ml,*mass of sorbent*=4gram)

Time (Min)	Square root of time(Min) <sup>½</sup>	Ce mg/l	q <sub>e</sub> mg/g	q mg/g	q <sub>e</sub> - q mg/g	Log(q <sub>e</sub> - q)
0.5	0.707	1.60	0.086	0.053	0.033	-1.481
1.0	1.000	1.16	Obtained	0.064	0.022	-1.658
2.0	1.414	0.80	After	0.073	0.013	-1.886
4.0	2.000	0.48	2 hrs of	0.081	0.005	-2.301
8.0	2.828	0.30	agitation	0.085	0.001	-3.000
16.0	4.000	0.28		0.086	0	-
30.0	5.477	0.28		0.086	0	-

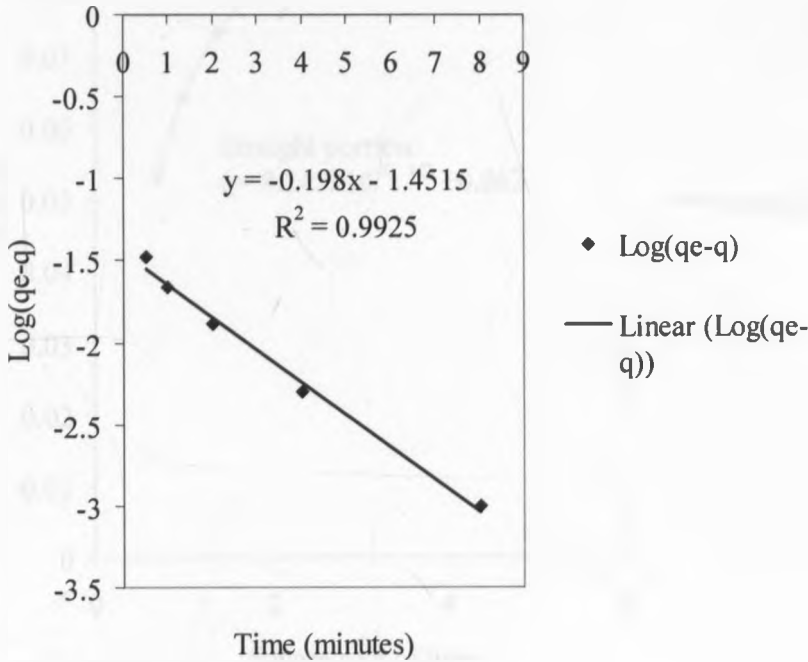


Fig 5.7 Lagergren plot for removal of iron ions by chokaa;(conditions;4g of zeolite per 100ml solution containing 3.7mg/l iron ions, particle size 0.3-0.6mm,pH=2.5).

In determining the kinetic parameters of the sorption process of iron on chokaa, a graph of log (q<sub>e</sub>-q) versus time in minutes was plotted as shown in Figure 5.7.

$$\text{Slope} = \frac{-K_{ad}}{2.303} = -0.198$$

$$K_{ad} = 0.456 \text{ Min}^{-1}$$

To determine whether intra particle diffusion is the rate-controlling step, the relative intra-particle diffusion constant,  $K_p$  was determined. This was done by plotting the amount of iron sorbed by the chokaa versus the square root of time Figure 5.8 (Weber and Morris, 1963). The slope of the linear portion of the graph gives the intra particle diffusion  $K_p$ , at room temperature.

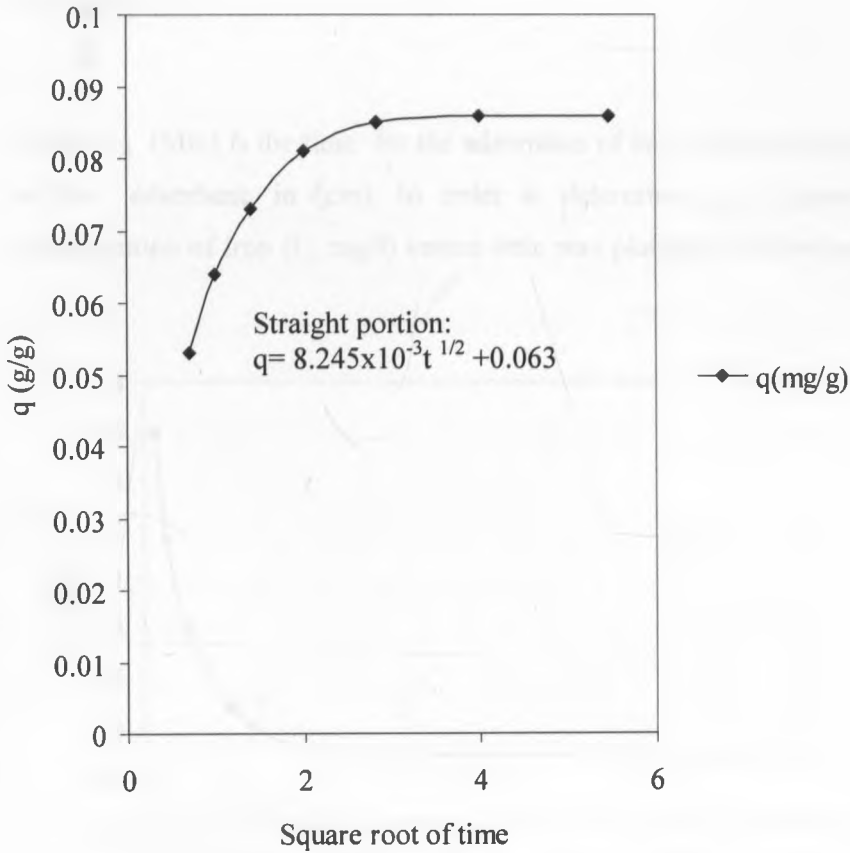


Fig 5.8 Weber and Morris Plot for the pore diffusion constant,  $K_p$  at room temperature. Conditions: 4g of Zeolite per 100 ml solution containing 3.70 mg/l of iron ions, Particle size of chokaa 0.3-0.6 mm, pH=2.5)

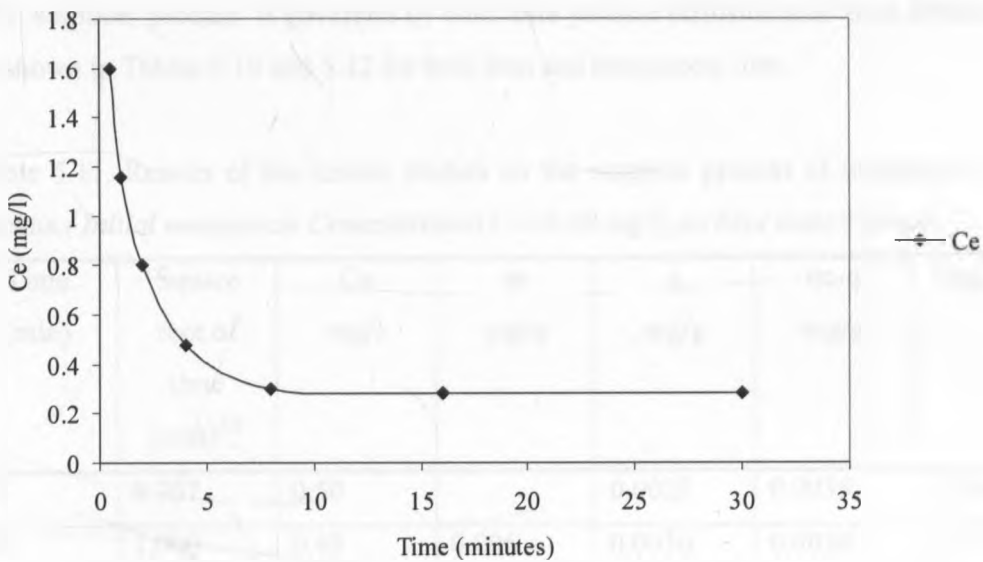
Intra -particle diffusion  $K_p = \text{Slope} = 8.245 \times 10^{-3} \text{ mgg}^{-1} \text{ min}^{-1/2}$

The initial curved portion of the graph is attributed to boundary layer diffusion effects (Crank, 1965) while the final linear portion is due to intra particle diffusion effects (Mckay et al., 1980)

The pore diffusion coefficient D was determined by using the following equation ( Bhattacharya et al.,1984)

$$t_{1/2} = \frac{0.03r^2}{D} \quad 5.2$$

Where  $t_{1/2}$  (Min) is the time for the adsorption of half the sorbate and r is the radius of the adsorbent, in (cm). In order to determine  $t_{1/2}$ , a graph of equilibrium concentration of iron ( $C_e$  mg/l) versus time was plotted as shown in Figure 5.9 using



data from Table 5.9.

Fig. 5.9 Plot of remaining concentration,  $C_e$  versus time, minute, for sorption of iron ions on chokaa. (Conditions; 4g, chokaa per 100mls solution containing 3.70 mg/l iron ions, Particle size 0.3 –0.6 mm: pH = 2.5)

From Figure 5.9,  $t_{1/2} = 27$  seconds

$$r = (0.3 + 0.6)/2/2 = 0.225\text{mm} = 0.0225 \text{ cm}$$

$$D = \frac{0.03 \times 0.0225}{2} = 5.625 \times 10^{-7} \text{ cm}^2 \text{ S}^{-1}$$

27

The kinetic parameters for the sorption of iron on chokaa are shown in Table 5.10.

Table 5.10. Adsorption kinetic parameters for iron sorbed on chokaa at room temperature.

$K_{ad} (\text{Min}^{-1})$	$K_p(\text{Mgg}^{-1} \text{Min}^{-1/2})$	$D (\text{cm}^2 \text{S}^{-1})$
0.456	$8.245 \times 10^{-3}$	$5.625 \times 10^{-7}$

The kinetic profiles in Figures 5.5, 5.6, 5.8, 5.9 and 5.11 reveal an early period of extensive exchange followed by a slowly proceeding uptake by the particles.

This suggest a very strong electrostatic attraction for iron and manganese ions and that there was a rapid ion concentration build-up in the diffuse double layer around the sorbent particles. These results seem to suggest that ion exchange is the dominant sorption mechanism and that intra particle diffusion is the rate controlling step.

The sorption process is governed by both intra particle diffusion and pore diffusion as shown in Tables 5.10 and 5.12 for both iron and manganese ions.

Table 5.11. Results of the kinetic studies on the sorption process of manganese on chokaa. (Initial manganese Concentration  $C_0=0.60 \text{ mg/l}$ , sorbent mass=4grams

Time (min)	Square root of time (min) <sup>1/2</sup>	Ce mg/l	qe mg/g	q mg/g	qe-q mg/g	Log(qe-q)
0.5	0.707	0.50		0.0025	0.0035	-2.456
1.0	1.000	0.48	0.006	0.0030	0.0030	-2.523
2.0	1.414	0.46	Obtained	0.0035	0.0025	-2.602
4.0	2.000	0.45	After	0.0038	0.0022	-2.658
8.0	2.828	0.44	2 hours of	0.0040	0.0020	-2.699
16.0	4.000	0.40	shaking	0.0050	0.0010	-3.000
30.0	5.478	0.36		0.0060	0	-



In order to determine the kinetic parameters for the sorption process of manganese ions on chokaa, a graph of  $\log(q_e - q)$  versus time in minutes was plotted as shown in Figure 5.10

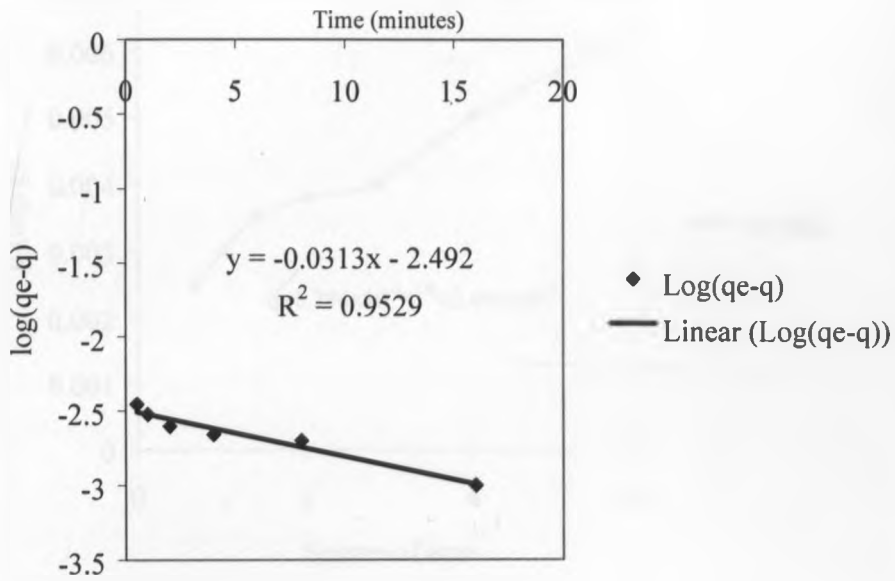


Fig. 5.10 Lagergren plot for removal of manganese ions by chokaa. (Conditions: 4g of Zeolite per 100 ml solution containing 0.60 mg/l Manganese ions, Particle size 0.3-0.6 mm, pH = 2.5)

To determine the value of  $K_p$  for the sorption process of manganese ions, a graph of  $q$  (mg/g) versus square root of time was plotted as shown in Figure 5.11.

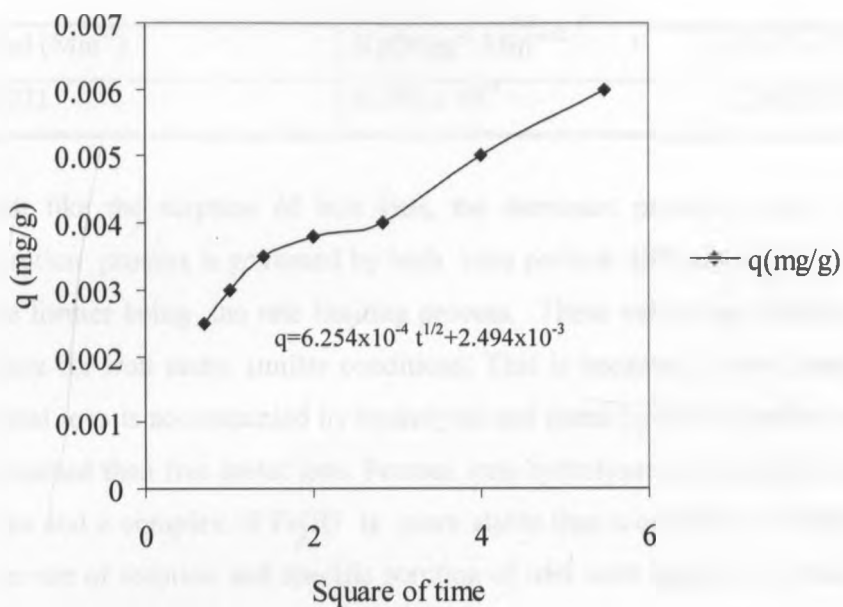


Fig 5.11 Weber and Morris plot for the pore diffusion constant,  $K_p$  at room temperature. (Conditions; 4g of Zeolite per 100 ml solution containing 0.6 mg/l of manganese ions; particle size of Zeolite 0.3-0.6 mm, pH =2.5)

From equation 5.1  $\frac{-K_{ad}}{2.303} = -0.031$

Manganese (rate constant)  $K_{ad} = 0.071 \text{ Min}^{-1}$

Intra particle diffusion constant)  $K_p = 6.254 \times 10^{-4} \text{ mg g}^{-1} \text{ min}^{-1/2}$

Pore diffusion coefficient;  $D = \frac{(0.03 \times 0.0225)}{120}$   
 $= 1.266 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$

the kinetic parameters for sorption process of manganese are shown in table 5.10.

Table 5.12 Adsorption kinetic parameters for manganese sorbed on chokaa at room temperature.

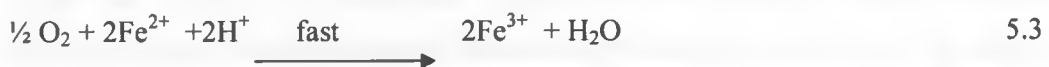
Kad (Min <sup>-1</sup> )	Kp(Mgg <sup>-1</sup> Min <sup>-1/2</sup> )	D (Cm <sup>2</sup> S <sup>-1</sup> )
0.071	6.254 x 10 <sup>-4</sup>	1.266 x 10 <sup>-7</sup>

Just like the sorption of iron ions, the dominant process is ion exchange. The sorption process is governed by both intra particle diffusion and pore diffusion with the former being the rate limiting process. These values are relatively smaller than those for iron under similar conditions. This is because in most cases adsorption of metal ions is accompanied by hydrolysis and metal hydroxo species are more readily adsorbed than free metal ions. Ferrous ions hydrolyses more readily than manganous ions and a complex of Fe(II) is more stable than a complex of Mn(II). This is why the rate of sorption and specific sorption of iron were higher than that for manganese under similar conditions.

### 5.6 Sorption rates of iron and manganese ions on chokaa sorbent

The rate of sorption of iron ions was found to be six times faster than that for manganese under similar conditions. During the removal of iron and manganese ions from water by the chokaa, the ferrous ions are oxidized to ferric ions and the manganous ions to manganic ions. The oxidised ions get attached to the chokaa (sorption process). Manganic oxide has a high sorption capacity for manganous ions. The two sorption processes therefore depends on both rate of oxidation of ferrous ions and manganese ions (Barnes, 1983).

The reaction of ferrous ions with Oxygen is fast and depends on the pH. On the other hand the reaction of manganaous ions with oxygen is considerably slower than the equivalent reaction with ferrous ions and the course of the reaction is different, and furthermore it requires high pH values to achieve significant rates. The oxidation of Fe(II) is as follows:-



$$\frac{-d[\text{Fe(II)}]}{dt} = \frac{K[\text{O}_2][\text{Fe(II)}]}{[\text{H}^+]} \quad 5.4$$

The reaction is fast and is found to be first order with respect to concentration of both Fe(II) and Oxygen [Stumm and Morgan, 1981]

The oxidation of Mn(II) is as follows



The rate law can be written as below:

$$\frac{-d[\text{Mn(II)}]}{dt} = K_0[\text{Mn(II)}] + K[\text{Mn(II)}] [\text{MnO}_2] \quad 5.5$$

The relative proportions of Mn(IV) and Mn(II) in the solid phase depends strongly on pH and other variables [Stumm and Morgan, 1981].

The reaction form is complex, because the reaction is autocatalytic, that is, it goes faster as the reaction proceeds, unlike majority of other reactions which are very fast initially when concentration is very high. Manganic oxide has high adsorptive capacity for manganous ions; for example at pH of 8, approximately 0.8 moles of manganous ions are adsorbed per mole of manganic oxide (Barnes, 1983).

In most cases adsorption of metal ions is accompanied by hydrolysis and metal hydroxo species are more readily adsorbed than free metal ions [James and Healy, 1972]. Ferrous ions hydrolyses more readily than manganous ions and a complex of Fe(II) is more stable than a complex of Mn(II) [Stumm and Morgan, 1981]. These are some of the reasons why both the rate of sorption and the specific sorption of iron ions are higher than manganese ions under similar conditions. Within the same group the affinity of adsorption increases with increasing atomic number [www.oceanag.co.za/articles/cation%20exchange%20capacity.pdf]. Since the atomic mass of iron is more than that of manganese and both are transitional elements we

expect that both the rate of sorption and specific sorption of iron to be higher than that of manganese. This was confirmed in this research.

### 5.7 Effect of temperature on equilibrium of iron removal.

The effect of temperature on equilibrium of iron removal was carried out at 15<sup>o</sup> C and 25<sup>o</sup> C and the results are presented in Appendix 1 and Figure 5.11.

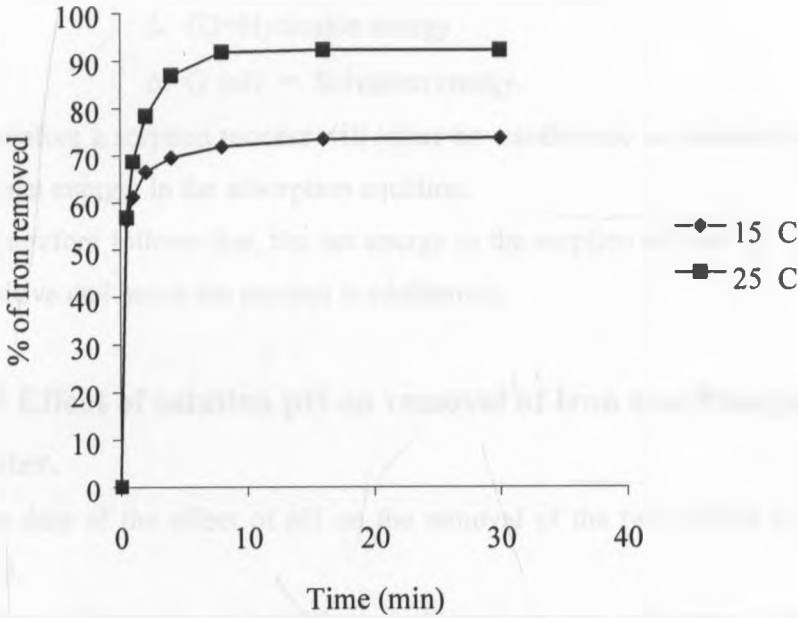


Fig 5.11 Effect of temperature on iron removal: (Conditions 4 g of sorbent per 100ml of sample; Particle size = 0.3-0.6, pH = 2.5)

The results show that the adsorption of iron by chokaa increases with increase in temperature and therefore the process is endothermic. Similar results were obtained by (Mwamachi, 2003), and (Adora, 2004). Adsorption at solid-liquid interface occurs when attractive force between the surface and the ionic solute is greater than that between solute and solvent (Zottlemeyer et al., 1971). The adsorption of an ionic solute is often the result of a thermodynamically favourable change in the enthalpy ( $\Delta H$ ) (Hassel et al., 1981).

The free energy of adsorption is given by:-

$$\Delta G_{ads} = \Delta G_1 - \Delta G_2 - \Delta G_{solv}$$

5.6

(Morgan, 1981)

Where  $\Delta G_{ads}$  = Adsorption energy

$\Delta G_1$  = Energy due to affinity of the surface.

$\Delta G_2$  = Hydration energy

$\Delta G_{solv}$  = Solvation energy.

Therefore a sorption process will either be exothermic or endothermic depending on the net energy in the adsorption equation.

It therefore follows that, the net energy in the sorption of iron by chokaa sorbent is positive and hence the process is endothermic.

## 5.8 Effect of solution pH on removal of Iron and Manganese from water.

The data of the effect of pH on the removal of the two cations is entered in Table 5.13.

Table 5.13: Results of the effect of pH on Iron and Manganese removal from water using chokaa. (Conditions; Initial iron concentration = 3.7 mg/L; Initial Manganese concentration = 0.6 mg/l, 4 g of sorbent per 100 ml of sample, Sorbent size=0.3-0.6mm Temperature = 25°C).

pH	2.5	3.0	4.0	5.0	7.0	9.0
Iron Concentration; mg/l	0.38	0.94	3.00	3.60	3.70	3.70
% of Iron removed	90	75	19	3	0	0
Manganese conc, mg/l	0.46	0.33	0.24	0.20	0.18	0.14
% of Manganese removed	23	45	60	67	70	77

The effect of solution pH on the removal of the two cations is presented in Figure 5.13 below.

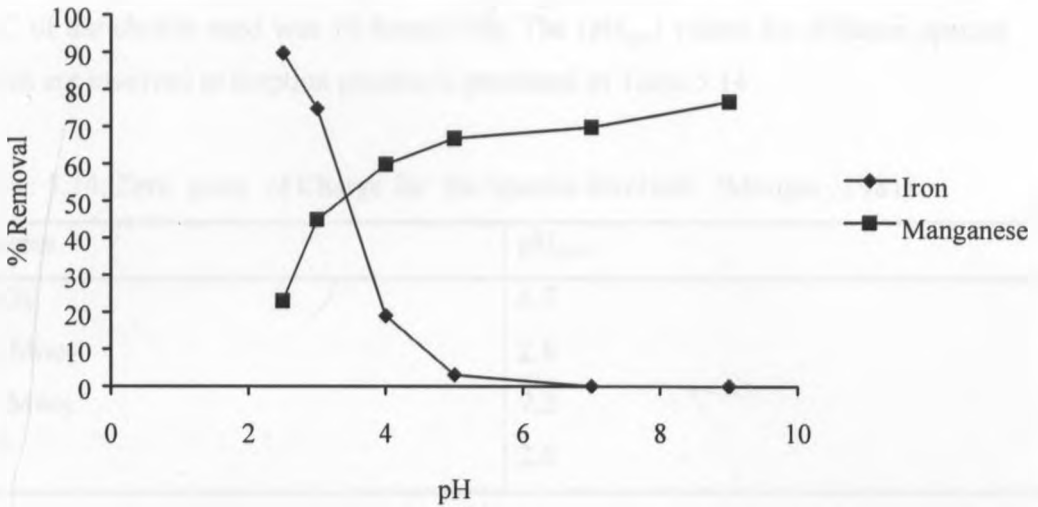


Fig 5.13 : Effect of pH on Iron and Manganese removal.

(Condition; 4g of Sorbent per 100mls of sample, temperature = 25°C) .

The extent of adsorption of a metal ion is strongly pH dependent (Kurbatov et al.,1951). This is because the fixed surface charge of a metal ion is a function of pH. The extent of adsorption of a metal ion by a given sorbent depends on the Zero point of charge ( $\text{pH}_{\text{zpc}}$ ) of both the metal ion and the sorbent. Zero point of charge ( $\text{pH}_{\text{zpc}}$ ) is related to the appropriate cationic charge and radius of the central ion and is approximately equal to the weighted average of the ( $\text{pH}_{\text{zpc}}$ ) values of the components making up a composite oxide ( Parks, 1965)

Manganese and iron are both transition elements, the latter is in group 8B and has an ionic radius of  $0.75 \text{ \AA}$ , while the former in group 7B and has an ionic radius of  $0.81 \text{ \AA}$

Furthermore manganese has three stable oxidation states, +2, +4, and +7 while iron has two stable oxidation states +2 and +3 (Ebbing et al.,1993). Therefore it is expected that , the two metal ions will react differently when subjected to the same sorbent under similar conditions.

Most of the adsorptive properties in a zeolite is due to the presence of  $\text{SiO}_2$ , which accounts for over 65% by mass in the chokaa sorbent used (Table 5.1). These adsorptive properties are mainly as a result of cation exchange capacity (CEC). The CEC of the chokaa used was 16.4meq/100g. The ( $\text{pH}_{\text{zpc}}$ ) values for different species which are involved in sorption process is presented in Table 5.14

Table: 5.14: Zero point of Charge for the Species involved (Morgan , 1981).

Species	$\text{pH}_{\text{zpc}}$
$\text{Fe}_2\text{O}_3$	6.7
d - $\text{MnO}_2$	2.8
B - $\text{MnO}_2$	7.2
$\text{SiO}_2$	2.0

At a pH between 6.7 and 2.0, the solution is acidic and the iron species will be positive while the  $\text{SiO}_2$  species will be negative. This will result to a net attractive force between the two species and hence the removal of Iron at low pH. Most of manganese exists as delta  $\text{MnO}_2$  with a  $\text{pH}_{\text{zpc}}$  of 2.8. which is closer to the  $\text{pH}_{\text{zpc}}$  of  $\text{SiO}_2$ . This will result to a very weak attractive force between the two ions and therefore very little removal of manganese ions at low pH.

At a pH of 7 and above, the solution is basic and most of the manganese exist as beta species with a  $\text{pH}_{\text{zpc}}$  of 7.2. Manganese ions are more electro negative than iron ions at this state. Therefore the net attractive force between manganese ions and  $\text{SiO}_2$  is much greater than that between iron ions and  $\text{SiO}_2$  and hence we have more manganese removal by chokaa sorbent at a pH of 7 and above. These results compare fairly well with the theoretical results of adsorption of metal ions on silica as a function of pH [Schindler et al., 1976].



## **5.9 Column Studies.**

### **5.9.1 Dosing the sample with Potassium Permanganate before passing it through a chokaa column.**

From section 5.10, it is evident that iron and manganese ions cannot be removed easily from water at normal pH. The results indicate that chokaa can easily remove iron at low pH while manganese can only be removed at high pH. Therefore there was a need to investigate further the possibility of removing both iron and manganese at normal operating conditions of neutral pH, (or neutral water pH).

### **5.9.2 Regeneration of chokaa.**

Re-oxidation or regeneration of the material was secured by back-washing with a solution of potassium permanganate. The manganous ions were re-oxidised to manganic Oxide. Manganic oxide has high adsorptive capacity for manganous ions (Barnes, 1983; Cox, 1994). The column was regenerated after 40 hours of operation. The concentration of the filtrate at the time was, iron= 0.42mg/l; manganese= 0.48mg/l.. After back-washing with potassium permanganate, the filtrate concentration was; iron=0.10mg/l and manganese=0.08mg/l.

The experimental data of the effect of treating the sample with potassium permanganate before passing it through a chokaa column is entered in Appendix 2 and presented in graphical form in Figure 5.14. At near neutral pH, the potassium permanganate will completely oxidise iron and the particles filtered by the column. Very little manganese will be oxidised at this pH and therefore most of it will be removed through ion exchange/sorption process.

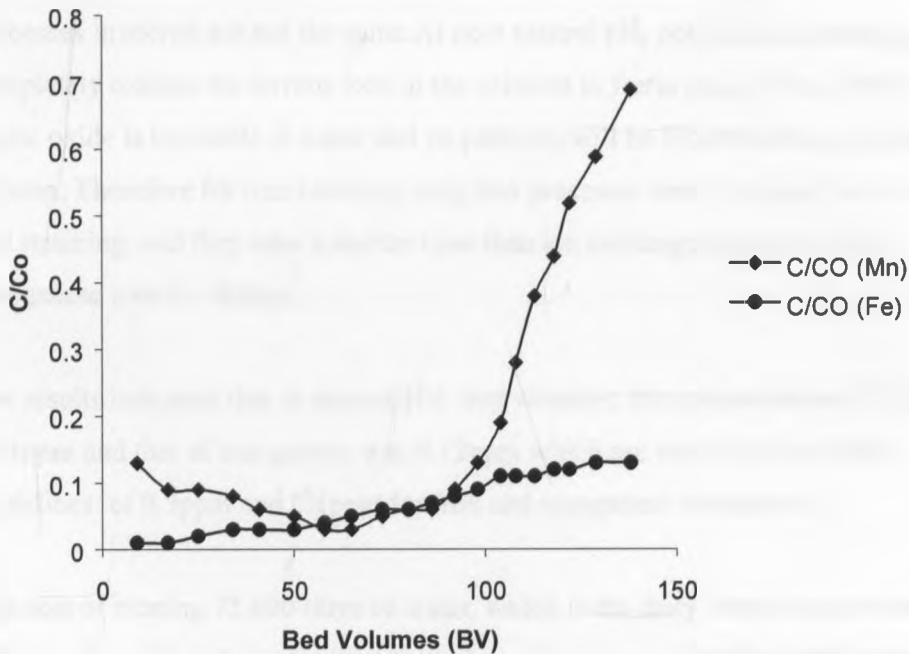


Fig 5.14 A graph of  $c/c_0$  versus bed volumes (BV) for manganese and iron removal.

The process of removal of the two metals is a complex one consisting of ion exchange, oxidation, straining and sorption of the two cations.

Manganese cations were removed through a combined process of oxidation, straining and ion exchange/adsorption, while iron cations were removed through a process of oxidation and straining. The potassium permanganate oxidised the ferrous ions to ferric oxide and manganous oxide to manganic ions (Barnes, 1983). The manganic oxide formed has a high sorption capacity for manganous ions (O'Connor, 1971; Barnes, 1983). At a pH of 8, approximately 0.8 moles of manganous ions are adsorbed per mole of manganic oxide (Barnes, 1983). This helps the resin to remove more metal cations from the water.

The initial part of the graph of  $c/c_0$  for manganese removals up to 50 bed volumes shows high levels of removal. This is because the removal is done through a combination of 3 processes, i.e. oxidation and filtration, sorption by manganic oxide and ion exchange/sorption by the chokaa. From 60 bed volumes onwards, the dominating removal process is sorption/ion exchange by the chokaa. At this stage the sorption capacity of manganic oxide has been exhausted.

The  $c/c_0$  graph for iron removal is different from that of manganese because the processes involved are not the same. At near neutral pH, potassium permanganate will completely oxidise the ferrous ions in the solution to ferric oxide (Cox, 1994). Ferric oxide is insoluble in water and its particles will be filtered out by the chokaa column. Therefore for iron removal, only two processes were involved, i.e.- oxidation and straining, and they take a shorter time than ion exchange/sorption of the manganese ions by chokaa.

The results indicated that at around 104 bed volumes, the concentration of iron was 0.34ppm and that of manganese was 0.12ppm which are very close to WHO guidelines of 0.3ppm and 0.1ppm for iron and manganese respectively.

The cost of treating 75,600 litres of water, which is the daily water requirement for Alliance Girls High School, utilizing chokaa column in conjunction with potassium permanganate works out to about KSh.300. This translates to about 24 cents per person per day (Appendix 3 of this report refers) This is a cheaper method of reducing iron and manganese from bore water. The chokaa is cheap and locally available and in addition the method can be simulated to the real water treatment process.

## **CHAPTER 6.0: CONCLUSIONS AND RECOMMENDATIONS.**

The following conclusions and recommendations were made based on the research findings presented here below.

### **6.1 Conclusions**

**1:** Chokaa has good potential for iron and manganese removal from water. The process of removal is a complex one, consisting of ion exchange, adsorption, oxidation and filtration of the two cations. Inter particle diffusion is the rate limiting step for the sorption process.

**2:** The removal of iron cations is favoured by low pH and is fast, while that of manganese is favoured by high pH and is slow.

**3:** Dosing the water sample first with potassium permanganate at near neutral pH before passing it through zeolite enhances the removal process of the two cations.

### **6.2 Recommendations**

**1:** The Alliance Girls High School management may consider using this

method to reduce the high levels of iron and manganese from their bore water.

**2:** A pilot plant should be set up to obtain the operational parameters for the process.

**3:** There are a number of instances in nature where iron bearing waters of pH considerably below 5 are encountered. Of special concern are waters in coal mining regions where pH values of 3 are not uncommon. The potential of zeolite to remove iron cations from such waters should be investigated.

# APPENDIX 1.0 Results of the effects of temperature on iron

## removal.

Sorbent mass, 4g per 100mls of sample, sorbent size =0.3-0.6 mm,

Initial Iron Concentration= 3.7 mg/l: pH=2.5

Time (min.)	0.5	1.0	2.0	4.0	8.0	16.0	30.0
Iron Conc: mg/l (15 °C)	1.62	1.44	1.24	1.12	1.04	0.98	0.98
Iron Conc: mg/l(25 °C)	1.60	1.16	0.80	0.48	0.30	0.28	0.28
% Iron Removed (15 °C)	56.2	61.1	66.5	69.5	71.9	73.5	73.8
% Iron Removed(25 °C)	56.8	68.7	78.4	87.0	91.9	92.4	92.4

**APPENDIX 2.0 Results of the effect of dosing the sample with potassium permanganate before passing it through a chokaa column.**

Initial concentration of iron=3.7mg/l; initial concentration of manganese 0.6mg/l, pH=7.35

Time Hrs	Volume treated cm <sup>3</sup>	Fe. conc, mg/l	% Fe. removal	Mn. conc, mg/l	% Mn. removal	BV	C/CO Mn.	C/CO Fe.
0	0	3.20	0	0.64	0	0	-	-
2	1345	0.04	98.8	0.08	87.5	9	0.13	0.01
4	2664	0.04	98.8	0.06	90.6	17	0.09	0.01
6	3968	0.06	98.2	0.06	90.6	25	0.09	0.02
8	5260	0.08	97.5	0.05	92.2	34	0.08	0.03
10	6546	0.10	96.9	0.04	93.8	41	0.06	0.03
12	7794	0.10	96.9	0.03	95.3	50	0.05	0.03
14	9016	0.12	96.3	0.02	96.9	58	0.03	0.04
16	10205	0.15	95.3	0.02	96.9	65	0.03	0.05
18	11344	0.18	94.4	0.03	95.3	73	0.05	0.06
20	12440	0.20	93.8	0.04	93.8	80	0.06	0.06
22	13445	0.22	93.1	0.05	92.2	86	0.06	0.07
24	14398	0.26	91.9	0.06	90.6	92	0.09	0.08
26	15290	0.30	90.6	0.08	87.5	98	0.13	0.09
28	16152	0.34	89.4	0.12	81.3	104	0.19	0.11
30	16955	0.36	88.8	0.18	71.9	108	0.28	0.11
32	17696	0.38	88.1	0.24	62.5	113	0.38	0.12
34	18405	0.40	87.5	0.28	56.3	108	0.44	0.13
36	19052	0.40	87.5	0.32	50.0	122	0.52	0.13
38	20155	0.42	86.9	0.38	40.6	129	0.59	0.13
40	21582	0.42	86.9	0.44	31.3	138	0.69	0.13

### APPENDIX 3.0 Approximate cost of treating Alliance Girls water per day.

- Students population = 760
- Teachers and other staff = 100
- Dependants to staff and teachers, say 4 per household = 400
- **Total population = 1,260**
- Average water use per capita, say 60 litres per day.
- Total water used per day =  $1260 \times 60 = 75,600$  litres
- Average iron concentration in the Bore – hole water = **3.70mg/l**
- Average manganese concentration in the Bore – hole water = **0.6mg/l**
- Approximate dose of potassium permanganate required to oxidise iron = two thirds the content of iron in raw water ( Cox, 1994) =  $\frac{2}{3} \times 3.70 = 2.467$ mg/l
- Approximate dose of potassium permanganate required to oxidise manganese = twice content of manganese in raw water (Cox, 1994) =  $2 \times 0.6$ mg/l= **1.2mg/l**
- Total dose of potassium permanganate required =  $(2.467 + 1.2) = 3.667$ mg/l.
- Total mass of potassium permanganate required per day =  $(75,600\text{l/day} \times 3.667\text{mg/l}) \times 10^{-3}\text{gm} = 277.2$ gm
- Cost of commercial/general purpose potassium – permanganate = Kshs 500 per gm at Laborama (K) Ltd on Kijabe street, Nairobi.

Therefore cost of potassium permanganate required per day=  $(277.2/500) \times 500$   
= **KSh. 277.20 per day.**

This is approximately Ksh 300 per day and translates to about 24 cents per person per day.

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