# ADSORBENT MATERIALS FROM RICE HUSKS AND WATER HYACINTH ASHES BLENDED WITH BONE CHAR FOR REMOVAL OF FLUORIDE IONS FROM CONTAMINATED WATER

**ROSE KAGWIRIA GITONGA (B.Ed. sc)**

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# DECLARATION

This thesis is my original work and has not been presented for any other degree award in any other university.

**ROSE KAGWIRIA GITONGA**

I56/22778/2010

Signature: ______________________________ Date: ________________________.

Department of Chemistry

Kenyatta University

## SUPERVISORS

The work reported in this thesis was carried by the candidate with our approval.

Dr. Harun M. Mbuvi
Department of Chemistry
Kenyatta University
Signature: _________________________________ Date: _________________________

Dr. Margaret Mwihaki Ng'ang'a
Department of Chemistry
Kenyatta University
Signature: _________________________________ Date: _________________________

# DEDICATION

I dedicate this work to my husband Francis Gitonga and my late father Misheck Kanake for the financial and moral support that they accorded to me and encouragement to enroll for Masters of Science Program and to my daughters Lorna, Linah and Mitchelle for their love and understanding demonstrated during the entire study period

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## ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| BBC: | Black bone char |
| WBC: | White bone char |
| NRC: | National Research Council |
| pH: | Potential Hydrogen |
| PPM: | Parts per million |
| RHA: | Rice husks ash |
| RPM: | Revolutions per minutes |
| TCP: | Tri calcium phosphate |
| UNICEF: | United Nations Children’s Funds |
| USPHS: | United States of Public Health Service |
| WHA: | Water hyacinth ash |
| WHO: | World Health Organization |
| XRF: | X-Ray Fluorescence Spectrometer |
| ZA: | Zeolite A |
| ZB: | Zeolite B |
| ZC: | Zeolite C |

## ABSTRACT

Safe and readily available water is important for public health, whether it is used for drinking, domestic use, food production or recreational purposes. Consumption of contaminated water may lead to acute and chronic health effects. The most common water pollutants include heavy metals, pesticides, and anions such as fluorides, arsenic, arsenite, chromate and selenate, which cause various diseases such as brain, liver and bone ailments. Among the pollutants, fluoride is the most occurring contaminant in water. Fluoride ions are absorbed by the body mainly through drinking water containing a concentration of more than 1.5 mg/L for a long period of time. At high levels, they cause health problems which range from mild to severe teeth and bone fluorosis. Many methods have been used for removal of anionic contaminants such as fluoride from drinking water. These methods include reverse osmosis, precipitation, electro dialysis and adsorption. Most of these methods are too expensive. This study aimed at synthesizing an adsorbent material from low cost agricultural waste products materials namely water hyacinth ash (WHA) and rice husks ash (RHA) blended with bone char and determine its effectiveness in removal of fluoride ions from contaminated water. Five zeolitic materials were prepared and labelled as zeolitic A (ZA), zeolitic B (ZB), zeolitic C (ZC), black bone char (BBC) and white bone char (WBC) by varying the amounts of rice husks and the water hyacinth ashes and blending with white and black char. Analysis of various oxides contained in the adsorbents was done by X-ray Fluorescence Spectrometer (XRF). Adsorption tests for fluoride ions by the five adsorbents were carried out based on the batch adsorption studies. These include varying the shaking speed, temperature, contact time, initial anion concentration and adsorbent dose. The concentration of fluoride ions remaining in the solution after adsorption was analysed using Fluoride Ion Selective Electrode (FISE). Results for the adsorption capacities for the five adsorbents fitted best onto Freundlich isotherm model which gave adsorption capacity (Kf) values as follows; ZA 1.181, ZB 1.281, ZC 1.061, BBC 1.142, BWC 1.112. The zeolite B had the highest adsorption capacity. This indicates that blending a zeolitic material by black bone char improves its adsorption capacity for fluoride ions from contaminated water. At optimum concentration of fluoride ion and optimum temperature, ZB removes 75.50% and 80.00% of the ion respectively. It gives 75.50% at a shaking speed of 120 rpm and 77.00% at optimum contact time. Therefore it is necessary to optimize use of locally available materials for application in defluoridation of water.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background of Study

Water is one of the most important substances found on earth. Purity of water is one of the necessary factors that determine its usefulness for human domestic uses such as drinking. In most rural communities in Africa, the main source of water supply is ground water. However, ground water has been found to be the major medium of introduction of fluoride ions into human beings (WHO, 1984). It has been discovered that the major water pollutants are heavy metals, arsenic, nitrates and fluorides but mostly the most serious pollutant of ground water is fluoride (Amini, 2008).

One of the most crucial questions to be asked most about drinking water is how safe that water is, and how its safety is ensured. The safe drinking water act as amended in 1996 (WHO, 1996) orders that each water supplier must give a report concerning the safety of the water it is supplying to people for domestic consumption once a year. It has been found that over 260 million people globally have been exposed to water used for drinking containing concentration of fluoride ions of more than 1.5 mg/ L which has been set as the maximum fluoride concentration necessary for healthy teeth and bone development (Bhatnegar, 2008). According to the World Health Organization (WHO), the maximum suitable amount of fluoride ions that should be contained in drinking water is 1.5 mg/L or below (WHO, 2000). It is important to note that fluoride if taken in small amounts, it is usually helpful to the body.

Depending on the concentration of ingested fluoride, it could have health benefits (Suyana, 2010). On the other hand, if for a long time the water which is being consumed has got a fluoride concentration higher than the recommended amount, fluorosis of teeth and bones will definitely occur (Jamodei, 2004).

The results of the 2006 National Research Council (NCR) panel categorized severe dental fluorosis that lead to pitting of the tooth enamel as a health problem that should raise an alarm (WHO, 2006).

Fluorides are released into the environment by some naturally occurring processes for example weathering and dissolution of materials, in emissions from volcanoes and aquatic aerosols (WHO, 2002; Ahmand *et al.*, 2010). Exposure of fluorides into the environment may also take place through burning coal and other waste materials from various industrial processes such as manufacture of steel and production of metals like aluminum, copper and nickel. In addition, the processing of the phosphate ore as well as production of phosphate fertilizers and use of glass bricks pollute the environment with fluorides (Nouri, 2006).

This study aimed at coming up with a means of reducing the high concentration of fluoride ions in contaminated ground water. There are various methods that have been in use currently. Examples of such methods are ion exchange, coagulation precipitation, reverse osmosis, electro dialysis and adsorption. Of all these methods, adsorption has been reported to be the most promising method for defluoridation due to the ease of operation and availability of a wide range of adsorbents. Among different types of adsorbent substances, bone char has been widely used due to its low cost, ease of preparation and bio compatibility (Nunes- Pereira *et al.*, 2018). Also, use of zeolites has been on the rise. This is because zeolites are biodegradable, readily available and show flexibility in terms of structure modification (Onyango *et al,* 2004)

## 1.2 Statement of the Problem

The various de-fluoridation methods that have been in use have shown various disadvantages. For instance, in reverse osmosis and electro dialysis, the disposal of brine is a problem. It removes all the ions present in water not withstanding that some minerals are essential for proper growth therefore, re-mineralization is required after the treatment (Palishahjee, 2013), since ions such as fluorides have beneficial effects if the amount present in water is that which has been recommended by WHO. This is because in its right amount, it prevents tooth decay and protects teeth against cavities. In precipitation technique, daily operations require a trained operator. These methods are too expensive to operate. On the other hand, the adsorbents that have been in use such as zeolites have shown low adsorption capacity. Therefore, this study aimed at providing an adsorbent material for reducing fluoride ions from water, from readily available waste materials. The study aimed at blending bone char with an adsorbent material prepared from ashes of water hyacinth and rice husks in order to improve its removal of fluoride ions from contaminated water.

## 1.3 Justification of the study

Most lakes found in areas such as rift valley region, have been found to contain a lot of fluoride. For instance, Lake Elementaita contains 1640 mg/L while lake Nakuru contains 2800 mg/L (Nair *et al.*, 1994). These findings and many others have resulted to Kenya being classified as a water scarce country (Marshall, 2011). The lack of clean water in Kenya is expected to rise due to the rate at which the population and industries are growing hence, makes it necessary to clean the available water. In addition, the health effects of high concentration of fluoride ions in drinking water are irreversible. The only way of reducing the negative health effects is by removing these ions from water. Most methods that have been in use to remove the fluoride ions are expensive and have shown low adsorption capacity.

Water hyacinth, rice husks and bones are waste materials that are difficult to dispose. This study provides information on developing an adsorbent material that has a higher capacity of removing fluoride ions from contaminated water using readily available waste material.

## 1.4 Hypothesis

Zeolitic material synthesized from ashes of water hyacinth, rice husk ash and blended with bone char are effective adsorbents of removal of fluoride ions from contaminated water.

## 1.5 Objectives of the study

### 1.5.1 General objective

To synthesize zeolitic materials from ashes derived from rice husks, water hyacinth and bone char and determine their effectiveness in reducing the concentration of fluoride ions from contaminated water.

### 1.5.2 Specific objectives

i. To investigate the chemical composition of adsorbent materials prepared from ashes of water hyacinth and rice husks and bone char.
ii. To determine adsorption capacities of the adsorbent materials on fluoride ions in contaminated water.
iii. To find out the percentage of fluoride ions removed from contaminated water by the adsorbents prepared.

## 1.6 Limitation of the study

The study focused on the preparation of water remediation zeolitic materials for fluoride adsorption. The chemical composition of the zeolitic materials was determined by X-ray Florescence Spectrometer. Types of bones used were not considered and the study only investigated the reduction of fluoride ions from water.

## 1.7 Significance of the study

Removing the ions of fluoride from drinking water will promote healthy living since people will be free from developing dental and skeletal fluorosis. Also, young children living in areas with high fluoride ion concentration will not have neurological damage as well as interference of DNA creation since the treated water will be safe for drinking. Consequently, use of water hyacinth in large scale will help reduce its population in water bodies thus enabling more fish farming in those lakes that are prone to this plant. In addition, use of rice husks and bones will reduce the problem of their disposal in urban areas. A new market for the materials made will also improve the economy and increase employment opportunities.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Water Pollution

Water pollution occurs when harmful substances such as chemicals or microorganisms—contaminate a stream, river, lake, ocean, aquifer, or other body of water, degrading water quality and rendering it toxic to humans or the environment (Gupta, 2009. Water, known as a universal solvent, is uniquely vulnerable to pollution and is able to dissolve more substances than any other liquid on earth.

Ground water gets polluted when contaminants from pesticides and fertilizers to waste leached from landfills and septic systems make their way into an aquifer, rendering it unsafe for human use. Ridding groundwater of contaminants can be difficult to impossible, as well as costly. Once polluted, an aquifer may be unusable for decades, or even thousands of years. Groundwater can also spread contamination far from the original polluting source as it seeps into streams, lakes, and oceans.

Water is said to be polluted when its quality changes due to additional substances thus becoming less suitable for drinking and other domestic uses, agriculture, industrial use, recreational use, wild life and other uses. Currently there is an increase in contamination of the little water that is available for use (Marshal, 2011).

On the other hand, water purification is the process of removing unwanted substances that may have found their way into it. Such substances involve heavy metals, fluorides, biological contaminants, pesticides and suspended solids and gases. Water is usually purified if it is polluted.

## 2.2 Fluoride in water

Fluorides are naturally organic occurring compounds released into the environment through various methods. These methods include weathering of minerals, emissions from volcanoes and release of marine aerosols (Symonds *et al*., 1988). Fluorides are also found in drinking water because of their presence in the earth's crust (Peterson, 2004).

The common minerals that contain fluoride are fluorite, apatite rock, phosphate and topaz (Teda, 1981). These minerals are usually the main natural distributors of fluoride that is contained in water. Fluoride occur in form of fluorspar, fluorapatite and cryolite within the earth's crust where it is widely distributed, but fluorine in its elemental form does not exist in the earth's crust, (WHO, 2006). Fluorides are also found in the atmosphere in form of vapor on various particles or in aerosols that are carried away by wind before being deposited to the environment. In ground water, presence of fluoride result when the rock minerals break down and release them into water (Kabata, 1984). In addition, high concentrations of fluoride ions found in urban areas come from regions surrounding aluminum smelting industry. Use of fertilizers contaminates water with fluoride ions (EPA, 1977).

## 2.3 Effects of Fluoride

Fluoride in drinking water may be of help or may harm the human body depending on how much of it is contained in the water (Srimurali *et al*., 1998). The World Health Organization (WHO) says that a helpful amount of the fluoride ion should be 1.5 mg per litre (WHO, 2008).

Excess fluoride results to skeletal and dental fluorosis (Gonzales, 2004). Concentration of fluoride ions of between 1.6 mg/ L and 4.0 mg/ L causes dental fluorosis because of prolonged intake of water with such high level of fluoride ions. This causes mottling and browning of teeth and with higher concentration of between 4.0 mg/L and 10.0 mg/L, skeletal fluorosis may occur. When water containing more than 10.0 mg/L of fluoride ions is consumed, crippling fluorosis develops (Ansari, 2011).

The characteristics of skeletal fluorosis include weak bones and malformed skeleton. Crippling fluorosis affects bone joints resulting to difficulties in movement. Taking of a lot of fluorides beyond the required level causes direct cellular poisoning, where fluoride ions bind on the calcium ions of the bones. It also interferes with the activity of glycolytic and proteolytic enzymes (Thole, 2011).

When fluoride is introduced into the digestive system, it causes abdominal pain, nausea and vomiting, seizures and muscle spasm and even death. This is as a result of the gastric acid present in the stomach reacting with fluoride to produce hydrofluoric acid in the system. Thus, exposure to high concentration of fluoride results to other immediate effects such as difficulties in breathing due to respiratory paralysis (Fawell, 2006). The following stage after fluorosis is esteoscelerosis; this is where bones harden and become more calcified. This is then followed by damage on the spine, major joints, muscles and nervous system (Barley, 2006). Whether dental or skeletal, fluorosis is never reversed and it does not have any treatment. The only way of controlling it is by preventing this intake, by maintaining fluoride level within the safe limit (Jamodei, 2004).

As explained earlier, the long-lasting negative effects or the desired helpful effects of fluoride on the structure of the human skeleton is based on the reactions of ion exchange between fluoride ions and hydroxide ions in the calcium hydroxy-phosphate structure which is usually the main component of the bone structure. The benefits of fluoride ions are as a result of the substitution of hydroxyl ions by fluoride ions leading in a fluoro apatite structure that is more resistant to acid attack. The exchange of ions in the structure is as shown in equation 1.

$$Ca_5\ (PO_4)_3\ OH + F \longrightarrow Ca_5\ (PO_4)_3F + OH^- \qquad \text{Equation 1}$$

Fluoroapatite structure is therefore more resistant to the attack by acid as compared to the hydroxyl apatite structure. This gives a layer of protection to the teeth enamel which protects it against the acids produced from food particles lodged in between them. This leads to prevention of dental carries. Taking in of too much fluoride enhances the reactions to exceed the replacement of hydroxyl ions only, and it goes beyond into replacing the phosphate ions as well. The reaction is as shown in the following equation; equation 2

$$Ca_5\ (PO_4)_3\ F + 9F^- \longrightarrow Ca_5F_{10} + 3PO_4\ 3^- \qquad \text{Equation 2}$$

In the equation 2, ion exchange takes place between phosphate and fluoride ions. The resulting product, calcium decafluoride, is a very hard and brittle substance which is not appropriate for the function of the structure of the skeleton (Thole, 2011). One of the regions that have been affected at a high degree in Kenya is the Rift Valley (Hellen *et al.*, 2013). This is as a result of minerals from the volcanic rocks in the region.

## 2.4 Methods of defluoridation

Many methods have been used for removing fluoride ions from their solution. These methods include; ion exchange, chemical precipitation (Jiang *et al*., 2013), reverse osmosis, electro dialysis (Menkouchi *et al*., 2007) and adsorption (Bhatgnar, 2011; Lorganathan *et al*., 2013). The method used in removing of fluoride ions depends on factors such as capital, operation cost, effect it has on the environment and the capacity it has for removing the ions from the solution.

### 2.4.1 Ion exchange

Ion exchange is a process where the contaminating ions are removed by exchanging them with other ions. In water treatment, ion exchange involves passing of water through an ion exchange resin which is insoluble in water and that is capable of exchanging some of its ions with ions of similar charge in a solution (Sanjeev, 2013; Mbugua *et al*., 2014).

This method has been useful for removing fluorides from water since there are many natural materials whose surfaces can be modified into various ion exchangers (Sanjeev and Sapna 2013), and most of the ion exchangers have been found to be environmentally friendly. Unfortunately, ion exchange alone has low efficiency for removal of trace concentration of fluorides (Zhang *et al*., 2012)

### 2.4.2 Electro dialysis

Electro Dialysis (ED) is a membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential (Oztekin and

Altin, 2016). It has a series of cation and anion exchange membranes which are positioned between the cathode and the anode (Tongwen, 2005). The positively charged ions move to the cathode while negatively charged ions move to the anode. These ions move through the membrane and are retained by the opposite charged electrodes (Zoulias *et al*., 2004). The disadvantage of electro dialysis is that it is costly and has low capacity for removal of fluorides and other pollutants from solutions (Zhang *et al*., 2012)

### 2.4.3 Chemical precipitation

This is where the removal of the contaminating species in solution is done by sedimentation transforming them into insoluble solids (Harrison, 2005). For example, calcium hydroxide and alumina are used as the precipitating substances (Meenakshi, 2006). This leads to precipitation of fluoride from aqueous phase as insoluble calcium fluoride (Palishahjee *et al*., 2013).

### 2.4.4 Reverse osmosis

Reverse osmosis method uses high pressure to force water molecules through a semi-permeable membrane (Amir *et al.,* 2010). The quantity of pressure required here depends on the concentration of the contaminant contained in the solution (Bina *et al*., 2014). This pressure must be able to overcome the osmotic pressure. However, the membrane is impermeable to salts and other contaminants so they get discharged through the concentrate stream. This is because the permeability of the membrane is based on the size and charge of the contaminating particles (Yeomin and Lueptol, 2005). The advantage of this method is that it is highly efficient and does not require pH balancing (Amir *et a*l., 2010). However, it requires high capital and operational cost (Feenastra *et al*., 2007)

### 2.4.5 Adsorption technique

The adsorption technique is one of the most useful and convenient method of reducing the fluoride ions from water. This is because most of the materials used in adsorption and others used in making adsorbents are readily available and it is possible to collect them from the environment at minimum cost (Jamode *et al.*, 2014). Many people involved in doing research work have focused very much on using adsorbents in their researches and they have developed a high degree of interest on the efficiency of the different types of adsorbent substances (Biswas *et al.*, 2007; Jamode *et al*., 2014).

This consideration is based on the initial cost, flexibility, availability and cost of operation. (Gupta, 2007; Biswas *et al.*, 2007). For example Pula has reviewed the method of adsorption of ions of fluoride on some adsorption substances, mainly those of clay which contain oxides of silicon, aluminium and iron (Pula, 2004) as his own background for experiments he did in his studies in order to illustrate and explain how fluoride ions interact with the adsorbent in the solution.

When using a solid adsorbent, there are three essential steps of adsorption of fluoride onto solid particles (Fan *et al*., 2003). These involves external mass transfer, adsorption of fluoride ions probably onto particle surfaces where the adsorbed fluoride ions probably exchange with the ions inside the adsorbent particles and intra-particle diffusion, that is, the adsorbed fluoride ions are transferred to the internal surfaces for a porous material.

Removing fluoride ions from water involves the use of a variety of adsorbents. Examples of such adsorbents are various oxides found on the earth crust (Raichur, 2001), alumina which has been activated (Das *et al*., 2005), activated clay (Argarwal *et al*., 2003), biosorbents (Mohan *et al*., 2007), silica (Wasay *et al*., 1996b) zeolites and related ion exchangers (Raw, 1988) as well as aluminium compounds (Sujuna *et al*., 1998).

## 2.5 Adsorbents for fluoride removal

### 2.5.1 Use of bone char

Bone charcoal is considered as a mixed adsorbent made up of tricalcium phosphate and carbon where both are in the hydroxyapatite form (Moreno, 2010; Fawell *et al*., 2006). This type of an adsorbent has given higher capacities in fluoride adsorption than in those other materials that have been made from carbon (Hermandez, 2012) and commercial adsorbents (Abe, 2007; Medallin, 2007). Several studies show that the properties of bone char for adsorbing fluoride ions are as a result of the chemical components of their structure, especially the hydroxyapatite structure (Medalin, 2007; Leyva, 2009).

The production of char from bone can be done by calcinations of bones at a temperature of 400$^o$ - 600$^o$ C. It can also be done in an environment where no oxygen at all is present during heating in the process of pyrolysis. Most researchers have found that the bone char that is made by particle calcinations are the most preferred for removing the fluoride ions provided that their temperature of synthesis is not below 400$^o$ C (Albertos, 2010). Phantumvanit and Legeros study (Phantumvanit, 1998) shows that bone char that is obtained at 400$^{o}$C exhibited the highest fluoride adsorption.

It is important to note that if bones from cattle are treated at a temperature above 600$^{o}$C the apatite structure of the bone is damaged. This affects the properties of the bone char in fluoride adsorption, while treatment of bones at a temperature below 400$^{o}$C result to production of a bone adsorbent material that has a bad taste and oduor which disqualifies it from defluoridation of water due to hygienic purposes (Kawasaki, 2009).

### 2.5.2 Use of zeolites

Zeolites are aluminosilicates that have porous crystalline usually made up of molecules of $SiO_4$ and $AlO_4$ forming a tetrahedra structure where these molecules are joined together by sharing of oxygen atoms (Yang, 1987).

The unique three-dimensional porous structures enables natural zeolite to have various applications (Smith, 1998). Certain zeolitic materials occur as minerals naturally. However, we have other zeolites which are synthesized and used in commercial work. Zeolites have unique adsorption properties due to the fact that their structure is porous. Zeolites with metals of valency three have a very good affinity for the ions of fluoride (shown *et al*., 2003; Onyango *et al*., 2009).

Researchers have preferred to modify the surfaces of some zeolites that have adsorption capacities for fluoride in order to improve their uptake of fluorides from their solution (Sun *et al*., 2011). Zeolites containing iron (III) oxide ($Fe_2O_3$) and aluminium oxide ($Al_2O_3$) are good adsorbents for fluoride (Biswas *et al*., 2007). The zeolitic materials that have been synthesized by hydrothermal methods have an oxide molecular sieve (Guliant, 2004), where some are micro porous and others meso porous as shown in the following figure, hence allowing adsorption by electrostatic attraction (Auerbach, 2003).

The hydrothermal method used during the synthesis involves both chemical and physical changes within the oxide. If low silica zeolites are loaded to aluminium oxide, as an adsorbent, defluoridation becomes very effective (Onyango *et al.*, 2006). Hydrated iron (III) oxide is presented as a scavenger of fluoride from fluoride containing water (Dey *et al.*, 2004). This therefore indicates that there is plenty of surface area over which the water interacts with these ions leading to reduction of their level from the contaminated water (Fawel, 2006).

### 2.5.3 Combining ashes of rice husks and water hyacinth

Water hyacinth ash and rice husks contain a number of oxides such as aluminium oxide, ferric oxide, zinc oxide and manganese (IV) oxide as shown in table 2.1 and 2.2 (Mbugua *et al* 2014). These oxides have molecular sieves which are microporous and mesoporous enabling them to have a large internal surface area that make them suitable for use as sorbent materials.

**Table 2.1: Chemical composition of rice husks ash**

| Compound | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ |
|---|---|---|---|---|---|---|---|
| % Oxide | 12.0% | 77.0% | 1.5% | 1.3% | 0.9% | 0.2% | 7.2% |

**Table 2.2: Chemical composition of water hyacinth ash**

| Compound | $Al_2O_3$ | $P_2O_5$ | Cl | $K_2O$ | CaO | MnO | $Fe_2O_3$ | ZnO |
|---|---|---|---|---|---|---|---|---|
| % Oxide | 1.0% | 6.0% | 21.0% | 35.8% | 27.0% | 7.1% | 1.8% | 0.2% |

Rice husks ash contains silica in a hydrous amorphous form which it is highly porous and reactive (Geneva *et al*., 2008). This silica is used as a powerful substance for making materials for use in adsorption such as zeolites (Thern, 2008). Silica is a polymer form of colloidal sililic acid which is partially hydrated with a formular of $SiO_2.nH_2O$. The water component in silica occurs in the structure as hydroxyl groups chemically combined. The surface of silica has got Si-OH and Si-O-Si groups which are polar and this is the reason as to why it is suitable for use as an adsorbent of anions (Yang, 2003).

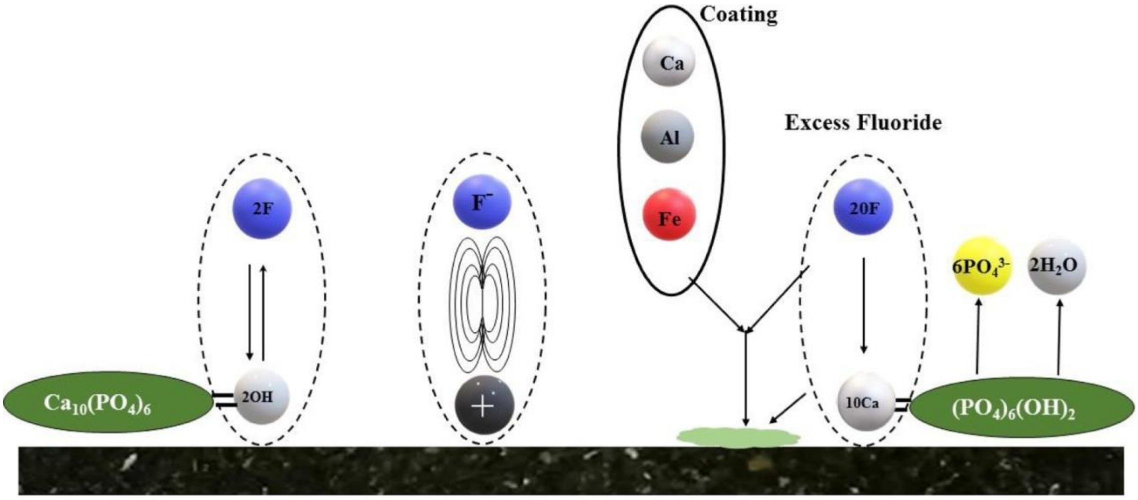
Since ashes of rice husks and water hyacinth contains a high percentage of silica and a number of oxides respectively, adsorbent materials prepared from them possess zeolitic characteristics (Mbugua *et al.*, 2014). Combining these two ashes by a hydrothermal treatment leads to a zeolitic material that has a surface modification with various positively charged species (Pollard, 1992; Oliveira, 2006; Mbugua *et al*., 2014). The process is environmentally friendly since these metal oxides have no harm to the environment (Doula, 2009; Guaya, 2015).

### 2.5.5 Mixing of bone char with ashes of rice husks and water hyacinth

Modified zeolitic adsorbent surfaces improve their adsorption abilities (Kragovi *et al*., 2012). Physical modification involving thermal treatment at a high temperature leads to reduction of the surface resistance of zeolites and promotes its ion exchange characteristics (Sannino *et al.*, 2012). Fahmy *et al*. 2016 in his studies used zeolites treated with microwave to remove divalent cadmium ions from waste water.

### 2.5.6 The mechanism of removal of the fluoride ions

There are three mechanisms of fluoride ions from the solution. These include; ion exchange, chemical precipitation and electrostatic interaction (Sternitzke *et al*., 2012).



**(a) Ion Exchange** **(b) Electrostatic** **(c) Precipitation**

**Figure 2.1:** The mechanism of the removal of fluoride ions **(Sternitzke *et al*., 2012)**

The ion exchange is due to the high affinity of fluoride ion to substitute the hydroxide group in the structure of the hydroxyappatite to form the fluoroappatite. The electrostatic interaction also plays a very important role in the removal process. The surface of the adsorbent is positively charged and this increases the affinity of the negatively charged fluoride ions to adsorb onto the char.

The formation of fluoride precipitates on the surface of the adsorbent takes place with high fluoride concentration (Herath *et al.,* 2018) or in the case of metal coated bone char with cations such as $Al^{3+}$ and $Fe^{3+}$. In this case, precipitates such as $CaF_2$, $AlF_3$ or $FeF_3$ will be formed on the char surface (Nigri *et al*., 2017; Rojas-Mayorga *et al.,* 2015; Zhu *et al*., 2011). Rojas – Myorga *et al.* (2013) explains that different metals doped onto the bone char surface contributes significantly to the improvement of anion removal efficiency.

Chatterjee *et al*. (2018) used aluminium sulphate in combination with calcium oxide to chemically treat bone char for fluoride removal. The new modified adsorbent resulted into enhancing the removal capacity from 14 to 150 mg/ L. Degadillo – Velasco *et al.* (2017) carried out studies on the effect of doping colloidal Ag onto commercial bone char samples at different temperatures ($300^oc$, $400^oC$, and $500^oC$) for fluoride removal from water. The results showed that thermal treatment at $400^oc$ was the most appropriate temperature for bonding Ag colloids to the bone char surface.

The capacity for the newly blend adsorption material increases because fluoride ions in solution are highly attracted to multivalent metal ions such as aluminium and iron due to their small size and high electronegativity (Tchomgui – Kamga *et al*., 2010)

## 2.6 Factors that influence removal of fluoride

Studies on variations of adsorption efficiency and equilibriums for removing of fluoride ions from their solution by an adsorbent is usually done by providing different parameters in experiment that involve their analysis (Yader, 2005) as discussed

### 2.6.1 Temperature

The temperature effect on the fluoride adsorption onto a solid is very significant. Decrease in temperature tends to decrease the kinetic energy of the particles of a substance while increase in temperature increases it. Studies have shown that at a very low temperature, the rate of adsorption of a substance is high and decreases with increase in temperature up to a certain level, after which the rate becomes constant. It is believed that this is because when the particles are vibrating at a very high rate as a result of increase in temperature, the contact between the adsorbent and the adsorbate is less hence low adsorption (Yader, 2005).

### 2.6.2 Initial anion concentration

Studies have showed that by increasing the concentration of the initial ion, the removal percentage of fluoride ion decreases (Choi, 1979). This may be explained by the fact that when the adsorbent dose is fixed, the adsorption sites that are available for adsorbing the ion are still the same regardless of how much of the adsorbate has been added (Wang, 2007).

### 2.6.3 Contact time

The time of contact is one of the most effective parameters in batch adsorption processes. In this particular parameter, all other parameters including adsorbent dose, initial fluoride concentration, shaking speed and temperature are kept constant (Cardon, 2000). Studies reveal that the maximum adsorption occurs in the first two hours after which there is almost no adsorption. This is probably because of the large surface area that is available at the start of the adsorption of fluoride ions.

### 2.6.4 Adsorbent dose

The study on effect of adsorbent dose is done by using different varying amounts of adsorbent doses. The other parameters are kept constant. These studies have shown that when the adsorbent dose is increased, an increase in the adsorption percentage occurs. This kind of an increase in the efficiency of removing the ions is as a result of increase in surface area. This gives more available active sites for the fluoride ions to attach themselves (Ayoob, 2006).

### 2.6.5 Shaking Speed

Studies done earlier have shown that removing fluoride ions from water depends on the shaking speed. At a particular time, as the speed of shaking increases, the percentage removal of fluoride ions also increases. (Dongre, 2006). However, the percentage increases up to an optimum level and at that point it remains constant. This may probably be due to an increase in the interaction between the fluoride ions and the zeolitic material at a relatively higher speed. (Bhargara, 1993).

## 2.7 Adsorption Isotherm

A sorption isotherm (also adsorption isotherm) is the isotherm describing the equilibrium of the sorption of a material on a surface (more generally at a surface boundary) at constant temperature. Adsorption isotherms describes a time when equilibrium is obtained between the amount of adsorbate adsorbed and that of adsorbate remaining in the solution if both of them have been given a long time to interact (Mead, 1981; Sposito, 1984).

## 2.8 Adsorption Equilibrium

An adsorption isotherm is usually a curve showing us the relationship between the equilibrium concentrations of a solute on the surface of an adsorbent, qe, to the solute concentration in the liquid, Ce, with which it is in contact (Kinniburgh, 1986). The adsorption isotherm is also an equation relating to the amount of solute adsorbed onto the solid and the equilibrium concentration of the solution at a given temperature (Dowd and Riggd, 1965). Qe÷ce relationship depends on the type of adsorption that occurs, multi-layer, chemical or physical adsorption.

## 2.9 Isotherm Models

There are various models that help us predict the equilibrium distribution. The most commonly used models include:

### 2.9.1 Linear Isotherm

This is the simplest adsorption isotherm equilibrium and also the most widely used (Travis, 1981). Such an adsorption isotherm equation is conventionally expressed in terms of the distribution coefficient, qe k= qece where k is the amount of ion adsorbed per unit mass and ce is the equilibrium solution of the concentration of the ion. Distribution coefficients are widely used in describing contaminant adsorption in flowing systems (Reardon, 1981). Graphically it can be shown as in Figure 2.2

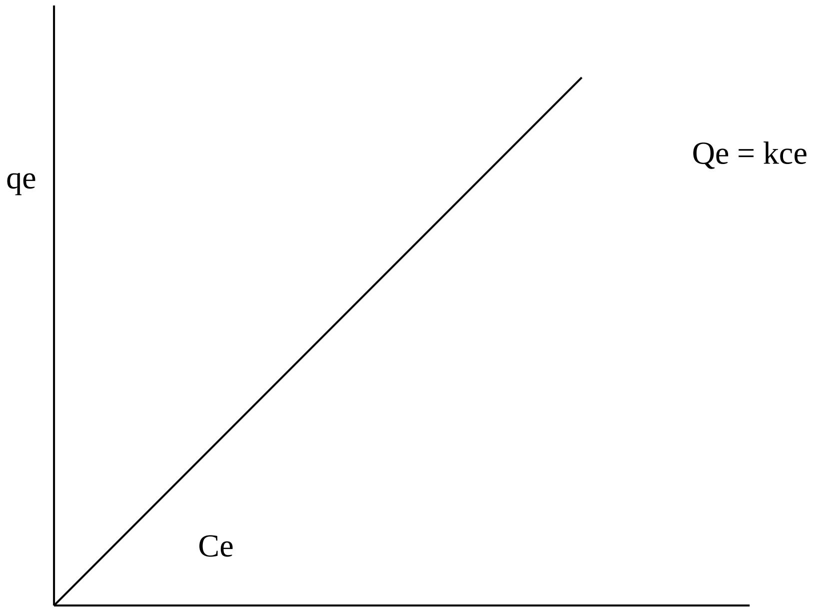


**Figure 2.2:** Linear isotherm model

qe= amount of solute adsorbed per unit weight of solid at equilibrium. Unit is either g/g or mg/g.
ce= Equilibrium concentration of solute remaining in solution when amount adsorbed equals qe.

### 2.9.2 Langmuir Isotherm

This adsorption isotherm takes the style of a monolayer coverage equilibrium model, where all sites of adsorbent are likely to adsorb (Sposito., 1984). Use of the Langmuir isotherm indicates a finite number of adsorption sites that are uniform and there are usually no lateral interactions (Mead, 1981). The linear form of Langmuir adsorption is given by the following equation.

$$qe = bQmax\frac{Ce}{1} + bCe \qquad equation\ 3$$

Where qe is the amount of solute which has been adsorbed (x) per unit weight of the adsorbent (m), ce (mg/l) is the equilibrium concentration of adsorbate in aqueous solution, b is a constant related to energy of adsorption, Qmax is the monolayer capacity. A plot of ce/qe versus 1/ce will give the value ce/Qmax the slope as b and ce/qe will be the y intercept.

### 2.9.3 Freundlich Isotherm

Freundlich Isotherm represents the isotherm variation of molecules adsorbed by unit mass of solid adsorbent with pressure. It is used for heterogeneous surfaces energy system (Westall, 1979). It is empirical and very widely used.

$$Qe = kfce^{\frac{1}{n}} \qquad \text{Equation 4}$$

Where; kf is an indicator of the capacity of the adsorption. The higher the maximum capacity, the higher the kf.

$^{1/n}$ is a measure of intensity of adsorption. Higher the 1/n value, more favorable is the adsorption. The linear form of Freundlich equation is,

$$Log\ qe = \log kf + \frac{1}{n}\log \text{ce} \qquad \text{Equation 5}$$

n and kf are system specific constants. A plot of log qe verses log ce gives values of log kf as the intercept and 1/n as the slope. The equation of this adsorption isotherm is among the oldest of the nonlinear isotherms and its use shows that the adsorption sites are heterogeneous (Kinniburgh, 1988).

### 2.9.4 Brunauer, Emmeh and Teller (BET) isotherm

This model is generally a multi-layer model. It assumes that a Langmuir isotherm applies to each layer and that no transmigration takes place between layers. It also assumes that there is equal energy of adsorption for each layer subsequent layers after the first layer has been dealt with (Cheo *et al.*, 1962).

## 2.10 Instrumentation

### 2.10.1 Fluoride ion selective electrode

A fluoride selective electrode is a type of ion selective electrode which is usually sensitive to the concentration of the fluoride ion (Truman, 1975). According to Martin, 1966 in the lanthanum fluoride electrode; the sensing element is a crystal of lanthanum fluoride $LaF_3$, doped with europium fluoride $EuF_2$ to create lattice vacancies. Such a crystal is an ionic conduction by the fact that the movement of the fluoride ions is by jumping between lattice vacancies”

An electrochemical cell may be made using a crystal such as that of a membrane which separates two solutions of fluoride. This electrochemical cell now behaves as a concentration cell with transference where the transport number of fluorides is one. The electrode is highly specific of fluoride ions as transference of charge though the crystal is almost exclusive. The hydroxide ($OH^-$) ion is the only ion which significantly interferes with the fluoride ion in the solution (Rich, 2006)

The interference of hydroxide ion can be avoided by buffering the sample below pH 7. The sensor that converts electrode is sensor or a transducer that is responsible of converting the activity of a specific ion which has been dissolved in a solution into an electric potential, which can be measured by a voltmeter or pH meter. (Eric, 2006 and Rich, 2006) agree that “the voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ionic-specific membrane, along with a reference. Electrode ion selective electrodes are used in biochemical and biophysical researches where measurements of ionic concentration in an aqueous solution are required”

#### 2.10.1.1 Calibration

The electrode must be calibrated before it is used, by measuring a series of known standard solutions which are prepared by diluting 1000ppm standard solution. For a full calibration, 50ml of fluoride solutions that contain concentrations of 200ppm, 100ppm, 10ppm, 1ppm and 0.1 ppm $F^-$ are prepared (Bralic, 2001). If the appropriate amounts of the ions in the samples are known, and this falls within the specific linear range of the ISE, then it becomes only necessary to make two solutions which are within this range (Lai, 2003).

#### 2.10.1.2 Electrode Characteristics

##### 2.10.1.2.1 The Response of the electrode

The electrode potential against concentration on semi – logarithmic paper results in a straight line with a slope of about 54 to 60 mV per decade change in concentration. (Radio, 2001).

The response time of the electrode is the time required to reach 99% of the stable potential reading which varies from a number of seconds on concentrated solutions to several minutes near the limit of detection.

### 2.10.1.2.2 Reproducibility

Reproducibility is usually affected by several factors which involves noise, drift and temperature changes. Within the range of operation of the electrode, reproducibility does not depend on concentration. When calibrations are done at the intervals of specified hours, direct electrode measurements reproducible to +2% can be obtained, (Ion, 2005).

### 2.10.1.3 Limits of detection

In solutions that are neutral, the concentration of fluoride ions can be measured down to $10^{-6}$moles$^{-1}$ (0.02 mg/L) fluoride. The upper most limit of detection is a fluoride solution that is saturated.

### 2.10.1.4 Temperature Effects

Since electrode potential is affected by change in temperature, samples and standard solutions should be within $_{+}^{-}1^{o}$C of each other. The absolute potential for the reference electrode changes slowly as the temperature varies as a result of solubility equilibrium on which the electrode depends upon (Zabban, 1975). Temperature also affects the slope of the fluoride electrode, as shown by factor S in the Nernst equation.When the temperature changes, the meter of the electrode should be recalibrated.

### 2.10.1.5 Interferences

The response to measurements of fluoride ions by the fluoride electrode is not interfered by most anions and cations. Such anions that do not interfere with electrode operation are $Cl^-$, $Br^-$, $I^-$, $SO_4^{2-}$, $HCO_3^-$, $PO_4^{3-}$ and acetate though they are commonly associated with fluoride. The $OH^-$ ions is the only group that causes electrode interference. Some anion such as $CO_3^{2-}$ or $PO_4^{3-}$ increases the pH of the sample, which increases $OH^-$ interference, but do not result to direct electrode interferences.

### 2.10.1.6 Effects of the pH

Solutions that are weakly acidic with a pH value of 4.5, will have hydrogen forming a complex with a portion of fluoride ions in the solutions resulting to formation of acids, HF and $HF_2$ which is usually not dissociated. Hydroxide ions interfere with fluoride response by the electrode when the level of hydroxide is greater than one tenth the level of fluoride ions present in the solution. At pH 7, when the hydroxide concentration is $10^{-7}$ moles/L or less, there is no interference by the hydroxide with fluoride measurement. At pH 10, where the hydroxide concentration is $10^{-2}$ moles/L fluoride, about 10% errors occur. At $10^{-4}$ moles/L fluoride, a bigger error will occur. Therefore, this makes it necessary to use a buffer solution in order to avoid this kind of interference. Addition of total ionic strength adjustment buffer (TISAB-2) to fluoride standards and samples will lead to formation of a buffer solution whose pH varies between 5.0 and 5.5 to avoid interferences of hydroxide ions and also to prevent formation of complexes of fluoride and hydrogen (Bulusu, 1990).

### 2.10.1.7 Complexation

Ions of fluoride form a complex structure with aluminum, silicon, iron$^{3+}$ and other cations that are polyvalent, and also hydrogen ions behave in the same manner. The degree of complex formation depends on the concentrations of the agents that are forming the complex, the total concentration of fluoride and the pH of the solution as well as the total ionic strength of the solution. (Alemayehu, 2001). A reagent referred to as CDTA which is found in TISAB II and III preferentially forms a complex with aluminum or iron in the sample.

### 2.10.1.8 Operation theory

This fluoride ion selective electrode consists of a sensing element adhered into an epoxy body. At the time when the sensing element comes into contact with fluoride ions contained in the solution, an electrode potential builds up across the sensing elements. The resulting potential, which builds according to the level of ions of fluoride which are free in the solution, is measured against a constant reference potential with a digital pH/mV meter on ISE concentration meter (Bailescu, 1990). The potential measured which builds to the level of fluoride ion in solution is described by the Nersnt equation.

$$E = Eo + S\log(A) \qquad Equation\ 6$$

Where;

E = Measured electrode potential

Eo= Reference potential (a constant)

A= Fluoride ion activity level in solution

S= Electrode slope (about 57 mV per decade)

### 2.10.2 X-ray Spectrometer

X-ray fluorescence (XRF) spectrometer is used often for analyzing the chemical components of rocks, minerals, sediments and fluids without destroying their chemical composition (Filton, 1997). It works on wavelength dispersive spectroscopic principles that are similar to an electron microbe (Fitton, 1977). However, an XRF cannot generally make analysis at the small spot sizes typical of electron microbe work (2-5 microns), so it is normally used for analyzing large amounts of organic materials. The relative case and low case of use of x-ray spectrometers make this one of the most widely used methods for analysis of major and trace elements in rocks, minerals and sediments (Potts, 1987).

Analyzing major and trace elements in these physical substances by XRF is usually possible because of how atoms behave when they come into contact with X-radiation. An XRF spectrometer work due to the fact that when a sample is illuminated by an intense X-ray beam, that is the incident, some of the energy is scattered, but some is also absorbed within the sample depending on the chemical and physical properties of the sample (Rollinson, 1993).

The sample is usually said to be excited when the primary x-ray beam illuminates it. (Rollinson, 1993) indicates that the excited sample as a result, emit x-rays along a spectrum of wavelengths whose characteristics are according to the types of atoms contained in that particular sample. This happens because the atoms that are within the sample in question absorb X-ray radiations by methods such as ionizing and pushing electrons from the lower energy levels which are usually energy level K and energy level L. He argued that “the pushed electrons are replaced by electrons from an outer, higher energy orbital. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared to the outer one". This energy release is in the form of emissions and is a characteristic of X-rays showing the type of atom present.

### 2.10.3 Magnetic Stirrer

The magnetic stirrer provides an extra degree of precision for your application. It allows for enhanced reproducibility of results and higher efficiency in the measuring process (Girolami, 2013). A magnetic stirrer (magnetic mixed) is a laboratory device that provides a rotating magnetic field to make a stir bar put into a liquid to spin quickly, this is the stirring (Arthur, 2003). Magnetic stirrers are mainly used in biology and chemistry. They are used more than the gear drivers' motorized stirrers. This is due to the fact that they show more efficiency and also, they don't have any external moving part which can easily be broken and wear out but instead, they have only a simple bar magnet. In addition to this advantage, the magnetic stirrer has another advantage of being small in size, easy to clean and sterilize than other devices that are used for stirring (Girolamis, 1999). This stirrer also does not need any lubricating substance which could result to contamination of the sample and the apparatus used. They can be used inside hermetically closed vessels and systems, without the need for using rotary seals that are complicated.

### 2.10.4 pH Meter

A pH meter is a type of voltmeter with a very high impendence of the input channels. PH meter has several inputs for indicators and reference electrode and temperature sensors (Hammond, 2005). This device is used to measure the activity of hydrogen ions in their solution (Butt, 2013). Basically, a pH meter contains a voltmeter attached to a pH response and a reference electrode. The pH electrode that responds to the activity of hydrogen ions is generally glass and the reference is usually mercury – mercury chloride (calomel) electrode, although silver – silver chloride electrode is sometimes used. These two electrodes behave as a battery when they are immersed in a solution.

The glass electrode creates an electric potential (charge) that directly depends on the hydrogen ion activity in the solution (59.2 millivolts per pH unit at 25$^{o}$C) and also the voltmeter measures the difference in potential between the glass and reference electrode (Hammond, 2005).

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Research design

The study aimed at blending zeolitic materials prepared from ashes of water hyacinth and rice husks with bone char, study the chemical composition of the blend material and undertake adsorption studies for removal of fluoride ions from contaminated water

## 3.2 Collection of materials

The biomass that was used for preparation of the zeolitic materials were obtained from rice husks, water hyacinth and bones. Rice husks were collected from Nice Rice Millers in Mwea West District, Kirinyaga County. They were then washed and rinsed with distilled water to remove dirt. They were dried in an oven at a temperature of 100°C for 6 hours. Water hyacinth plants were uprooted from Nairobi Dam. They were washed and rinsed with distilled water to remove soil. They were sundried for one month according to the procedure described by Kruatrachue *et al.*, 2004. The bones were collected from Maua town in Meru County. They were taken to the laboratory where they were cleaned with boiled tap water to remove fat and flesh residue and then rinsed with hot de-ionized water.

## 3.3 Preparation of standard solutions

The 1000 ppm stock solution of fluoride ions was prepared by dissolving 2.21 g of sodium fluoride salt in 1000 ml of distilled water in a volumetric flask. The solution was then diluted to obtain standard solution of 100 ppm. Total ionic strength adjustment buffer (TISAB) II solution was added to the fluorides in order to maintain the solution to pH value of 5.0-5.5.

### 3.4 Generation of black and white bone char

300 g of clean bone samples were dried for 24 hours in an oven at a temperature of 100°C. Bone char was synthesized by heating the cleaned bones at a temperature of 400°C and 600°C in order to obtain black bone charcoal and white bone charcoal respectively (Abe, 2009).

### 3.5 Preparation of ashes

Dried rice husks and water hyacinth were burnt separately in a furnace at 500°C in excess air for 12 hours to obtain the ashes (Kruatrachue *et al*., 2004). The ashes were ground, screened through a sieve and then stored in desiccators for further tests.

### 3.6 Hydrothermal synthesis of zeolitic materials

#### 3.6.1 Zeolitic material A

Zeolitic material A was prepared by adding 20 g of each ash of water hyacinth ash and rice husks in 500 ml de-ionized water and then conditioned into a stainless-steel digestion bomb. The closed bomb was introduced into a pre-heated oven at the temperature of crystallization (100 °C) for 24 hours. The resulting solid was saturated in de-ionized water in a period of 24 hours for the salts to dissolve and it was then dried at 100 ˚C for 24 hours to get rid of any organic material. The sample was stored in a dry place at room temperature.

### 3.6.2 Zeolitic material B

To prepare zeolitic material B, 20 g of black bone charcoal, 20 g of water hyacinth and 20 g of rice husks were added to 500 ml deionized water. The mixture was then conditioned into a steel bomb, closed and put into a pre-heated oven at a temperature of 100°C for 24 hours. The resulting product was put in distilled water for 24 hours and later dried at 100°C. The sample was then stored.

### 3.6.3 Zeolitic C

Zeolitic material C was prepared by adding 20 g of white bone charcoal 20 g of each ash of water hyacinth and of rice husks were put into a stainless-steel digestion bomb. Then closed bomb introduced into the oven at a temperature of 100°C, and heated for 24 hours. The sample was stored at room temperature.

## 3.7 Preparation of the total ionic strength adjustment buffer (TISAB II)

500 ml of distilled water was put in a 1000 ml beaker and placed on a magnetic stirrer. 84 ml of concentrated hydrochloric acid (36-38%) was added slowly to the distilled water. 242 g of tris (hydroxymethyl) amino methane was added to the mixture followed by 230g of sodium titrate ($Na_2C_4H_4O_6.2H_2O$). When the solid dissolved, the solution was allowed to cool to room temperature, then transferred to a 1 litre volumetric flask and then filled to the mark with distilled water. Before measurements of fluoride ions, equal volumes of TISAB-II and standards were combined in order for the solution pH to remain constant (Liberti, 1969).

## 3.8 Instrumentation

Analysis of fluoride ions was done using Fluoride ion selective electrode (FISE). The FISE used was the EDT instrument type (3221). A pH meter-model (PHEP Hanna instrument Italy) was used at pH values of 5.0-5.5 and at a temperature of 25 °C. A Magnetic stirrer model MH-4 mrc laboratory equipment of serial number 2.42-03-10 was used. The accuracy of the instrument was checked using triplicates of samples. Three samples of similar concentration were put in three different plastic bottles, the FISE was dipped into each of the samples at different times and the readings were recorded.

A series of standards were prepared for instrumental calibration by serial dilution of a working solution of the 100 ppm that was prepared from analytical grade stock solution, 1000 ppm. Standard and blank samples were run after every one hour of analysis to check on the change of the instrumental analysis principle. Calibration curve method was used to quantify the fluoride ion concentration.

## 3.9 Determination of chemical composition using X-ray fluorescence spectrometry

The chemical composition of the adsorbent materials prepared was determined using X-ray fluorescence spectrometry. This involved the determination of the oxides present in the materials.

## 3.10 Batch experiments

In the batch experiments, a water-bath temperature-controlled shaker (DKZ-1 No 1007827-USA) was used for the batch adsorption study. Data for sorption isotherm were generated by contacting 0.3 g ZA, ZB, ZC, BCB and BCW with fluoride containing aqueous solution at pH 5.5. Samples of 50 ml fluoride solution at concentration of 100 ppm were transferred into 120 ml plastic container and placed in a magnetic stirrer and stirred at a fixed temperature of 25°C. A piece of asbestos sheet was placed between the stirrer and the plastic container containing the fluoride solution. This was to control the effect that may be brought about by change of solution temperature that might be as a result of magnetic stirrers that may produce heat as the stirring continues. TISAB-II was added to samples and standards to adjust the pH of solutions to 5.0-5.5. The plastic containers containing the solutions were agitated at a constant shaking rate of 120 rpm.

Triplicate of sample solutions of 100 ppm $F^-$ ions solutions were mixed with 0.3 g of absorbent and shaken for 2 hours at a temperature of 25°C and thereafter, they were filtered. Fluoride concentrations in the filtrates obtained were measured using the Fluoride Ion Selective Electrode.

### 3.10.1 Effect of adsorbent dosage of the adsorbents

The effect of the dosage on the adsorption of fluoride ions were investigated by agitating $F^-$ ion solutions at various dosages from 0.05 g to 0.40 g at fixed contact time. Initial anion concentration was maintained at 100 ppm and the temperature at the shaker remained 25°C. These samples were in triplicates and the agitation period was 2 hours on the water bath shaker. The samples were taken out of the shaker at the end of the 2 hour period and were then filtered using the Whatman No.1 filter papers. The concentration of the fluoride ions in the filtrates was determined.

### 3.10.2 Effect of initial concentration of fluoride ions

The experiments on the effect of initial concentration of fluoride ions on the uptake of fluoride ions by the adsorbents was done by agitating 50 ml samples of $F^-$ions solutions of 0.1ppm, 10 ppm, 20 ppm, 50 ppm, 80 ppm and 100 ppm in 120 ml plastic bottles with 0.3 g of ZA, ZB, ZC, BCB and BCW adsorbents in a water bath shaker at 25˚C. All other parameter such as contact time, shaking speed, dose of adsorbent and temperature were kept constant. This was done in triplicates and removed 2 hours later and filtered using the Whatman No.1 fitter papers. The samples were then measured for the residue of $F^-$ ions remaining in the filtrate.

### 3.10.3 Effects of Contact Time

Studies undertaken on effect of contact time on the fluoride removal was done by varying the time from 10, 20, 30, 60, 90, 120, 720 and 1440 minutes using 50 ml of 100 ppm sample solutions in plastic containers. Temperature was kept at 25˚C for each of the samples and the shaking speed set at 120 rpm. The adsorbent dosage was retained at 0.3 g of all the adsorbents. The solutions were then filtered and the filtrates were subjected to fluoride ion selective electrode for analysis of the ions of fluoride remaining.

### 3.10.4 Effect of shaking speed

Effect of shaking speed on the fluoride removal efficiency was investigated by varying the shaking speed from 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200 rpm at a temperature of 25 ˚C. The contact time was 2 hours and adsorbent dose was retained at 0.3 g for all the adsorbents and the fluoride ion concentration was 100 ppm. At the end of 2 hours period per every shaking speed, the solutions were filtered and the filtrate was analyzed for fluoride ions.

### 3.10.5 Effect of Temperature

Effect of temperature on the removal of fluoride ion solution at various temperature levels from 25 ˚C, 35 ˚C, 45 ˚C, 55 ˚C, 65 ˚C and 75 ˚C was investigated. The dosage used was 0.3 g for the adsorbents while the concentration of the fluoride ion solutions also remained 100 ppm. The shaking speed for all these samples was kept at 120 rpm and contact time was 2 hours for each sample. After two hours for each temperature level, the samples were removed from the water bath shaker and filtered. The fluoride ion concentration of the filtrates was then determined.

### 3.11 Determination of fluoride ion removed from water

The amount of fluoride ion uptake by blended adsorbent substances during the batch experiment was determined using equation 3.1

$$qe = \frac{(\mathrm{Co}-\mathrm{Ce})\mathrm{V}}{\mathrm{W}} \qquad \text{Equation 7}$$

Where;

$\mathrm{qe} = \text{Amount of fluoride ion uptake per mass of modified material at equilibrium}$

$\mathrm{Co} = \text{Initial concentration of fluoride ions in } \frac{\mathrm{mg}}{\mathrm{L}}$

$\mathrm{Ce} = \text{Concentration fluoride ions at equilibrium in } \frac{\mathrm{mg}}{\mathrm{L}}$

$\mathrm{W} = \text{Mass ofthe modified adsorbent material in grams}$

$\mathrm{V} = \text{Volume of solution in litres}$

# CHAPTER FOUR

# RESULTS AND DISCUSSIONS

## 4.1 Chemical composition of the adsorbent's materials

The chemical composition of synthesized zeolitic materials was determined using x-ray fluorescence spectrometer and the results are shown in tables 4.1and 4.2. These materials contained compounds including calcium carbonate ($CaCO_3$), calcium phosphate ($Ca_3(PO_4)_6$, aluminium oxide ($Al_2O_3$), potassium oxide ($K_2O$), iron (II) oxide ($Fe_2O_3$), and silicon dioxide ($SiO_2$) in varying amounts.

**Table 4.1**: **Chemical composition of synthesized Zeolitic materials**

| **Compound / % Oxide** | **$CaCO_3$** | **$CaSO_4$** | **$Ca_3(PO_4)_2$** | **$Al_2O_3$** | **$P_2O_3$** |
|---|---|---|---|---|---|
| **ZA** | 0.00 | 0.00 | 0.00 | 10.00 | 5.00 |
| **ZB** | 4.00 | 0.05 | 30.00 | 10.00 | 1.00 |
| **ZC** | 8.00 | 0.08 | 15.00 | 7.50 | 10.00 |
| **BCB** | 15.00 | 0.50 | 71.00 | 0.00 | 0.00 |
| **BCW** | 45.00 | 0.25 | 40.00 | 0.00 | 0.00 |

**Table 4.2: Oxides in synthesized zeolites**

| **Compound / % Oxide** | **$K_2O$** | **CaO** | **$Fe_2O_3$** | **ZnO** | **MnO** | **$SiO_2$** |
|---|---|---|---|---|---|---|
| **ZA** | 15.00 | 2.00 | 10.10 | 0.01 | 0.10 | 55.00 |
| **ZB** | 0.00 | 0.00 | 10.10 | 0.50 | 0.01 | 43.50 |
| **ZC** | 0.00 | 0.00 | 8.00 | 0.50 | 0.01 | 51.00 |
| **BCB** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **BCW** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Bone charcoal adsorbents charred at 400 °C display a surface that is rich in heterogeneous components, allowing for physi-sorption, chemi-sorption or ion exchange to occur on them (Castillo *et al.*, 2007). Bone char has been shown to have specific ability to take up fluoride by the three processes due to its chemical composition. This is because it is a granular and porous material and their main inorganic constituent is calcium hydroxyapatite ($Ca_{10}$ $(PO_4)$. $6(OH)_2$. The ability to adsorb fluoride ions from water is because it contains the hydroxyl groups which are the active sites for fluoride adsorption in its hydroxyapatite structure (Fawell, 2006). The ion exchange takes place due to the high affinity of fluoride ion to substitute the hydroxide group in the structure of the hydroxyappatite to form the fluoroappatite. Another compound which is present in the bone structure is calcium carbonate (Deydier, 2003). The carbonate in the structure is not structural but it has been adsorbed on the apatite surface (Elliot, 1994) so they are very well exchanged with fluoride ions in the solution.

The newly formed zeolitic material also has surfaces containing Si-O-Si and Si-OH sites which are usually polar. They also have alumina ($Al_2O_3$) and ferric oxide ($Fe_2O_3$) that have micro porous and meso porous molecular sieves that make them have cage-like structures that adsorb ions onto themselves (Tang *et al.*, 2009). Aluminium oxide has a high surface area, with a lot of tunnel-like pores that run all through it (Fawell, 2006). Ferric oxide has been presented as a scavenger for fluoride ions from its solution (Dey *et al.*, 2004). Adsorption of fluoride ions using these sites is by electrostatic attraction (Bahena, 2002).

From Table 4.2, it was noted that the adsorbent material ZB**,** contained 10.10% ferric oxide and 10.00% alumina. Previous report illustrated adsorption of fluoride ions by activated alumina though it was reported to have a limitation of low adsorption capacity (Onyango *et al.,* 2004). Hence, to improve their adsorption characteristics, modification of their surfaces is necessary.

## 4.2 Effect of adsorption parameters on percentage removal of fluoride ions

### 4.2.1 Effect of Initial Concentration of Fluoride ions on its percentage removal

The graph in Figure 4.1 shows the effect of initial concentration of fluoride ions on its percentage removal. The results reveal that the percentage removal of fluoride ion by various adsorbent materials increased initially as the concentration progressed from 0.1, 10.0, 20.0 and 50.0 ppm. This is probably because of the availability of many active sites on the adsorbent at the beginning of the adsorption process which become saturated with increased concentration (Appel and Lena, 2002). At 50-80 ppm for all the materials, the adsorption percentage removal decreases.

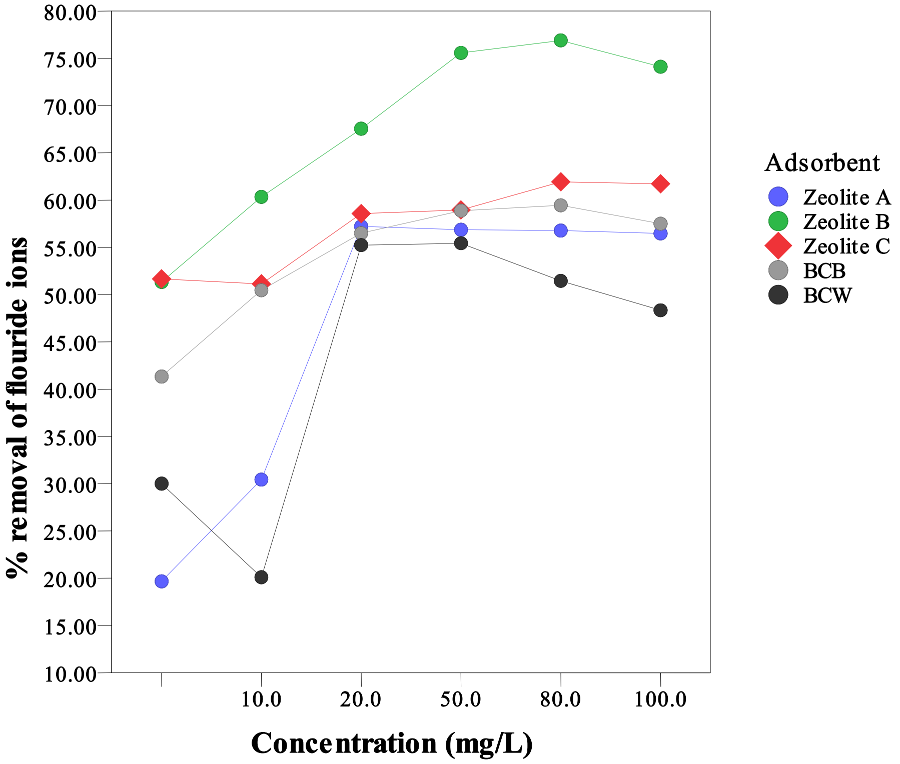


**Figure 4.1:** Effects of varying fluoride ion concentration on percentage removal of fluoride ions at conditions of 25°C, 120 min, dosage of 0.3 g and 120 rpm.

For zeolite A, initial removal of fluoride ions increases from 19.6% to 57.2% at the concentration of 0.1 ppm to 20 ppm but the rate becomes almost constant towards 50 ppm through 80 ppm. For zeolite B, the adsorption percentage is 51.3% at a concentration of 0.1 ppm and increases to 60.3% at 10ppm, 67.5% at 20 ppm and becomes constant at 50 ppm with 75.5% but drops to 73% at 80 ppm. For Zeolite C the adsorption percentages are 51.6%, 51.1%, 58.5% and 58.0% for concentrations of 0.1, 10, 20, 50, and 80 ppm respectively. BBC gives 41.3%, 50.4% 56.5%, 58.8% and 55.0 % for the initial concentrations of 0.1, 10, 20, 50 and 80 ppms respectively. WBC follows the same trend as there is 30.0% at 0.1 ppm, 20.1% at 10 ppm, 55.2% at 20 ppm 55.4% at 50 ppm and 51.4% at 80 ppm. There is a clear indication that further increase of the initial ions' concentration decreases the percentage removal of all the adsorbents. This could be as a result of the capacity of adsorbent material getting exhausted sharply with the increase in the initial fluoride ion concentration (Palanisamy *et al.,* 2012; Namasivayan, 2003). This was demonstrated by the studies done earlier by Kadirvelu, 2003). They demonstrated that there is a limited number of high energy sites on the surface of the absorbent on which adsorption takes place. As the initial ion concentration increases the sites become saturated resulting in a decrease in the efficiency of adsorption and consequently the percentage of fluoride adsorbed lowers

### 4.2.2 Effects of Temperature

The effect of temperature on the percentage removal of fluoride ions at the same conditions of 120 minutes contact time, 100 mg/L initial concentration and stirring at 120 rpm is as shown in Figure 4.2. The percentage removal of the fluoride ions decreased from 60% to 36%, 80% to 50%, 70% to 37%, 60% to 35%, and 57% to 24% for adsorbents ZA, ZB, ZC, BCB and BCW respectively as temperature was increased from 25°C to 75°C. Decreased adsorption at increased temperature is associated to adsorption processes that are exothermic and may be physi-sorption in nature (Poshusta *et al*., 2000). This means that adsorbent is held together by weak van der Waal forces. The maximum absorbance was observed at 25°C while an increase in temperature decreases the absorbance.

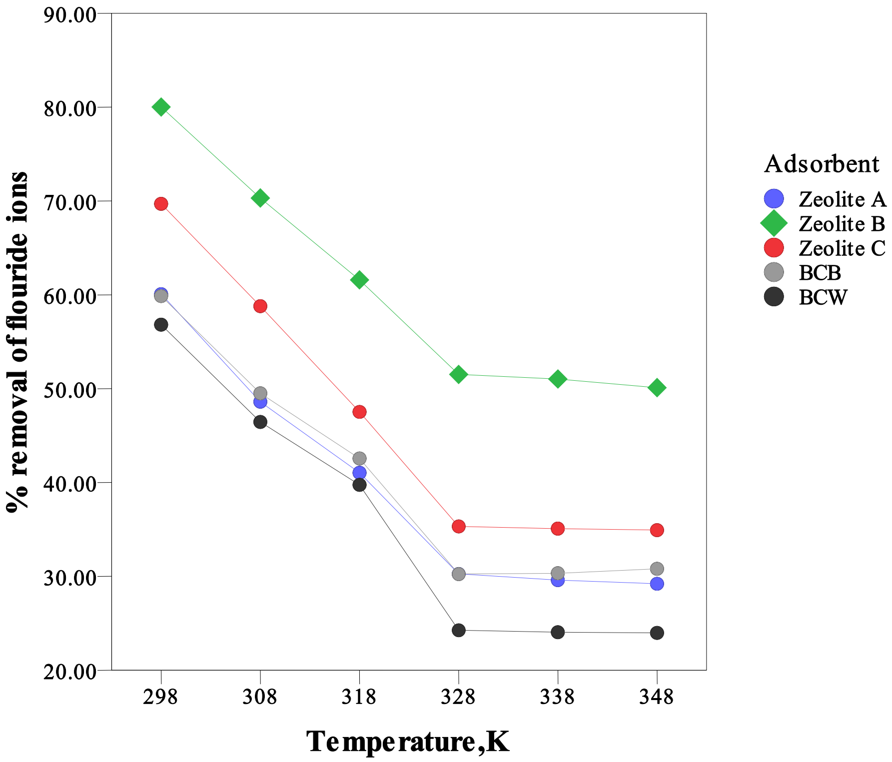


**Figure 4.2:** Effects of temperature on the percentage removal of fluoride ions at conditions of 100 ppm, 120 min, 120 rpm and a dosage of 0.3 g.

### 4.2.3 Effect of shaking speed

The effect of shaking speed on percentage removal of fluoride was determined. The shaking speed was adjusted from 40 rpm to 200 rpm at a dosage of 0.3 g adsorbent with a time of contact of 120 minutes and initial concentration of 100 ppm. The effect of shaking speed on the degree of adsorption indicates that the removal of fluoride is affected by the shaking speed (Bhargave, 1993). As shown in Figure 4.3, the percentage removal increased from 14% to 43%, 60% to 75%, 47% to 65%, 43% to 60% for ZA, ZB, ZC and BCW respectively. As the shaking speed increases to 160 rpm, the adsorption decreases. Earlier studies have shown that at a given time, fluoride removal increase with the rate of shaking up to a certain level and then decrease at a further increase of the shaking speed (Tembhurkar, 2006). This is because shaking the mixture makes the solid adsorbent particles to move rapidly in the solution therefore increasing the concentration of the fluoride ions around the surface of the solid zeolite probably to a level near that of bulk concentration (Argun *et al*., 2005)

Further, Chuah *et al*. (2005) reported that shaking the mixture results in an increase of fluoride ion diffusion into the boundary layer between the adsorbent particles and the surrounding solution increasing the speed of the external mass transfer and rapidly reaching the equilibrium. Above the speed of 160 rpm the rate of diffusion decreases due to very high shaking speed which provides energy that is sufficient to break the newly formed bonds between the fluoride ions and the adsorbent surface (Erdem *et al*., 2004).

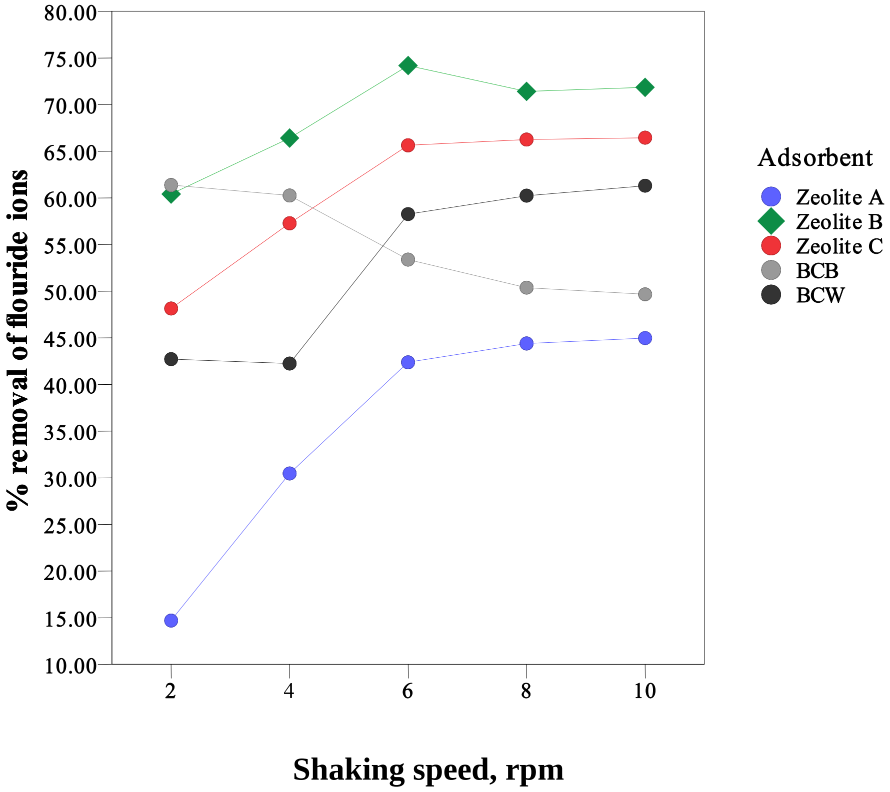


**Figure 4.3:** Effects of shaking speed on the percentage removal of fluoride ions at conditions of 100 ppm, 25$^o$ C, 0.3 g dosage and 120 min

### 4.2.4 Effect of the contact time

Studies on effects contact time on the percentage removal of fluoride ions was done by varying the contact time from 10 to 1440 minutes maintaining the dosage of the adsorbent at 0.3 g, initial concentration of fluoride of solution of 100 ppm, and temperature of $25^{\circ}$ C. Rate of shaking was kept to its optimum value of 120 rpm. From the graph in Figure 4.4, the percentage removal of fluoride ions increases from 19% to 47% between 10 and 90 minutes and then remained constant up to 1140 minutes for the white bone char. Black bone char has a percentage removal of 21% to 57%, zeolitic material A has 20% to 51%, zeolitic material C has 23% to 58% and zeolitic material B has the highest percentage removal of 40% to 77%. Murugan (2006) demonstrated that removal of fluoride ions increases with increase in contact time to some extent, but further increase in the contact time does not increase the uptake due to deposition of fluoride ions on almost all the vacant sites of adsorbent.

In this particular study, most adsorption takes place during the first 30 minutes and thereafter increases to their maximum during 90 to 120 minutes, then remains constant. Therefore, this contact time, 120 minutes, was taken as the equilibrium time.

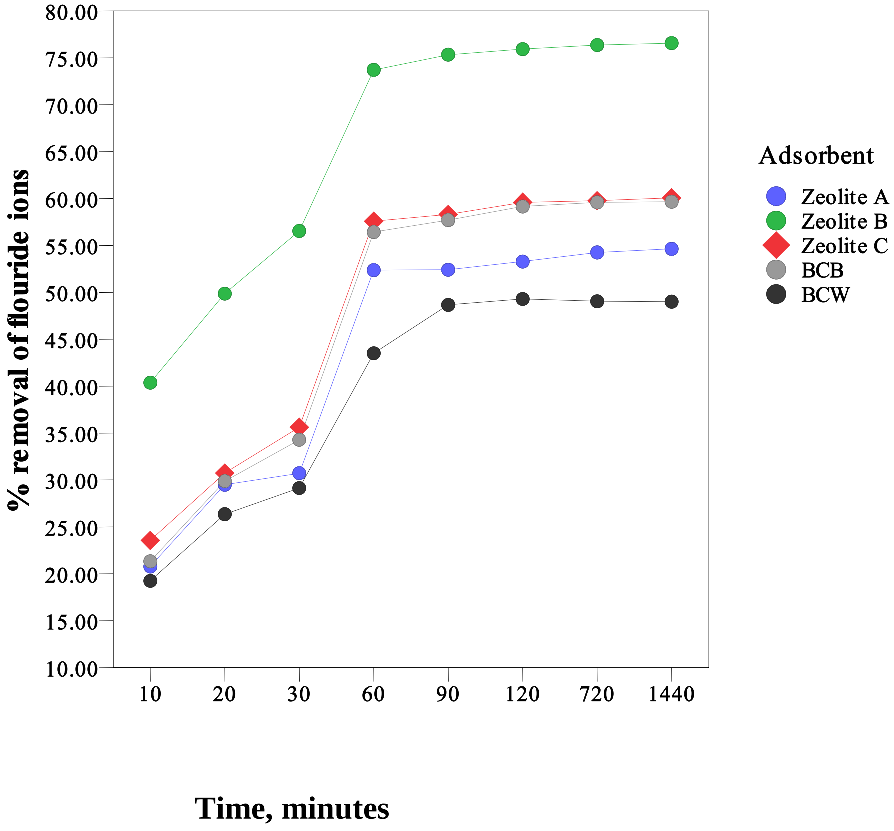


**Figure 4.4:** Effect of varying contact time on the percentage removal of fluoride ions at conditions of 100 mg/L, 25 ˚C, 120 rpm, and a dosage of 0.3 g

The change in the degree of adsorption is due to the fact that at first all the adsorbent sites were open and the concentration of the solute was high within the first 30 minutes (Altum, 2006). As the adsorption sites became fewer due to saturation, the fluoride ion uptake was controlled by the rate at which the adsorbate was transported from the exterior to the interior sites of the adsorbent particles (Mbugua *et al*., 2014). The results indicate that “the possible monolayer of fluoride ions in the other surface is formed, pores of the adsorbent are blocked and pore diffusion onto inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment is restricted” (Tadar *et al*., 2005).

As in figure 6, the percentage removal of fluoride ions increased from 19% to 47%, 21% to 57%, 23% to 58%, 40% to 77% and 20% to 51% as time increased from 10 min to 90 min for adsorbents BCW, BCB, ZC, ZB and ZA respectively. After the percentage removal reaches its maximum time, the percentage removed remains constant or decreases.

These results show that the rate of percentage removal of fluoride ions increases with increasing contact time. Zeolite B remains the best adsorbent as it gives the highest percentage removal of 77% at the 90th minute. White bone char is the poorest adsorbent as its maximum percentage removal is 47%. This is probably because the hydroxyapatite structure of the white bone char was destroyed by high temperature of 600°C during the calcination process (Leyva, 2009).

### 4.2.5 Effects of adsorbent dose on fluoride removal

The study on the effect of varying the dose of the adsorbent on removing fluoride ion was done by maintaining fluoride ion concentration constant at 100 ppm. Changing the amount of the dose of the adsorbent during the removal of fluoride ions indicates that an increase in the degree of adsorption occurs with the corresponding increase in the adsorbent dose as can be seen from graphs given in Figure 4.5. This is because the percentage of fluoride ions adsorbed is greatly dependent on the adsorbent dose (Mouni *et al.*, 2011). The increase in the removal efficiency with the simultaneous increase in adsorbent dose is due to increase in the surface area, and hence more active sites available for adsorption of fluoride (Kurnian, 2004) resulting to increased adsorption capacity.

The adsorbent dose was varied from 0.05 g, 0.10 g, 0.15 g, 0.20 g, 0.25 g, 0.30 g, 0.35 g and 0.40 g for all the adsorbents, by maintaining contact time of 120 minutes and a shaking speed of 120 rpm. The results show that the maximum dose of adsorbent of 0.3 g gave the highest adsorption. The percentage adsorption of a dose of 0.3 g of the adsorbents were 54%, 74%, 61%, 55%, 49%, For ZA, ZB, ZC, BCB & BCW respectively as illustrated in Figure 4.5. When the dosage was increased above 0.3 g which was the point where the adsorbent reached their maximum adsorption capacity, the adsorption becomes constant.

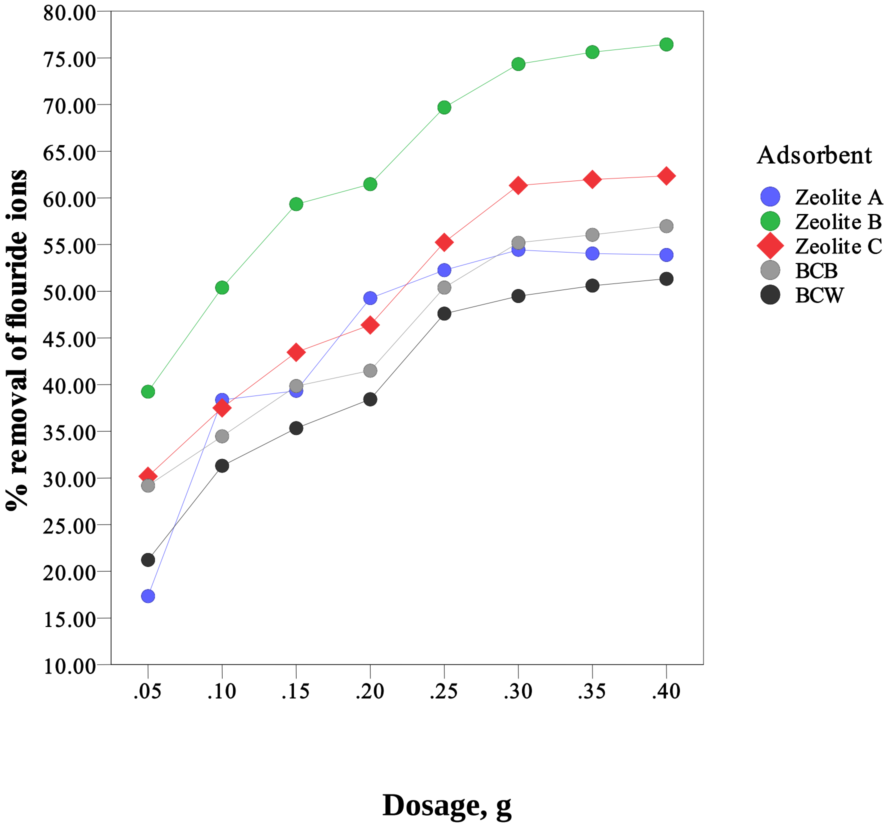


**Figure 4.5:** Effects of Adsorbent dosage on the percentage removal of fluoride ions at conditions of 25°C, 120 rpm, 120 min and 100 ppm

These findings also corresponded to those reported by Najua *et al*. 2008, confirming that a further increase in the adsorbent dose has no effect on adsorption since equilibrium has already been established and the amounts of free ions remain the same even with further addition of the adsorbent dose (Duvnjak and Al-Asheh, 1998). Furthermore, very high adsorbent dosage results in the shielding effect on the dense outer layer of the cells leading to a screening of the fluoride ions from the binding sites of the adsorbent as already reported by Bishnoi *et al*., (2004)

## 4.3 Adsorption Isotherms

The data obtained from sorption studies where the fluoride ion concentration was varied from 0.1 mg/L to 100 mg/L with a fixed adsorbent dosage of 0.3 g, shaking speed of 120 rpm and a temperature of 25°C were fitted to Langmiur and Freundlich isotherm models. The thermodynamic constants of the two models are given in Table 4.3.

From the table, the sorption data for the fluoride ions for adsorbents ZA, ZB, ZC, BCB and BCW best fitted Freundilich model on the basis of coefficient factor $R^2$ of 0.986, 0.995, 0.998, 0.999 and 0.960 respectively. Values of $1/n$ less than 1 show favorable nature of physical adsorption of anions onto the adsorbents while values of $R^2$ close to one as much as possible show a good relationship between absorbance and concentration (Bering *et al*., 1972).

The data also shows that the adsorption capacities of the five adsorbents for fluoride ions were 1.177, 1.281, 1.061, 1.142 and 1.112 for adsorbents ZA, ZB, ZC, BCB and BCW respectively. This shows that the best adsorbent for fluoride ions was ZB because it had the highest adsorption capacity. This could be attributed due to the presence of the alumina and ferric oxide in the zeolitic material B. There is also the presence of tricalcium phosphate which is in form of hydroxyapatite from the black bone charcoal whose –OH group actively exchange with fluoride ions in the solution (Mareno, 2010).

**Table 4.3:** Langmuir and Freundilich adsorption constants for fluoride ions

| | **Langmuir** | | | **Freundlich** | | |
|---|---|---|---|---|---|---|
| **Adsorbent** | **$Q_{max}$ (mg/g)** | **b($dm^3$/g)** | **$R^2$** | **1/n** | **Kf(mg/g)** | **$R^2$** |
| Zeolite A | 4.46 | 0.021 | 0.482 | 0.118 | 1.177 | 0.986 |
| Zeolite B | 11.90 | 0.028 | 0.652 | 0.413 | 1.281 | 0.995 |
| Zeolite C | 28.82 | 0.010 | 0.744 | 0.301 | 1.061 | 0.998 |
| BBC | 20.83 | 0.011 | 0.494 | 0.234 | 1.142 | 0.999 |
| WBC | 7.62 | 0.014 | 0.266 | 0.138 | 1.112 | 0.960 |

The graphs in appendix 1 and appendix 6 are best examples of adsorption isotherms. These are the Langmuir and Freundlich isotherms for the adsorption of fluoride ions using zeolitic material B. From the graphs it can be seen that there is a linear relationship between the log of qe and log of ce in Figure 6 but there is a non linear relationship in Figure 1 between the log of qe and ce, and this explains why the data was fitted in Freundlich isotherm and not in the Langmuir isotherm.

# CHAPTER FIVE

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

From the results obtained from this study, it is clear that the adsorbent materials prepared from ashes of rice husks and water hyacinth demonstrated zeolitic characteristics and showed ability to remove fluorides. Blending these adsorbent substances with bone char increases their capacity for removal of fluoride ions from their solution. The adsorbent material blended with black bone char, zeolitic material B, **(ZB)**, has 43.50% of $SiO_2$, 10.10% of $Fe_2O_3$ and 30% of $Ca_3(PO_4)_2$. It has the highest percentage removal of fluoride ions. It gave 80% fluoride removal at optimum temperature and 77% removal at optimum time.

Zeolitic material B gave the highest adsorption capacity as well. The optimum temperature and contact time were found to be 25°C and 120 minutes, respectively. The study of fluoride removal by zeolitic material A, zeolitic material B, zeolitic material C, black bone charcoal and white bone charcoal best fitted in Freundlich adsorption model. In conclusion, this study shows that ZB can be used effectively to remove fluoride ions from water.

## 5.2 Recommendations

i. More work should be done to optimize use of locally available materials for application in defluoridation of water.
ii. More studies on surface modifications of zeolites to improve their adsorption capacities for more water pollutants are necessary.

iii. Use of other methods in determination of functional group present in the blend material.
iv. Educate the public on the use of locally available agricultural waste materials in water treatment.

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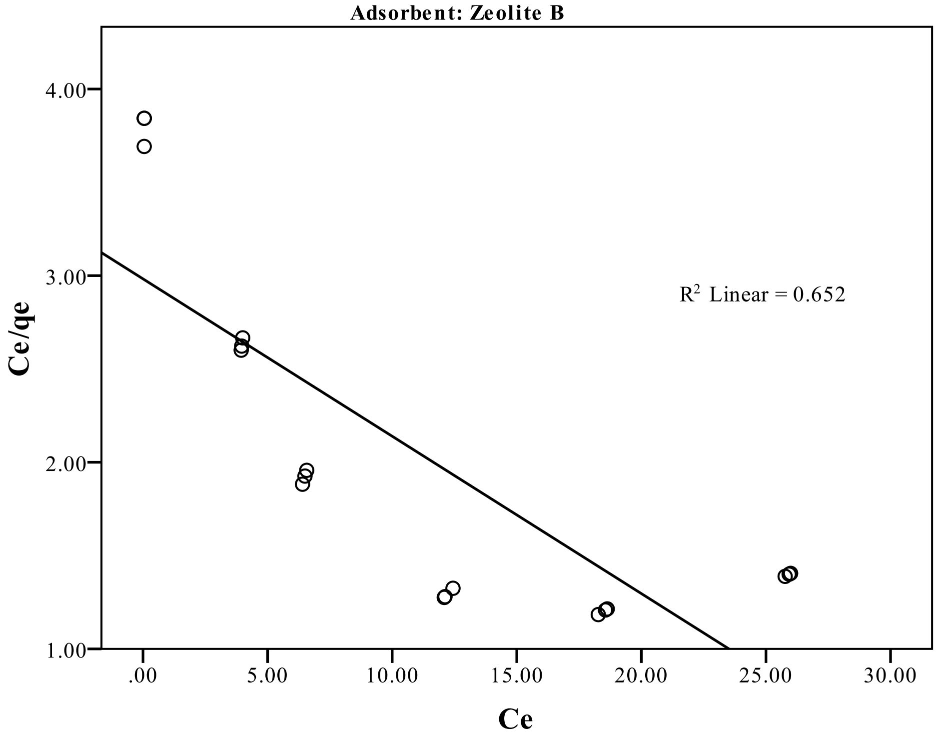
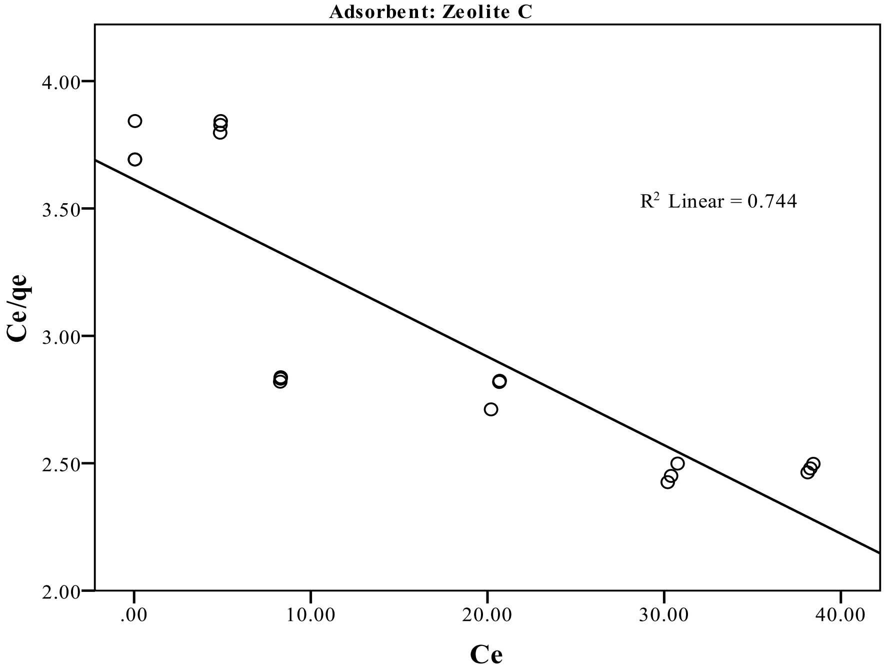
# APPENDICES

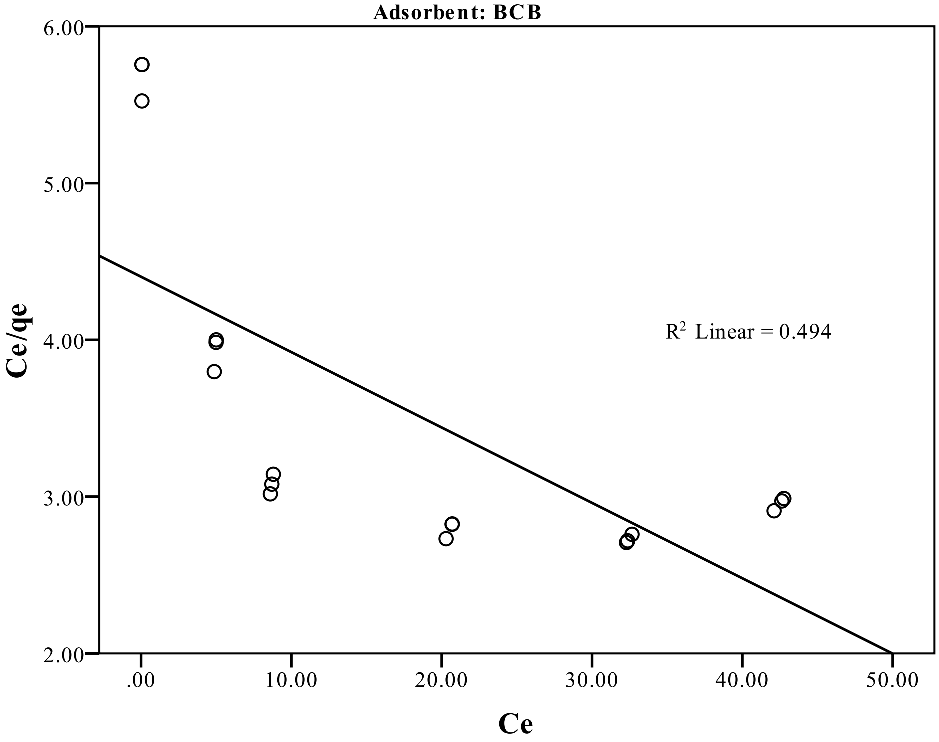
Appendix 1: Langmuir adsorption isotherm for fluoride ions by Zeolite B



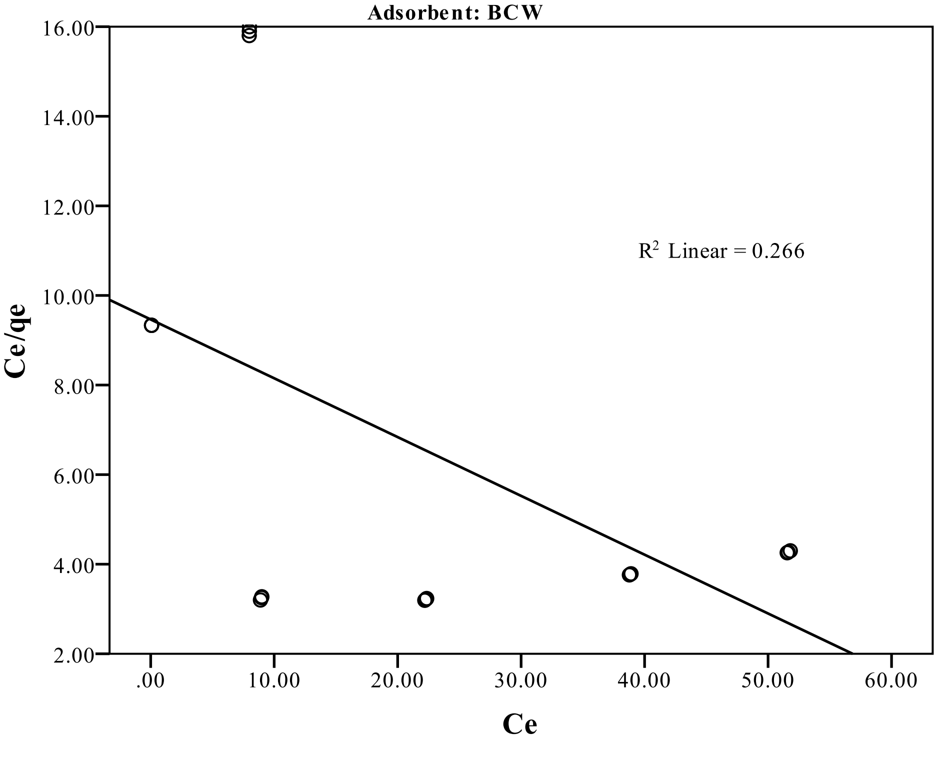
Appendix 2: Langmuir Adsorption isotherm for fluoride ions by Zeolite C



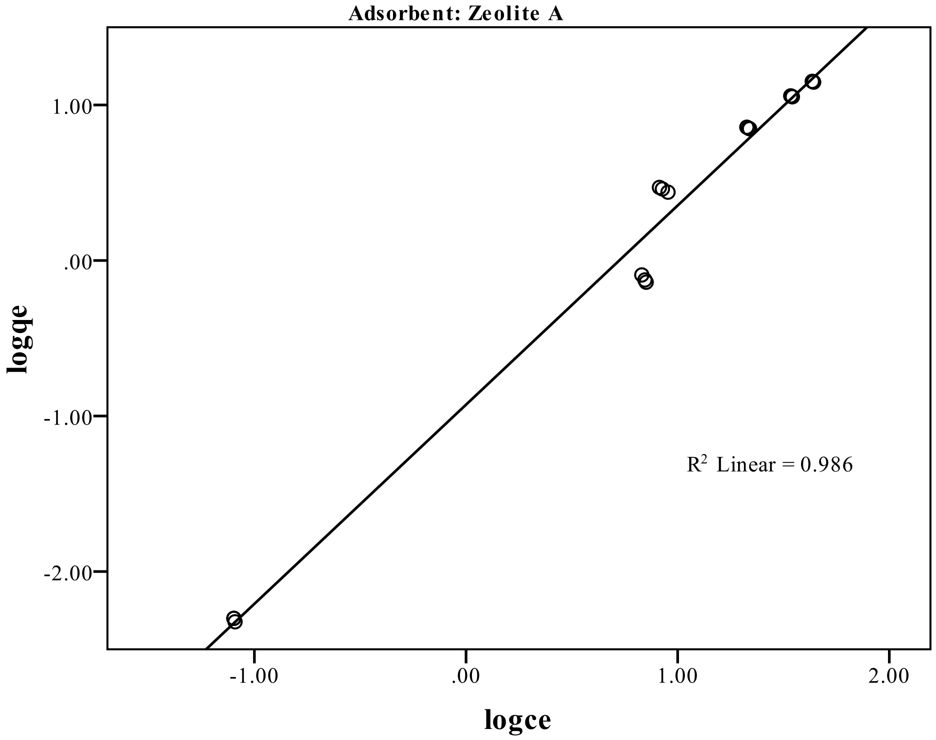
Appendix 3: Langmuir adsorption isotherm by Black Bone Charcoal



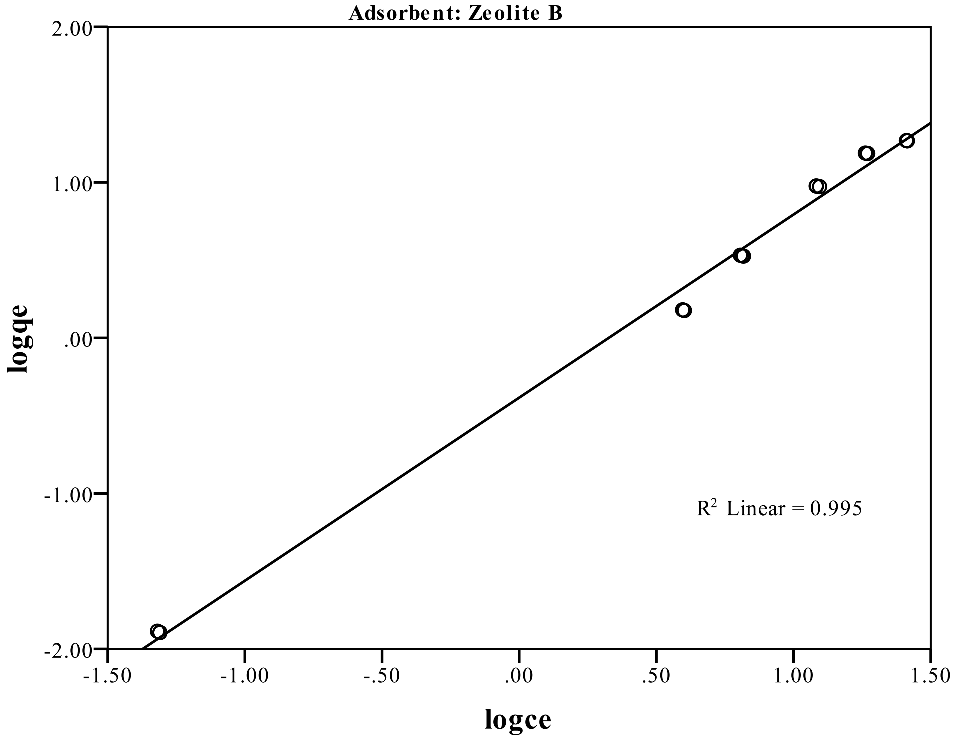
Appendix 4: Langmuir adsorption isotherm by White Bone Charcoal



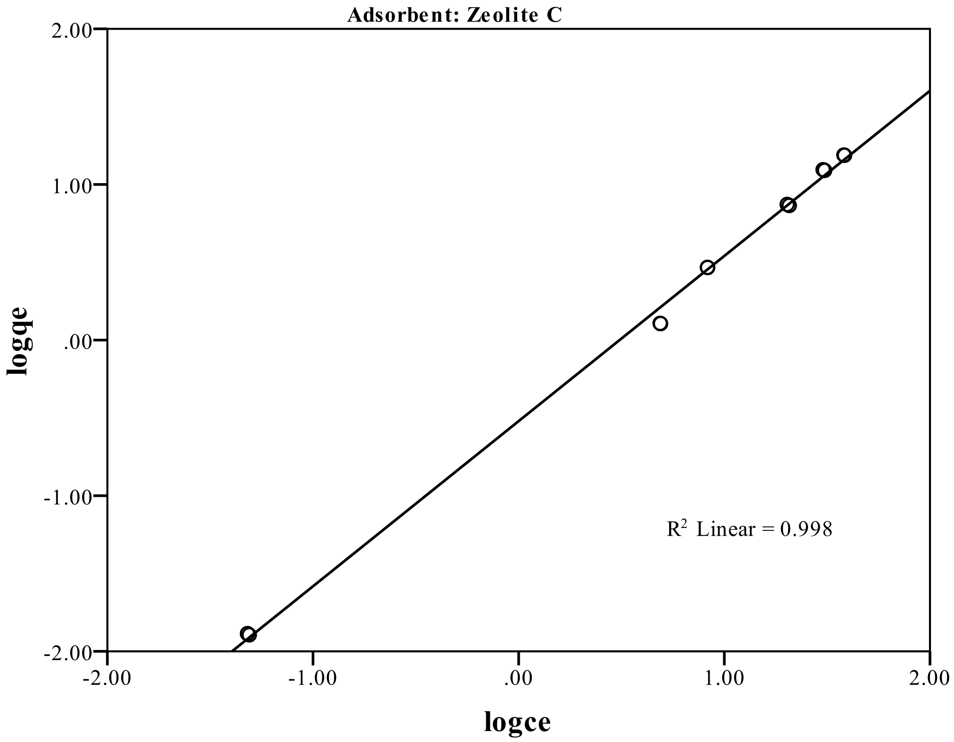
Appendix 5: Freundlich adsorption isotherm of fluoride ions by Zeolite A.



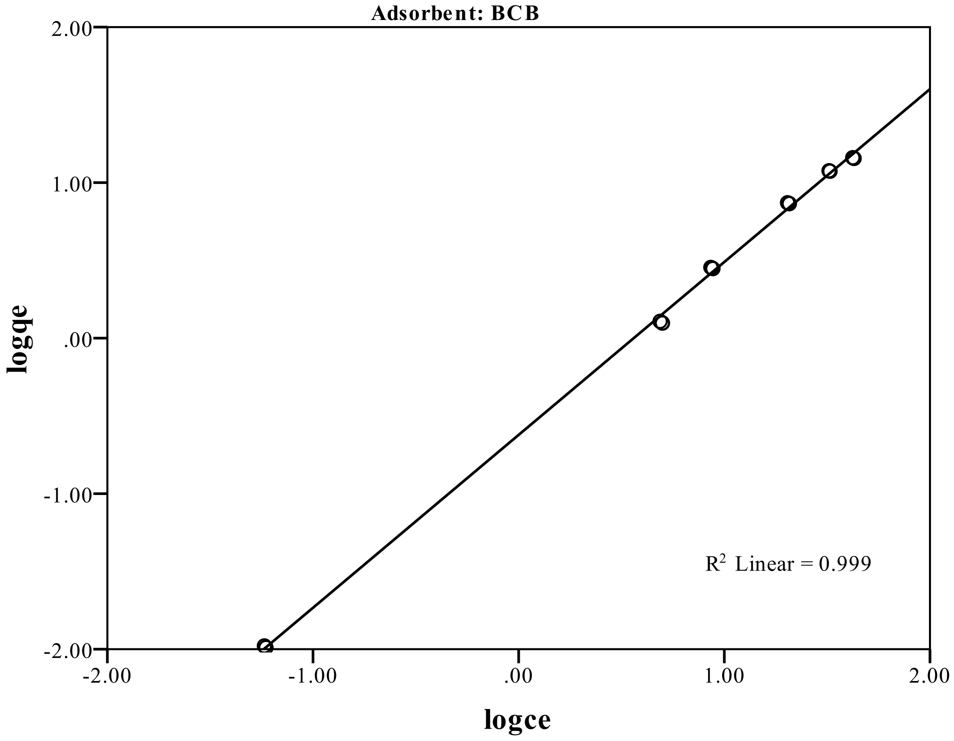
Appendix 6: Freundlich adsorption isotherm for fluoride ions by Zeolite B



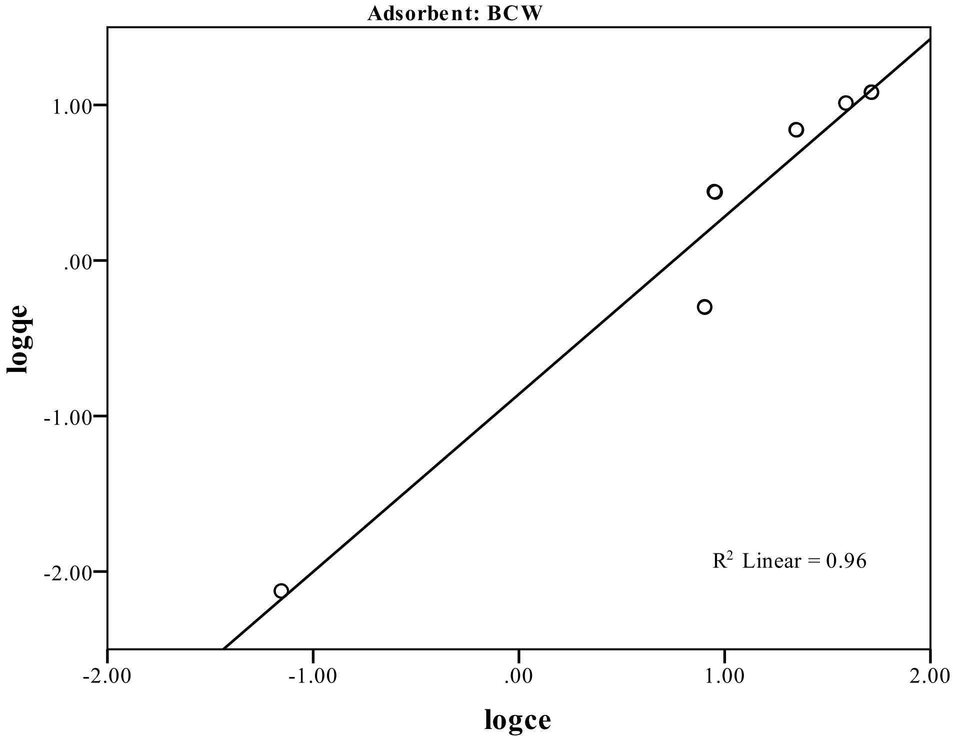
Appendix 7: Freundlich adsorption isotherm for fluoride ions by zeolite C



Appendix 8: Freundlich adsorption isotherm for fluoride ions by black bone charcoal.



Appendix 9: Freundlich adsorption isotherm for fluoride ions by white bone charcoal



Appendix 10: Effects of varying initial ion concentration on removal of fluoride ions.

| **Conc,mg/L** | **Zeolite A (Mean±SD)%** | **Zeolite B (Mean±SD)%** | **Zeolite C (Mean±SD)%** | **BCB (Mean±SD)%** | **BCW (Mean±SD)%** | **P-value** |
|---|---|---|---|---|---|---|
| 0.1 | 19.67±0.58$^{a}$ | 51.33±0.58$^{d}$ | 51.67±0.58$^{d}$ | 41.33±0.58$^{c}$ | 30.00±0.00$^{b}$ | <0.001 |
| 10.0 | 30.43±1.69$^{b}$ | 60.33±0.31$^{d}$ | 51.13±0.15$^{c}$ | 50.47±0.72$^{c}$ | 20.10±0.10$^{a}$ | <0.001 |
| 20.0 | 57.22±2.03$^{ab}$ | 67.55±0.43$^{c}$ | 58.57±0.08$^{b}$ | 56.50±0.50$^{ab}$ | 55.23±0.28$^{a}$ | <0.001 |
| 50.0 | 56.86±0.65$^{b}$ | 75.57±0.39$^{d}$ | 58.96±0.55$^{c}$ | 58.88±0.47$^{c}$ | 55.43±0.15$^{a}$ | <0.001 |
| 80.0 | 56.78±0.40$^{b}$ | 76.89±0.24$^{e}$ | 61.94±0.36$^{d}$ | 59.45±0.24$^{c}$ | 51.45±0.08$^{a}$ | <0.001 |
| 100.0 | 56.47±0.34$^{b}$ | 74.10±0.11$^{e}$ | 61.72±0.16$^{d}$ | 57.50±0.34$^{c}$ | 48.34±0.13$^{a}$ | <0.001 |

**% mean values within the same row followed by different small letter(s) do not differ significantly from one another (One-way ANOVA, SNK-test, α=0.05.**

Appendix 11: Effects of varying temperature on the percentage removal of fluoride ions.

| **Temp,K** | **Zeolite A (Mean±SD)%** | **Zeolite B (Mean±SD)%** | **Zeolite C (Mean±SD)%** | **BCB (Mean±SD)%** | **BCW (Mean±SD)%** | **P-value** |
|---|---|---|---|---|---|---|
| 298 | 60.07±0.26$^{b}$ | 80.01±0.22$^{d}$ | 69.70±0.02$^{c}$ | 59.86±0.05$^{b}$ | 56.82±0.01$^{a}$ | <0.001 |
| 308 | 48.60±0.12$^{b}$ | 70.32±0.30$^{e}$ | 58.79±0.13$^{d}$ | 49.50±0.14$^{c}$ | 46.45±0.16$^{a}$ | <0.001 |
| 318 | 41.04±0.91$^{b}$ | 61.59±0.12$^{e}$ | 47.52±0.24$^{d}$ | 42.56±0.24$^{c}$ | 39.75±0.29$^{a}$ | <0.001 |
| 328 | 30.26±0.19$^{b}$ | 51.51±0.13$^{d}$ | 35.32±0.10$^{c}$ | 30.24±0.08$^{b}$ | 24.25±0.17$^{a}$ | <0.001 |
| 338 | 29.59±0.30$^{b}$ | 51.03±0.04$^{e}$ | 35.08±0.04$^{d}$ | 30.33±0.23$^{c}$ | 24.04±0.05$^{a}$ | <0.001 |
| 348 | 29.21±0.27$^{b}$ | 50.11±0.12$^{e}$ | 34.93±0.06$^{d}$ | 30.80±0.11$^{c}$ | 23.97±0.02$^{a}$ | <0.001 |

**% mean values within the same row followed by different small letter(s) do not differ significantly from one another (One-way ANOVA, SNK-test, α=0.05)**

Appendix 12: Effects of varying the shaking speed on the percentage removal of fluoride ions

| **Shaking speed** | **Zeolite A (Mean±SD)%** | **Zeolite B (Mean±SD)%** | **Zeolite C (Mean±SD)%** | **BCB (Mean±SD)%** | **BCW (Mean±SD)%** | **P-value** |
|---|---:|---:|---:|---:|---:|---|
| 2 | 14.70±0.10$^{a}$ | 60.41±0.08$^{d}$ | 48.14±0.14$^{c}$ | 61.37±0.08$^{e}$ | 42.71±0.60$^{b}$ | <0.001 |
| 4 | 30.46±0.32$^{a}$ | 66.41±0.35$^{e}$ | 57.28±0.27$^{c}$ | 60.25±0.13$^{d}$ | 42.24±0.25$^{b}$ | <0.001 |
| 6 | 42.37±0.18$^{a}$ | 74.18±4.93$^{e}$ | 65.63±0.24$^{d}$ | 53.38±0.21$^{b}$ | 58.26±0.23$^{c}$ | <0.001 |
| 8 | 44.39±0.35$^{a}$ | 71.41±0.30$^{e}$ | 66.25±0.28$^{d}$ | 50.37±0.36$^{b}$ | 60.23±0.06$^{c}$ | <0.001 |
| 10 | 44.97±0.06$^{a}$ | 71.84±0.29$^{e}$ | 66.45±0.40$^{d}$ | 49.66±0.06$^{b}$ | 61.30±0.10$^{c}$ | <0.001 |

**% mean values within the same row followed by different small letter(s) do not differ significantly from one another (One-way ANOVA, SNK-test, α=0.05)**

Appendix 13: Effects of varying the adsorbent dosage on the percentage removal of fluoride ions

| **Adsorbent dosage** | **Zeolite A (Mean±SD)%** | **Zeolite B (Mean±SD)%** | **Zeolite C (Mean±SD)%** | **BCB (Mean±SD)%** | **BCW (Mean±SD)%** | **P-value** |
|---|---:|---:|---:|---:|---:|---|
| 0.05 | 17.34±0.26$^{a}$ | 39.23±0.41$^{e}$ | 30.18±0.04$^{d}$ | 29.18±0.15$^{c}$ | 21.22±0.57$^{b}$ | <0.001 |
| 0.10 | 38.36±0.44$^{d}$ | 50.38±0.25$^{e}$ | 37.50±0.17$^{c}$ | 34.46±0.13$^{b}$ | 31.30±0.04$^{a}$ | <0.001 |
| 0.15 | 39.33±0.41$^{b}$ | 59.32±0.25$^{e}$ | 43.46±0.13$^{d}$ | 39.84±0.15$^{c}$ | 35.33±0.08$^{a}$ | <0.001 |
| 0.20 | 49.26±0.47$^{d}$ | 61.47±0.11 $^{e}$ | 46.38±0.15$^{c}$ | 41.49±0.15$^{b}$ | 38.43±0.18$^{a}$ | <0.001 |
| 0.25 | 52.26±0.24$^{c}$ | 69.69±0.42$^{e}$ | 55.23±0.14$^{d}$ | 50.39±0.24$^{b}$ | 47.59±0.05$^{a}$ | <0.001 |
| 0.30 | 54.44±0.30$^{b}$ | 74.33±0.28$^{e}$ | 61.33±0.11$^{d}$ | 55.19±0.11$^{c}$ | 49.48±0.29$^{a}$ | <0.001 |
| 0.35 | 54.04±0.09$^{b}$ | 75.61±0.26$^{e}$ | 61.97±0.06$^{d}$ | 56.04±0.07$^{c}$ | 50.59±0.52$^{a}$ | <0.001 |
| 0.40 | 53.89±0.11$^{b}$ | 76.44±0.50$^{e}$ | 62.35±0.20$^{d}$ | 56.97±0.12$^{c}$ | 51.33±0.33$^{a}$ | <0.001 |

**% mean values within the same row followed by different small letter(s) do not differ significantly from one another (One way ANOVA, SNK-test,α=0.05)**