Removal of Fluoride from Drinking Water Using Thermally Activated Mixture of Bone and Banana Peel

by

Belayneh Kassaw Tareke

Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

Presented in Partial Fulfillment of the Requirements for the Master's Degree of Science in Industrial Chemistry

Office of Graduate Studies

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December, 2020

Adama, Ethiopia

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Approval of Board of Examiners

We, the undersigned, members of the board of examiners of the final open defense by Belayneh Kassaw Tareke have read and evaluated his thesis entitled “Removal of Fluoride from Drinking Water using Thermally Activated Mixture of Bone and Banana Peel” and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the degree of Masters of Science in chemistry.

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I hereby declare that this MSc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

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Subject: Thesis Submission

This is to certify that the thesis entitled "Removal of fluoride from drinking water using thermally activated mixture of bone and banana peel" submitted in partial fulfillment of the requirements for the Masters of Science in Chemistry, the Graduate program of the department of Chemistry, and has been carried out by Belayneh Kassaw Id. No PGR/18205/11, under our supervision. Therefore, we recommend that the student has fulfilled the requirements and hence hereby he can submit the thesis to the department.

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LIST OF ABBREVIATIONS

AA	Activated Alumina
ASTM	American Society for Testing Materials
BC	Bone Char
BC-BPC	Bone Char – Banana Peel Char
BPC	Banana Peel Phar
CDN	Catholic Diocese Nakuru
CD's	Developing Countries
DNA	Deoxyribonucleic Acid
FAP	Calcium Fluoroapatite
HAP	Calcium Hydroxyapatite
RBCs	Red Blood Cells
WHO	World Health Organization
UNICEF	United Nations International Children's Emergency Fund
NEERI	National Environmental Engineering Research Institute
US-EPA	United States Environmental Potential Agency
SPADNS	trisodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate
ANOVA	Analysis of Variance

ABSTRACT

The present investigation was dealt with fluoride removal from drinking ground water by thermally activated biosorbents prepared from bone and banana (Musa paradisiaca) peel. Double beam UV-spectrometry was used for the determination and monitoring of fluoride ion concentration. Batch experiments were conducted to establish the optimal conditions like pH, dose of the adsorbent, and contact time. To conduct the experiment, the bones and banana peel mixtures with 2:1 (100-to-50 g) bone-to-banana peel ratio was charred at six different temperatures (300 ^{o}C, 400 °C, 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C) for 1.5 h and 100 g of each adsorbent were also separately charred at 500^{o}C for the same pyrolysis time in a muffle furnace. The product obtained was then ground in a grinding machine, and sieved through a mesh size of 250 μm. The proximate analysis, point of zero charge and specific surface area of the prepared adsorbent was also determined. The adsorption efficiency of adsorbent which pyrolyzed in a mixture of 2:1 bone-banana peel at a pyrolysis temperature of 500 ^{o}C (89.2 % efficiency) was better than that of 1:1 ratio (78.4 % efficiency) of bone-banana peel char, respectively. The less fluoride uptake below 400 ^{o}C was due to incomplete conversion of organic carbons to inorganic carbons whereas, beyond 600 ^{o}C was due to the distortion (damage) of hydroxyapatite structure of the bone. The adsorption efficiency of bone-banana peel char for fluoride removal was increased with adsorbent dosage and contact time before equilibrium and it was appreciable around neutral pH. Freundlich isotherm model equation was found to fit the equilibrium data for fluoride adsorption and the linear regression analysis of kinetic data confirmed that pseudo-second order rate expression was best fitted.

Keywords: defluoridation, fluorosis, adsorption, fluoride.

CHAPTER ONE

1. INTRODUCTION

1.1 Background Information

Water is one of the basic necessities for human being; however, developing countries have a problem of accessing clean water. Water covers almost ¾ of the earth's surface. However, most of it is salinized and contains toxic substance like arsenic, leads, chromium, manganese, fluoride, and others which cause health disorder if used as drinking water (Schwarzenbach, 2010). Water bodies around the world contain fluoride concentration with more than 1.5 mg/L (WHO, 2004).

Very small quantity of fluorine is required for hardening of enamel and protection against dental caries. When the concentration of fluoride in drinking water is above 1.5 mg/L, it results in dental, skeletal, and non-skeletal fluorosis due to its strong attraction by positively charged calcium ion in teeth and bones (Mohan et al, 2007; Shahid et al, 2008). Apart from dental and skeletal fluorosis, fluoride can bind to the functional amino acid groups located around the active center of an enzyme to cause an in inhibitory effect which leads to decrease enzyme activity (Trivedi et al, 2007). The main source of fluoride in the environment is entirely geogenic in nature (Peckham et al, 2015). However, recently, literature cited that it enters through anthropogenic activities such as industrial drains (Koilraj & Kannan, 2013).

Ethiopia is one of the 23 countries in the world, where a significant number of its population suffers from the toxic effects of high level of fluoride in drinking water (Mitiku- Tadele, 2015). Concentration of fluoride greater than the WHO guideline value of 1.5 mg/L were detected in several groundwater of Ethiopia, but fluoride concentrations greater than 10 mg/L were found in waters from the rift valley (Kloos & Teklehaymanot, 1993). Analysis of the water samples taken along the roads from Addis to Hawassa and from Addis to Adama showed that the fluoride concentration ranged from 5 to 25 mg/L (Ayenew, 2008). Therefore, it is required to develop and implement appropriate water treatment technology using local resources that are accessible and technically feasible to the rural community.

There are different methods for the removal of fluoride such as chemical treatment, membrane separation, electrolytic defluoridation, electrodialysis, membrane filtration, precipitation, nano-filtration, coagulation, electrocoagulation, chemical precipitation, reverse osmosis, and ion exchange. However, these techniques have certain disadvantages

such as complicated treatment process, high cost, high energy requirement and operational cost, use of chemicals, and generation of toxic sludge or other waste products that again require disposal ((Dubey & Shiwani, 2012); Kumar et al, 2012). Adsorption processes using natural adsorbents or agricultural waste products are becoming the new alternatives for the removal of fluoride from aqueous solution as they are cheap, simple, sludge-free, re-generable, environment friendly, require small initial cost, and minimal chemical use (Saka & Sahin, 2012). Therefore, treatments capable to combine effectiveness, technical simplicity and low costs are necessary (Shannon, 2010). A good number of low cost materials have been tested such as sugarcane ash (Mondal, 2013), Tea ash (Mondal, 2012), coconut fiber dust (Bhaumik & Mondal, 2015) lemon leaf dust (Bhaumik & Mondal, 2013), egg shell dust (Bhaumik, et al., 2012) and rice husk ash (Mondal, et al., 2012).

The use of banana peel is a cost-effective adsorbent and may provide an alternative method for removal of fluoride from water (Mondal, 2017; Poudyal & Babel, 2016). Adsorbents prepared from banana peels are suitable for the removal of fluoride ions (Getachew, et al., 2015). Mitiku (2015) studied the optimization and characterization of synthesis conditions of adsorbent from bone for removal of fluoride from drinking and waste water in order to find low cost treatment material (Mitiku-Tadele, 2015). However all thus studies were used chemical activation methods for preparation of adsorbents and most of the adsorbents based technologies for fluoride removal works at acidic pH which is not possible condition for application to rural areas. No report is found in the literature regarding utilization of mixture of bone char and banana peel char for defluoridation. However, these materials are available aplenty in this region. Thus, in the present work, a study of fluoride removal efficiency and adsorption capacity of bone char and banana peel char is undertaken. Therefore, in this study the potential of using thermally activated mixtures of cattle bones and banana peel char as a low cost defluoridation adsorbent is investigated.

1.2 Statement of the Problem

Fluorosis is known to be endemic in the Ethiopian Rift Valley because People in several areas of the Ethiopian Rift Valley are consuming water with up to 33mg/l of fluoride (Ashish-Tikariha & Omprakash-Sahu, 2013). It is estimated that about 14 million people are potentially at risk of fluorosis in Ethiopia mainly in the Rift Valley area, The scarcity of surface water in the main Ethiopian Rift Valley exacerbated the vulnerability to fluorosis as the communities become highly dependent on the fluoride rich groundwater sources for drinking water supply (Johnson et al, 2011).

Mitigation of this health problem has been hampered mainly by the lack of a suitable and inexpensive removal method. Yet, fluoride removal systems in rural communities are necessary since successful implementation of such systems is still inexistent in Ethiopia (Annette-Johnson et al, 2011).

Accumulation of bone wastes causes environmental pollution that can be manifested in number of ways such as deterioration of the natural beauty of an environment, blockage of sewerage systems of cities and towns in developing countries which in turn creates foul smells and favorable habitats for mosquitoes and other vectors that could spread various diseases (Hamer, 2003). Banana peel is a major waste in many countries including Ethiopia. Very handful of researcher tried to use banana peel as an adsorbent for removal of fluoride. In fact, different separate studies indicate that bone char and chemically activated carbon from banana peel are very important for the removal of fluoride by adsorption. Especially bone char is an excellent adsorbent for removal of fluoride from drinking water. However the quality of drinking water treated by bone char is low due to the presence of some organic impurities and these organic impurities can be removed using activated carbon (Mohamed et al, 2004; National Research Council Committee, 1990).

Therefore, the aim of this research was focused on the removal of fluoride from drinking ground water using adsorbents prepared from mixtures of cattle bones and banana peel char under thermal activation to find low cost water treatment and locally abundant materials

1.3 Objectives

1.3.1 General Objective

The general objective of this study was to remove fluoride from drinking ground water samples using thermally activated mixture of bone and banana peel adsorbents.

1.3.2 Specific Objectives

- To characterize adsorbents prepared by mixing cattle bone and banana peel.
- To determine optimum activation temperature, pH, adsorbent dose, contact time and initial fluoride concentrations of selected adsorbent for efficiently remove fluoride from drinking water samples.
- To determine adsorption isotherm and adsorption kinetics for fluoride removal by selected adsorbent.

1.4 Significance of the Study

The significance of this study is comprised of both economy and environment. Since the adsorbent produced from bone and banana peel, this study is considered as one way of transforming a solid waste into useful material. Beside to this the produced adsorbent when it is used in drinking and waste water treatment, will contributed in keeping the countries ecosystem safer. Generally, this study is providing information on the application of mixture of bone-banana peel char for fluoride removal from drinking water by adsorption process. Moreover, it provides initial information for the researchers who are interested to conduct further studies on this area.

1.5 Scope and Limitation of the Study

1.5.1 Scope of the Study

This study was mainly focused on the preparation of mixture of adsorbents from cattle bone and banana peels at optimum activation temperature and activation time, and characterization of the produced adsorbents by proximate analysis, zero point charge determination, specific surface area determination, and SEM, and FTIR test. Finally, the study was being completed by performing adsorption test for fluoride removal using synthetic water and real ground water sample which were taken from Mojo and Meki to determine the efficiency of the prepared mixture of bone and banana peel char.

1.5.2 Limitation of the Study

The study was limited to the thermally activated mixture of bone and banana peel for removal of fluoride ion from ground water and aqueous solution. Lack of important materials like fluoride ion selective electrodes and automated stirrer was also another limitation.

CHAPTER TWO

2. REVIEW OF THE LITERATURE

2.1 Fluorine

Fluorine is the lightest member of the halogen group and one of the most reactive of all chemical elements. It is therefore not found as fluorine in the environment. Fluorine is also the most electronegative of all elements and therefore, has a strong tendency to acquire a negative charge to form a monovalent ion, fluoride (F^-) (Fawell et al, 2006). Water is one of the major elements essential for sustenance of all forms of life and is available in abundance in nature covering approximately three fourth of the surface of the earth. The chemical nature of water is one of the most important criteria that determines its usefulness for a specific need and as such not all the waters are fit for drinking; hence the problems of scarcity of drinking water (Rao & Nagendra, 2003). Water related problems continue to affect the human population the world over. Most of these afflictions are associated with contaminants of water, which extends from microbial to chemical and being both natural and anthropogenic with their effects ranging from crippling to death. The chemical contaminants include but not limited to mercury, arsenic, lead, cyanide, fluoride and sulphate ions (Ayoob & Gupta, 2006). Deprived sections of the society consume contaminated water and fall ill periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride is a salt of the element fluorine (Jamode et al, 2013).

Fluoride occurs in practically all natural ground waters, in concentrations varying from trace to as high as 2,800 mg/L in environments such as the Soda Lakes of the East African Rift System (Mamatha & Rao, 2010). Fluorine is a common element that does not occur in the elemental state in nature because of its high reactivity. It accounts for about 0.3 g/kg of the Earth's crust (WHO, 2004) and it is present in the soil and rock formation in the form of fluoroapatite, fluorspar, amphiboles and micas weathering rock-alkali contribute fluoride natural waters. The fluoride present in these minerals is substituted by (OH^-) ion under redox conditions resulting in the release of fluoride ions to the circulating water (Sunil-Kumar et al, 2008). Fluorine is found in the soil and the content of fluorine in the lithosphere varies between 100 and 1500 g/ton (Vivek & Karthkyan, 2011).

Fluoride is highly toxic and is considered as an accumulative toxin (Tarundeep Gill et al, 2014). Fluoride is present universally in almost every water body (higher concentrations

are found in ground water). It is also present in most of every day needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes, and so on (Dongre, et al., 2006). Geological formation is the main source of fluoride in the groundwater. The other sources of fluoride occurrence in water are industrial discharge from aluminum industries, phosphate industries, coal plants as well as due to water, food, medicament and cosmetics (Jadhav, 2014). Fluoride bearing rocks are fluorspar, cryolite, fluoroapatite and hydroxyapatite. The fluoride content in the ground water is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature, and concentration of calcium and bicarbonate ions in water (Metre et al, 2012).

2.2 Fluoride and Human Health

2.2.1 Beneficial and Harmful Effects of Fluoride

Fluoride has both beneficial and harmful effects on the human health depending upon its level. Among the beneficial effects of fluoride in human body, strengthening of bones and prevention from tooth decay are significant (Sorg, 1978). Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as fluorosis, and long-term damage to the brain, liver, thyroid and kidney (Fordyce, 2011). Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electronegativity (Larsen et al, 1994).

High fluoride levels indicator in ground water are pH beyond 7, and high sodium and bicarbonate concentrations in the water. High fluoride waters often have low calcium and magnesium concentrations as such are fairly soft (Bernard-Thole, 2013). About 95% of fluoride in the body is deposited in hard tissues and calcified structure even after other bone constituents (Ca, P, Mg, carbonates and citrate) have reached the steady state. Due to such deposition, bones deformation causes irreversible damages (Anil-Shrivastava & manoj-Sharma, 2012).

Other problems arise due to the excessive intake of fluoride are fiber degeneration, low hemoglobin levels, deformities in red blood cells (RBCs), excessive thirst, headache, skin rashes, nervousness, neurological manifestation, depression, gastro intestinal problems, urinary tract malfunctioning, nausea, tingling sensation in fingers and toes, repeated abortions, male sterility and destruction of about 60 enzymes (Anil-Shrivastava & manoj-Sharma, 2012). The structural inorganic part of bones and teeth consist mainly of apatite, a

mixture of more hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6(OH)_2$) and less fluoroapatite (FAP), ($Ca_{10}(PO_4)_6F_2$). In this structure F_2 and $(OH)_2$ are interchangeable. The parts of the apatite molecules which are FAP determine the properties of this hard tissue. At very low FAP ratios, teeth are easily soluble under acidic conditions, meaning a higher risk of dental carries. At higher FAP ratios, the solubility is reduced. However, too high a ratio causes dental fluorosis (Kaseva, 2006).

World Health Organization (WHO) recommends that the fluoride content in drinking water should be in the range of 1-1.5 mg/L. An intake of more than 6 mg/day of fluoride results in multidimensional health manifestations, the most common being dental, skeletal fluorosis (Tembhurkar & Shilpa-Dongre, 2006) and crippling (Metre et al, 2012). Fluoride is more toxic than lead and less toxic than arsenic and is an accumulative toxin. Thus the requirement of fluoride content varies among countries and depends on the geography and the age of people involved (Jadhav, 2014). Fluoride is more toxic than lead, and just like lead, even in minute doses, accumulates in and is damaging to brain/mind development of children, i.e. produces abnormal behavior in animals, reduces intelligence quotient (IQ) in humans (Metre et al, 2012), damage to liver, thyroid and kidney (Roberto Lavecchia et al, 2012). Fluoride can also damage the fetus if the mother consumes water and food, with a high concentration of fluoride during pregnancy/breast feeding, infant mortality due to calcification of blood vessels can also occur (Rao & Nagendra, 2003).

Dental fluorosis is characterized by browning and mottling of teeth caused by prolonged consumption of water with fluoride concentrations between 1.5 and 4.0 mg/L. Skeletal fluorosis also caused by Prolonged drinking of water (ground water) with concentrations of fluoride between 4.0 and 10 mg/L and when water of concentrations beyond 10.0 mg/L is taken for a long time crippling fluorosis may follows. Skeletal fluorosis is characterized by weakening of bones and malformation of the skeleton (Bernard-Thole, 2013). Symptoms of crippling fluorosis are the growing together of bone junctions causing immobility.

The science behind the beneficial and harmful effects of fluoride on the skeletal structure is based on the possible ion exchange reactions between hydroxide and fluoride ions in the calcium hydroxy-phosphate, the main skeletal structure compositional material. The replacement of hydroxide ions with fluoride ions results in a more acid resistant structure, fluoroapatite (Bernard-Thole, 2013).

$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3 F + OH^-$ ----------[Reaction 2.1]

Fluoroapatite being more resistant to acid attack compared to hydroxyapatite offers a protective layer to the tooth enamel against acids from foods. This prevents dental caries. Excessive fluoride intake however may enhance the reaction to go beyond replacement of hydroxide (Bernard-Thole, 2013).

$$Ca_5(PO_4)_3\,F + 9F^- \rightarrow Ca_5F_{10} + 3PO_4^{3-}$$ ----------[Reaction 2.2]

The resultant compound due to ion exchange between phosphate and fluoride ions, calcium deca-fluoride, is a very hard and brittle material not appropriately suited for the functions of the skeletal structure. Dental and skeletal fluorosis has however attracted greater attention as compared to the other effects of fluoride because of its obvious manifestations (Bernard-Thole, 2013). It may even interfere with carbohydrates, proteins, vitamins and mineral metabolism and to DNA creation as well if intake excessively (Metre et al, 2012). The excessive fluoride intake leads to the loss of calcium from the tooth matrix, aggravating cavity formation throughout life (Bhaumik et al, 2012).

The requirement of fluoride content in ground water changes and it depends on the geographical condition and the age of human beings (Tarundeep-Gill et al, 2014). According to current knowledge, a fluoride concentration of about 0.5 mg/L is beneficial in preventing dental caries during tooth development, while levels higher than 1.5 mg/L may result in fluorosis or other health problems. A maximum fluoride concentration of about 4 mg/L is considered adequate for the prevention of skeletal fluorosis and secondary maximum contaminant level of 2 mg/L is recommended to minimize the cosmetic risk of dental fluorosis, which can occur when fluoride is incorporated into enamel (Metre et al, 2012).

After oral uptake, water-soluble fluorides are rapidly and almost completely absorbed in the gastrointestinal tract. Absorbed fluoride is transported via the blood; with prolonged intake of fluoride from drinking-water, concentrations in the blood are the same as those in drinking water, a relationship that remains valid up to a concentration in drinking-water of 10 mg/L. Distribution of fluoride is a rapid process. It is incorporated into teeth and bones; there is virtually no storage in soft tissues. Incorporation into teeth and skeletal tissues is reversible: after cessation of exposure, mobilization from these tissues takes place. Fluoride is excreted via urine, faeces and sweat. Fluoride in inhaled particles is also absorbed, the extent of absorption depending on the size of the particles and the solubility of fluoride compounds present (WHO, 2004). For a total intake of 14 mg/day, there is a

clear excess risk of skeletal adverse effects; and there is suggestive evidence of an increased risk of effects on the skeleton at total fluoride intakes above about 6 mg/day (WHO, 2004).

2.2.2 Factors Affecting Fluorosis

The science behind the beneficial and harmful effects of fluoride on the skeletal structure is based on the possible ion exchange reactions between hydroxide and fluoride ions in the calcium hydroxyl-phosphate, the main skeletal structure compositional material. The replacement of hydroxide ions with fluoride ions results in a more acid resistant structure, fluoroapatite (Angmar Månsson & Whitford, 1990).

$$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^-$$ ----------[Reaction 2.3]

Excessive fluoride intake however may enhance the reaction to go beyond replacement of hydroxide.

$$Ca_5(PO_4)_3F + 9F^- \rightarrow Ca_5F_{10} + 3PO_4^{3-}$$ ----------[Reaction 2.4]

In the above reaction ion exchange occurs between phosphate and fluoride ions. The resultant compound, calcium decafluoride, is a very hard and brittle material not appropriately suited for the functions of the skeletal structure (Shruthi-Anil, 2018). Skeletal fluorosis includes severe pain in the backbone, severe pain in the joints, severe pain in the hip region, Stiffness of the backbone, immobile /stiff joints, and increased density of bones, besides calcification of ligaments, Construction of vertebral canal and intervertebral foramen-pressure on nerves and Paralysis (Shruthi-Anil, 2018).

Fluoride, when consumed in excess can cause several ailments besides skeletal and dental fluorosis (Rao & Negendra, 2003). Some of non-skeletal fluorosis is: neurological manifestations, muscular manifestations, allergic manifestations, gastro intestinal problems, head-ache, and loss of teeth (edentate) at an early age (Shruthi-Anil, 2018).

The World Health Organization recommends that in mitigating for fluorosis in endemic areas the approach should be hierarchical in the following order; first to identify alternative source of potable water with low fluoride content, secondly to dilute high fluoride water with low fluoride water to attain a mass balance of within 1.5 mg/L, thirdly to use high calcium, magnesium and vitamin C diets and finally, when all these may not be feasible; to remove fluoride from water to meet the required level of 1.5 mg/L (Bernard-Thole, 2013; WHO, 2004).

2.3 Available Fluoride Removal Technologies

Due to the permanent risk and the lack of known effective treatment for fluorosis, fluoride removal from contaminated drinking water is necessary, to avoid taking of excess fluoride as a preventive measure (Sahli, 2007; Fawell et al, 2006). Several defluoridation technologies have been developed in many places around the world, some of which are described as best available technologies. The current methods, however, have some limitations which generally make their use unsustainable under most given conditions, particularly in remote areas in developing countries (Feenstra et al, 2007; Fawell et al, 2006).

Membrane filtration, precipitation, nano-filtration, ion-exchange, electro coagulation, flotation, reverse osmosis and adsorption have been used for fluoride removal. Most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations (Biswas, 2007).

2.3.1 Activated Alumina (AA)

The technology which uses activated alumina as a filter media has been described by the United States Environmental Protection Agency as a best available technique for water defluoridation (Dysart, 2008). The use of the technique which started in the 1930's, remains popular and has become the method of choice for water defluoridation in industrialized countries including the USA and Australia. The technology has also gained attention in some less developed countries particularly in India where its use is propagated in villages with the support of UNICEF. The technique has a fluoride removal performance of about 85-95% (Feenstra et al, 2007; Dysart, 2008; Meenakshi & Maheshewari, 2006).

The activated alumina is aluminum oxide (Al_2O_3) grains prepared to have a large sorptive surface. The media is prepared by a controlled thermal treatment of granules of hydrated alumina to produce a highly porous media. It consists essentially of a mixture of amorphous and crystalline phases of aluminum oxide referred to as aluminum trihydrate. Alumina has a high pH point of zero charge (pH_{PZC} = 8.2) indicating it has an adsorption

affinity for many negatively charged particles including fluoride ions (Dysart, 2008; Fawell et al, 2006).

The mechanisms of fluoride removal by the activated alumina method has been described as complex, mainly involving an adsorption and an ion exchange processes where hydroxyl ions (OH^-) are exchanged for fluoride ions in solutions (Dysart, 2008; Feenstra et al, 2007).

The fluoride removal capacity of alumina is highly sensitive to pH, hence defluoridation systems based on activated alumina often need pH adjustment in their operations in order to optimize the fluoride removal (Meenakshi & Maheshewari, 2006). Generally, the optimum fluoride removal has been found to occur in the range of pH 5 to 6 (Chiou Ku, 2002). At pH above 7 the uptake of fluoride by the activated alumina media decreases. This is because the exchange reactions between surface hydroxyl groups and the adsorbing fluoride ion become less favorable, as silicates and hydroxides in solution become a stronger competitor of the fluoride ion for exchange sites on the activated alumina surface. Increasing pH also favors the electrostatic repulsion between the negatively charged alumina surface and the anionic fluoride. At pH< 5, activated alumina gets dissolved in the acidic environment leading to loss of the media and hence a decrease in the uptake of fluoride (Chiou Ku, 2002; Meenakshi & Maheshewari, 2006).

When activated alumina is used for the fluoride removal it eventually becomes exhausted and has to be regenerated. The regeneration process is carried out by exposing the media to an alkaline solution, typically caustic soda (NaOH), to strip of the fluoride and restore the removal capacity. As the fluoride removal capacity is strongly dependent on pH, an acid solution typically sulfuric acid or hydrochloric acid is subsequently used to neutralize and reactivate the media. During regeneration cycle about 5-10% of the alumina is lost, and usually results in a reduction of the capacity of the media by 30-40%. The media often has to be replaced after 3-4 regenerations (Dysart, 2008).

The activated alumina technique has been noted to have the following limitations/shortcomings:

- ✓ The technology is expensive to acquire, operate and maintain for sustainable use in developing countries (Ayamsegna, 2008). Because the process works best in a narrow pH range, chemical feed equipment, storage and handling of corrosive chemicals, and skills are required for pH adjustment if the fluoride removal process

is to be optimized. These additional requirements have been found to be problematic for rural level operations in developing countries. Moreover this also increases the operational cost of the system (Dysart, 2008);

- ✓ Less purified AA products have relatively low fluoride removal capacity (Meenakshi & Maheshewari, 2006);
- ✓ Spent regeneration solution contains high F^- concentrations (Feenstra et al, 2007) and is difficult to dispose off.

2.3.2 Bone Char (BC) Defluoridation Method

Bone char is a granular material produced by charring animal bones: the bones are heated to high temperatures (in the range of 400 to 500 °C) in an oxygen-depleted atmosphere to control the quality of the product as related to its adsorption capacity for applications such as defluoridation of water and removal of heavy metals from aqueous solutions. The quality of the bone char can be easily determined by its color (Jacobsen & Dahi, 1997). Black charcoals are usually under charred bones that still contain organic impurities which may impart undesired odor and color to treated waters. White bone chars are over charred bones that present low fluoride removal capacity. Grey-brownish bone char is the best quality chars for adsorption applications (Korir et al, 2009).

Bone charcoal has the ability to improve the color, taste, and odor of water. Most importantly, it can remove fluoride from water. The major components of bone charcoal are calcium phosphate 57-80 %, calcium carbonate 6-10 %, activated carbon 7-10 %. The fluoride removal process is mainly by the replacement of the hydroxide groups of hydroxyapatite by fluoride (Standard, 2012; Fawell et al, 2006).

$$Ca_{10}(PO_4)_6(OH)_{2\,(s)} + 2F^-(aq) \rightarrow Ca_{10}(PO_4)_6F_{2\,(S)} + 2OH^-_{(aq)} \text{ ---------- [Reaction 2.5]}$$

OH^- and PO_4^{3-} ions in BC are the only ionic species that could be exchanged by fluoride ions (Abe et al, 2004). High fluoride sorption capacity, local availability, and cheapness of animal bones are some of the advantages of using bone char. Also, no chemicals are added during the defluoridation process. Sorption on bone char, manufactured by the pyrolysis of crushed cattle bone, had been somewhat used to defluoridate drinking water since 1953. However, this process was abandoned due to cost of the adsorbent and regeneration chemicals. Furthermore, bone char has not been applied broadly due to the problems related to the bad taste of the treated water, and the availability, cost, and quality of this adsorbent material. Nowadays, bone char is being reconsidered as a potential adsorbent for

defluoridation of drinking water since bone char can be manufactured in a sufficient amount and quality (Medellin-Castillo et al, 2014).

The principal active component of bone char is $Ca_3(PO_4)_2$. Raw bone char, prepared from animal skeletons by calcination at 300-600^oC is a mixture of three macroscopically different forms i.e. black, grey, and white fragments, which exhibit considerable differences in their efficiency for defluoridation. Black bone char is best, and white bone char is ineffective for removal of fluoride (Cao, 1996). Bone Char formed at lower temperatures and containing undecomposed organic matter, which may impart an unpleasant taste to the treated water. In addition, bone char is less effective when used alone in a batch method, a technique that is more appropriate where there is no reticulated (piped) water supply (Cao, 1996).

Several studies have concluded that the fluoride adsorption properties of bone char are attributed to their content of mineral components, especially, the hydroxyapatite content (Leyva-Ramos et al, 2010). Limitations of the bone charcoal defluoridation method have been found to include the following:

- The process depends on the local availability of adequate quantities of bones as raw material for the preparation of the media (Dysart, 2008)
- If the bone charring process is not properly done the resulting filter media will have low fluoride removal capacity (Fawell et al, 2006)
- When water is treated with a poorly prepared bone charcoal media, it may taste and smell like rotten meat and may also be aesthetically not acceptable. Any occurrence of such taste and odour problems may put consumers off and could result in a total rejection of the bone charcoal treatment method (Feenstra et al, 2007).

2.3.3 Contact Precipitation

Contact precipitation is a recently reported technique in which fluoride is removed from water through the addition of calcium and phosphate compounds. The process involves the addition of calcium and phosphate compounds to the raw water prior to its flow through the fluoride saturated bone char filter (Bernard-Thole, 2013). The presence of a saturated bone charcoal medium acts as a catalyst for the precipitation of fluoride either as CaF_2, and/or fluoroapatite. It gives high efficiency (Biswas, 2007). The exact chemical process of contact precipitation are not known, but it is assumed that it is basically a combination of precipitation of fluoroapatite, $Ca_{10}(P0_4)_6F_2$, and fluorite, CaF_2. Precipitation of fluorite can

occur if there already are precipitated compounds to initiate the process e.g. bone char. Precipitation of fluoroapatite will only occur in contact with the apatite structure in the bone char and is dependent of the pore water velocity and contact time in the filter (Vivek Vardhan & Harthikyan, 2011).

Calcium and fluoride concentrations will decrease due to precipitation of both fluorite and fluoroapatite as parallel reactions. The precipitation products depend on the concentrations of phosphate and calcium. At high concentrations both fluoroapatite and fluorite will precipitate while at lower concentrations the solubility constant for fluorite will be reached and further removal of fluoride must be due to precipitation of fluoroapatite alone (Vivek-Vardhan & Harthikyan, 2011). The following reactions illustrate the removal of fluoride

$CaCl_2.2H_2O(s) \rightarrow Ca^{2+} + Cl^- + 2H_2O$ ----------[Reaction 2.6]

$NaH_2PO_4.H_2O(s) \rightarrow PO_4^{3-} + Na^+ + 2H^+ + H_2O$ ----------[Reaction 2.7]

$Ca^{2+} + 2F^- \rightarrow CaF_2(s)$ ----------[Reaction 2.8]

$10Ca^{2+} + 6PO4^{3-} + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2(s)$ ---------- [Reaction 2.9]

However, if some soluble parameters are changed by the treatment process such as total phosphorus levels may exceed limits as PO_4^{3-} increases pH. Water quality taste and smell have been sometimes reported to be poor (Bernard-Thole, 2013).

It is therefore possible that the manufacture of good quality bone char for contact precipitation is less complicated and cheaper to manufacture than bone char for adsorption (Vivek Vardhan & Harthikyan, 2011).

2.3.4 Membrane Filtration Processes: Reverse Osmosis (RO)

Reverse osmosis process is a type of membrane separation technology which has been noted to be highly effective for fluoride removal. It has a fluoride removal performance of 85-95%, and has been recommended by the US-EPA as one of the best available techniques for fluoride removal (Fawell et al, 2006).

In the reverse osmosis process, pressure is applied to force feed water through a semi-permeable membrane thereby removing dissolved solutes (including fluoride) through rejection by the membrane, based on particle size and electrical charges. The technique is a physical process and the reverse of natural osmosis as a result of pressure applied to the

concentrated side of a membrane to overcome osmotic pressure (Feenstra et al, 2007; Dysart, 2008). The reverse osmosis technique is also noted to have the following limitations:

- The process is complex for rural water supply in developing counties: it requires special equipment, a continuous supply of electricity and, skilled personnel which are mostly not available in rural areas of developing countries (Dysart, 2008).
- High capital, operation and maintenance cost (Meenakshi & Maheshawari, 2006).
- There is a significant loss of water (typically 10-35%) by the process which can have implications on groundwater resources and any water conservation measures (Meenakshi & maheshawari, 2006).
- The process also removes most ions present in the water though some are required as essential minerals for the human body (Feenstra et al, 2007).
- Disposal of concentrate with rejected contaminants (fluoride) is difficult.

2.3.5 The Nalgonda Technique

The Nalgonda technique is a defluoridation method adapted and developed by the National Environmental Engineering Research Institute (NEERI) in India, and named after the village where it was first pioneered. The technique has been described as probably the best known and most established fluoride removal method. It is the most widely used defluoridation method in India (Iyengar, 2003).

The Nalgonda method is an aluminum sulfate-based coagulation-precipitation-sedimentation-filtration process. In the Nalgonda technique, alum ($Al_2(SO_4)_3$. $18H_2O$) is added as a coagulant to the fluoride-contaminated water under efficient mixing conditions to ensure complete mixing. This induces the development of insoluble aluminum hydroxide ($Al(OH)_3$) micro-flocks which gather together into large settleable flocks. The removal of fluoride is accomplished by the adsorption of the negatively charged fluoride ions (F^-) in a solution onto the aluminum hydroxide particles by electrostatic attraction and are subsequently separated from the water by sedimentation and filtration (Dysart, 2008; Fawell et al, 2006). When alum is added to water, the resulting solution becomes acidic. Simultaneous addition of lime ($Ca(OH)_2$) is required for pH adjustment to ensure a neutral pH (Dysart, 2008; Fawell et al, 2006)

Some limitations/short comings of the Nalgonda defluoridation technique include:

- ✓ The efficiency of the technique is limited to about 70%. It is therefore not suitable in situations where the fluoride concentration in raw water is very high (Fawell et al, 2006).
- ✓ The operational costs of the Nalgonda technique are high (Meenakshi & Maheshwari, 2006).
- ✓ The process requires correct dosing of chemicals, regular attendance and close monitoring to ensure effective fluoride removal. The labor, skills and time requirements on a sustainable basis, has been noted by UNICEF to be problematic at the rural community level (Dysart, 2008; Fawell et al, 2006).
- ✓ It produces sludge which is toxic and requires to be disposed of safely.
- ✓ A large dose of aluminium sulphate may be required for the process and it may get to a point where users complain of the taste of the treated water (Fawell et al, 2006). This can result in the users either by-passing the treatment unit and using the raw water directly or returning to their traditional and contaminated water sources.
- ✓ Excess residual aluminum in treated water, which could result from the use of aluminium sulphate in the technique, can cause dangerous dementia disease as well as neurobehavioral, structural and biochemical changes (Meenakshi & Maheshwari, 2006). It can also affect respiratory, cardiovascular, endocrine and reproductive systems. Excess aluminum in drinking has also been linked to the causes of Alzheimer's disease (Sarkar, 2007).

2.4 The Adsorption Process

Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. The process of adsorption arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. These unbalanced residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface. Adsorption is essentially a surface phenomenon (Raj-Gurdeep, 2005).

2.5 Isotherm Modeling of Fluoride Adsorption

Adsorption isotherms are viable for describing the relationship between solute molecules and adsorbent surface, highlighting the distribution of solute molecules between the liquid

and solid phases when an adsorption process reaches an equilibrium state. The analysis of isotherm data by fitting different isotherm models is a significant step to determine the suitable model which can be used for design purposes. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for interpretation and prediction of the extent of adsorption, in deciding the maximum adsorption capacity of adsorbate for a given adsorbent (Sivarajasekar & Baskarl, 2014). The Freundlich and Langmuir isotherms are useful models for the description of the adsorption process by different adsorbents. The Freundlich model refers to surface heterogeneity of the adsorbent, whereas the Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface (Getachew et al, 2015).

The Freundlich isothermal model is expressed in equation (2.1)

$$q_e = Kf{C_e}^{1/n} - 2.1$$

The linearized Freundlich adsorption isotherm can be expressed as,

$$\log(q_e) = log\left(K_f\right) + \frac{1}{n}\log(C_e) - - - - - - - - - - - - - - - 2.2$$

Where:- q_e (mg/g) is the amount of fluoride ions adsorbed per unit weight of adsorbents, K_f and 1/n are the Freundlich constants. If 1/n < 1, bond energies increase with surface density, if 1/n > 1, bond energy decreases with surface density and if 1/n = 1, all surface sites are equivalent. C_e (mg/L) is the equilibrium concentration. Linear plots of log q_e vs log C_e at different adsorbent doses are applied to confirm the applicability of Freundlich models (Mittal, 2007).

The Langmuir isotherm is based on the assumption that the point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as

$$q_e = \left(\frac{q_m k_1 C_e}{1 + C_e}\right) - 2.3$$

Where; q_e is the amount adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L), q_m and k_1 are the Langmuir constants related to capacity and energy of adsorption, respectively (Mittal, 2007).

The linear form of the Langmuir isotherm can be expressed as,

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{k_1 q_m} \quad \text{---------- 2.4}$$

Where; C_e/q_e is plotted against C_e, a straight line with slope $1/q_m$ is obtained which shows that the adsorption follows the Langmuir isotherm. The Langmuir constants q_m and k_1 are calculated from the slope and intercept with Y-axis. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by

$$R_L = \frac{1}{1 + K_1 C_o} \quad \text{---------- 2.5}$$

where Co is the initial concentration of fluoride (mg/L) and k_1 is the Langmuir constant (in g/L).The value of separation factor R_L, indicates the isotherms shape and the nature of the adsorption process as unfavorable (R_L>1), linear (R_L =1), favorable (0<R_L<1) (Mittal, 2007).

The basic assumptions of Langmuir isotherm are:

1. Intermolecular forces decrease rapidly with increase of distance and consequently predict the existence of monolayer coverage of the adsorbate at the outer of the adsorbent.
2. Adsorption occurs at specific homogeneous sites within the adsorbent.
3. Once adsorbate molecule occupies active sites, no further adsorption can take place at that site.
4. All adsorption sites are identical and energetically equivalent.

2.6 Kinetic Modeling of Fluoride Adsorption

Adsorption kinetics describes the solute uptake rate (chemical reaction), which in turn governs residence time of the adsorption process (Leyva-Ramos et al, 2010). Throughout recent years, three kinetic models have been widely used in the literature for adsorption processes, namely the pseudo-first-order kinetic model (Lagergren model), pseudo-second order kinetic model (Ho and McKay model) and intra-particle diffusion model (Weber and

Morris model). Parameters of the kinetic constants are identified by linearization followed by both linear and non-linear regression analysis.

One of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase is the Lagergren's first order rate equation. When adsorption is preceded by diffusion through a boundary, the kinetics in most systems follow the pseudo-first-order rate equation. The linear form of pseudo first-order rate expression of Lagergren is given as,

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad \text{----------} \quad 2.6$$

Where, q_e and q_t are the amounts of fluoride adsorbed on adsorbent (mg/L) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo first-order kinetics. The good correlation coefficients from the plot t vs. log ($q_e - q_t$) indicate the applicability of pseudo first order model. The pseudo first-order rate constant k_1 and q_e values were determined from the slope and the intercept of corresponding plot (Rao, 2010).

The pseudo-second-order equation predicts the behavior over the whole time of adsorption, with the adsorption (chemisorption) mechanism being the rate controlling step (Baskar & Sivarajasekar, 2015), which involves valence forces through electrons sharing or exchange (between adsorbate and adsorbent). The model has the advantage that without knowing any parameters beforehand, adsorption capacity, pseudo-second-order rate constant, and initial adsorption rate can be determined from the equation. The pseudo-second order kinetic equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}(t) \quad \text{----------} \quad 2.7$$

Where, k_2 is the rate constant for the pseudo second-order kinetics. The value of correlation coefficients from the plot (t/q_t) vs t indicates the significance of pseudo second-order model and in the determination of the values q_e and k_2 from the slope and intercept of the corresponding plot (Rao, 2010).

CHAPTER THREE

3. MATERIAL AND METHOD

3.1 Equipments

Equipment required for the completion of this study was double beam SM-1600 UV-spectrometer (double beam spectrophotometer), pH meter (HANNA-Hl5521 USA), grinding materials (mortar and pestle), syringe filter paper, ceramic crucibles, plastic beakers (different size), glass rod, spatula, tongs, measuring cylinder (different size), magnetic stirrer (PMC-502, USA), oven, volumetric flask (different size), muffle-furnace (SX-2.5-12), desiccator, Electronic balance (GF-610, Japan), measuring cylinders, sieve (250μm mesh size).

3.2 Reagents

Analytical grade reagents were used in this research: sodium fluoride (99.9% Samir tech-Chem pvt ltd), sodium chloride (99.5%), sodium hydroxide (97% Sigma-Aldrich Germany), hydrochloric acid (37% Merk India), sodium-2-(para-sulfophenylazo)-1,8-dihydroxy-3,6-3,6-naphtalene-disulfonate (SPADNS) (HACH, USA) zirconyl chloride octahydrate ($ZrCl_2.8H_2O$) (Vetec, Rio de Janeiro, Brazil) and distilled water were used throughout the experiment.

3.3 Preparation of Adsorbents

3.3.1 Preparation of Bone-Banana Peel Char Adsorbent

Bone-banana char adsorbent was produced from cattle bones (from slaughter house) and banana peel (from market) which was collected from Mojo town. Firstly, the bones were degreased with boiling water in a heat resistant beaker for one hour and dry in an oven at 105^{o}C (in Adama science and technology university chemistry lab) and secondly, the collected banana peels were washed with water to remove dust and other impurities and dried in the sun. Then 2:1 ratio (100-to-50 g) of bone samples to the banana peel each was mixed together and placed in a muffle-furnace at temperatures (300, 400, 500, 600, 700, and 800 ^{o}C) for 1.5 hours optimum time (in ASTU chemical engineering lab). The charred materials were then ground in a grinding machine, and sieved through 250 μm sieve, in order to have uniform particles. The bone-banana peel char powder was kept in a closed plastic bottle before use to prevent any interaction with air. Finally, their performance towards fluoride removal and other physical properties were investigated.

3.3.2 Preparation of Bone Char

The rest bone samples in step 3.3.1 were charred with the optimum temperature of 500 ^{o}C. Then, it was ground and sieved using standard sieves having a mesh size of < 250 μm to get uniform size powder of bones. Finally, the sample was stored in a plastic bag until further use.

3.3.3 Preparation of Banana Peel Char

The rest banana peel samples in step 3.3.1 were charred at a temperature of 500 ^{o}C. Then, it was ground and sieved using standard sieves having a mesh size of < 250 μm to get uniform size powder of banana peel chars. Finally the sample was stored in a plastic bottle until further use. The fluoride removal efficiency of individually charred bone and banana peel was conducted as a preliminary test to ensure how a thermally activated mixture of bone and banana peel enhances the efficiency of fluoride removal from aqueous fluoride solution.

3.4 Characterization of Bone and Banana Peel Char

3.4.1 Proximate Analysis

Proximate analysis was carried out for the determination of moisture, volatile matter, fixed carbon, and ash content by prescribed methods in ASTU chemical engineering lab.

Moisture Content

Moisture content was determined according to ASTM, D2867-89 (ASTM-D2867-99, 1999). Each sample of adsorbent samples (2 g) was weighed and dried in an oven continuously for 4h at 120 ^{o}C and weighed. The drying sample was then constantly re-weighed at 1h interval until a constant weight (w_d) was obtained. The crucible and its content was retrieved and cooled in desiccator. The difference in mass was recorded and the moisture content (M_C) calculated from Eq. (3.1) as loss in mass on drying divided by initial weight of the sample multiplied by 100.

$$Mc = \frac{Ww - Wd}{Ww} * 100 \quad ---------- 3.1$$

Where; W_w is weight of the bone and banana peel char before drying in gram, W_d is weight of dried bone and banana peel char in gram, Mc is moisture content.

Volatile Matter Content

The percentage of volatile matter of bone and banana peel char samples was determined by the standard method of ASTM, D5832-98 (ASTM-D5832-98, 2014). 2 g of each sample was measured on the balance and placed in a crucible. And then, both the sample and the crucible were weighed (w_1). It was heated up to 950 ^{0}C for exactly 7 minutes in a furnace. After heating, the sample was removed, cooled in desiccators and then weighed (w_2). The volatile matter content was determined by the following formula:

$$\%VM = \frac{(W_1 - W_2)}{(W_1 - w_3)} * 100 \quad ---------- 3.2$$

Where, %VM = percentage of volatile matter content, W_1 = weight of sample and crucible before heating, W_2 = weight of sample and crucible after heating, W_3 = weight of empty crucible.

Ash Content

The ash content was found by method ASTM, D2866-94 (ASTM-D2866-94, 2004). Its determination was done by taking 2 g of each sample together with the crucible and weighed them on the balance (w_1) and kept for 4 h in the furnace at 550 ^{0}C. After heated, the sample was removed, cooled in desiccator and then weighed to obtain new weight (w_2). The ash content was then be determined by the following the formula:

$$\%ash = \frac{(w_2 - w_3)}{(W_1 - w_3)} * 100 \quad ----------3.3$$

Where, W_1 = Mass of crucible + sample before heating

W_2 = Mass of crucible + ash sample after heating, W_3=Mass of empty crucible

Fixed Carbon Content

Fixed carbon is a calculated value and it is obtained by subtracting the summation of percentage of moisture content, ash content, and volatile matter content from 100.

% fixed carbon = 100 – (% moisture + % ash + % volatile matter) ----------3.4

3.4.2 Zero Point Charge (pH_{zpc})

The pH, at which the sorbent surface charge density has a zero value, is referred to as the point of zero charge (pH_{pzc}). The Isoelectric point or Zero point charge (pH_{zpc}) of the selected samples was measured by using the method described by (Duran-Valle, 2012;

Vanloon & Duffy, 2003). 0.1 M of 10 mL NaCl solutions having the initial pH values ranging from 2 to 11 with 1 increment was prepared in duplicate using 0.1M HCl and 0.1M NaOH. While in on each duplicate 0.5 g of bone-banana peel char was added and mixed for a specified period of time (2 h). Then the solutions were filtered off and the adsorbent was separated. The final pH values of the ten solutions were then measured and thereby calculation of ΔpH was made by subtracting the initial pH values from final pH values. The graph was drawn by plotting the final pH values against ΔpH. From the graph plotted, the pH_{zpc} (point of zero charge) of the adsorbent was determined.

3.4.3 Specific Surface Area

Sear's method was used for the determination of the surface area (Saer, 1983). A sample containing a one gram mixture of bone and banana peel char with {2:1} ratio was acidified with 0.1M HCl to pH 3 – 3.5, the volume was made up to 100 cm^3 with deionized water after addition of 20.0 g of NaCl. The titration was carried out with standard 0.1M NaOH at room temperature to pH 4.0, and then to pH 9.0 with continuous measurements of pH by pH meter. The volume, V required to raise the pH from 4.0 to 9.0 was noted and the surface area was calculated from the following equation:

S = 32V-25---------- 3.5

Where S = Surface area of adsorbent per gram (m^2/g), V =Volume of 0.1 M NaOH required to rise the pH of the sample from 4 to 9.

3.4.4 Scanning Electron microscopy (SEM) Characterization of the Adsorbent

To study the effect of activation on porosity and observe the surface physical morphology of the activated carbon, Scanning Electron Microscopy was employed (Aji et al, 2015) (performed in ASTU Biology lab). The scanning electron micrographs enable the direct observation of the surface microstructures of the adsorbent (Ahamed et al, 2013).

3.4.5 Fourier Transforms Infrared (FTIR) Characterization of the Adsorbent

FTIR technique is an important tool for identifying types of chemical bonds (functional groups). Some of the infrared radiation is absorbed by the sample and some of it is transmitted. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in qualitative identification of every different kind of material.

Detection of the surface functional groups for the bone and banana peel char before and after the uptake of fluoride was carried out in Bahir-Dar university using Fourier Transform Infrared (FT-IR, JASCO- FT/IR 6600) technique (Smith, 2011), The scanning range was 400–4000 cm^{-1} with a resolution of 1 cm^{-1}.

3.5 Preparation of Adsorbate Solutions

Anhydrous sodium fluoride (2.210 g) was weighed and transferred into 1000 mL volumetric flask. It was dissolved in deionized water and then diluted to 1 L. The resultant solution containing 1000 mg/L of fluoride was considered as stock fluoride solution. Five standard solutions 5, 10, 15, 20 and 30 mg/L were prepared from the stock solution (1000mg/L) in the range of 5–30 mg/L by serial dilution (dilution law, $C_1V_1 = C_2V_2$) (Yadav et al, 2013). Where, C_1 and V_1 were concentration and volume of stock fluoride solution, respectively and C_2 and V_2 were concentration and volume of standard solutions that were prepared, respectively.

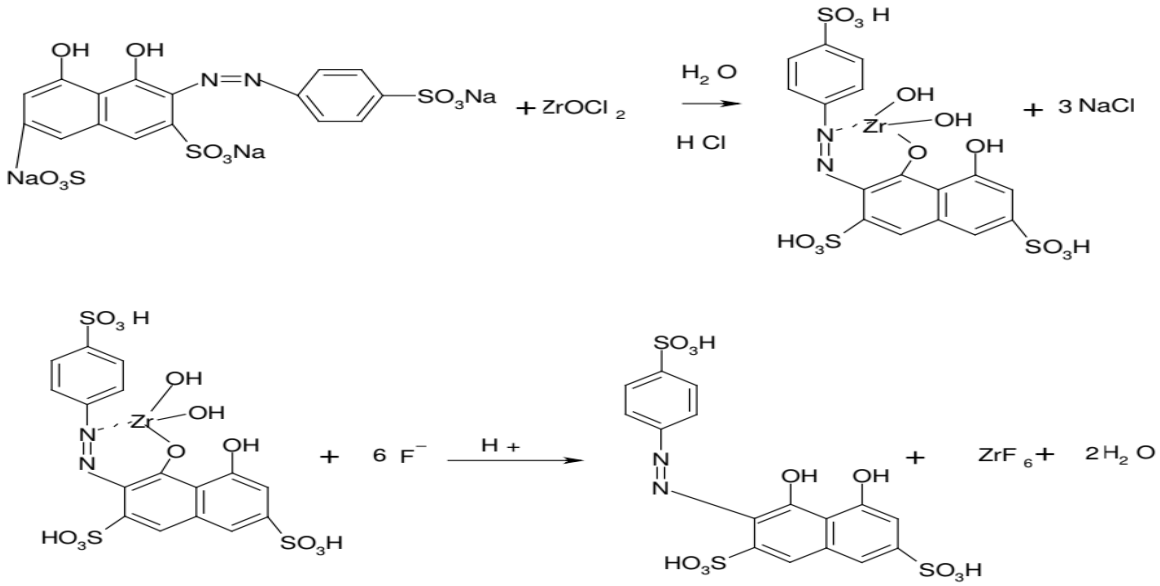
3.6 Preliminary Test

Before conducting optimization experiment, preliminary test was carried out to evaluate the adsorption performance of mixture of charred materials at the specified mass ratio of bone char (BC) and banana peel char (BPC) (3:0, 3:1, 2:1, 1:1, 1:2, 1:3, 0:3), respectively. For this purpose, 100 mL of 10 mg/L of fluoride standard solution was transferred to seven different 250 mL plastic beakers containing 4 g of BC and BPC mixture added at each ratio. Then, the samples were steered on magnetic stirrer at contact time of 1 h. Finally, residual fluoride concentration was determined.

The residual fluoride concentration was measured by taking 40 mL of sample filtrate or standards and 10 mL of trisodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6- napthalene disulfonate solution (zirconyl-SPADNS reagent) in a 100 mL plastic beaker, and the mixture was stirred uniformly using magnetic stirrer. The same amount of sample was used throughout the experiment.

The indicator solution was prepared by diluting 958 mg of SPADNS in 500 ml distilled water. 133 mg of zirconyl chloride octahydrate ($ZrCl_2.8H_2O$) is dissolved in 25 ml distilled water and 350 ml of conc.HCl is added and diluted to 500 ml with distilled water. Equal volumes of SPADNS solution and zirconyl acid solutions are mixed. SPADNS Reagent contains enough arsenite to eliminate interference up to 5 mg/L chlorine.

In the SPADNS method, zirconium reacts with SPADNS to form a red coloured complex. Fluoride bleaches the red colour of the complex due to the reaction of fluoride with a red zirconium-dye solution and hence the change in absorbance can be measured using a spectrophotometer, thus bleaching the red color in an amount proportional to the fluoride concentration (Moradi et al, 2020).



Reaction of the formation of the SPADNS-$ZrOCl_2$ complex and SPADNS - $ZrOCl_2$ complex with fluoride ions, respectively

3.7 Calibration of the UV-Vis Spectrophotometer

From the standard 40mL of fluoride solutions with different fluoride ion concentrations (0.5, 1.0, 1.5 and 2.0 mg/L) were prepared in constant intervals, 10 mL of trisodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6- napthalene disulfonate (SPADNS) was added to each solution and mixed well. The absorbance reading of each concentration was taken at 570 nm and the graph of absorbance versus concentration (mg/L) was drawn using Microsoft Excel program. Then from the graph, the slope of regression equation (R^2 = 0.998) value verified the accuracy of the measurement (Figure 3.1).

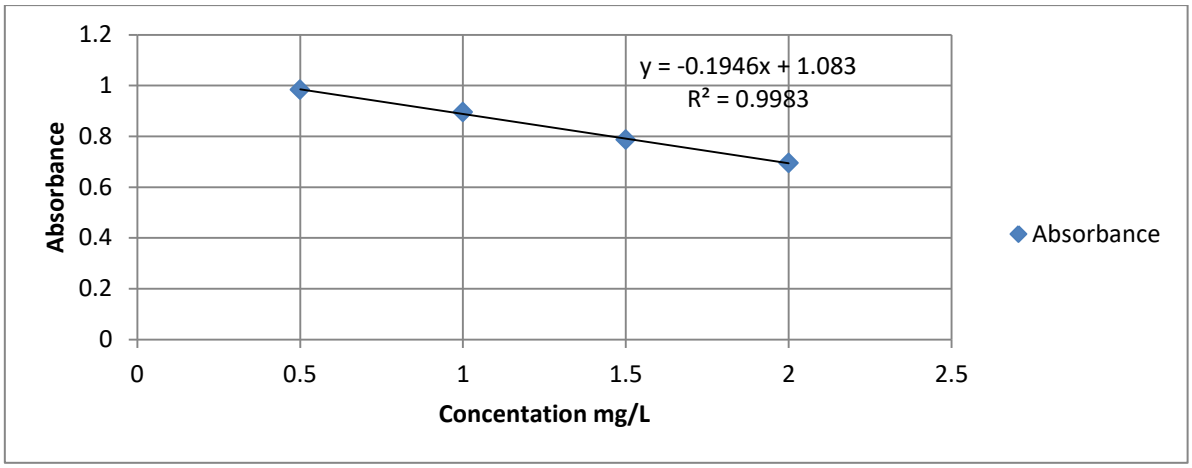


Figure 3. 1 Calibration of absorbance of UV-vis spectrophotometer at 570 nm

3.8 Adsorption Study

Adsorption experiments were conducted using 100 mL of aqueous solution containing known fluoride concentration in different plastic beakers to which a weighed fixed mass of bone-banana peel char (B-BPC) and weighed amount of fixed ratio of bone char (BC) and banana peel char (BPC) was added. This solution was then stirred continuously at room temperature to achieve equilibrium and was periodically taken out from each beaker and filtered through a filter paper before fluoride analysis. All the adsorption studies were performed in triplicate, and average values were used to plot the graphs. The adsorption efficiency (%) and the defluoridation capacity (mg F^- adsorbed/g of adsorbent) at a given contact time for the selected adsorbents were determined using the Equations (3.6) and (3.7), respectively (Solangi et al, 2009).

$$Percentage\ removal = \left(\frac{Co - C}{m}\right) 100 \quad ---------- \quad 3.6$$

$$Adsorption\ capacity(AC) = \left(\frac{Co - C}{m}\right) V \quad ---------- \quad 3.7$$

Where; AC is the amount of fluoride ion adsorbed, Co is initial concentration of fluoride (mg/l), C is the equilibrium concentration (mg/L), V is volume of solution (L) and m is mass of the adsorbent in gram.

3.9 Effect of Different Parameters

Optimization was carried out in innovative Technology Center for Sustainable Development (iTCSD) lab to make some parameters function at their best by varying one parameter while keeping other parameters constant. The effect of major parameters like adsorbent dose, contact time, pH, and initial fluoride concentration was optimized.

3.9.1 Effect of Contact Time

Residual F^- concentrations were measured for different contact times of adsorption (0.5, 1, 2, 4, 6, 8, 12 and 24 hours) with the selected adsorbent mixture in 100 mL of fluoride solution in order to investigate the effect of contact time. Other parameters, pH (6.75), dose (4 g) and concentration (10 mg/L) of the solution were remaining constant.

3.9.2 Effect of pH

To study the effect of solution pH on fluoride removal, the test solutions containing 10 mg/L of fluoride and pH of 6.75 (pH of adsorbent solution without adjustment) was adjusted to pH values of 3, 5, 7, 9, and 11 using 1M HCl and 1M NaOH. Then 4 g of the mixture of adsorbent (bone-banana peel char) was added to 100 mL of the test solutions separately and steered for constant contact time (2 h). Residual fluoride ion concentration was analyzed in each experiment after 2 h contact time. Finally pH versus percentage removal was plotted to describe the adsorption behavior of the adsorbent at each pH.

3.9.3 Effect of Adsorbent Dosage

Experimental investigations was carried out at different dosages of adsorbent 2, 4, 6, 8 and 10 grams in 100 mL of fluoride solution with 10 mg/L initial fluoride concentration at 2 h contact times.

3.9.4 Effect of Initial Fluoride Concentration

To investigate the effect of initial fluoride concentration, experiments were conducted at various initial fluoride concentrations (5, 10, 15, 20, 25 and 30 mg/L). Then 4 g of selected adsorbents were added to each solution (100 mL) keeping pH (6.75), temperature (25 ℃) and contact time (2 h) constant.

3.10 Experiments for Adsorption Isotherms

Adsorption isotherms were determined using adsorbents at room temperature. Data for plotting isotherm was obtained by mixing 100 mL a constant fluoride ion concentration of 10 mg/L with the selected adsorbent dosages of (3, 6, 9, 12 and 15 g). And it was agitated for 1 h to ensure the equilibrium, and residual fluoride was determined after filtration and adsorption isotherms were plotted.

3.11 Adsorption Kinetics for Fluoride Removal

Adsorption kinetics was determined using constant surface loading of 6, 9 and 15g to the initial fluoride concentration of 10, 20, and 30 mg/L, respectively. Residual fluoride concentrations were measured at different time intervals of 0.5, 1, 2, 4, 6, 10, 14, 16 and 24 h by taking 10 mL of samples periodically.

3.12 Statistical Analysis

Analyses were performed in triplicate and results were reported as mean ± standard deviation (SD) and graphs were drawn using Microsoft Excel program. One-way analysis of variance (ANOVA) (using SPSS software), tukey post hoc test (using SPSS software) and t-test (using Microsoft excel) were used for means comparison of fluoride removal at the 95% confidence level.

CHAPTER FOUR

4 RESULT AND DISCUSSION

4.1 Result of Preliminary Test

Preliminary tests were carried out to optimize the best ratio of the adsorbent mixtures. Seven different doses of adsorbent mixtures were taken for the test. For this test 4 grams of different ratios was taken. The adsorbent mixture was tested by 100 mL of 10 mg/L initial fluoride concentration and the results are given in table (4.1) bellow.

Table 4. 1; The different ratio of bone char (BC) and banana peel char (BPC) mixture and their percentage removal of fluoride

BC-BPC ratio respectively	Final concentration				% removal	q_e (mg/g)
	t1	t2	t3	Mean ± SD		
3 to 0	2.88	2.89	2.9	2.89 ± 0.01	71.1	0.178
3 t0 1	2.48	2.47	2.49	2.48 ± 0.01	75.2	0.188
2 to 1	1.09	1.08	1.07	1.08 ± 0.01	89.2	0.223
1 to1	2.14	2.18	2.16	2.16 ± 0.02	78.4	0.196
1 to 2	3.39	3.4	3.38	3.39 ± 0.01	66.1	0.165
1 to 3	3.9	3.88	3.9	3.89 ± 0.01	61.1	0.153
0 to 3	4.6	4.58	4.59	4.59 ± 0.01	54.2	0.135

Where, q_e is amount of fluoride adsorbed per gram of BC-BPC adsorbent and BC-BPC is bone char to banana peel char mixture, respectively.

For Bach adsorption study sample 2 to 1 ratio was selected considering the following three basic reasons.

- Percentage removal of fluoride
- Quality of treated water
- Accessibility of the raw material for preparation.

4.2 Effect of Temperature on the Removal Efficiency of Adsorbents

Based on the preliminary test sample BC-BPC (2:1) was selected for this batch adsorption study considering some reasons like its high percentage removal capacity, good fluoride removal efficiency, and relatively moderate consumption of heat energy and time compared to those prepared at higher temperature of B-BPC adsorbents.

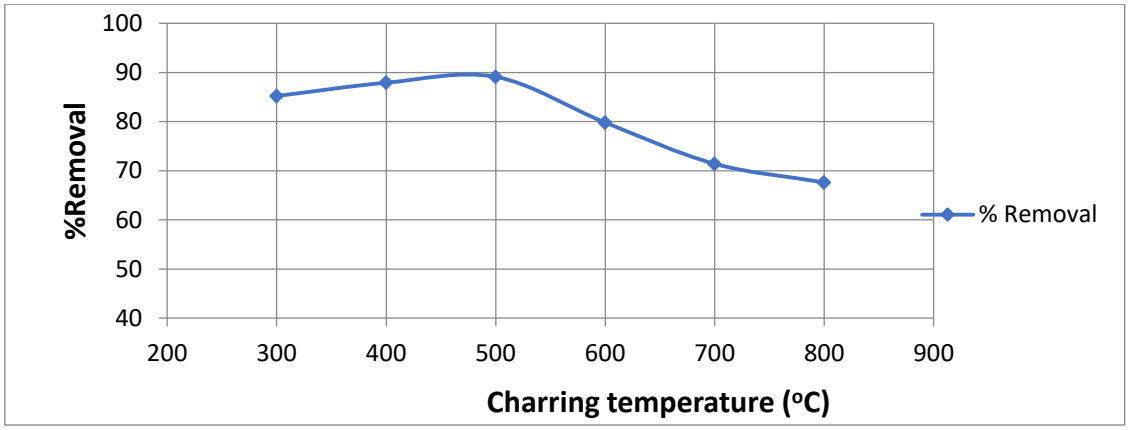


Figure 4. 1; The effect of pyrolysis temperature on the adsorption capacity of the adsorbents

The highest fluoride removal efficiency was observed in range 400 to 500℃ and for temperatures up to 400℃, the bone char might be incompletely burned, thus resulting in less fluoride uptake by the bone char material. Removal capacity at temperatures beyond 500℃ (600 – 800℃) was again reduced, which is in agreement with the hypothesis that generation of bone char material at high temperatures damages the hydroxyapatite structures (Kaseva, 2006). The graph also shows that pyrolyzing temperature strongly affects the adsorption efficiency of bone char on fluoride and also the analysis of variance (ANOVA) indicated that the charring temperatures had significant effect on the adsorption efficiency of bone-banana peel char, $F(5,12) = 7156.628$, $p = 4.12 * 10^{-20} < 0.05$, also the tukey hoc test showed that all the means were significantly different $p < 0.05$ (see appendices table 7.3A). In this study the best adsorbent was obtained at pyrolysis temperature of 500 ℃ which resulted adsorption of 89.1%, this implies that as the temperature increased from 400 ℃ to 500 ℃ the volatile components were released and more vacant spaces were produced and that enhanced the adsorption capacity of the adsorbent. But, increasing the activation temperature above 500 ℃ results in decreasing the performance of bone-banana peel char, since at high temperature the hydroxyapatite structure starts to collapse and this result in losing ions that play role in ion exchange (Liao et al, 1999).

$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O$, decomposition of HAP in bone char at high temperature (>500 ℃).

4.3 Characterization of Thermally Activated Bone-Banana Peel Char Adsorbents

4.3.1 Proximate Analysis

Table 4. 2; Proximate analysis of adsorbents prepared at a temperature of 500^{o}C

Temperature (^{o}C)	Treatments	%Moisture content (mean ± SD)	%Volatile matter content (mean ± SD)	%Ash content (mean ± SD)	%Fixed Carbon content
500	2:1	4.84 ± 0.02	3.76 ± 0.01	25.9 ± 0.01	65.50
500	1:1	3.67 ± 0.05	4.92 ± 0.03	30.25 ± 0.06	61.16

The presence of high moisture content on the adsorbent surface is known to reduce the adsorption capacity due to adsorption of water on to these groups by means of hydrogen bonding (Hassen & Ahmedin, 2007). The increase in number of oxygen-containing surface functional groups increases the polarity of carbon surfaces. Hence, the selectivity of carbon surface for water increases, and thus adsorbed water clusters may block active site of the carbon (Johnson et al, 2011). Also there was a significant difference between the two ratios, for 2:1 ratio (mean = 4.84) for 1:1 ratio (mean = 3.67); t(2) = 39.38, p = 0.00064

Volatile content in activated carbon is mainly due to the presence of non-carbonaceous matters and there was a significant difference between the two ratios, for 2:1 ratio (mean = 3.76) for 1:1 ratio (mean = 4.92); t(2) = -116, p = 0.000074. The elimination of non-carbonaceous matters is controlled by temperature. Ash is non-carbon or mineral additives that do not combine chemically with the carbon surface. The high in ash content of adsorbent have negative effect on the absorptivity of adsorbents (Duran-Valle, 2012). Also there was a significant difference between the two ratios, for 2:1 ratio (mean = 25.9) for 1:1 ratio (mean = 30.25); t(2) = -9.063, p = 0.01196.

The proximate analyses presented in Table: 4.2 showed that adsorbent prepared in 2:1 ratio is better than that of 1:1 ratio, (P(T<=t) was < 0.001) which indicated the result was significant (see appendices table 7.4). Because the sum of the factors that hindered/reduce adsorption capacity (moisture content, volatile matter content and ash content) were

relatively low whereas higher in its fixed carbon content, this in turn shows that the prepared char in 2:1 ratio can be an excellent raw material for adsorbents to be used in defluoridation of drinking water.

4.3.2 Zero Point Charge (pH_{zpc}) for Selected Adsorbent

Table 4. 3; Experimental data for determination of zero point charge

$pH_{initial}$	2	3	4	5	6	7	8	9	10	11
pH_{final}	3.5	4.21	4.86	5.76	6.73	7.46	7.98	8.82	9.43	9.81
$\Delta pH(pH_f - pH_i)$	1.5	1.21	0.86	0.76	0.73	0.46	-0.02	-0.18	-0.57	-1.19

As shown in table 4.3 and figure 4.2, prepared adsorbent has a high pH point of zero charge (pH_{PZC} ~ 8.0). This indicates that it has an adsorption affinity for many negatively charged particles including fluoride ions (Dysart, 2008). The pH values of the adsorbents generally fall in the slightly basic region and values of pH_{pzc} >7 show dominancy of basic groups over acidic groups. The presence of basic functional group such as hydroxyl on the surface of thermally activated B-BPC may cause the basic property of activated carbon. Net surface charge of the thermally activated carbon under pH_{pzc} is positive, while it is negative above pH_{pzc}. Therefore, this value helps deciding at which pH value one should work during adsorption studies.

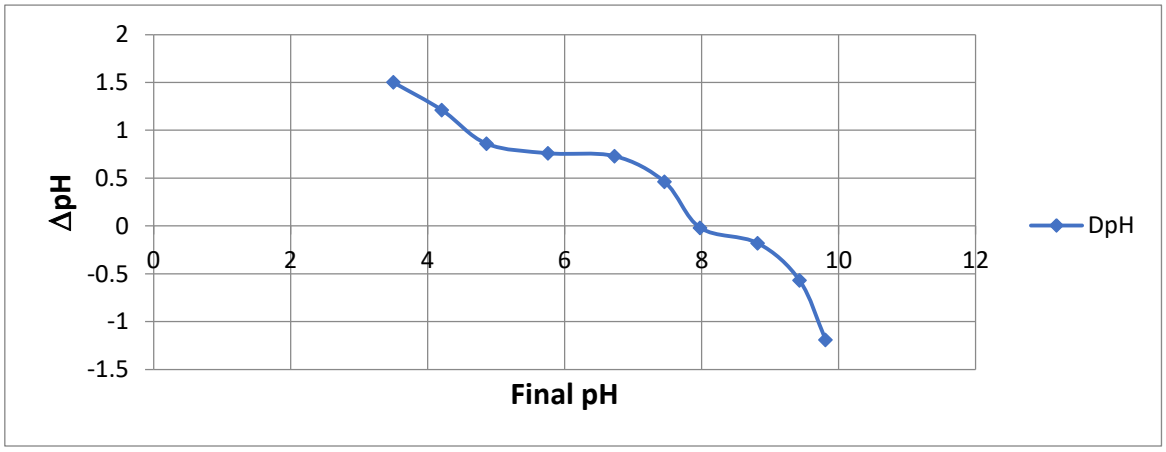


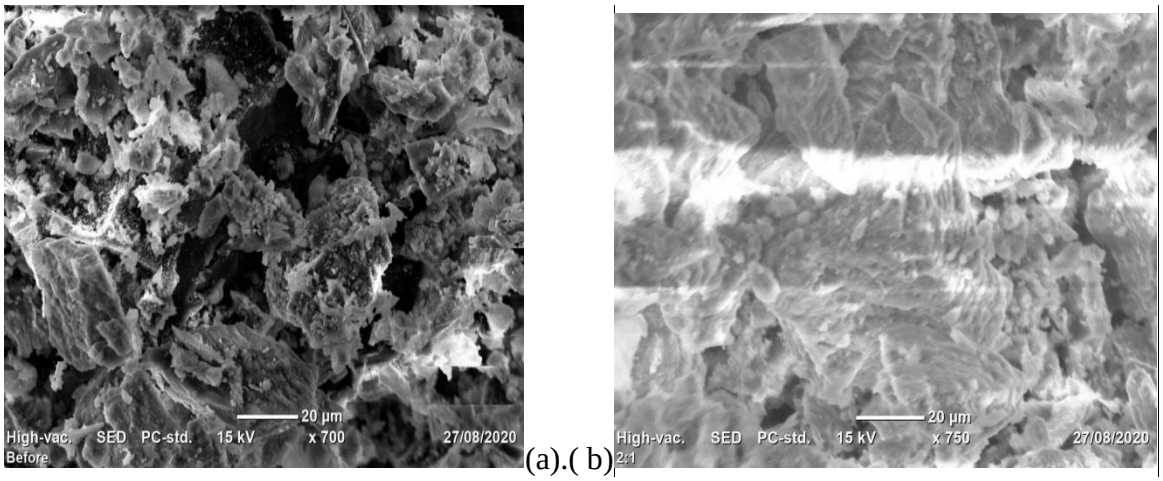
Figure 4. 2; Plot of ΔpH vs. pH final of the adsorbent to determine zero point charge

4.3.3 Specific Surface Area (S)

The specific surface area of the selected adsorbent was estimated using Equation 3.5. The volume of NaOH was measured in replicate and found to be 4.6 mL whereas the corresponding surface area was 122.2 m^2/g. this result verified that the prepared adsorbent of particle size <250 μm has large surface area which can perform better fluoride adsorption capacity.

4.3.4 Scanning Electron Microscopy (SEM) Analysis

Scanning electron micrograph has immense potentiality for understanding the surface morphology of the adsorbents. Figure 4.3 (a) and (b) represents the SEM images of the B-BPC before and after fluoride adsorption at a resolution of x700 and x750. Before adsorption, the adsorbent exhibited irregular and rough porous surface. These characteristics increase the adsorption capacity of the adsorbent and act as reactive adsorption centers for fluoride adsorption. After adsorption, the surface morphology of the adsorbent was significantly changed. B-BPC appears to have smooth surface as the pores and caves were partially covered by fluoride. This observation clearly indicates that B-BPC has great role towards the affinity of fluoride binding (Poudyal & Babel, 2016).



(a).(b)

Figure 4. 3; Scanning electron microscopy (SEM) images for bone – banana peel char mixture: (a) Before adsorption; (b) After adsorption

4.3.5 Fourier Transforms Infrared Spectroscopy (FTIR) Analysis

The spectrum of a mixture of bone char (BC) and banana peel char (BPC) was measured at 400-4000 cm^{-1}. FTIR test of the adsorbent displays a number of absorption peaks as shown in (Table 4.4). The FTIR spectrum analysis of a mixture of bone char and banana peel char displays a number of functional groups on its surface indicating the complex nature of the

adsorbent. The adsorption capacity of the adsorbent depends upon porosity as well as chemical reactivity of functional groups at the adsorbent surface (Teshome, 2015).

Bone char contains about 10% carbon (C) by weight with the remainder comprising mainly hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$) but also a significant percentage of calcium carbonate (Rao & Nagendra, 2003). In banana peel char structure, many heteroatoms (oxygen, hydrogen, nitrogen and others) exist as in the form of functional groups (Chen, et al., 2019). Oxygen is the most dominant heteroatom in the carbon matrix. Carbon–oxygen surface compounds are the most important centers having an effect on surface reactions and surface behaviors of activated carbon. Adsorption properties of activated carbon can be controlled by modification of surface groups (Teshome, 2015).

Table 4. 4; Frequencies and respective functional groups present on the surface of the adsorbent a mixture of BC and BPC.

Wave number (cm^{-1})	Bond	Functional group
3600-3000	Stretching O-H	Hydroxyl, carboxylic acid
3000-2850	Stretching C-H	Aliphatic, olefin, and aromatic hydrocarbons
1770-1650	Stretching C=O	Carbonyl
1700-1600	Stretching C=C	Olefin structures
1480-1420	Bending C-H	Aliphatic structure
1430-1360	Bending O-H and C-H	Hydroxyl, carboxylic acid, Olefins, methyl
1120-1070	Stretching C-O	Secondary Hydroxyl
1060-1000	Stretching C-O	Primary Hydroxyl
1100-950	Stretching P-O	Hydroxyl apatite
850-800	Stretching Ca-H	Calcium hydride
750-100	Stretching Ca-F	Calcium Fluoride
610-540	Stretching P-O	Phosphate group

The FT-IR spectroscopic study of the produced adsorbent is shown in Figure (4.4). The sample showed three major absorption bands at 3600-2900 cm^{-1}, 1630-1391 cm^{-1} and 1036-500 cm^{-1}. A wide band with maximum peaks can be noticed at 3450 cm^{-1}. The band at 3438 cm^{-1} represents of an O-H stretching mode of hydroxyl groups of hydroxyl apatite and adsorbed water by activated carbon, while the band at 2928 cm^{-1} is attributed to C-H interaction with the surface of the carbon. However, it must be indicated that the bands in the range of 3200-3650 cm^{-1} has also been attributed to the hydrogen-bonded -OH groups (Rao, 2010). Peaks at 598 and 680 cm^{-1} are assigned to the out of plane C-H bending

mode. Band between 620-550 cm^{-1} and another one, sharper, around 1030 and1100 cm^{-1} these two bands correspond to the PO_4^{3-} ions. A weak band at 872 cm^{-1} corresponding to aromatic rings has also been identified. A band at 1410 and 1440 cm^{-1} can be characteristic of C = C and O-H (Saer, 1983).

After adsorption, the shifting of -OH and the slight decrease in intensity indicate the involvement of -OH in the fluoride adsorption because of exchanging of some -OH with fluoride ion after adsorption.

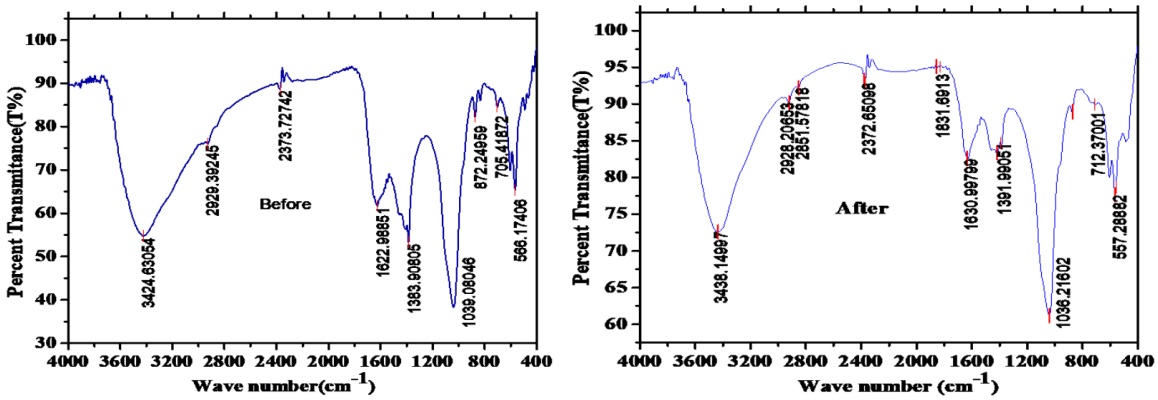


Figure 4. 4; Fourier transform infrared spectrophotometer (FTIR) spectra before and after adsorption of a mixture of bone char and banana peel char, respectively

4.4 Effect of Different Parameters on the Adsorption of Fluoride

4.4.1 Effect of Solution pH on the Adsorption

Table 4. 5; The effect of pH on percent removal of fluoride

pH	Dose	Volume (mL)	C_o(mg/L)	Final F-concentration Ct (mg/L)				% Removal	qe (mg/g)
				Ct_1	Ct_2	Ct_3	mean ± SD		
3	4	100	10	0.77	0.75	0.76	0.76 ± 0.01	92.4	0.231
5	4	100	10	0.90	0.89	0.88	0.89 ± 0.01	91.1	0.22775
6.75	4	100	10	1.08	1.07	1.09	1.08 ± 0.01	89.2	0.223
7	4	100	10	1.23	1.23	1.23	1.23 ± 0.00	87.7	0.21925
9	4	100	10	1.37	1.34	1.34	1.35 ± 0.02	86.5	0.21625
11	4	100	10	1.50	1.47	1.47	1.48 ± 0.02	85.2	0.213

Table 4.5 revealed that the maximum adsorption capacity occurred at pH = 3 so that should be the optimal pH. However, this value is in highly acidic range of pH, it is not advisable to treat drinking water. Therefore as the pH_{pzc} of the selected adsorbent are around 8.0, it is better to work at the pH of 6.75 which is the pH without adjusting and normal pH of the sodium fluoride solution. This is because at this pH, the bone-banana peel char adsorbent achieved 89.2% removal capacity gives 0.223 mg/L residual fluoride concentration for this batch experiment. The analysis of variance (ANOVA) indicated that pH had significant effect on the adsorption efficiency of bone-banana peel char, $F(5,12) = 1511.53$, $p = 2.32256*10^{-16} < 0.05$, also tukey post hoc test showed that each means are significantly different ($p< 0.05$), see appendices table 7.3B.

The adsorption capacity diminished gradually while increasing the pH from 3 to 11. This is because in acidic condition, OH^- groups in the bone char can interact with H^+ in solution to form positively charged surfaces (Jadhav, 2014), hence, the ionic interaction between the bone-banana peel char surface and the fluoride ion could be another way fluoride is adsorbed onto the bone- banana peel char in addition to substitution of the active functional groups (Hezron et al, 2014).

The effect of pH on the adsorption was due to electrostatic interactions between the F^- anions in solution and the surface charge of bone-banana peel char (Hezron et al, 2014). When the solution pH is below 7, the F^- anions were attracted to the positively charged surface of the bone-banana peel char, caused by the protonation of the hydroxyapatite hydroxyl groups, thus favoring F^- accumulation onto the surface. The surface charge of bone-banana peel char became more positively charged while decreasing the pH below 7. Hence, more F^- anions were attracted to the surface causing an increase in the adsorption capacity of the bone-banana peel char. At pH above 7, adsorption of F^- was very slight because the bone-banana peel char surface is negatively charged, due to deprotonating of the hydroxyapatite hydroxyl groups, causing a mutual repulsion between F^- anions and the bone-banana peel char surface. If adsorption occurred at all, it was not due to an electrostatic attraction but to a chemical interaction with sufficient energy to overcome the surface-fluoride repulsion forces.

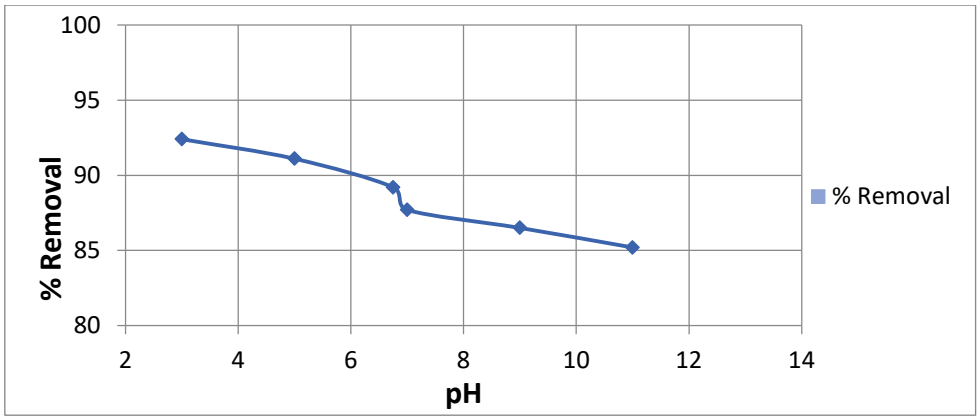


Figure 4. 5; The effect of pH on percent removal of fluoride

4.4.2 The Effect of Contact Time

Table 4. 6; The effect of contact time on percent removal of fluoride

Contact time (hr)	Dose (g)	Volume (mL)	Co (mg/L	Final fluoride concentration (mg/L)				Average % removal	qe (mg/g)
				C_t1	C_t2	C_t3	Mean ± SD		
0.5	4	100	10	1.12	1.11	1.13	1.12± 0.00	88.8	0.222
1	4	100	10	1.05	1.06	1.06	1.06 ± 0.02	89.4	0.224
2	4	100	10	0.98	0.97	0.95	0.97± 0.01	90.3	0.226
4	4	100	10	0.91	0.94	0.92	0.92 ± 0.01	90.8	0.227
6	4	100	10	0.87	0.89	0.9	0.89 ± 0.02	91.1	0.228
8	4	100	10	0.43	0.46	0.45	0.45 ± 0.02	95.5	0.239
12	4	100	10	0.45	0.45	0.44	0.45 ± 0.00	95.5	0.239
24	4	100	10	0.46	0.43	0.45	0.45 ± 0.02	95.5	0.239

Table 4.6 was shown that, as contact time increases, percentage removals also increases initially and gradually attains almost an equilibrium condition and remains more or less constant thereafter. The fluoride concentrations in the solution continued to decrease steadily from 0.5 to 24 hours due to adsorption by bone-banana peel char. The change in rate of fluoride removal is because of reason that initially all the surface was available of adsorbent and solute concentration was high. After some time, the fluoride adsorption by adsorbent reduced significantly, due to lesser surface area of adsorbent. This implies that the bone-banana peel char has specific number of active sites, which eventually are saturated after prolonged exposure to fluoride solution. Therefore contact time was found to have an effect on the amount of fluoride removed per unit weight of bone-banana peel

char and the analysis of variance (ANOVA) indicated that contact time had significant effect on the adsorption efficiency of bone-banana peel char, $F(7,16) = 1522.0$, $p = 2.26 * 10^{-21} < 0.05$. The tukey post hoc test showed that the means were significantly different ($p < 0.05$) except the mean at contact time of 8, 12 and 24 h ($p = 1.00$, which was greater than 0.05), see appendices table 7.3C.

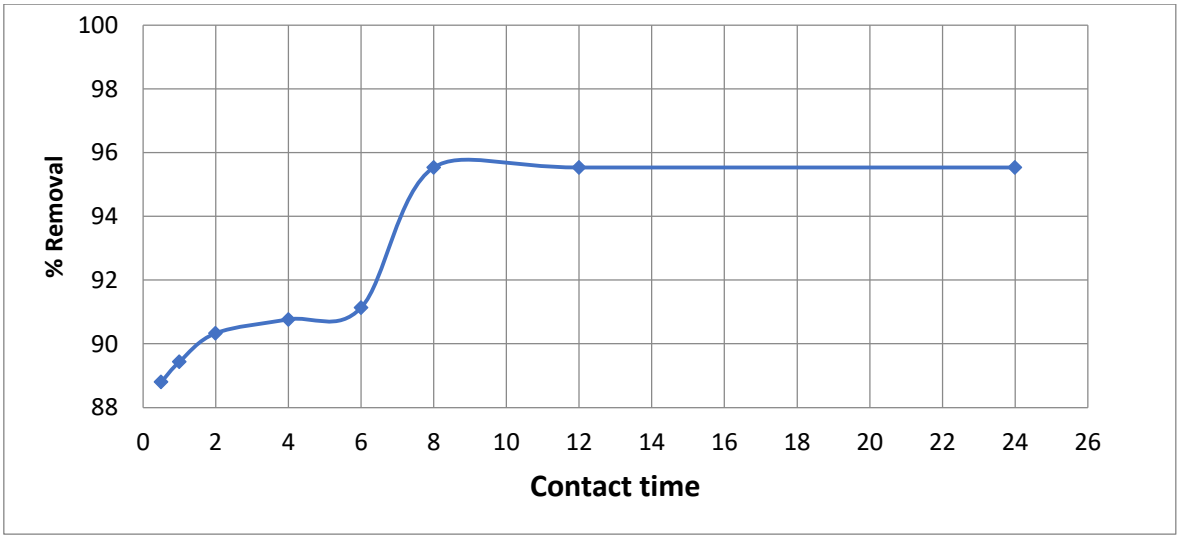


Figure 4. 6; Effect of contact time on percent removal of fluoride

4.4.3 The Effect of Adsorbent Dose

Table 4. 7; Effect of adsorbent dose on fluoride removal

Dose (g)	volume (mL)	Co (mg/L)	Final fluoride concentration (mg/L)				%removal	q_e (mg/g)
			C_1t	C_2t	C_3t	Mean ± SD		
2	100	10	2.01	1.98	1.99	1.99± 0.02	80.1	0.400
4	100	10	1.01	1.20	0.98	1.06 ± 0.10	90.2	0.223
6	100	10	0.62	0.59	0.59	0.60 ± 0.02	94.0	0.157
8	100	10	0.43	0.42	0.44	0.43± 0.01	95.7	0.119
10	100	10	0.28	0.30	0.29	0.29± 0.01	97.1	0.097

As shown in Table 4.7, the removal capacity of the adsorbent for fluoride increased with increasing the B-BPC dose. The reason is that, the increase of adsorbent dose can be attributed to increasing the number of active sites to which fluoride ions were adsorbed (Hezron et al, 2014). The gradual increase of the removal efficiency is due to possible overlapping of the active sites which makes any further increase in the dose insufficient for adsorption process. The analysis of variance (ANOVA) indicated that adsorbent dose had

significant effect on the adsorption efficiency of bone-banana peel char, $F(4,10) = 566.58$, $p = 9.78 * 10^{-12} < 0.05$. The tukey post hoc test showed that the means were significantly different ($p < 0.05$) except the mean at adsorbent dose of 8 g and 10 g ($p = 0.064$, which was greater than 0.05), see appendices table 7.3D.

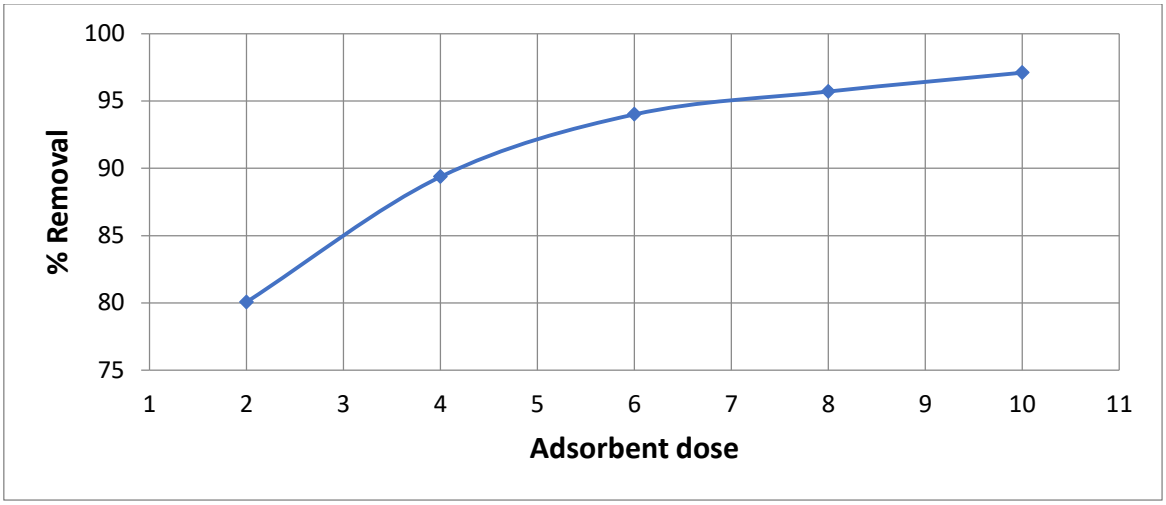


Figure 4. 7; Effect of adsorbent dose on percentage removal of fluoride

4.4.4 The Effect of Initial Fluoride Concentration

Table 4. 8; The effect of initial fluoride concentration on % fluoride removal

Co (mg/L)	Volume (mL)	Time	Dose	Final fluoride concentration (mg/L)				% removal	qe (mg/L)
				C_t1	C_t2	C_t3	Mean ± SD		
5	100	2	4	0.15	0.21	0.17	0.177±0.03	98.7	0.246
10	100	2	4	0.98	1.02	1.01	1.003±0.02	97	0.243
15	100	2	4	1.86	1.79	1.83	1.827±0.03	90.2	0.225
20	100	2	4	3.98	4.01	3.99	3.993±0.02	80.0	0.200
25	100	2	4	6.95	6.98	6.97	6.967±0.02	72.1	0.180
30	100	2	4	11.01	11.08	11.06	11.050±0.03	63.2	0.158

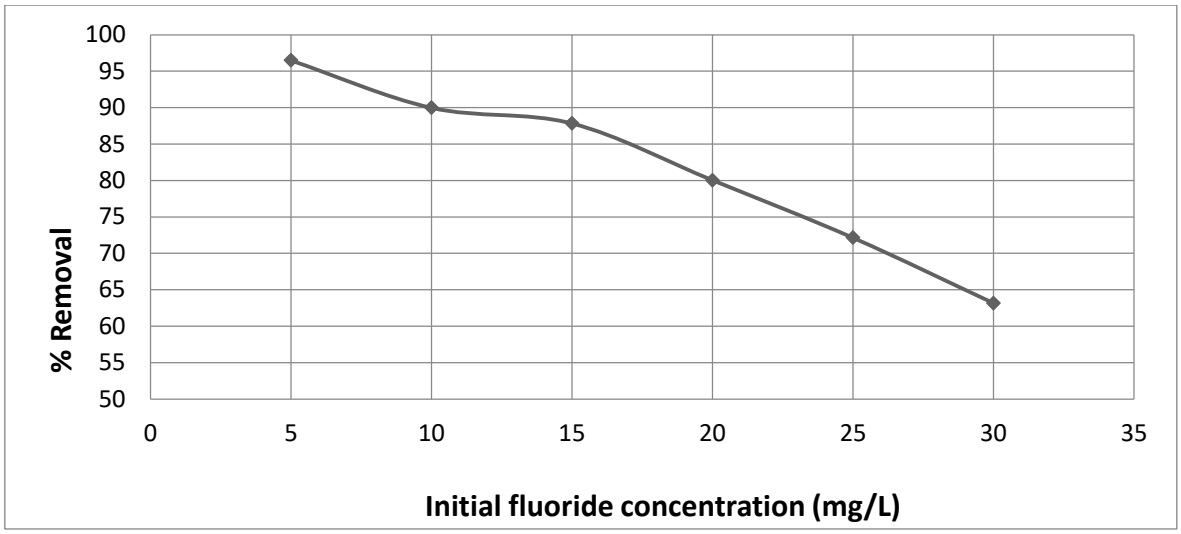


Figure 4. 8; Effect of initial fluoride concentration on percentage removal

As shown in Figure 4.8, the removal efficiency (%removal) of the adsorbent decreases with increasing initial fluoride concentration. The higher percentage removal efficiency at lower initial fluoride concentration is due to higher ratio of active surface area to total fluoride ions, which leads to the utilization of more accessible energetically active sites on the adsorbent surface. The reason for the decrease of percentage removal efficiency with the increase in initial fluoride concentration is lack of sufficient surface area to accommodate more fluoride ions available in the solution (Getachew et al, 2015). The analysis of variance (ANOVA) indicated that initial fluoride concentration had significant effect on the adsorption efficiency of bone-banana peel char, $F(5,12) = 71438.83$, $p = 2.11 * 10^{-26} < 0.05$. The tukey post hoc test showed that all the means were significantly different ($p < 0.05$), see appendices table 7.3E.

4.5 Application to Real Water Samples

Two different ground water samples were investigated to determine the amount of fluoride in the sample. Mojo water and Meki water collected from three different sites and mixed for determination of fluoride for each Meki and Mojo site. The water samples were analysed in ITCSD using double beam uv-vis spectrophotometer and found to contain 1.92 mg/L and 5.04 mg/L fluoride respectively. This concentration of fluoride ion in both water samples collected were observed to be higher than the permissible level according to WHO. Taking the water samples, adsorption capacity of thermally activated bone-banana peel char prepared at 500 ^{o}C was investigated. All test results indicated in less than 1.5 milligrams of fluoride per litter (mg F^-/L) remaining after adsorption for contact time of 8

h. These results show that thermally activated bone- banana peel char is a suitable material for the removal of fluoride ion. The result of percentage removal is given below in the Table 4.9.

The maximum fluoride required in drinking water according to World Health Organization (WHO) is 1.5 mg/L (WHO, 2004). This requirement can be achieved by bone-banana peel char since the residual fluoride concentration is below 1.5 mg/L for 1.92 mg/L and 5.04 mg/L initial F^- concentration.

The result obtained for naturally fluoridated water differs with that of synthetically fluoridated water (as shown in Table 4.9) for some points. The reason for this might be attributed to the presence of other ions competing with fluoride for the active site. The condition resulting in low fluoride removal may be the best condition for another ion removal rather than fluoride ion.

Table 4. 9; Adsorption test result for naturally fluoridated water at neutral pH

Name of sample water	Initial fluoride concentration (mg/L)	Final fluoride concentration (mg/L)	Adsorbent dose in 1L of water	Percentage % removal	Smell of treated water	Test of treated water
Mojo water	1.92	0.57	4g	70.3	Normal	Normal
Meki water	5.04	1.21	4g	75.9	Normal	Normal
Synthetic water	10	0.98	4g	90.2	normal	-------

4.6 Adsorption Isotherm Model

The analysis of isotherm data by fitting different isotherm models is a significant step to determine the suitable model which can be used for design purposes. The correlation of equilibrium data using either a theoretical or empirical equation is essential for interpretation and prediction of the extent of adsorption, in deciding the maximum adsorption capacity of adsorbate for a given adsorbent (Sivarajasekar & Baskarl, 2014). The Freundlich and Langmuir isotherms are useful models for the description of the adsorption process by different adsorbents. The Freundlich model refers to surface heterogeneity of the adsorbent, whereas the Langmuir model assumes uniform energies of

adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface (Getachew et al, 2015).

Table 4. 10; Experimental results of adsorption isotherm model

Co (mg/L)	Dose (g)	Ce (mg/L)	qe (mg/g)	logCe	logqe	Ce/qe
20	3	0.98	0.471	0.061	-0.327	2.44
20	6	0.71	0.241	-0.143	-0.618	2.99
20	9	0.53	0.163	-0.367	-0.788	2.64
20	12	0.32	0.123	-0.553	-0.910	2.28
20	16	0.25	0.099	-0.638	-1.00	2.32

4.6.1 Langmuir Isotherm

The Langmuir isotherm model estimates the maximum adsorption capacity produced from complete monolayer coverage on the adsorbent surface. The linear equation of Langmuir isotherm model can be expressed using Equation (2.4).

A plot of C_e/q_e Vs. C_e (Figure 4.9) should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then give the values of q_m = 6.2 mg/g and k_1= 0.067 L/mg.

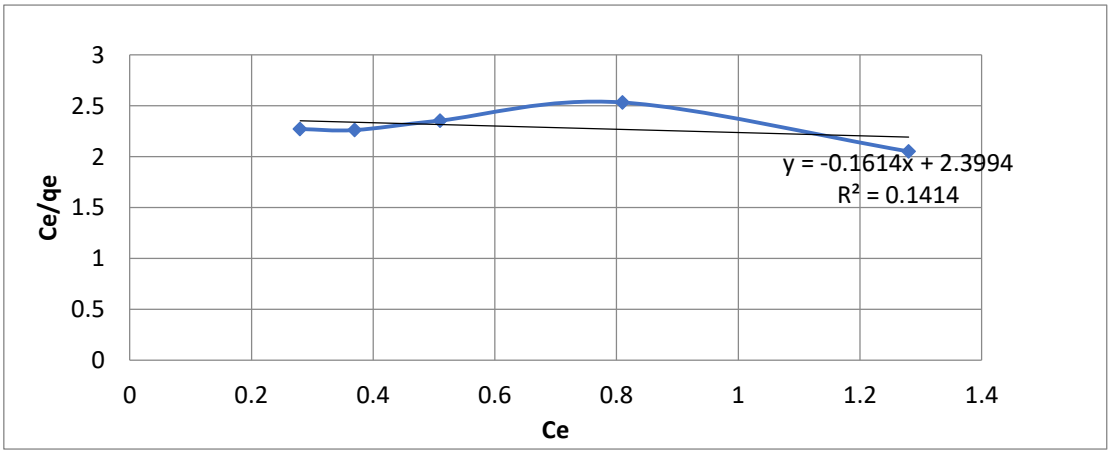


Figure 4. 9; Plot of fitting equilibrium data on Langmuir isotherm

4.6.2 Freundlich Isotherm

The Freundlich isotherm is an empirical model that is based on adsorption on heterogonous surface and the information to be obtained from this model were determined using Equation 2.2.

In this equation, K_f and n are Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. The k_f value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The Freundlich constants were determined from the slope and intercept of a plot of $\log q_e$ versus $\log C_e$ (Figure 4.10).

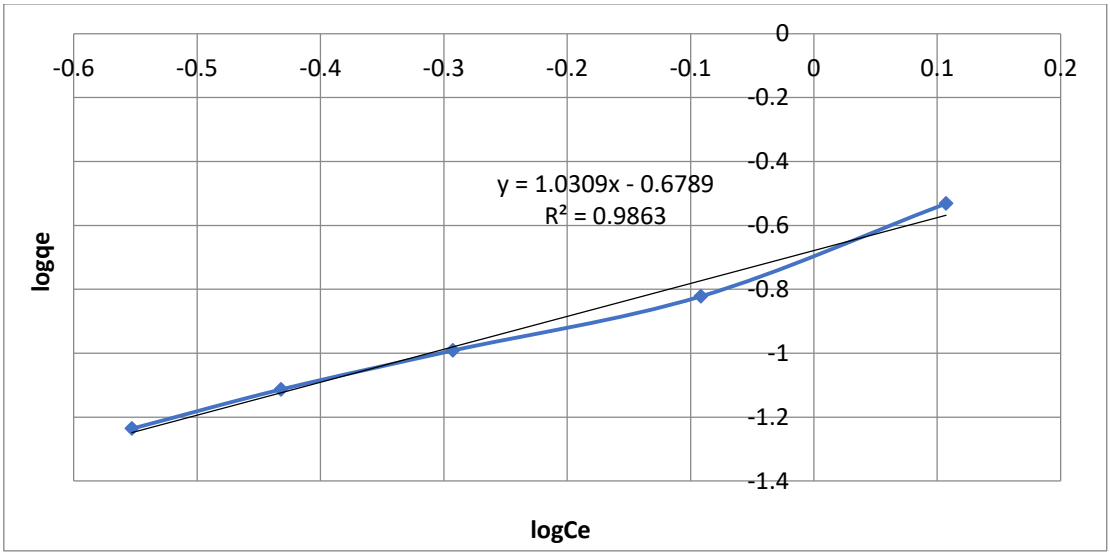


Figure 4. 10; Plot of fitting equilibrium data on Freundilich isotherm

Table 4. 11; Adsorption isotherm model parameters

Freundlich model	Langmuir model
K_f = 0.209 mg/g	q_m = 6.20 mg/g
n = 0.970	K_l = 0.067 L/mg
R^2 = 0.986	R^2 = 0.1414

The constant parameters for the Langmuir and Freundlich models are calculated and presented in Table 4.11. From the table it can be concluded that the Freundlich isotherm model best fits for the product. The R^2 value of the Langmuir model for the B-BPC is 0.1414 and R^2 value of the Freundlich model for the bone-banana peel char (B-BPC) is 0.986. It is evident from a comparison of the values of coefficient of correlation (R^2) that the equilibrium adsorption of fluoride on to bone-banana peel char follows Freundlich adsorption isotherm model which reflects adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved (Said, 2017). Based on these results, it can be concluded that fluoride is effectively adsorbed on bone-banana peel char and that the Freundlich model provides a satisfactory description of the adsorption equilibrium.

Therefore, Freundlich model is selected to be the best model for describing the adsorption of fluoride by the bone-banana peel char. The adsorption capacity (q_e) and adsorption intensity (n) for the Freundlich model at equilibrium are 0.209 mg/g and 0.970 respectively.

4.7 Adsorption Kinetics Models

Modeling adsorption with isotherms allows for a better understanding of the factors that affect equilibrium and maximum adsorption capacity for a particular system. However, equilibrium isotherms do not provide information about the time response or kinetics of the system. An understanding of adsorption kinetics is important to system design parameters such as residence time, which dictate the physical size and flow rates for many unit operations. The kinetics of physical and chemical reactions can be described by a series of models including: Pseudo-first order and Pseudo-second-order models. The different parameters of pseudo first order kinetics and pseudo second order kinetics are given in Table 4.12 and 4.13 , from the table comparing the correlation coefficients of pseudo first and pseudo second order kinetics the best kinetics that fits the experimental data is preferably selected.

4.7.1 Pseudo First Order Kinetics Model

Lagergren was first to develop and publish a rate equation to describe the Kinetics of adsorption from a liquid phase onto a solid adsorbent (Lagergren, 1898). Lagergren's first-order rate equation, presented below, is most commonly referred to as a Pseudo-first-order rate equation. The term pseudo is applied to differentiate rate equations using adsorption capacities, q_e, from other first-order equations using liquid phase concentrations. The commonly used linear form of the pseudo first order kinetics is mentioned in unit two, Equation 2.6.

The pseudo first-order rate reaction has been used to study the adsorption of fluoride onto activated banana peel (Lee et al, 2011) and bone char (Murthy et al, 2010). The values of log (qe – qt) were linearly correlated with time. The plot of log ($q_e - q_t$) versus time should give a linear relationship from which k_1 and q_e can be determined from the slop and intercept of the plot, respectively.

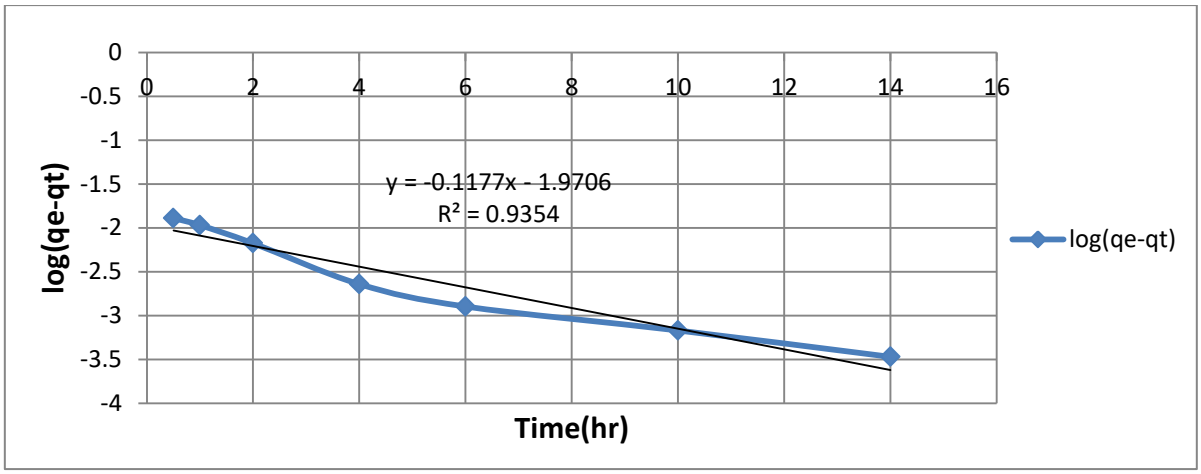


Figure 4. 11; Pseudo first order kinetics curve for 10 mg/L

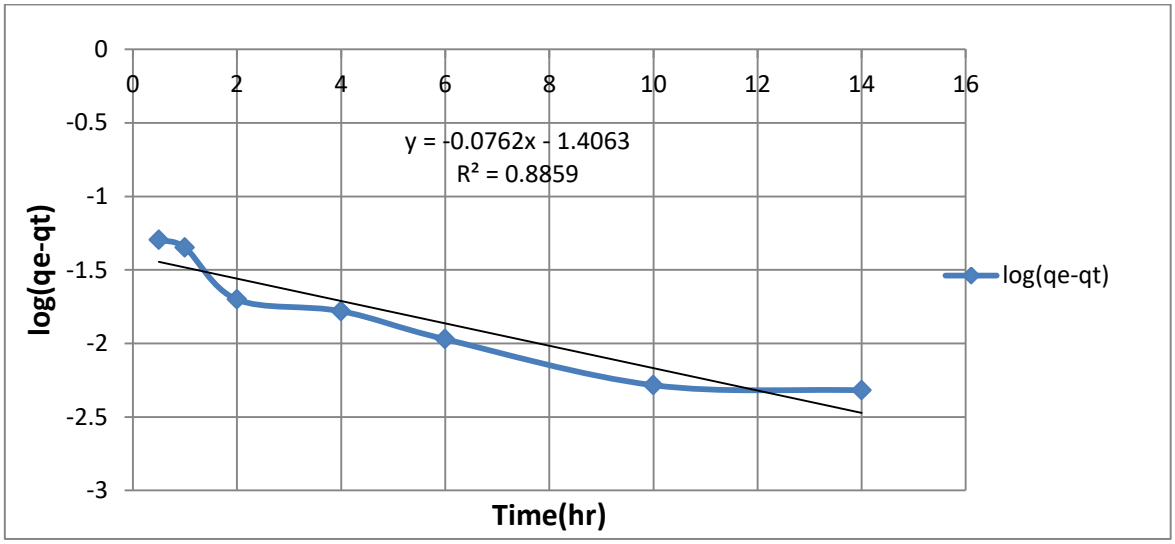


Figure 4. 12; Pseudo first order kinetics curve for 30 mg/L

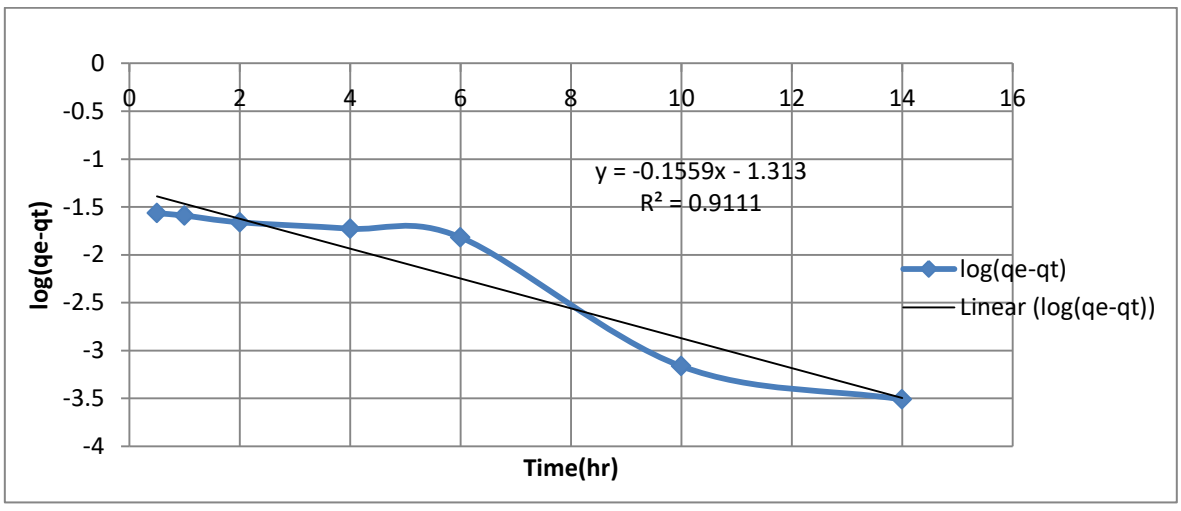


Figure 4. 13; Pseudo first order kinetics curve for 30 mg/L

Table 4. 12; The pseudo first order kinetic data

time (min)	Initial fluoride concentrations					
	10 mg/L		20 mg/L		30 mg/L	
	qt (mg/g)	log(qe-qt)	qt (mg/g)	log(qe-qt)	qt (mg/g)	log(qt-qe)
30	0.1467	-1.8879	0.1660	-1.2964	0.1632	-1.5660
60	0.1489	-1.9688	0.1717	-1.3485	0.1646	-1.5901
120	0.15296	-2.1750	0.1966	-1.7018	0.1685	-1.6604
240	0.1574	-2.6413	0.1999	-1.7810	0.1716	-1.7272
360	0.1584	-2.8965	0.20583	-1.9715	0.1751	-1.8178
600	0.1590	-3.1695	0.2113	-2.2843	0.1896	-3.1642
840	0.1593	-3.4706	0.2117	-2.3191	0.1900	-3.5109
960	0.1596	-	0.2165	-	0.1903	-
1440	0.1596	-	0.2165	-	0.1903	-
Pseudo first order adsorption kinetics parameters						
Intercept(logqe)	-1.9706		-1.4063		-1.313	
k_1	0.271		0.176		0.359	
R^2	0.9354		0.8859		0.9111	

4.7.2 Pseudo Second Order Kinetics

The term ‘pseudo’ is applied to indicate the use of adsorption capacity as opposed to concentration in the second-order rate equation. The linearized form of the pseudo second-order rate equation is expressed in unit two as Equation 2.7.

The plot of (t/q_t) and t of this equation should give a linear relationship from which k_2 and q_e can be determined from the slope and intercept of the plot, respectively. Similar to the pseudo first order kinetics, here also the experimental data are plotted in a graph as shown below, then from the given curves the parameters for pseudo second order kinetic model were calculated and put in a Table 4.13.

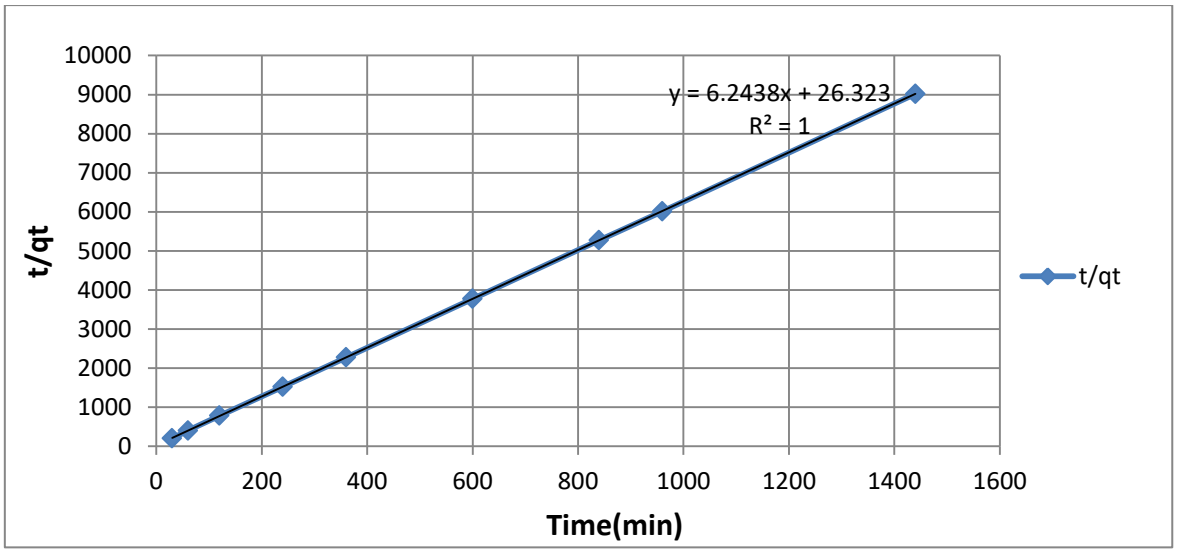


Figure 4. 14; Pseudo second order kinetics curve for 10 mg/L

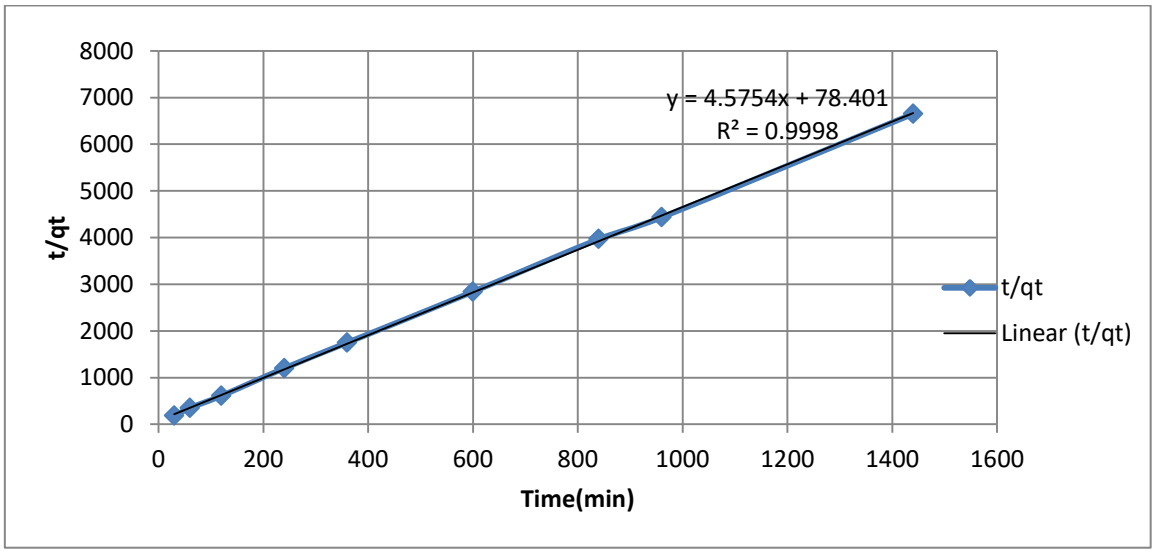


Figure 4. 15; Pseudo second order kinetics curve for 30 mg/L

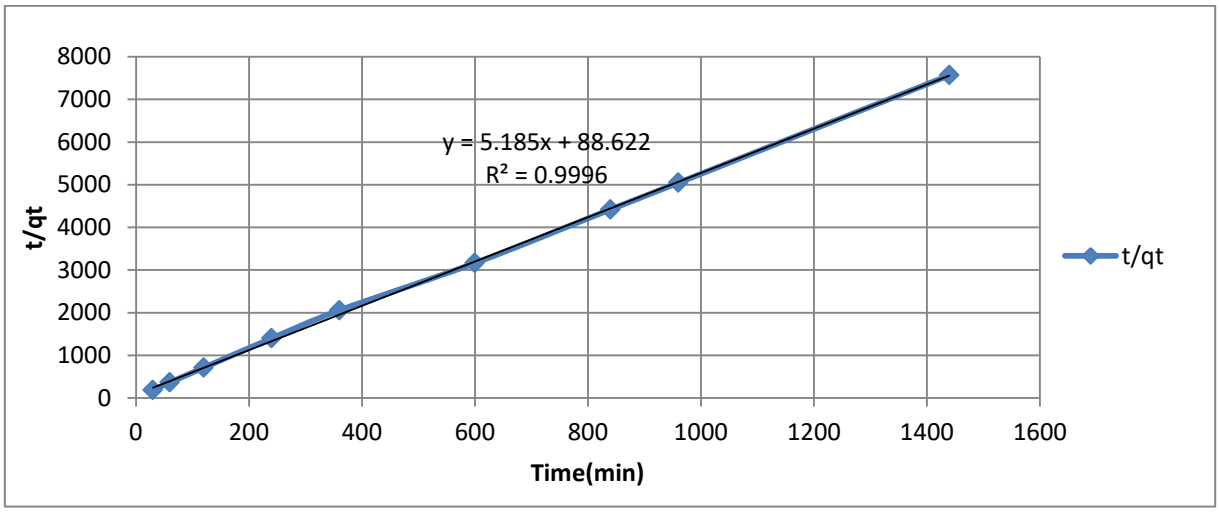


Figure 4. 16; Pseudo second order kinetics curve for 30 mg/L

Table 4. 13; The pseudo second order kinetic data

time (min)	Initial fluoride concentrations					
	10 mg/L		20 mg/L		30 mg/L	
	qt (mg/g)	t/qt	qt (mg/g)	t/qt	qt (mg/g)	t/qt
30	0.1467	204.498	0.1659	180.743	0.1632	183.854
60	0.1489	402.955	0.1716	349.465	0.1646	364.419
120	0.1529	784.513	0.1966	610.244	0.1685	712.241
240	0.1574	1525.161	0.1999	1200.274	0.1716	1398.603
360	0.1584	2273.077	0.2058	1748.971	0.1751	2055.634
600	0.1589	3774.348	0.2113	2839.341	0.1896	3163.656
840	0.1593	5272.862	0.2117	3967.573	0.1900	4420.335
960	0.1596	6013.355	0.2165	4433.924	0.1903	5043.629
1440	0.1596	9020.032	0.2165	6650.886	0.1903	7565.443
Pseudo second order adsorption kinetics parameters						
Intercept($1/K_2qe^2$)		26.323		78.401		88.622
K_2		1.48		0.267		0.303
R^2		1		0.9998		0.9996

The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t versus t. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.999$). So, it was inferred that the adsorption of fluoride onto thermally activated bone-banana peel char followed pseudo-second-order kinetics.

The correlation coefficient for pseudo second order kinetics is compared with correlation coefficient of pseudo first order kinetics and the best model that fits the experimental data is selected. The correlation coefficient (R^2) is found to be 1, 0.9998 and 0.9996 for the concentration of 10 mg/L, 20 mg/L and 30 mg/L respectively.

From the given graphs shown above and the parameters in Table 4.12 and Table 4.13, the best kinetic model that fits to the adsorption process is obtained to be pseudo second order kinetics model since the value of R^2 is very closer to unity and the adequate linear fitting of the plots. Therefore, this model is selected to be the best model for the adsorbent used and similar results have been reported by other researchers (Mitiku-Tadele, 2015; Said, 2017).

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the results of this work, it is concluded that thermally activated mixture of bone char and banana peel char are used for fluoride removal from water. The pyrolysis temperature has major effect in the removal efficiency of thermally activated mixture of bone char and banana peel char. As the temperature increased from 400 to 500 ℃ the percentage removal also increased. Beyond temperature of 500℃, percentage removal decreased. Since the organic components of bone and banana peel add color and taste to drinking water it is better to heat until all organic components converted into inorganic matter. Hence it is better to use 500 ℃ in order to avoid color and taste effect with 89% removal of fluoride.

Based on the results of this work, it is concluded that fluoride removal efficiency of bone and banana peel can be improved by thermal activation of the two mixtures. The char prepared by mixing bone and banana peel showed best defluoridation capacity than individual.

The experimental parameters such as pH, initial concentration, adsorbent dose and contact time were investigated for their potential impact on up taking capacity for fluoride. The results indicated that increase in adsorption with increase in initial concentration, adsorbent dose and contact time. pH has indicated better adsorption efficiency at 3 but for this study around normal pH value (6.75) of fluoride solution was considered.

Furthermore, when considering the adsorption isotherm, thermally activated mixture of bone char and banana peel char was found to be best fitted with the Freundlich isotherm better than the Langmuir isotherm.

The adsorption kinetics was also determined and the kinetic results obtained from this study fitted well with the pseudo second order kinetic model.

Generally thermally activated mixtures of bone and banana peel char can be effectively remove fluoride with appropriate selection of adsorption parameters and charring conditions.

5.2 Recommendation

The future efforts in this field should include the investigation of the Regeneration process to either reuse the sample or safely disposal in economic and environmental safe manner. Natural water may contain many anions that compete with fluoride for adsorption such as HCO_3^{-}, SO_4^{2-}, and Cl^{-} (Hanumantharao, et al., 2011). Therefore the effect of other ions should be investigated so that it helps to selectively use the sorbent in preference to other ions. The design of appropriate and automated equipment is required for future studies. To increase the adsorptive efficiency of the adsorbent produced it is recommended to carry out experiments with different experimental parameters. Some of the most critical parameters are the heating rate, inlet nitrogen pressure and holding time. The future efforts in this field should include the investigation of the effect of activating agents.

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APPENDICES

Table 7. 1 Proximate Analysis of bone to banana peel char at 500 ^{o}C.

I. Moisture content, %MC.

Temperature (^{o}C)	Ratio (BC-BPC)	t1	t2	t3	%Moisture content (mean ± SD)
500	2:1	4.83	4.86	4.83	4.84 ± 0.02
500	1:1	3.62	3.68	3.72	3.67 ± 0.05

II. Percentage volatile matter, %VM.

Temperature (^{o}C)	Ratio (BC-BPC)	t1	t2	t3	%Volatile mater (mean ± SD)
500	2:1	3.75	3.76	3.77	3.76 ± 0.01
500	1:1	4.89	4.93	4.94	4.92 ± 0.03

III. Percentage ash content, %Ash.

Temperature (^{o}C)	Ratio (BC-BPC)	t1	t2	t3	%Ash content (mean ± SD)
500	2:1	25.9	25.8	26	25.9 ± 0.1
500	1:1	29.7	30.2	30.86	30.25 ± 0.6

IV. Percentage fixed carbon content, %FC.

Temperature (^{o}C)	Ratio (BC-BPC)	%MC	%VM	%Ash	Sum	%FC 100-sum
500	2:1	4.84	3.76	25.9	34.5	65.50
500	1:1	3.67	4.92	30.25	38.84	61.16

Table 7. 2 Effect of pyrolysis temperature on the color and smell of treated fluoridated water

Treated B-BPC 2:1 ratio, at charring temperature (^oC)	Color of treated water	Smell of treated water
300	yellow	Bad
400	Slightly yellow	Bad
500	normal	none
600	Normal	none
700	Normal	none
800	Normal	none

Table 7. 3 ANOVA and post hoc test for different effects

```
A. ONEWAY concentration BY temperatures /POSTHOC=TUKEY ALPHA(0.05.
```

ANOVA

concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	12.723	5	2.545	7156.628	.000
Within Groups	.004	12	.000		
Total	12.727	17			

Multiple Comparisons

Dependent Variable: concentration

Tukey HSD

(I) tempreture	(J) tempreture	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
	400.00	.79000*	.01540	.000	.7383	.8417
	500.00	.66000*	.01540	.000	.6083	.7117
300.00	600.00	-.34000*	.01540	.000	-.3917	-.2883
	700.00	-1.11000*	.01540	.000	-1.1617	-1.0583
	800.00	-1.48333*	.01540	.000	-1.5350	-1.4316
	300.00	-.79000*	.01540	.000	-.8417	-.7383
400.00	500.00	-.13000*	.01540	.000	-.1817	-.0783
	600.00	-1.13000*	.01540	.000	-1.1817	-1.0783

	700.00	-1.90000*	.01540	.000	-1.9517	-1.8483
	800.00	-2.27333*	.01540	.000	-2.3250	-2.2216
	300.00	-.66000*	.01540	.000	-.7117	-.6083
	400.00	.13000*	.01540	.000	.0783	.1817
500.00	600.00	-1.00000*	.01540	.000	-1.0517	-.9483
	700.00	-1.77000*	.01540	.000	-1.8217	-1.7183
	800.00	-2.14333*	.01540	.000	-2.1950	-2.0916
	300.00	.34000*	.01540	.000	.2883	.3917
	400.00	1.13000*	.01540	.000	1.0783	1.1817
600.00	500.00	1.00000*	.01540	.000	.9483	1.0517
	700.00	-.77000*	.01540	.000	-.8217	-.7183
	800.00	-1.14333*	.01540	.000	-1.1950	-1.0916
	300.00	1.11000*	.01540	.000	1.0583	1.1617
	400.00	1.90000*	.01540	.000	1.8483	1.9517
700.00	500.00	1.77000*	.01540	.000	1.7183	1.8217
	600.00	.77000*	.01540	.000	.7183	.8217
	800.00	-.37333*	.01540	.000	-.4250	-.3216
	300.00	1.48333*	.01540	.000	1.4316	1.5350
	400.00	2.27333*	.01540	.000	2.2216	2.3250
800.00	500.00	2.14333*	.01540	.000	2.0916	2.1950
	600.00	1.14333*	.01540	.000	1.0916	1.1950
	700.00	.37333*	.01540	.000	.3216	.4250

*. The mean difference is significant at the 0.05 level.

```
B. ONEWAY Concentration BY pH
  /POSTHOC=TUKEY GH ALPHA(0.05).
```

ANOVA

Concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.093	5	.219	587.155	.000
Within Groups	.004	12	.000		
Total	1.097	17			

Multiple Comparisons

Dependent Variable: Concentration

Tukey HSD

(I) pH	(J) pH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
3.00	5.00	-.13000*	.01575	.000	-.1829	-.0771
	6.75	-.32000*	.01575	.000	-.3729	-.2671
	7.00	-.47000*	.01575	.000	-.5229	-.4171
	9.00	-.55667*	.01575	.000	-.6096	-.5038

	11.00	-.72000*	.01575	.000	-.7729	-.6671
	3.00	.13000*	.01575	.000	.0771	.1829
	6.75	-.19000*	.01575	.000	-.2429	-.1371
5.00	7.00	-.34000*	.01575	.000	-.3929	-.2871
	9.00	-.42667*	.01575	.000	-.4796	-.3738
	11.00	-.59000*	.01575	.000	-.6429	-.5371
	3.00	.32000*	.01575	.000	.2671	.3729
	5.00	.19000*	.01575	.000	.1371	.2429
6.75	7.00	-.15000*	.01575	.000	-.2029	-.0971
	9.00	-.23667*	.01575	.000	-.2896	-.1838
	11.00	-.40000*	.01575	.000	-.4529	-.3471
	3.00	.47000*	.01575	.000	.4171	.5229
	5.00	.34000*	.01575	.000	.2871	.3929
7.00	6.75	.15000*	.01575	.000	.0971	.2029
	9.00	-.08667*	.01575	.001	-.1396	-.0338
	11.00	-.25000*	.01575	.000	-.3029	-.1971
	3.00	.55667*	.01575	.000	.5038	.6096
	5.00	.42667*	.01575	.000	.3738	.4796
9.00	6.75	.23667*	.01575	.000	.1838	.2896
	7.00	.08667*	.01575	.001	.0338	.1396
	11.00	-.16333*	.01575	.000	-.2162	-.1104
	3.00	.72000*	.01575	.000	.6671	.7729
	5.00	.59000*	.01575	.000	.5371	.6429
11.00	6.75	.40000*	.01575	.000	.3471	.4529
	7.00	.25000*	.01575	.000	.1971	.3029
	9.00	.16333*	.01575	.000	.1104	.2162

*. The mean difference is significant at the 0.05 level.

C. `ONEWAY concentration BY time /POSTHOC=TUKEY ALPHA(0.05).`

ANOVA

concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.776	7	.254	1522.000	.000
Within Groups	.003	16	.000		
Total	1.778	23			

Multiple Comparisons

Dependent Variable: concentration

Tukey HSD

(I) time	(J) time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
.50	1.00	.06333*	.01054	.000	.0268	.0998
	2.00	.15333*	.01054	.000	.1168	.1898
	4.00	.19667*	.01054	.000	.1602	.2332
	6.00	.23333*	.01054	.000	.1968	.2698
	8.00	.67333*	.01054	.000	.6368	.7098
	12.00	.67333*	.01054	.000	.6368	.7098
	24.00	.67333*	.01054	.000	.6368	.7098
1.00	.50	-.06333*	.01054	.000	-.0998	-.0268
	2.00	.09000*	.01054	.000	.0535	.1265
	4.00	.13333*	.01054	.000	.0968	.1698
	6.00	.17000*	.01054	.000	.1335	.2065
	8.00	.61000*	.01054	.000	.5735	.6465
	12.00	.61000*	.01054	.000	.5735	.6465
	24.00	.61000*	.01054	.000	.5735	.6465
2.00	.50	-.15333*	.01054	.000	-.1898	-.1168
	1.00	-.09000*	.01054	.000	-.1265	-.0535
	4.00	.04333*	.01054	.014	.0068	.0798
	6.00	.08000*	.01054	.000	.0435	.1165
	8.00	.52000*	.01054	.000	.4835	.5565
	12.00	.52000*	.01054	.000	.4835	.5565
	24.00	.52000*	.01054	.000	.4835	.5565
4.00	.50	-.19667*	.01054	.000	-.2332	-.1602
	1.00	-.13333*	.01054	.000	-.1698	-.0968
	2.00	-.04333*	.01054	.014	-.0798	-.0068
	6.00	.03667*	.01054	.048	.0002	.0732
	8.00	.47667*	.01054	.000	.4402	.5132
	12.00	.47667*	.01054	.000	.4402	.5132
	24.00	.47667*	.01054	.000	.4402	.5132
6.00	.50	-.23333*	.01054	.000	-.2698	-.1968
	1.00	-.17000*	.01054	.000	-.2065	-.1335
	2.00	-.08000*	.01054	.000	-.1165	-.0435
	4.00	-.03667*	.01054	.048	-.0732	-.0002
	8.00	.44000*	.01054	.000	.4035	.4765
	12.00	.44000*	.01054	.000	.4035	.4765
	24.00	.44000*	.01054	.000	.4035	.4765
8.00	.50	-.67333*	.01054	.000	-.7098	-.6368
	1.00	-.61000*	.01054	.000	-.6465	-.5735

	2.00	-.52000*	.01054	.000	-.5565	-.4835
	4.00	-.47667*	.01054	.000	-.5132	-.4402
	6.00	-.44000*	.01054	.000	-.4765	-.4035
	12.00	.00000	.01054	1.000	-.0365	.0365
	24.00	.00000	.01054	1.000	-.0365	.0365
	.50	-.67333*	.01054	.000	-.7098	-.6368
	1.00	-.61000*	.01054	.000	-.6465	-.5735
	2.00	-.52000*	.01054	.000	-.5565	-.4835
12.00	4.00	-.47667*	.01054	.000	-.5132	-.4402
	6.00	-.44000*	.01054	.000	-.4765	-.4035
	8.00	.00000	.01054	1.000	-.0365	.0365
	24.00	.00000	.01054	1.000	-.0365	.0365
	.50	-.67333*	.01054	.000	-.7098	-.6368
	1.00	-.61000*	.01054	.000	-.6465	-.5735
	2.00	-.52000*	.01054	.000	-.5565	-.4835
24.00	4.00	-.47667*	.01054	.000	-.5132	-.4402
	6.00	-.44000*	.01054	.000	-.4765	-.4035
	8.00	.00000	.01054	1.000	-.0365	.0365
	12.00	.00000	.01054	1.000	-.0365	.0365

*. The mean difference is significant at the 0.05 level.

```
D. ONEWAY concentration BY Dose /POSTHOC=GH ALPHA(0.05).
```

ANOVA

concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5.706	4	1.427	476.562	.000
Within Groups	.030	10	.003		
Total	5.736	14			

Multiple Comparisons

Dependent Variable: concentration

Tukey HSD

(I) Dose	(J) Dose	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
2.00	4.00	.93000*	.06944	.015	.4148	1.4452
	6.00	1.39333*	.01333	.000	1.3336	1.4531
	8.00	1.56333*	.01054	.000	1.5124	1.6143
	10.00	1.70333*	.01054	.000	1.6524	1.7543
4.00	2.00	-.93000*	.06944	.015	-1.4452	-.4148
	6.00	.46333	.06960	.061	-.0479	.9746
	8.00	.63333*	.06912	.034	.1099	1.1568
	10.00	.77333*	.06912	.023	.2499	1.2968

6.00	2.00	-1.39333*	.01333	.000	-1.4531	-1.3336
	4.00	-.46333	.06960	.061	-.9746	.0479
	8.00	.17000*	.01155	.002	.1114	.2286
	10.00	.31000*	.01155	.000	.2514	.3686
8.00	2.00	-1.56333*	.01054	.000	-1.6143	-1.5124
	4.00	-.63333*	.06912	.034	-1.1568	-.1099
	6.00	-.17000*	.01155	.002	-.2286	-.1114
	10.00	.14000*	.00816	.000	.1037	.1763
10.00	2.00	-1.70333*	.01054	.000	-1.7543	-1.6524
	4.00	-.77333*	.06912	.023	-1.2968	-.2499
	6.00	-.31000*	.01155	.000	-.3686	-.2514
	8.00	-.14000*	.00816	.000	-.1763	-.1037

*. The mean difference is significant at the 0.05 level.

```
E. ONEWAY Final concentration BY Initial concentration /POSTHOC=TUKEY
   ALPHA (0.05).
```

ANOVA

Final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	259.958	5	51.992	71438.829	.000
Within Groups	.009	12	.001		
Total	259.967	17			

Multiple Comparisons

Dependent Variable: Final concentration

Tukey HSD

(I) Initial concentration	(J) Initial concentration	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
5.00	10.00	-.82667*	.02203	.000	-.9007	-.7527
	15.00	-1.65000*	.02203	.000	-1.7240	-1.5760
	20.00	-3.81667*	.02203	.000	-3.8907	-3.7427
	25.00	-6.79000*	.02203	.000	-6.8640	-6.7160
	30.00	-10.87333*	.02203	.000	-10.9473	-10.7993
10.00	5.00	.82667*	.02203	.000	.7527	.9007
	15.00	-.82333*	.02203	.000	-.8973	-.7493
	20.00	-2.99000*	.02203	.000	-3.0640	-2.9160
	25.00	-5.96333*	.02203	.000	-6.0373	-5.8893
	30.00	-10.04667*	.02203	.000	-10.1207	-9.9727
15.00	5.00	1.65000*	.02203	.000	1.5760	1.7240
	10.00	.82333*	.02203	.000	.7493	.8973
	20.00	-2.16667*	.02203	.000	-2.2407	-2.0927
	25.00	-5.14000*	.02203	.000	-5.2140	-5.0660

	30.00	-9.22333*	.02203	.000	-9.2973	-9.1493
	5.00	3.81667*	.02203	.000	3.7427	3.8907
	10.00	2.99000*	.02203	.000	2.9160	3.0640
20.00	15.00	2.16667*	.02203	.000	2.0927	2.2407
	25.00	-2.97333*	.02203	.000	-3.0473	-2.8993
	30.00	-7.05667*	.02203	.000	-7.1307	-6.9827
	5.00	6.79000*	.02203	.000	6.7160	6.8640
	10.00	5.96333*	.02203	.000	5.8893	6.0373
25.00	15.00	5.14000*	.02203	.000	5.0660	5.2140
	20.00	2.97333*	.02203	.000	2.8993	3.0473
	30.00	-4.08333*	.02203	.000	-4.1573	-4.0093
	5.00	10.87333*	.02203	.000	10.7993	10.9473
	10.00	10.04667*	.02203	.000	9.9727	10.1207
30.00	15.00	9.22333*	.02203	.000	9.1493	9.2973
	20.00	7.05667*	.02203	.000	6.9827	7.1307
	25.00	4.08333*	.02203	.000	4.0093	4.1573

*. The mean difference is significant at the 0.05 level.

Table 7. 4 T-Test for proximate analysis

T-Test: Paired Two Sample for Means for moisture content, volatile mater and ash content

	Moisture content		*Volatile mater*		*Ash content*	
	2: 1 ratio	*1:1 ratio*	*2: 1 ratio*	*1:1 ratio*	*2: 1 ratio*	*1:1 ratio*
Mean	4.84	3.673333	3.76	4.92	25.90	30.24667
Variance	0.0003	0.002533	0.0001	0.0007	0.0090	0.552533
Observations	3	3	3	3	3	3
Pearson Correlation	0.114708		0.944911		-0.90212	
Hypothesized Mean Difference	0		0		0	
df	2		2		2	
t Stat	39.37808		-116		-9.06283	
P(T<=t) one-tail	0.000322		3.72E-05		0.005979	
t Critical one-tail	2.919986		2.919986		2.919986	
P(T<=t) two-tail	0.000644		7.43E-05		0.011957	
t Critical two-tail	4.302653		4.302653		4.302653	

Figure 7. 1 Mixture of bone char and banana peel char, charred at 500 ^{o}C {2:1} ratio.

Figure 7. 2 Photograph of dried raw bones and banana peel, respectively.

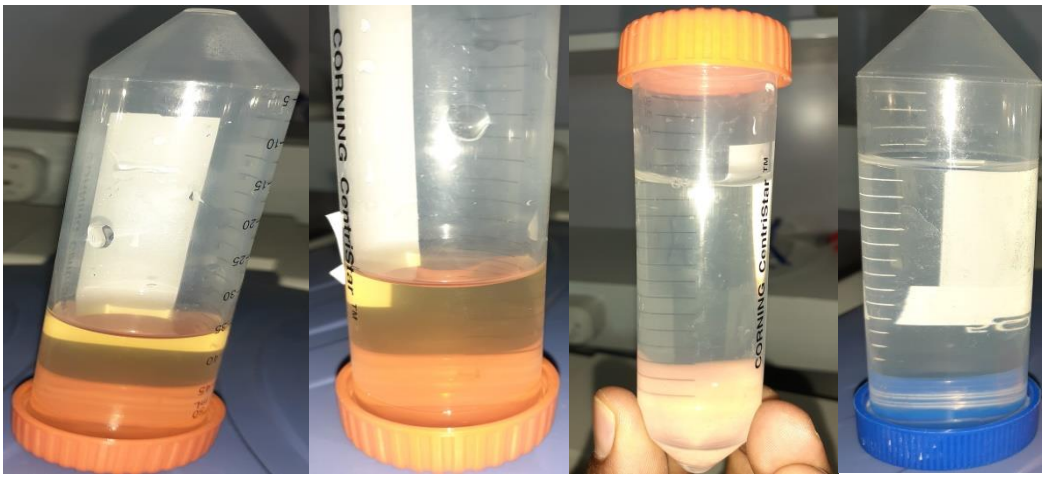

Figure 7. 3 Photograph of treated fluoride water colors with 2:1 ratio of B-BPC prepared at pyrolysis temperature of 300, 400, 500, 600 ^{o}C, respectively.