REMOVAL OF FLUORIDE FROM DRINKING WATER USING THERMALLY ACTIVATED MIXTURE OF BONE AND COFFEE HUSK

BY TAMIRU GUDA LEMA

A THESIS SUBMITTED TO

THE DEPARTMENT OF APPLIED CHEMISTRY

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PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY

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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 Tamiru Guda Lema have read and evaluated his thesis entitled “removal of fluoride from drinking water using thermally activated mixture of bone and coffee husk ” 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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Declaration

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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Supervisor's/Advisor's approval sheet

To: Chemistry department

Subject: Thesis Submission

This is to certify that the thesis entitled "removal of fluoride from drinking water using thermally activated mixture of bone and coffee husk" 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 Tamiru Guda Lema Id. No GSU/0507/06, 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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Name of major Advisor/supervisor	Signature	Date
_____	_____	_____
Name of Co-advisor	Signature	Date

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TABLE OF CONTENTS

CONTENTS **PAGE**

LIST OF TABLES

TABLE **PAGE**

LIST OF FIGURES

FIGURE **PAGE**

LIST OF ABBREVIATIONS AND ACRONYMS

AA	Activated Alumina
ASTM	American Society for Testing Materials
BATs	Best Available Technologies
BC	Bone char
B-CHC	Bone-Coffee Husk Char
CHC	Coffee husk char
DNA	Deoxyribonucleic acid
EDTA	Ethylene diaminetetra acetate
FAP	Fluorapatite
HAP	hydroxyapatite
IQ	Intelligent Quotient
ISE	Ion Selective Electrode
ISO	International Standards Organization
NEERI	National Environmental Engineering Research Institute
NGO	Nongovernmental Organization
OSHO	Oromo Self Help Organization
ppm	Parts per million
rpm	revolution per minute
RBCS	Red Blood Cells
TISAB	Total Ionic Strength Adjustment Buffer
WHO	World Health Organization
UNICEF	United Nations International Children's Emergency Fund
US-EPA	United States Environmental Potential Agency

ABSTRACT

Due to the negative health impacts of high level of fluoride in drinking water, the search for an appropriate and locally available technology for its removal from contaminated water still remains very critical. Therefore, this research investigates the potential of thermally activated mixtures of cattle bones and coffee husk as technically simple, cost effective and easily transferable technology for defluoridation of drinking water. To conduct the experiment, the bones and coffee husk mixtures with 1:1 (100g each) and 2:1 (150-to-75 g) bone-to-coffee husk ratio were pyrolysised at six different temperatures (300 ^{o}C, 400 °C, 500 ^{o}C, 600 °C, 700 ^{o}C and 800 ^{o}C) for 2h and 200g of each adsorbents were also separately charred at pyrolysis temperature of 500^{o}C for the same pyrolysis time in a muffle furnace. The pyrolysis product obtained were then ground in a grinding machine, and sieved through a mesh size of 250μm. The prepared adsorbent were characterized by its percentage removal of fluoride ions from artificial fluoridated water and naturally fluoridated water under the optimized contact time, adsorbent dosage, pH and initial concentration of fluoride. The proximate analysis, point of zero charge and specific surface area of the prepared adsorbent were also determined. The adsorption efficiency of adsorbent which pyrolyzed in a mixture of 2:1 bone-coffee husk at a pyrolysis temperature of 500^{o}C was better than that of 1:1 ratio and all ratios of separately charred bone and coffee husk. This indicates that the chemical composition of bone may activate carbons from coffee husk when they are pyrolyzed together. The less fluoride uptake below 400^{o}C was due to incomplete conversion of organic carbons to inorganic whereas, beyond 600^{o}C was due to the distortion (damage) of hydroxyapatite structure of the bone. The adsorption efficiency of bone-coffee husk char for fluoride removal was increased with adsorbent dosage and contact time before equilibrium and it was appreciable around neutral pH. The linear regression analysis of kinetic data confirmed that pseudo-second order rate expression best fitted while Freundlich isotherm model equation was found to fit the equilibrium data for fluoride adsorption.

Keywords: *adsorption, defluoridation, drinking water, fluoride, fluorolysis, pyrolysis.*

1. INTRODUCTION

1.1. Background of the study

Fluoride is anion of the chemical element fluorine, which belongs to the halogen group. It is the most electronegative of all the elements and it is never found in elemental gaseous form except in industrial processes.

The level of fluoride in drinking water is a very important factor in evaluating the quality of water for human consumption. Depending on the level of fluoride, the ingestion of fluoride containing drinking water can be either beneficial or detrimental to human health. Among the beneficial effects of fluoride in human body, strengthening of bones and prevention from tooth decay are significant [1]. Excessive fluoride exposure (greater than 1.5mg/L) may cause fluorosis and long term damage to the brain, liver, thyroid and kidney [2]. Some studies have also reported that long term exposure to levels of between 3-6mg/L of fluoride concentrations can result in skeletal fluorosis, which is characterized by severe pain and stiffness of the backbone as well as pain in the joints [3]. Fluoride levels beyond 10mg/L resulted in crippling fluorosis, which is characterized by bending of the bones and difficulties in walking [4]. Moreover, fluoride taken at concentration levels less than 0.5mg/L may result in lack of protection against dental caries, especially for children.

The occurrence of high fluoride concentrations in groundwater and the risk of fluorosis associated with using such water for human consumption is a problem faced by many countries, notably India, Sri Lanka, and China, the Rift Valley countries in East Africa, Turkey, and parts of South Africa [5]. The total number of people is not known, but a conservative estimate would number in the tens of millions.

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 [6]. Concentration of fluoride greater than the WHO guideline value of 1.5mg/L were detected in several groundwater of Ethiopia, but fluoride concentrations greater than 10mg/L were found in waters from the rift

valley [7]. A resent analysis of the water samples taken along the roads from Addis to Hawasa and from Addis to Adama showed that the fluoride concentration ranged from 5 to 25mg/L [8]. So it is required to develop and implement appropriate water treatment technology using local resources that are accessible and technically feasible to the rural community.

Related to this a number of studies has been conducted. Yadav *et al.* 2013, studied removal of fluoride from aqueous solutions and groundwater by activated carbon from wheat straw. They studied to design and develop a new cost effective strategy for fluoride removal, applicable to rural areas of developing countries. Awugchew T. 2015, presented coffee husk as new low-cost, locally abundant material for production of activated carbon and investigated its application for adsorption of fluoride and Cr (VI) from aqueous solution. Also Mitiku T. 2015, was 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. Enyew 2017, studied removal of fluoride from water samples using mixture of bone char and chemically activated carbon from coffee husk. Teshome L.2017 conducted his dissertation on low-cost chemically activated cow bone for fluoride removal from drinking water: batch, field-scale column and business model studies. However, all these studies were used chemical activation method 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. Therefore, in this study the potential of using thermally activated mixtures of cattle bones and coffee husk char as a low cost defluoridation adsorbent were investigated.

1.2. Statement of the problem

Around 200 million people worldwide rely on drinking water that is contaminated with excess fluoride [9]. People in several areas of the Ethiopian Rift Valley are consuming water with up to 33mg/L of fluoride as a result fluorosis is known to be endemic in the Ethiopian Rift Valley[10]. The scarcity of surface water in the main Ethiopian Rift Valley complicated the susceptibility to fluorosis as the communities become highly dependent on the fluoride rich groundwater sources for drinking water supply [11].

Mitigation of this health problem has been hindered mainly by the lack of a suitable and inexpensive removal method [12].Yet, fluoride removal systems in rural communities are necessary since successful implementation of suitable and cost effective systems is still inexistent in Ethiopia [13]. Thus, it is important to explore low-cost adsorbents for the adsorption of fluoride from drinking water.

City of Addis Ababa generates a solid waste more than 200,000t/year and about 550t/day of wastes are collected out of this 2% is bone waste [14]. 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 like mosquitoes.

Since Ethiopia is one of major coffee producing countries in the world, large amount of coffee husk is produced as waste. In addition to its low-cost, coffee husk has shown better adsorptive capacity, property of high carbon contents and low inorganic compound levels [15, 16, and 17].

In fact, different separate studies indicate that bone char and chemically activated carbon from coffee husk 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. These organic impurities can be removed using activated carbon from coffee husk [18].

Therefore the aim of this research focused on the removal of fluoride from drinking water using adsorbents prepared from mixtures of cattle bones and coffee husk under thermal activation (without chemical use) to find low cost treatment and locally abundant materials.

1.3. Objectives of the study

1.3.1. General objective

The general objective of this study is:

- To remove fluoride from drinking water samples using thermally activated mixture of bone and coffee husk adsorbents.

1.3.2. Specific objectives

- To prepare adsorbents using cattle bones and coffee husk for removal of fluoride.
- To characterize adsorbents prepared by mixing cattle bone and coffee husk that activated at different temperature.
- 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. Significant of the study

The significance of this study is comprised of both economy and environment. Since the adsorbent is going to be produced from bone and coffee husk, this study can be considered as one way of transforming a solid waste (a waste that could have been dispersed in the environment so easily) into useful material. Beside to this the produced adsorbent when it is used in drinking water treatment, will contribute in keeping the countries ecosystem safer.

Generally this study will provide information on the application of composite of bone-coffee husk char for fluoride removal from drinking water by adsorption process. Moreover, it can provide initial information for the researchers who are interested to conduct further studies on this area.

2. REVIEW OF THE LITERATURE

2.1 Occurrence and Origins of Fluoride

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^-) [19; 20].

Fluorine is widely distributed in the earth's crust as the fluoride ion and constitutes about 0.06-0.09% weight of the upper layers of the lithosphere [20; 21]. Fluoride and hydroxide ions both have the same charge and similar ionic radii, and can therefore replace each other in many mineral structures to form fluoride-mineral complexes. Over 150 minerals are known to contain fluoride but with a great variation in content from as high as 73% in the rare mineral griceite (LiF) to less than 0.2% in many others [21, 22]. The most common fluoride-bearing minerals, which are the natural sources of fluoride include; fluorite (CaF_2), fluoroapatite ($Ca_{10}(PO_4)6F_2$), villianmite (NaF), cryolite (Na_3AlF_6), topaz ($Al_2SiO_4(F,OH)_2$), the micas including muscovite (K $Al_2(Si_23Al)O_{10}(OH,F)_2$) and biotite ($K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2$), the amphiboles including hornblende ($NaCa_2(Mg,Fe,Al)_3(Si,Al)_8O_{22}(OH,F)_2$) and rock phosphate. Clay minerals such as illite, chlorite and smectites also represent excellent anion exchange media that can contribute to fluoride enrichment of groundwater [21, 23, 24, and 25]. Due to its favorable dissolution properties, however, fluorite (CaF_2) seems to be the main mineral that predominantly controls aqueous fluoride geochemistry in most environments [21, 24, 26].

Fluoride occurs in practically all natural groundwaters, 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 [24, 27, 28].

The dominant factors that control the concentration of fluoride in natural groundwater include: the geological setting and types of rocks/minerals traversed by the groundwater, solubility of fluorine-bearing minerals in the aquifer matrix and the amount of leachable fluorine they contain,

anion exchange capacity of aquifer materials (OH^- for F^-), and the chemical composition of the traversing groundwater and its contact time or reaction time with fluorine-bearing materials [23, 24, 28, 29].

The climatic conditions of an area of interest may also have an influence on the fluoride concentration of the groundwater [23, 24, 28, 29]. Arid regions are more vulnerable to high fluoride concentrations. In these regions groundwater flow is slow and reaction times with rocks (including fluoride-bearing minerals) are therefore longer [30].

High fluoride concentrations can also build up in ground waters which have long residence times in host aquifers. Such ground waters are usually associated with deep aquifer systems and slow groundwater movement. On the other hand shallow groundwaters, which represent young and recently infiltrated rain water generally, have low concentrations of fluoride. Such groundwaters are usually found in hand dug wells [30].

Fluoride contamination of groundwater can also result from anthropogenic sources and/or industrial activities such as application of phosphatic fertilizers, processing of phosphatic raw materials, uses of clays in ceramic industries, electroplating, and aluminum smelting operations and burning of coal [23, 31, 32, 33].

2.2. Health Effect 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 [1]. 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 [2]. Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electronegativity [34].

High fluoride waters often have low calcium and magnesium concentrations as such are fairly soft [35]. About 95% of fluoride in the body is deposited in hard tissues and it continues to be deposited in calcified structure even after other bone constituents (Ca, P, Mg, carbonates and

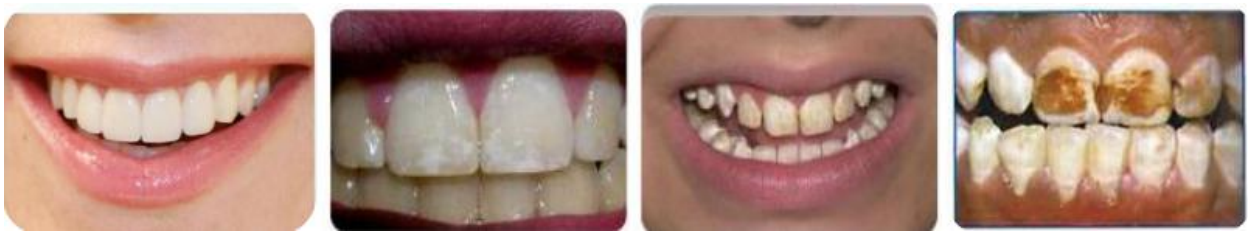
citrate) have reached the steady state. Due to such deposition, bones deformation causes irreversible damages [36].

The other problems associated with health impact of fluoride are generally overlooked because of the notion prevailing that fluoride only affects bones and teeth. 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 etc. It is also responsible for destruction of about 60 enzymes [36]. 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 fluorapatite (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 [37].

World Health Organization (WHO) and ISO: 10500 recommend that the fluoride content in drinking water should be in the range of 1-1.5mg/L. An intake of more than 6mg/L of fluoride results in multidimensional health manifestations, the most common being dental, skeletal fluorosis [38] and crippling [39]. 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 [35]. 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 IQ in humans [39], damage to liver, thyroid and kidney [40]. 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 [41].

Dental fluorosis is caused by prolonged consumption of water with fluoride concentrations between 1.5 and 4.0mg/L. This is characterized by browning and mottling of teeth (Figure 2.1).

Prolonged drinking of water with concentrations of fluoride between 4.0 and 10mg/L causes' skeletal fluorosis and when water of concentrations beyond 10.0 mg/L is taken for a long time crippling fluorosis may ensue. Skeletal fluorosis is characterized by weakening of bones and malformation of the skeleton [42].



Normal **Slight mottling** **Obvious mottling** **Sever mottling**

Figure 2.1 Degree of dental fluorosis

(This lady is only 40 years old, but looks 80 years!!) (Source: UNICEF, 2001)

Figure 2.2 Photographs Showing Skeletal Fluorosis

Symptoms of crippling fluorosis (Figure 2.2) 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 hydroxyl-phosphate, the main skeletal structure compositional material. The replacement of hydroxide ions with fluoride ions results in a more acid resistant structure, fluoroapatite [42].

$$Ca_5(PO_4)_3OH + F^- \longrightarrow Ca_5(PO_4)_3F + OH^-$$

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 [42].

$$Ca_5(PO_4)_3F + 9F^- \longrightarrow Ca_5F_{10} + 3PO_4^{3-}$$

That means 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. Dental and skeletal fluorosis has however attracted greater attention as compared to the other effects of fluoride because of its obvious manifestations [42]. It may even interfere with carbohydrates, proteins, vitamins and mineral metabolism and to DNA creation as well if intake excessively [43]. The excessive fluoride intake leads to the loss of calcium from the tooth matrix, aggravating cavity formation throughout life [44].

There are many sources of fluoride in the diet. Dentists apply fluoride to teeth; some municipal water systems add fluoride to the water supply; and some toothpaste have fluoride as an additive; and some foods also have elevated fluoride such as fish and tea [41]. The requirement of fluoride content changes and it depends on the geographical condition and the age of human beings [45]. According to current knowledge, a fluoride concentration of about 0.5mg/L is beneficial in preventing dental caries during tooth development, while levels higher than 1.5mg/L may result in fluorosis or other health problems. A maximum fluoride concentration of about 4mg/L is considered adequate for the prevention of skeletal fluorosis [43].

A secondary maximum contaminant level of 2mg/L is recommended to minimize the “cosmetic” risk of dental fluorosis, which can occur when fluoride is incorporated into enamel. The World Health Organization (WHO) guidelines suggest optimum levels of fluoride concentration at 1 and 1.5mg/L for warmer and cooler climates, respectively [39].

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 10mg/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 [36]. For a total intake of 14mg/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 6mg/day [36].

Nutritional status and physical strain also play vital role in deciding total effects of fluoride pollution. A diet poor in calcium, for example, increases the body's retention capacity of fluoride. Environmental factors include annual mean temperature, humidity, rainfall, tropical climate, duration of exposure etc. Besides, other factors such as pH in terms of alkalinity, age, calcium in diet, fresh fruits and vitamin-C reduces fluoride toxicity. Whereas, trace elements like molybdenum enhances the fluoride toxicity [36].

2.3 Available fluoride removal technologies

Because of the permanent risk and also the lack of known effective treatment for fluorosis, fluoride removal from contaminated drinking water is a necessity, to avoid ingestion of excess fluoride as a preventive measure [46, 47].

Several defuoridation technologies have been developed in many places around the world, some of which are described as "Best Available Technologies" (BATs). The current methods, however, have some limitations which generally make their use unsustainable under most given conditions, particularly in remote areas in developing countries [20, 48, 49]

The common fluoride removal techniques include those based on sorption process, coagulation-flocculation-filtration, contact precipitation and membrane filtration processes [20, 50, 51].

2.3.1 Techniques based on adsorption process

The most popular fluoride removal technologies based on the adsorption process include fluoride adsorption on activated alumina and bone charcoal.

2.3.1.1 Activated alumina (AA)

The technology which uses activated alumina as a filter media has been described by the United States Environmental Protection Agency (US-EPA) as a Best Available Technique for water defluoridation [50]. 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% [49, 50, 51, 52]

The activated alumina (Fig. 2.3) 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 [20, 50].

Figure 2.3 Activated alumina grains

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 [20, 49, 50]

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 [20, 50, 51]. Generally the optimum fluoride removal has been found to occur in the range of pH 5 to 6 [50, 51, 53] 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 [50, 51, 53]

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 each 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 [20, 50].

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 [20, 48]. 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 [50];

- Less purified AA products have relatively low fluoride removal capacity [20, 51];
- Spent regeneration solution contains high F concentrations [20, 49] and is difficult to dispose off.

2.3.1.2 Bone charcoal defluoridation method

Bone charcoal is a blackish, porous, granular material used as filter media for defluoridation. It has been described as the oldest known defluoridation agent and was used in the USA in the 1940s through to the 1960s. It is reported as working very well in Thailand and in some African countries (e.g Tanzania) at the domestic level [49, 20, 50].

Bone charcoal is prepared from animal bones by heating in specially designed kilns at temperatures ranging from 400 to 600 ^{o}C at controlled air supply. The heat treatment process removes organic materials (fats, oils and meat remains) from the bones and also activates or improves its fluoride removal capacity [54]. The major components of bone charcoal are calcium phosphate (57-80%), calcium carbonate (6-10%), and activated carbon (7-10%) [20, 49].

When in contact with water, bone charcoal is able to remove a wide range of pollutants (colour, taste, odour components), and has a specific ability for the up-take of fluoride from solution. The removal capability is thought to be due to its chemical composition, mainly as hydroxyapatite where one or two of the hydroxyl groups can be replaced by fluoride [20, 50]. In addition, it is also thought that the fluoride removal can be due to the reaction between calcium phosphate and fluoride or the replacement of the carbonate by fluoride to form an insoluble fluoroapatite. According to Fawell et al. (2006) the principal reaction for fluoride removal can be represented as:

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \longrightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-$$

$$(Ca_3(PO_4)_2)\,nCaCO_3 + 2F^- \longrightarrow (Ca_3(PO_4)_2)\,nCaF_2 + CO_3^{2-}$$

The appropriate preparation of the bone charcoal is crucial to optimizing its properties as a fluoride removal agent [50, 49, 20, 55].

The two charring techniques are calcination and pyrolysis.

Calcination:-is known as a process of high temperature heating in the presence of atmospheric oxygen. The end product being pure bone mineral, a compound related to hydroxyapatite. All organic carbon material is combusted to CO_2.

Pyrolysis:- is a charring process with no or very limited access to oxygen. In the organic phase the bone is converted into inorganic carbon and graphite, which makes this bone char black whatever charring temperature is used. However, the fluoride uptake is mostly ascribed to the bone mineral phase (apatite).

Pyrolysed bones are therefore always totally black while calcined bones are brown-grey-white, depending on the access of oxygen and thereby degree of charring. Pyrolysis is much more fuel demanding and therefore more expensive [56].

Recently, a study presented by Dahi and Bregnhøj showed that when bone has free access to oxygen in the atmosphere (calcination), the defluoridation capacity is drastically reduced when heated at temperatures higher than 550^{o}C. They found that pyrolysis provides the best bone char defluoridation capacity demonstrated by a linear correlation between surface area and defluoridation capacity [57].

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^{o}C 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 [58]. 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 [58].

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 [20, 50]
- If the bone charring process is not properly done the resulting filter media will have low fluoride removal capacity [20]
- 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 [20, 49, 50].

2.3.2 Coagulation-flocculation-filtration process: 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 [49, 52].

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 [20, 50]. 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 [20, 50, 51]

The various reactions which occur in the Nalgonda defluoridation process are presented by four equations below [20, 50].

Dissolution of Alum:

$$Al_2(SO_4)_3.\ 18H_2O \longrightarrow 2Al^{3+} + 3SO_4^{2-} + 18H_2O$$

Precipitation of aluminum hydroxide:

$$2Al^{3+} + 6H_2O \longrightarrow 2Al(OH)_3 + 6H^+$$

Co-precipitation of fluoride:

$$F^- + Al(OH)_3 \longrightarrow \text{Al-F complex + undefined product}$$

pH adjustment:

$$6Ca(OH)_2 + 12H^+ \longrightarrow 6Ca^{2+} + 12\ H_2O$$

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 [20, 49].
- The operational costs of the Nalgonda technique are high [51].
- The process requires correct dosing of chemicals, regular attendance and close monitoring to ensure effective fluoride removal. The labour, skills and time requirements on a sustainable basis, has been noted by UNICEF to be problematic at the rural community level [20, 50].
- 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 [20]. 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.

- According to Meenakshi et al. (2006), 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. 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 [47, 59, 60].

2.3.3 Contact precipitation process

In this technique fluoride removal is accomplished by the addition of calcium chloride and sodium dihydrogen phosphate or monosodium phosphate (MSP) to the raw water and then bringing the solution in contact with a bone charcoal medium already saturated with fluoride. The technique is reported as having high fluoride removal efficiency [20, 49].

In a solution containing calcium, phosphate and fluoride, the precipitation of calcium fluoride and/or fluoroapatite is theoretically feasible. The precipitation process is however, practically impossible due to the slow nature of the reaction kinetics. Though the mechanism of the fluoride removal by the contact precipitation process is not fully understood, it is thought that the saturated bone charcoal acts as a catalyst for the calcium fluoride and/or fluoroapatite precipitation process. It also acts a filter media for the resulting precipitate, thereby accomplishing the fluoride removal [20].

According to Fawell et al. (2006), the reactions which occur in the contact precipitation defluoridation process can be represented as follows:

Dissolution of calcium chloride:

$$CaCl_2\,2H_2O(s) + 2H_2O \longrightarrow Ca^{2+} + 2Cl^- + 2H_2O$$

Dissolution of monosodium phosphate:

$$NaH_2PO_4\,H_2O(s) \longrightarrow PO_4^{3-} + Na^+ + 2H^- + H_2O$$

Precipitation of fluoroapatite:

$$10\ Ca^{2+} + 6PO_4^{3-} + 2F^- \longrightarrow Ca_{10}(PO_4)_6F_2(s)$$

Precipitation of calcium fluoride:

$$Ca^{2+} + 2F^- \longrightarrow CaF_2(s)$$

The saturated bone charcoal acts as a catalyst in the above reactions.

The limitations of the contact precipitation process include:

- Chemicals and trained staff are required for the process, which is often problematic and unsustainable if the process is to be used for water defluoridation in rural communities in developing countries.
- The process is new and still under investigation. It has so far been implemented only at the domestic level in Kenya and Tanzania [61]
- The use of bone char as contact bed also has similar limitations/shortcomings as indicated for the bone charcoal defluoridation method [20, 49].

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 [20, 50]

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 [49, 50, 51].

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 countrie [50].
- High capital, operation and maintenance cost [51].
- 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 [49,51].
- The process also removes most ions present in the water though some are required as essential minerals for the human body [49, 50, 51].
- Disposal of concentrate with rejected contaminants (fluoride) is difficult.

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.

Adsorption is a term which is completely different from Absorption. While absorption means uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. When both Adsorption and Absorption processes take place simultaneously, the process is called sorption. Adsorption process involves two components, which are adsorbent and adsorbate. Adsorbent is the substance on the surface of which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of adsorbent.

Adsorbate + Adsorbent give rise to Adsorption. For this study the adsorbate is fluoride which can adsorb by adsorbent mixture of thermally activated bone-coffee husk char.

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 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 [62, 63]. The Freundlich and Langmuir isotherms are useful models for the description of 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 [64].

2.5.1 Freundlich Isotherm

The Freundlich isotherm has the general form,

$$q_e = K_f C_e^{\frac{1}{n}} \quad \text{----------(2.1)}$$

The linearised Freundlich adsorption isotherm can be expressed as,

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

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 increases with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$, all surface sites are equivalent. Ce (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 [65].

2.5.2 Langmuir Isotherm

The Langmuir isotherm is based on the assumption that 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,

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

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. 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 C_o 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) and irreversible (R_L = 0) [65].

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 [66, 67]. 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.

The Lagergren's first order rate equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. 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,

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

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_m) indicate the applicability of pseudo first-

order model. The pseudo first-order rate constant k_1 and q_e values were determined for each adsorbent from the slope and the intercept of corresponding plot [68]

Contrary to the other model, the pseudo-second-order equation predicts the behavior over the whole time of adsorption, with the adsorption (chemisorption) mechanism being the rate controlling step [69, 70] which involves valency 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:

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

where, k_2 is the rate constant for the pseudo second-order kinetics. The value of correlation coefficients from the plot (t/q_e) 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 [68].

3. MATERIALS AND METHODS

3.1. Chemicals and Equipments

Equipments

Equipments required for the completion of this study were fluoride ion selective electrode (Orion model 940 Expandable Ion Analyzer), pH meter (mettle Toledo Mp220), grinding materials (mortar and pestle), filter paper (Whatman number 1), ceramic crucibles, plastic beakers (different size), glass rod, spatula, tongs, measuring cylinder (different size), magnetic stirrer, hot air oven (Contherm 260), volumetric flask (different size), Muffle furnace (Sx-2.5-12), Electronic beam balance (OHAUS Switzerland), measuring cylinders, sieve (250μm mesh size)

Chemicals

Analytical grade working chemicals used in this research include: sodium fluoride (99.9%), sodium chloride (99.5%), sodium hydroxide (99.8% E-Merck, India), hydrochloric acid (GR grade, Merck, India), glacial acetic acid, sodium citrate ($Na_3C_6H_5O_7.2H_2O$), EDTA, TISAB, and distilled water were used throughout the experiment.

3.2. Preparation of adsorbents

3.2.1. Preparation of bone-coffee husk char adsorbent

Bone-coffee husk char adsorbent were produced from cattle bones collected from Adama town and dried coffee husk sample collected from West Wollega, Nejo town; Ethiopia following a procedure developed by [71]. At the university laboratory, firstly, the bones were degreased with boiling water in a heat resistant beaker for one hour and dry in an oven at 105^oC.Then the dried bones were crushed in mortar. Secondly, the coffee husk was washed several times (at least 10 times) with distilled water to remove dirt particles and any water soluble materials present and then it was kept in air oven at 90^0C for 12h to dry. Then on the bases of previous findings and preliminary test result, 1:1 ratio (100g each) and 2:1 ratio (100-to-50g) of bone samples to coffee

husk each were mixed together and placed in a pyrolyzer at temperature (300, 400, 500, 600, 700 and 800 ^{o}C) in absence or limited presence of oxygen for two hours. The pyrolyzed (charred) materials were then ground in a grinding machine, and sieved through 250μm sieve, in order to have uniform particles. The charcoal powder was then kept in closed plastic bottle before use to prevent any interaction with air. Finally their performance towards fluoride removal and other physical properties was investigated.

3.2.2. Preparation of Bone Char

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

3.2.3. Preparation of coffee husk Char

The rest coffee husk samples in step **3.3.1** were pyrolyzed at a temperature of 500^{o}C. Then, it was ground and sieved using standard sieves having a mesh size of 250μm to get uniform size powder of bones. Finally the sample stored in a plastic bottle until further use.

Fluoride removal efficiency of individually pyrolyzed bone and coffee husk were conducted as a preliminary test to ensure how thermally activated mixture of bone and coffee husk enhance the efficiency of fluoride removal from aqueous fluoride solution. (See appendix B)

3.3. Characterization of adsorbents

3.3.1. Proximate Analysis

Proximate analysis of activated carbon provides a good idea about the physical properties of sample. According to ASTM D121, proximate analysis is the determination of moisture, volatile matter, fixed carbon, and ash content by prescribed methods.

Moisture content

Moisture content was determined according to ASTM 2867-99. Each mixture of BC and coffee husk char samples (2g) was weighed and dried in an electric muffle (Sx-2.5-12) furnace continuously for a 4h at 120^{o}C and weighed. The drying sample was then constantly reweighed at a 1h interval until a constant weight (w_2) is obtained. The crucible and its content were retrieved and cooled in desiccators. The difference in mass (∂w) was recorded and the moisture content (MC) calculated from Eq. (3.1) as loss in mass on drying divided by initial weight of the sample multiplied by 100.

$$\%MC = \left(\frac{w_1 - w_2}{w_1 - w_3}\right) X\ 100 \quad \text{----------(3.1)}$$

Where, %MC = percentage of moisture 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

Volatile matter content

The percentage of volatile matter of the mixture of BC and coffee husk char samples was determined by the standard method (ASTM D5832 – 98). 2g of each sample was measured on the balance and placed in a crucible. And then, both the sample and the crucible 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 then determined by following the formula:

$$\%VM = \frac{100[100(w_1 - w_2) - M(w_1 - w_3)]}{[(w_1 - w_3)(100 - M)]} \quad \text{----------(3.2)}$$

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

M = % of moisture determined above.

Ash content

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

$$\%Ash = \left(\frac{w_2 - w_3}{w_1 - w_3}\right) x \quad 100 \quad \text{----------(3.3)}$$

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)

3.3.2. Zero point charge (pH_{zpc})

The pH at which the sorbent surface charge has a zero value, is referred to as the point of zero charge (pHpzc). The Isoelectric point or Zero point charge (pH_{zpc}) of the selected samples was measured by using the method described by [72]. 0.1 M of 10 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 one each duplicate 0.5 g of B-CHC was added and mixed for a specified period of time. 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 graphs plotted, the pH_{zpc} (point of zero charge) of the adsorbent would be determined.

3.3.3. Specific surface area

Sears' method was used for the determination of the surface area [73]. A sample containing a one gram mixture of bone and coffee husk char with optimum ratio was acidified with 0.1M HCl to pH 3 – 3.5, the volume was made up to 100cm^3 with deionized water after addition of 20.0g 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. The volume, V required to raise the pH from 4.0 to 9.0 was noted and the surface area would be computed from the following equation:

$$S = 32V-25 \quad (3.5)$$

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. Preparation of adsorbate solutions

A stock solution of 1000mg/L sodium fluoride has been prepared by dissolving 2.21g of sodium fluoride in double distilled water. Standards at a required concentration range have been prepared by appropriate dilution of the stock solution with double distilled water.

The total ionic strength adjustment buffer (TISAB) was prepared following the procedure developed by Agarwal [74]. Accordingly 57mL of glacial acetic acid, 58g of NaCl, 7g of sodium citrate, and 2g of EDTA would be added to 500mL of double distilled water and allowed to dissolve, and then, the pH was adjusted to 5.3 with 6 M NaOH. Finally, the solution was adjusted up to 1,000mL in a volumetric flask mark with double distilled water.

3.5 Calibration of the electrode

30mL of fluoride solutions with different fluoride ion concentrations were prepared in constant intervals 3mL of TISAB was added to each solution. The potential reading of each concentration were taken and the graph of potential (reading in mv) versus the logarithm of concentration (mg/L) was drawn using Microsoft Excel program. Then from the graph, the slope and correlation coefficient (R^2) were used to check the accuracy of the measurement (Figure 3.1).

The prepared concentration of standard fluoride solutions, (2mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L) were used for calibration of fluoride ion selective electrode. For good accuracy, the slope should be 59.2 ± 3mv and the correlation coefficient value close to 1during calibration. Hence as shown from figure 3.1, the slop of regression equation and R^2 value verified that the electrode was well calibrated.

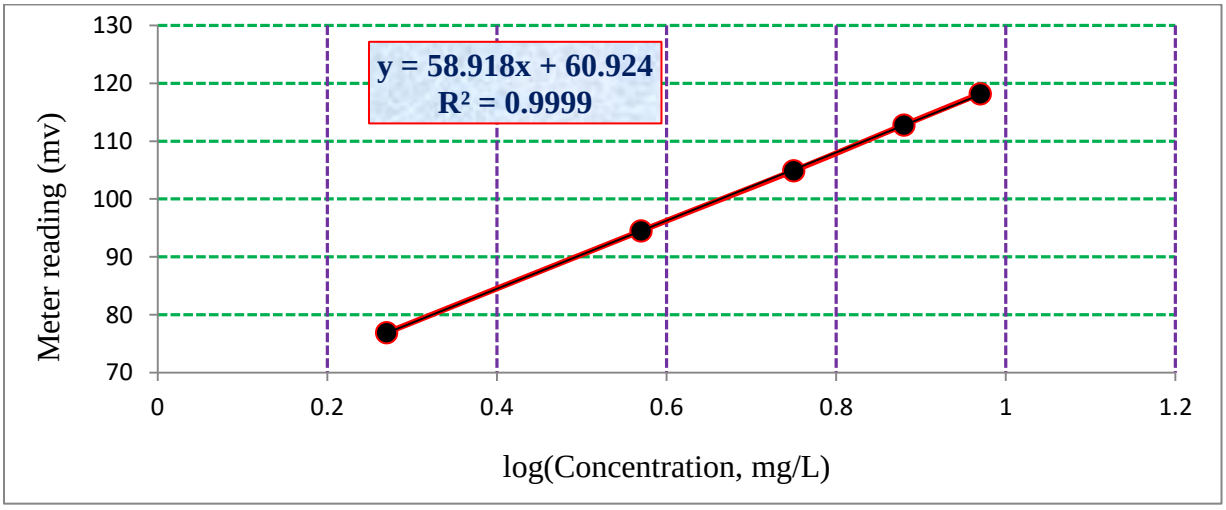


Figure 3.1 Plot for calibration of fluoride ion selective electrode

3.6 Preliminary test

Before conducting optimization experiment, preliminary test were carried out to evaluate the adsorption performance of mixture of individually charred materials at the specified ratio of BC and CHC (3:0, 3:1, 2:1, 1:1, 1:2, 1:3, 0:3) and thermally activated cattle bone and coffee husk mixtures. For this purpose, 50mL of 10mg/L of fluoride standard solution was transferred to two different 100mL plastic beakers containing 6g of BC and CHC mixture added at two different ratios (The ratio of BC and CHC were 1:1 and 2:1). Then, the samples were steered on magnetic stirrer at speed of 200rpm and at contact time of 0.5h. Finally residual fluoride concentration was determined and the results were indicated in appendix B, Table 1. Similarly, 50mL of 10mg/L of fluoride standard solution was transferred to two different 100mL plastic beakers containing 6g of thermally activated cattle bone and coffee husk mixtures prepared at the specific ratio of raw bone to coffee husk ratios of 1:1 and 2:1 to determine the residual fluoride concentration. The results were indicated in appendix B.

The liquid-phase fluoride concentration was measured by taking 40mL of sample filtrate or standards and 10mL of total ionic strength adjustment buffer (TISAB) in a 100mL plastic beaker, and the mixture was stirred uniformly (at stirrer speed of level 3 for 1 min) using magnetic stirrer. The same amount of sample was used throughout the experiment.

3.7 Adsorption study

Batch experiments were conducted using 100mL of aqueous solution containing known fluoride concentration in different plastic beakers to which a weighed fixed mass of B-CHC and weighed amount of fixed ratio of BC and CHC was added. This solution was then stirred continuously at room temperature to achieve equilibrium. A sample were periodically taken out from each beaker and filtered through a Whatman No. 1 filter paper before fluoride analysis. 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 Equation (3.6) and (3.7) respectively.

Percentage removal $= \frac{[Co-Ct]}{Co} * 100$ ..... (3.6)

Adsorption capacity (AC) $= \frac{[Co-Ct]}{m} * V$ ..... (3.7)

Where Co is initial fluoride concentration, Ct is residual fluoride concentration at time t, m is mass of the adsorbent, and V is volume of the solution used in the batch.

3.8 Optimization of different parameters

Optimization is carried out to make some parameters function at their best by varying one parameter while keeping other parameters constant. The dosage range was selected based on the preliminary test results in the optimum ratio of 2:1 bone-to-coffee husk char at 500^{o}C. The effect of major parameters like adsorbent dose, contact time, pH, and initial fluoride concentration were optimized.

3.8.1 Effect of Contact Time

Residual F^- concentrations were measured for different contact time of adsorption (0.5, 1, 4, 6, 8, 14 and 24 hours) with 4g of the selected adsorbent mixture in 50mL of fluoride solution in order to investigate the effect of contact time. Other parameters, pH, concentration of the solution remain constant.

3.8.2 Effect of adsorbent dosage

Experimental investigations were carried out at different dosages of adsorbent 2, 4, 6 and 10 grams in 50mL of fluoride solution with 10mg/L initial fluoride concentration at 2h contact times.

3.8.3 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 6.73 was adjusted to pH values of 3, 5, 7, 9, and 11 using 1M HCl and 1M

NaOH. Then 4g of the selected mixture of adsorbent (B-CHC_{500} {21}) was added to 40mL of the test solutions separately and steered for 1h to reach equilibrium. Residual fluoride ion concentration was analyzed in each experiment after 1h contact time. Finally pH versus percentage removal was plotted to describe the adsorption behavior of the adsorbent at each pH.

3.8.4 Effect of initial fluoride concentration

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

3.9 Experiments for adsorption isotherms

Adsorption isotherms were determined using treated adsorbents at room temperature. Data for plotting isotherm were obtained by mixing 50mL a constant fluoride ion concentration of 20 mg/L with the selected adsorbent dosages of (4, 8, 12, 16 and 20 g). The mixture was agitated for 5 h to ensure the equilibrium, and residual fluoride was determined after filtration. Based on the data generated, adsorption isotherms were plotted.

3.10 Experiments for adsorption kinetics

Adsorption kinetics was determined using constant surface loading of 6, 12 and 15 g selected adsorbents corresponding to the initial fluoride concentration of 10, 20 and 30 mg/L, respectively with 50mL volume of the solution. Residual fluoride concentrations were measured at different contact time intervals of 0.5, 1, 2, 4, 6, 8 and 12h by taking 7 samples periodically.

4. RESULTS AND DISCUSSION

4.1 Effect of temperature on the removal efficiency of adsorbents

Based on the preliminary test shown in appendix B and Figure 4.1 , sample B-CHC_{500} {21} 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-CHC adsorbents.

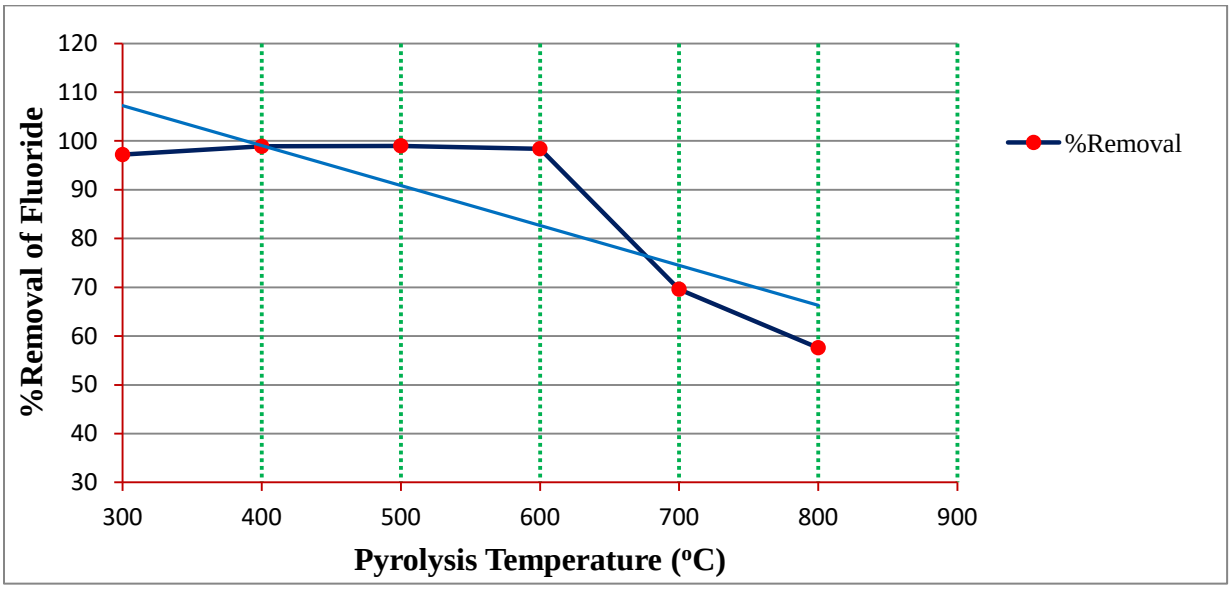


Figure 4.1 The effect of pyrolysis temperature on the adsorption capacity of the adsorbents B-CHC (21).

As shown in Figure 4.1, the highest fluoride removal efficiency was observed for B-CHC (21) adsorbents prepared in range of 400^{o}C to 600^{o}Cand less removal efficiency was obtained for the adsorbent produced below 400^{o}C and above 600^{o}C. The best adsorbent (B-CHC) was relatively obtained at pyrolysis temperature of 500^{o}C which resulted adsorption of 99.00% fluoride (Figure 4.1, Appendix B). This implies that as the temperature increased from 400^{o}C to 500^{o}C 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^{o}C results in decreasing the performance of bone-coffee husk char, since at high temperature the

hydroxyapatite structure starts to collapse and this result in losing ions that play role in ion exchange. In addition to best percentage removal, the color and odor of treated fluoride water was clear and normal (refer appendix B). This is in agreement with the hypothesis that generation of bone char material at high temperatures damages the hydroxyapatite structures [75].

4.2 Characterization of Thermally Activated Bone-Coffee Husk Char Adsorbents

4.2.1 Proximate analysis

Table 4.1 Proximate analysis of adsorbents prepared at a temperature of 500^{o}C (B-CHC$_{500}$)

Temperature (^{o}C)	Treatments	%Moisture content (mean ± SD)	%Volatile matter content (mean ± SD)	%Ash content (mean ± SD)	%Fixed Carbon content
500	2:1	5.00 ± 0.01	2.63 ± 0.01	23.00 ± 0.02	69.37 ± 0.013
500	1:1	3.67 ± 0.04	3.80 ± 0.04	28.33 ± 0.18	64.20 ± 0.087

The proximate analyses presented in Table: 4.1 showed that adsorbent prepared in 2:1 ratio is better than that of 1:1 ratio. 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 charcoal in 2:1 ratio can be an excellent raw material for adsorbents to be used in defluoridation of drinking water. (Refer appendix D for more information)

Volatile content in activated carbon is mainly due to the presence of non carbonaceous matters. 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 adsorptivity of adsorbent since it reduces the mechanical strength of carbon [72].

The presence of high moisture content (heterogeneous oxygen groups) on the adsorbent surface is known to reduce the adsorption capacity due to adsorption of water onto these groups by means of hydrogen bonding [2]. 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 [13].

4.2.2 Zero point Charge (pH_{zpc}) for selected adsorbent

Table 4.2 Experimental data for determination of zero point charge

$pH_{initial}$	2	3	4	5	6	7	8	9	10	11
pH_{final}	3.12	3.80	4.74	5.61	6.51	7.42	8.09	8.68	9.11	9.51
ΔpH (pH_f - pH_i)	1.12	0.80	0.74	0.61	0.51	0.42	0.09	-0.32	-0.89	-1.49

As shown in table 4.2 and figure 4.2, prepared adsorbent has a high pH point of zero charge (pH_{PZC} ~ 8.2). This indicates that it has an adsorption affinity for many negatively charged particles including fluoride ions [20, 50]. 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-CHC 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, knowledge of this value helps deciding at which pH value one should work during adsorption studies.

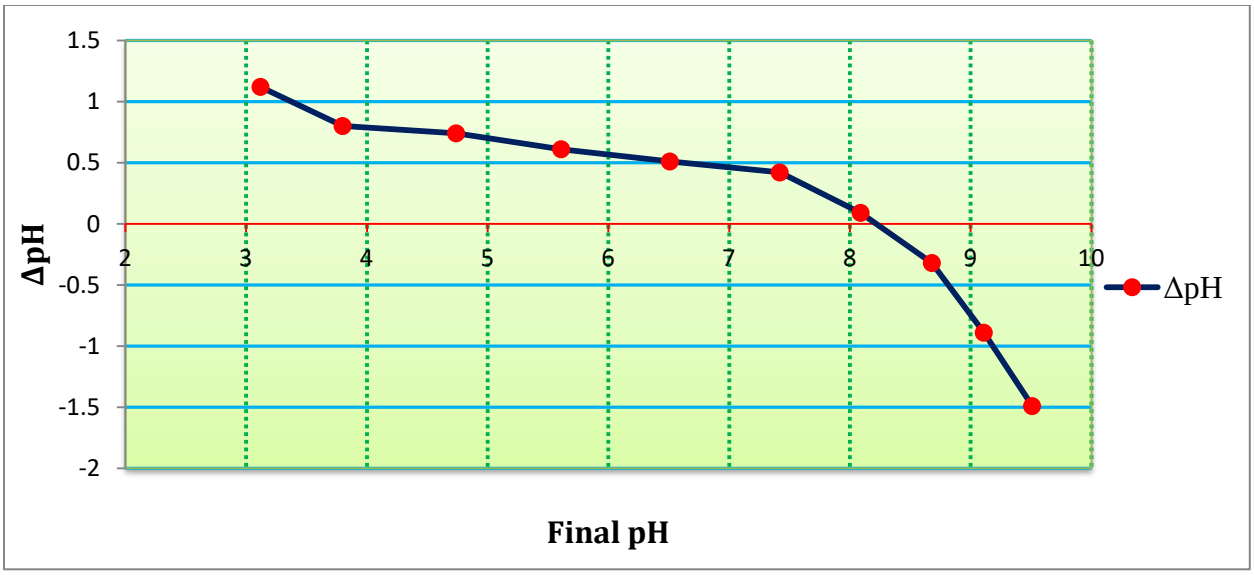


Figure 4.2 Graph of ΔpH versus final pH of the selected adsorbent to determine pH_{pzc}.

4.2.3 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 5.4ml whereas the corresponding surface area is 147.8m^2/g. As compared with Enyew *et al.*, 2017 result (112.6m^2/g) for adsorbent's particle size of <425µm, this result verified that the prepared adsorbent of particle size <250µm has large surface area which can perform better fluoride adsorption capacity.

4.3 Effect of Different Parameters on the Adsorption of Fluoride

4.3.1 Effect of Solution pH on the Adsorption

Table 4.3 The effect of pH on percent removal of fluoride

pH	Dose (g)	Volume (mL)	C_o (mg/L)	Final fluoride concentration, C_t (mg/L)				% removal	AC (mg/g)
				C_t1	C_t2	C_t3	Mean ± SD		
3.00	4.00	40.00	10.00	0.09	0.13	0.11	0.11±0.02	98.9	0.0989
5.00	4.00	40.00	10.00	0.14	0.13	0.12	0.13±0.01	98.7	0.0987
6.73	4.00	40.00	10.00	0.14	0.14	0.14	0.14±0.00	98.6	0.0986
7.00	4.00	40.00	10.00	0.15	0.12	0.15	0.14±0.02	98.6	0.0986
9.00	4.00	40.00	10.00	0.21	0.17	0.19	0.19±0.02	98.1	0.0981
11.00	4.00	40.00	10.00	0.24	0.22	0.21	0.22±0.02	97.8	0.0978

Table 4.3 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 treate drinking water. Therefore as the pH_{pzc} of the selected adsorbent is around 8.2, it is better to work at the pH of 6.73 which is the pH without adjusting and normal pH of the sodium fluoride solution. This is because at this pH, the WHO guide line value (1.5mg/L) is well achieved since 98.6% removal capacity gives 0.14mg/L residual fluoride concentration for this batch experiment. In addition to this the color of treated fluoride water was appeared light yellow. This may arise because of the solubility of HA in highly acidic solution. (See appendix C, figure 2)

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 [76], hence, the ionic interaction between the bone-coffee husk char surface and the fluoride ion could be another way fluoride is adsorbed onto the bone-coffee husk char in addition to substitution of the active functional groups [77].

The effect of pH on the adsorption was due to electrostatic interactions between the F^- anions in solution and the surface charge of bone-coffee husk char [78]. When the solution pH is below 7, the F^- anions were attracted to the positively charged surface of the bone-coffee husk char, caused by the protonation of the hydroxyapatite hydroxyl groups, thus favoring F^- accumulation onto the surface. The surface charge of bone-coffee husk 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-coffee husk char. At pH above 7, adsorption of F^- was very slight because the bone-coffee husk char surface is negatively charged, due to deprotonation of the hydroxyapatite hydroxyl groups, causing a mutual repulsion between F^- anions and the bone-coffee husk 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.

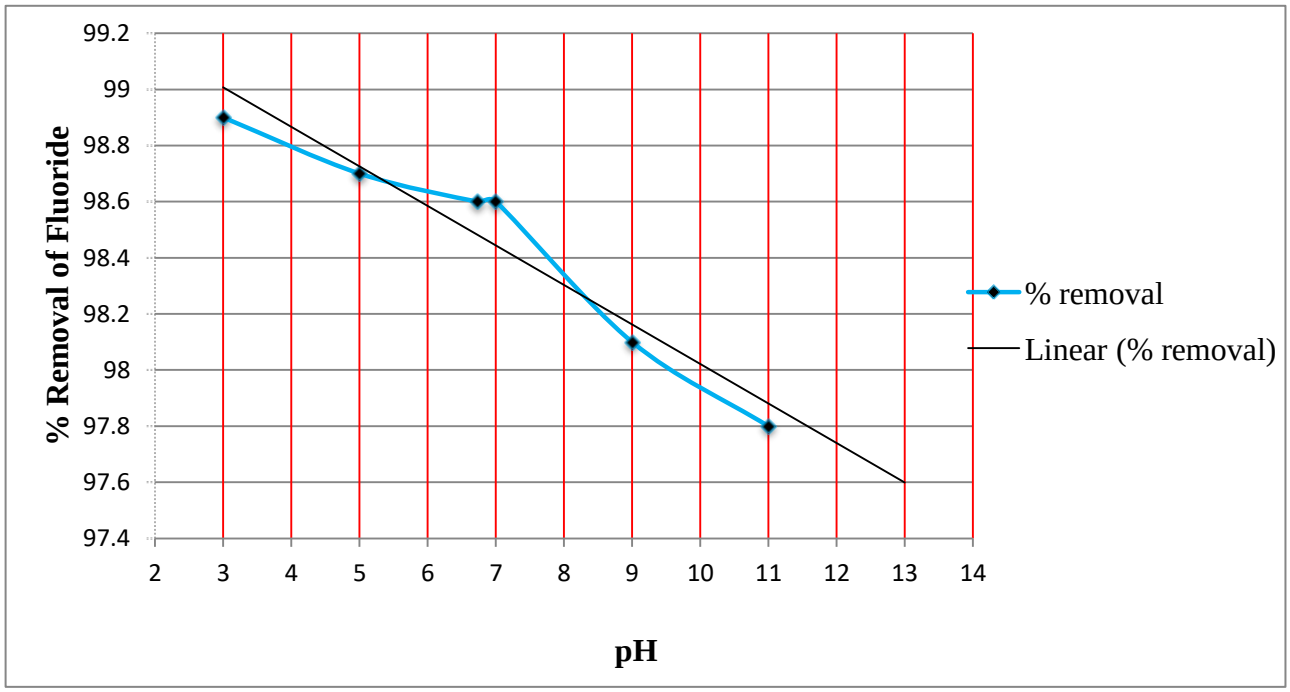


Figure 4.3 The effect of pH on percent removal of fluoride

4.3.2 The Effect of Contact Time

Table 4.4 The effect of contact time on percent removal of fluoride

Contact time (hr)	Dose (g)	Volume (mL)	C_o (mg/L)	Final fluoride concentration (mg/L)				Average % removal	Average AC (mg/g)
				C_t1	C_t2	C_t3	Mean ± SD		
0.50	4.00	50	10.00	0.59	0.60	0.61	0.60±0.01	94.0	0.1175
1.00	4.00	50	10.00	0.53	0.50	0.54	0.52±0.02	94.8	0.1185
2.00	4.00	50	10.00	0.31	0.32	0.36	0.33±0.03	96.7	0.1209
4.00	4.00	50	10.00	0.15	0.19	0.18	0.17±0.02	98.3	0.1228
6.00	4.00	50	10.00	0.13	0.12	0.12	0.12±0.01	98.8	0.1235
8.00	4.00	50	10.00	0.09	0.10	0.08	0.09±0.01	99.1	0.1239
14.00	4.00	50	10.00	0.08	0.09	0.09	0.09±0.01	99.1	0.1239
24.00	4.00	50	10.00	0.09	0.09	0.09	0.09±0.00	99.1	0.1239

It was shown in Table 4.4 that, as contact time increases, percentage removal also increases initially and reduces gradually with time and 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-coffee husk char. This trend was also reported by other studies on defluoridation processes [6, 71]. This is due to faster saturation of the active sites with time. This implies that the bone-coffee husk 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-coffee husk char.

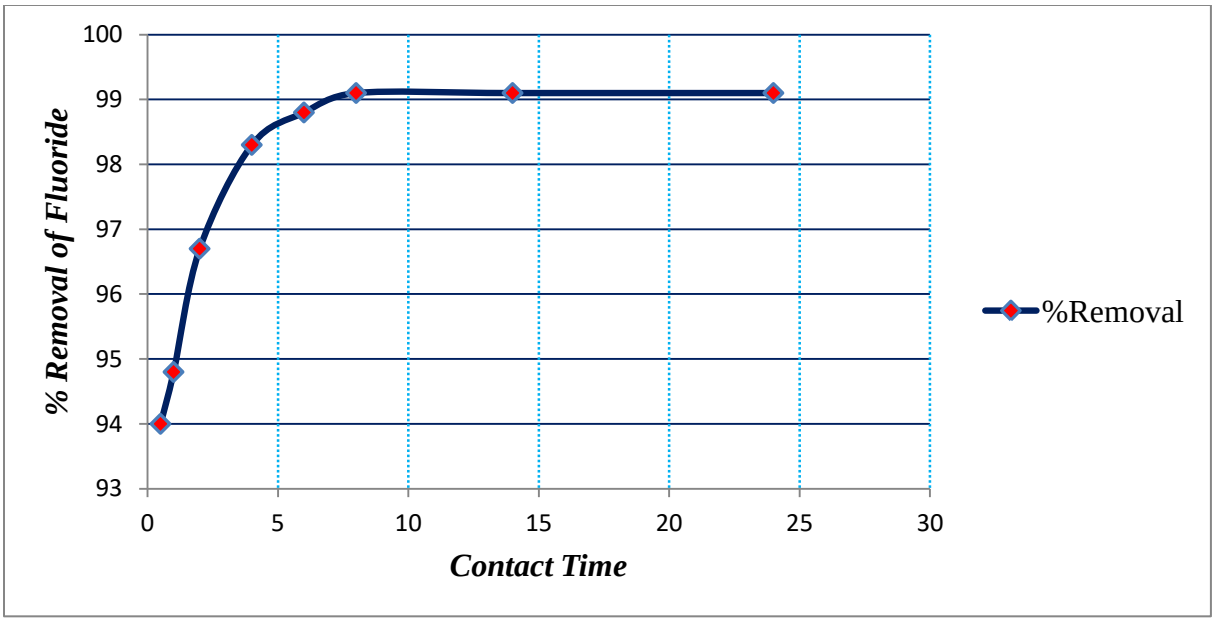


Figure 4.4 Effect of contact time on percent removal of fluoride

4.3.3 The Effect of Adsorbent Dose

Table 4.5 Effect of adsorbent dose on fluoride removal

Dose (g)	Volume (mL)	C_o (mg/L)	Final fluoride concentration (mg/L)				% removal	AC (mg/g)
			C_t1	C_t2	C_t3	Mean ± SD		
2.00	50.00	10.00	1.89	1.9	1.93	1.91±0.02	80.9	0.2023
4.00	50.00	10.00	0.93	0.97	0.94	0.95±0.02	90.5	0.1132
6.00	50.00	10.00	0.45	0.46	0.46	0.46±0.01	95.4	0.0795
10.00	50.00	10.00	0.25	0.3	0.34	0.30±0.05	97.0	0.0485

As shown in Table 4.5, the removal capacity of the adsorbent for fluoride increased with increasing the B-CHC 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 [77]. 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.

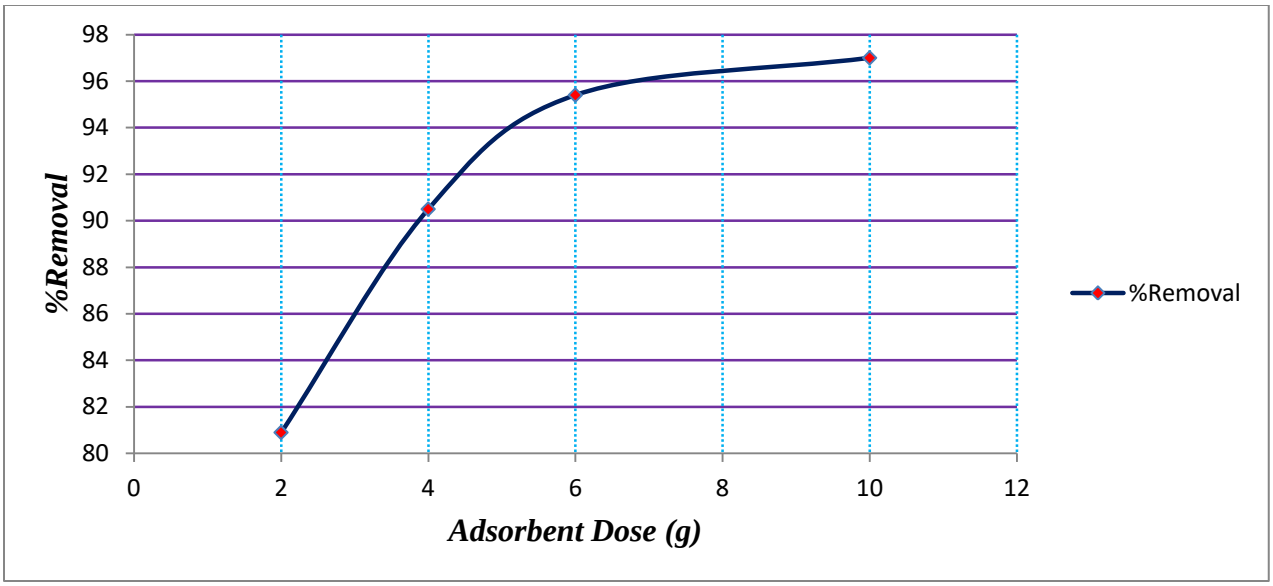


Figure 4.5 Effect of adsorbent dose on percentage removal of fluoride

4.3.4 The Effect of Initial Fluoride Concentration

Table 4.6 The effect of initial fluoride concentration on %fluoride removal

C_o (mg/L)	Volume (mL)	Time	Dose (g)	Final fluoride concentration (mg/L)				% removal	AC (mg/g)
				C_t1	C_t2	C_t3	Mean ± SD		
5	30.00	4.00	6.00	0.08	0.08	0.07	0.08±0.01	98.4	0.0369
10	30.00	4.00	6.00	0.31	0.32	0.35	0.33±0.02	96.7	0.0726
15	30.00	4.00	6.00	1.50	1.45	1.49	1.48±0.03	90.1	0.1014
20	30.00	4.00	6.00	4.18	4.21	4.16	4.18±0.03	79.1	0.1186
25	30.00	4.00	6.00	7.20	7.20	7.50	7.30±0.07	70.8	0.1328
30	30.00	4.00	6.00	10.38	10.42	10.44	10.41±0.03	65.3	0.1469

As shown in table 4.6, for a given mass of adsorbent the fluoride removal capacity increases with increasing initial fluoride concentration. This is because, due to increased diffusion of fluoride to adsorption sites and utilization of less active sites of the adsorbent [83].

As shown in the Table 4.6, the initial fluoride concentration showed influence on the removal capacity of the B-CHC, where the amount of fluoride adsorbed increased with increasing initial fluoride concentration from 0.037 to 0.147 mg/g at initial concentration ranging from 5-30mg/L. This is attributable to the increased concentration gradient between the liquid and the solid phases which increasingly go beyond the mass transfer resistance between the solution and the B-CHC.

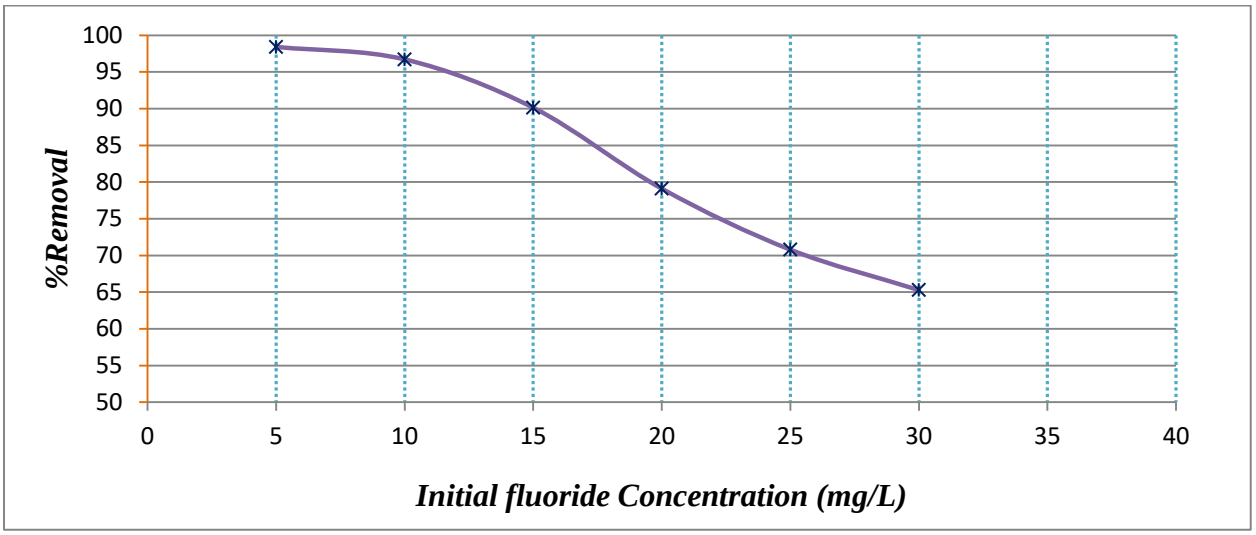


Figure 4.6 Effect of initial fluoride concentration on percentage removal

As shown in Figure 4.6, the removal efficiency (%removal) of the adsorbent decreases with increasing initial fluoride concentration. The higher percent 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 percent removal efficiency with the increase in initial fluoride concentration is lack of sufficient surface area to accommodate more fluoride ions available in the solution [71].

4.4 Application to Real Water Samples

As an approximation of the results of the present work for application to a real problem, fluoride containing water collected from East Shoa zone farm area which is located near to Mojo town,

Ethiopia. Two different water samples were investigated to determine the amount of fluoride in the sample. One of the water samples is called Bofo water which is found in Meki woreda whereas the other water sample is called Huluka water which is found in Dugda-bora woreda. The water samples were found to contain 8.30mgF^-/L and 6.61mgF^-/L 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 B-CHC prepared at 500^oC was investigated. All test results indicated in less than one milligrams of fluoride per litter (mg F^-/L) remaining after adsorption for contact time of 8h. These results show that thermally activated B-CHC is a suitable material for the removal of fluoride ion. The result of percentage removal is given below in the Table 4.7.

The maximum fluoride required in drinking water according to World Health Organization (WHO) is 1.5mg/L. This requirement can be achieved by 85% removal capacity of bone-coffee husk char since the residual fluoride concentration at this percent is below 1.5mg/L for 8.30mg/L and 6.61mg/L initial F^- concentration.

The result obtained for naturally fluoridated water differs with that of synthetically fluoridated water (as shown in Table 4.7) for some points. The reason for this might be attributed to the presence of other ions competing with fluoride for active site. The condition resulting low fluoride removal, it may be the best condition for other ion removal in prefers to fluoride ion.

Table 4.7 Adsorption test result for naturally fluoridated water at neutral pH.

Name of sample water	Intial 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
Bofo water	8.30	0.513	6g	93.82	Normal	Normal
Huluka water	6.61	0.294	6g	95.55	Normal	Normal
Artificially fluoridated water	10.00	0.100	6g	99.00	Normal	-

4.5 Adsorption Isotherm Model

Table 4.8 Experimental results of adsorption isotherm model.

C_o (mg/L)	Dose (g)	C_e (mg/L)	q_e(mg/g)	logC_e	logq_e	C_e/q_e
20	4	1.15	0.471	0.061	-0.327	2.44
20	8	0.72	0.241	-0.143	-0.618	2.99
20	12	0.43	0.163	-0.367	-0.788	2.64
20	16	0.28	0.123	-0.553	-0.910	2.28
20	20	0.23	0.099	-0.638	-1.000	2.32

4.5.1 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 logq_e versus logC_e (Figure4.7)

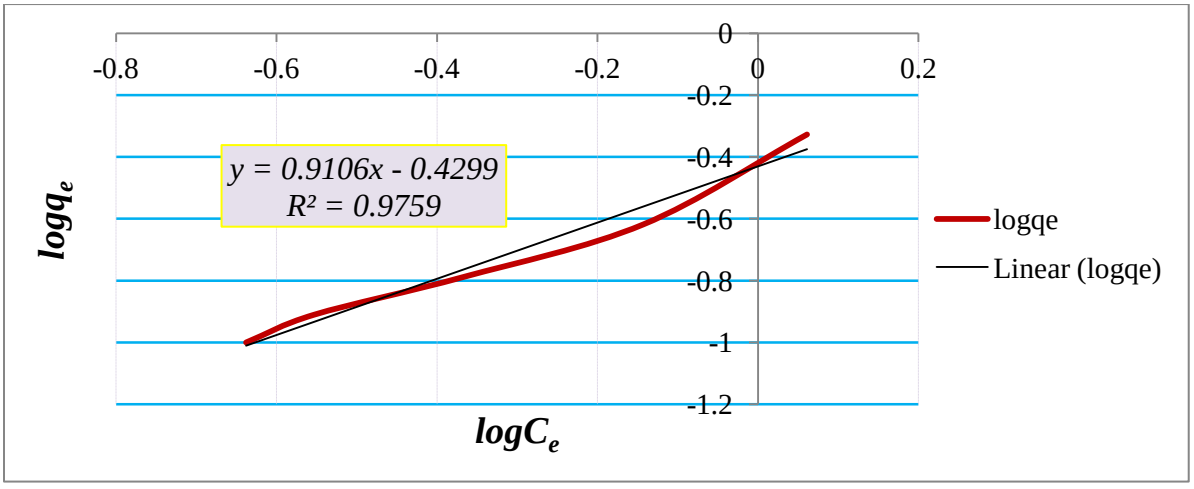


Figure 4.7 Plot of fitting equilibrium data on Freundilich isotherm.

4.5.2 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 4.8) 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 and k_1.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L also known as the separation factor, given by equation (2.5). The value of equilibrium parameter R_L (Table 4.9) is in the range of $0<R_L<1$ which reflects the favorable adsorption process. This indicated to the fact that the sorption process was favorable and the adsorbent employed exhibited a good potential.

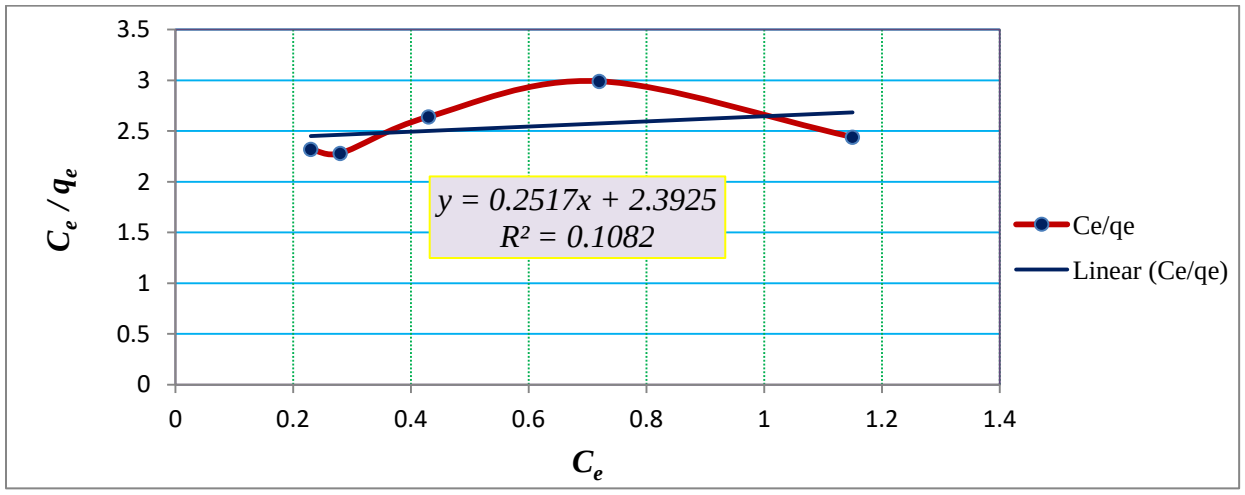


Figure 4.8 Plot of fitting equilibrium data on Langmuir isotherm.

The constant parameters for the Langmuir and Freundlich models are calculated and presented in Table 4.9. 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-CHC is 0.1082 and R^2 value of the Freundlich model for the B-CHC is 0.9759. It is evident from a comparison of the values of

coefficient of correlation (R^2) that the equilibrium adsorption of fluoride on to bone-coffee husk 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 [79]. Based on these results, it can be concluded that fluoride is effectively adsorbed on bone-coffee husk 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 B-CHC. The adsorption capacity and adsorption intensity for the Freundlich model at equilibrium (q_e) are 0.372mg/g and 1.098 respectively.

Table 4.9 Adsorption isotherm model parameters

Freundlich Model	**Langmuir Model**
K_f = 0.372mg/g	q_m = 3.97mg/g
n = 1.083	K_l = 0.105L/mg
R^2 = 0.9759	R^2 = 0.1082
	R_L = 0.3226

4.6 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 4.10 and 4.11 , 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.

4.6.1 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 [80]. 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, from other first-order equations using liquid phase concentrations, C. 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 coffee husk [81] and bone char [82]. The values of log ($q_e - q_t$) were linearly correlated with t. The plot of log ($q_e - q_t$) versus t should give a linear relationship from which k_1 and q_e can be determined from the slop and intercept of the plot, respectively.

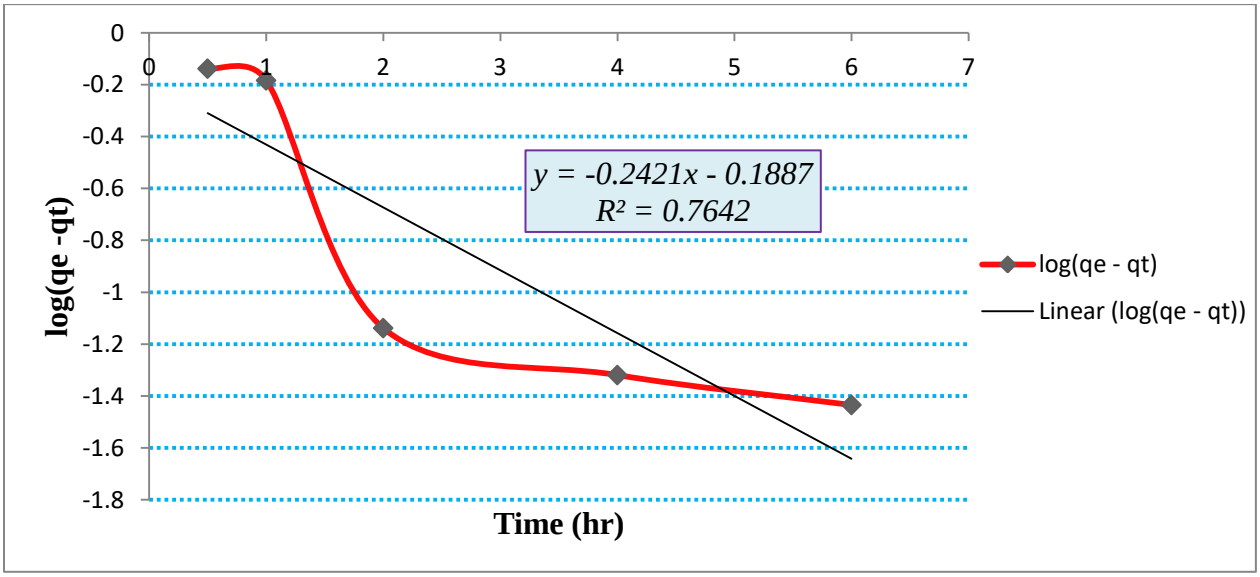


Figure 4.9 Pseudo first order kinetics curve for 30mg/L

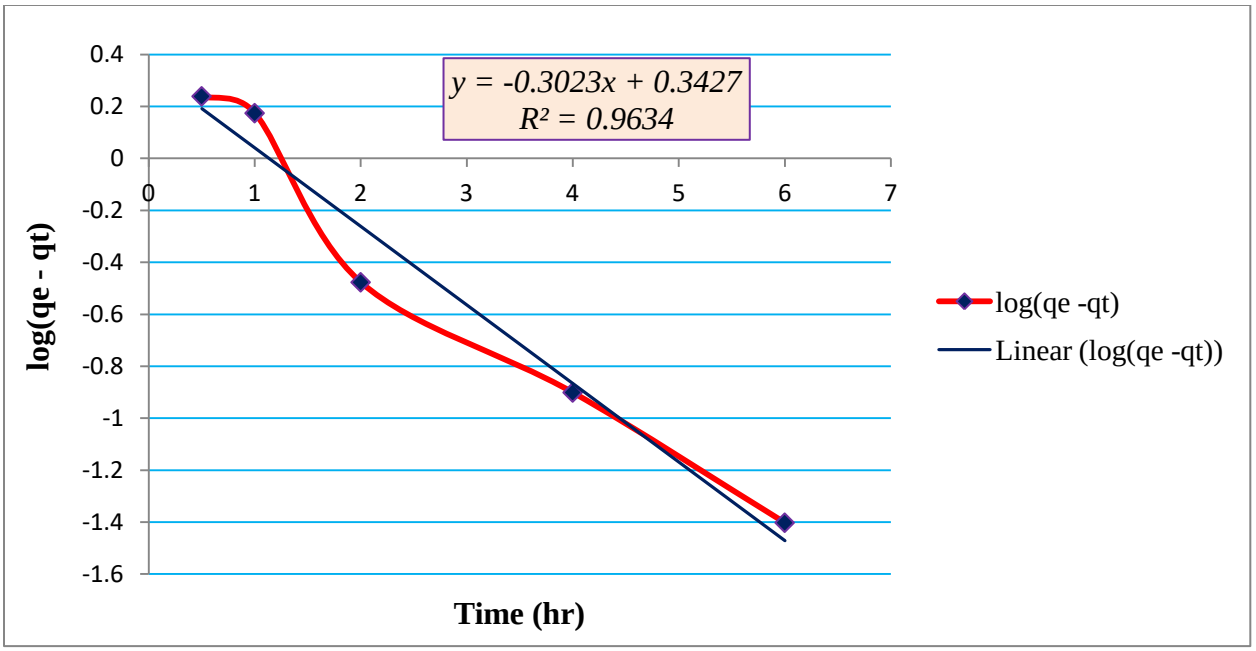


Figure 4.10 Pseudo first order kinetics curve for 20mg/L

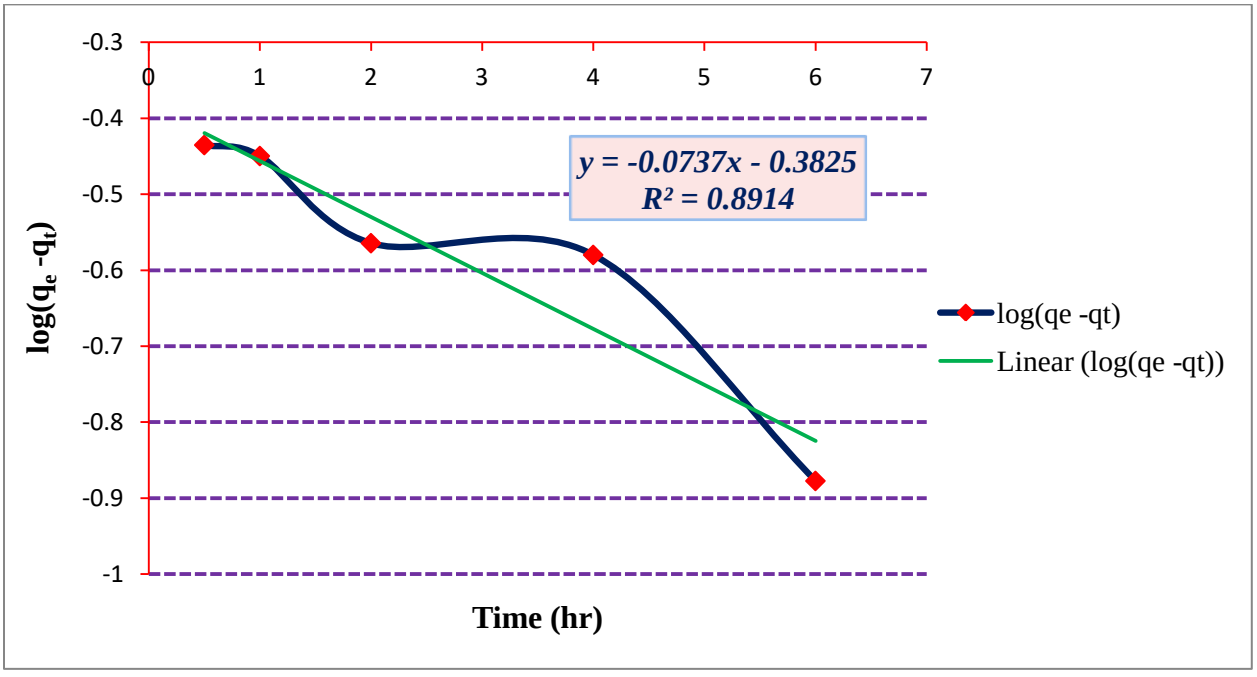


Figure 4.11 Pseudo first order kinetics curve for 10mg/L

Table 4.10 Pseudo first order kinetics model data

Time (min)	Initial fluoride concentrations					
	(30mg/L)		(20mg/L)		(10mg/L)	
	q_t (mg/g)	$\log(q_t - q_e)$	q_t (mg/g)	$\log(q_t - q_e)$	q_t (mg/g)	$\log(q_t - q_e)$
30	5.20	-0.1379	2.248	0.2389	1.748	-0.4353
60	5.272	-0.1831	2.488	0.1742	1.760	-0.4498
120	5.8552	-1.1379	3.648	-0.4768	1.8424	-0.5645
240	5.880	-1.3188	3.856	-0.9010	1.8520	-0.5800
360	5.8912	-1.4342	3.942	-1.4023	1.9824	-0.8775
480	5.9280	-	3.9816	-	2.1150	-
720	5.9280	-	3.9816	-	2.1150	-
Pseudo first order adsorption kinetics parameters						
Intercept($\log q_e$)	-0.189		0.343		-0.383	
K_1	0.558		0.696		0.170	
R^2	0.7642		0.9634		0.8914	

4.6.2 Pseudo second order kinetics

Again 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 q_e and k_2 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 are calculated and put in a Table 4.11.

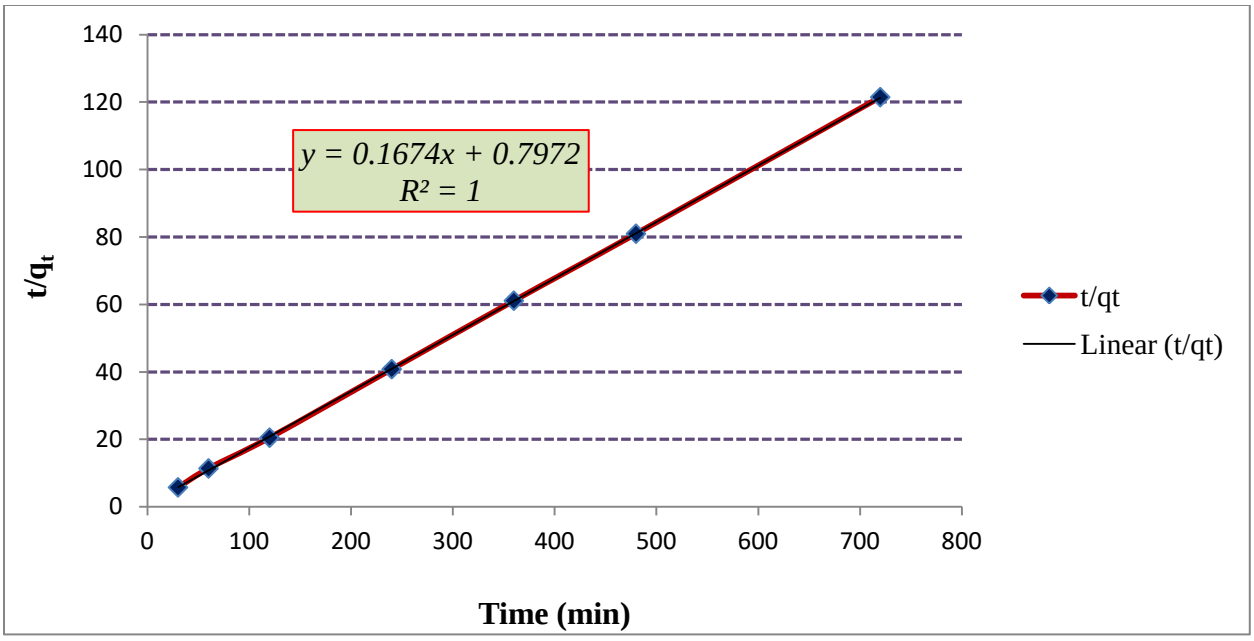


Figure 4.12 Pseudo second order kinetics curve for 30mg/L

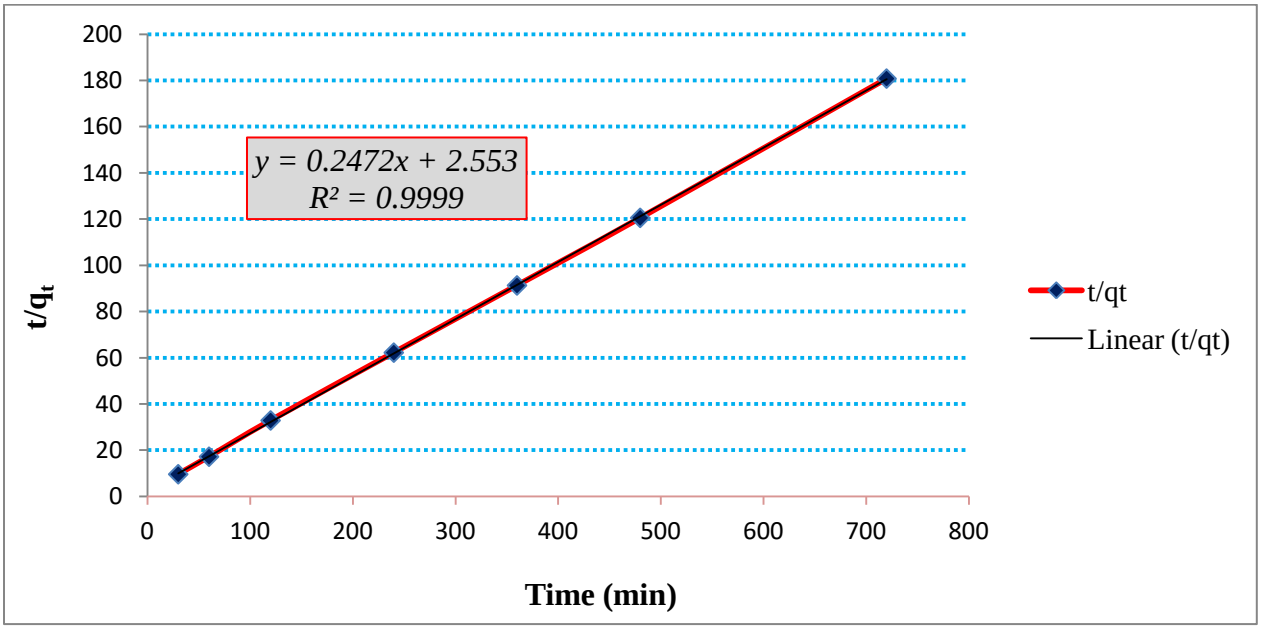


Figure 4.13 Pseudo second order kinetics curve for 20mg/L

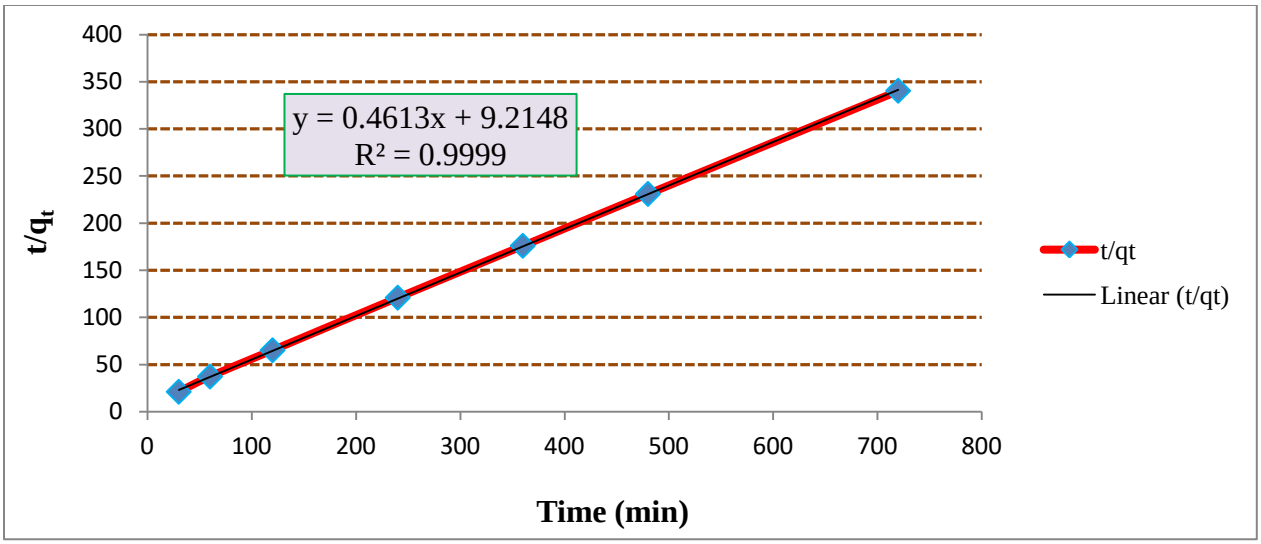


Figure 4.14 Pseudo second order kinetics curve for 10mg/L

Table 4.11 Pseudo second order kinetics model data

Time (min)	Initial fluoride concentrations					
	(30mg/L)		(20mg/L)		(10mg/L)	
	q_t (mg/g)	t/q_t	q_t (mg/g)	t/q_t	q_t (mg/g)	t/q_t
30	5.20	5.7692	3.1180	9.6216	1.5420	21.0822
60	5.272	11.3809	3.4880	17.2018	1.6110	37.2439
120	5.8552	20.4946	3.6480	32.8947	1.8424	65.1324
240	5.880	40.8163	3.8560	62.2407	1.9850	120.9068
360	5.8912	61.1081	3.9420	91.3242	2.0460	175.9531
480	5.928	80.9717	3.9816	120.5546	2.0780	230.9913
720	5.928	121.4575	3.9816	180.8318	2.0780	346.4870

Pseudo first order adsorption kinetics parameters			
	(30mg/L)	(20mg/L)	(10mg/L)
Intercept($1/K_2qe^2$)	0.797	2.55	9.215
K_2	3.52×10^{-2}	2.39×10^{-2}	2.31×10^{-2}
R^2	1	0.9999	0.9999

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-coffee husk 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, 0.9999 and 0.9999 for the concentration of 30mg/L, 20mg/L and 10mg/L respectively.

From the given graphs shown above and the parameters in Table 4.10 and Table 4.11, 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 [83, 6].

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

- Based on the results of this work, it is concluded that fluoride removal efficiency of bone and coffee husk can be improved by thermal activation of the two mixtures. The char prepared by mixing bone and coffee husk showed best defluoridation capacity than individually (separately) pyrolyzed coffee husk or bone char.

- The pyrolysis temperature has major effect in the removal efficiency of bone-coffee husk char and the highest removal efficiency was obtained in the temperature range of 400^{o}C and 500^{o}C. Beyond temperature of 500^{o}C, percentage removal decreased. However, it is better to use 500^{o}C in order to avoid color and taste effect. The results also indicated that increase in adsorption with increase in initial concentration, adsorbent dose and contact time.

- The pH_{ZPC} indicated that the activated adsorbent has basic surface functional group. Hence, the pH has indicated better adsorption efficiency at 3 but for this study around normal pH value (6.73) of fluoride solution was considered.

- Furthermore, when considering the adsorption isotherm, the fluoride adsorption was found to be best fitted with the Freundlich isotherm than the Langmuir isotherm which indicating that the bone char media was not a homogenous media. Moreover, the kinetic results obtained from this study fitted well with the pseudo second order kinetic model.

- In general, bone-coffee husk charcoal can be used efficiently and effectively for fluoride removal from drinking water with appropriate selection of synthesis conditions and preparation processes.

5.2 Recommendations

Even though the research covered some areas concerning fluoride, including the occurrence and distribution, health effects, as wells as the development of fluoride adsorbent material, there are still many aspects that were either not covered or require further understanding as indicated below, and recommendations for further research studies:

- Further improvements of the adsorption capacity of the bone-coffee husk charcoal-based fluoride adsorbent need to be investigated to enhance the practical and economic capability, and for its possible use in large centralized systems.
- Many researchers reported only a first cycle of adsorbent regeneration however further investigation need to be conducted on the possibility of multiple regeneration.
- An environmental impact assessment of the production and disposal after use of bone-coffee husk charcoal also needs to be conducted, and mitigation measures have to be identified for any potential negative impacts on the environment.
- Natural water may contain many anions that compete with fluoride for adsorption such as HCO_3^-, SO_4^{2-}, and Cl^- [84]. Therefore the effect of other ions should be investigated so that it helps to selectively use the sorbent in preference to other ions.
- The processes in this thesis is basically done on the small scale so it can be tried to extend it to large scale process, that way it can be used to remove fluoride from drinking water on a mass level.
- The design of appropriate and automated equipments is required for future studies.

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7. APPENDICES

Appendix A. Effect of charring temperature on charcoal color

Figure 4.1 Charcoal obtained from bone and coffee husk at different pyrolysis temperature

Appendix B Preliminary test results

Table 1 Effect of pyrolysis temperature on the color and smell of treated fluoridated water.

Treated sample ID	Color of treated water	Smell of treated water
B-CHC_{300}{21}	yellow	Bad
B-CHC_{400}{21}	Slightly yellow	Bad
B-CHC_{500}{21}	normal	none
B-CHC_{600}{21}	Normal	none
B-CHC_{700}{21}	Normal	none
B-CHC_{800}{21}	Normal	none

Table 2 different ratios of BC-to-CHC both at 500^{o}C and their percentage removal of fluoride at constant pH=6.73, 6g adsorbent dose, volume (100mL) and particle size of <250µm with initial concentration of 10mg/L

Adsorbents ratio BC : CHC	C_o (mg/L)	Final fluoride concentration (mg/L)				%removal	AC (mg/g)
		Trial 1	***Trial 2***	***Trial 3***	***Average***		
3-to-0	10.00	0.14	0.12	0.11	0.12	98.77	0.1646
3-to-1	10.00	0.13	0.12	0.14	0.13	98.70	0.1645
2-to-1	10.00	0.16	0.14	0.15	0.15	98.50	0.1642
1-to-1	10.00	0.60	0.64	0.62	0.62	93.80	0.1563
1-to-2	10.00	1.13	1.15	1.14	1.14	88.60	0.1477
1-to-3	10.00	2.52	2.54	2.55	2.54	74.63	0.1244
0-to-3	10.00	8.98	9.01	8.86	8.95	10.50	0.0175

Table 3 1:1 ratio of B-CHC and their percentage removal of fluoride at constant pH=6.73, 6g adsorbent dose, volume (100mL) and particle size of <250µm with initial concentration of 10mg/L.

Treated sample ID	C_o (mg/L)	Final fluoride concentration (mg/L)				%removal	AC (mg/g)
		Trial 1	***Trial 2***	***Trial 3***	***Average***		
B-CHC_{300}{11}	10.00	0.20	0.19	0.18	0.19	98.10	0.1635
B-CHC_{400}{11}	10.00	0.16	0.16	0.19	0.17	98.30	0.1638
B-CHC_{500}{11}	10.00	0.12	0.13	0.11	0.12	98.80	0.1647
B-CHC_{600}{11}	10.00	0.14	0.16	0.15	0.15	98.50	0.1642
B-CHC_{700}{11}	10.00	0.30	0.29	0.28	0.29	97.10	0.1618
B-CHC_{800}{11}	10.00	0.85	0.86	0.84	0.85	91.50	0.1525

Table 4 2:1 ratio of B-CHC and their percentage removal of fluoride at constant pH=6.73, 6g adsorbent dose, volume (100mL) and particle size of <250µm with initial concentration of 10mg/L.

Treated sample ID	pH	C_o (mg/L)	Final fluoride concentration (mg/L)				Average % of F^- removal	Average value of q_e (mg/g)
			Trial 1	Trial 2	Trial 3	Mean ± SD		
B-CHC_{300}{21}	6.73	10.00	0.28	0.27	0.29	0.28±0.01	97.20	0.1620
B-CHC_{400}{21}	6.73	10.00	0.11	0.12	0.10	0.11±0.01	98.90	0.1648
B-CHC_{500}{21}	6.73	10.00	0.09	0.10	0.11	0.10±0.01	99.00	0.1650
B-CHC_{600}{21}	6.73	10.00	0.16	0.15	0.17	0.16±0.01	98.40	0.1640
B-CHC_{700}{21}	6.73	10.00	3.00	3.08	3.04	3.04±0.04	69.60	0.1160
B-CHC_{800}{21}	6.73	10.00	4.22	4.26	4.24	4.24±0.02	57.60	0.0960

Note that {21} represents 2:1 ratio of bone-to-coffee husk and the subscripts from 300-800 represents the pyrolysis temperature, (C_t1, C_t2 and C_t3) are residual fluoride concentration at trial 1, 2, and 3, respectively. SD is standard deviation.

Appendix C: Colors of treated fluoride water.

Figure 1 Photograph of treated fluoride water colors with 2:1 ratio of B-CHC prepared at pyrolysis temperature of 300-800 ^{o}C.

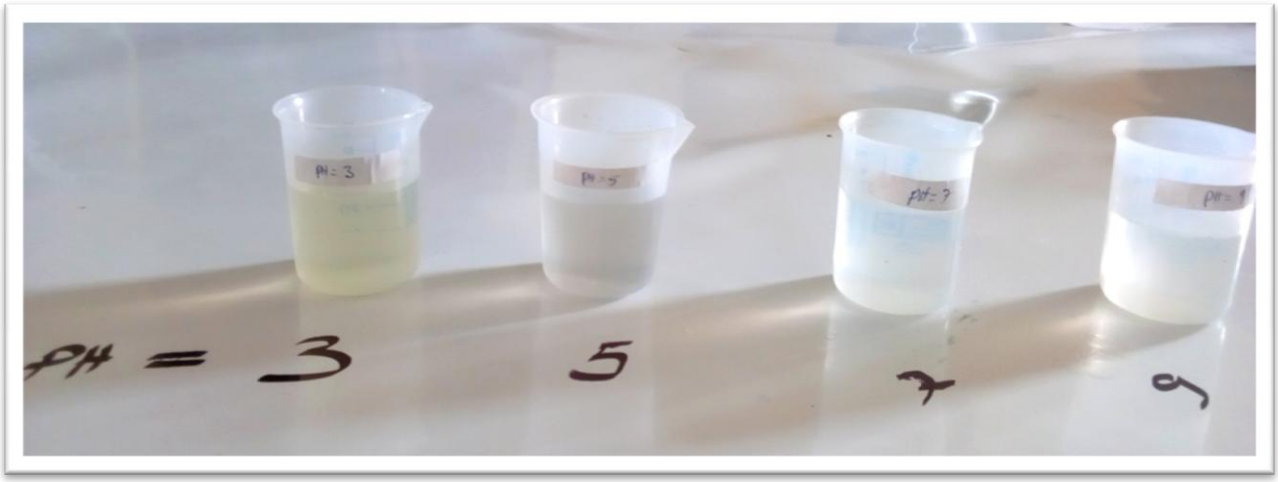

Figure 2 Photograph of treated fluoride water colors with B-CHC$_{500}${21} at pH 3, 5, 7 and 9.

Appendix D: Proximate Analysis of 2:1 bone to coffee husk char at different temperatures.

I. Moisture content, %MC.

Charring temperature(^oC)	W_3 (g)	Mass of sample(g)	W_1 (g)	W_2 (g)				%MC
				C_t1	C_t2	C_t3	Ave.	
800	23.80	2.00	25.80	25.65	25.76	25.66	25.69	5.50
700	29.20	2.00	31.20	31.00	31.16	31.12	31.09	5.33
600	24.80	2.00	26.80	26.74	26.73	26.70	26.72	3.83
500	27.80	2.00	29.80	29.69	29.70	29.71	29.70	5.00
400	26.30	2.00	28.30	28.20	28.19	28.15	28.18	6.00
300	24.00	2.00	26.00	25.77	25.88	25.79	25.81	9.33

II. Percentage volatile matter, %VM.

Charring temperature(^oC)	W_3 (g)	Mass of sample(g)	W_1 (g)	W_2 (g)				%VM
				C_t1	C_t2	C_t3	Ave.	
800	27.80	2.00	29.80	29.70	29.75	29.33	29.59	5.11
700	30.20	2.00	32.20	31.98	32.13	31.88	32.00	5.11
600	27.70	2.00	29.70	29.51	29.60	29.53	29.55	3.99
500	27.80	2.00	29.80	29.65	29.64	29.66	29.65	2.63
400	28.40	2.00	30.40	30.21	30.18	30.20	30.20	4.43
300	29.80	2.00	31.80	31.12	31.63	31.55	31.43	9.93

III. Percentage ash content, %Ash.

Charring temperature(^oC)	W_3 (g)	Mass of sample(g)	W_1 (g)	W_2 (g)				%Ash
				C_t1	C_t2	C_t3	Ave.	
800	28.40	2.00	30.40	28.99	29.13	29.19	29.10	35.17
700	27.80	2.00	29.80	28.62	28.50	28.31	28.48	33.83
600	27.80	2.00	29.80	28.51	28.30	28.11	28.31	25.33
500	30.20	2.00	32.20	30.68	30.66	30.64	30.66	23.00
400	27.70	2.00	29.70	28.25	28.19	28.33	28.26	27.83
300	29.70	2.00	31.70	30.44	30.12	29.97	30.18	23.83

IV. Percentage fixed carbon content, %FC.

Charring temperature(^{o}C)	***%MC***	%Ash	***%VM***	***Sum***	%FC (100 – sum)
800	5.50	35.17	5.11	45.78	54.22
700	5.33	33.83	5.11	44.27	55.73
600	3.83	25.33	3.99	33.15	66.85
500	5.00	23.00	2.63	30.63	69.37
400	6.00	27.83	4.43	38.26	61.74
300	9.33	23.83	9.93	43.09	56.91