Enhancement of Defluoridation Efficiency of Bone Char using Surface Modification and Sequential application with Bamboo Char

By: Bundi Roba Lemu

A thesis submitted to

Chemical Engineering Department, School of Mechanical, Chemical and Material Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

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This is to certify that the thesis prepared by Bundi Roba Entitled: **Enhancement of Defluoridation Efficiency of Bone Char using Surface Modification and Sequential application with Bamboo Char** and submitted in partial fulfillments of the requirements for the Degree of Masters of Science in Chemical Engineering complies with the regulations and meets the accepted standards with respect to originality and quality.

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DECLARATION

I, Bundi Roba, author of the thesis **" Enhancement of Defluoridation Efficiency of Bone Char using Surface Modification and Sequential application with Bamboo Char"** hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name: **Bundi Roba Lemu**

Signature: _____

This MSc Thesis has been submitted for examination with my approval as thesis advisors
Advisor: Dr. **Tatek Temesgen**

Signature_____

Date of submission _____

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Abstract

For this study, ground water source from five selected boreholes around Adama were chosen and their chemical properties were characterized. The average of the five selected boreholes water sample was taken to prepare synthetic fluoride ion. In this study, low cost bone and bamboo were used as an adsorbent, in which the bone char was calcined at temperatures of {300, 450, 600, 750 and 900^{o}c} and bamboo char was carbonized at temperature of {350, 400, 500 and 600 ^{o}c} in muffle furnace parameters like resident time, calcination temperature and activation chemical were considered in case of bamboo to prepare the adsorbent. Parameter on the adsorption test for fluoride removal capacity like contact time, adsorbent dosage and particle size for each adsorbent was investigated. The adsorption test was compared with that of Modjo defluoridation center. The experiments were conducted at conditions of adsorbent dosage 0.5, 1, 1.5 and 2 g, particle size of {355-500, 500-700, 700-1000 and 1000-2000micrometer} and contact time of {30, 60, 90 and 120 min}. The adsorption was rapid at initial time. The adsorption efficiency was obtained at adsorbent dose of 2 g, particle size of 355-500µm and 2hr contact time. For this research, the comparison of fluoride removal efficiency on bone char (11.01 mg/l) and bamboo char (8.26 mg/l) was removed and effects of different adsorbent preparation and adsorption operation parameters were tested on both adsorbent bases. Moreover, an alternative modification was done on bone char to enhance its property by coating the bone char with Aluminum Hydroxide and its adsorption capacity (11.64 mg/l) was removed. The removal efficiency of a grey (3.61 mg/l) and white bone char (7.51 mg/l) as well as hydroxyapatite (10.22 mg/l) was compared with synthesized adsorbent. The morphology, crystalline phase and functional group synthesized adsorbent was further characterized using SEM, XRD and FTIR. Kinetic studies revealed that fluoride adsorption fitted well to pseudo-second-order model for all adsorbent.

Key words: *Adsorption; batch experiments; fluoride removal; bone char; bamboo char; coated bone char ; kinetics model*

CHAPTER ONE

Introduction

1.1 Background

Water is one of the most important natural resources present on the earth. It is available in abundance. Even though earth's surface is covered with 71% of water, 96.5% of the water resource is in oceans while 0.9 % is within other saline waters and 2.5% is fresh water. This shows that availability of fresh water is very less [1]. Groundwater is often contaminated by natural as well as man-made sources. Fluorine is a 13th most abundant element on earth and it is not found in the elemental state in nature due to its high reactivity and it exists in ion form in an aqueous solution. Fluorine accounts for about 0.3 g/kg of the earth's crust and exists in the form of fluorides in a number of minerals, of which fluorite (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$) are the most common. It exists in higher concentrations in ground water compared to surface waters [2].

In 2006, the World health organization (WHO) registered 28 countries associated with exposure to high fluoride concentration in drinking water. Among these, the most affected countries are India, Ethiopia, and China [3]. There are different technologies to treat water with Fluorine ion contamination. These technologies are chemical precipitation, ion exchange, membrane separations (ultrafiltration, reverse osmosis, electro dialysis), and adsorption.

Adsorption is considered to be the simplest and most cost-effective relative to other techniques. Adsorption is a process in which atoms, ions, and molecules are attached to the surface of a material. Due to this, a layer of adsorbate (atoms to be adsorbed) is formed on the adsorbent (material which adsorbs). Adsorption is a surface phenomenon and its process arises due to presence of unbalanced or residual forces at the surface solid phase. These unbalanced residual forces have a tendency to attract and retain the molecular species with the surface it comes in contact. Adsorption mechanisms are divided in two types; physical adsorption which involves adsorption of materials on the solid surface via weak van der Waal's forces and chemical adsorption in which materials, molecules or atoms are held to the solid surface via chemical bonds. Several studies have identified adsorbents that are suitable for de-fluoridation, those include activated alumina, bone char, raw bauxite, activated carbon, natural clays etc.

Bone char is locally available low-cost adsorbent. Bone char have been good adsorbents because of the existence of several types of active sites on the surface, which have ion exchange sites. Their sorption capabilities come from their high surface areas and exchange capacities [4]. Bone char has proven to be a promising economic material for de-fluoridation of groundwater due to its, availability, lower cost and have high efficiency to absorb fluoride from water. It consists of a poor crystalline structure and has been proposed for adsorption [5].

1.2 Statement of the problem

Currently, fluoride containg groundwater has been a big challenge for a large population living in the rift valley part of Ethiopia. Different attempts have been done to solve this problem. Oromo Self-help Organization (OSHO) produces bone char as an adsorbent and tried to address clean water needs of more than 94,000 people around Mojo and nearby zones. Despite the effort the efficiency of the adsorbent produced is very low and huge amount of bone char is required for a limited volume of fluorinated water. The produced bone char has an effect of causing odor and color despite its removal efficiency. This problem is assumed to arise from poor control of calcination time, temperature and other preparation parameters. In Modjo Defluoridation Center, a 600kg bone per batch is introduced into concrete chamber furnace at 450^{o}C for 10days. This operation takes high energy and longtime for production of bone char. Despite its energy and time consuming operation, the produced bone has poor adsorption capacity. Therefore to solve the problem and optimize the production parameters, this study investigates the calcination system and the effect of temperature and calcination time for production of bone char. The study also tried to assess the potential of substitution of bone char by an alternative material, bamboo, to improve fluorine ion removal efficiency. This thesis mainly aimed to study the optimum production parameters of bamboo char and possibility of enhancing defluoridation efficiency for bone char using surface modification and Sequential application with bamboo char for selected ground waters around Adama.

1.3 Objectives of the research

1.3.1 General objective

Enhancement Defluoridation efficiency of bone char using surface modification and Sequential application with bamboo char.

1.3.2. Specific objectives

- Characterization of representative groundwater around Adama
- Production of bone char at different temperature as well as time and bamboo char at different temperature, activation chemical and time for comparison of its fluoride removal efficiency
- Surface modification of produced bone char by using locally available chemical
- Sequential application of bone char with bamboo char
- Characterization of the adsorbent

1.4. Significance of the study

This project has benefit for the population living in the rift valley of Ethiopian under the problem of fluorosis. The research is assumed to have a significance of

- Providing baseline information for the optimization of bone char and bamboo application.
- Providing technically improved option for defluoridation processes through the modification of Bone char and also help organizations working on de-fluoridation for adaption of the optimized technique

1.5. The scope of the study

The main scope of this research was directed towards enhancing defluoridation efficiency of bone char using surface modification and Sequential application with bamboo char. Through this study, the modification effects of bone char by the surface coating of aluminum hydroxide precipitation was investigated for the removal of fluoride ions from groundwater through batch experiments (jar test). The effects of contact time, adsorbent dosage and particle size have been studied. Sequential application of bamboo char with bone char was tested to see the improvement possibility of fluorine ion removal. Characteristics of coated bone char and bone char as well as bamboo char produced were evaluated to know the reason for the change of removal efficiency.

CHAPTER TWO

LITERATURE REVIEW

2.1 Water resource

Water is a natural resource and all living things need water in order to live. It is used for various purposes ranging from domestic and agricultural, to industrial and allied purposes. Water is available in two basic forms; surface-water and ground-water. Groundwater plays an important role in the supply of drinking-water to rural communities whereas acceptable surface water quality is not abundantly available. The use of groundwater is usually preferable to that of surface water because well managed groundwater resources are less vulnerable to contamination than surface water and usually require less treatment [6].

Due to various ecological factors, either natural or anthropogenic, the groundwater is being polluted because of deep percolation from intensively cultivated fields, disposal of hazardous wastes, liquid and solid wastes from industries, sewage disposal, surface impoundments, etc.

2.1.1 Drinking Water as a Source of Essential Minerals

Drinking water contains several essential mineral elements; among them some 21 mineral elements are known or suspected to be essential for humans. This number includes four that function physiologically as anions or in anionic groupings
(chlorine as Cl^-, phosphorus as PO_4^{-3}, molybdenum as MoO_4^{-2}, fluorine as F^-), eight that function in their simple cationic forms {calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), potassium (K^+), ferrous iron (Fe^{+2}), copper (Cu^{+2}), zinc (Zn^{+2}), manganese (Mn^{+2})) and which are subject to chelation by either intact proteins or a variety of small, organic molecules; ions of two nonmetals (iodine (I) and selenium (Se)) that function as constituents of covalent compounds (e.g., iodothyronine, selenocysteine) that are formed metabolically; and ions from five additional elements (boron (B), chromium (Cr), nickel (Ni), silicon (Si), vanadium (V)) the nutritional significance of which remain to be fully elucidated. Thus, fourteen mineral elements are established as being essential for good health; these elements in combined form affect bone and membrane structure (Ca, P, Mg, F), water and electrolyte balance (Na, K, Cl), metabolic catalysis (Zn, Cu, Se, Mg, Mn, Mo), oxygen binding (Fe), and hormone functions (I, Cr) [7].

Minerals in water are subject to most of the same determinants of bioavailabilty that affect the utilization of those minerals in foods. For example, phytate, phosphorus and triglycerides can each reduce the lumenal solubility and, hence, the absorption of calcium [7].

2.1.2 Optimal value of Fluoride as mineral in Drinking Water

Most drinking waters contain some fluoride. Fluoride is present in groundwater at concentrations from nil to about 67 mg/l, and in surface waters sometimes at concentrations as low as 0.1mg/l or less. The amount of fluoride in treated drinking water is also affected by treatment processes such as anion exchange that will remove it along with the target contaminant (e.g. Arsenic). Demineralization and some other treatment processes will also remove fluoride. Fluoride intake has been known for the past 50 to 60 years to play a beneficial role in dental health; there is some evidence that it may be beneficial for bone formation, but this has not been proven. The optimal drinking water concentration of fluoride for dental health is generally between 0.5 to 1.0 mg/L and depends upon the volume of drinking water consumed and the uptake and exposure from other sources [7].

2.1.3 Fluoride Global Condition

Geogenic occurrence of fluoride is often linked to volcanic activity, fumaric gases and presence of thermal waters. Proxy indicators of high fluoride levels in groundwater are; low levels of calcium and magnesium, high levels of sodium and bicarbonate ions, and high pH above 7 [8].Fluoride occurs in ground water all over the world. Areas with high fluoride in groundwater includes: Syria, Jordan, Egypt, Libya, Algeria and Morocco. It also includes the Rift Valley areas in Africa from Sudan through Kenya to Tanzania and Malawi. Another geographical area extends from Turkey through Iraq, Iran and Afghanistan to India, Northern Thailand and China [9].

High fluoride content in the groundwater is caused mainly due to fluoride bearing minerals in the rocks and soils. The problem of elevated concentrations of fluoride in natural water, especially groundwater, is severe and widespread in the Rift Valley region of Kenya [10].

2.1.4 Status of Groundwater Fluoride Occurrence in the World

In the two largest countries India and China of the world, fluorosis is most severe and well known. High concentration of fluoride, often above 1.5 mg /l, constitutes a severe problem over

a large part of India. About 80 % of the diseases in the world are due to the poor quality of drinking water, and the fluoride contamination in drinking water is responsible for 65 % of endemic fluorosis around the globe [11]. Furthermore, 50 % of the groundwater sources in India have been contaminated by fluoride and more than 90 % of the villages use groundwater for drinking purposes [12]. In fact, more than 40 million people in India are affected due to the prevalence of dental fluorosis [13].

The Yuncheng basin in the southern part of the Shanxi province is one of the most extensively studied areas in China for fluoride contamination in groundwater. [14] have reported a high fluoride level of 6.6 mg/L in Yuncheng basin. Fluoride in groundwater in this basin is originated from the dissolution of fluorine-bearing minerals and desorption of exchangeable fluoride from the loess [15].

In Ethiopia, associated with rift valley and semiarid climate are two major factors responsible for the high concentration of fluoride in both surface and subsurface water system. [16] have reported the high fluoride concentration of 264 mg/L in hot springs.

In Malawi, the fluoride concentrations were analyzed by [17]. They observed fluoride concentration ranging from 0.50 to 6.98 mg/L in the rainy season and between 2 and 7.02 mg/L. In Kenya, some areas such as lake Elementaita (1640 mg/L) and lake Nakuru (2800 mg/L) were reported to have extremely high level of fluoride [18].

In the Republic of South Africa, researchers have reported that around 803 sites are affected by endemic fluorosis. These include locations in western and Karoo Regions of Cape Province, north western, northern, eastern and western areas of Transvaal, western and central Free State. Fluoride levels as high as 6 mg/L were reported in groundwater of Madibeng local municipality in northwest Province of South Africa [8]. [19] reported the prevalence of fluorosis in Arizona, Arkansas, California, Colorado, Idaho, Illinois, Iowa, Kansas, Minnesota, Nevada, New Mexico, North Carolina, North Dakota, Oklahoma, Oregon, South Carolina, South Dakota, Texas, Utah and Virginia. In 1980's the United States incorporated several recommendations to reduce fluoride ingestion. But concentrations [20] has not declined even more than ten years after the recommendations. High concentration of fluoride (>3.5 mg/l) was noticed in South Carolina where 40% of the people depend on groundwater for their needs [21]. The groundwater of Lake

Saint-Martin area, Manitoba represented geochemical signature of groundwater originating from a deep regional aquifer, which are upwelling in a previously unrecognized discharge zone created by structural uplift associated with the impact event [22].

The volcanic ash deposits in Texas which was the reason behind high fluoride in groundwater up to 6.27 mg/l showed better correlation with well depth [23]. Emission from phosphate fertilizer production factory which was the cause of high fluoride in groundwater in southern Brazil was found to be influenced by vegetation cover i.e. places with grasslands had higher fluoride than those with eucalyptus plantation [24].

2.1.5 Ethiopia's Fluoride Condition

According to [25], in Ethiopia, the regions that are facing excessive fluoride in ground water are Afar, Oromia and Southern Nations and Nationalities Regional States (SNNPRS) – (Table 2.1).

Table 2. 1 Fluoride content of water in various areas of Ethiopian rift valley

Sample sites	Fluoride (mg/l)
Gewane (town)	0.7-2.5
Abadir (farm)	4.0
Koka (town)	26
Alem tena (village)	9
Abernosa (village)	36
Jido (village)	33.6

Source: [16]

2.1.6 Industrial fluoride pollution

Fluoridated mineral deposits generally contaminate groundwater but an industrial emitted fluoride pollutes not only the air or atmosphere but also the plants (forage), crops (fodder), vegetables, soil, and freshwater bodies. These fluoride contaminated sources are potential to develop toxic or diverse adverse health effects (fluorosis) in both man and domestic animals. Industrial fluoride contamination can be evaluated and inferred by the estimation of fluoride content in biological (milk, blood serum, urine, teeth, bones, nails, etc.) and environmental (soil,

water, forage, fodder etc.) samples collected from the surrounding areas of potential sources of fluoride emission [26]. The presence of fluoride content in any of these samples confirms the persistence of industrial fluoride pollution in the surrounding environment.

2.1.7 Standards for Fluoride in Drinking Water

According to World Health Organization (WHO) guideline optimum value or a general standard concentration of fluoride in water ranges from 1.0–1.5 mg/L [27]. According to World Health Organization (WHO), fluoride is considered as a contaminant in water when its concentration exceeds the limit of 1.5 mg/L [28].

2.2 Effects of fluoride on human health

There are various studies [29] on the beneficial and harmful effects of fluoride. The typical health impact of fluorosis is dental caries. Table 2.2 shows impact of fluoride in drinking water according to variation in concentration.

Table 2. 2 Harmful effects of Fluoride

Fluoride (mg/l)	Impacts
0.5-1.5	Dental caries and optimum dental health, works against dental caries
1.5-3	Dental fluorosis, blackening and pitting of enamel and teeth from long term exposure, mottled enamel, roentgen graphic bone changes, polydipsia.
3-8	Skeletal fluorosis, damages fetus, increase in F^- concentration in milk, infant mortality due to calcification of blood vessels, lack of intelligence quotient in children, renal diseases, and elevated serum alkaline phosphates, stiffness of knees and hips, increased bone mineral density, bone and joint pains.
10-100	Within this range it leads to gastroenteritis, skin irritation, deformation of bones and other skeletal abnormalities, thyroid changes, growth retardation, kidney damage, crippling fluorosis.

Source: [29]

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 [30]. Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as fluorosis, and longterm damage to the brain, liver, thyroid and kidney [31].

Some of the health conditions that manifest due to skeletal fluorosis are:-

- Severe pain in the backbone
- Severe pain in the joints
- Severe pain in the hip region
- Stiffness of the backbone.
- Immobile /Stiff joints
- Increased density of bones, besides calcification of ligaments
- Paralysis

This aspect of fluorosis is often overlooked because of the misconception prevailing that fluoride will only affect bone and teeth. Fluoride, when consumed in excess can cause several ailments besides skeletal and dental fluorosis [29].

- Neurological Manifestations
- Muscular Manifestations
- Allergic Manifestations
- Gastro intestinal problems
- Head-ache and Loss of teeth (edentate) at an early age

Taking of fluoride through food and air is relatively small compared to fluoride ingestion through water. Attention has thus been drawn to controlling fluoride concentrations in water supplied for drinking. The World Health Organization recommends that in mitigating for fluorosis in endemic areas the approach should be hierarchical in the following order; first to identify alternative source of potable water with low fluoride content, secondly to dilute high fluoride water with low fluoride water to attain a mass balance within 1.5 mg/l, thirdly to use high calcium, magnesium and vitamin C diets and finally, when all these may not be feasible; to remove fluoride from water to meet the required level of 1.5 mg/l [8].

2.3 Fluoride Removal Technologies

De-fluoridation is a process of removal of fluoride from drinking water. Different methods have been described with various materials for the fluoride removal since 1930‟s [32]. Methods for Defluoridation of water includes coagulation – precipitation, membrane separation processes, ion exchange, adsorption techniques and others (electro-dialysis and electrochemical).

Adsorption method

Adsorption processes involve the passage of water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. After a period of operation, a saturated column must be refilled or regenerated [33]. Adsorption seems to be economical and user-friendly especially in the developing world where point of use treatment is recommended. Different adsorbents have different limitations [34]. Adsorption is considered to be a viable approach due to its simplicity and cost-effectiveness [30].

Comparatively, adsorption seems to be the most attractive method for the removal of fluoride below 1mg/l. The criteria for the selection of adsorbent mainly include its potential (adsorption capacity) for fluoride removal and the cost. Various low-cost materials such as activated alumina, clay, soil, bone char, bentonite and other materials have been tested for removing fluoride from drinking water, but the fluoride adsorption capacities of those materials are not high enough for wide application[32].

2.4 Surface Chemistry and Forces Involved in Adsorption

Adsorption is a mass transfer operation in which a spontaneous accumulation of a gas or vapor (adsorbate) at the solid surface (adsorbent or substrate) as compared to the bulk phase. Adsorption processes are used in drinking water treatment for the removal of taste- and odor-causing compounds, synthetic organic chemicals, color-forming organics, and disinfection byproduct precursors. Inorganic constituents, including some that represent a health hazard, such as perchlorate, arsenic, fluoride, and some heavy metals, are also removed by adsorption [35].

Adsorption is based on the capability of porous solids with large surfaces such as silicone gel, activated carbon, to selectively retain and release compounds on the surface of the solid. The adsorption process is classified as either physical adsorption or chemical adsorption. Physical adsorption is adsorption in which the forces involved are intermolecular forces (van der

Waals forces) and which do not involve a significant change in the electronic orbital patterns of the species involved". Chemical adsorption is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds" [36]. There are three interfaces involved in adsorption. These are adsorbate- adsorbent, adsorbate – water, and water–adsorbent. Compounds that are less water soluble (hydrophobic) are more likely to be adsorbed to a solid [36].

2.4.1 Fluoride Removal from Drinking Water by using Bone Char as Adsorbent

Bone char is a solid granular material which is produced by the calcination of animal bones [37]. Low cost adsorption techniques are gaining interest in recent years because of their proven efficiency in purification [38]. The adsorption efficiency depend on its pore structure, pore volume and surface chemistry [38]. In most of the countries, animals are slaughtered for meeting people demands of eating meat. This ultimately results in big amounts of bone wastes affecting the environment. Hence, these waste bones need to be disposed in a safe way. Nowadays, animal bone char which consists of a poor crystallite structure is been proposed for adsorption [5]. The fluoride removal capacity of bone char is attributed to the presence of hydroxyapatite in its structure [39]. Bone char contains about 10% carbon (C) by weight with the remainder comprising mainly hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$), but also a significant percentage of calcium carbonate[39].

The beneficial and harmful effects of fluoride on the skeletal structure are based on the ion exchange reactions between hydroxide and fluoride ions in the calcium hydroxy-phosphate of the main skeletal structure compositional material. The replacement of hydroxide ions with fluoride ions results in a more acid resistant structure, fluoroapatite [8].

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

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 [8].

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

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 [40].

2.4.2 Mechanisms of Bone char Adsorption

Reactions involved are direct adsorption of fluoride on the empty sites of the bone char surface. Ion exchange mechanisms where fluoride ion exchange position with OH^- or it exchanges with hydrogen carbonate/carbonate ion/ phosphate ion. Recrystallization processes where the hydroxyapatite and bone minerals dissolve and precipitate with fluoride as fluorapatite [41].

The anion exchange between the fluoride ions with the hydroxyl ions and carbonate ion:

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

$$(Ca_3(PO_4)_2)nCaCO_3 + 2F^- \longrightarrow (Ca_3(PO_4)_2)nCaF_2 + CO3^{2-}$$

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. Moreover bone charcoal has the specific ability to adsorb fluoride from water. This is believed to be due to its chemical composition mainly as hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, where one or both the hydroxyl groups can be replaced with fluoride.

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 [3].

2.4.3 Empirical review on the study of bone char for water treatment

Bone char was synthesized from used cattle bone by thermal treatment [42]. In this study, they reported that bone char was synthesized at different temperatures including {350, 400, 500, 600 and 700 °C} and the calcination time was maintained at 2 h. The authors used XRD, FTIR, SEM and BET to characterize the bone char adsorbent and selected 350^{o}c due to higher surface area and adsorption capacity, by using BET instrument. The adsorption isotherm test was performed by adding 1 g of BC in to 1 L fluoride solution of different initial concentrations, i.e., 5, 10, 20, 30, 40 and 50 mg L^{-1}. The solutions were kept on continuous stirring at {250 rpm} for 24 h. Temperature and pH were controlled at 20 °C and 7, respectively. For the kinetic study, 1 g of

BC was added into the solution having 10 mg L^{-1} initial fluoride concentration. BC having two different size ranges, {75–150 μm and 150–300 μm} was examined for time dependent adsorption study. The mixture was allowed to stir at 250 rpm for 2 h. Followed by startup, samples were collected 6 times, at {sampling interval is 5 min}. About 79.38% of the fluoride concentration was adsorbed on 1 g of bone char (BC) from the solution having 5 mg L^{-1} initial concentration. For the solution having higher initial concentration i.e., 50 mg L^{-1}, the maximum adsorption quantity was 10.56 mg of fluoride on 1 g of BC.

Recently, animal bone char which consists of a poor crystallite structure is being proposed for adsorption[5].Also some researchers [43] compare bone char to egg char for the purpose of fluoride removal from water. In this regard, they compared percentage of calcium and Phosphorous of both chars using solar thermo elemental atomic absorption spectrophotometer (Flame AAS) and spectrophotometer respectively. The reported results were calcium content of {53.12%} and {39.68%} for bone char and egg char while phosphorous content was {4.08%} and {2.71%} for Bone char and Egg char (EC) respectively [43].

In their study, the Parameters used by the authors were contact time of {60, 120, 180, 240 and 300min}, temperature {25, 30, 40 and 50^0C}, mass dosage {5, 10, 15 and 20g} and constant particle size of 2.12 micrometer. Calcination temperature was 300^0C and both adsorbent were modified with 1.0M HNO_3 (trioxonitrate (v)) acid. Final percentage of fluoride ion removal capacity from water was highest at room temperature with 74% for activated BC and 73.77% for activated EC respectively [43].

2.5 Fluoride Removal by Bamboo Char as Adsorbent

Activated carbons are carbonaceous materials that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces [44]. Bamboo's growth is more rapid than any other tree species on the planet, even faster than Eucalyptus species that can be annually self-renewable and harvestable, if managed properly. Bamboo is a high-yield renewable natural resource for agro-forestry and engineering based products [45].

The development of cost-effective and efficient adsorbent methods is still under investigation. In recent years, the use of inexpensive, easily available adsorbents with high carbon content and low inorganic composition have been used as potential raw material for the preparation of

activated carbon. Special attention is given for locally developed adsorbents that are promising raw materials for the removal of contaminants from water and wastewater [46].

Activated carbon (AC) has been widely used as a good adsorbent for various applications including water treatment and desalination, wastewater treatment and air purification due to its unique characteristics [47] [48]. The extensive application of activated carbon is mainly due to its high adsorption capacity and cheap for starting carbonaceous materials used for the preparation activated carbon. Starting materials to prepare activated carbon includes bamboo, bagasse, coconut husk and palm shell etc. AC has a high degree of porosity, an extensive surface area, and a high degree of surface reactivity. Its large specific surface area of {500 – 2000m^2/g} is in fact the most important physical property of AC which allows the physical adsorption of gases or vapors and dissolved or dispersed substances from liquids. Bamboo can be converted into charcoal and activated carbon via carbonization followed by activation[49, 50] [51-53].

The carbonization process is to enrich the carbon content and create an initial porosity, and the activation process helps in enhancing the pore structure. Carbonization takes place in the temperature range of 300–400 °C. During carbonization, primary carbonization gases are produced. The residue of the carbonization process is the primary charcoal which serves as base material for the activation step [54].

A summary of bamboo application for various uses is given in Table 2.3 below.

Table 2. 3 application of bamboo char

Advantage	Cited from
Used for electrodes in dye sensitized solar cell	[55]
Used to purification contaminated water	[55]
Used for electromagnetic waves absorber	[55]
Used in industrial applications, including gas and air cleaning	[56]
It's used for treatment, purification and decolourization of liquids, which is particular importance in the pharmaceuticals, food, beverage and other industries.	[56]

2.6 Bamboo Resource in Ethiopia

Ethiopia has the greatest bamboo resources in Africa representing a significant proportion of Africa's total bamboo resources. The country has more than 1 million hectares of bamboo, which is 67% of African bamboo resources and more than 7% of the world total area covered by bamboo is found in Ethiopia [57]. Bamboo is one of the non-timber forest products, which support the livelihood of millions of local people in small cottage industries in Ethiopia [57]. Bamboo is very important to Ethiopia, because of the fact that, the country's high forest coverage is estimated at only 3.56%, which is still alarmingly decreasing, while bamboo can be a substitute for almost all wood products and share this pressure since it is fast growing. Dawuro zone which one of the 14 zones of Southern, Nationalities, and Peoples Region (SNNPR), has 3 medium and 2 high bamboo potential highland districts. In the districts, cattle fattening, sugarcane production, cotton and oil crops, poultry, coffee plantations and crop production are the main agricultural activities. Forestry activities are also one of income generating ways of most residents in Dawuro. Forest covers an area of about 32,000 hectare. Highland and lowland bamboo (Yushania alpine and Oxytenantheria abyssinica) are widely cultivated and covers more than 2,008.7 hectares of bamboo which is about 0.43% of total area. Out of total bamboo resource, highland bamboo (Yushania alpine) covers 92% hectare

CHAPTER THREE

3. Methodology

3.1 Materials and Equipment used

The major equipment used were muffle furnace (model: SX-2.5-12) which can operate up to a temperature of 1200ºC, oven (model:- NE9-56S), sieve (model: CEN-MKII-00-A), size reduction (ROHS), analytical balance (JA203H), beaker plastic bottles, Micro Processor pH-mV meter (SL-145), tray, vacuum pump, filter paper, magnetic stirrer (XMTD-231), jar test (SW6), crucible, deionized water, aluminum foil, conical and Erlenmeyer flasks, Measuring cylinders, and fluoride ion selective electrode (S-613F). Instrumental equipment such as x-ray diffractometer (model: XRD700s), scanning electronic microscope (SEM) and Fourier transform infrared (FTIR) (model: JASCOFTIR-6600typeA).

Table 3. 1 List of chemical reagents

No.	Reagent	Source of product
1	Sodium hydroxide (NaOH)	AR source from Turkey
2	Potassium hydroxide (KOH)	Carelabmed
3	Hydrochloric acid (HCL)	Blulux analytical reagent
4	Sodium fluoride	Abron chemicals
5	Magnesium chloride	SRL
6	Sodium bi carbonate	Neolab life science co.
7	Aluminum sulphate	Alpha chemika
8	Calcium chloride	Blulux laboratories (p) Lted.-121005
9	Phosphoric acid (H_3PO_4)	Blulux laboratories (p) Lted.-121005

Overall Flow Diagram or structural frame work of Bone char

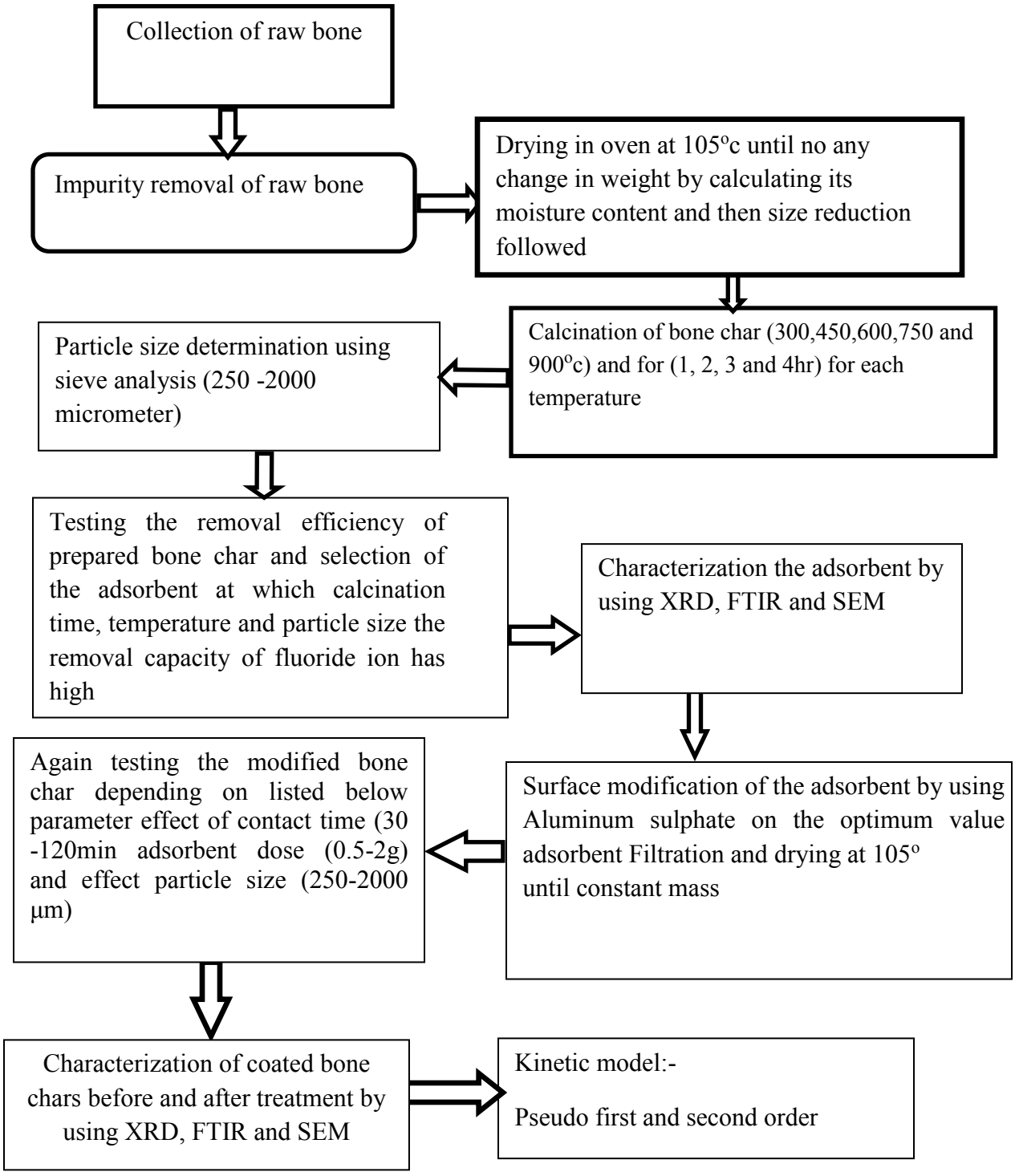


Figure 3. 1 Overall Flow Diagram or structural frame work of Bone char

3.2 Characterization of selected representative groundwater around Adama

In this study fluoride containing water was conducted in the Rift Valley part of Ethiopia. Raw ground waters were collected from five different areas which are given in table 3.2.

Table 3. 2: - five selected representative ground water around Adama Town

No.	Site Name	Location
1	Anano	Ziway 10 km to Shashemene
2	Garba fila	Ana Dugda 3 km before Maki town
3	Gura	14 km after Maki
4	Serity	Ana Dugda 15 km on the way to Batu
5	Meja	Ana Dugda 17 km from Maki to the west

In this thesis work, eight ions which co-exist with to fluoride ions wer investigated. Those co-existing ions are Sodium (mg/l Na^{+}), Potassium (mg/l K^{+}), Calcium (mg/l Ca^{2+}), Magnesium (mg/l Mg^{2+}), Alkalinity (mg/l $CaCO_3$), Carbonate (mg/l CO_3^{2-}), Bicarbonate (mg/l HCO^{3-}) and Chloride (mg/l Cl^{-}) were analyzed.

3.3 Batch adsorption tests for bone char, surface modified bone char and bamboo char

In this study the effect of different controlling parameters particle size, contact time and adsorbent dosage on defluoridation capacity of the adsorbent was examined. Adsorption studies were carried out through batch process. This is due to its simplicity of equipment needed, flexibility and relatively inexpensive.

3.4 Experimental procedure for preparation of bone chars at different temperature and time

The cattle bones were collected from Adama city Hateric restaurant, which is located around 04 keble. Raw animal bones were boiled, washed, dried in order to remove fat and meat residues. The cleaned and dried bone was transferred in to box type resistance muffle furnace (model: SX-2.5-10, supply voltage 220v and having power rating 2.5KW). The bone was carbonized at temperatures of {300, 450, 600, 750 and 900^{o}c} at different calcination time of {1, 2, 3 and 4 hr} and at heating rate was 12 ^{o}c/min. After collecting the product, the charcoal was further crushed into fine particle using grinding machine. Bone char was screened using sieve of 355, 500, 710,

1000 and 2000 μm size in order to obtain particles below 2000 μm. Average of five selected groundwater fluoridated water was prepared using NaF. Adsorption test results were analyzed for different char and conditions suspected to affect adsorption.

3.5 Method of coating of aluminum hydroxide on bone char

Aluminum hydroxide has been coated on bone char by using stirred tank reactor and filtered by using vacuum filter and dry it using oven/drier. Initially, one gram bone char was taken and mixed with 10, 20 and 30 mL of 0.1, 0.5, 1 and 1.5M aluminum sulfate solution in stirred tank reactor. The reactor was stirred at 80rpm by using magnetic stirrer with 1 molarity (M) sodium hydroxide solution. In this condition, sodium hydroxide reacts with aluminum sulfate to produce aluminum hydroxide which gets deposited on bone char. In this process, the addition of sodium hydroxide is very vital and it was controlled by proper checking of pH of the mixture. Once the pH of the reaction media reaches the desired value of 5–7, sodium hydroxide addition was stopped. Finally the resulting adsorbent contains the mixture of sodium sulfate and aluminum hydroxide coated bone char. Thereafter, the whole slurry was filtered and subsequently dried at 105^{o}c until constant mass was achieved to get the desired adsorbent. However, for further use the bone char was thoroughly washed with deionized water for complete removal of sodium sulfate and it was dried again in oven at 105 ^{o}c.

3.6 Experimental procedure for preparation of bamboo char

The raw bamboo used in this study was collected from arbegona area of Sidama regional state and it was cut into pieces of approximately 1.5x1cm in size and its thickness and diameter was 1x3.5cm. Raw bamboo was first dried in an oven at 110°C for 12hr, and then crushed manually. Crushing provided smaller particles with increased surface area and it also enabled more efficient chemical activation of the raw material. Chemical activation of the bamboo was then done using different activating agents, namely NaOH, KOH and H_3PO_4. Next the mixture was immersed 25, 30, 35 and 40% by volume for each three chemical activation 1:4 bamboo precursor to activator was soaked for 24 hr and dehydrated in oven at 105°C for 12 hr.

The impregnated dried sample was carbonized in box type resistance muffle furnace at different temperature of {350, 400, 500 and 600^{o}c} for each three activator and activation time was for 0.5, 1, 1.5 and 2 hr. After collecting the product, the charcoal was further crushed into fine particle using grinding machine. Bamboo char was screened using sieve of 355, 500, 710, 1000

and 2000 μm size in order to obtain particles below 2000 μm. Average of five selected groundwater fluoridated water was prepared using NaF. Adsorption test results were analyzed for different char and conditions suspected to affect adsorption.

To remove remaining impurities such as ash, the synthesized activated carbon, activated by KOH and NaOH, was washed with a hydrochloric acid (HCl) aqueous solution (5% by weight) and activated carbon carbonized by H_3PO_4 was washed with NaOH (5% by weight) followed by washing with distilled water several times until the pH of the washing solution become neutral. Then, treated activated carbon was dried at 105 °C for 12 h in oven. The resulting samples were washed with distilled water, dried and ground to particle size of 0.5mm, 0.71mm, 1mm and 2mm stored for further coating and analysis. The bamboo charcoals were kept in closed plastic bottle to prevent any interaction with air.

3.7 Removal of fluoride from aqueous solution

Contact time

The influence of the contact time of adsorbent on the fluoride removal was investigated by varying the contact time from 30, 60, 90 and 120 min in order to investigate the effect of contact time. In this part the kinetics of the adsorption data was also analyzed based on reaction kinetics of pseudo-first-order and pseudo second-order mechanisms. .

Dose

The effect of dosage was studied by varying adsorbent dose of 0.5, 1, 1.5 and 2 g, by increasing by 0.5 intervals with contact time of 2 h (optimum time) and pH 7.

Particle size

The effect of particle size was studied by considering the adsorbent size from 355-500, 500-710,710-1000 and 1000-2000μm to investigate the removal capacity.

3.8 Characterization of adsorbent

3.8.1 X-ray diffraction (XRD)

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure. X-ray crystallography is used in two main areas, namely fingerprint characterization of crystalline materials, and determination of their

structure. When a beam of X-ray strikes the crystal, it gets scattered elastically into many specific directions, with its wavelength remaining unchanged.

A Crystalline phase of bone char and bamboo char synthesis were identified by powder XRD (XRD 7000S) using CuKα radiation (40 kV and 100 mA).

3.8.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). Analysis functional group of raw bone, calcined bone char before treated and after treated and also surface modified bone char before and after treatment. In this study it also analysis the morphology of bamboo char before treatment and after treatment.

The wavelength of light absorbed is characteristic of the chemical bond and can be seen in this spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler.

3.8.3 Scanning electron microscope analysis

A scanning electron microscope (SEM) is a type of electron microscope that determine the images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography or morphological change. Analysis morphology of raw bone, calcined bone char and surface modified bone char before treatment. In this study it also analysis the morphology of bamboo char before treatment.

3.9 Adsorption Kinetic Model

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations were applied to model the kinetics of fluoride adsorption onto bone char and bamboo char.

3.9.1 Pseudo-First Order Kinetic Model

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations were applied to model the kinetics of fluoride adsorption onto bone charcoal powder. This model is also known as Largergren model, proposed in 1898, which assumes a first order adsorption kinetics and can be represented by equation given below [58].

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

Where q_e and q_t (mg/g) are the amounts of fluoride ions adsorbed at equilibrium or adsorption capacity at equilibrium and the adsorption at time t, respectively, and K_1 is the kinetic constant of pseudo-first-order adsorption (min^{-1}). 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.

3.9.2 Pseudo second order kinetic model

The pseudo-second-order equation is expressed as follows:

$$\frac{1}{q_t} = (\frac{1}{q_e})t + \frac{1}{k2}\frac{(1)}{(q_e)^2}$$

Where $\mathbf{q_t}$ (mg/g) is the amount of fluoride ions adsorbed at time **t**, K_2 is the pseudo-second-order rate constant of adsorption (g/ (mg min)), qe is the adsorption capacity at equilibrium (mg/g) and **t** is the contact time (min). If the second order kinetic equation is applicable, the plot of t/q_t against **t** of above equation should give a linear relationship. The q_e and K_2 can be determined from the slop and intercept of the plot $\mathbf{1/q_e}$ versus **t** respectively.

Chapter Four

Result and Discussion

4.1 Preparation of synthetic Fluorinated water

The treatment of water is site specific and it is highly dependent on the properties of the water to be treated. Considering this, the first task done for this thesis was selection and characterization of the water to be treated. Groundwater from five selected boreholes around Adama were chosen and characterized for their chemical properties. The selected areas are chosen by communication with Oromo Self- Help Organization (OSHO) staffs for high concentration of fluoride presence. Groundwater from Meja, Anano, Garba fila, Gura and Serity areas were tested and characterized as shown in Table 4.1.

	Meja	Anano	Garba fila	Gura	Serity
Sodium (mg/l Na^+)	180.00	190.00	400.00	375.00	169.00
Potassium (mg/l K^+)	11.8	8.80	20.00	19.50	11.80
Calcium (mg/l Ca^{2+})	9.98	4.16	24.96	9.98	9.98
Magnesium (mg/l Mg^{2+})	2.00	1.00	7.99	2.00	1.50
Alkalinity (mg/l $CaCO_3$)	422.3	576.8	854.9	824.00	424.36
Carbonate (mg/l CO_3^{2-})	Nil	Nil	Nil	Nil	Nil
Bicarbonate (mg/l HCO_3^-)	515.21	703.7	1042.98	1005.28	517.72
Chloride (mg/l Cl^-)	5.96	14.91	133.2	16.90	42.74
Fluoride (mg/lit)	13.76	10.93	9.09	12.55	8.29

Table 4. 1 Characterization of five ground waters from different areas around Adama

Based on the average amounts of each species present in the five groundwater samples, a representative synthetic water with the formulation presented in Table 4.2 was prepared as a surrogate for a ground water to be tested in all the analysis in this study.

Table 4. 2 Formulation recipe of a synthetic ground water used

Chemicals Used	Concentration (mg/l)
KCl	27.47
$MgCl_2$	11.4
NaF	33.6
NaHCO3	1,041
$CaCl_2.2H_2O$	44.5

	KCl	$MgCl_2$	NaF	$NaHCO_3$	$CaCl_2.2H_2O$
Molecular Weight g/mol	74.5	94	42	84	111
In the synthetic water (mg/l)	27.47	11.4	33.6	1041	44.5
Initial fluoride concentration (mg/l)					11.72

The initial Fluoride ion concentration of the synthetic water is 11.72 mg/l.

4.2 Evaluation of Removal Efficiency

For this research, adsorption of fluoride ion on bone char and bamboo char was done and effects of different adsorbent preparation and adsorption operation parameters were tested on both adsorbent bases. Moreover, an alternative modification was done on bone char to enhance its property by coating the bone char with aluminum hydroxide and its adsorption capacity was checked. To compare the efficiency of each synthesized adsorbents a grey and white bone char as well as hydroxyapatite (HAP) produced at OSHO as an adsorbent were used as reference adsorbents. All the tests were done in Jar test for a predetermined time with 200 rpm mixing speed of an impeller.

4.2.1 Removal Efficiency of Hydroxyapatite (HAP)

HAP produced by OSHO for the purpose of fluoride removal was applied as a reference material because of its presence application in the company as it was highly recommended as their efficient adsorbent for fluoride removal. The company synthesis HAP because of its high adsorption capacity compared to the white and Grey bone char they use as an adsorbent. Despite its high removal efficiency its cost of production is high and cannot be afforded by local communities.

The adsorbent dose of 2 g of HAP was used in 250 ml synthetic water having initial fluoride concentration of 11.72 mg/l and for a contact time of 110 min and 10.22 mg/l removal was achieved, as shown in Figure 4.1. The result of the percentage removal fluoride ion showed that adsorption was rapid in the first 10 min followed by a gradual increase with time until equilibrium was attained. The fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbent in the solution and the concentration of vacant sites available on the HAP surface. The attainment of equilibrium adsorption might have been due to reduction in the available active adsorption sites on the adsorbent.

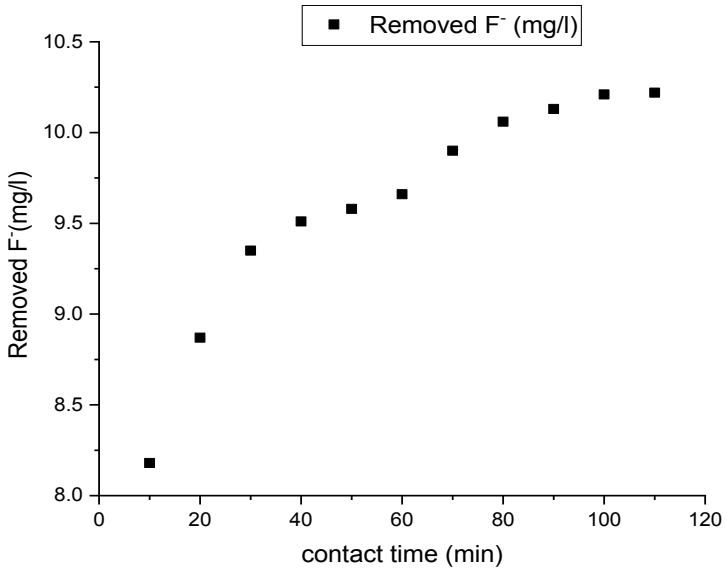


Figure 4. 1 Fluoride ion removal efficiency of HAP

4.2.2 Removal Efficiency of Grey and White Bone Chars

OSHO produces product bone char at a temperature of 400ºc and 450ºC in a house shaped furnace for ten days. The system of calcination is poor in limiting the entrance and flow of oxygen in the system. The difference in temperature produces two different types of bone chars. With the former temperature the type of bone char produced is grey in color and named after its color as grey bone char while the later type is named as a white bone char. For a synthetic ground water of 11.72 mg/l initial fluoride concentration, Figure 4.2 showed the percentage removal efficiency of the grey bone char with adsorbent dose of 2 g of grey bone char in 250 ml synthetic water. The maximum removal capacity of 7.51 mg/l was achieved.

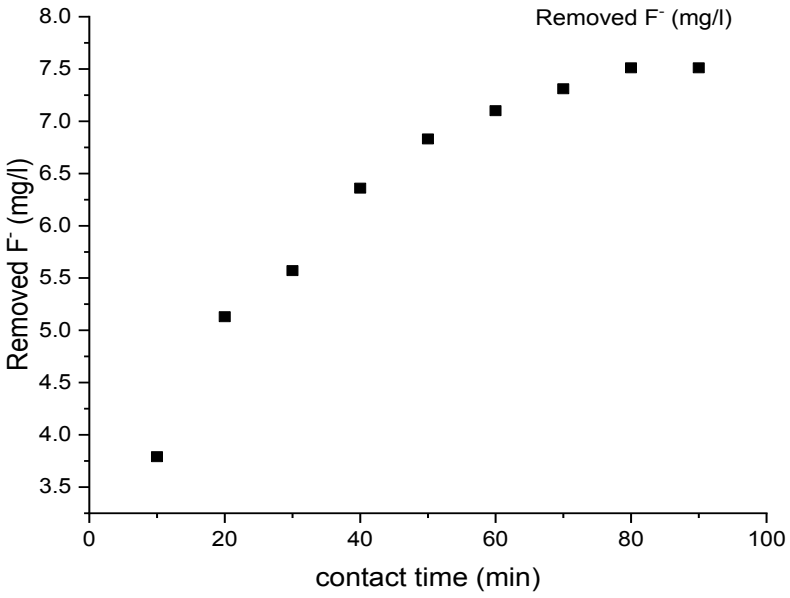


Figure 4. 2 Fluoride ion removal efficiency of grey bone char

Similarly, the adsorption efficiency of a white bone char for a fluoride ion was tested and presented in Figure 4.3. The removal efficiency of white bone char for fluoride ion from synthetic water with initial fluoride concentration of 11.72 mg/l, was found to be 3.61 mg/l.

The low removal efficiency in comparison with HAP and Grey bone char is probably due to negative effect of calcination temperature. As the calcination temperature increases the active surface of the adsorbent might be damaged resulting in decrease of the removal capacity. Moreover, the

uncontrolled presence of oxygen could facilitate a complete removal of active functional groups resulting in the ash content of a bone.

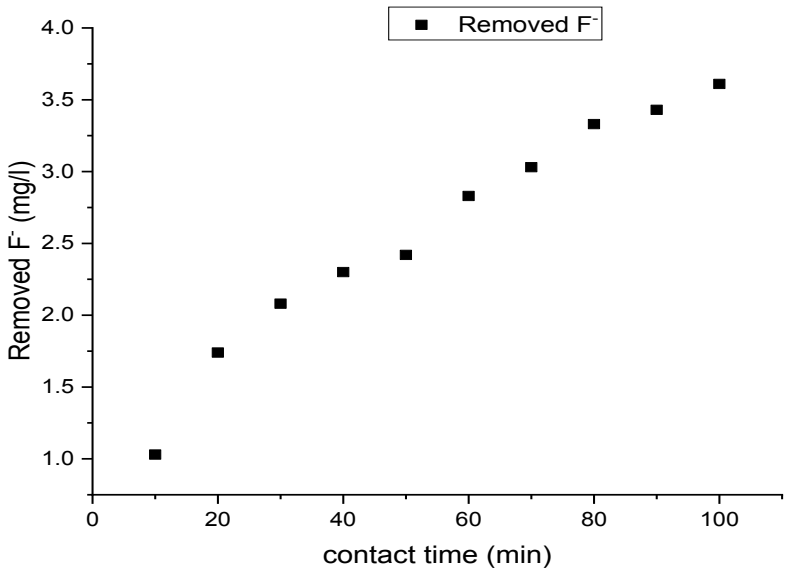


Figure 4. 3 Effect of contact time on white bone char for the removal efficiency fluoride ion

4.3 Effect of parameters on Bone char calcination

From the bone char adsorbents collected from OSHO it can be observed that the adsorption capacity of a bone char is highly dependent on its calcination parameters. Therefore, this research evaluates the effect of calcination temperature and time on the fluoride ion adsorption capacity of the bone char produced. Five calcination temperatures and four calcination times were tested to identify the optimum temperature for the production of a bone char in a limited oxygen furnace. The adsorbent samples were prepared at a calcination temperature of 300, 450, 600, 750 and 900^{o}c and calcination time of 1, 2, 3 and 4hr. The result found was plotted in Figure 4.4.

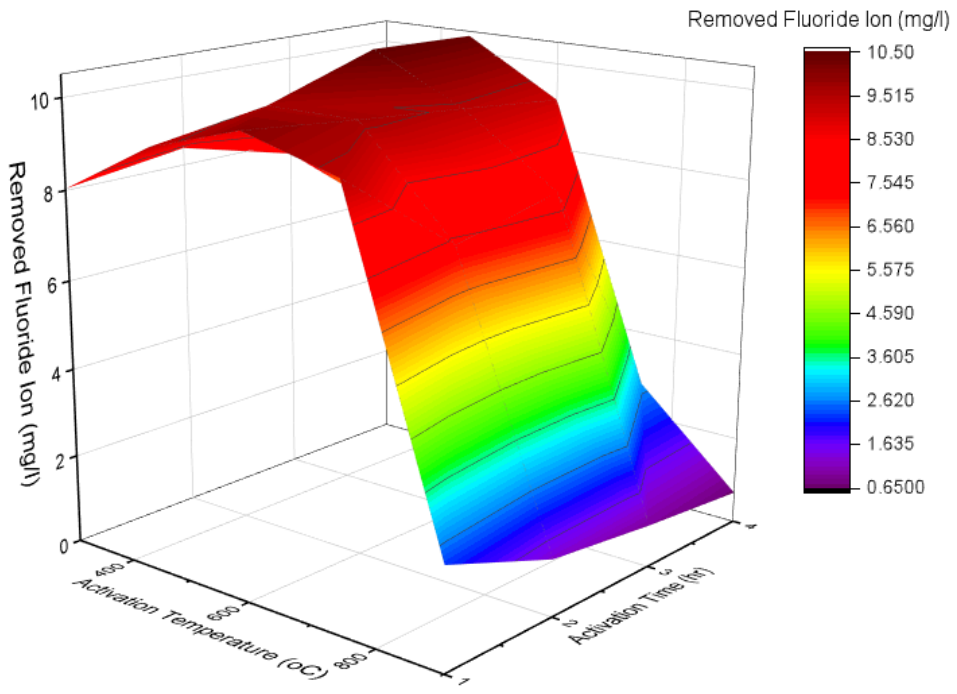


Figure 4. 4 Effect of Calcination temperatures and calcination time on bone char removal efficiency

4.3.1 Effect of Calcination Temperature

In Figure 4.4, it is observed that the bone char produced at a temperature of 450°c for a calcination time of 3 hr had the highest adsorption capacity of fluoride ion. As the calcination temperature increases beyond 450°C the fluoride ion removal efficiency of the bone char decreased. The smallest removal efficiency of the bone char was obtained at a calcination temperature of 900°c. This is probably because of the high temperature degradation of surface functional groups. More volatile components are expected to be removed and also at high temperatures the hydroxyapatite structures are assumed to be damaged since high temperature tend to collapse the hydroxyapatite structure resulting in losing ions that play role in ion exchange. The physical observation of calcined bone char shows that the color of the bone char changes from dark black to grey and then to white as calcination temperature increases as shown samples in figure 4.5.

(a) (b) (c)

Figure 4. 5 Bone char image after calcination at different time and temperature a) 300^{o}C, 1 hr b) 450^{o}C, 4 hr and c) 900^{o}C, 4 hr.

4.3.2 Effect of Calcination Time

As it is shown in Figure 4.5, the effect of calcination time on the adsorption capacity of bone char is not significant compared to the effect of temperature. The results in general show that, as the time of calcination for a given constant temperature activation increases the adsorption efficiency tends to decrease. This implies that production of a bone char at a given temperature for a prolonged time has a negative impact on the active surfaces of the bone char.

4.4 Effect of parameters on Bamboo char activation

In a similar fashion, the effect of activation parameters on the fluoride ion adsorption of bamboo char was tested. Activation temperature, time, and chemical were the main production or activation parameters tested against produced activated bamboo char for fluoride ion removal efficiency. The activation chemicals selected was, 11.4M Sodium hydroxide (NaOH), 7.8M Potassium Hydroxide (KOH) and 5.75M Phosphoric acid (H_3PO_4).

4.4.1 Effect of Calcination Temperature

Carbonization of bamboo char at different temperature (350, 400, 500 and 600°c) was done for a 30 % concentration of each activation chemical calcined for 1hr to evaluate the effect of temperature in relation to the percentage removal of fluoride ion. From figure 4.6, the effect of temperature for different activation chemicals exhibit different properties. For the basic activation chemicals as a temperature of activation increases the fluoride ion adsorption efficiency of the bamboo char tends to decrease. Bamboo char activated by KOH and H_3PO_4 at temperature of 400 and 500 °c their removal efficiency was high and then after decrease respectively. But, in cause of NaOH calcination temperature of 350 °c found to be high and then decrease This is may be because of the penetration efficiency of the basic solution helping the surface active functional groups to be removed during activation as a volatile matter. An increase in temperature facilitates the removal of functional groups easily.

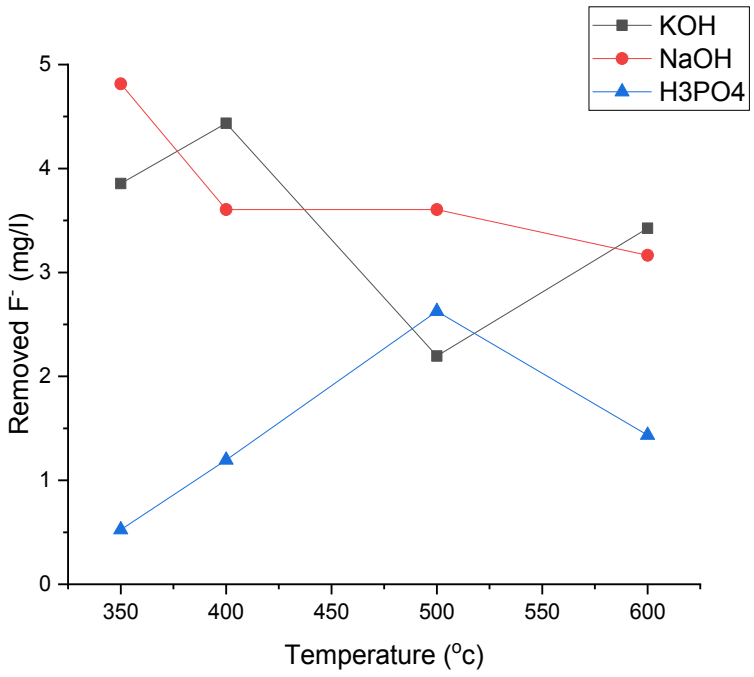


Figure 4. 6 Effect of temperature on synthesis of bamboo char for 1hr and 30% by volume chemical activation

4.4.2 Effect of Calcination Time

The effect of carbonization time was also tested to observe its effect on the adsorption efficiency of the bamboo char. Carbonization time of 0.5, 1, 1.5 and 2hrs were used for all the three activation chemicals at a concentration of 30 % with a constant carbonization temperature of 400 ^{o}C. In Figure 4.7, the effect of calcination time shows less effect on the adsorption efficiency for NaOH activated bamboo char. But for both KOH and H_3PO_4 activated bamboo chars, an increase in activation time has a tendency of improving the adsorption efficiency of the bamboo char. This effect could be because of the tendency of an increase in carbonization of more volatile matters while the carbonization time increases, creating enough porous active surfaces. .

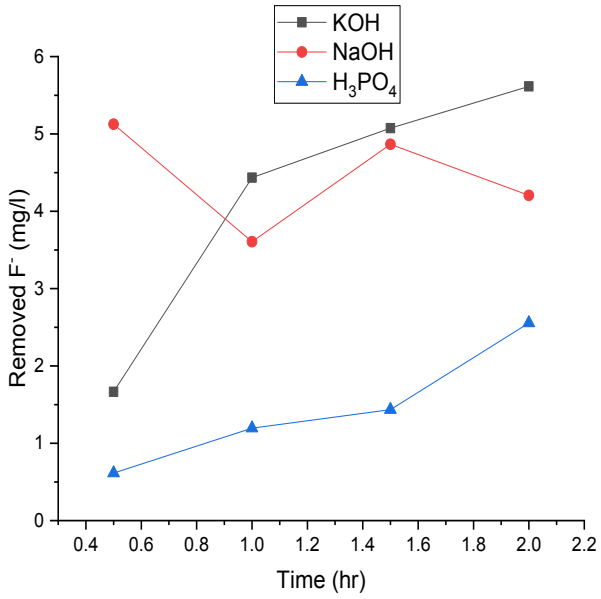


Figure 4. 7 Effect of carbonization time at a temperature of 400^{o}c and 30% by volume chemical activation

4.4.3 Effect of activation Chemical

The main importance of activation was to develop porosity (pore volume and active surface area) and also to control the pore size distributions of the prepared activated carbon.These are believed to increase the removal capacity. From the results on figures 4.6 and 4.7, KOH has a better activation performance for higher temperature and contact times. The effect of activation chemical on the fluoride ion adsorption efficiency was analyzed for four concentration levels (25, 30, 35, and 40%). The comparison of the three activation chemicals further shows that as the percent by volume of each activation chemical increases, the effect of activation tends to reach its maximum at 30 % by volume, at calcination temperature of 400 ^{o}c and contact time of 90 min for all chemicals starts to drop down. From the result shown on figure 4.8 the maximum fluoride ion removal efficiency of bamboo was 5.62 mg/l. This is greater than the removal efficiency of the white bone char from OSHO.

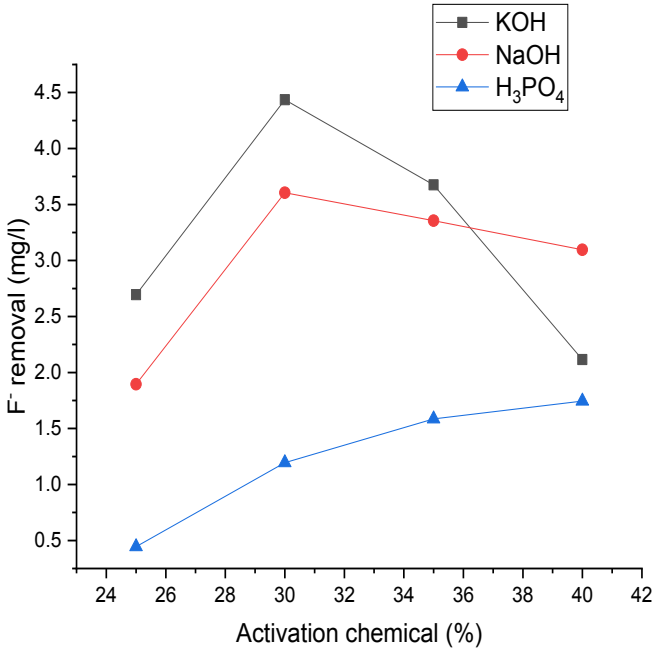


Figure 4. 8 Effect of percent by volume of activation chemical on the removal efficiency of fluoride ion at 400^{o}c for 1hr

4.5 Effect of adsorption parameters on removal efficiency of Bone char for Fluoride ion

Three adsorption parameters were selected and tested for their effect on the removal efficiency of bone char for fluoride removal. Adsorbent dose, contact time and particle size were examined to evaluate the effect of each parameter. These experiments were done for a bone char prepared at 450^{o}C calcination temperature and for 3hrs found to have a higher efficiency from the previous experiments.

4.5.1 Effect of adsorbent dose

The effect of synthesized bone char dose on the fluoride ion removal is presented in Figure 4.9. It was tested at the agitation time of 120 min by varying the adsorbent dosage. The graph of fluoride ions removed versus amount of bone char dose showed that the removal of the fluoride ions increases with an increase in the amount of bone char dose. The increase of fluoride removal capacity with increase of bone char dose can be attributed to increasing number of active sites with an increase in the adsorbent dose.

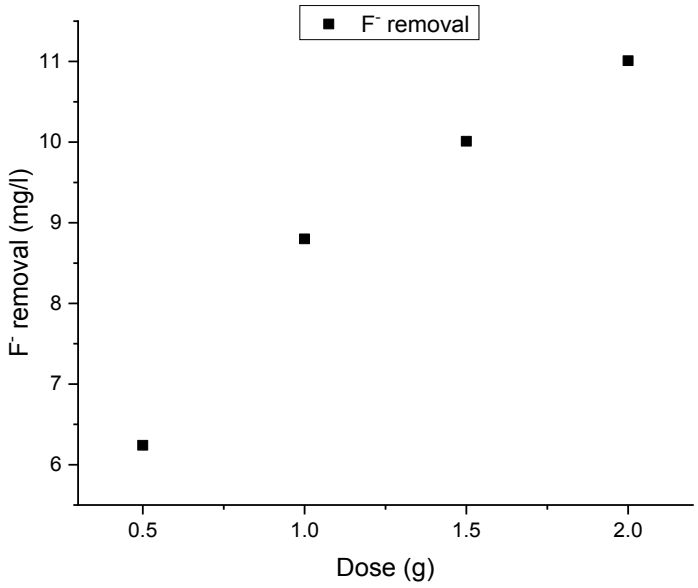


Figure 4. 9 Effect of adsorbent dose on the removal efficiency of fluoride ion

4.5.2 Effect of contact time

The adsorption capacity of fluoride ion onto bone char at different contact time is presented in Figure 4.10. As contact time increases, the percentage removal also increases initially and starts to get constant or changes the slope of the graph for the contact time range selected. The concentration of fluoride ion in the solution continued to decrease steadily from 0 to 120 min due to adsorption by bone char. Since the bone char has specific number of active site the fast adsorption at the initial stage was probably due to the initial concentration gradient between the fluoride ion in the bulk solution and the surface of the vacant active sites on the adsorbent. The reduction in removal efficiency rate for higher contact time could be due to the reduction in the available active sites on the adsorbent resulting in reduction the mass transfer of the fluoride ion in the bulk liquid to the external surface of adsorbent. The removal of fluoride ions reaches 10.69 mg/l at 2 hr.

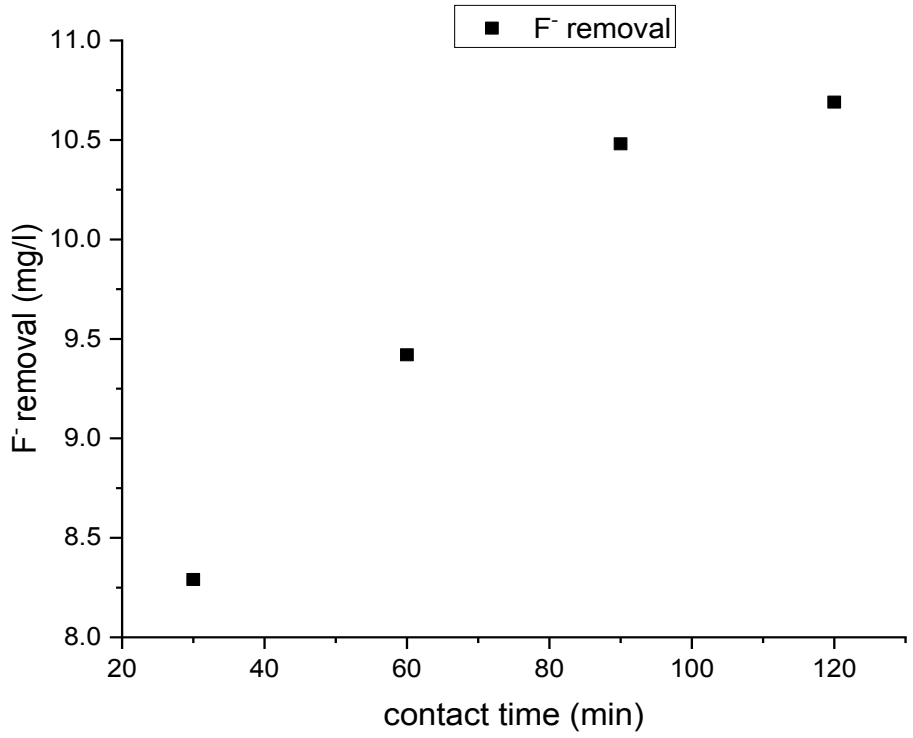


Figure 4. 10 Effect of contact time on fluoride removal efficiency of bone char

4.5.3 Effect of particle size

Effect of adsorbent particle size was tested for its effect on fluoride removal efficiency of bone char. A decrease of bone char particle size resulted in an increase in fluoride adsorption from water. Thus, reducing the bone char particle size increases the effective surface area, provides more active sites for fluoride removal and eases the exposure of more active sites to the adsorbent. The test was made using different ranges of particle sizes. The residual fluoride decreased from 11.01 mg/l to 10.69 mg/l and 10 mg/l to 8.52 mg/l after a contact time of 120 min using 355-500 μm to 500-710μm and 710-1000 μm and 1000-2000 μm sieve particle size, respectively. Since, the effect of particle size is highly dependent on operation parameters like pressure drop during continuous processes further investigation is important for to identify optimum particle size for adsorption.

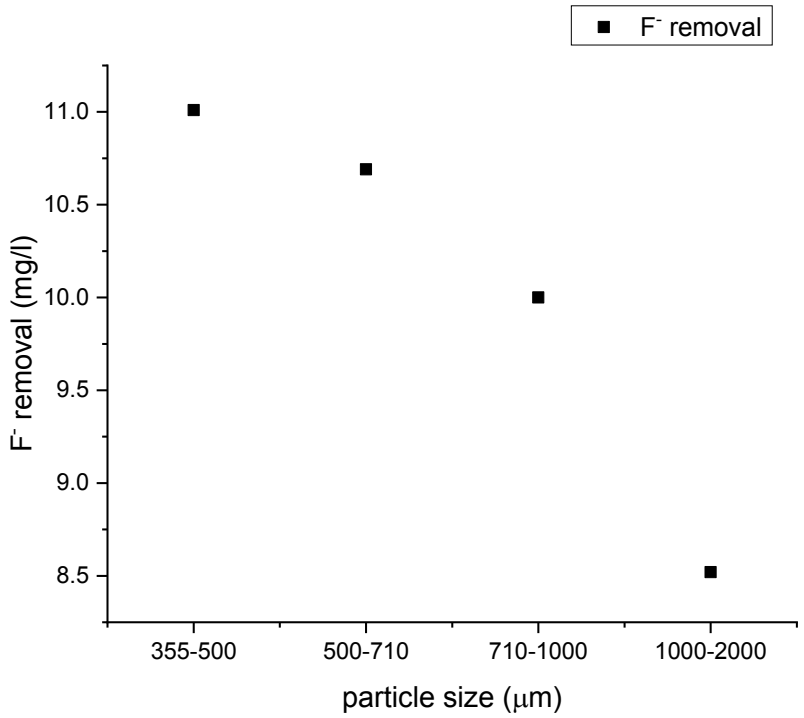


Figure 4. 11 Effect of particle size on removal efficiency of bone char on fluoride removal

4.6 Effect of adsorption parameters on removal efficiency of bamboo char for Fluoride ion

The operation parameters for adsorption processes in this section and type of bamboo char selected from previous experiments is presented in table 4.3

Table 4. 3 Operation parameters for bamboo char adsorption test

pH of initial synthetic water	8.9
Volume of Water treated (ml)	250
Activation Chemical and %	KOH and 30% by volume
Mixing Speed (rpm)	200
Carbonization time(hr)	2
Optimum Activation Temperature (^oC)	400
Initial Fluoride conc. (mg/l)	11.72

4.6.1 Effect of adsorbent dose

Figure 4.12 displays the effect of synthesized bamboo char dose on removal of fluoride ion. The effect of the adsorbent dose on fluoride ion was tested at the agitation time of 120 min by varying the adsorbent dosage. The effect of amount of adsorbent on the uptake of fluoride ion was examined. The result showed that the removal of the fluoride ions increases with an increase in the amount of bamboo char dose. The increase of fluoride removal capacity with increase of bamboo char dose can be attributed with an increasing number of active sites because of an increase in the adsorbent dose.

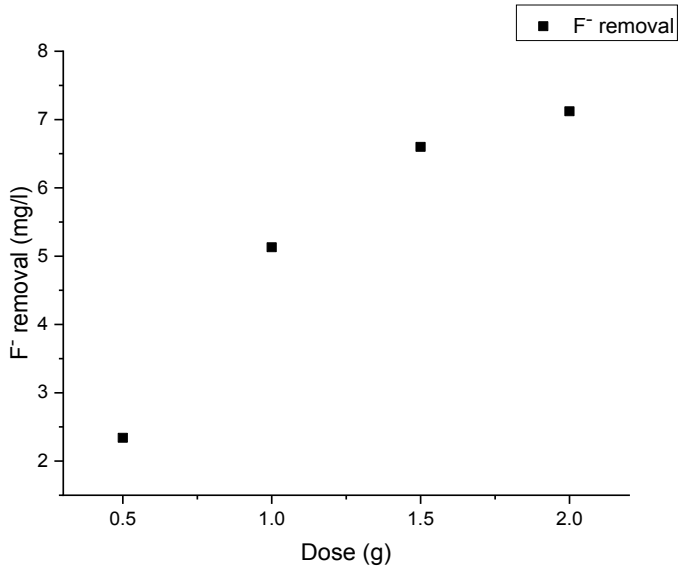


Figure 4. 12 Effect of adsorbent dose on the removal efficiency of Bamboo char

4.6.2 Effect of contact time

Effect of contact time for which the fluoride ion is in contact with the bamboo char was examined. The sorption effect of fluoride ion on the activated carbon, given in Figure 4.13 illustrates that the percentage of fluoride removal by bamboo char increases linearly as a function of contact time in the time interval examined showing the possibility of relatively high removal as the time of contact increases. In comparison to bone char the mass transfer or adsorption rate to the surface of the active sites is slower for bamboo char.

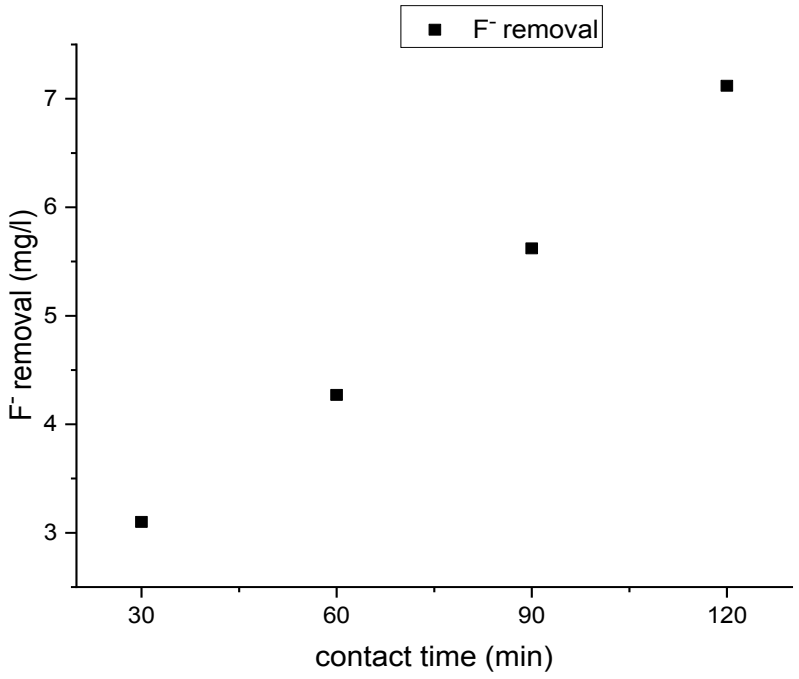


Figure 4. 13 Effect of contact time on fluoride removal efficiency of bamboo char

4.6.3 Effect of particle size

The effect of bamboo char particle size on fluoride removal efficiency was presented in Figure 4.14. A decrease of bamboo char particle size resulted in an increase in fluoride adsorption. Because reducing the bamboo char particle size is believed to increases the effective surface area providing more active sites for fluoride removal. The examinations were made using different ranges of particle sizes. The fluoride removal decreased from 8.259 mg/l to 7.1199 mg/l and 4.819 to 3.5 mg/l after a contact time of 120 min for sieve particle size ranges of 355-500, 500-710,710-1000 and 1000-2000 micrometer sizes respectively.

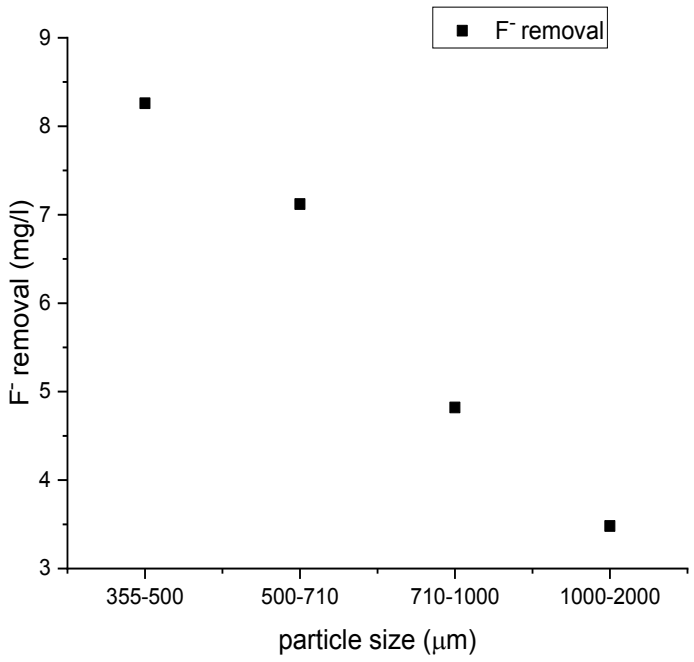


Figure 4. 14 Effect of particle size on bamboo char for fluoride removal capacity

4.7 Removal Efficiency of Coated Bone char

4.7.1 Effect of aluminum sulfate ($Al_2(SO_4).18H_2O$) Concentration

Aluminum sulfate was applied on the surface of the best performing bone char from the previous experiments in the presence of sodium hydroxide to create a coating layer of aluminum hydroxide on the surface of the bone char. Then the effect of concentration of aluminum sulfate for surface modification of bone char with different molarity (0.1M, 0.5M, 1M and 1.5M) and adsorbent dose of 2g was examined. The result shown on the figure 4.15 indicates that an increase in the molarity of coating material tends to reach maximum fluoride ion removal efficiency at 1M concentration of aluminum sulfate and tends to decrease. The maximum percentage removal capacity of fluoride ion at 1M coating solution was 11.63 mg/l. Compared to the maximum absorption efficiency of bone char from the previous experiments which is 10.48 mg/l and the HAP produced by OSHO the coating improved the removal efficiency by almost 1.172 mg/l. For the case of reduction in adsorption efficiency of a coated bone char while increasing the coating chemical concentration could be due to the possibility of aluminum

hydroxide precipitates blocking pores and limit access to internal surfaces clogging active site of bone char.

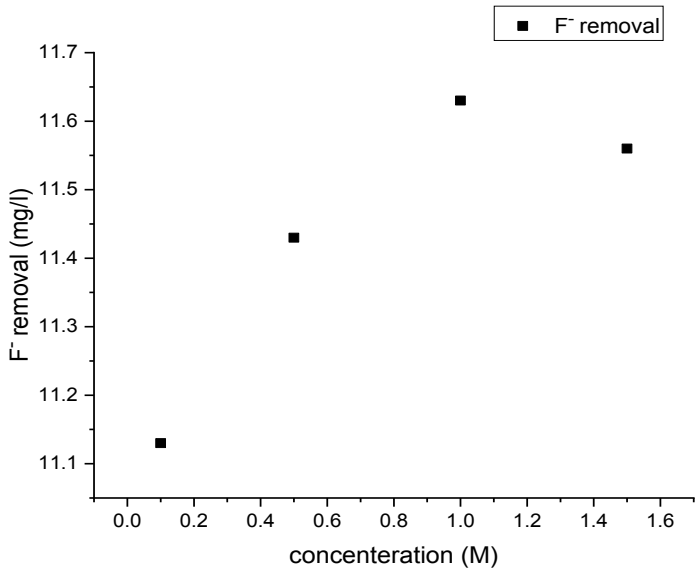


Figure 4. 15 Effect of $Al_2(SO_4).18H_2O$ concentration on the removal efficiency of activated bone char

4.7.2 Effect of time on impregnation of bone char

The percentage removal of fluoride ion has been investigated as a function of contact time of {1, 2, 4 and 6 hr} with 11.72 mg/L initial fluoride concentration and 2.0 g of adsorbent. Figure 4.16 shows that as coating time increased the amount of fluoride adsorbed increased. The removal of fluoride ion coating time for 6 hr (11.66 mg/l) showed in the Figure 4.16, which had high adsorption capacity. Compared to the HAP produced in OSHO and bone char produced in laboratory where the first hour absorption was around 9.61 and 9.38 mg/l, respectively, the coating has shown an improvement in increasing the affinity of fluoride ion attraction towards the active sites.

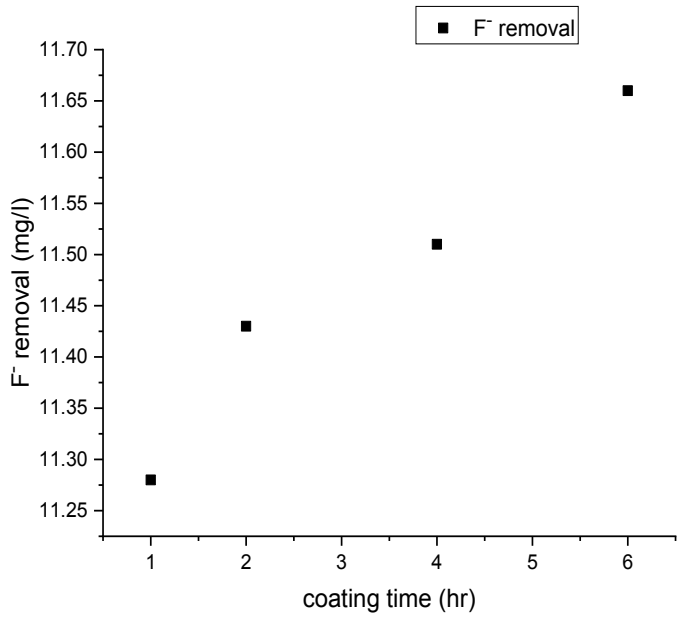


Figure 4. 16 Effect of reaction time on fluoride removal capacity

4.7.3 Effect of coating ratio

For this experiment the concentration of aluminum sulfate was maintained at 0.5 M and the bone char to the coating solution ration was varied to see the effect of coating chemical ratio. The results on figure 14.17 showed that as bone char to aluminum sulphate ratio increases percentage removal capacity of fluoride ion increased. This is due to an increased contact of the bone char to be coated with the coating solution resulting in facilitation of the coating efficiency.

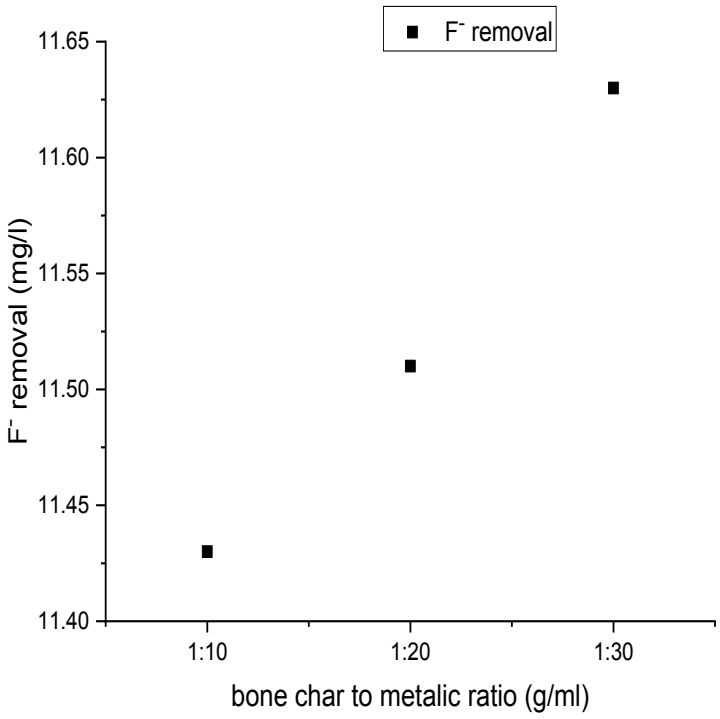


Figure 4. 17 Effect of bone char to coating solution ratio on fluoride removal efficiency

4.7.4 Effect of impregnation temperature

In this study, the bone char was coated at temperature of {30, 40 and 50^{o}c} and the result shows that for the range of temperatures chosen, the effect of coating temperature was analyzed. As the reaction temperature increased the fluoride removal efficiency also increased as shown in Figure 4.18. This might be because of the effect of temperature on the facilitation of the reaction between aluminum sulphate and sodium hydroxide to speed up the coating of aluminum hydroxide on bone char. For higher temperature above 40^{o}C the effect seems not significant.

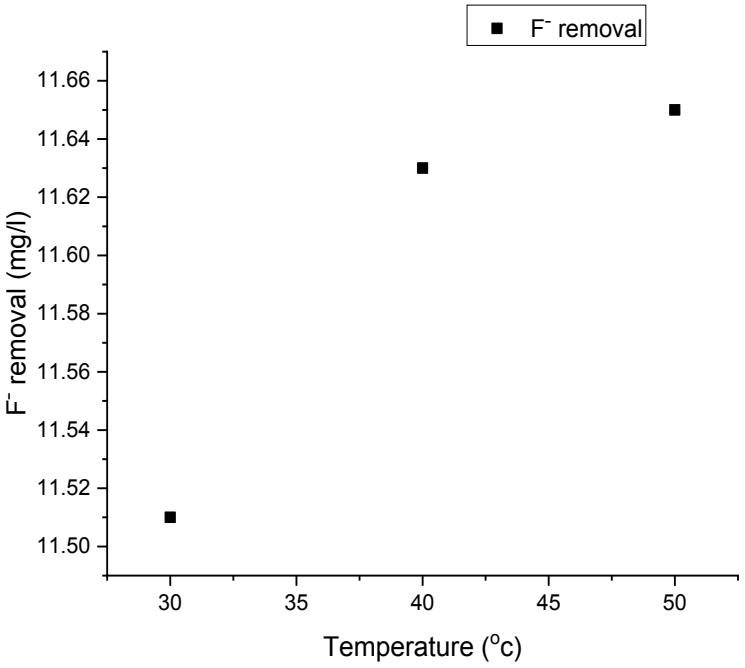


Figure 4. 18 Effect of Bone Char Coating Temperature on fluoride removal efficiency

4.8 Characterization of produced Bone Char, coated bone char, grey bone char and raw bone

4.8.1 X-ray diffraction (XRD):-

The XRD patterns of raw bone (RB), bone char (BC), grey bone char (GBC) and coated bone char (CBC) samples are presented as shown in Figure 4.19. The XRD patterns confirmed that the diffraction peaks correspond to the crystal structure of the adsorbent in all samples. From the XRD patterns observed, the raw bone powder consists of a poorly crystalline phase compared to the calcined and coated ones. This is probably due to the presence of organic substances resulting in less or relatively no visible peak splitting. A decrease in the peak width and a considerable increase in the peak height were observed with coating. This indicates an increase in the crystalinity. The peak positions for $2\theta^{o}$ angles for raw bone 25.90, 31.02, 40.1, 46.58 and 49.6 and for grey bone char 26.04, 29.12, 31.94, 33.14, 34.22, 39.86, 46.82, 48.22, 49.76, 50.66, 51.5, 52.46 and 53.22 and peak position for bone char 26, 31.94, 40.34, 46.84 and 49.72 and final peak position for coated bone char 14.82, 25.78, 29.76, 31.94, 40.02, 42.34, 46.58 and 49.46. The new peaks on the XRD pattern of the coated bone char could be due to the formation of aluminum oxide on the bone char surface. This is confirmed by cross checking with EDX chemical

composition results. New peak occurred having peak position for 2θ^{o} angles of 14.82 in case of coated bone char this is most probable due to coating.

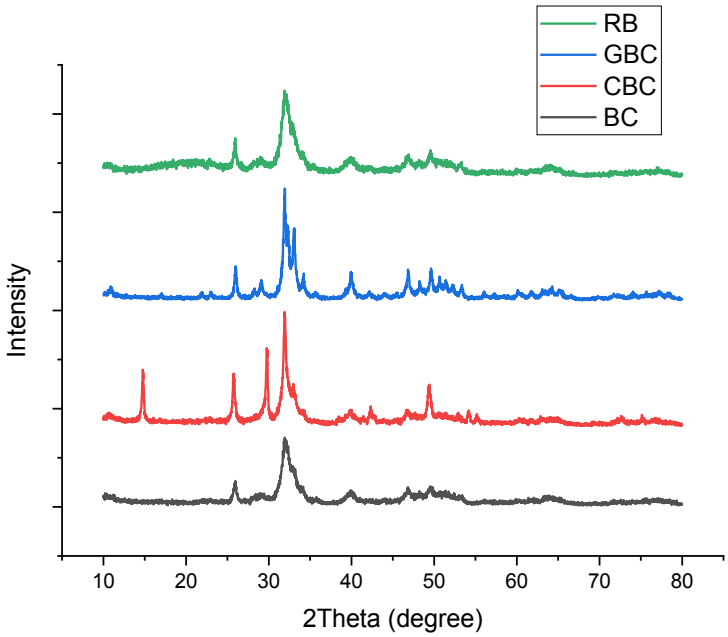
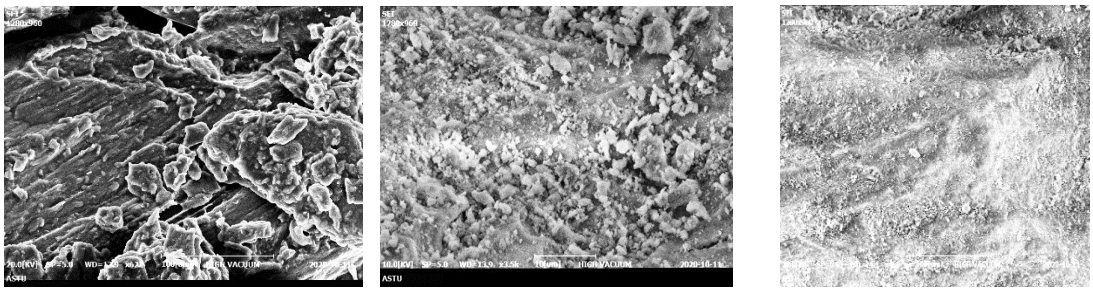


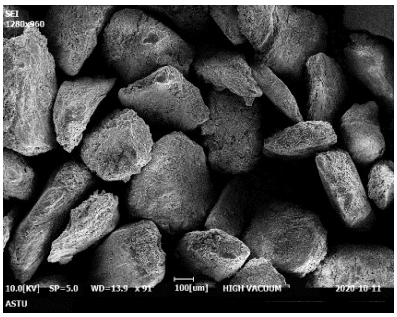
Figure 4. 19 XRD pattern of raw bone (RB), grey bone char before treatment (GBC), coated bone char before treatment (CBC) and bone char before treatment (BC)

4.8.2 Scanning electron microscope analysis (SEM):-

The results showed in figure 4.20 that raw bone, Bone Char and modified bone char by impregnation with aluminum hydroxide. Figure 4.21 show that the composition of BC and modified BC was analyzed by energy dispersive X-ray (EDX) measurement. The surface morphology shows a change through every step of activation. The surface of the raw bone is covered by a relatively thick layer probably organic residue. After calcination the bone char showed a relatively clean surface exposing the active sites of the bone. On the coated bone surface a relatively clean and neat surface is observed. The peaks obtained in EDX spectra identified phosphorous, calcium, carbon, sodium, magnesium and oxygen as the main constituents of BC. But modified bone char has aluminum in addition to constituents of bone char without modification. EDX analysis confirmed that 4%wt aluminum coated on bone char. This is because of the modification done on the surface of the bone char using aluminum hydroxide. This confirms that the coating was successful and the resulting improvement of the adsorption capacity after coating is due to the presence of aluminum coating.

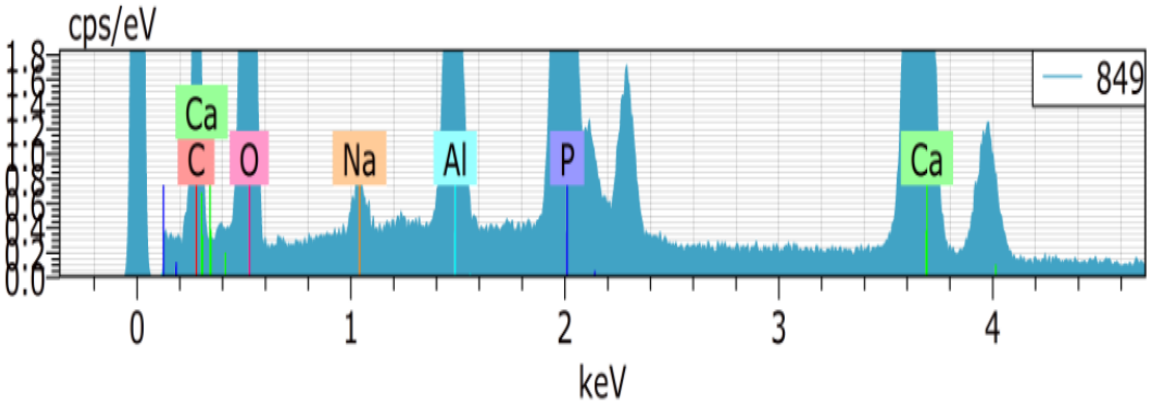


a) **B)** **c)**

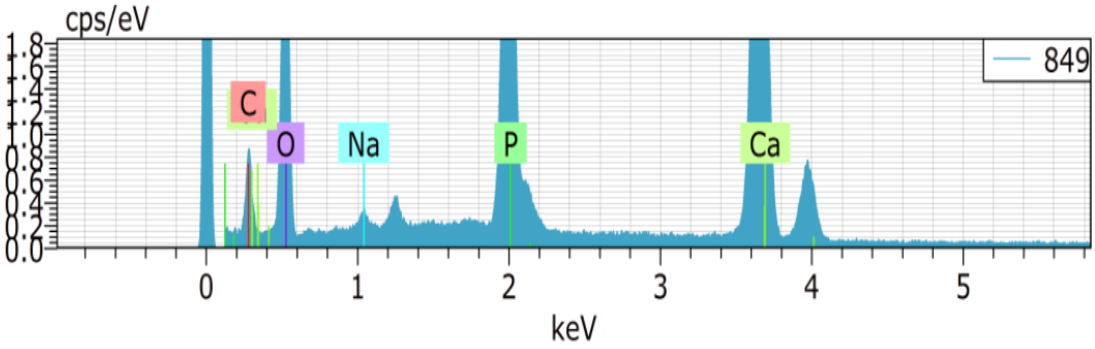


d)

Figure 4. 20 Scanning electron micrographs of raw bone (a), bone char before treatment (b), grey bone char before treatment (c) and coated bone char before treatment (d)



a,



b,

Figure 4. 21 EDX spectra of (a) modified BC before treatment and (b) BC before treatment

4.8.3 Fourier Transform Infrared Spectroscopy (FTIR):

Raw bone (RB) in Figure shows the FT-IR spectrum of the raw precursor where the band at 3435 cm^{-1} corresponds to the stretching of O-H and the absorption band at 2921 - 2854 cm^{-1} is assigned to the C-H stretching which were present in all the samples with reduced intensities.. Additionally, the bands of groups C = O, C = C and C = N corresponding to the organic phase of the bone matrix are identified at 1459–1741 cm−1. The band of the phosphate group PO_4^{3-} was observed at 1046 cm^{-1}, the peaks of the carbonate group CO_3^{2-} are evident at 875, 1231 and 1442 cm^{-1}. Coated bone char (CBC) in red color showed on the figure the broad band observed at 3553 cm-1 could be attributed due to aluminum hydroxide coated on bone char and other function group bonded with hydrogen. The OH-stretching vibration was observed at 3610 cm^{-1} whereas 1621 cm^{-1} is been assigned to physically adsorbed water molecules. The C-O stretching vibrations at 1461 and 1419 cm^{-1} has been assigned to CO_3^{2-} group, which appears under all the temperatures indicating that CO_3^{2-} is present until 600ºC. The bands of C = O and C = C (protein and collagen) were assigned to the peaks at 1621 cm^{-1} corresponding to the organic phase of bone material. This peak disappears at high temperature, indicating its removal from the bone material during calcination. The bands at 1152 and 1094 cm^{-1} has been assigned to the P -- O stretching vibrations of PO_4^{3-} group. The band at 874 cm^{-1} for coated bone char, bone char and grey bone char (GBC) has been assigned to CO_3^{2-} group. The bands at 660, 601 and 564cm^{-1} corresponds to PO_4^{3-} bending vibrations. Bone char (BC) without coating on the figure showed the band at 601 and 566 cm^{-1} corresponds to PO_4^{3-} bending vibrations. And in similar fashion the band occurred 604 and 568 cm-1 corresponds to PO_4^{3-} bending vibrations in grey bone char.

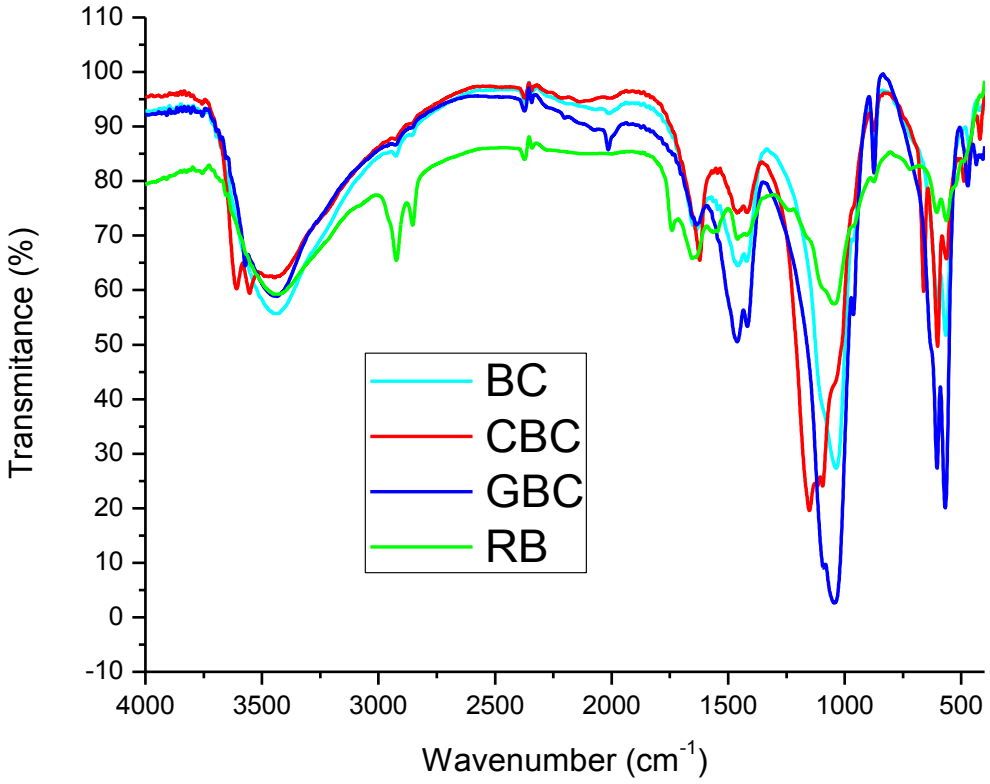


Figure 4. 22 FT-IR spectra of raw bone (RB), bone char before treatment (BC), coated bone char before treatment (CBC) and grey bone char before treatment (GBC)

Coated bone char after treatment (CBCAT) showed in figure 4.23 the OH-stretching vibration was observed at 3444 cm^{-1}. The OH vibration peaks was varied compered to coated bone char before treatment. This is due to fluoride ions adsorbed on its surface. The C - O stretching vibrations at 1461 and 1421 cm^{-1} has been assigned to CO_3^{2-} group, which appears under all the temperatures indicating that CO_3^{2-} is present until 600^oC. The bands at 1038 cm^{-1} has been assigned to the P -- O stretching vibrations of PO_4^{3-} group. The band at 875 cm^{-1} has been assigned to CO_3^{2-} group. The bands at 605 and 566cm^{-1} corresponds to PO_4^{3-} bending vibrations. Bone char after treatment (BCAT) showed in figure 4.23 the OH-stretching vibration was observed at 3445 cm^{-1}. This also in similar to CBCAT shows a change in OH stretching vibration peaks due to the vacant space occupied by fluoride ion. The bands at 1041 cm^{-1} has been assigned to the P -- O stretching vibrations of PO_4^{3-} group. The band at 873 cm^{-1} of the bone char after treatment has been assigned to CO_3^{2-} group. Bone char after treatment in the

figure showed the band at 605 and 565 cm^{-1} corresponds to PO_4^{3-} bending vibrations. Grey Bone char after treatment (GBCAT) showed in figure 4.23 the OH-stretching vibration was observed at 3441 cm^{-1}. This also in similar to CBCAT and BCAT shows a change in OH stretching vibration peaks due to the vacant space occupied by fluoride ion. The bands at 1042 cm^{-1} has been assigned to the P -- O stretching vibrations of PO_4^{3-} group. The band at 873 cm^{-1} of the grey bone char after treatment has been assigned to CO_3^{2-} group. Grey Bone char after treatment in the figure showed the band at 603 and 567 cm^{-1} corresponds to PO_4^{3-}bending vibrations.

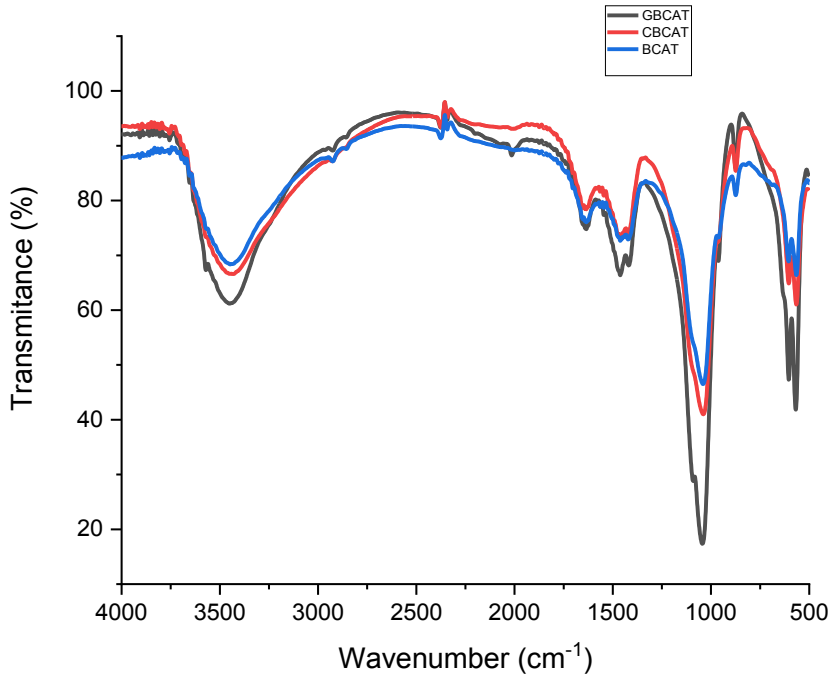


Figure 4. 23 FT-IR spectra of bone char after treatment (BCAT), coated bone char after treatment (CBCAT) and grey bone char after treatment (GBCAT)

4.9 Kinetic Model Prediction

4.9.1 Kinetic models for fluoride removal on Bone char

During adsorption two main processes are involved; physical (physisorption) or chemical (chemisorption). Physical adsorption is as a result of weak forces of attraction (van der Waals), while chemisorption involves the formation of a strong bond between the solute and the adsorbent that involves the transfer of electrons. Kinetic model can be classified in to two;

pseudo first and pseudo second order kinetic model. In this study, the adsorption process is physiorption and all bone char are fit with pseudo second order kinetic model. This indicate, that the rate adsorption of solute is proportional to the available sites on the adsorbent and the reaction rate is dependent on the amount of solute on the surface of the adsorbent—the driving force ($q_e - q_t$) is proportional to the number of active sites available on the adsorbent.

Based on the mathematical analysis done on the fluoride adsorption efficiency data, the resulting linear regression of pseudo first and second order kinetic models are shown in Figure {4.24} and Figure {4.25}. Contrary to the pseudo-first-order equation the pseudo second order fitting of the kinetic data showed excellent fit with high correlation coefficient (R^2 =0.99666). So, the adsorption of fluoride ion onto bone char followed pseudo-second-order kinetics.

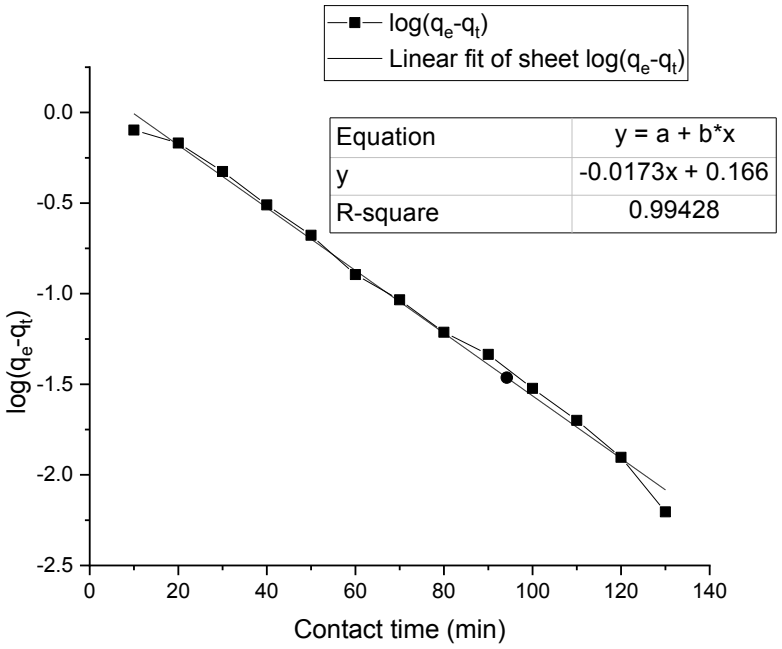


Figure 4. 24 Pseudo first order kinetic model for fluoride adsorption on bone char

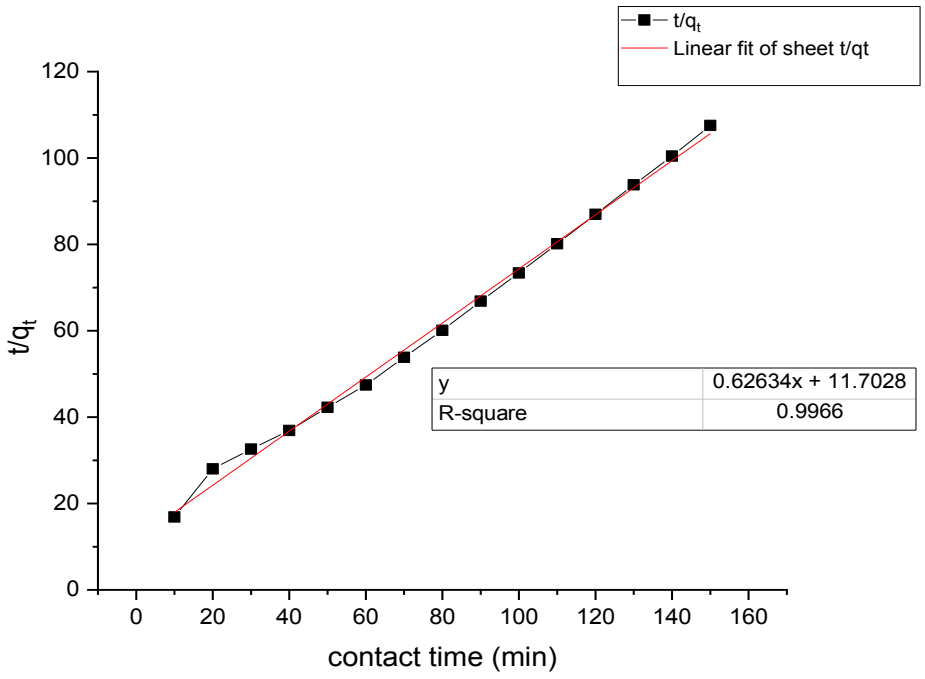


Figure 4. 25 Pseudo second order kinetic model of fluoride adsorption on bone char

4.9.2 Kinetics models for fluoride removal on coated Bone char

The regression coefficient for pseudo first order kinetics (R^2 =0.95517) was compared with correlation coefficient of pseudo second order kinetics (R^2 =0.99714) and the result showed that pseudo-second-order kinetic model is the governing adsorption kinetic model for the adsorption of fluoride onto a coated bone char.

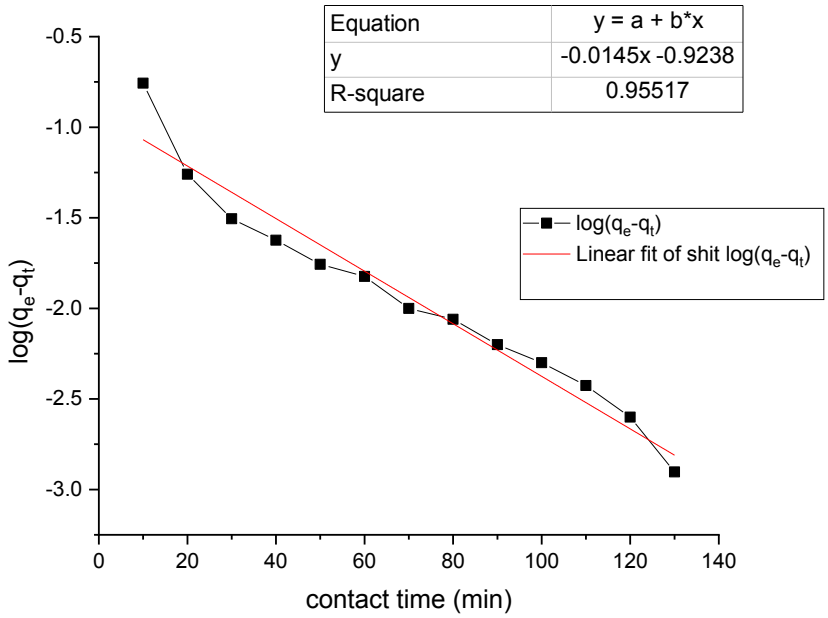


Figure 4. 26 Pseudo first order kinetics models for fluoride adsorption on coated Bone char

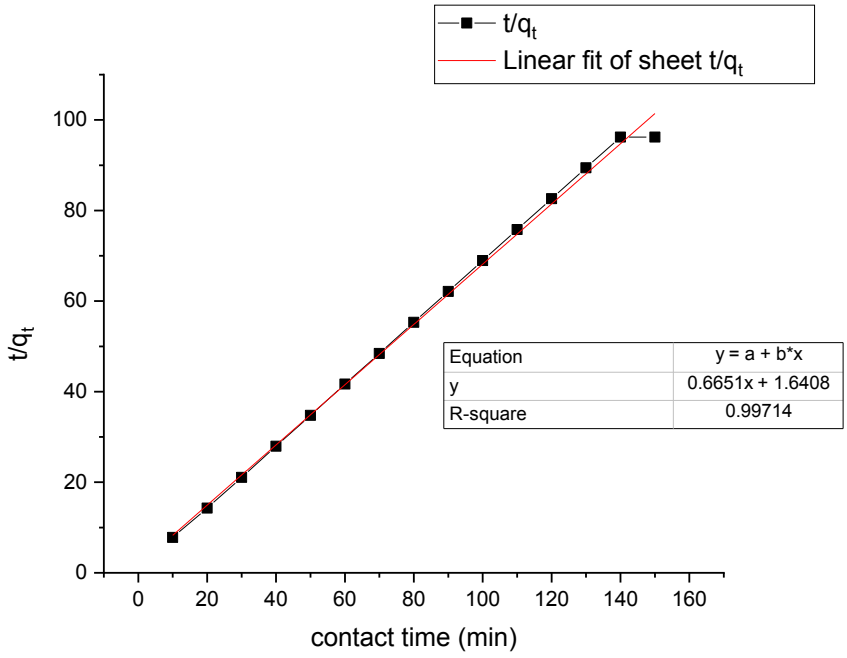


Figure 4. 27 Pseudo second order kinetics models for fluoride adsorption on coated Bone char.

4.9.3 Kinetic models for fluoride removal on HAP

The regression coefficient square showed on figure 4.28 and figure 4.29 depicted that the second order kinetic model (R^2= 0.99946) had excellent fit compared to first order kinetic model (R^2 = 0.91951). Therefore, the adsorption of fluoride onto HAP followed pseudo-second-order kinetics and the best model that fits the experimental data selected in this study was pseudo-second-order kinetics.

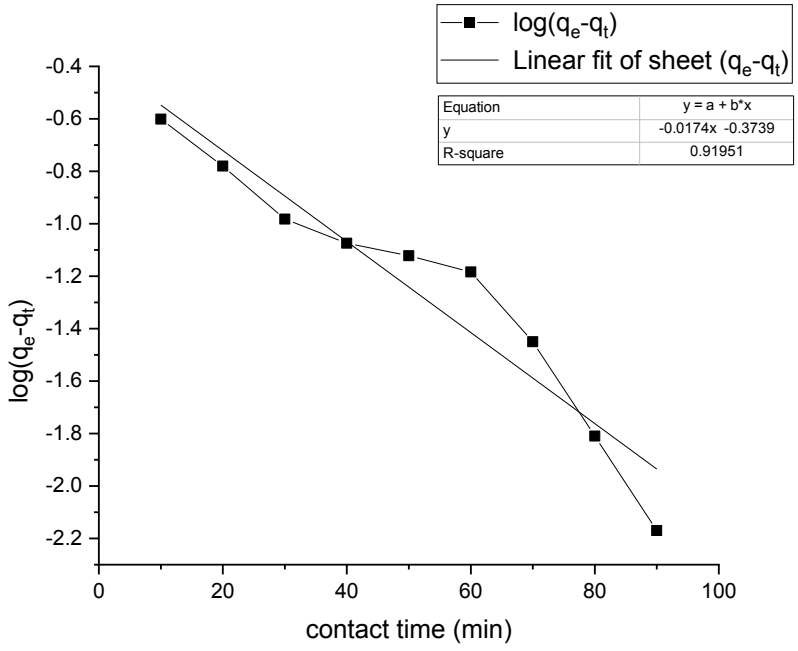


Figure 4. 28 Pseudo first order kinetics models for fluoride adsorption on HAP

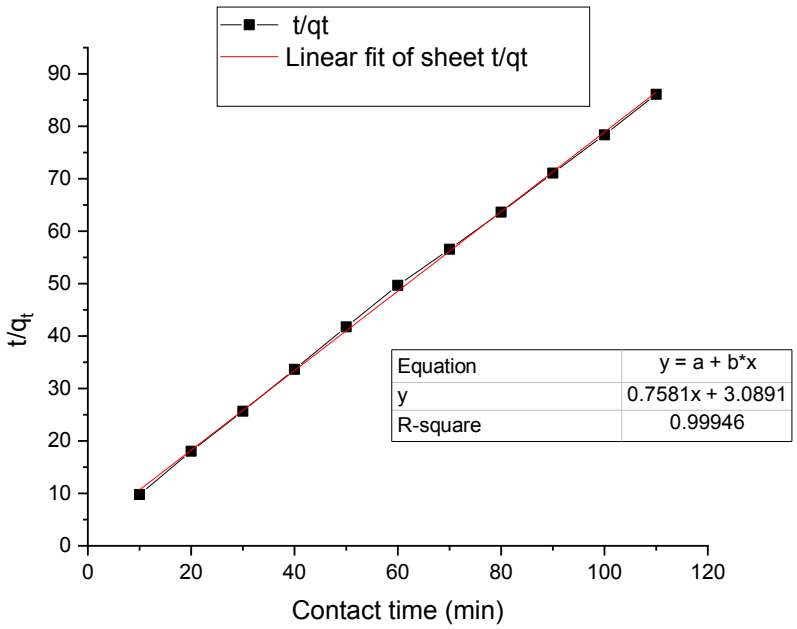


Figure 4. 29 Pseudo second order kinetics models for fluoride adsorption on HAP

4.9.4 Kinetics models for fluoride removal on Grey bone char

The regression coefficient showed in Figure 4.30 and Figure 4.31 depicted that the second order kinetic model (R^2= 0.98031) had excellent fit compared to first order kinetic model (R^2 = 0.96854). Therefore, the adsorption of fluoride onto grey bone char followed pseudo-second-order kinetics and the best model that fits the experimental data selected in this study was pseudo-second-order kinetics.

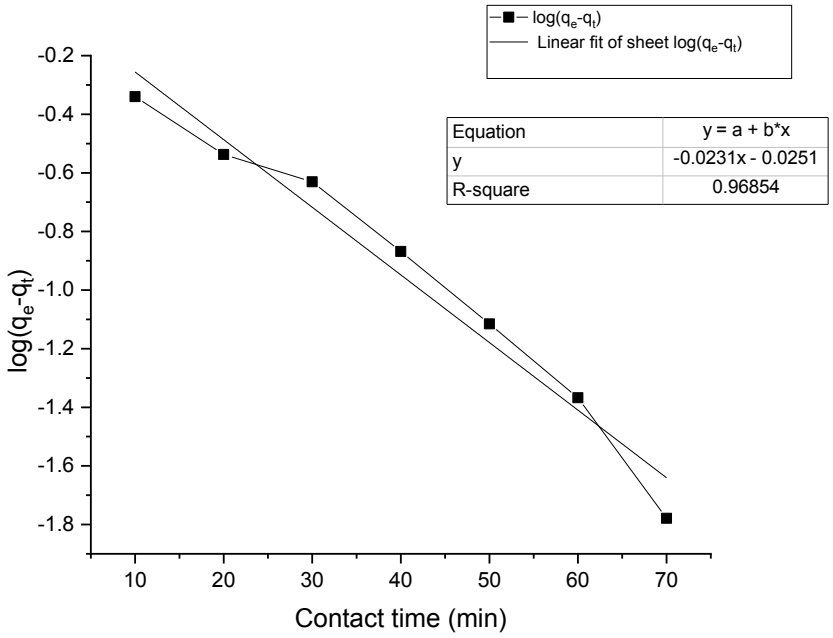


Figure 4. 30 Pseudo first order kinetics models for fluoride adsorption on Grey bone char

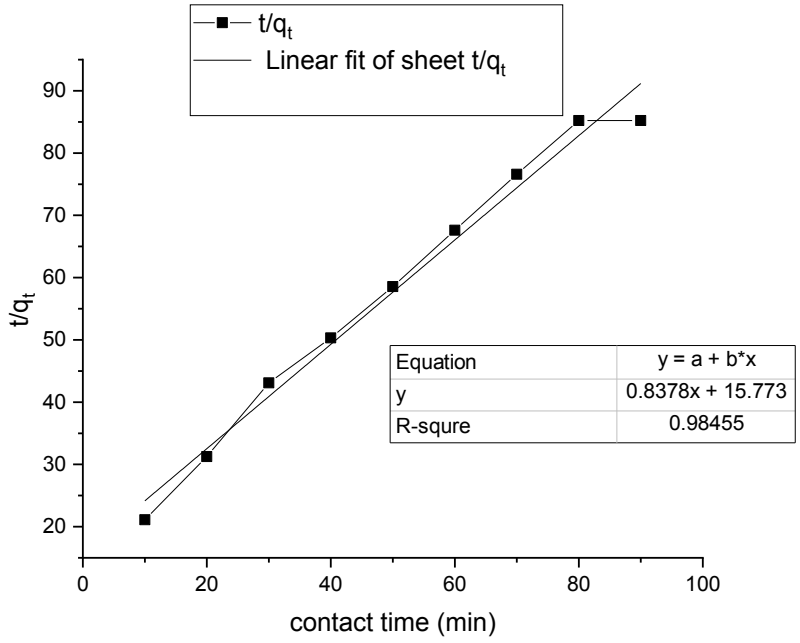


Figure 4. 31 Pseudo second order kinetics models for fluoride adsorption on Grey bone char

4.9.5 Kinetics models of for fluoride adsorption on white bone char

The regression coefficient showed in Figure 4.32 and Figure 4.33 depicted that the second order kinetic model (R^2= 0.988031) had excellent fit compared to first order kinetic model (R^2 = 0.91658). Therefore, the adsorption of fluoride onto white bone char also followed pseudo-second-order kinetics and the better model that fits the experimental data selected in this study was pseudo second-order kinetics.

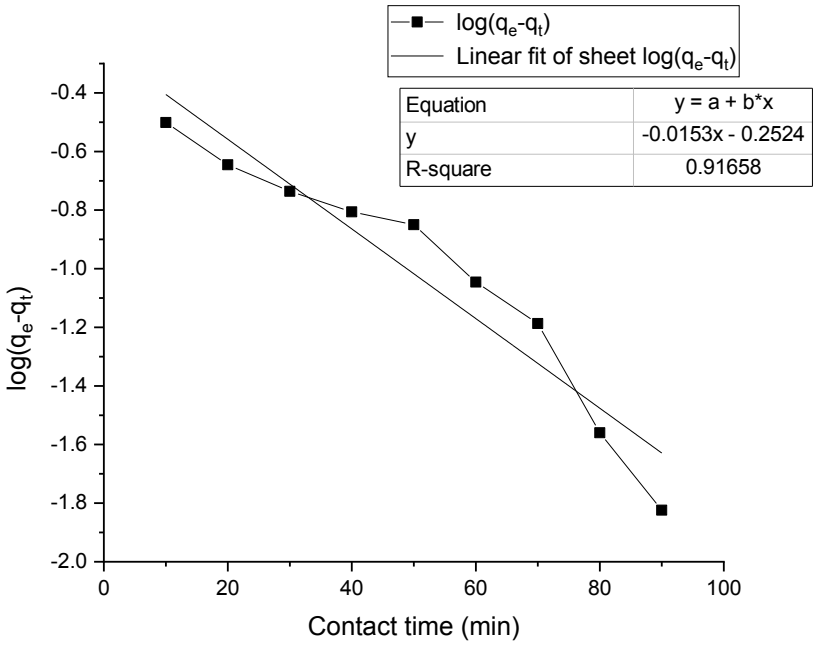


Figure 4. 32 Pseudo first order kinetics models for fluoride adsorption on white bone char

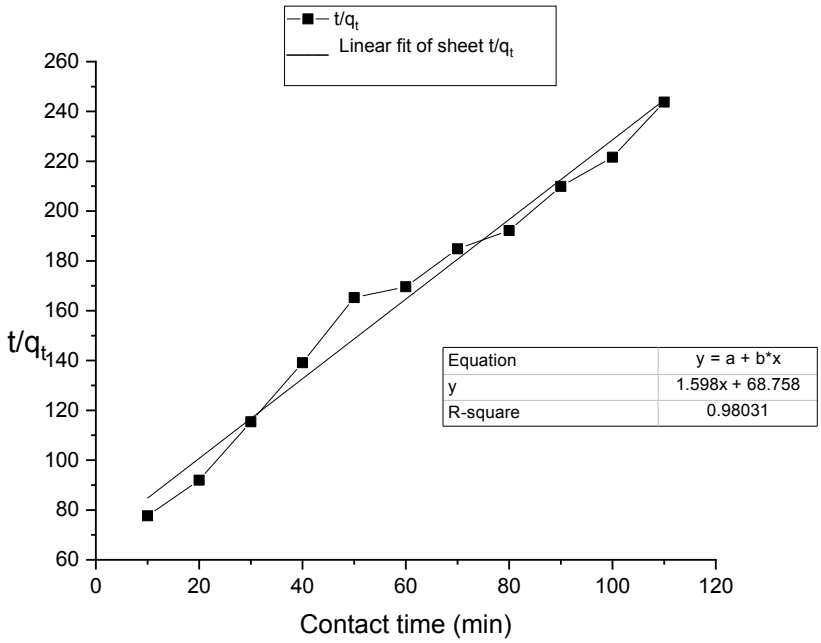


Figure 4. 33 Pseudo second order kinetics models for fluoride adsorption on white bone char

4.9.6 Kinetics models for fluoride adsorption on bamboo char

The regression coefficient shown from Figure 4.34 and Figure 4.35 depicted that the second order kinetic model (R^2 = 0.99101) had a better fit than the first order kinetic model (R^2 = 0.95424). The better kinetic model that fits to the adsorption process is obtained to be pseudo second order kinetics model for this adsorbent.

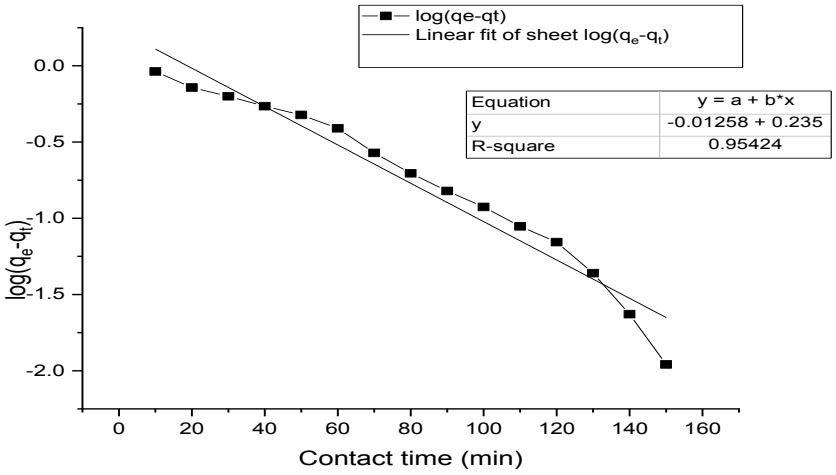


Figure 4. 34 Pseudo first order kinetics models for fluoride adsorption on bamboo char

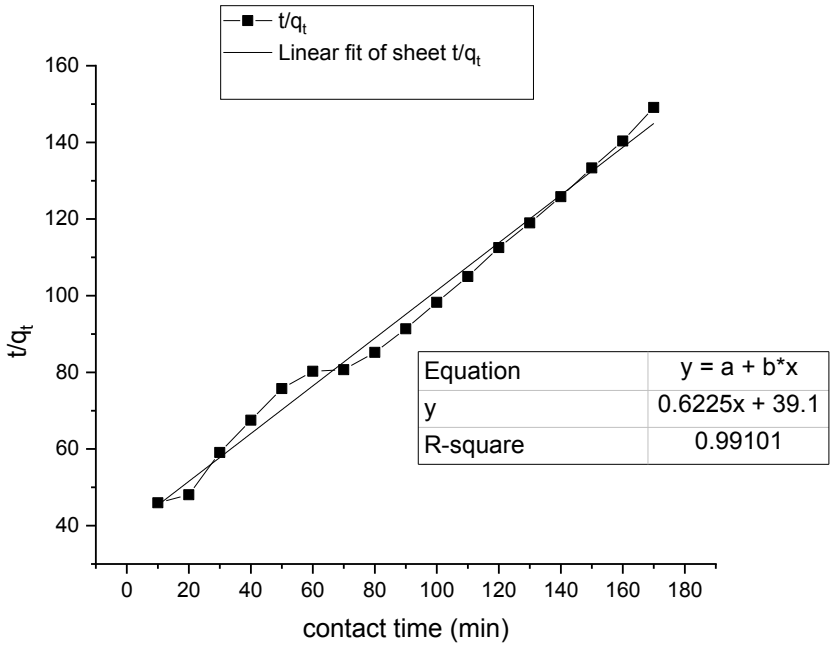


Figure 4. 35 Pseudo second order kinetics models for fluoride adsorption on bamboo char

4.10 Comparison of fluoride removal efficiency of prepared bone char and coated bone char with adsorbents from OSHO

Modjo Defluoridation center prepared three types of adsorbents for fluoride removal from ground water. Those adsorbent are HAP (hydroxyl apatite), White and grey bone char. The fluoride removal efficiencies of those adsorbent (HAP, Grey and White bone) were 10.22, 7.51 and 3.61 mg/l, respectively. Figure 4.35 showed that prepared bone and coated bone char had high fluoride removal efficiency of 11.01 and 11.66 mg/l, respectively which higher than the adsorbents prepared from industry. The removal capacity of those adsorbents were measured for the same particle size (355-500µm), adsorbent dose (2g/250ml) and contact time of 2 hr. Optimal value for prepared coated bone char of 1M aluminum sulphate which is locally available chemical and at a reaction temperature of 40^{o}c.

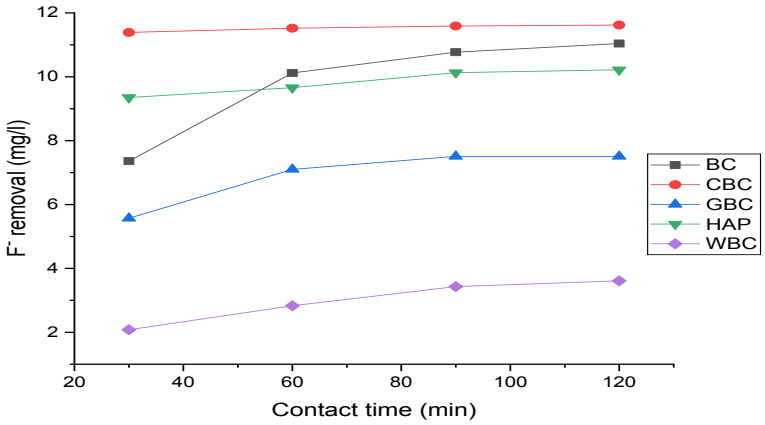


Figure 4. 36 Effect of contact time on prepared bone char and coated bone char in comparison to commercial

4.11 Fluoride removal efficiency on bone char and Sequential application with bamboo char

In this study two adsorbent bone char and bamboo char were used for fluoride removal.by taking in to account the adsorbent dose of {2 g}, contact time of {2 hr}, mixing speed {200 rpm}, particle size of {355-500µm} and initial fluoride concentration of {11.72 mg/l} of bamboo char was taken. To minimize the error, the testes done were triplicated and their average was taken. Then fluoride removal efficiency was found to be {8.31 mg/l}.

After 8.31 mg/l fluoride ion was removed by bamboo char the remaing fluoride ion was removed by bone char by taking similar bamboo char particle size {355-500µm}, adsorbent dose {2 g}, mixing speed {200 rpm} and contact time of {2 hr} was takes place on bone char but the only difference is initial fluoride concentration in case of bone char adsorbent 3.41mg/l. final fluoride removal capacity after treated by bone char was 10.98 mg/l.

The important use of this sequential application treatment of fluoride removal on bamboo char followed by bone char: (1) bamboo char removes co-existing ion in addition to fluoride ion (2) removal of odor or test and (3) to increase the removal efficiency

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Excess amount of fluoride in drinking water is a public health concern globally and especially in the Rift Valley part of Ethiopia. Under this study, as a low-cost adsorbent for water treatment, fluoride removal from drinking water was assessed using locally available adsorbents, bone char, bamboo char and bone char which was surface modified by using locally available chemical, aluminum sulphate (from Awash Melkasa aluminum sulphate chemical factory).

Collecting bone from different area can solve environmental pollution in addition to fluoride removal. The results show that the calcination temperature and the calcination time play a very significant role in changing the properties of bone and bamboo chars. In this study the optimization parameters during charcoal preparation included, calcination temperature, calcination time for bone char preparation and effect of chemical activation, carbonization temperature and carbonization time for bamboo char during charcoal preparation. After adsorbent preparation fluoride removal efficiency was checked and the optimum calcination time, calcination temperature and activation chemical were determined and then after the main parameter to select fluoride removal capacity like contact time, dosage and particle size was determined. This thesis work also confirmed that preparation of the best optimal adsorbent, bone char with co-application of bamboo char and surface modification of bone char to enhance fluoride removal efficiency. Results obtained from this study showed that, the calcination temperature and calcination time were major effect in the removal efficiency of bone char and bamboo char and also the chemical activation has similar effect as temperature and time for the removal of fluoride in case of bamboo char. Fluoride removal capacity of prepared adsorbent in comparison with industry (Modjo Defluoridation center or Oromo Self – Help Organization) is the other confirmed part of this study. In this study bone char adsorbent was prepared at calcination temperature {300, 450, 600, 750 and 900 ^{o}c} and calcination time {1, 2, 3 and 4 hr}. Maximum fluoride removal efficiency was achieved at a temperature of 450^{o}c for 3 hr with initial fluoride concentration of 11.72 mg/l, particle size 355-500 μm, contact time 2 hr and mixing speed 200 rpm. The maximum removal capacity of bone char was determined to be

11.01 mg/l and after coating the removal capacity was (11.64 mg/l). The removal capacity of bone char with sequential application of bamboo char in this study the fluoride ion was first removed by bamboo and the remained fluoride ion was removed by bone char (8.767 to 11.5 mg/l) and this result shows significant change. In comparison to the industry (Modjo Defluoridation center) the maximum removal capacity of fluoride ion was 10.22 mg/l using HAP adsorbent, 7.51 mg/l grey bone char and 3.61 mg/l using white bone char adsorbent which is less removal capacity when compared to the prepared bone char and coated bone char. The morphology, crystalline phase and functional group synthesized adsorbent was characterized using SEM, XRD and FTIR. The adsorption kinetics was also determined and the kinetic results obtained from this study fitted well with the pseudo second order kinetic model. The increase in surface area and volume of the bone char enhanced the adsorption efficiency.

5.2. Recommendation

- ✓ For future study it's better to activate bone char to increase the removal capacity.
- ✓ To determine specific surface area, pore volume and pore diameter using Brunauer, Emmett and Teller (BET) instrument
- ✓ To evaluate the effect of other parameter like agitation by varying mixing speed is other future recommendation.
- ✓ Other future study or recommended part of this is also designing and scale up of adsorption column and applying the prepared adsorbent to the existing site.
- ✓ To determine the relevant adsorption isotherm for produced and modified adsorbent.
- ✓ To test the recommended bone char, bamboo char and coated bone char in continuous adsorption.
- ✓ Other future study also cost analysis determination of the adsorbent
- ✓ Determine regeneration of the adsorbent

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APPENDICES

Appendix A

Solution preparation of aluminum sulphate on bone chars coating

Aluminum sulfate is a chemical compound with the formula $Al_2(SO_4)_3$. It is soluble in water.

Formula: $Al_2(SO_4)_3.18H_2O$

Molar mass: 666.42 g/mole

To prepare 0.1M of aluminum sulphate in 0.1L (100ml)

Molarity (M) = $\frac{moles}{volume\ (liter)}$ ……………………………………….. (1)

But mole (n) = $\frac{given\ mass}{molar\ mass}$ ………………………………………… (2)

By substituting equation (2) in to equation (1)

Molarity = $\frac{given\ mass}{molar\ mass\ Al2(SO4)3.18H2o * volume(lit)}$

Therefore to prepare 0.1M of aluminum sulphate in 0.1liter (100ml)

$0.1 \frac{mole}{volume\ (lit)} = \frac{given\ mass}{\frac{666.42g}{mol} * 0.1lit}$

Given mass = 6.66g

To prepare 0.5M of aluminum sulphate in 0.1liter (100ml)

$0.5 \frac{mole}{lit} = \frac{given\ mass}{\frac{666.42g}{mol} * 0.1lit}$

Given mass = 33.321 g

For 1M of aluminum sulphate in 0.1liter (100ml)

Given mass = 66.642 g

Solution preparation of sodium hydroxide (NaOH) for pH adjustment

Molar mass of NaOH = 40.0 g/mole

Then after to prepare 1M of sodium hydroxide in 0.1liter (100ml) distilled water

$$\text{Molarity (M)} = \frac{moles}{volume\ (liter)}$$

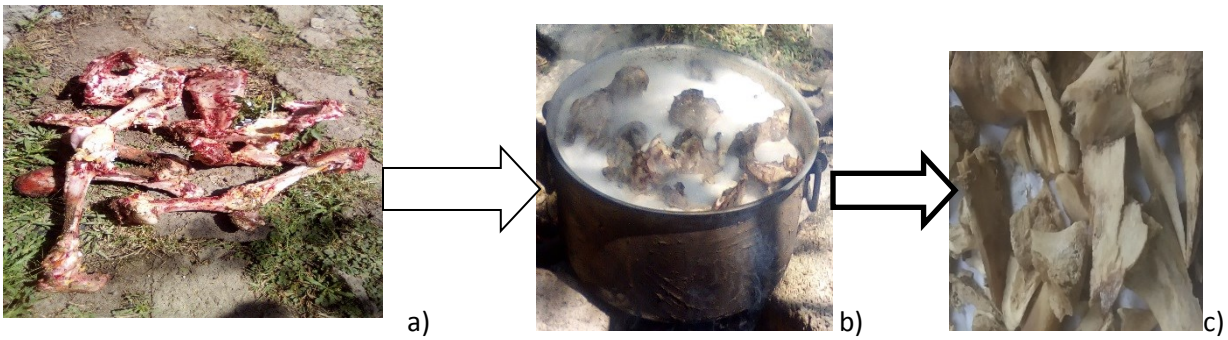
$$\text{Molarity} = \frac{given\ mass\ (g)}{volume\ (lit) * molar\ mass\ \text{NaOH}\ (\frac{g}{mol})}$$

$$1\ \frac{mole}{volume\ (lit)} = \frac{given\ mass}{\frac{40.0g}{mol} * 0.1lit}$$

Given mass = 4.0g

Therefore 4.0g of NaOH to be add in one liter distilled water

Appendix B



a) b) c)

a) Raw bone b) boiling raw bone c) Bone after removal of fat part including oven drying

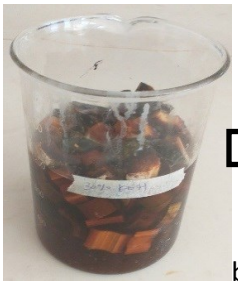

a)

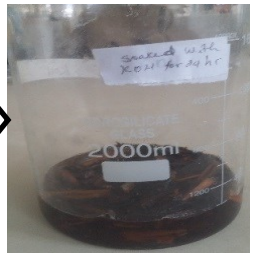

b)

a) Calcined bone char b) after size reduction

Appendix C


a)


b,


c)

a) Cutting of bamboo into small pieces b) Soaking of bamboo and oven drying

Carbonization of bamboo chars by using muffle furnace


a)


b)


c)

a) Muffle furnace b) after carbonization c) P^H checking

d) After size reduction e) jar test f) fluoride ion selective electrode

Appendix D

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	36.56	46.89	55.92	5.02
Ca	20	K-series	17.00	21.80	10.38	0.54
C	6	K-series	11.07	14.19	22.54	2.00
P	15	K-series	8.84	11.33	6.98	0.38
Al	13	K-series	4.00	5.13	3.63	0.23
Na	11	K-series	0.51	0.66	0.55	0.07
		Total:	77.98	100.00	100.00	

a)

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	29.57	42.24	55.94	4.12
Ca	20	K-series	23.35	33.36	17.64	0.72
P	15	K-series	10.48	14.97	10.24	0.44
C	6	K-series	6.23	8.90	15.69	1.21
Na	11	K-series	0.37	0.53	0.49	0.06
		Total:	69.99	100.00	100.00	

b)

Constituents of modified bone char (a) and bone char (b)