# PREPARATION OF COMPOSITE MATERIALS FROM ACTIVATED CARBON, BONE CHAR AND PUMICE FOR DEFLUORIDATION OF DRINKING WATER

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**JULY, 2020**

# Preparation of Composite Materials from Activated Carbon, Bone Char and Pumice for Defluoridation of Drinking Water

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**A Thesis Submitted to the Department of Applied Chemistry, School of Applied Natural Sciences in Partial Fulfillment for the Requirements of Degree of Master of Science in Chemistry (Industrial Chemistry)**

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**Adama, Ethiopia**

**July, 2020**

## DECLARATION

I hereby declare that this M.Sc. Thesis entitled "Preparation of composite material from activated carbon, bone char and pumice for defluoridation of drinking water" in partial fulfillment of the requirement of the degree of Master of Science in Industrial Chemistry is an authentic record of my own work under supervision of Dr. Enyew Amare and professor Neeraj Gupta at Adama Science and Technology University. The matter embedded in this thesis has not been submitted for the award of a degree or diploma in any other university. All relevant resource information used in this paper has been duly acknowledged.

…….…… ……

Student Name Signature

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief. This has been submitted for department of chemistry with my approval.

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Advisor Signature

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Co-advisor Signature

## APPROVAL SHEET

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## ACKNOWLEDGEMENT

First and foremost, I would like to express my special appreciation and thanks to my advisor Dr. Enyew Amare and Prof. Niraj Gupta for their support, follow up comments and suggestions. They have been tremendous mentors for me.

Second I would also thank my school members Mengistu Taddese and Andualem Mergia full time helping me during laboratory work.

I would especially like to thank my friend's Lijalem Abeble associate researcher at Ethiopian agricultural research institute, Ketema Alemayehu lecturer at Wolaita Sodo University, Mekides Merkebu, Melkamu Embiale, Getaneh Mehari and Asmare Getaneh all of you were with me in all type of support I need. I also thank staff members of Ethiopian Conformity Assessment Enterprise Adama Main Branch.

A special thanks to my family, words cannot express how grateful to my mother and my father, for all of the sacrifices that you have made on my behalf. Your prayer for me was what sustained me thus far.

Finally I thank my God, my good father and his mother St. Mary for letting me all the difficulties; you are the one who let me finish my degree.

I will keep on trusting you for my future. Thank you, Lord.

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## LIST OF ACRONYMS

| | |
|---|---|
| AC | Activated carbon |
| AD | Adsorbent dose |
| APHA | American public health association |
| BC | Bone char |
| CT | Contact time |
| EDTA | Ethylene di-amine tetra acetic acid |
| EDX | Energy dispersive x-ray |
| EPA | Environment Protection Agency |
| FTIR | Fourier transformed infrared |
| HAP | Hydroxyl Apatite |
| ISE | Ion selective electrode |
| LOI | Loss of ignition |
| NTU | Nephelometric turbidity unit |
| OSHO | Oromo Self Help Organization |
| PU | Pumice |
| Rpm | Revolution per minute |

| | |
|---|---|
| SEM | Scanning electron microscopy |
| TDS | Total dissolved solid |
| TISAB | Total ionic strength adjustment buffer |
| WHO | World Health Organization |
| XRD | X-ray diffraction |
| XRF | X-ray fluorescence |

## ABSTRACT

*Excessive fluoride exposure from drinking water is a major problem in many parts of the world including Rift valley region of Ethiopia. Preparations of composite material from activated carbon (AC), bone char (BC) and pumice (PU) for fluoride removal from drinking water was studied using batch adsorption. The main focus of the research work lies on preparation of new fluoride adsorbent material having good adsorption capacity. AC, BC and PU were uniformly mixed, grinded and sieved in three different ratio (% mass) based on their fluoride removal efficiency, $C_1$ (25:50:25), $C_2$ (25:40:35) and $C_3$ (25:30:45) respectively.The composites were fired in muffle furnace for at 350℃, 400℃, 450°C and 500°C, cooled down over night and grounded. The material having grain size between 250 µm – 280 µm was used for defluoridation of water. Optimum firing temperature (350 $^0$C) and appropriate mixing ratio of AC, BC and PU by % of mass (25:50:25) respectively was found to be good condition to get the best composite for defluoridation of water. The composite is amorphous non crystalline solid with large surface area mainly composed of oxygen, calcium, carbon, phosphorus and silicon. The composite had good removal efficiency both from real water sample (94.88) and laboratory fluorinated water (95.26) at neutral pH value. The effect of pH of the solution, contact time, adsorbent dose and initial fluoride concentration on the adsorption efficiency of the composite were analyzed. The equilibrium data have been analyzed by the Langmuir and Freundlich isotherm models while the kinetics of adsorption have been investigated by the pseudo-first-order and pseudo-second-order kinetic models. The adsorption experiment best fitted with Freundlich isotherm model and pseudo second order kinetics.*



**Keywords**: Adsorption, defluoridation, composite material, activated carbon, bone char and pumice

# CHAPTER ONE

## 1. INTRODUCTION

### 1.1. Background of the Study

Purified water is essential for leading a healthy life as such everyone should have access to it. With an increasing global usage and growing demand for high purity, effective management, distribution, storage, recycling and purification of water are critical to ensure the sustainable use of this resource in the future (Lopamudra 2013).

As all water used is collected from natural sources, a proper treatment and purification process is required before its consumption. Conventionally the treatment process has been applied to remove natural organic material, sediments and harmful pathogens from water prior to distribution. The rapidly decreasing quality of water and the growing global demand for this scarce resource has driven the pursuit of high-performance purification materials, particularly for application as point-of-use devices (Martin et al., 2017).

Drinking water contaminated by anionic constituents such as nitrate, phosphates, fluoride, arsenates, chromate, sulphate, bicarbonate etc. are a menace to both human health and environmental safety. Prolong consumption of drinking water polluted by excessive concentrations of fluoride (above 1.5 mg/L) causes teeth mottling, skeletal fluorosis and crippling fluorosis (Edmunds & Smedley 1996, Buamahet al., 2013).

Fluoride is one of the most widespread geogenic contaminant in groundwater. Fluoride is the cause of serious health problems such as dental and skeletal fluorosis, spontaneous abortion or congenital malformations for pregnant women and possible renal deficiencies. Once a person is affected by fluorosis, the damage is irreversible, which is why prevention is essential (Ariane 2013).

Several materials have been used to remove fluoride from water: activated alumina (Srimurali and Karthikeyan 2008), bone char (Bertha 2016), hydroxyl apatite (Manzola et al., 2015), geomaterials such as clay (Hariprasad et al., 2016) and pumice (Malakootian et al., 2011) and other materials. In order to implement defluoridation materials in rural communities, technological and economic aspects must be considered. The material should be affordable, simple to implement and maintain, cost effective and locally produced. Technologies such as reverse osmosis and electro dialysis are not suitable due to the high investment and maintenance costs and skill requirements (Hariprasad et al., 2016).

### 1.2. Statement of the Problem

Desirable concentration of fluoride (0.5 – 1.5 mg/L) in drinking water is beneficial for bone development and prevention of dental caries in humans (WHO 2006). The excessive intake of fluoride has adverse effect for human health resulting dental, skeletal and nonskeletal fluorosis, chronic and endemic disease. Defluoridation should be taken up where there is no alternative source of safe drinking water. Though many defluoridation techniques are developed and applied, most of these methods are expensive and technically non-feasible for rural communities. Therefore areas with high fluoride concentration are exposed to the adverse effects of its long-term consumption. Preventive measures are thus required to reduce fluoride concentration in drinking water to the acceptable level. People affected by excessive and undesirable levels of fluoride up to 33 mg/L (Worku 2006) in the Rift Valley of Ethiopia are in small and poor communities that rely on underground water as a source of drinking water. Therefore, there is a need for a material for the removal of fluoride from water at neutral pH which is cheap, simple to use and adaptable to either household or village scale.

### 1.3. Objectives

#### 1.3.1. General Objective

The general objective of this study was preparation of composite adsorbent from locally available cheap materials; activated carbon, pumice and bone char for the removal of fluoride from drinking water.

#### 1.3.2. Specific Objectives

Specifically, this study aimed:

- To prepare composite adsorbent materials from activated carbon, bone char and pumice for defluoridation
- To investigate structure, composition, and morphology of the prepared composite material by XRD, XRF, SEM/EDX and FTIR
- To evaluate the defluoridation efficiency of the composite material
- To investigate the fluoride removal potential of the composite under varying parameters (pH of solution, contact time, fluoride concentration and adsorbent dose) using batch adsorption experiment

### 1.4. Relevance of the study

In Ethiopia even though many defluoridation techniques have been developed and applied from time to time, still more work is needed to bring competent alternative, cost effective, easily available defluoridation material. The results of this study will provide useful baseline data on the development of composite material for fluoride removal.

### 1.5. Scope of the study

This study was preparation of composite material from easily available indigenous activated carbon, bone char and pumice at different mixing ratio and firing temperature for fluoride removal. The structure, composition and morphology of the prepared composite material were investigated using XRD, XRF, SEM/EDX and FTIR. The fluoride removal efficiency of the composite at different parameters and its effect on the quality of water was studied on this work.

### 1.6. Limitation of the study

The limitation of this study emanates from laboratory equipment, instrument and financial support to investigate more alternative mixing ratio of activated carbon, bone char and pumice.

# CHAPTER TWO

## 2. LITERATURE REVIEW

Fluorine is a pale yellow gas, has a strong and characteristic odour that can be detected in very small amounts, as low as 20 parts per billion. It is the thirteen most abundant and the most reactive elements that exist in different form of complex compounds on the earth's crust, as a result of strong affinity for calcium and other metals. Fluorine never occurs as a free element in nature; combines easily with every other element except helium, neon, and argon. It reacts with most compounds, often violently. The distribution of fluoride in the natural environment is very uneven, largely a result of the geochemical behavior of this element. Fluorine is preferentially enriched in highly evolved magmas and hydrothermal solutions, which explains why high concentrations are often found in syenites, granitoid plutonic rocks, alkaline volcanics, and hydrothermal deposits. It can also occur in sedimentary formations that contain fluoride-bearing minerals derived from the parent rock, fluoride-rich clays or fluorapatite. Dissolved fluoride levels are usually controlled by the solubility of fluorite ($CaF_2$), thus high concentrations are often associated with soft, alkaline, and calcium-deficient waters (David 2015). Fluoride in ground drinking water and the pooled prevalence of dental fluorosis among residents in Ethiopian rift valley is expectedly high, because the East African Rift Valley which cuts through Ethiopia is geomorphologically still an active volcanic region. East African Rift Valley is still an active volcanic region; fluoride concentration is expected at high level in ground water for the future (Habtamu et al., 2019).

### 2.1. Exposure of Human to Fluoride

The major sources of internal exposure of human beings to fluorides are the diet (food, water, beverages) and fluoride-containing dental products (toothpaste, fluoride supplements). Internal exposure to fluorides can also occur from inhalation (cigarette smoke, industrial emissions), dermal absorption (from chemicals or pharmaceuticals), ingestion or parental administration of fluoride-containing drugs, and children also exposed through ingestion of fluoride-containing soil. The major dietary source of fluoride for most people is from drinking water, including water consumed directly, food and beverages prepared at home or in restaurants from drinking water, and commercial beverages and processed foods (EPA 2006). The amount of fluoride occurring naturally in groundwater is governed principally by

climate, composition of the host rock and hydrogeology (Pal et al., 2012) and when 0.8-1.5 mg/L of fluoride is added intentionally to the drinking water body as supplements (EPA 2006).

### 2.2. Health Impacts of Fluoride in Potable Water

Major fluoride exposure comes from drinking water and minor amounts from food staffs and water based beverages contribute a significant fluoride concentration for total dietary intake (Liu et al., 2014). Fluoride exposure from different sources has both acute and chronic effects for human beings. Fluoride has both beneficial and detrimental effects on human health, particularly, for the formation and development of dental and skeletal parts of human body. Fluoride beyond desirable amount (0.5-1.5 mg/L) in ground water is a major problem in many parts of the world (Yadav et al., 2012). Excess amounts of fluoride in potable water may cause irreversible demineralization of bone and tooth tissues, a condition called fluorosis, and long-term damage to the brain, liver, thyroid, and kidney (Krishna et al., 2018).The public health problem of fluorosis is prevalent in the high water fluoride levels found in the Rift Valley region of Ethiopia, which is characterized by relatively high volcanic activity (Kloos and Tekle-Haimanot 1999). Particularly, drinking water has been considered the main reason for the development of fluorosis, but dietary intake may also be a contributor in areas with high concentration of fluoride in water, soil, and biota (Dessalegne and Zewge 2013). The onset of fluorosis and the severity of symptoms are governed by chronic fluoride ingestion. When immature teeth and bones exposed with elevated amount of fluoride for a long time, fluorosis risk will be observed. The formation of fluoroaptite/ hydroxylfluorapatite from hydroxyapitite causes the change in structural and functional characteristics of calcified tissue mainly teeth and bones due to the following chemical reactions (Kanyora et al., 2014).

Fluoroaptite forms according to the reaction:

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^- \quad (2.1)$$

Or hydroxylfluorapatite according to the reaction;

$$Ca_{10}(PO_4)_6(OH)_2 + F^- \rightarrow Ca_{10}(PO_4)_6FOH + OH^- \quad (2.2)$$

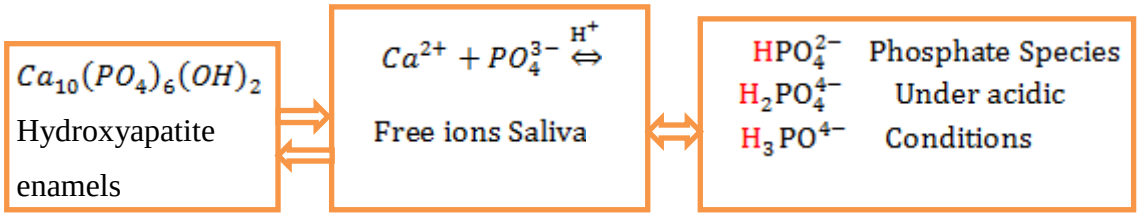
Fluoride and calcium interact in a negative manner; calcium intake through diet decreases the retention of fluoride in teeth and bones. The percentage of calcium in vegetables, cereals and fruits are rich in calcium, while milk is known to be the richest

source of calcium, therefore these food items considerable decreases the effect of fluorosis (Bhargava and Bhardwaj 2009).

### 2.2.1. Dental Fluorosis

Dental fluorosis is a developmental disturbance of dental enamel, caused by successive exposures to high concentrations of fluoride during tooth development, leading to enamel with lower mineral content and increased porosity. The severity of dental fluorosis depends on when and for how long the over exposure to fluoride occurs, the individual response, weight, nutritional factors and bone growth. The risk period for esthetic changes in permanent teeth is between 20 and 30 months of age. The recommended level for daily fluoride intake is 0.05 - 0.07 mg fluoride/Kg/day, which is considered of great help in preventing dental caries, acting in remineralization. A daily intake above this safe level leads to an increased risk of dental fluorosis (Jenny et al., 2009). Enamel fluorosis is a dose-related mottling of enamel that can range from mild discoloration of the tooth surface to severe staining and pitting. The condition is permanent after it develops in children during tooth formation. Severe enamel fluorosis is characterized by dark yellow to brown staining and discrete and confluent pitting, which constitutes enamel loss (EPA 2006).

Dental caries is an infectious disease caused by the complex interaction of cariogenic (caries causing) bacteria with carbohydrates (i.e. sugars) on the tooth surface over time. Cariogenic bacteria metabolize carbohydrates for energy and produce organic acids as by products. The hydroxyapatite of tooth is primarily composed of phosphate ions ($PO_4^{3-}$) and calcium ions ($Ca^{2+}$). Under normal conditions, there is a stable equilibrium between the calcium and phosphate ions in saliva and the crystalline hydroxyapatite that comprises 96% of tooth enamel. When the pH drops below a critical level (5.5 for enamel, and 6.2 for dentin), it causes the dissolution of tooth mineral (hydroxyapatite) in a process demineralization. When the pH is elevated by the natural buffer capacity of saliva, mineral gets reincorporated into the tooth through the process of remineralization shown in scheme 2.1 (Fejerskov 1997, Silverstone 1980, Featherstone 2004).




Scheme 2. Demineralization/remineralization cycles of tooth

Fluoride ions ($F^-$) replace hydroxyl groups ($OH^-$) in the formation of the apatite crystal lattice. In fact, the presence of fluoride increases the rate of remineralization (Curly 2009). Fluorapatite is inherently less soluble than hydroxyapatite, even under acidic conditions (Koenigs et al., 2013).

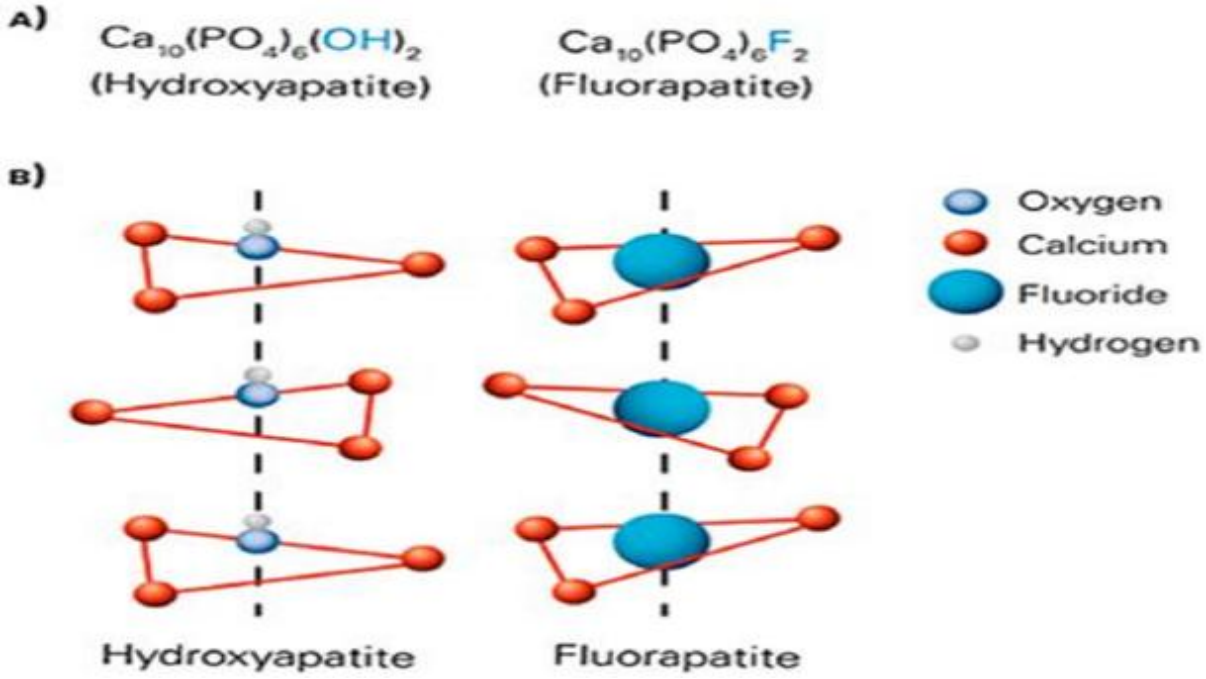



Figure 2. 1. Fluorapatite formation

(A) Fluoride ions ($F^-$) replace hydroxyl groups ($OH^-$) in hydroxyapatite to form fluorapatite in the tooth enamel. (B) A portion of the apatite crystal lattice is depicted showing the replacement of hydroxide for fluoride (Posner 1985).

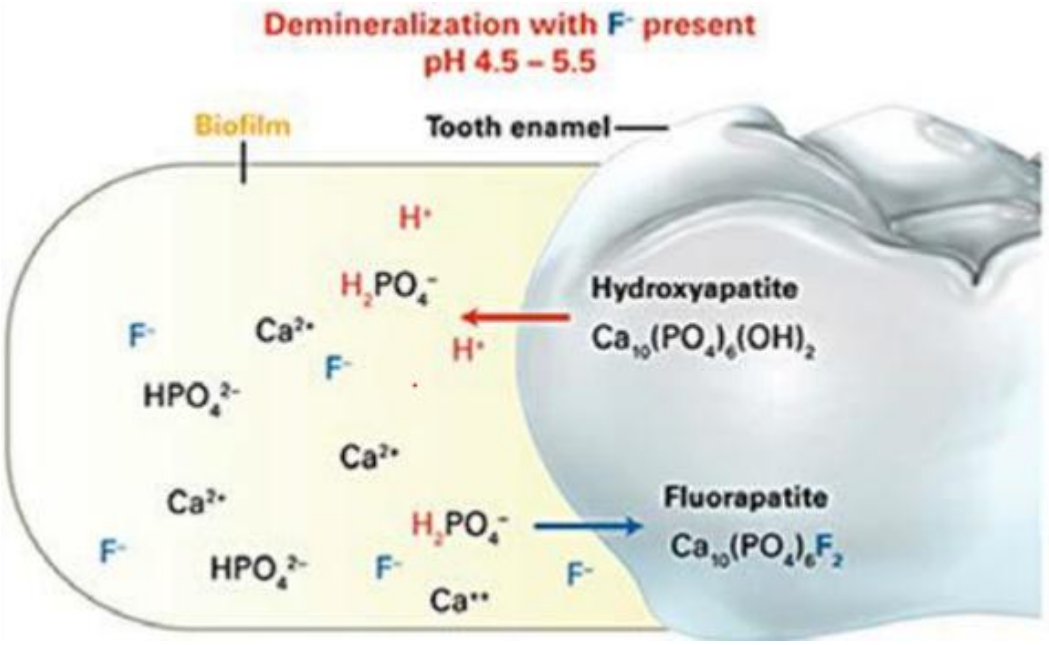



Figure 2. 2. Fluoride reactivity on tooth enamel

Under cariogenic conditions, carbohydrates are converted to acids by bacteria in the plaque biofilm. When the pH drops below 5.5, the biofilm fluid becomes under saturated with phosphate ion and enamel dissolves to restore balance. When fluoride ($F^-$) is present, fluorapatite is incorporated into demineralized enamel and subsequent demineralization is inhibited (Clarkson 1993 and Curly 2009).

### 2.2.2. Skeletal Fluorosis

Endemic skeletal fluorosis is a chronic metabolic bone and joint disease caused by chronic exposure to high doses of fluoride either through water or rarely from foods of endemic areas. The total quantity of ingested fluoride is the single most important factor which determines the clinical course of the disease. Skeletal fluorosis has several stages: two preclinical symptomatic stages characterized by slight radiographically detectable increases in bone mass; early symptomatic stage characterized by sporadic pain and stiffness of joints and osteosclerosis of the pelvis and vertebral column; a second clinical phase associated with chronic joint pain and arthritic symptoms and slight calcification of the ligaments. These features may mimic the diagnosis of seronegative arthritis (Gupta et al., 2007, Whyte et al., 2008).

The most severe stage (clinical stage III) historically has been referred to as the "crippling" stage (EPA 2006). Crippling skeletal fluorosis characterized by marked limitation of the joint movements, considerable calcification of ligaments, crippling

deformaties of the spine and major joints, muscle wasting and neurological defects associated with compressing of the spinal cord (Yamaguchi 2007).

Table 2. 1. Effect of prolonged use of drinking water on human health related to fluoride content (Dissanayake 1991).

| $F^-$ concentration, mg/L | Health outcome |
|---|---|
| <0.5 | Dental caries |
| 0.5-1.5 | Optimum dental health |
| 1.5-4.0 | Dental fluorosis |
| 4.0-10 | Dental and skeletal fluorosis |
| >10 | Crippling fluorosis |

Defluoridation of drinking water is the only pragmatic approach to solve the fluoride pollution problem as the use of alternate water sources and improvement of nutritional status of population at risk have their own limitations and are expensive affairs (Emmanuel et al., 2008).

### 2.3. Removal of Fluoride from Water

The process of removal of fluoride is generally termed as defluoridation. Numerous methods have been described employing various materials for the fluoride removal since 1930's. Due to all previously mentioned fluoride health problems (table 2.1), various technologies are currently available that reduces the concentration of fluoride in water to make it safe for human consumption such as coagulation and precipitation, membrane processes, electrochemical treatments, ion-exchange and its modification, but the adsorption process is generally accepted as the cheapest and most effective method for removal of fluoride from water (Mirna et al., 2014).

#### 2.3.1. Precipitation and Coagulation

Precipitation methods employ the addition of coagulant which aids to precipitate sparingly soluble salts of fluoride as fluorapatite. A well-known defluoridation technique that uses this method is the Nalgonda technique. It was developed by the National Environmental Engineering Research Institute (NEERI) in India (1975) in

response to fluorosis concerns in the endemic village of Nalgonda and its surrounding areas (Suneetha et al., 2008, Appropedia.org. 2013).

During the process, prescribed quantities of lime, alum and bleaching powder are added to the raw water, followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection (Lyengar 2002). Lime and alum are the most commonly used coagulants. Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride. The formation of fluoride precipitate follows this reaction:

$$(Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \quad (2.3)$$

### 2.3.2. Membrane Filtration (Reverse Osmosis and Electrodialysis)

In reverse osmosis process pressure is applied on the feed water to force it through a semipermeable membrane leaving the fluoride contaminated salts behind. The pressure applied on the membrane is relative to the size of the pollutants left behind (Renuka & Pushpanji 2013).

Electro dialysis is an electrochemical separation process whereby ions are separated via a semipermeable membrane by applying a potential gradient. The electrical charges on the fluoride ions allow them to be driven through the membranes fabricated from ion exchange polymers. The membranes used in electro dialysis for fluoride treatment have the potential to selectively transport the negatively charged fluoride ions and reject opposite ions (Meenakshi & Maheshwari 2006).

### 2.3.3. Ion- Exchange

The use of ion-exchange to remove fluoride from water involves the application of a synthetic anion exchange resin. During the process, the fluoride contaminated water is made to pass through the resins packed in a column. The fluoride removal uptake proceeds according to the following reaction:

$$Matrix - NR_3^+Cl^- + F^- \rightarrow Matrix - NR_3^+F^- + Cl^- \quad (2.4)$$

Where; $NR_3^+$ is the ion exchange group, $Cl^-$ is the chloride exchangeable ion and $F^-$ is the fluoride ion

The fluoride ($F^-$) in the water substitutes the chloride ($Cl^-$) in the resins and the defluoridated water is received at an outlet. The process proceeds until all the free sites on the resin are occupied. The fluoride saturated resin could then be regenerated for

reuse by backwashing with dissolved supersaturated sodium chloride salt solution (Khandare 2013, Meenakshi & Maheshwari, 2006).

Table 2. 2. Comparison of fluoride removal technologies (Chakrobortty et al., 2013, Tomar and Kumar 2013)

| Technologies | Advantages | Disadvantages |
|---|---|---|
| Coagulation/precipitation<br>Calcium hydroxide;<br>Aluminium hydroxide | High efficiency;<br>Commercially available chemical | Expensive, efficiency depends on pH and presence of co-ions in water, adjustment and readjustment of pH is required, elevated residual aluminium concentration, formation of sludge with high amount of toxic aluminium fluoride complex and high amount of retained water |
| Membrane filtration<br>reverse osmosis<br>Nano filtration | High removal efficiency, removes other contaminants<br>No chemicals required | High capital, running and maintenance cost<br>Toxic waste water produced<br>Clogging, scaling and fouling problems |
| Electrochemical treatments;<br>dialysis, electro-dialysis, electro-coagulation | High efficiency<br>High selectivity | High cost during installation and maintenance<br>Skilled labour required<br>Polarization problem |

| | | |
|---|---|---|
| Ion exchange; strong basic anion exchange resin with quaternary ammonium functional groups | Simplicity and flexibility design<br>Effective, at pH< 7 | Expensive, vulnerable to interfering ions ($SO_4^{-2}$, $PO_4^{-3}$, $Cl^-$, $HCO_3^-$)<br>Replacement of media after multiple regeneration, used media present solid toxic waste, regeneration creates toxic liquid waste, efficiency highly depends on pH |
| Adsorptive materials; activated alumina, activated carbon, bone char and others | High accessibility, low cost, simple operation, | High efficiency, often demand adjustment and readjustment of pH and other ion interference |

### 2.3.4. Fluoride Removal by Adsorption

Adsorption is one of the most efficient water treatment technologies because of its low cost, it's simple operation and it does not produce large amount of sludge. It is defined as a mass transfer process which involves the accumulation of substance at the interface of two phases such as liquid-liquid, gas-gas, gas-solid, or liquid-solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed as adsorbent (Gupta et al., 1998). It occurs when the attractive forces at the adsorbent surface overcome the attractive forces of the liquid. As contaminated water or air flows through adsorbent, the contaminants sorb (stick) to the surface of the granules and are removed from the water or air (Mitiku 2015).

Adsorption retains a major place in defluoridation research and practice because of its greater accessibility and lower cost. Thus even in the past decade, when interest in alternative defluoridation approaches has been increasing rapidly, many researchers have continued to explore the development of low-cost and effective adsorbents and to improve the efficiency of all adsorbents (Vivek 2011). Theoretically, the adsorption of fluoride on to solid particles takes three essential steps (Fan et al., 2003):

- Diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle, called external mass transfer;
- Adsorption of fluoride ions on to particle surfaces;
- The adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion).

Evaluating an adsorbent for practical purposes, however, requires consideration of adsorption capacity in dilute solutions, pH, time for fluoride removal, stability of adsorbent, regeneration and loading capacity in presence of other anions and cations, finally the overall cost for fluoride removal (Mohapatra et al., 2009). Adsorption is considered to be a viable approach due to its simplicity and cost-effectiveness. It seems to be economical and user-friendly especially in the developing world. Different adsorbents have different limitations. Comparatively, adsorption seems to be the most attractive method for the removal of fluoride below 1 mg/L. The criteria for the selection of adsorbent mainly include its potential (adsorption capacity) for fluoride removal and the cost (Hanumantharao et al., 2015).

## 2.4. Adsorbents for Fluoride Removal

A wide variety of both conventional and non-conventional adsorbent materials have been tested in the past to find out an efficient and economical defluoridating agent.The effectiveness of fluoride adsorption from drinking water by using various adsorbents, the method used for the assessment, the kinetics and equilibrium models that best explained the adsorption process, factors affecting the efficiency of the adsorbent (pH, adsorbent dose, fluoride concentration contact time competing ions..) are main considerations during defluoridation of drinking water. An ideal adsorbent that can be used to remove fluoride ion must have the following characteristics; low cost, high $F^-$ adsorption capacity, rapid adsorption of $F^-$, easily regenerated for reuse and rapid water flow without filter clogging (Paripurnandaet al., 2003).

Table 2. 3. Adsorbents for defluoridation of water

| Defluoridation material | Mechanism | Advantage | Limitation | Reference |
|---|---|---|---|---|
| Activated carbon | Manufactured from carbonization and activation of carbonaceous materials High porosity amorphous nature<br>High surface area | High adsorption or filtration capacity (55%)<br>Removes other organic impurities too. | Highly PH dependant (effective at a pH less than 3 and little removal at pH 7 | Martin.et al., 2017<br>Jasmine 2013 |
| Bone char | Made from animal bones<br>Charred at 300-500$^oC$ and<br>Crushed to 0.5-0.4 mm<br>Blackish, Grey and white porous granular | High removal capacity up to 91.8%<br>Low-processing temperature<br>Low cost | Unpleasant taste of treated water,<br>Unavailability and short shelf life<br>Socio-cultural acceptance | Bertha 2016 |

| | | | | |
|---|---|---|---|---|
| Clay Soil | Bed of clay/soil and the fluoride is accumulated in a thin layer on surface of the clay/soil | Low cost,<br>Ease preparation<br>Ready availability of materials<br>environmental stability | Used only in small scale treatment<br>Variable efficacy ,unproven and scalability<br>Less effective with time (media need to be replaced after about 1 month) | Hariprasad. et al., 2016 |
| HAP | Made from lime, $H_3PO_4$ acid and $H_2O$<br>Calcium (22.80)<br>Phosphorus (10.15)<br>Moisture (1.96)<br>Ash content (6.58) | High removal capacity (6.8-7.5 mg/g)<br>Lowers-salinity<br>High lifetime<br>Less adverse effect on total water quality | High cost 120 birr/kg | OSHO 2018<br>Manzola et al., 2015 |
| Natural Pumice | Volcanic stone<br>Chemical composition<br>$SiO_2$, $Al_2O_3$,CaO, MgO $Fe_2O_3$ , $K_2O$ | Low cost and low processing $T^0$ (105 $^oC$), Best absorbs (85.75%) at<br>pH 7 | Low absorbance capacity 0.31 mg/g | Malakootian. et al., 2011<br>Sanghratna 2015 |
| Cement paste | Prepared by 28 day old cement paste block of OPC and sieving with less than 0.15mm sieve | Easy to prepare<br>Cheap and abundant | Low adsorption efficiency (50-67%)<br>pH dependent, optimum pH ranges 7-11.5 | Kang et al., 2007 |

| | | | | |
|---|---|---|---|---|
| Red mud | Fine grained mixtures of oxides and hydroxides | Easy/zero price<br>Can be reused many times | Unconventional<br>Effective at low fluoride ion concentration<br>pH dependent, maximum removals achieves at pH 4.7 | Tor et al., 2009 |
| Bleaching powder | White powder consists of calcium hypo-chloride | Can be used both as disinfectant and defluoridation agent<br>Effective at wide pH range (6-10) | Effective at high amount adsorbent dose (>50 g/L) | Kagne et al., 2009 |
| Activated alumina | Highly porous material made by dehydroxylation of aluminum hydroxide | Cost, ease of operation, High adsorption capacity<br>Potential for reuse<br>Removes arsenic and selenium contaminants too | Increasing pH, alkalinity, calcium and carbonate decreases its sorption capacity<br>Chlorides, sulphates, $K^+$, $Na^+$ and $Mg^{2+}$ marginally influence adsorption potassium sodium and magnesium | Srimurali& Karthikeyan 2008 |
| Limestone | Limestone acidified with citric acid and acetic acid generates $Ca^{2+}$ and $F^-$ precipitates as $CaF_2$ and the layer adsorbs fluoride ion | Cost and availability of the material<br>Ease of preparation<br>Don't affect taste and color of treated water | Removal efficiency is poor in repeated use | Suresh and Robin 2010 |

| | | | | |
|---|---|---|---|---|
| Natural zeolite | Crystalline microporous aluminum silicate | Adsorb $F^-$ in wide range of pH<br>Removes other organic and inorganic impurities too | Needs surface modification with multivalent cations<br>Low adsorption capacity | Mohammeai et al., 2015 |

Most water defluoridation media need some kind of processing before they are ready for use. The processing may be an entire chemical synthesis, like the preparation of alumina from alum and the preparation of synthetic apatite, or more simple physical preparation like the selection, heating, crushing, drying, sieving, and cleansing, in the case of the preparation of organic media from plant materials. In any case, one would need a simple procedure to test if the resulting product met expectations, in particular with respect to the defluoridation capacity and the quality of the treated water. Selection of defluoridation method and material is mainly based on cost, regulatory compliance, appropriateness, environmental burden and public perception and acceptance (Eli 2015).

### 2.4.1. Activated Carbon

Activated carbon is the generic term used to describe a family of amorphous carbonaceous adsorbents with a highly non-crystalline form and well developed internal pore structure. It can also be defined as any porous material formed in the major part of carbon and characterized by a well-developed porosity. It is predominantly an adsorbent with a large internal pore volume and surface area (Jasmankaur 2013). All-inexpensive residues with high carbon and low inorganic content can be considered as starting materials for the production of activated carbon, one of the most known used adsorbent (Javier 2011). Activated carbons are commonly prepared by two basic processes: physical or gas activation and chemical activation. The choice of activation method also depends on the starting material and whether a low or high density, powdered or granular carbon is desired (Mohammad and Ansari 2009).

Physical activation of activated carbon powder is prepared by the pyrolysis of carbonaceous materials having appreciable carbon content at a temperature ranging between 600-900 $^{0}$C in the abescence of oxygen follows treatment with oxidizing agents (steam, carbon dioxide, or oxygen). It's collected, washed, dried, and crushed before carbonizing in uniform nitrogen flow in a horizontal tube furnace, while the chemical activation method applies impregnation the raw material before carbonization using certain chemicals such as $H_3PO_4$, $H_2SO_4$, KOH, NaOH, $K_2CO_3$, $ZnCl_2$ and others (Subramani and Revathi 2015). Chemical activants promote crosslinking, forming a rigid, less volatile matrix with smaller volume contraction at high temperature. Among numerous chemicals used as activating agent $H_3PO_4$ has been most preferred activating agent because it promotes depolymerisation, dehydration and redistribution of biopolymers and also favours the conversion of aliphatic to aromatic compounds thus increases percentage of activated carbon. It also reacts with the char and volatile matter and diffuses quickly out of the surface Phosphoric acid accelerates the pyrolytic decomposition of the initial material and promotes the formation of cross linked structure, more over $H_3PO_4$ helps for the development of both micropores and mesopores (Sait and Derya 2015).

It is largely used as versatile adsorbent with so many applications, purification of water, air and many chemicals and natural products and it's also widely used for adsorption and removal of pollutants from gaseous and liquid phases. It has several applications in medical, industrial and pharmaceutical processes (Martin et al., 2017).

Although activated carbons are the most used adsorbents worldwide with high capacities, they are generally characterized by low selectivity for fluoride ions due to physical adsorption, so in most studies, prior examination of fluoride removal efficiency, activated carbons are modified by oxidation and subsequent impregnation with high valent ions such as zirconium, titanium, iron, calcium. Oxidation is one of the most conventional modifications used for activated carbons. It is mainly used to introduce carbon–oxygen surface groups in activated carbon. Oxidation methods involve the utilization of oxidizing gases (oxygen, steam, carbon dioxide) or oxidizing solutions such as nitric acid, hydrogen peroxide, chlorine water (Jaramillo et al., 2010).

Batch adsorption dynamics and equilibrium studies for the removal of fluoride ions from aqueous solution using indigenously Acacia farnesiana carbon has been carried out under various experimental conditions at room temperature. Results found that, initially, the percentage removal of fluoride ions increased with a decrease in initial concentration and increased with an increase in contact time and, after 40–45 min, the percentage removal is found to be almost constant. Adsorption is highly pH sensitive and the optimum pH range for appreciable or maximum adsorption of fluoride ion is found to be 6.5–7.0, with maximum absorption around 6.9 then decreases with increasing pH. At the same pH, fluoride adsorption follows the Freundlich isotherm, indicating that the Acacia farnesiana carbon surface is highly heterogeneous (Hanumantharao et al., 2011).

Activated carbon prepared from cashew nut shell for fluoride removal from aqueous solution time of 180 min has a maximum percentage of fluoride removal 72.67% from 3 mg/L fluoride concentrated solution using 2 g adsorbent at room temperature (Alagumuthuet al., 2011).

Khat(Catha *edulis*) is a good precursor for preparation of activated carbon and has a good adsorption capacity from aqueous solution. Chemically ($H_2SO_4$) activated C. *edulis* under batch adsorption mode have 73% fluoride removal efficiency at optimum conditions of adsorbent dose 1.5 g in 100 mL, 60 min contact time and pH 2 (Jemal et al., 2019).

Graphene is a single flat atomic sheet of carbon with the atoms arranged in a two-dimensional (2D) honeycomb configuration. It has drawn much scientific attention since its discovery due to its unique electronic and mechanical properties, specific magnetism, excellent mobility of charge carriers, and high thermal conductivity. The

adsorption capacities and rates of fluoride onto graphene at different initial pH, contact time, and temperature were evaluated. It is an excellent fluoride adsorbent with an adsorption capacity of up to 17.65 mg/g at initial fluoride concentration of 25 mg/L and temperature of 25℃ (Li et al., 2011).

. This microcrystalline structure has been described as defective graphene assemblies or alternatively stacks of aromatic sheets

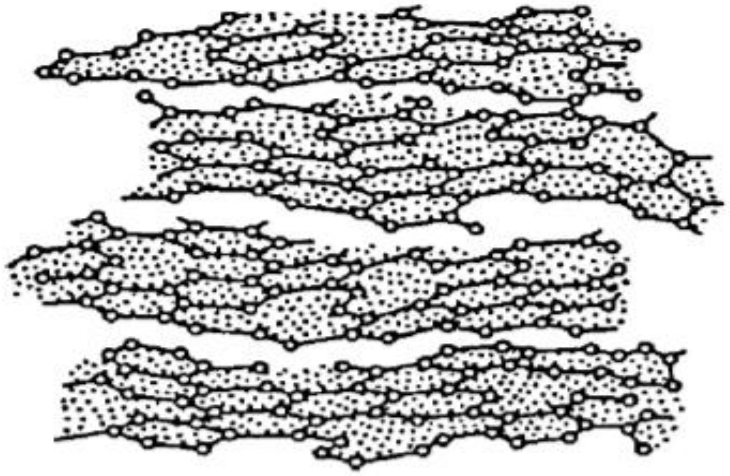


Figure 2. 3. Typical structure of graphene activated carbon (Li et al., 2011)

Coffee husk is potential raw material for the production of effective, good quality and suitable activated carbon (Maina 2001). The production could be of great interest in Ethiopia because the coffee consumption was around 500,000-700,000 tonnes annually (Berhanu 2017). Activated carbon prepared from coffee husk and activated with $H_2SO_4$ exhibits highest fluoride removal efficiency (up to 86%) for less than 10 mg/L of initial fluoride concentration at pH 2 (Getachew et al., 2015).

Activated carbon is also used as effective adsorbent for $NO_3^-$ (Mohammad et al., 2015), $SO_4^{2-}$ and other ions that bring hardness to drinking water (Hanna et al., 2016).

### 2.4.2. Bone Char

The amorphous bio sorbent bone char powder can be prepared mainly by heating the biomass-bone, which contains the elements oxygen, calcium and phosphorous.

It is an effective material for removing fluoride, provided the bone char is of high quality. Bone charring process, "unless carried out properly, may result in a product of low defluoridation capacity and / or deteriorated water quality". Hence the production of bone char is one of the most important steps for a future, successful defluoridation treatment (Das et al., 2003). The elemental chemical analysis reveals that the bone

char was composed of P, Ca, C, O, Si, Al, Na, and Mg. This is due to the main components of bone char being the hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), carbon, and calcite ($CaCO_3$), and their weight percentages may be up to 76%, 11%, and 9%, respectively (Nahum et al., 2007).

Bone char was be prepared by pure pyrolysis, at 700℃ without the admission of oxygen. In such a process, all the organic material in the bone cracks. Some of the organic carbon is lost as volatile smoke but the main part remains in the charred bone as graphite, i.e., active carbon. The graphite content gives the charred bone its characteristic black color. Later, bone char was reported to change color during heating from black to grey to white as the temperature increased (Eli 2015). Bone fired up to 500℃ had the highest percentage of fluoride removed (91.8 %) at pH 3 and the adsorption capacity diminished drastically while increasing the pH from 3 to 12. The adsorption equilibrium is not obtained at pH < 3 since bone char dissolves in a solution having pH value less than 3. At higher temperature of pyrolysis, the percentage was less decreasing with increasing temperature. At 800°C the percentage of fluoride removed was less than 50% (Puangpiya and Osiriphan 2011).

Pyrolysis temperature is a critical operating parameter for the synthesis of bone char for fluoride removal from water. Specifically, this temperature has a major effect on the fluoride adsorption properties of bone char due to the dehydroxylation process of the hydroxyapatite contained in this adsorbent at higher temperature. Higher pyrolysis temperature reduces the $OH^-$ groups (dehydroxylation) and this decreases the exchange between ions $OH^-$ and $F^-$ directly affecting the adsorption capacity of the bone char obtained from a pyrolysis process. Therefore, the synthesis of bone char at 700℃ helps to reduce the effect of the hydroxyapatite dehydroxylation on its fluoride adsorption properties (Rojaset al., 2013).

In order to produce good quality bone char one should therefor aim at a pyrolysis process, that preserves the defluoridation capacity, but where the accompanying poor smell, poor taste, and discoloration are removed by a post-treatment of the charred bone. The colour of the charred bone indicates the quality of the medium with respect to its defluoridation capacity. Black and brown bone char are most capable in removing fluoride from the water, while grey and white bone char are less effective and the result of poor firing. Black bone char, in particular, may produce coloured

water, while white bone char produce water with an elevated pH and increased concentrations of dissolved solids. An acid wash followed by a water wash may alleviate these negative effects on the quality of the treated water (Eli 2015). The color of the bone char has been proven to be a simple indicator for its ability to remove fluoride and stripping of the bone char minerals to the water. It is examined with respect to grain size distribution, density, color and porosity.

Based on its color bone char can be classified as:

- Black bone char: Highest defluoridation capacity, while the bones still contain organic impurities, which cause odor/color to the treated water and released some dissolved solids to the water.
- Grey-brownish bone char: low fluoride removal capacity and releases dissolved solids.
- White bone char: lowest fluoride removal capacity and released more solids

Figure 2. 4. Different colors of bone char (Eli 2015)

Once the bone char is saturated with fluoride, it can theoretically be regenerated using caustic soda solution:

$$Ca_5(PO_4)_3F + OH^- \rightleftarrows Ca_5(PO_4)_3OH + F^- \quad (2.5)$$

Table 2. 4. Effect of bone char prepared at different temperature on the quality of water (Eli 2015 Puangpinyo and Osiriphan 2006):

| Temp. °C | Bone color | Property of treated water | | | % $F^-$ removal |
|---|---|---|---|---|---|
| | | Color | Smell | Taste | |
| 300 | brown : black (4:1) | dark yellow | bad odor | undrinkable | 97 |
| 400 | black : brown (4:1) | dark yellow | bad odor | undrinkable | 93.4 |
| 500 | black : brown (3:1) | light yellow-clear | bone | normal | 91.8 |
| 600 | black : grey (4:1) | clear | none | normal | 75.0 |
| 700 | black : grey (3:1) | clear | none | normal | 62.5 |
| 800 | black : grey : white (3:2:1) | clear | none | normal | 45.3 |

Ground water in rift valley of Ethiopia is associated with high fluoride concentration causing endemic fluorosis. People living around this region have no other alternative source of drinking water thus community training and monitoring producers were done to use bone char for defluoridation of the available water. After repeated monitoring even 8% of the users express negative experience related to odor, taste and turbidity of treated water (Samual et al., 2009). Disadvantages of this adsorbent are, the adsorption efficiency is strongly pH dependent (defluoridation is satisfactory at lower pH value), the char harbors bacteria and hence unhygienic, short life span, pre and post treatment of water, effect of co and counter ions, efficiency of bone char as adsorbent for fluoride is a function of charring producers which should be done cautiously (table 2.4) and more over use of bone char invites cultural and religious objections (Larsen and Pearce 2002).

### 2.4.3. Pumice

Pumice is a low cost natural adsorbent which has been widely tested and used in water treatment as an adsorbent, filter bed, and support media. It is volcanic stone comprised of irregularly connected as well as separated cavities and often composed from high amount of silica (69%) than other minerals. Pumice has a light appearance and a porous structure which is due to the release of gases during solidification. The main

use for pumice continued to be as an aggregate in lightweight building blocks and assorted building products. Other major applications for pumice and pumicite included abrasives, absorbents, concrete aggregate and admixture, filter aids, horticulture (including landscaping), stonewashing of denim and as a traction enhancer for tires. Imports were used primarily as a lightweight aggregate, but a small percentage of pumice imports were used in abrasive applications (Alan 2004).

Pumice can be used as effective adsorbents for fluoride removal from aqueous solutions because the surface structure of pumice has been banded with metal cations which are resistant towards absorbent rinse. The main advantage of pumice in comparison with other natural or synthetic adsorbent is its lack of toxicity (Mohammad et al., 2016). Defluoridation of water by using pumice mineral is simple design and low cost investment, the adsorption process has more advantage than other methods in removal of fluoride. Fluoride removal by pumice is more effective at increasing adsorbent dose, contact time and pH while the efficiency declines as initial fluoride concentration increases. The main advantage of pumice over the other adsorbents of fluoride is it has high fluoride removal efficiency at neutral pH (Malakootian et al., 2011). As pumice is highly porous material besides to defluoridation of water it removes nitrates ($NO_3^-$) (Lokesh and Singh 2017) and pumice with high content of calcium oxide (CaO) removes phosphate ($PO_4^{3-}$) from water (Onaret al., 2010).

Figure 2. 5. Pumice stone (Alan 2004)

## 2.5. Composite Material

Composite materials (composites) are inherently heterogeneous and represent a defined combination of chemically and structurally different constituent materials, ensuring the required properties such as mechanical strength, stiffness, low density, or other specific characteristics depending on their purpose. There is an increasing requirement for advanced materials with enhancement properties to meet new requirements or to replace existing materials. The composites have prognosed electrochemical, ion-exchanging and adsorption properties, as very sensitive structural and surface properties for water treatment (Hany et al., 2017).

Basic factors affecting properties of composites are as follows (Marjan et al., 2012):

- Properties of phases
- Amount of phases
- Bonding and the interface between the phases
- Size, distribution and shape (particles, flakes, fibers, laminates) of the dispersed phase reinforcement
- Orientation of the dispersed phase-reinforcement (random or preferred)

The properties of a composite material depend upon the relative quantities and properties of its constituents.

$$P_{CM} = f_i p_i \tag{2.6}$$

Where $P_{CM}$ is property of the composite material, f is volumetric fraction of each i ($\sum fi=1$), p is property of each material and i is the $i^{th}$ component

The composites are connected by chemical bonds, Van der Waals forces and mechanical interlocking. Good bonding (adhesion) between matrix and dispersed phase provides a high level of mechanical properties of the composite via the interface. In addition, interfaces are responsible for numerous processes of electron transfers and play crucial role in redox processes, heterogeneous catalysis, adsorption etc. In this field of application, composites usually have the role of adsorbent, electrochemically active materials, catalysts, and photo catalysts (Hany et al., 2017).

A novel material for fluoride adsorption has been synthesised by incorporating hydroxyapatite (HAP) in to montmorillonite (MMT). The resultant material has a high fluoride adsorption capacity in the pH range of drinking water compared to a physical mixture of HAP and MMT due to the expansion of layers of MMT and incorporation

of HAP into the layers (Shanika et al., 2019), While another novel clay composite material prepared from clay, grog, sawdust and bone char with volume ratio 3:3:3:1 fired at 400°C was found to have 91.6% at pH 3.0 and 73% at pH 7.03 fluoride removal efficiency (Lechisa et al., 2019).

Areca nut AC prepared by chemical activation with phosphoric acid and composited with $Fe_2O_3$ shows a maximum fluoride adsorption capacity of 4.8mg/g. The composite has comparatively higher adsorption efficiency than commercial areca nut AC and it can be promising adsorbent for fluoride removal from water (Sahira and Mandira 2016).

According the report by (Asgari et al., 2018) carbon modified pumice (CP) prepared from sucrose and pumice mix heated from room temperature to 500°C at a rate of 2°C/min and kept at this temperature for 4 hours resulted with the maximum fluoride removal efficiency **(**21.64 mg/g**)**. Bone is a nanocomposite constituted of hydroxyapatite (HA) nanocrystals. One method to improve properties of HA is the incorporation of glass–ceramics derived from silica that resulted with a composite material of higher strength and improved properties. In this study, natural pumice (NP) a naturally occurring glass–ceramic of volcanic origin was used to reinforce bone-derived hydroxyapatite.

With all this in mind, it stands to reason to investigate a new composite material fabricated from sustainable indigenous resources such as natural pumice; bone derived activated hydroxyapatite and activated carbon for deflouridation.

### 2.6. Mechanism of Adsorption

The mechanism of adsorption involves the sorption of sorbant molecules on the surface of sorbents through molecular interaction and diffusion of sorbent molecules from the surface into the interior of the sorbent materials, either by monolayer or multilayer surface (Rani and Mohammad 2017).

#### 2.6.1. Physical Adsorption

Physical adsorption is a general incident and occurs in any solid/liquid or solid/gas system. It is a process in which binding of adsorbate on adsorbent surface is caused by Van der Waals force of attraction. The adsorbed molecule is not affixed to a particular site on the solid surface but is free to move over the surface. In addition, the absorbed

material may condense and form several superimposed layers on the surface of the adsorbent. It is readily reversible (Adam and Abhoyjit 2011).

### 2.6.2. Chemical Adsorption

It is a kind of adsorption which involves a chemical reaction between the adsorbent and adsorbate. The strong interaction creates new electronic bonds (covalent, ionic) comparable with those leading to the formation of a chemical compound. Normally, the adsorbed material forms a layer over the surface, which is only one molecule thick, and for which molecules are not free to move from one surface site to another. When the monomolecular layer covers the surface of the adsorbent, the adsorption capacity is essentially exhausted. Chemical adsorption is seldom reversible (Kitchener 2016).

## 2.7. Adsorption Isotherm

The equilibrium adsorption isotherms are of fundamental importance in the study of adsorption. It is a function of both characteristics and concentration of adsorbate and temperature. The relationship between the amount of the substances adsorbed at constant temperature and its concentration in equilibrium solution is called adsorption isotherm. It is a quantitative relationship describing the equilibrium between the concentration of adsorbate in a solution C (mass/volume) and its sorbed concentration q (mass adsorbate/mass absorbent) in a given temperature (Nethaji et al., 2012).

$$q_e = \frac{v\,(C_o - C_e)}{m} \qquad (2.7)$$

Where $q_e$ = Adsorbent phase concentration after equilibrium i.e. mg adsorbate/g adsorbent

$C_o$ = Initial concentration of the adsorbate, mg/L

$C_e$ = Final equilibrium concentration of the adsorbate after adsorption occurred, mg/L

$V$ = Volume of liquid in the reactor, L

$m$ = Mass of adsorbent, g

The adsorption isotherm is described by using data collected from adsorption capacity ($q_e$) and the equilibrium concentration of adsorbate ($C_e$). Different adsorption models were developed based on theoretical explanations and assumptions. Commonly used

isotherms are; Langmuir, Freundlich, BET and Temkin. BET isotherm developed by Brunaur, Emmett and Teller applies to systems of a multilayer adsorption and usually utilizes probing gases that don't chemically react with material surfaces as adsorbate to quantify specific surface area. It is extension of Langmuir theory which is a theory for monolayer molecular adsorption to multilayer adsorption (Ajay et al., 2016). Temkin isotherm contains factors that explicitly taking into the account of adsorbent-adsorbate interaction. The model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Dada 2012). However Langmuir and Freundlich adsorption isotherm have been commonly used models to describe surface coverage adsorption equilibrium characteristics.

### 2.7.1. Langmuir Adsorption Isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and no further adsorption takes place. Thereby, it represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites (Eder et al., 2015).

Langmuir adsorption isotherm model is based on the assumption that adsorbates are chemically adsorbed at a fixed number of energetically equivalent well-defined sites that can hold only one adsorbate species so that the layer of the adsorbent would have a monolayer thickness. Once the adsorbate matter occupies the sites (saturated), no further adsorption is expected (Jemal et al., 2019).

Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \frac{Q_e K_L C_e}{1 + K_L C_e} \tag{2.8}$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (2.8) into linear form:

$$\frac{1}{q_e} = \frac{1}{Q_e} + \frac{1}{Q_e K_L C_e} \quad \rightarrow \quad \frac{C_e}{q_e} = \frac{1}{K_L Q_e} + \frac{1}{Q_e} C_e \tag{2.9}$$

Where:

$C_e$ =Equilibrium concentration of adsorbate (mg/L$^{-1}$)

$q_e$ =Amount of ion adsorbed per gram of the adsorbent at equilibrium (mg/g).

$Q_e$ =Maximum monolayer coverage capacity (mg/g)

$K_L$ =Langmuir isotherm constant (L/mg) which is related to the adsorption energy and quantitatively reflects the affinity between the sorbent and the sorbate

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_L$ which is a dimensionless constant referred to as separation factor or equilibrium parameter

$$R_L = \frac{1}{1 + K_L C_o} \qquad (2.10)$$

Where:

$C_0$ =Initial concentration

$R_L$ = Constant related to the energy of adsorption (Langmuir Constant). $R_L$ value indicates the adsorption nature to be either unfavourable if $R_L$>1), linear if $R_L = 1$, favourable if 0< $R_L$<1 and irreversible if $R_L$=0 (Dada et al., 2012).

### 2.7.2. Freundlich Adsorption Isotherm

Freundlich model is an empirical equation that applies to non-ideal adsorption equilibrium on heterogeneous surfaces and also multilayer adsorption, suggesting that binding sites are not equivalent and independent (Oliveira et al., 2005). The model assumes there is an infinite supply of unreacted adsorption sites, that the stronger binding sites are occupied first, binding strength decreases with increasing degree of site occupation, and that there is a logarithmic reduction of the affinity between adsorbate and adsorbent during surface coverage (Paggnanelli 2011).

The nonlinear form of this model is expressed as:

$$Q_e = K_f C_e^{\,1/n} \qquad (2.11)$$

Where,

$K_f$= Freundlich isotherm constant (mg/g) which indicates the relative adsorption capacity of the adsorbent

n = Heterogeneity factor, and its reciprocal indicates adsorption intensity

$C_e$= Equilibrium concentration of adsorbate (mg/L)

$Q_e$= Amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g).

Linearizing equation 2.11

$$LogQ_e = LogK_f + {}^{1}/_{n} LogC_e \quad (2.12)$$

$K_f$ and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where $1/n$ is a heterogeneity parameter, the parameter $n$ gives an indication of the adsorption type whether is linear ($n$=1) or a physical process ($n$>1) is favourable, or a chemical process $(n < 1)$. On the other hand, the value of $\frac{1}{n} < 1$ or $\frac{1}{n} > 1$ indicates a normal Langmuir isotherm and cooperative adsorption, respectively (Dada et al., 2012).

**2.8. Adsorption Kinetics Model**

Adsorption kinetics describes the rate of adsorbate uptake by the adsorbent from the aqueous solution helps to determine the overall rate of the adsorption process.

$$q_e = \frac{(c_0 - c_t)v}{m} \quad (2.13)$$

Where $C_o$ and $C_t$ are the liquid-phase concentrations at an initial and predetermined time (mg/L), respectively, is the volume of solution (L) and m is the dry weight of the added adsorbent (g) (Ismail 2014).

The kinetic equation of chemical reaction is determined experimentally by using gathered data from the experiment. The study of adsorption kinetics is important because it provides valuable information and describes the mechanism of the reaction.

Pseudo-first and pseudo-second-order reactions were observed, as the most common cause for adsorption modeling (Eduard, 2013).

**Pseudo-first-order Kinetic Model**: A reaction which is not first- order reaction naturally but made first order by increasing or decreasing the concentration of one or more reactants. It is based on the assumption that the rate of sorption is proportional to the number of free active sites on the sorbent surface (Febrianto et al., 2009).

The rate constant of adsorption can be determined from the pseudo-first-order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2.14)$$

Where $q_e$ and $q_t$ (mg/g) are the amounts of solute adsorbed (mg/g) at equilibrium and at time (min), respectively and $k_1$ is the adsorption rate constant ($min^{-1}$), larger adsorption rate constant $k_1$ usually represents a quicker adsorption rate.

**Pseudo-Second-Order Kinetic Model**: It is based on the assumption that the rate controlling step is the adsorption on the surface that involves chemisorption, where the removal from a solution is owing to physiochemical interaction between the two phases (Ho and Mckay 1999).

The pseudo-second-order equation based on the equilibrium adsorption is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \quad (2.15)$$

Where, $K_2$ (g/mg. min) is the rate constant of second-order adsorption, the larger $K_2$ value the slower the rate of adsorption.

### 2.9. Factors Affecting Defluoridation Process

Apart from the mineral and chemical composition of the adsorbent affecting adsorption properties, the solution parameters play a major role in determining the performance of the adsorbent in an adsorptive system. The effect of pH, contact time, adsorbent dose and adsorbate concentration on uptake of fluoride ion from aqueous media were investigated on different adsorbents and the effects discussed in the subsequent sections 2.9.1-2.9.4

#### 2.9.1. pH

The pH value of the solution plays an important role in the whole adsorption process and particularly on adsorption capacity. It would affect both aqueous chemistry and surface binding sites of adsorbents. The pH intern depends on the charge on the adsorbent surface. If the adsorbent surface is negatively charged, at lower pH, hydrogen ion ($H^+$) neutralizes the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion, and better adsorption. If the surface charge of the

adsorbent is positively charged, the $H^+$ compete effectively with the cations of the solution causing a decrease in the amount of metal ion adsorbed (Ushakumary 2013).
The solution of pH changes as fluoride adsorption progressed, necessitating $HNO_3$ or NaOH addition of solutions to keep the pH constant. During defluoridation of drinking water using bone char the solution pH always increases during the adsorption at $pH \leq 7$, but always diminishes slightly at $pH \geq 8$. This observation indicates that $H^+$ ions were adsorbed on the bone char at $pH \leq 7$ causing an increase in in the pH while the $H^+$ ions were released at $pH \geq 8$ causing a decrease in the pH of solution. This behaviour is due to the amphoteric character of the bone char since it has acidic and basic sites (Nahum et al., 2007).

### 2.9.2. Contact Time

The amount adsorbed on to the adsorbent is in a state of dynamic equilibrium with the amount desorbed from the adsorbent. The time required to attain this state of equilibrium is termed as equilibrium time. Contact time is the time for which fluoride is in contact with the adsorbent .In adsorption fluoride gets adsorbed in the vacant spaces in the adsorbent, so when the spaces are filled and no more fluoride can go inside, the adsorption stops and it is possible also that desorption may takes place (Indra et al., 2005).

### 2.9.3. Effect of Initial Fluoride Concentration

Concentration is the abundance of constitute or solute in a known volume of a mixture (Martin et al., 2017). Fluoride removal efficiency decreases with an increase in fluoride concentration. This is due to free sites on the adsorbent surface in lower initial fluoride concentrations (Mohammad et al., 2017).

### 2.9.4. Effect of Adsorbent Dose

Adsorbent dose is the mass of adsorbent prepared for adsorption for a specific amount of adsorbate. It has the greatest regression coefficient and the greatest effect on fluoride removal. An increase in the adsorption with an increase adsorbent dosage can be attributed to a greater surface area and more available adsorption sites at higher adsorbent dosage (Mohammad et al., 2017).

# CHAPTER THREE

# 3. MATERIALS AND METHODES

## 3.1. Materials and Chemicals

### 3.1.1. Instruments and Apparatus

Instruments and apparatus used in this study included; fluoride ion selective electrode (Metrohm, Sweeden), Muffle furnace (Audiotronics, Wagtech International Ltd. UK temperature upto 1200°C), weighing balance (Sartorius AG, 0.1 mg-320 g Germany), ball mill (MXC-11 Armfild, UK) Tubular oven (Schwabach, Germany), XRF (NEX De Advanced XRF Malvern Panalytical Ltd. UK), (XRD (Bruker D8 Advance diffractometer. Germany), FTIR (Perkin Elmer KBr 65 spectrophotometer USA), SEM-EDX (Carl Zeiss Naon-40 FESEM/FIB, Germany), pH meter (HANNA instrument, HI 9025, Malaysia), mortar and pestle, sieves with receiver (150 µm, 212 µm, 250 µm, 280 µm, 1 mm, 3 mm and 5 mm Impact test sieves (ASTM E11 ISO 3310), ceramic crucible, Orbital shaker (L0422SOI UK), measuring cylinders (5-500mL Duran, Germany), pipettes (15-100 mL Pyrex, USA), volumetric flasks (50, 100, 250, 500 and 1000mL Dragonmed Shangai China), 50ml plastic beaker, polyethylene plastic bags

### 3.1.2. Chemicals and Reagents

The chemicals and reagents used in this work were all analytical grade. Distilled water was used throughout the experiments. Sodium fluoride (NaF 99%, Analar, NaF, BDH Chemicals Ltd, England), hydrochloric acid (HCl 36% Fisher Scientific UK Limited), Sodium hydroxide (NaOH 98% Scharlau Chemie S.A. Sentmenat, Spain), phosphoric acid ($H_3PO_4$ 85% Fisher Scientific UK Limited ), sodium chloride (NaCl 99% Fisher Scientific UK), trisodium citrate ($Na_3C_6H_5O_7$ BDH Laboratory Supplies, Poole, England), glacial acetic acid ($CH_3COOH$ 100%, Sigma-Aldrich Laborchemikalien, Germany), EDTA ($C_{10}H_{16}N_2O_8$ Scharlau Chemie S.A. Barcelona, Spain), tap water

## 3.2. Methods and Procedures

### 3.2.1. Sample Collection

The raw materials used for the preparation of the composites were activated carbon (AC) prepared from coffee husk, stored in Debub farmers association warehouse Hawassa, bone char (BC) was prepared from cow bone supplied from Alem hotel

Adama, pumice (PU) obtained from National Cement Share Company, Koka Branch and ground real water sample was collected from Tejitu village, Modjo Street.

### 3.3. Raw Material Preparation

#### 3.3.1. Preparation of Activated Carbon

Three kilogram coffee husk was washed with tap water, sun dried for 2 days then crushed and ground to less than 1000 µm sieve size. This was then impregnate with 40% phosphoric acid ($H_3PO_4$) overnight, decanted through 212 µm sieve and air dried for 12 h at room temperature. After drying the husk was placed in 50 mL ceramic crucible and activated over night at 105℃ in a tubular oven, carbonized in a furnace for 1 h at 500℃ at constant heating rate (5℃/min) and cooled overnight in the furnace. Finally it was neutralized with 0.1 M sodium hydroxide (NaOH) and dried over night at 105℃ in a tubular oven, ground to pass through a150µm sieve (Derya 2015 and Maraisa et al., 2013).

#### 3.3.2. Preparation of Bone Char

Five kilogram cow bone was washed with hot tap water and scraped using knife to remove all the meat remnants, lipids and tendons then dried in the sun for 3 days. The bone was cut into pieces put in 50 mL crucible and fired at 500℃ for 1 h in a muffle furnace, cooled overnight. The fired bone was ground in a mortar manually, washed with 0.1 M sodium hydroxide (NaOH) and sieved to obtained 3-5 mm grain size for fluoride removal experiments and composites preparation (Eli 2015, Puangpinyo and Osiriphan 2006).

#### 3.3.3. Pre-treatment of Pumice

Two kilograms of pumice was crushed using 10mm ceramic ball mill and rinsed with de-ionized water for dust removal, dried at 105℃ for 24 h then sieved to pass through 40 meshes (Malakootian et al., 2011). The sample was used for both fluoride removal experiments and composites preparation.

### 3.4. Preparation of Composites

Dry samples of AC, BC and PU prepared above were mixed in in three different ratio (% mass) based on fluoride removal efficiency of the constituents, $C_1$ (25:50:25), $C_2$ (25:40:35) and $C_3$ (25:30:45) respectively. The mixing ratio was based on fluoride

removal efficiency of the constituents (Eq. 2.6). The samples were uniformly mixed, grinded with mortal to pass through 150 µm sieve and three drops of 0.9 M poly vinyl alcohol (PVA) solution was added to each composites powder samples to bind together and circular paste was prepared by pressing at 20 N. Then each composite was fired in muffle furnace for 1h at 350℃, 400℃, 450℃ and 500℃ and allowed to cool down overnight. This firing temperature range is expected to induce interlocking between the composite materials without deteriorating their chemical and physical characteristics**.**

Table 3. 1. Preparation of composites from AC, BC and PU

| Composite Code | Mixing ratio of AC, BC and PU respectively (% mass) | Firing temperature (℃) |
|---|---|---|
| $C_1$-350 | 25:50:25 | 350 |
| $C_1$-400 | 25:50:25 | 400 |
| $C_1$-450 | 25:50:25 | 450 |
| $C_1$-500 | 25:50:25 | 500 |
| $C_2$-350 | 25:40:35 | 350 |
| $C_2$-400 | 25:40:35 | 400 |
| $C_2$-450 | 25:40:35 | 450 |
| $C_2$-500 | 25:40:35 | 500 |
| $C_3$-350 | 25:30:45 | 350 |
| $C_3$-400 | 25:30:45 | 400 |
| $C_3$-450 | 25:30:45 | 450 |
| $C_3$-500 | 25:30:45 | 500 |

Twelve different samples (composite adsorbents) were ground and washed with distilled water till they became clean and dried at 100℃ for 24 h. The dried composite powders were sieved using 280 µm and 250 µm sieves. The composite powders that passed through 280 µm sieve and retained on the 250 µm sieve were used for defluoridation of water experiments (Scheme 3.1). The powdered composites that passed through the 250 µm sieve were very fine that increase total dissolved solid (TDS) of the water and reused back for composite paste preparation.

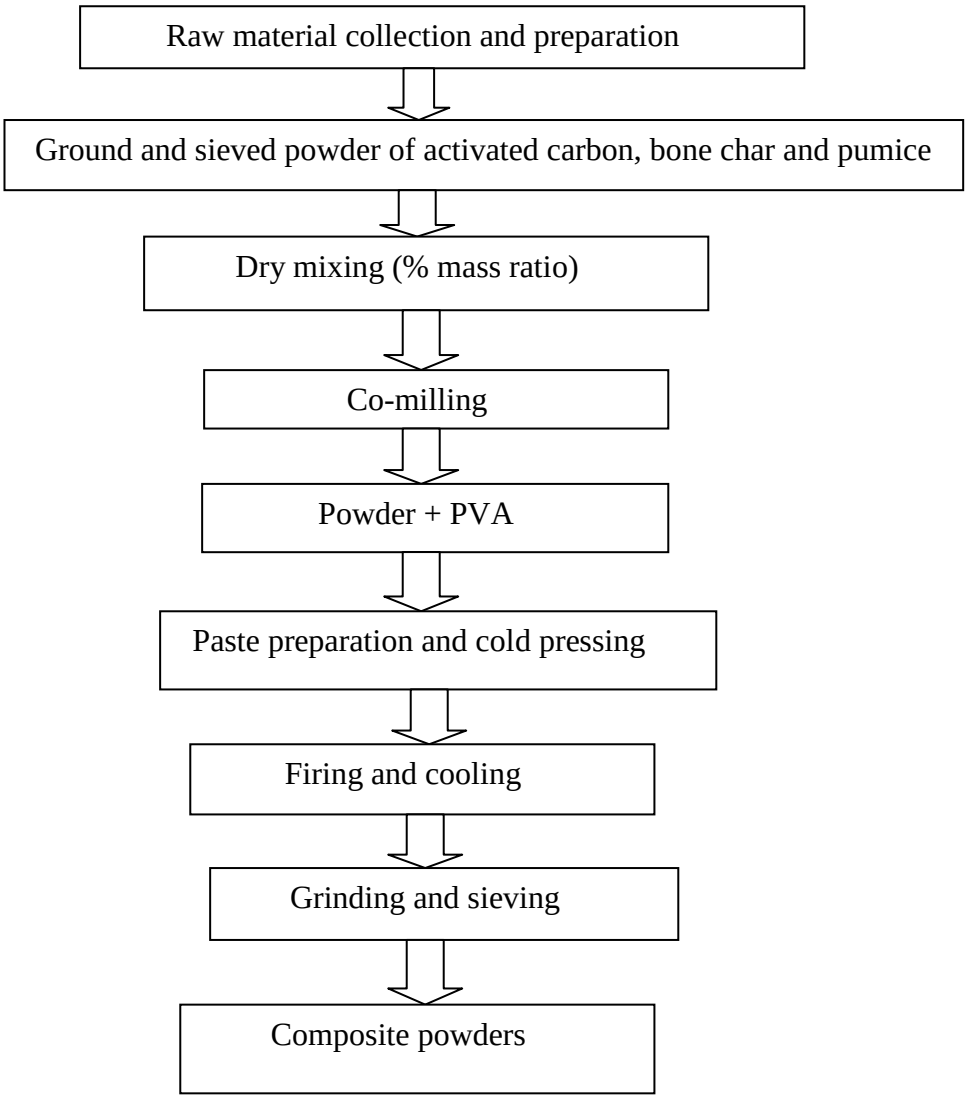



Figure 3. 1. Scheme of the preparation of composites from BC, PU and AC

### 3.5. Determination of Fluoride Concentration

#### 3.5.1. Preparation of Standard Solutions

A stock solution of 1000 mg/L sodium fluoride solution was prepared by dissolving 2.21 g of anhydrous sodium fluoride (NaF previously dried for 2hrs at 105℃ and

cooled in desiccators) in double distilled water (Yucel et al., 2015). Standards at required concentration (2 mg/L, 4 mg/L, 6 mg/L, 7 mg/L, 8 mg/L, 10 mg/L and 13 mg/L) were prepared by appropriate serial dilution from the stock solution with double distilled water.

### 3.5.2. Preparation of TISAB

TISAB II was prepared by dissolving 56 g sodium chloride, 7 g hydrated trisodium citrate ($Na_3C_6H_5O_7$. $2H_2O$), 2 g ethylene di-amine tetra acetic acid (EDTA) ($C_{10}H_{16}N_2O_8$) in 500 mL de-ionized water. After shaking and stirring for 10 minutes the solution was mixed with 57 mL glacial acetic acid in a 1000mL volumetric flask. The pH was adjusted to 5.3 using 5 M sodium hydroxide and 1 M hydrochloric acid (Agarwalet al., 2003).

### 3.5.3. Calibration of Fluoride Ion Selective Electrode

Standard fluoride solutions were prepared from 1000 mg/L of sodium fluoride stock solution by diluting with double distilled water. 2 mL of TISAB II was added to 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L standard fluoride solution. The ISE was placed in the plastic beakers containing 30 mL of standard fluoride solutions and continuous stirring and rotates at 20 rpm at room temperature. The potentiometric readings for each concentration were noted and calibration curve of the potential (E in mv) versus the logarithm of concentration of fluoride ([Log C]) was plotted in figure 3.2 (APHA 2012). The slope and coefficient of determination ($R^2$) value of the graph were 58.62 and 0.996 respectively.

Table 3. 2. Calibration of fluoride ion selective electrode

| Standard solutions ($[F^-]$ (mg/L)) | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|
| Log $[F^-]$ | 0.3 | 0.6 | 0.78 | 0.9 | 1 |
| Potentiometric reading (mv) | -80.6 | -97.7 | -109.6 | -114.1 | -122.3 |

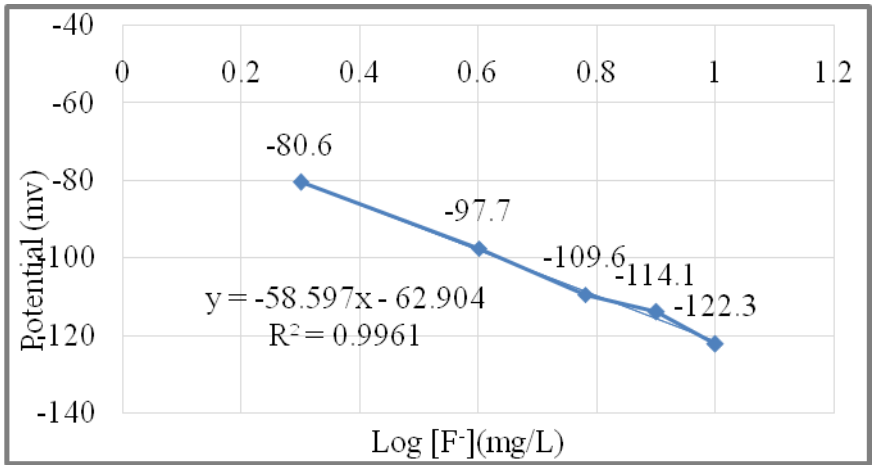



Figure 3. 2. Fluoride ion selective electrode calibration curve

The potential developed in ion selective electrode (ISE) and the concentration of fluoride ion ([$F^-$]) in the solution was correlated using Nernst equation:

$$E = E^0 - (2.303\ RT/zF)\log [F^-] \qquad (3.1)$$

Where: E is the measured electrode potential in the solution, $E^o$ is the standard potential of the reference electrode, R is the gas constant (8.314 joules/mole), T is the absolute temperature (K); z is the charge of fluoride ion in the solution, F is faraday's constant (96,500 coulombs/mole) and [$F^-$] is the concentration of fluoride ion in a particular sample solution.

### 3.5.4. Defluoridation of Water

Batch adsorption preliminary test was carried out at the same fluoride concentration (13 mg/L $F^-$), pH 7 contact time (1 h) and amount of composite powders (2.5 g) to identify the sample having highest percentage fluoride removal. Twelve 50 mL sample solutions (13 mg/L F-) was mixed with 2 mL of TISAB II in 100 mL plastic beaker for pretest. 2.5 g of each composite ($C_1$-350—$C_3$-500) adsorbent was added to each sample solution. The mixtures were under stirring for 50 minutes and then centrifuged at 20 rpm for 10 minutes; decanted and filtered using Whatman No.1 filter paper. The residual fluoride concentration in the samples were determined by mixing an aliquot of 20 mL filtered water sample with 2 mL of TISAB II solution into 50 mL of plastic beaker with continuous stirring using ISE combined with glass electrode. The potential readings (mV) of the sample were converted into concentration of fluoride (mg/L) using Microsoft excel program

The composite material which had high fluoride percentage removal (adsorption efficiency) and adsorption capacity ($q_e$) was identified to study factors that affect its deflouridation efficiency, adsorption kinetics, adsorption isotherm model, physic-chemical nature and its adverse effect on the quality of water. .

$$\% F^- \text{ removed} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3.2)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3.3)$$

Where, $C_0$ is initial fluoride concentration, $C_e$ is residual fluoride concentration, $q_e$ is the adsorption capacity (mg $g^{-1}$), m is mass of adsorbent (g) and v is volume (L) of the solution.

The adsorbent prepared by mixing treated pumice, charred bone and chemically activated coffee husk with ratio of 25:50:25 respectively fired at 350°C ($C_1$-350) was found to had better performance in deflouridation of water and used for other parameter optimization.

### 3.6. Effect of Different Parameters on Fluoride Removal Efficiency of $C_1$-350

Different factors affect the defluoridation efficiency of an adsorbent including adsorbent dose, pH level of the solution; fluoride concentration and contact time are main factors that should be deal during deflouridation.

#### 3.6.1. Effect of pH

The effect of solution pH on the fluoride removal efficiency of $C_1$-350 by adsorption, experiments were carried out using 2.5 g of composite adsorbent, contact time 1 h and 13 mg/L fluoride ion concentration by varying the pH of the solutions from 3, 5, 7 and 9 using 1 M NaOH and/or 1 M HCl at room temperature

#### 3.6.2. Effect of Adsorbent Dose

The effect of adsorbent dose on the adsorption capacity and adsorption efficiency were carried out using 2.5 g, 5 g, 7.5 g and 10 g of the screened out best composite ($C_1$-350) adsorbent/50ml of 13 mg/L fluoride ion solution at 1 h contact time and pH 7.

### 3.6.3. Effect of Initial Fluoride Concentration

The effect of initial concentration of fluoride ion on the adsorption capacity of composite ($C_1$-350) was investigated at room temperature by varying fluoride ion concentration from 4 mg/L to 13 mg/L (4 mg/L, 7 mg/L, 10 mg/L and 13 mg/L) using 2.5 g composite at 1 h and at pH of 7.

### 3.6.4. Effect of Contact Time

The residual fluoride ion concentration that remains in the solution depends on the length of contact time between adsorbent and adsorbate. Contact time of 1, 3, 5 and 7 h were selected to study the effect of contact time on the adsorption of fluoride ion.

## 3.7. Adsorption Isotherms

Both Langmuir $\frac{C_e}{q_e}$ $vs$ $C_e$ and freundlich ($\log q_e$ vs $\log C_e$) isotherm models for fluoride ion adsorption by the composite ($C_1$-350) were plotted at room temperature. Data for isotherms was obtained by mixing a serious of increasing composites ($C_1$-350) dosage (0.15, 0.20, 0.25 and 0.30 g) at 5 mg/L constant fluoride ion concentration using 50 mL solution. The mixtures were agitated at 200 rpm for 5 h (a time which percentage of fluoride adsorption occurs) to ensure equilibrium at constant values of pH 7, and residual fluoride was determined after filtration. Based on the data generated, the adsorption isotherms were plotted

## 3.8. Adsorption Kinetics Models

The rate of fluoride ions uptake (kinetics of fluoride adsorption) by the composite ($C_1$-350) was characterized by the pseudo first order and pseudo second order models using 30mL solution with 13 mg/L initial fluoride ion concentration, 2.5 g $C_1$-350 composite, pH of 7 at room temperature. The residual fluoride ion concentration was measured at different time intervals of 1, 3, 5 and 7 h.

## 3.9. Physico-chemical Parameters of $C_1$-350

### 3.9.1. Surry pH

0.2 g of the dry, grinded $C_1$-350 composite was mixed with 25 mL of distilled water and allowed to boil for 30 min in stoppered glass bottle. After cooling, the pH of the adsorbent was measured using a digital pH meter, allowing 5 min for the pH probe to equilibrate (ASTM D3838-80).

### 3.9.2. Moisture

Moisture content of $C_1$-350 composite was determined according to ASTM 2867-99. This was done by weighing 0.5 g of the composite into a crucible. The crucible was placed in oven and heated for 5hours at constant temperature of 105℃. The crucible was then removed and placed rapidly into a desiccator in order to prevent more moisture uptake from atmosphere. The sample was re-weighed. The difference in the mass constitutes the amount of moisture content of the adsorbent.

$$\% \text{ moisture} = \frac{w_2 - w_3}{w_2 - w_1} \times 100 \qquad (3.4)$$

Where, $W_1$ is weight of crucible $W_2$ is initial weight of crucible with sample and $W_3$ is final weight of crucible with sample with dry sample

### 3.9.3. Bulk Density

The bulk density of $C_1$-350 composite was determined using Archimedes' principle by weighing a 10g of $C_1$-350 composite. This mass of composite was impressed into a 25 mL measuring cylinder filled with 10 mL water ($V_0$) hence the water level rises to $V_1$. The difference in levels $V_1$-$V_0$ corresponds to the volume of impressed composite.
The bulk density was determined as:

$$\text{Bulk density} = \frac{\text{mass of composite}}{V_1 - V_0} \qquad (3.5)$$

Where, $V_0$ is volume of water in measuring cylinder $V_1$ is volume of after impressing the composite

### 3.9.4. Specific Surface Area

Sears Method was used to determine the surface area. 0.5 g of the $C_1$-350 composite was acidified with 0.1M hydrochloric acid to pH 3 – 3.5, the volume was made up to 50$cm^3$ with de-ionized water after addition of 10 g of sodium chloride. The titration was carried out with standard 0.1M sodium hydroxide in a thermostated bath at room temperature to pH 4.0, and then to pH 9.0. The volume V required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed as:

$$S\ (m^2/g) = 32V - 25 \qquad (3.6)$$

### 3.9.5. Point zero charge determination

0.2 g of $C_1$-350 composite was added to 40 mL of 0.1 M $NaNO_3$ solution. The pH was adjusted with 0.1 M $HNO_3$ and 0.1 M NaOH to obtain a pH range of 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 (± 0.1pH unit). The pH values of the supernatant in each tube were denoted as $pH_i$. The samples were shaken for 24 h using rotary agitator at 200 rpm. After settling, the pH values of the supernatant in each tube were measured and denoted as $pH_f$. The PZC was obtained from the plot of ΔpH ($pH_f$ - $pH_i$) against $pH_i$. Point zero charge is the pH at which the initial pH with minimum ΔpH (Tan et al., 2008).

### 3.10. Characterization techniques

1) **X-ray fluorescence (XRF)**: The chemical composition of pumice sample was determined by XRF (NEX De Advanced EDXRF Malvern Panalytical Ltd. UK).
2) **X-ray diffraction (XRD)**: Identification of the crystal structure of pumice, bone char, activated carbon and $C_1$-350 composite were analyzed using XRD (Bruker D8 advance diffractometer). The radiation was operated at 40Kv and 30mA. The diffraction pattern was recorded from $10^0$ to $80^0$ with 2θ angle of diffraction.
3) **Fourier transform infrared spectrometry (FT-IR)**: This study was conducted on bone char, activated carbon and $C_1$-350 composite to identify the groups on the surface before adsorption using FTIR (Perkin Elmer KBr 65 spectrophotometer) at the scanning range of 4000 $cm^{-1}$- 400 $cm^{-1}$.
4) **Scanning electron microscopy (SEM)**: The surface morphology of the materials was observed using SEM (Carl Zeiss Naon-40 FESEM/FIB) at different magnification power. The analysis was done by spraying dried sample powders onto aluminum stubs using double-sided adhesive carbon discs. The morphology was examined under the following analytical conditions: EHT = 2.00 kV beam current =100 μA Signal A =SESI, WD = 8.5 mm, 8.6 mm, 8.7 mm, 8.8 mm and 8.9 mm.
5) **Energy dispersive x-ray spectroscopy (EDX):** An x-ray produced by a sample in an electric beam is detected. The electric beam excites the atoms in the sample to produce x-rays to discharge the excess energy. The energy of the x-ray is typical of the atoms that produced them, creating peaks in the spectrum and thus allowing the chemical composition of the sample to be established.

# CHAPTER FOUR

## 4. RESULTS AND DISCUSSION

### 4.1. Defluoridation of Water by Adsorption

The defluoridation efficiency of AC, BC, PU and composites were examined in the experiment. It has reported in literature that fluoride removal by bone char is associated with the two main mechanisms of ion exchange and chemical precipitation as calcium fluoride (Rojaset et al., 2013) while fluoride-pumice interaction concurred was expected due to the attraction of fluoride ion to metal cations (Mohammad et al., 2016). Adsorption of fluoride on the surface of activated carbon occurs by physical adsorption on the porous structure (Jaramillo et al., 2010). It has reported (table 4.1) that BC is the most effective defluoridation material than AC and PU.

Fluoride adsorption by the composite materials has been proposed to occur via ion exchange with lattice $OH^-$, chemical precipitation as $CaF_2$, interaction with cationic centers and physical adsorption on the porous structure. The adsorption capacity of the composites ($C_1$, $C_2$ and $C_3$) fired at temperature range of 350℃ - 500℃, were evaluated for defluoridation of water. Out of these twelve composite materials $C_1$ fired at 350℃ ($C_1$-350) removes fluoride significantly shown in the table 4.1. The experimental result shows that the fluoride removal efficiency and capacity of the composites depend on the percentage of components in the composites and intensity of firing temperature. $C_1$-350 prepared by mixing 25:50:25 AC, BC and PU respectively fired at 350 ℃ had 95.26% fluoride removal efficiency while the efficiency of $C_2$-350 composed from 25:40:35 AC, BC and PU fired at the same temperature was 93.57%. The difference in their removal efficiency is due to the percentage of constituents, $C_1$-350 that contains 50% BC had high removal efficiency than $C_2$-350 that contains 40% BC. The other factor that affects defluoridation capacity of the composites was intensity of firing temperature which can be understood by observing $C_1$-350 and $C_1$-400. These two composites were prepared from the same percentage of AC, BC and PU (25:50:25). $C_1$-350 fired at 350 ℃ had 95.26% defluoridation efficiency whereas fluoride removal efficiency of $C_1$-400 fired at 400 ℃ was 90.19. As firing temperature increases fluoride removal efficiency/capacity of the composite decreases due to the

dehydroxylation of hydroxyapatite (fluoride exchanger) in bone char (Rojaset al., 2013) that is contained in the composite.

Mean well composite containing high percentage of bone char and fired at low temperature was found to be effective fluoride removal thus $C_1$-350 was better adsorbent for fluoride than other composite. Fluoride removal efficiency of AC (62.54%) and PU (40.23%) increase to 95.26% when they are incorporated with 50% BC composite ($C_1$-350) while the efficiency of BC (97.46%) declines to 95.26% when it was composited with 25% AC and 25% PU.

Table 4. 1. Fluoride removal efficiency and adsorption capacity of the composite materials ($C_1$-350 – $C_3$-500) AC, BC and PU at pH 7, 1h contact time, 13 mg/L fluoride concentration using 2.5 g of adsorbents in 50 mL laboratory fluorinated water

| Firing temperatur(°C) | Sample code | Measured value of $C_e$ (mg/L) | | Average value of $C_e$ | Removed $F^-$ (%) | Average value of $q_e$ |
|---|---|---|---|---|---|---|
| | | $C_{e1}$ | $C_{e2}$ | | | |
| 500 | AC | 2.31 | 2.56 | 2.435 | 62.54 | 0.1626 |
| 500 | BC | 0.18 | 0.15 | 0.165 | 97.46 | 0.2534 |
| 105 | PU | 3.78 | 3.99 | 3.885 | 40.23 | 0.1046 |
| 350 | $C_1$-350 | 0.51 | 0.72 | 0.615 | 95.26 | 0.2477 |
| | $C_2$-350 | 0.85 | 0.82 | 0.835 | 93.57 | 0.2433 |
| | $C_3$-350 | 1.2 | 1.17 | 1.185 | 90.88 | 0.2363 |
| 400 | $C_1$-400 | 1.27 | 1.28 | 1.275 | 90.19 | 0.2345 |
| | $C_2$-400 | 1.28 | 1.35 | 1.315 | 89.88 | 0.2337 |
| | $C_3$-400 | 1.47 | 1.51 | 1.49 | 88.54 | 0.2302 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | $C_1$-450 | 1.56 | 1.53 | 1.545 | 88.11 | 0.2291 |
| 450 | $C_2$-450 | 1.89 | 1.82 | 1.855 | 85.73 | 0.2229 |
| | $C_3$-450 | 2.74 | 2.57 | 2.745 | 78.88 | 0.2051 |
| | $C_1$-500 | 1.73 | 1.76 | 1.745 | 86.57 | 0.2251 |
| 500 | $C_2$-500 | 1.98 | 1.9 | 1.94 | 85.07 | 0.2212 |
| | $C_3$-500 | 2.23 | 2.39 | 2.31 | 82.23 | 0.2138 |

Where, $C_e$ is final equilibrium concentration of fluoride after adsorption and $q_e$ is adsorbent phase concentration after equilibrium/ mg of fluoride ion per gram of adsorbent.

### 4.2. Effect of Different Parameters on Fluoride Sorption by Composite $C_1$ – 350

#### 4.2.1. Effect of pH

The effect of pH on removal of fluoride was shown in figure 4.1. Test mixtures containing 13 mg/L fluoride concentration and 2.5 g of the composite material were adjusted to various pH values: acidic, neutral and alkaline range (3, 5, 7 and 9) mixed for 1 h and the residual fluoride concentration was analyzed. The adsorption data was not performed at pH < 3 since bone char dissolved at pH < 3.

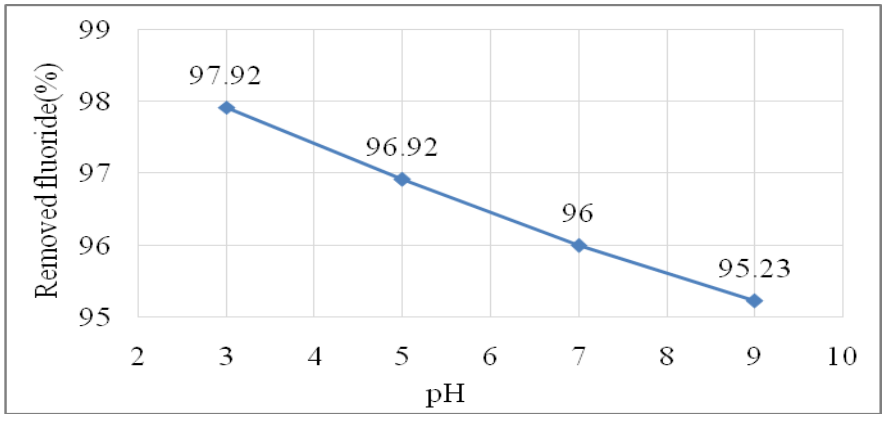



Figure 4. 1. Effect of pH on fluoride removal efficiency of $C_1$-350

In this figure, it can be noticed that the adsorption capacity of the composite is affected by the solution pH. The results also revealed that the maximum adsorption capacity occurred at pH 3. The adsorption efficiency diminished drastically while increasing the pH from 3 to 9 because change in pH alters the surface charge of the adsorbent and

electrostatic interactions between the $F^-$ anions in solution. In the acidic medium, the surface of the adsorbent is highly protonated, and hence more $F^-$ ions can be attracted, at higher pH the surface of the adsorbent becomes negatively charged (deprotonated) and fluoride leads to comparatively low adsorption. The effect of pH on the adsorption efficiency can be clearly illustrated by dealing surface charge of composite (PZC). When the solution pH is below the PZC of 8.1, the $F^-$ anions were attracted to the positively charged surface of the composite, caused by the protonation of the hydroxyapatite hydroxyl groups, thus favoring $F^-$ accumulation onto the surface. The surface charge of composite became more positively charged while decreasing the pH below its PZC. Hence, more $F^-$ anions were attracted to the surface resulting in an increase in the adsorption capacity of the composite. At pH above the PZC, adsorption of $F^-$ was slightly decrease because the bone char surface was negatively charged, due to deprotonation of the hydroxyapatite hydroxyl groups, causing a mutual repulsion between $F^-$ anions and the composite surface. Adsorption at pH value above the PZC was not due to an electrostatic attraction but to a chemical interaction with sufficient energy that overcome the surface-fluoride repulsion forces. The composite shows higher fluoride removal efficiency (97.92%) at pH 3 and 96% at neutral pH.

### 4.2.2. Effect of Adsorbent Dose

Figure 4.2 shows percentage removal of fluoride ion from water on $C_1$-350 composite adsorbent at pH 7, 1 h contact time and 13 mg/L initial fluoride concentration at varied adsorbent dose. The dose of the adsorbent increases from 2.5 g -10 g (2.5, 5, 7.5 and 10 g). Defluoridation increases as adsorbent dose increases due to the availability of more active sites to absorb fluoride ion. Percentage of defluoridation increases from 93.69 to 99.23 as the amount of $C_1$-350 used increases from 2.5 g to 10 g.

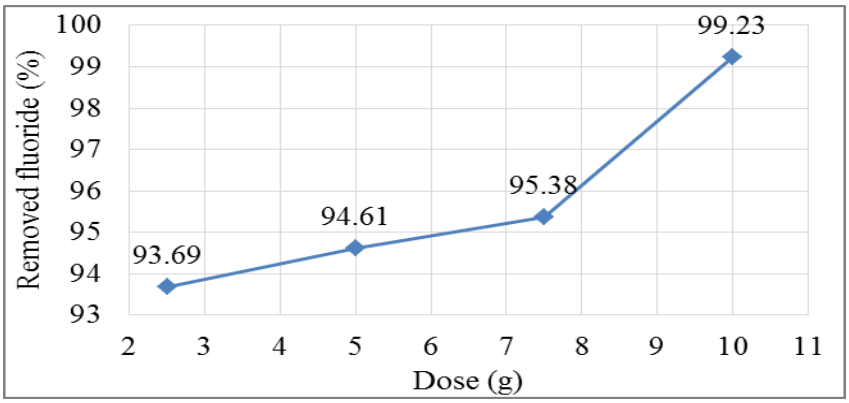



Figure 4. 2. Effect of adsorbent dose on fluoride removal efficiency of $C_1$-350

### 4.2.3. Effect of Initial Concentration of Fluoride

For a fixed mass of adsorbent (2.5 g), at constant contact time (1 h) and pH 7 the removal efficiency of the adsorbent decreased as concentration of fluoride increases shown in figure 4.3. Significant change was not observed for fluoride concentration less than 10 mg/L (4, 7 and 10 mg/L) this is due to the availability of active adsorbent site up to some range of fluoride ion concentration. But there is a sharp decrease in fluoride removal efficiency for a solution having fluoride concentration more than 10 mg/L (13 mg/L) this is because of the utilization of all the energetically active site of the adsorbent. The adsorption capacity (mg/g) the adsorbent increases as initial fluoride concentration increases as more active sites were not occupied, the whole fluoride ion was adsorbed from the solution still unoccupied active sites were accessible.

The removal efficiency was highest at lower and desired concentration of fluoride and decreased as concentration gets over the optimum range indicating the specific adsorption sites were available for $F^-$ adsorption.

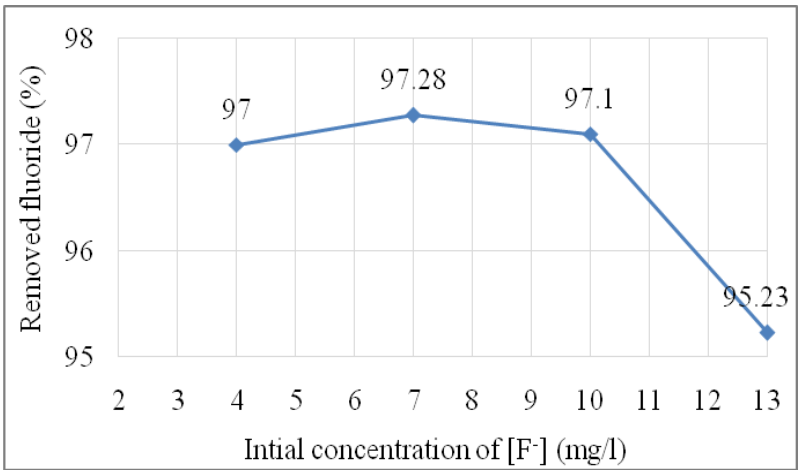



Figure 4. 3. Effect of concentration of fluoride on fluoride removal efficiency of $C_1$-350

### 4.2.4. Effect of Contact Time

The effect of the length of contact time between fluoride water and the composite on percentage removal of fluoride could be observed at figure 4.4; as time increases more fluoride ions from the solution would have more probability to stick to the available active site of the adsorbent until equilibrium reached. After equilibrium no more fluoride ion would be adsorbed rather desorption incident occurred on prolonged contact time.

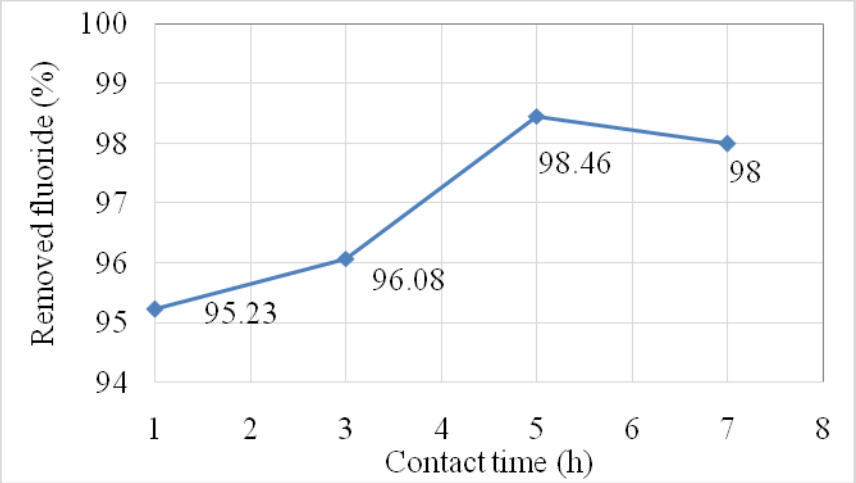



Figure 4. 4. Effect of contact time on fluoride removal efficiency of $C_1$-350

### 4.3. Adsorption Isotherm Models

#### 4.3.1. Langmuir and Freundlich Isotherm Model

Both Langmuir ($\frac{C_e}{q_e}$ vs $q_e$) and freundlich ($\log q_e$ vs $\log C_e$) for fluoride ion adsorption on the composite adsorbent ($C_1$-350) were done at room temperature. Data for plotting isotherms were obtained by mixing a constant fluoride ion concentration of 5 mg/L with a serious of increasing adsorbent ($C_1$-350) dosage (0.15, 0.20, 0.25 and 0.30 g) using 50 mL solution. Based on the data generated, adsorption isotherms were plotted in Fig 4.5.

a) Langmuir isotherm model b) Freundlich isotherm model

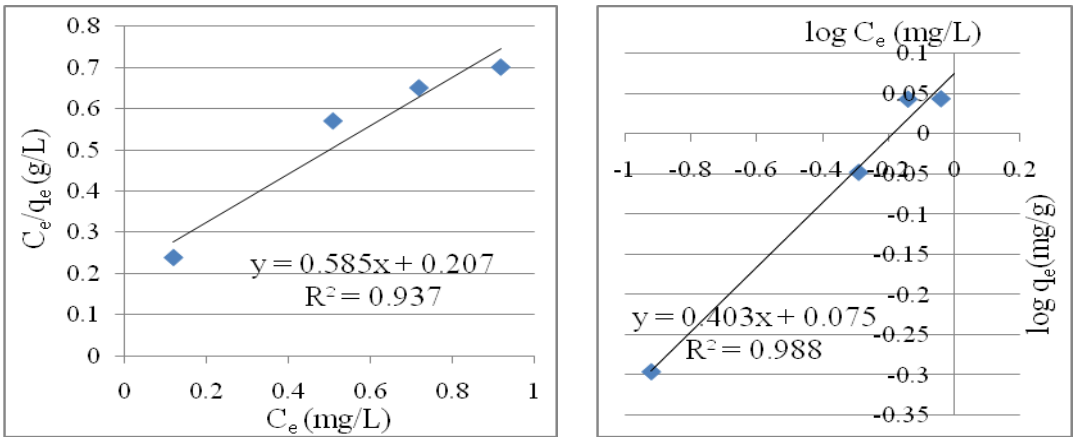



Figure 4. 5. Langmuir and Freundlich isotherm models

Figure 4.5a) shows the results of the Langmuir adsorption isotherm model of fluoride ion from water using composite $C_1$-350. The graph shows the good adsorption

isotherm for fluoride removal. This can be proved by looking at the coefficient of determination; $R^2$ where it is 0.9372.The effect of isotherm shape can be used to predict whether an adsorption system is 'favorable' or 'unfavorable'. The essential features of Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter, the isotherm is unfavorable when $R_L > 1$, linear when $R_L=1$, favorable when $0<R_L<1$ and irreversible when $R_L=0$. In this work the $R_L$ value calculated was 0.361 (table 4.2), which suggests the favorable adsorption of fluoride onto $C_1$-350 absorbent, under the conditions used for the experiment.

Freundlich's isotherm model for fluoride ion is shown in figure 4.5b above. $K_f$ and 1/n are obtained from the equation of linear line plotted, 1/n is obtained from the slope and $K_f$ value is from antilog value of log $C_e$. Large $K_f$ value indicates greater adsorption capacity, while 1/n is a function of the strength of the used adsorbent material ($C_1$ - 350) and high value of 1/n showed adsorption bond is weak. When 1/n >1, the adsorption coefficient $K_f$ increases with increasing concentration of the solution and $\frac{1}{n} < 1$, $K_f$ decreases with concentration. From the result (table 4.2) the value of 1/n and $K_f$ obtained were 0.4033 and 1.078 respectively. Based on these values it can be concluded that the removal of fluoride ion using $C_1$-350 from water is satisfactory at low concentration of the solution.

In comparison fluoride adsorption on $C_1$ - 350 was fitted more with Freundlich isotherm ($R^2$ = 0.9887) indicates that the adsorption is characterized with a multilayer adsorption which is shown by a system with heterogeneous surface.

Table 4. 2. Langmuir and Freundlich isotherm constants for the adsorption of $F^-$ ion by $C_1$ – 350 composite at room temperature

| Ion | Adsorbent | Langmuir isotherm parameters | | | | Freundlich isotherm parameters | | |
|---|---|---|---|---|---|---|---|---|
| $F^-$ | $C_1$-350 | $Q_e$(mg/g | $K_L$ (L/mg) | $R_L$ | $R^2$ | $K_f$ (mg/g) | $\frac{1}{n}$ | $R^2$ |
| | | 1.707 | 0.354 | 0.361 | 0.9372 | 1.078 | 0.4033 | 0.9887 |
| | | $C_e/q_e = 0.5859C_e + 0.2075$ | | | | $Logq_e = 0.4033LogC_e + 0.0758$ | | |

### 4.4. Adsorption Kinetics Modelling of $F^-$ sorption on $C_1$-350

In addition to the adsorption isotherms, kinetics data were obtained from the composite material $C_1$-350. The rate at which dissolved fluoride ions are removed from aqueous solution using the composite matter is a significant factor. The rapid adsorption processes are quite useful for practical use due to the need of short contact time in the actual process. Figure 4.6 shows the pseudo first order and pseudo second order kinetics of fluoride ion sorption experiment at room temperature.

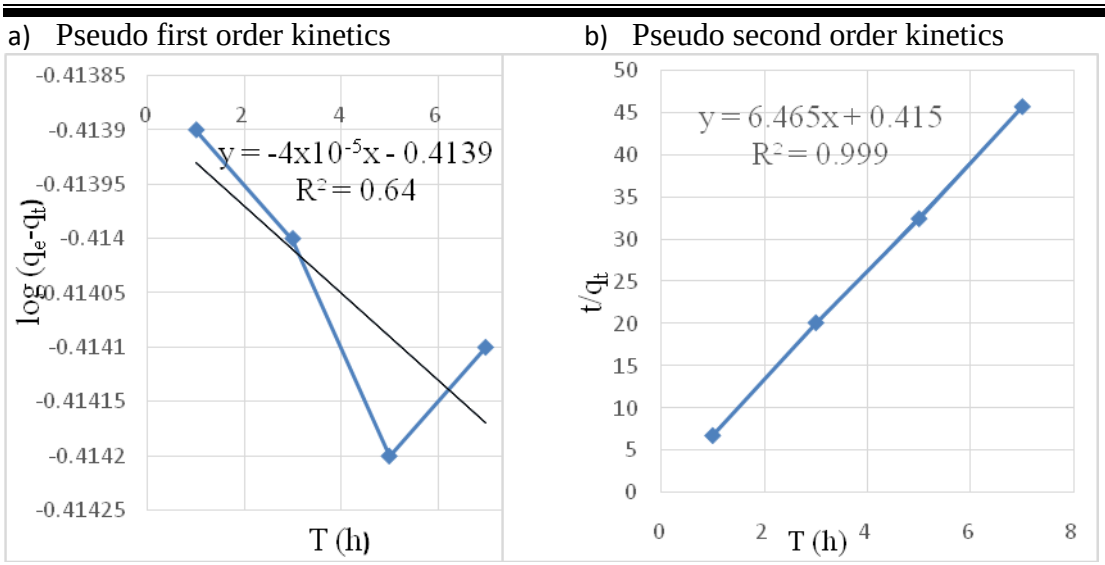



Figure 4. 6. Pseudo first and second order kinetics model

Figure 4.6 above shows a plot of pseudo first order model and pseudo-second order model for the sorption of fluoride ion onto $C_1$-350 composite at 13 mg/L initial fluoride ion concentrations for the initial 1h then 3, 5 and 7 hrs.

The kinetic constants of pseudo first order and pseudo second order isotherm models ($K_1$ and $K_2$), the adsorption capacity calculated $Q_e$ (cal) from the kinetics model and the experimentally resulted adsorption capacity $Q_e$ (exp) and correlation coefficients ($R^2$) are calculated from the slope and intercept of Eq. 2.13, Eq. 2.14 and tabulated in table 4.3. According to the results, the correlation coefficient for the plot of pseudo first order ($R^2$ =0.64) is less than that of the correlation coefficient of pseudo second-order reaction ($R^2$ =0.9998). In addition the kinetic data shows that the values of $Q_e$ (cal) and $Q_e$ (exp) by pseudo second order kinetics model are closer than the values at first pseudo order model. Those findings indicate that kinetic data for adsorption of fluoride by the adsorbent prepared is better fitted to pseudo second-order rate equation than pseudo first-order rate equation. Therefore, it is concluded that the adsorption of

fluoride by this adsorbent follows the pseudo second order reaction kinetics which implies that the chemical adsorption controls the rate of fluoride adsorption onto the composite ($C_1$-350) without transmigration of the adsorbate ($F^-$). The larger value of $K_2$ (107.5 g $mg^{-1}$ $min^{-1}$) shows that the rate of adsorption is slower.

Table 4. 3. Kinetics constants for $C_1$-350 composite on fluoride adsorption

| | | |
|---|---|---|
| Experimental data | $Q_e$ (exp) (mg $g^{-1}$) | 0.19 |
| Pseudo first order | $Q_e$ (cal) (mg $g^{-1}$) | 0.66 |
| | $K_1$ ($min^{-1}$) | $9.21x10^{-5}$ |
| | $R^2$ | 0.64 |
| Pseudo second order | $Q_e$ (cal) (mg $g^{-1}$) | 0.15 |
| | $K_2$ (mg $g^{-1}$ $min^{-1}$) | 107.5 |
| | $R^2$ | 0.9998 |

### 4.5. Defluoradation of Real water Using $C_1$-350 and Raw Materials

The adsorption process of the real water (taken from Tejitu village, Modjo Street, pH 7.31 and ([$F^-$] 8.6 mg/L)) was done at 26 $^0$C, 200 rpm for 1hr using 2.5 gram of BC, AC PU and $C_1$-350 adsorbents. The composite material $C_1$-350 removed fluoride from real water significantly than the raw materials. This is because activated carbon and pumice hinders the effect of coexisting ions $Cl^-$, $CO_3^{2-}$, $PO_4^{3-}$ $SO_4^{2-}$ and particulate matter as stated in literature part 2.4.1, 2.4.2 and 2.4.3 while bone char removes fluoride effectively.

Table 4. 4. Fluoride removal efficiency of raw materials (BC, AC, and PU) and the $C_1$-350 composite form real water

| Water samples | Removed fluoride (%) | | | |
|---|---|---|---|---|
| | BC | AC | PU | $C_1$-350 |
| Real water ([$F^-$] 8 mg/L) | 82.5 | 55.63 | 2.88 | 94.88 |

### 4.6. Characterization of Raw Materials and $C_1$-350

#### 4.6.1. Characterization of Raw Materials

4.6.1.1. Pumice

The XRF analysis in table 4.4 shows $SiO_2$ (67.4%) and $Al_2O_3$ (13.69%) are the main constituents of pumice whereas the percentage composition of MgO, $TiO_2$, $P_2O_5$ and MnO is less than 1%. The higher percentage of silica is an indicative of pure pumice (Ersoy et al., 2010).

Table 4. 5. Chemical composition of the pumice by XRF

| Oxides | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | MnO | $P_2O_5$ | $TiO_2$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wt. (%) | 67.4 | 13.69 | 2.76 | 1.04 | 0.54 | 1.80 | 4.98 | 0.06 | 0.08 | 0.20 | 6.89 |

The EDX analysis carried out in the PU particle is shown in table 4.5 and figure 4.7, where it can be observed that the concentration of oxygen (O), silicon (Si) and aluminum (Al) is higher which confirms its XRF analysis.

Table 4.5: EDX analysis showing percentage abundance of elements in pumice

| Element | O | Na | Mg | Al | Si | K | Ca | Ti | Fe | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| Weight % | 59.65 | 1.42 | 0.17 | 6.51 | 26.00 | 0.06 | 3.88 | 0.29 | 1.57 | 100 |
| Atomic % | 72.96 | 1.21 | 0.14 | 4.72 | 18.12 | 1.94 | 0.25 | 0.12 | 0.55 | |

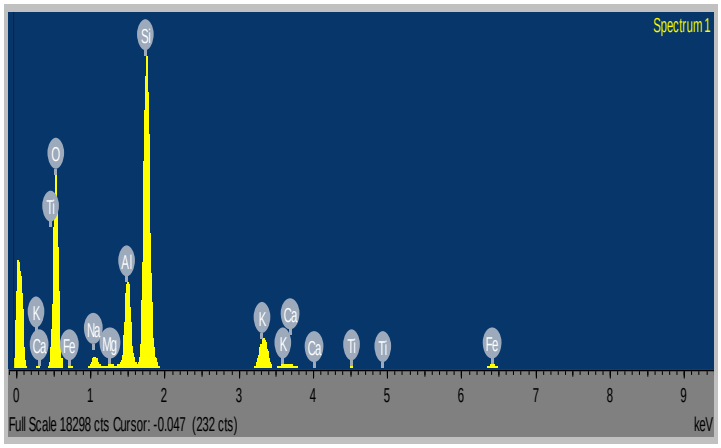



Figure 4. 7. EDX spectra showing the elemental composition of pumice

The XRD diffraction pattern shown in fig. 4.8 indicates that pumice stone has no crystalline structure and the broad peak reflection between $20^o$ and $30^o$ (2θ) confirmed

the presence of amorphous silica (Mucip et al., 2012). The main structure is amorphous confirming the characteristic property of oxides (table 4.4) of the pumice which allows a better accessibility to fluoride and thus a better activity.

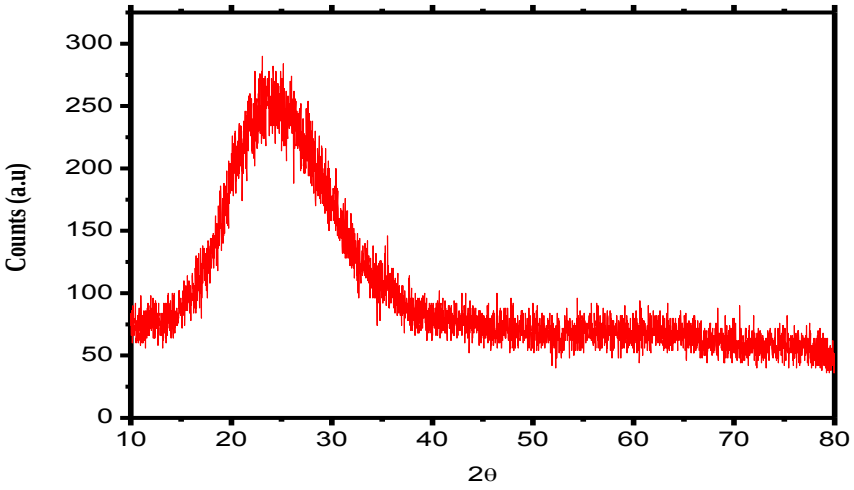



Figure 4. 8. XRD diffraction of pumice

4.6.1.2. Activated Carbon

As shown in table 4.6 and figure 4.9 EDX detects the presence of high percentage (wt. %) of carbon (C) and oxygen (O) in activated carbon prepared from coffee husk. The percentage (wt. %) of these two elements was investigated to be 98.44% while the other elements were found in a very small amount.

Table 4. 6. EDX analysis showing percentage abundance of elements in activated carbon

| Element | C | O | Na | Mg | Al | Si | P | S | K | Ca | Cu | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Weight % | 77.11 | 21.33 | 0.17 | 0.08 | 0.05 | 0.06 | 0.41 | 0.05 | 0.22 | 0.43 | 0.09 | 100 |
| Atomic % | 82.30 | 19.09 | 0.10 | 0.04 | 0.02 | 0.03 | 0.17 | 0.02 | 0.07 | 0.14 | 0.02 | |

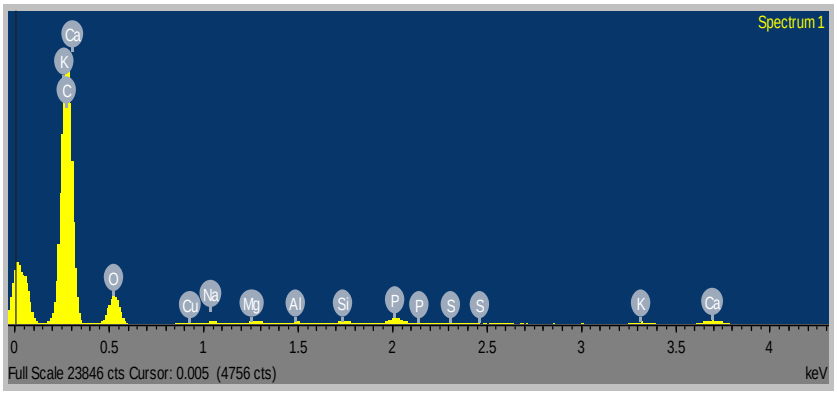
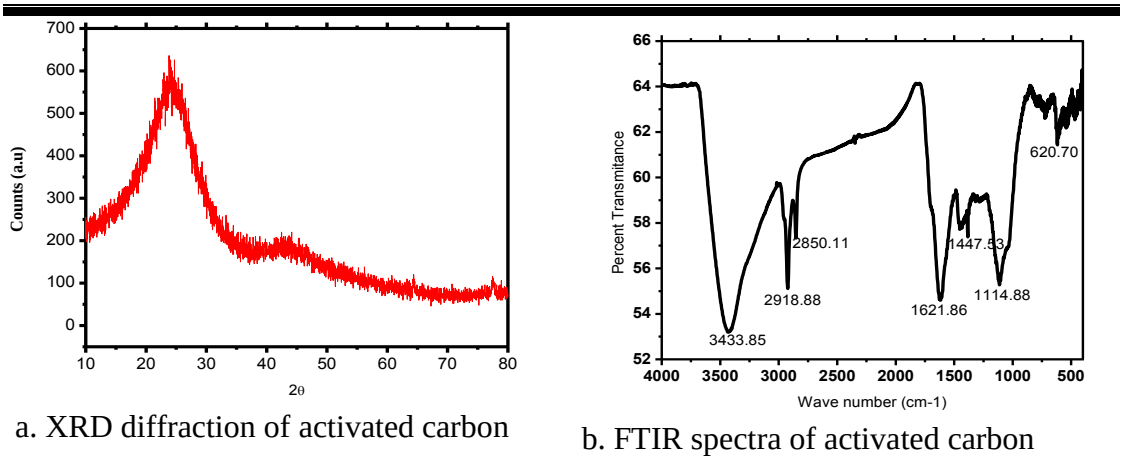



Figure 4. 9. EDX spectra showing the elemental composition of activated carbon

Figure 4.10a illustrates the XRD diffraction of activated carbon. This activated carbon exhibits very board diffraction peaks and the absence of sharp peak revealed a predominant amorphous structure. The two broad diffraction background corresponding to 2θ = 25$^{o}$ and 2θ = 43$^{o}$ in the spectrum showed in synthesized AC from coffee husk is in amorphous state with very low crystallinity (Shamsuddin et al., 2016).

The FTIR spectra of activated carbon prepared from coffee husk shown in figure has many characteristics peaks. The first peak was observed at 3433.85 cm$^{-1}$ indicates the presence of hydroxyl functional group associated to organic acid, alcohol or phenol. The bands between 2800 – 3000 cm$^{-1}$ denote aliphatic –CH stretching. The bands at 1621.21 cm$^{-1}$, 1447.53 cm$^{-1}$ and 1114.88 cm$^{-1}$ indicates carbonyl/carboxyl group, C-C stretched aromatic group and C-C vibrations respectively. The last peak observed at 620.70 cm$^{-1}$ is attributed to C=C functional group.




a. XRD diffraction of activated carbon

b. FTIR spectra of activated carbon

Figure 4. 10. XRD diffraction and FTIR spectra of activated carbon

The observation of samples by SEM (figure 4.11a and b) allowed to get an idea about the texture of the carbonaceous materials. It was observed that there is irregular variety of forms, some are granular, large cavity pores produced by aggressive attack of $H_3PO_4$ during activation and substantial removal of volatiles (Hong et al., 2012). Pore development in AC during pyrolysis was also important as this would enhance the surface area and pore volume by promoting $H_3PO_4$ molecules into the pores and thereby increasing $H_3PO_4^-$ carbon reaction, which would then create more pores.

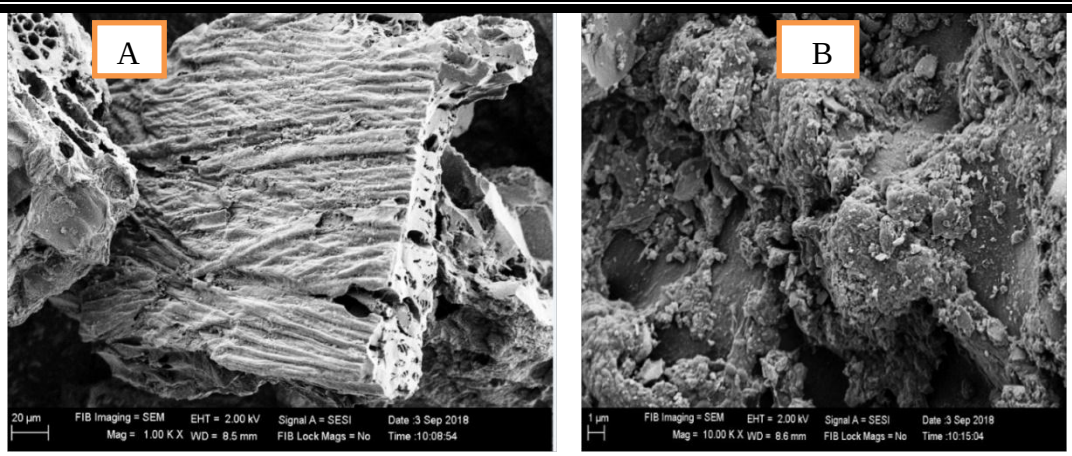



Figure 4. 11. SEM images of activated carbon prepared from coffee husk

4.6.1.3. Bone Char

EDX analysis of BC is reported in table 4.7 and figure 4.12 indicates that the adsorbent is mainly composed of calcium (Ca), oxygen (O) and phosphorous (P) where there is also minor component of carbon (C).

Table 4. 7. EDX analysis of showing percentage abundance of elements in bone char

| Element | C | O | P | Ca | Totals |
|---|---|---|---|---|---|
| Weight % | 2.93 | 15.15 | 11.19 | 70.73 | 100 |
| Atomic % | 7.35 | 28.56 | 10.89 | 53.20 | |

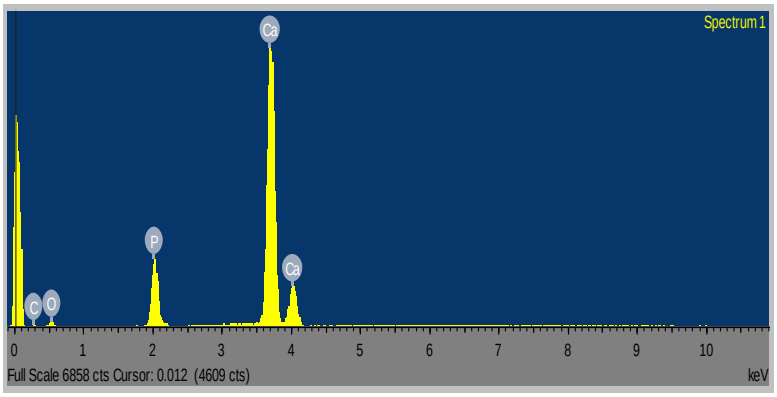
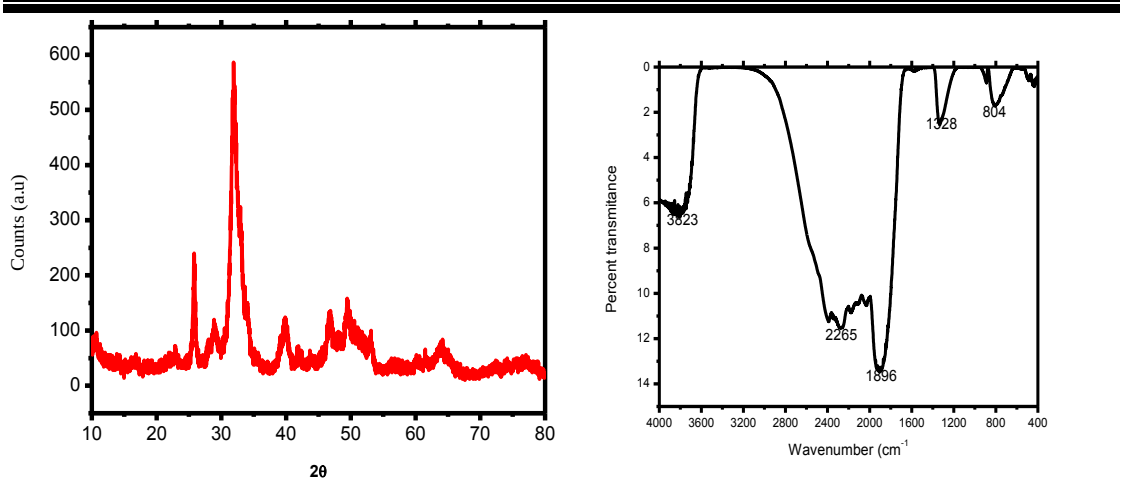



Figure 4. 12. EDX spectra showing the elemental composition of bone char

The XRD pattern of bone char is depicted in figure 4.13a. The crystalline species were identified comparing the characteristic peaks with the data base of the diffractometer. The characteristic peaks corroborated the presence of calcium phosphate hydrate ($Ca_3(PO_4)_2).xH_2O$, calcium phosphate hydroxide ($Ca_9HPO_4(PO_4)_5OH$), Calcium Phosphate Hydroxide/Apatite $Ca_5(PO_4)_3(OH)$ and calcium oxide (CaO).

The FTIR spectrum of bone char in figure 4.13b shows that the bands observed at 3623 $cm^{-1}$ is inner hydroxyl group $OH^-$ in bone char. The bands appearing at 2265 $cm^{-1}$, 1898 $cm^{-1}$ and 1328 $cm^{-1}$ are indicative of carbonates ($CO_3^{2-}$). The Band located at 804 $cm^{-1}$ is related with hydrogen phosphate ($HPO_4^{2-}$) or HAP with deficiency of calcium by decomposition and non-stoichiometric structure.




a. XRD diffraction of bone char

b. FTIR spectra of bone char

Figure 4. 13. XRD diffraction and FTIR spectra of bone char

The morphology of bone char particles observed in the SEM image shown (figure 4.14) are irregular, and the particle size distribution is not uniform moreover, the surface is porous.

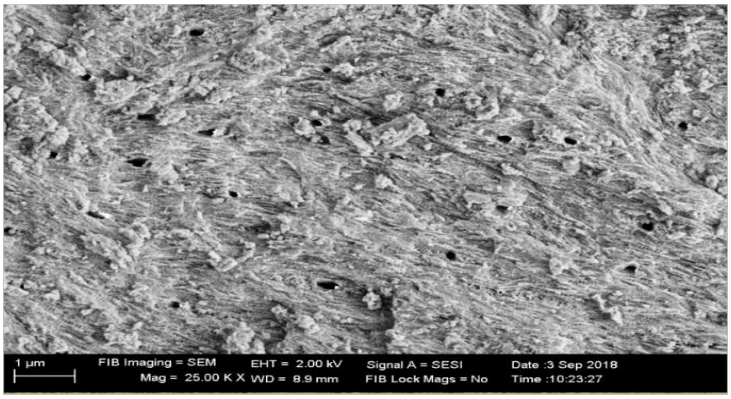



Figure 4. 14. SEM image of cow bone char

### 4.6.2. Characterization of the Composite ($C_1$-350)

The physico-chemical properties of $C_1$-350 composite was analysed and the results obtained were displayed in table 4.8. Basically the intension of the experiment was to determine the PZC and surface area of the composite. The surface area (109.8 $m^2/g$) and low moisture content (1.4%) was recorded which indicates the adsorbent is good.

Table 4. 8. Physico-chemical parameters of $C_1$-350 composite

| Properties | Value |
|---|---|
| Slurry pH | 8.8 |
| Point zero charge | 8.1 |
| Moisture Content (%) | 1.4 |
| Bulk density ($g/cm^3$) | 0.74 |
| Surface Area ($m^2/g$) | 109.8 |

Figure 4.15 shows the point zero charge (PZC) of $C_1$-350 composite determined by salt addition method. PZC of $C_1$-350 composite is 8.1 which implies that the surface of the material will have positive charge at a solution pH values less than the PZC (8.1) and thus be a surface on which it absorbs anions (anionic exchanger). On the other hand the material surface will have negative charges at a solution pH value greater than the PZC and thus be a surface which absorbs cations (cationic exchanger).

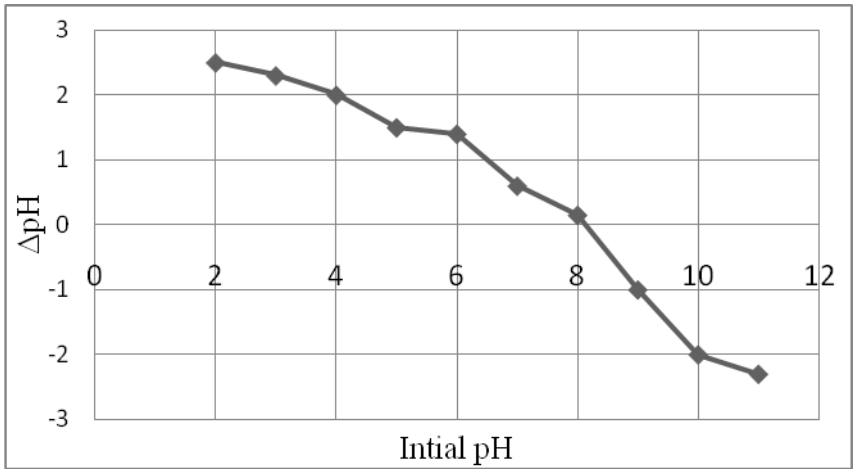



Figure 4. 15. Point zero charge of $C_1$-350 composite

The EDX analysis of $C_1$-350 composite in table 4.9 shows that the composite mainly consists of oxygen (O), carbon (C), calcium (Ca), Phosphorous (P) and silicon (Si). Oxygen (O) and silicon (Si) where major component of pumice, calcium (Ca) and Phosphorous (P) were from bone char while carbon (C) is derived from activated carbon.

Table 4. 9. EDX analysis showing percentage abundance of elements in $C_1$-350 composite

| Element | C | O | Na | Mg | Al | Si | P | S | K | Ca | Fe | Cu | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Weight % | 20.80 | 46.22 | 0.74 | 0.21 | 0.98 | 3.59 | 4.77 | 0.56 | 0.57 | 19.76 | 1.01 | 0.79 | 100 |
| Atomic % | 31.29 | 52.19 | 0.58 | 0.15 | 0.66 | 2.31 | 2.78 | 0.32 | 0.26 | 8.91 | 0.33 | 0.23 | |

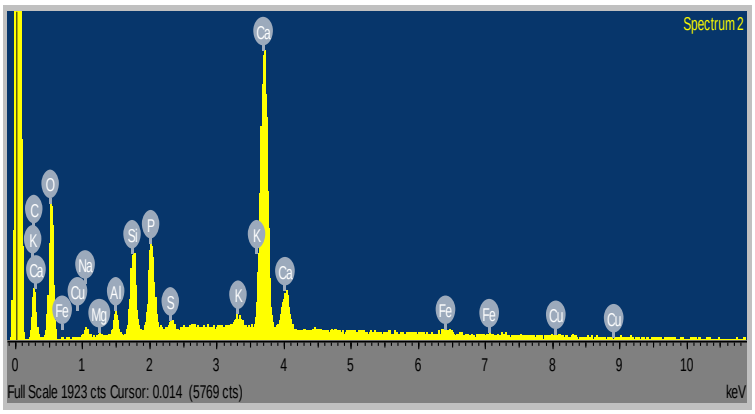
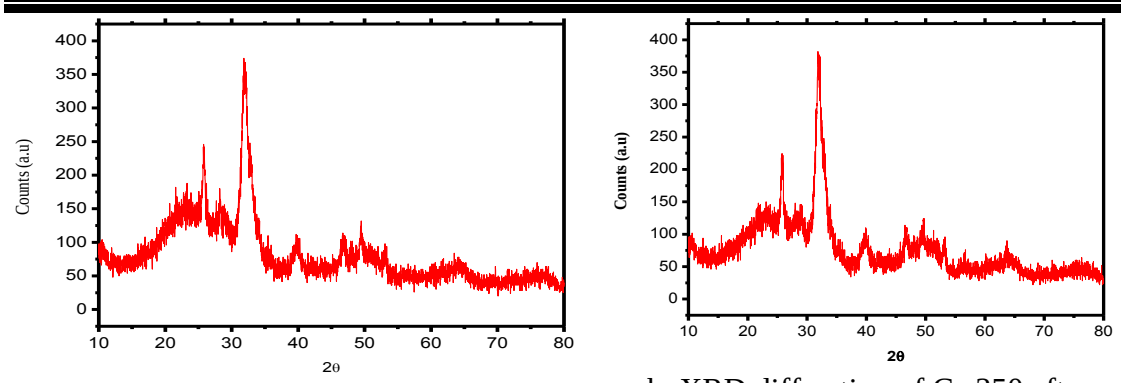



Figure 4. 16. EDX spectra showing the elemental composition of $C_1$-350 composite

The XRD diffraction of $C_1$-350 in Figure 4.17a and 4.17b shows multiple peaks. The peaks in figure 4.19 indicates the presence of calcium phosphate hydrate ($Ca_3(PO_4)_2$).x$H_2O$, calcium phosphate hydroxide ($Ca_9HPO_4(PO_4)_5OH$), Calcium Phosphate Hydroxide/Apatite $Ca_5(PO_4)_3(OH)$, hydrogen phosphate ($H_4P_2O_7$).The peaks in figure 4.17 shows the presence of calcium phosphate, calcium fluoride phosphate (fluoroapatiet$Ca_5(PO_4)_3F$)), phosphorous, calcium and all oxides observed in figure 4.17a. According to the figures the two X-ray diffraction patterns overlapped, showing that the crystal structure of $C_1$-350 before adsorption and after adsorption was similar because fluoride ion and hydroxide ion consists of the same charge and a similar size of radius (Brunson and Sabatini 2009).

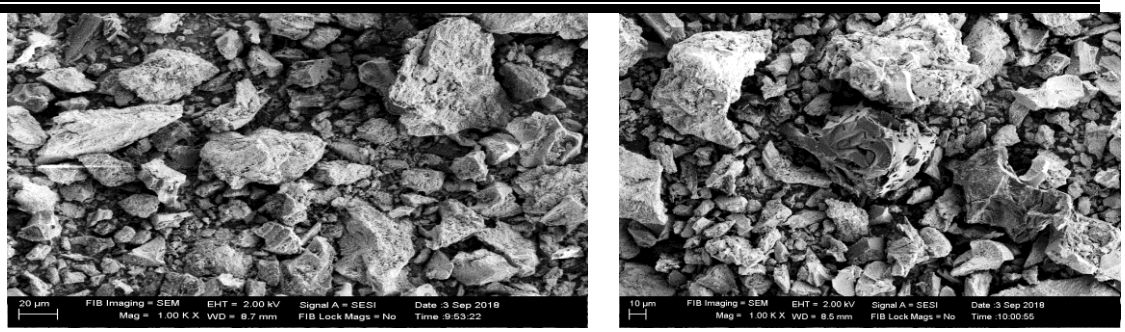



a. XRD diffraction of $C_1$-350 before adsorption

b. XRD diffraction of $C_1$-350 after adsorption

Figure 4. 17. XRD diffraction of $C_1$-350 before and after adsorption

As shown in figure 4.18a and 4.18b $C_1$-350 before and after adsorption of fluoride ion from water had the same non uniform particle distribution and heterogeneous surface which is an evident from the similar X-ray diffraction patterns.



a. SEM image of $C_1$-350 before adsorption

b. SEM image of $C_1$-350 after adsorption

Figure 4. 18. SEM image of $C_1$-350 before and after adsorption

### 4.7. Effect of $C_1$-350 Adsorbent on Water Quality

Different adsorbents have their own adverse effect on the quality of water mainly on color, pH, conductivity and turbidity. In real life the impurities in water increase its conductivity and turbidity. The current is carried out almost entirely by dissolved ions. The effect of the composite was analyzed in table 4.10 and Figure 4.19, the slight difference in conductivity and turbidity of water after treatment is due to dissolution of small fine particles from the composite and this effect can be reduce by washing the composite with fluoride free water before using. The increase in pH value is mainly because of the substitution of fluoride ion from water with hydroxide ion ($OH^-$). The parameters of the treated water using $C_1$-350 are still in WHO permissible range so the water can be directly used for drinking or washing without further color, conductivity and turbidity post treatment.

Table 4. 10. Water quality parameters before and after defluoloridation using $C_1$-350

| Property of Water | Before Treatment (fluoride water) | After Treatment (defluoridation) | WHO permissible limit |
|---|---|---|---|
| pH | 7.03 | 7.05 | 6.5-8.5 |
| Conductivity | 400 µs/cm | 425 µs/cm | ---- |
| Turbidity | 0.04 NTU | 0.05 NTU | <1 NTU |
| Taste | tasteless | tasteless | tasteless |
| Odor | none | none | none |

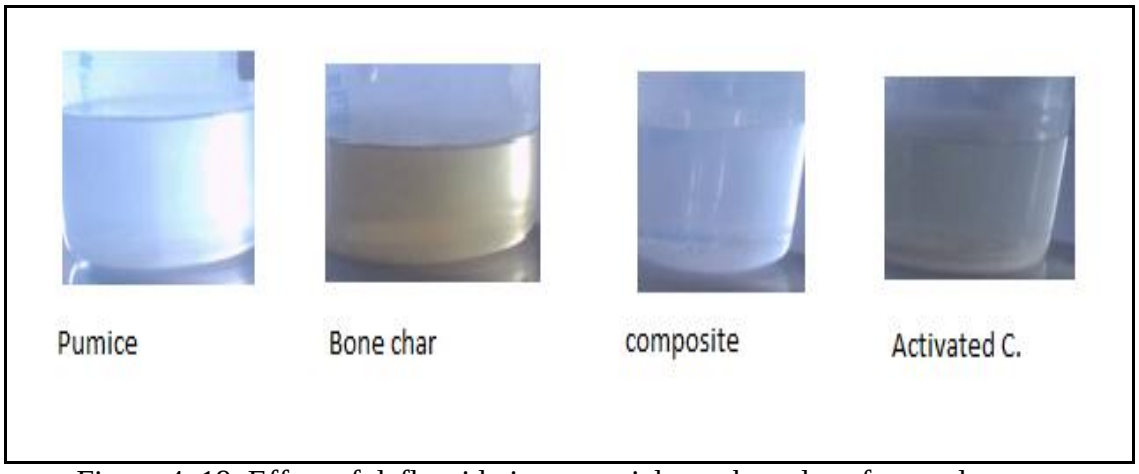



Figure 4. 19. Effect of deflouridation materials on the color of treated water

# CHAPTER FIVE

# 5. CONCLUSION AND RECOMMENDATION

## 5.1. Conclusion

The study shows that composite material developed from activated carbon, bone char and pumice (% mass 25:50:25 respectively) fired at 350℃ was found to have better fluoride removal efficiency both from laboratory fluorinated and real water pH range of drinking water. This material was not also found to bring change in pH, conductivity, turbidity and color of water significantly after treatment, thus taken as better fluoride adsorbent. The fluoride adsorption capacity of $C_1$ fired at 350℃ was comparable to those traditional and novel adsorbents. The composite is a porous material with a surface area of 109.8$m^2$/g. The concentration of the basic site is higher than that of the acidic site causing its PZC to be basic (8.1). Defluoridation of drinking water in batch absorber shows that fluoride can be effectively removed and the experiment can be used for large scale adsorption process.

## 5.2. Recommendations and Future Works

The composite was prepared from locally available cheap raw materials without high investment cost and it can be alternative defluoridation material for low economic living society in rural areas.

The research done was limited on three different mixing ratio of activated carbon, bone char and pumice taking four firing temperature ranges (350, 400, 450 and 500 ℃), if the composite is prepared using more alternative mixing ratio and firing temperature range, it may be found to be more capable adsorbent than done.

Developing re-geration method for the composite material should be also the main concern of the future study.

As such porous materials can trap microbes; packing the composite in a column and evaluating microbial removal test is recommended to be done.

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# APPENDICES

Appendices 1: Calibration of fluoride ion selective electrode

| [ ]$F^-$in mg/L | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|
| Reading in mv | -80.6 | -97.7 | -109.6 | -114.1 | -122.3 |
| Equation of calibration graph | Y = 58.62X+111.58 | | | | |

Appendices 2: Defluoridation of water using the prepared adsorbents (concentration of fluoride =13mg/l, PH 7, contact time 1h and adsorbent dose 2.5gram)

| S.NO | Sample code | Reading in mv | | $F^-$ concentration in mg/l | | Remark |
|---|---|---|---|---|---|---|
| | | Test 1 | Test 2 | Test 1 | Test 2 | |
| 1 | $C_1$350 | -31.7 | -40.4 | 0.51 | 0.72 | |
| 2 | $C_2$350 | -44.7 | -43.7 | 0.85 | 0.82 | |
| 3 | $C_3$350 | -53.4 | -52.8 | 1.2 | 1.17 | |
| 4 | $C_1$400 | -55.0 | -55.1 | 1.27 | 1.28 | |
| 5 | $C_2$400 | -55.1 | -56.4 | 1.28 | 1.35 | |
| 6 | $C_3$400 | -58.7 | -59.4 | 1.47 | 1.51 | |
| 7 | $C_1$450 | -60.2 | -59.7 | 1.56 | 1.53 | |
| 8 | $C_2$450 | -65.0 | -64.1 | 1.89 | 1.82 | |
| 9 | $C_3$450 | -74.5 | -72.9 | 2.74 | 2.57 | |
| 10 | $C_1$500 | -62.8 | -63.2 | 1.73 | 1.76 | |
| 11 | $C_2$500 | -66.2 | -65.1 | 1.98 | 1.9 | |
| 12 | $C_3$500 | -69.2 | -71.0 | 2.23 | 2.39 | |

Appendices 3: Effects of adsorbent dose, initial fluoride concentration, contact time and pH on the defluoradation efficiency of $C_1$ - 350

| S. NO | Sample code | Reading in mv | $F^-$ concentration mg/L | Remark |
|---|---|---|---|---|
| 1 | $Dose_{2.5}$ | -43.7 | 0.82 | |
| 2 | $Dose_5$ | -39.9 | 0.7 | |
| 3 | $Dose_{7.5}$ | -35.9 | 0.6 | |
| 4 | $Dose_{10}$ | 10.3 | 0.1 | |
| 5 | $[F-]_4$ | 4.4 | 0.12 | |
| 6 | $[F-]_7$ | -6.4 | 0.19 | |
| 7 | $[F-]_{10}$ | -17.4 | 0.29 | |
| 8 | $CT_3$ | -31.6 | 0.51 | |
| 9 | $CT_5$ | -8.4 | 0.2 | |
| 10 | $CT_7$ | -14.6 | 0.26 | |
| 11 | $PH_3$ | -15.5 | 0.27 | |
| 12 | $PH_5$ | -25.5 | 0.4 | |
| 13 | $PH_9$ | -32.2 | 0.52 | |

Appendices 4: Defluoradation of both synthetic ($F^-$ = 13mg/l and raw water ($F^-$ = 8.6mg/L) using PU, BC, AC and $C_1$-350 (composite) where S = synthetic water and R = raw water

| | Sample code | | | | | | |
|---|---|---|---|---|---|---|---|
| | P-S | P-R | B-S | B-R | AC-S | AC-R | $C_1$-350-R |
| Reading in mv | -101 | -111 | -20.3 | -57.4 | -89.1 | -81.1 | -26.4 |
| [ ]$F^-$in mg/L | 7.77 | 11.5 | 0.33 | 1.4 | 4.87 | 3.55 | 0.41 |