JIMMA UNIVERSITY
JIMMA INSTITUTE OF TECHNOLOGY
FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING
ENVIRONMENTAL ENGINEERING CHAIR

SORPTIVE REMOVAL OF FLUORIDE FROM WATER USING ACTIVATED SUGARCANE BAGASSE (BIOCHAR)

BY TEWODROS MANYAZEWAL

A THESIS SUBMITTED TO JIMMA UNIVERSITY, JIMMA INSTITUTE OF TECHNOLOGY, FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING, ENVIRONMENTAL ENGINEERING CHAIR IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENVIRONMETAL ENGINEERING

OCTOBER, 2017
JIMMA, ETHIOPIA

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Main advisor: Prof., Dr. Ing ESAYAS ALEMAYEHU
Co-advisor: Mr. MENBERU YITBAREK (MSc, PhD Fellow)

OCTOBER, 2017
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DECLARATION

I, Tewodros Manyazewal, hereby declare that the thesis, entitled "*Sorption removal of fluoride from water using activated sugarcane bagasse (Biochar)*", is entirely my original work done for the award of MSc. degree in Environmental Engineering. To the best of my knowledge, the work has not been presented for the award of MSc. degree or any other degree either in Jimma University or any other Universities. Thorough acknowledgment has been given where reference has been made to the work of others.

Tewodros Manyazewal

__________________________ _______________________ _____________________

Name (Researcher) Signature Date

This Thesis has been submitted for examination with my approval as University supervisor.

Esayas Alemayehu (Prof. PhD, Ing.)

________________________________ ___________________________ ______________

Name (Main advisor) Signature Date

The Thesis has been submitted for examination with my approval as University co-supervisor.

Menberu Yitbarek (PhD fellow)

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Name (Co-supervisor) Signature Date

As chair Holder of Environmental Engineering I approved the submission of the Thesis for examination

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Name (Chair Holder) Signature Date

ABSTRACT

Drinking water contaminated by fluoride is recognized as a major public health problem in many parts of the world. Thus, the aim of this study was to investigate fluoride (F^-) adsorption onto activated sugarcane bagasse and investigated in a batch system by considering the effects of various parameters like contact time, initial concentration, pH, agitation speed and absorbent dose. The result of the study showed that the optimum contact time for adsorption of F^- on activated sugarcane bagasse reached to equilibrium at 60 min, at optimum adsorbent dose of 15 g/L, optimum pH ~5, equilibrium initial concentration of 5 mg/L, and shaking speed of 200 rpm. The sorption kinetics was found to follow pseudo-second-order model with $R^2 = 0.993$ rate and the experimental equilibrium sorption data fitted well to Freundlich isotherm model with $R^2 = 0.983$. The efficiencies of the activated sugarcane bagasse towards the removal of fluoride from real sample were also examined and the fluoride content of groundwater sample were reduced from 16.75 mg/L to 8.95 mg/L without the pH adjustment. When the pH of the groundwater sample readjusted to optimum pH 5 the fluoride concentration was reduced from the original 16.75 mg/L to 5.62 mg/L. The study concludes application of activated sugarcane bagasse for the synthesis of an effective and low-cost adsorbent for water defluoridation. Enough attention should be given to defluoridation of water using locally available bisorbents.

Key words: Activated Sugarcane Bagasse, Defluoridation, Kinetics, Isotherm and Sugarcane Bagasse

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

F^-	Fluoride
ASB	Activated Sugarcane Bagasse
RADWQ	Rapid Assessment of Drinking Water Quality in the Federal Democratic Republic of Ethiopia
SB	Sugarcane Bagasse
JMP	Joint Monitoring Program
MOWR	Ministry of Water Resource
TISAB	Total Ionic Strength Adjustment Buffer
WHO	World Health Organization
FISE	Fluoride Ion Selective Electrode

CHAPTER ONE

INTRODUCTION

1.1. Back ground of the study

Fluoride is one of the very few chemicals that has been shown to causes significant effects on people through drinking water. Fluoride has beneficial effects on teeth at low concentrations in drinking water, but excessive exposure to fluoride in drinking water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects (WHO, 2004).

Around the world, millions of people are exposed to high levels of fluoride in drinking water (Amini, *et al.*, 2008). Even though the microbial quality of groundwater is generally better than surface water, chemical contaminants, such as fluoride, can pose an additional health risk. Aquifer rocks can release fluoride into the groundwater in concentrations above the WHO guideline of 1.5 mg/L (Tekle-Haimanot, 2005).

It has led to endemic fluorosis, which has become a major geo-environmental health issue in many developing countries. According to a recent estimate, 62 million people are affected by various degrees of fluorosis in India alone. Water with high fluoride content is generally soft, has high pH and contains large amount of silica. That is why in many cases, the water sources have been rendered unsafe not only for human consumption but also for other activities such as irrigation and industrial needs (Susheela, 2001).

The most well-known and documented area associated with volcanic activity follows the East African Rift system from the Jordan valley down through Sudan, Ethiopia, Uganda, Kenya and the United Republic of Tanzania which are prone to higher concentration of fluoride in water (Nair *et al.*, 1984).

The intake of high fluoride doses, mostly through drinking and cooking water, over a longer time can cause dental and skeletal fluorosis. It is estimated that in the Ethiopian Rift Valley alone 8.5 million people are at risk of developing dental or skeletal fluorosis (Tekle-Haimanot, 2005).

The numerous methods for defluoridation can be grouped in physical and chemical categories. Frequent chemical methods based on the principle of precipitation, adsorption, ion exchange, electrochemical and membrane process have been described for the fluoride removal (Chhabra, 1997).

Adsorption technology is an efficient method for fluoride removal from water and has been widely studied. Recent research work has been devoted to develop low cost adsorbents to enhance the cost effectiveness for defluoridation Fluoride adsorption efficiency of bio-sorbents usually depends of type of multifunctional group and modification that has been conducted with aim to increase adsorption capacity. Most of the tested bio-sorbents showed good results in bench scale studies but only some of them were tested with real water samples (Ma *et al.,* 2007).

1.2. Statement of the problem

Pure water is scarce and is not easily available to all. The water may be contaminated by natural sources or by industrial effluents. One of such contaminant is fluoride (Malay and Salim, 2011).

Fluoride if taken in small amount is usually beneficial, but the beneficial fluoride concentration range for human health is very small. Long-term consumption of water containing excessive fluoride may cause dental and skeletal disorders (Gonzales *et al.,* 2004 & Solangi *et al,* 2009).

In some of the cases it may even interfere with carbohydrates, proteins, vitamins and mineral metabolism and DNA formation as well if intake excessively (Zhou, 2004).

Exposure to fluoride in drinking water has a number of adverse effects on human health including crippling skeletal fluorosis that is a significant cause of morbidity in a number of regions of the world. Fluoride is more toxic than lead, and just like lead, even in minute doses, accumulates in and is damaging to brain/mind development of children, i.e. produces abnormal behavior in animals and reduces IQ in humans (Parlikar, and Mokashi, 2013).

Further, osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder can attack human body on excessive intake of fluoride. Fluoride contamination in ground water is a worldwide issue. Excessive presence of fluoride in potable water continues to be a serious public health concern in many parts of the world, including Ethiopia (MOWR, 2008).

Treatment of water and wastewater containing fluoride ions requires a suitable and effective method. Membrane filtration**,** precipitation, nano-filtration, ion exchange, electro coagulation, flotation, reverse osmosis and adsorption have been used for fluoride removal. Most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment (Koteswara and Mallikarjun, 2014).

1.3. Objectives

1.3.1. General Objective

The main objective of this study was to investigate the capacity and efficiency of activated sugarcane bagasse (Biochar) for fluoride removal from water under batch experimental setup.

1.3.2. Specific Objectives

- To evaluate fluoride removal efficiency of activated sugarcane bagasse using both aqueous solution and natural water samples under batch adsorption setup
- To determine optimum conditions (contact time, pH, shaking speed, and dose) of activated sugarcane bagasse
- To determine the adsorption isotherm and kinetics that best fit to describe the relationship between solution fluoride and adsorbed fluoride

1.4. Research questions

Based on the objective of the study, the following research questions can be addressed.

- What is the adsorptive removal efficiency of F^- using ASB?
- What are the major factors that influence the adsorptive removal efficiency of F^- using ASB?
- Which adsorption isotherm and kinetics best fits with experimental data?

1.5. Significance of study

Defluoridation of drinking water is the only practicable option to overcome the problem of excessive fluoride in drinking water. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations (Koteswara and Mallikarjun, 2014).

Develop appropriate technology which is suitable and effective for the treatment of water with fluoride ions. This study also gives a great advantage for developing countries those that have low income and cannot access high technology for their drinking water treatment. It will initiate them to use locally available material with low cost for effective removal of fluoride (F^-) to meet internationally acceptable guidelines for water.

Since our country Ethiopia is one of low-income Sub-Saharan country with accelerated economic growth and industrial establishments but difficulty of advanced water treatment, this research will give a key to use locally available material for water treatment. Specially, for countries with number of sugar factories and where sugarcane bagasse is abundantly found. In addition, it will give good information to use as one of Fluoride removal technology and can be used as a secondary source of information for further study.

CHAPTER TWO

LITERATURE REVIEW

2.1. General description

Scientists estimate groundwater accounts for more than 95% of all fresh water available for use. Nearly 95% of rural residents rely on groundwater for their drinking supply. Groundwater can be contaminated in many ways. If surface water that recharges the aquifer is contaminated, the groundwater will also become contaminated. This can, in turn, affect the quality of surface water at discharge areas. Groundwater can also be contaminated by liquid hazardous substances (or solids that can dissolve in water) that filter through the soil into groundwater, by salt water moving in from the ocean, or by minerals that are naturally present in the area. (Hengsdijk & Jansen, 2006).

Fluoride is a naturally occurring mineral found in soil, air, plants, animals and water supplies. Individuals are exposed to small amounts of fluoride by breathing air, drinking water, and eating food (Dace *et al.,* 2002). In particular, fluorides are frequently added to drinking water supplies and to dental products such as toothpaste, mouth rinses and professionally applied fluorides to prevent dental decay. Fluoride is considered a beneficial nutrient based on its proven effects on dental health (Khichar and Kumbhat, 2015). Depending on the amount and type of clay content, soil pH, soil OM content, reaction time, exchangeable Al^{3+}, soil redox condition characteristics soil can influence ground water concentration of fluoride (Sanchez and Uehara, 1980).

Fluoride pollution in the water environment occurs through two different channels which are natural and anthropogenic sources. Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into subsoil water sources by the slow natural degradation of fluorine contained in rocks. Fluorine and its compounds are very valuable and extensively used in industry. While some fluoride in water is good for people, consuming too much fluoride causes a condition called fluorosis. Fluorosis negatively affects human health, particularly the teeth and bone. Children under eight whose teeth are still forming under their gums are particularly susceptible to having dental problems, and prolonged consumption of water with too much fluoride can lead to abnormal bone fragility (Chen *et al.,* 2010).

Toxicity of hazardous ions, such as fluoride, is of interest for public health (Tomar and Kumar, 2013). It is the strongest electronegative elements & in gaseous form is a very powerful oxidizing agent. The natural abundance of fluoride ranges from 0.065 % to 0.09 % by weight in the earth's crust and it exists naturally as fluoride ion (F^-) which is extremely reactive (Sivasankar *et al.,* 2014). Geological sources are among the main that contaminates human drinking water by fluoride (Ayoob and Gupta, 2006). Skeletal fluorosis was first reported in Ethiopia in 1973 in the Wonji-Shoa sugar estates in the Ethiopian Rift Valley (Lester, 1974).

Although the major cause of fluorosis is the elevated level of fluoride in drinking water, temperature, nutrition and health status, and deficiency of calcium and vitamins have been found to be important contributory risk factors for developing skeletal and dental fluorosis (Tekle-Haimanot, 2005). Consuming milk on a daily basis, and breastfeeding in the early phase of dental formation led to a less severe form of dental fluorosis. They also found that the severity of dental fluorosis increased with age, probably due to the increasing exposure to excessive F^- in water and food (Kravchenko *et al.*, 2014).

Almost all parts of the world have reported high concentration of fluoride in drinking water. North America, Africa and Asia are the mostly affected continents of the world. Countries like India, Srilanka and China have reported high concentrations of fluoride. Rift valley countries in Africa have reported high concentrations of fluoride due to the weathering of alkaline volcanic rocks. In the World, 1.1 billion people did not access to water sources or systems with a higher likelihood that the water is not polluted (WHO, 2007). Due to fluoride pollutions and health problems that it causes World Health Organization (WHO) specified the acceptable limit of fluoride in drinking water not to exceed 1.5 mg/L (WHO, 2004). According to UNESCO more than 200 million people worldwide rely on drinking water with F^- concentrations exceeding the present World Health Organization guideline (Feenstra and Griffioen, 2007).

Ethiopia is one of the 23 countries in the world, where a significant number of its population suffers from the toxic effects of high levels of fluoride in drinking water. The toxic effect of excess amount of fluoride in the drinking water of several towns in the Ethiopian Rift Valley has been in evidence since the 1970s. This was due to the fact that the people in these areas were accustomed to drinking water that contains as much as 33 mg/L (Hassen, 2007).

The access to drinking water and sanitation in Ethiopia is the lowest in the world. Nearly 50 million people lack access to safe water while 56 million lack access to sanitation according to the Ethiopian water sector report in 2008. In 2008 only, 38 percent of population; that is 98% of urban and 26% of rural population have improved water coverage (JMP, 2010). According to The Ethiopian Ministry of Water Resource, the total water coverage of the country in 2008 is only 53% and they are planned to increase the potable water and, sanitation coverage in rural country to 98% by 2012 (MOWR, 2010).

In Ethiopia, well water, spring water, and Tap water are the common water supply source used in both urban and rural areas (Gebrekidan & Samuel, 2011). The amount of fluoride present naturally in non-fluoridated drinking water is highly variable, being dependent upon the individual geological environment from which the water is obtained (Facts, 2007). However, water is epidemiologically most essential sources of fluoride in most areas, considerable exposure risk is also associated with the consumption of fish bones, canned meat, vegetables, grains and other staples, local salt, drinks (especially tea) and air (WHO, 2004)

Fluoride is one of the most important chemicals to affect the quality of drinking water. In the Rift Valley region of Ethiopia, the problem of high fluoride concentrations in natural waters, especially groundwater, is severe and widespread (Samson, 2004).

Fluoride content of drinking water poses a major public health problem, particularly in the Rift Valley of Ethiopia, a fact confirmed by the RADWQ project findings. The main areas affected by excessive fluoride concentrations in drinking water were the East Shewa Zone (maximum average fluoride concentrations of 10.5 mg/l) and some areas in the Somali Region (Tadesse, *et al.,* 2010).

The high fluoride concentrations are primarily associated with:

- ✓ Volcanic and fumarole activity, which adds fluoride to the ground waters
- ✓ Water interacting with fluoride-bearing volcanic and sedimentary rocks, such as pumice, ignimbrite, obsidian and rhyolite and,

- ✓ Low calcium concentrations, which restrict the precipitation of fluoride as fluorite (CaF_2).

In addition to the Rift Valley region, groundwater resources in a few isolated pockets in Oromiya were shown to contain significant fluoride concentrations. In some areas of the Somali region (e.g. Deghabur, Kebri Dehar, Jerer Valley, Hargele and Warder), historical water-quality data indicate that fluoride concentrations in groundwater resources are well above the WHO guideline value or the national standard. The cause is believed to be of geological origin (FMOWR, 2000; 2001).

In Oromiya, fluoride concentrations exceeded the WHO guideline value and the national standard at almost all the water supplies in the East Shewa Zone, which is located in the main Rift Valley system of Ethiopia. The RADWQ results are consistent with historical national water quality data and with numerous study findings and all agree that fluoride levels pose a major water quality problem in the Zone (Tamiru, 2000 and Berhanu, 2004).

Fluoride content in water depends on not only the geochemical background, climate and biological factors such as hydrological condition, landform, rainfall, and evaporation, but also on the adsorption and leaching of fluoride in soil. The adsorption-leaching process directly affects fluoride migration and exchange from soil to water. Studies on adsorption or desorption of fluoride have shown that the nature of soil or rock relates to the release of fluoride from soils and rocks (Totsche, *et al,* 2000).

A number of defluoridation techniques have been developed. Among them reverse osmosis (RO), is one of the well-known techniques applied for removal of F^- (Ndiaye *et al.*, 2005). However, RO has serious drawback for its high operational and maintenance cost. Application of Solar distillation for defluoridation demonstrated approximately 97% fluoride removal (Antwi, *et al.*, 2011). But the method doesn’t produce large volume of potable water, which is its drawback on the other hand Nano-filtration have remarkable suitability for defluoridation of water. However, the use of inorganic components, such as CaCO3, as filter membrane produces a smell in the water. In addition, this method requires a huge maintenance cost (Fang *et al.*, 2009). Application of precipitation and coagulation method for defluoridation of water has also been investigated (Haung and Liu, 1999). However, shortcoming of most of these methods are high operational and maintenance cost, secondary pollution (generation of toxic sludge, etc.) and complicated procedure involved in the treatment (Bibi, *et al.*, 2015). In comparison with the above-mentioned techniques for defluoridation of water, adsorption is a simple, low cost and easily applicable method (Kumar *et al.*, 2009).

In developing countries, the logistical challenges and the high cost associated with defluoridation technology, including the cost of power supply, chemicals, regeneration, and consumables can be a constraint to the implementation and sustainability of schemes. In addition, local issues including acceptance of the technology by the community may result in rejection or incorrect usage of the scheme (Huber and Mosler, 2013).

2.2. Fluoride removal by adsorption

Adsorption is the bond of molecule species from bulk solution with a surface of a solid by physical or chemical forces. Depending on the nature of the interactions, ionic species and molecular species carrying different functional groups may be held to the surface through electrostatic attraction to sites of opposite charge at the surface or physiosorbed due to action of van der Waals forces or chemisorbed involving strong solute and adsorbent bonding. So, it may lead to attachment of solute molecules at specific functional group on adsorbent surface (Sivarajasekar and Baskar, 2014).

Adsorption has shown considerable potential in defluoridation of water and wastewater because; it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations (Das, 2005). Several adsorbent materials have been tried in the past to find out an efficient and economical defluoridating agent. The viability of such technique is greatly dependent on the development of suitable adsorptive materials. Hence, the use of an alternative and cheaper local building material to substitute the ones being traditionally used may facilitate solving the problems relating to water treatment (Koteswara and Mallikarjun, 2014).

A number of agricultural and forest wastes/by-products and industrial waste products have been proposed by a number of researchers for the fluoride removal from aqueous wastewater. These low-cost adsorbents are abundant in nature, inexpensive, require little processing, and are effective for fluoride removal (Tomar and Kumar, 2013). Activated carbon/charcoal is one of the most widely used adsorbents for the removal of fluoride ions from aqueous solutions. The adsorption capacity of activated carbon depends on various factors, such as surface area, pore size distribution, surface functional groups on the adsorbent, polarity, solubility and molecular size of the adsorbate, solution pH and the presence of other ions in solution (Sivarajasekar and Baskar, 2014).

Proponents of adsorption technology argue that the technique is economically efficient and produces high quality water. The removal of fluoride by adsorption methods has been widely studied in recent years and interest is growing in the use of high-valency metals to functionalized sorbents (Onyango *et al.,* 2004).

Adsorption of fluoride on to solid adsorbent usually occurs through three phases (Mohapatra *et al.,* 2009).

1. 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;
2. Adsorption of fluoride ions on to particle surfaces
3. 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).

Adsorption depends on ions (adsorbate) in fluid diffusing to the surface of a solid (adsorbent), where they bond with the solid surface or are held there by weak intermolecular forces (Li *et al,* 2011). Adsorption studies pointed most important characteristics which determined adsorbent suitability for practical application: adsorption capacity, selectivity for fluoride ions, regenerability, compatibility, particle and pore size, and cost while fluoride removal efficiency always depends on raw water quality profile, *i.e.,* initial fluoride concentration, pH, temperature, contact time and adsorbent dosage (Bhatnagar *et al.,* 2011)

However, with fluoride concentration decreasing, a lot of adsorbents lose the fluoride removal capacity, the lowest limit for fluoride reduction by most of the adsorbents is 2 mg/L. Therefore, they are not suitable for drinking water, especially as some of them can only work at an extreme pH value, such as activated carbon, which is only effective for fluoride removal at pH < 3.0 (Li *et al.*, 2001).

2.3. General descriptions of sugarcane bagasse

Sugarcane bagasse is an agro-industrial waste by-product that is left in the sugar manufacturing process after extraction of sugar juice from crushed sugarcane. Sugarcane is the most harvested crop in the world. As consequence, its residual bagasse is the most abundant agricultural waste. The sugarcane bagasse is the solid and fibrous fraction which remains from usual milling of sugarcane (Santos, 2016).

Basic characteristic features of the residues which are important for analysis and designing a biomass conversion unit includes proximate analysis used for calculation of chemical composition of the residue including (ash content, moisture content, volatile matter & fixed carbon), Ultimate analysis or elemental compositions (carbon, hydrogen, oxygen, sulphur, calcium, nitrogen etc.) & heating value determination. Proper evaluation of these properties consequently enhances the overall plant efficiency. The detailed analysis of the characteristics also needs to be carried out for exploring their future potential (Shukla, 1997).

Bagasse, the fibrous residue of the cane stalk after crushing and extraction of the juice, consists of water, fibers and relatively small quantities of soluble solids. Its composition varies according to the variety of cane, its maturity, the method of harvesting, and finally the efficiency of the milling plant and average estimate comprises moisture 46-52 %, Fiber 43-52 %, Soluble solids (mostly sugar) 2-6 % (Bon, 2007).

Bagasse contains mainly cellulose, hemi-cellulose, pentosanes, lignin, sugars, wax and minerals. Sugar cane bagasse is composed of fibers, module, fine particles and soluble materials, the natural bagasse chemically composed of 44.5 % of lignocellulosic fibers; 50 % of moisture; 2.5 % of soluble solids in water and 3.0 % of ash (Santana and Teixeira, 1993).

CHAPTER THREE

MATERIALS AND METHODS

3.1. Study area and study period

The study was conducted at Environmental Health Science and Technology laboratory, Jimma University, South West of Ethiopia from December, 2016 to July, 2017.

3.2. Study design

Laboratory based experimental study was used to investigate the objectives of the study.

3.3. Chemicals

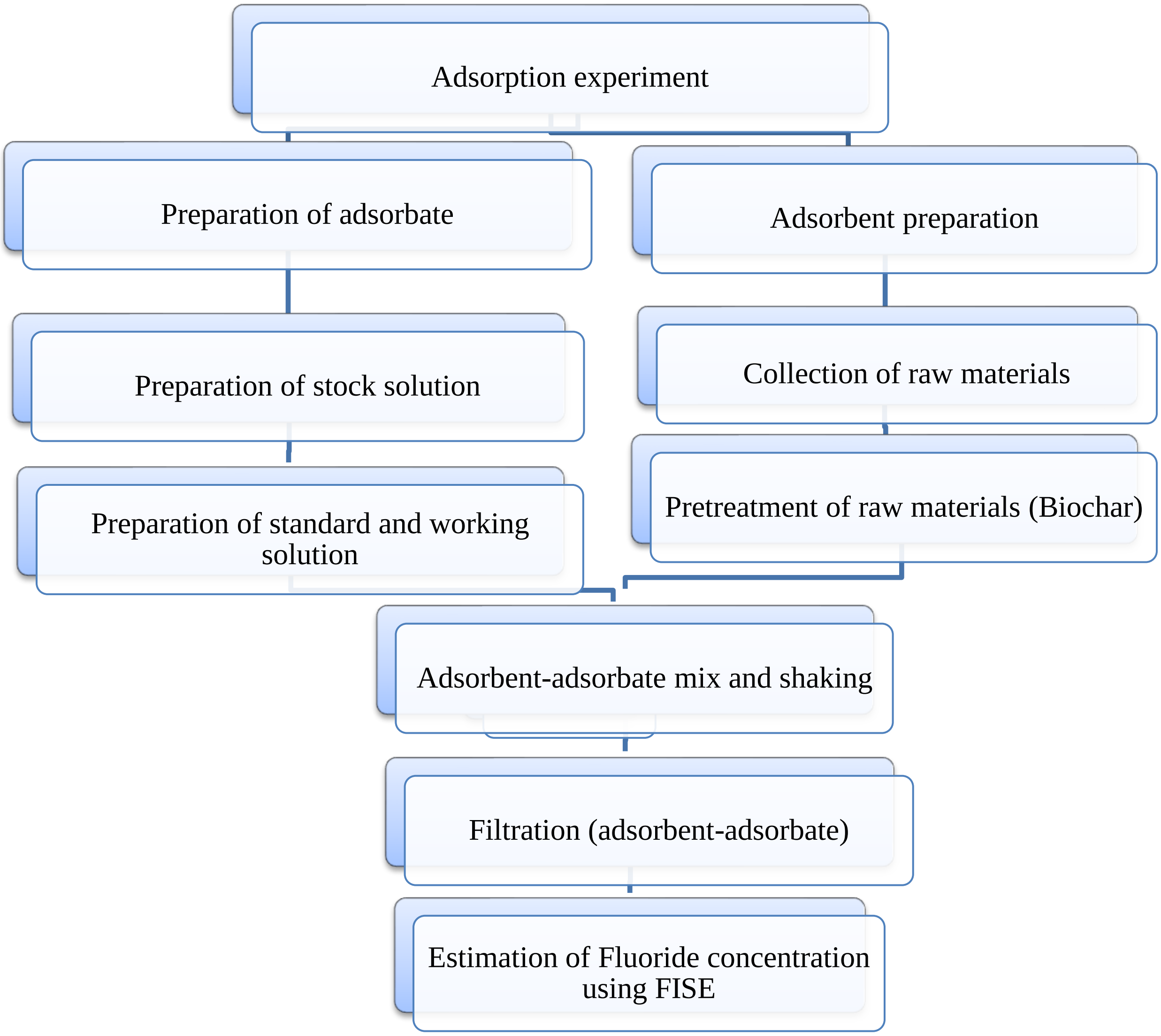
All chemicals used in this study were analytical reagent grade and were used without further purification. The chemicals used for this study were: NaF, NaOH, EDTA, NaCl, HCl (37 %, Riedel-deHaën, Germany), CH_3COOH (glacial, 99.99%, Riedel-deHaën, Germany).

3.4. Instruments

Analytical balance (Model BP110S), pH meter (Model EN 16-102, WAGTECH), Fluoride Ion Selective Electrode (METTLER TOLEDO) with a detection limit of 0.02 mg/L, Magnetic stirrer (Model HI 300N, HANNA), Vacuum gas pump (Model VWR Electric vacuum pump), Suction filtration setup, Oven (GP/150/CLAD/F/VIS/SD/100/DG, WAGTECH), Furnace (model MR 260 E) and Horizontal shaker (Edmund Buhler GmbH, SM – 30 A model) were used.

3.5. Methods

Adsorption experiment flow chart



3.5.1. Preparation of stock and standard solutions

A stock solution of fluoride with a concentration of 1000 mg/L was prepared by 2.21 g of sodium fluoride (NaF) measured on analytical balance and dissolved in to 1000 mL distilled water. The stock solution of fluoride was further diluted in a serial dilution system with distilled water as required (i.e., 100, 10, 1, 0.1, 0.01 mg/L) for the calibration of the ion selective fluoride electrode (i.e. detection limit of 0.02 mg/L) to be used for sample reading. In addition, working solution of different fluoride concentration were prepared from the stock solution as required for adjustment of initial concentration.

3.5.2. Preparation of untreated and treated sugarcane bagasse

Sugarcane bagasse obtained from Metahara Sugar Factory, Oromia Reginal State, Ethiopia were washed repeatedly with distilled water to remove any water-soluble deposits and dried at room temperature. Then crushed and sieved to an average particle size 0.3 mm (300 microns) which is in between 0.075 and 0.425 mm. Particle size analysis of the sample was performed in to different particle size which is silt (< 0.075 mm), fine (0.075 – 0.425), medium (0.425 – 2.0 mm), and coarse (> 4.75) based on the soil textural classification system (ASTM D 422). The powdered sugarcane bagasse passing through 0.3 mm sieve were collected and subjected to chemical treatment followed by pyrolysis. The activation was carried out by impregnation of the sugarcane bagasse sample with phosphoric acid in a ratio of 1:1 (w/w) for 24h. After that, the impregnated sample were dried at 106^{o}C then pyrolyzed in a muffle furnace in absence of air at 500^{o}C for 1h to produce the biochar. After pyrolysis, the resulting samples were washed with distilled water several times until the washing solution pH reached 6.5-7 (Alagumuthu *et al.*, 2010). Then the activated samples were dried at 106^{o}C and packed in an airtight plastic bottle for later investigation.

3.5.3. Determination of fluoride by FISE

Fluoride stock solution of NaF containing 1000 mg/L solution was further diluted with distilled water as required (i.e. 100, 10, 1, 0.1, 0.01 mg/L) for the calibration of the ion selective fluoride electrode to be used for sample reading. After calibration of the fluoride ion selective electrode it was used to determine the fluoride concentrations of the filtered water sample. The samples and fluoride standard solutions were diluted 1:1 with the TISAB. The solutions, which contained 25 mL of the sample and 25 mL of TISAB solutions, were mixed with a magnetic stirrer for about 2-3 min. The electrode potentials of the sample solutions directly compared with those of fluoride standard solutions in milligram per liter (Serife *et al.*, 2003).

3.5.4. Determination of adsorption efficiency

The adsorption efficiency studies were carried out after adjusting the pH values before adding a measured mass of the adsorbent of interest into 50 mL of the fluoride solution and shaken in horizontal shaker at the speed of 200 rpm. Depending on the parameters under study, the pH, adsorbent dose, initial fluoride ion concentration, contact time was varied to study the adsorption efficiencies. Known concentration of fluoride and desire amount of ASB were mixed in 50 mL solution in plastic bottles and all-important parameters were considered before separation of the clear supernatant solution from the adsorbent by using Whatman filter paper (0.45 µm). Then the concentrations of samples were determined by using fluoride ion selective electrode (Mettler Toledo model) with a detection limit as low as 0.02 mg/L. Throughout the study particle size of < 0.3 mm, 10 mg/L fluoride concentration (except in the study of the effect of initial fluoride concentration), 2 g/L of ASB (except in the investigation of the effect of adsorbent dose), solution pH ~ 3 (except in the study of the effect of solution pH), 60 min (except in the study of the effect of contact time) and 200 rpm (except in the study of the effect of agitation speed) in 50 mL solution were used for optimization of the first parameter and the optimized values were used for the optimization of the succeeding parameters.

Analytical grade chemicals and reagents were used throughout the study. All glassware and sample bottles were washed with tap water and rinsed three times with distilled water. Then plastic bottles were filled with distilled water over night before conducting the next parameter to minimize contamination (Maduakor *et al.*, 1995). All experiments were conducted in duplicate and the average values were used for data analysis. The pH of solution was adjusted using 0.1 M NaOH and/or 0.1 M HCl. The supernatant solution samples were then filtered with 0.45µm filter paper for the analysis of residual fluoride. Then the amount of fluoride ion adsorbed at equilibrium, q_e (mg g^{-1}) and at time t (min), q_t (mg g^{-1}), and the adsorption efficiency (%), were calculated according to the equations (Eqs. 1 and 2), respectively given below (Meenakshi *et al.*, 2008).

$$q_t = \frac{(C_0 - C_t)}{m} * V \qquad (1)$$

$$A\ (\%) = \frac{(C_0 - C_t)}{C_0} * 100 \tag{2}$$

Where C_0 (milligrams per liter) is the initial concentration of fluoride in the solution, Ct (milligrams per liter) is the concentration of fluoride in the aqueous phase at any time, t (minutes), V (liters) is the volume of the solution, and m (grams) is the mass of the adsorbent.

3.5.5. Effect of contact time

The effect of contact time on fluoride removal was examined by varying the contact time (10, 20, 30, 40, 50, 60, 90, 120, and 180 min) until equilibrium achieved, while all other adsorption experimental factors were kept constant (i.e. adsorbate concentration, 10 mg/L, pH ~ 3, adsorbent amount, 2 g/L and shaking speed of, 200 rpm). The supernatant solution samples were then filtered with 0.45-µm filter paper for the analysis of residual fluoride to determine equilibrium time, the percentage of fluoride removed, A %, (adsorption efficiency) and amount of fluoride adsorbed per unit mass of the adsorbent, q_t, (adsorption capacity, milligrams per gram) of ASB.

3.5.6. Effect of shaking speed

Effect of agitation speed on fluoride adsorption was analyzed at different shaking speed (100, 150, 200 and 250 rpm) while all other experimental parameter was kept constant (agitation time, 60 min, solution pH ~ 3, Initial fluoride concentration, 10 mg/L, adsorbent dose, 2 g/L and particle size < 0.3mm).

3.5.7. Effect of solution pH

Solution pH was investigated to determine the optimum pH for maximum adsorptive removal of fluoride over the pH range of (3, 5, 6, 7, 9 and 11). Known adsorbent of dose, 2 g/L, shaking speed of, 200 rpm, agitation time, 60 min, initial fluoride concentration, 10 mg/L, particle size < 0.3 mm and clear supernatant was taken to determine effective optimum pH.

3.5.8. Effect of adsorbent dose

In order to optimize the dosage for bringing down fluoride concentration from aqueous solution, ASB with 2, 4, 6, 8, 10, 15, 20, and 25 g/L were used to adsorb fluoride under identical experimental conditions. Whereas the solution at pH ~ 5, adsorbate concentration of 10 mg/L, shaking speed 200 rpm, agitation time of 60 min and particle size < 0.3 mm are kept constant. At the end clear, supernatant solution was taken to examine effective dose.

3.5.9. Effect of initial fluoride concentration

The influence of initial concentration was experienced varying fluoride initial concentration (2.5, 5, 10, 15, 20, 25 and 30 mg/L). While maintaining the solution pH ~ 5, adsorbent dose 15 g/L, shaking speed 200 rpm, equilibrium contact time 60 min and particle size < 0.3 mm.

3.5.10. Adsorption kinetics

The adsorption kinetics of the system was explained by pseudo-first-order and pseudo-second-order equation (Eqs. 3 and 4) when the removal of an adsorbate from aqueous solution increases during the initial agitation time, and followed by a slow increase until the equilibrium time was reached (Lagergren, 1898).

$$q_t = q_e[1 - \exp(-k_f t)] \tag{3}$$

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \tag{4}$$

Where q_t (mg/g) is the amount of F^- adsorbed per unit mass of the adsorbent at any time t (minutes), q_e (mg/g) is the calculated equilibrium capacity, and k_2 (g/(mg.min)) is the equilibrium rate constant based on the pseudo-second-order equation. Integrating (Eq. 4) for the boundary conditions q_t = 0 to q_t = qt and t = 0 to t = t is simplified and linearized to find out the following equation.

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{5}$$

The values of k_2 and q_e were calculated from the intercept and the slope of the graph of t/q_t versus t, respectively.

3.5.11. Adsorption Isotherms

The F^- sorption capacity of ASB, the relationship between the amount of F^- adsorbed at equilibrium per unit mass of the adsorbent and the concentration of F^- in the aqueous phase at equilibrium was analyzed with well-known sorption isotherm models namely, the Langmuir and Freundlich isotherms. Langmuir sorption isotherm assumes the monolayer coverage on a structurally homogeneous surface of the adsorbent. Whereas, Freundlich isotherm model commonly used to describe the adsorption characteristics for the heterogeneous surface. The nonlinear forms of the two widely used isotherms namely, the Langmuir (Eq. 6) (Langmuir, 1916) and the Freundlich (Eq. 9) (Freundlich, 1906) were used to estimate the F^- adsorption capacity of the adsorbent.

$$q_e = \frac{Q_{max} b C_e}{1 + bC_e} \tag{6}$$

C_e is the equilibrium concentration (mg/L) and q_e the amount adsorbed at equilibrium (mg/g). Q_{max} is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg/g) and b (L/mg) Langmuir constant relates the heat of adsorption (Chen *et al.*, 2013). Q_{max} represent a practical limiting adsorption capacity when the surface fully covered with adsorbate molecules and assists in the comparison of adsorption performance. Eq. (6) rearranged to a linear form;

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{\max}} + \frac{C_e}{Q_{\max}} \tag{7}$$

The values of Langmuir constant of K_L and Q_{max} were calculated from the intercept and the slope of Linear plots of C_e/q_e vs C_e, respectively.

In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter R_L.

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

b (L/mg) is the Langmuir isotherm constant and C_o (mg /L) is the initial concentration of F^-. There are four probabilities for the R_L value:

For favorable adsorption $0 < R_L < 1$, unfavorable adsorption $R_L > 1$, linear adsorption $R_L = 1$ and irreversible adsorption for $R_L = 0$ (Foo & Hameed, 2010).

$$q_e = K_F C_e^{1/n} \tag{9}$$

K_f indicates adsorption capacity (mg/g) and 1/n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < 1/n < 1$, adsorption is favorable. The higher the values of K_f the better favorability of adsorption (Attar, 2010) (Eq. (9) can be rearranged to linear form;

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{10}$$

The values of Freundlich constant *K_f* and q_e were calculated from the intercept and the slope of linear plots of log q_e vs log C_e, respectively.

All the model parameters were evaluated by both non-linear regression and linear least-squares method. The correlation coefficient (R^2) was also used to determine the best-fitting isotherm to the experimental data, illustrated on equation (11).

$$r^2 = \frac{\sum\left(q_m - \overline{q_e}\right)^2}{\sum\left(q_m - \overline{q_e}\right)^2 + \sum\left(q_m - q_e\right)^2} \tag{11}$$

Where q_m is the constant obtained from the isotherm model, q_e is the equilibrium capacity obtained from experimental data, and $\overline{q_e}$ is the average of q_e.

3.5.12. Real water analysis

A water sample with F^-concentration of 16.75 mg/L was collected from Jimma University (Kolo Ber), Southwest Ethiopia. Using the water sample with and without adjusting its pH and keeping All other parameter at optimum and equilibrium, adsorption experiments were carried out. Besides, important physicochemical parameters for the ground water were measured both at the field and in laboratory using standard water and wastewater sampling and analyses methods (Stephenson *et al.,* 1985).

3.6. Data quality control and assurance

Duplicate experiments were carried out during each set of experiments and the average values of the result were reported. At each set of experiments, calibration (standardization) was conducted for analysis.

3.7. Ethical consideration

Ethical considerations were taken in to account for the study to be sound and ideal. Each of data collection, processing, and analysis followed scientific methods and procedures. Furthermore, all concerned bodies were informed prior to the study get started. Finally, the result of laboratory analysis honestly recorded and interpreted based on scientific procedures.

3.8. Dissemination plan

The result of this study will be submitted to Department of Civil and Environmental Engineering, School of Graduate Studies, Jimma University Institute of Technology, and disseminated to all concerned bodies. Correspondingly, could be published in National and International Journals.

CHAPTER FOUR

RESULTS AND DISCUSSION

Characterization of sugarcane bagasse

Sugarcane bagasse have porous specific surface along with a mass of carboxyl, hydroxyl and carbonyl groups. These special structure and functional groups which possess favorable adsorption as a result of hydrogen bonding, chelation and electrostatic adsorption methods (Khoramzadeh, 2013).

Typical proximate (dry basis) and ultimate analysis (dry ash free basis) of sugarcane bagasse (Anukam *et al.,* 2013)

Proximate analysis (wt %)		Ultimate analysis (wt %)	
Moisture	1.14	Carbon (C)	44.1
Volatile matter	69.99	Haydrogin (H)	5.7
Fixed carbon	16.39	Oxygen (O)	47.7
Ash	1.42	Nitrogen (N)	0.2
		Sulfur (S)	2.3

Preliminary test

Preliminary test was done to check the efficiency of the untreated sugarcane bagasse for sorpion removal of fluoride from water. Removal efficiency was determined by using contact time 60 min, adsorbent dose 2 g/L, pH 3, initial fluoride concentration 10 mg/L and agitation speed 200 rpm. The final result for fluoride was 7.78 mg/L with removal efficiency 22.2 % which is not satisfactory to go for further optimization of the adsorption parameters. Therefore, activation of the biosorbent was required and activated sugarcane bagasse was used to find out the optimum parameters for fluoride removal.

Based on the pre-test, optimizations of important parameters such as effect of contact time, pH, adsorbents dose, initial fluoride ion concentration and agitation speed were studied in order to determine the efficiencies of adsorbents to remove fluoride both from aqueous solution and real water sample. The data collected from these studies is used to describe the responsible adsorption isotherm models and to assess the kinetic of the adsorption of fluoride onto activated sugarcane bagasse (Biochar).

4.1. Effect of contact time

The time profile of adsorption of F^- onto ASB was investigated by varying the contact time from 5 to 180 min under 10 mg/L fluoride concentration at pH ~ 3 and 2 g/L adsorbent dose and is presented in Fig. 4.1. As agitation time increases from 10 to 60 min, fluoride removal also increases initially from 32.8 % to 64.2 % correspondingly. However, gradually approaches a more or less constant value, denoting attainment of equilibrium. Obviously, the equilibrium was attained after shaking for about 60 min, beyond which there is no further significant increase in the adsorption efficiency were observed. Likewise, fluoride adsorption capacity of ASB was high ~ 0.428 mg/g at agitation time of 60 min, whereas the amount adsorbed increases from ~ 0.219 to ~ 0.449 mg/g with the increase in the contact time from 10 to 180 min respectively.

These changes in the rate of removal may be because, initially all adsorbent sites were vacant and the solute concentration gradient was high. Afterwards, the fluoride uptake rate by the adsorbent decreases significantly, due to decrease in adsorption sites. A decreasing removal rate, particularly towards the end of the experiment, indicates a possible monolayer of fluoride ions on the outer surface and pores of ASB and pore diffusion onto the inner surface of adsorbent particles through the film due to continuous agitation maintained during the experiment (Li *et al.*, 2003).

The sorption of fluoride is very rapid in less than 60 min. This may be the result of the instantaneous sorption reaction in which fluoride sorbed quickly on to the surface of ASB. Moreover, the sudden rise in removal of fluoride from 10 min to 60 min indicates that the adsorption of fluoride probably is due to the diffusion taking place into the pores on the surface of the adsorbent (Das *et al.,* 2003). After 60 min, fluoride removal rate leveled off significantly, denoting attainment of equilibrium and the non-availability of sorption sites (Nasr *et al.,* 2011). As no further, significant removal of fluoride was recorded after 60 min, an equilibrium time of 60 min was chosen and this was used in all subsequent experiments.

Therefore, the uptake and un-adsorbed F^- concentrations at the end of 60 min are given as the equilibrium values. Similar results were also reported by other researchers where the fluoride adsorption was found to increase with increase in contact time and after reaching to equilibrium time, adsorption remained constant (Regassa *et al.*, 2016).

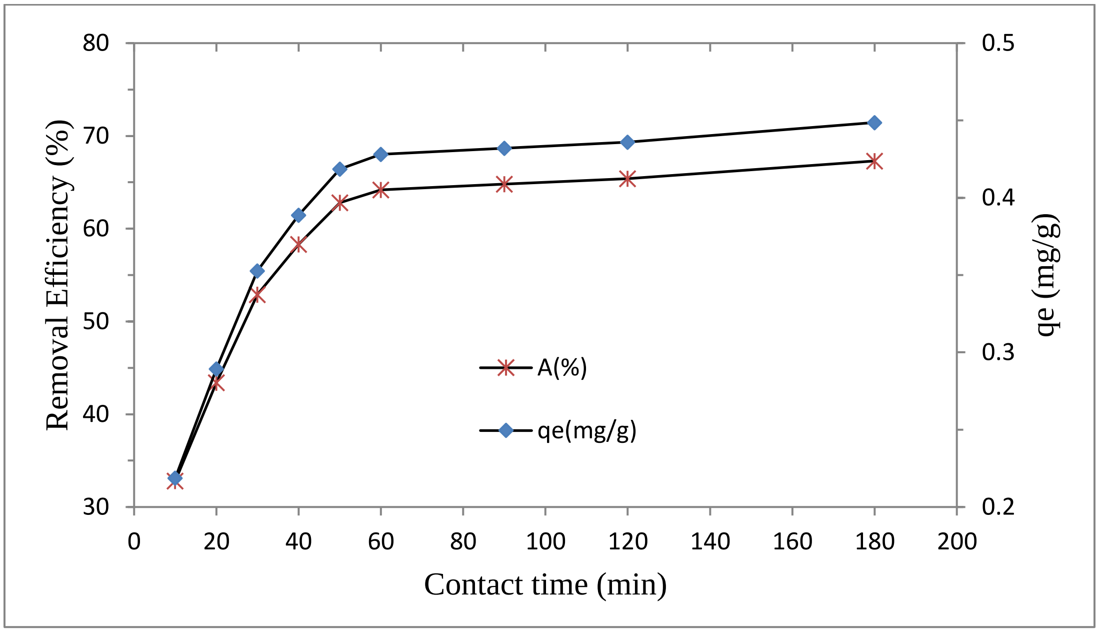


Figure 4.1 Effect of contact time on fluoride removal by ASB (F^- initial concentration, 10 mg/L; dose, 2 g/L; $pH_{initial}$, 3; volume of solution, 0.05 L; and shaking speed, 200 rpm)

4.2. Effect of shaking speed

Effect of shaking speed was tested using a horizontal shaker and result is presented graphically on Fig. 4.2. Result indicates removal efficiency rises within raise of shaking speed. The value obtained was 57.1 % and 67.1 % for 100 and 200 rpm respectively. However, further increases of shaking speed were resulted in the reduction of removal efficiency. For instance, at the shaking speed of 250 rpm it was 44.6 %, which decreases, by a margin of ~ 22.5 %, compared to 200 rpm and this might be due to over shaking that possibly because, of desorption.

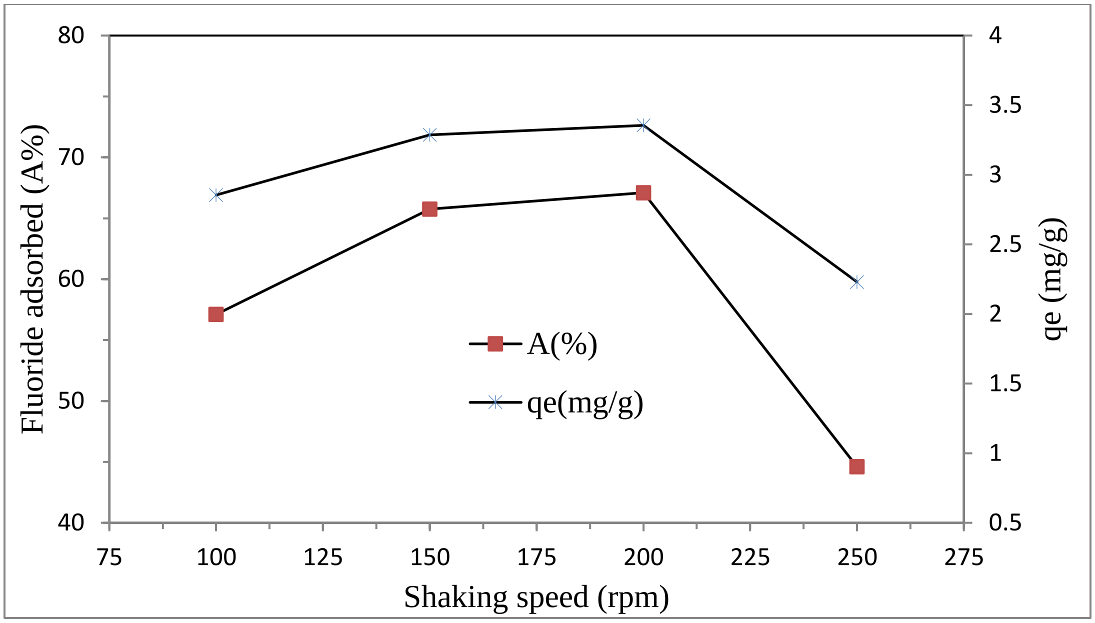


Figure 4.2 Effect of shaking speed on fluoride removal by ASB (Shaking speed, 100 - 250 rpm F^-; initial concentration, 10 mg/L; dose, 2 g/L; $pH_{initial}$, 3; volume of solution, 0.05 L and contact time, 60 min)

4.3. Effect of pH

The effect of pH on the adsorption removal efficiency was studied by varying the pH from 3 to 11 and constant parameters of 10 mg/L F^- concentration, 60 min contact time, 200 rpm shaking speed, F^- 2 g/L ASB. The result showed that the fluoride removal efficiency was high (76.1 %) at pH 3 (Figure 4.3). However, percentage removal significantly decreased from 74.2 % to 41 % upon the pH increase from 5 to about 11. Furthermore, fluoride adsorption capacity of ASB was high (~ 0.35 mg/g) at the pH 3, whereas the amount adsorbed decreased from ~ 0.186 to ~ 0.11 mg/g with the increase in the initial pH from 7 to 11.

Fluoride removal decreases with increasing pH and the maximum removal of fluoride was observed at pH 3. More adsorption at acidic pH indicates that an increase in H^+ on the adsorbents surface results in electrostatic attraction between positively charged adsorbents surface and negatively charged fluoride ions. However, the decrease in the adsorption capacity in the basic region (pH greater than 7) is due to the decrease in positive charges of the adsorbent and increase in competition of fluoride ion with the hydroxide ion (OH^-) since both have the same charge and ionic radii (Mahramanlioglu *et al.*, 2002). Therefore, lower values of adsorption were observed at higher pH because of repulsion between the fluoride and the adsorbent's negative charge surface which goes align with the findings (Zazouli *et al.,* 2014).

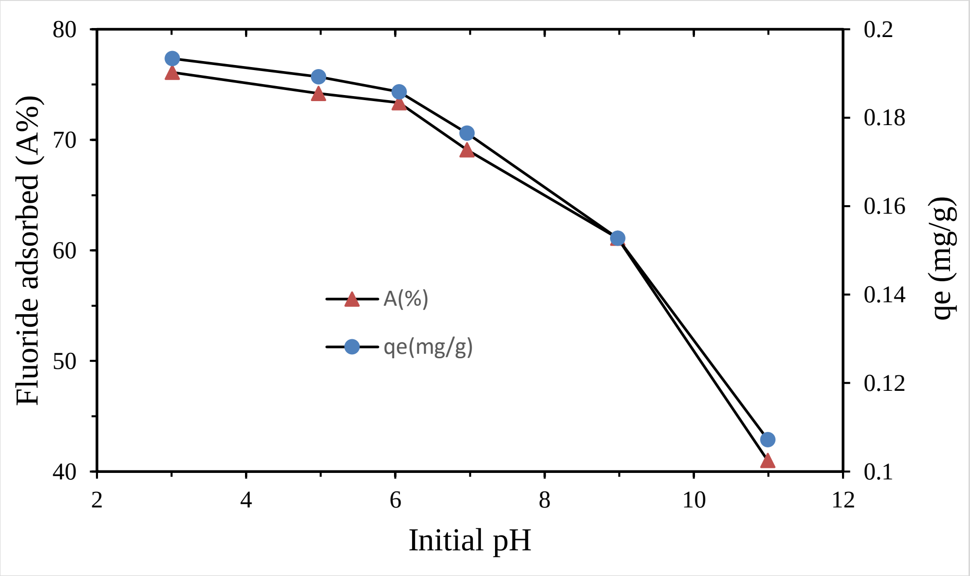


Figure 4.3 Effect of initial pH on fluoride removal by ASB ($F^-_{initial}$ concentration, 10 mg/L; dose, 2 g/L; volume of solution, 0.05 L; contact time, 60 min; and shaking speed, 200 rpm)

4.4. Effect of activated sugarcane bagasse (ASB) dose

In the optimization of dose for bringing down fluoride concentration from aqueous solution, various amount of ASB (2 to 25 g/L) were used while keeping the other experimental conditions constant to adsorb fluoride under identical experimental conditions. It can be seen from the results in Figure 4.4 that the dose of ASB in adsorbate significantly influenced the adsorption capacity of adsorbent. Adsorbate with ASB dose of 15 g/L possessed an adsorption capacity of 0.027 mg/g, whereas ASB with 2.0 g/L & 25 g/L had 0.129 mg/g and 0.017 mg/g, respectively. As the dosage of adsorbent is increased, the adsorption sites remain unsaturated during the adsorption reaction leading to drop in adsorption capacity (*q*e) (Sharma and Forster, 1993).

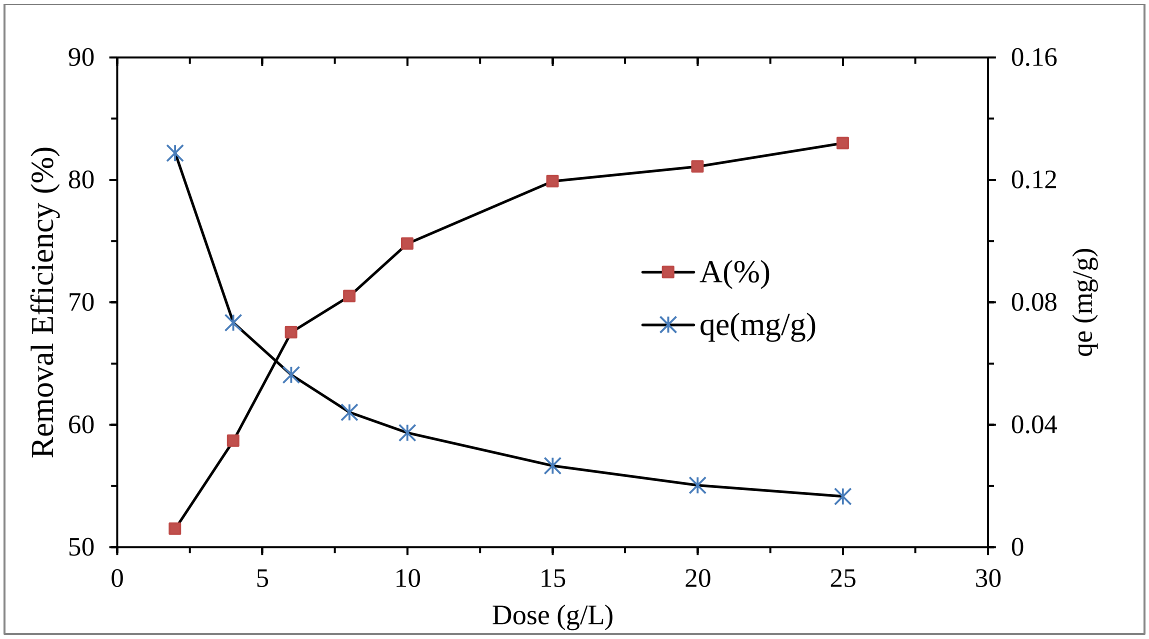


Figure 4.4 Effect of adsorbent dose on fluoride removal by ASB (F^- initial concentration, 10 mg/L; $pH_{initial}$, 5; volume of solution, 0.05 L; contact time, 60 min; and shaking speed, 200 rpm)

Although, the amount of adsorbed F^- per unit mass (g) of adsorbent decreased from 0.129 mg/g to 0.017 mg/g with increasing the adsorbent dose. As illustrated in the Figure 4.4 above the adsorption efficiency increased from ~ 51.5 % to ~ 83 % with increasing the adsorbent dose from 2 to 25 g/L. The treated SB (ASB) was efficient for 79.9 % removal of fluoride ions, at 15 g/L and maximum removal of 81.1 % and 83 % was observed at 20 and 25 g/L, respectively. This is due to enhanced active sites with an increase in amount of adsorbent. Increase in adsorbent dosage increases adsorption of adsorbate from the solution which is due to the availability of more active sites and increase in surface area at higher dosage (Hu *et al.*, 2015). However, the decrease in adsorption capacity can be due to a lack of saturation of the active sites in the adsorbent. By increasing the adsorbent dose, the capacity of all the available active sites of adsorbent surface is not completely used and there is a reduction in the adsorption amount per unit mass of adsorbent (Tang *et al.*, 2009). Hereafter, 15 g/L of ASB was fixed as the optimal dosage in all subsequent experimental studies.

4.5. Effect of initial concentration

The effect of the initial concentration on removal efficiency was investigated at different initial F^- concentration (2.5, 5, 10, 15, 20, 25 and 30 mg/L) by keeping all other parameters constant. The effect of initial fluoride concentration on percent removal of fluoride along with the amount of adsorbate adsorbed per unit mass of adsorbent illustrated on Figure 4.5.

The amount of adsorbate in the solid phase with lower initial concentration of adsorbate was smaller than the amount when higher concentrations were used. It is seen that the removal of fluoride was dependent on the concentration of fluoride as the decrease in the initial concentration increased the amount of fluoride removed. While the percentage of fluoride removal was found to be 61.8 % for 10 mg/L initial concentration, this value was 45.73 % for that of 30 mg/L. On the other hand, the total amount of adsorbate adsorbed per unit mass of adsorbent increases with an increase in initial concentration i.e. 0.12 mg/g for 2 mg/L and 0.91 mg/g for 30 mg/L of initial fluoride concentrations.

At low adsorbate concentration, the ratio of surface active sites to total fluoride is high hence, the fluoride ions could interact with the sorbent to occupy the active sites on the ASB surface sufficiently and removed from the solution. Nevertheless, with the increase in adsorbate concentration, the number of active adsorption sites is not enough to accommodate fluoride ions. Comparable results were testified for fluoride removal using brick powder and $KMnO^-_4$ modified activated carbon derived from steam pyrolysis of rice straw (Daifullah *et al.*, 2007).

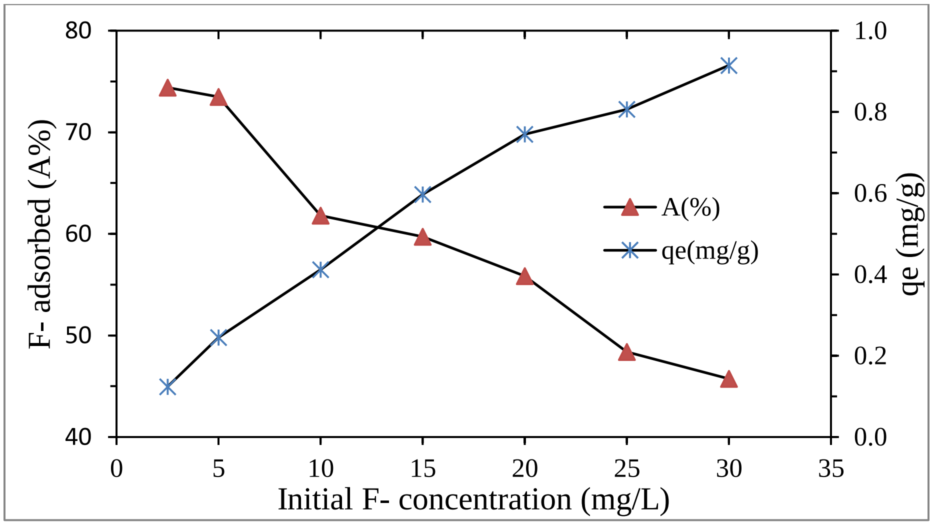


Figure 4.5 Effect of initial F^- concentration on fluoride removal by ASB (Dose, 15 g/L; $pH_{initial}$, 5; volume of solution, 0.05 L; contact time, 60 min; and shaking speed, 200 rpm.

4.6. Adsorption kinetics of fluoride

Pseudo-first-order and Pseudo-second order

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations are applied to model the kinetics of fluoride adsorption onto ASB using 10 mg/L adsorbate, 15 g/L adsorbent, at pH 5 for 60 min contact time. The kinetic experimental data of fluoride ions on activated sugarcane bagasse sorbent is simulated by the pseudo-first-order (Equation 5) and pseudo second-order (Equation 6) rate equation (Ho and McKay, 1999).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{5}$$

Where q_t and q_e are the amount adsorbed (mg/g) at time, t, and at equilibrium respectively and k_1 is the rate constant of the pseudo-first-order adsorption process (min^{-1}). The pseudo-first-order rate constant, k_1 can be obtained from the slope of the graph of log (q_e-q_t) versus time (t) on Fig.4.6. The calculated k_1 values and corresponding linear regression correlation coefficient values are shown in table 4.1.

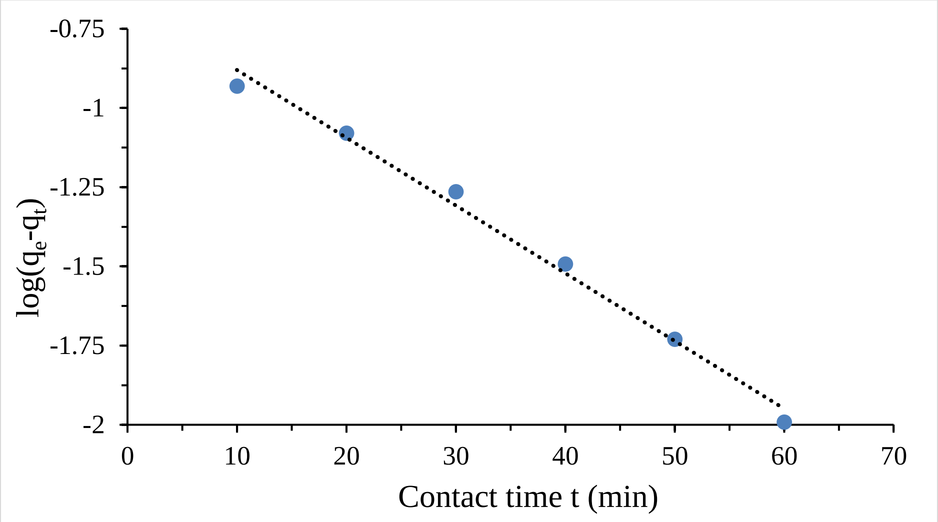


Figure 4.6 Pseudo-first-order plots of fluoride adsorption kinetics (F⁻initial concentration, 10 mg/L; dose, 15 g/L; pH$_{initial}$, 5; volume of solution, 0.05 L; contact time, 60 min; and shaking speed, 200 rpm)

With correlation coefficients, R^2 of 0.990, it was seen that adsorption of F^- on ASB did follow both pseudo first-order kinetics and pseudo second order kinetics compared with having correlation coefficient, R^2 of 0.993. Though, the value of coefficient of determination from kinetic data analysis are nearly equal for each plot, the values of q_e,cal (calculated) and q_e,exp (experimental) in the case of pseudo second order kinetics were almost equal. Hence, it could be concluded that the sorption system of fluoride on ASB more or less followed the pseudo second order kinetics equation, based on the assumption that the rate-limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between anions and adsorbent (Gucek *et al.*, 2005). Ruixia *et al.* obtained similar results for the adsorption of fluoride onto ion-exchange fiber (Ruixia *et al.*, 2002).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

Where q_t and q_e are the amount of adsorbed fluoride (mg/g) at time t (min) and at equilibrium time, respectively, and k_2 is second order rate constant of adsorption (g mg^{-1} min^{-1}). Fig. 6 shows the linear relationship of the graph plot of t/q_t versus time t, from which q_e and k_2 can be determined from the slope and intercept, respectively.

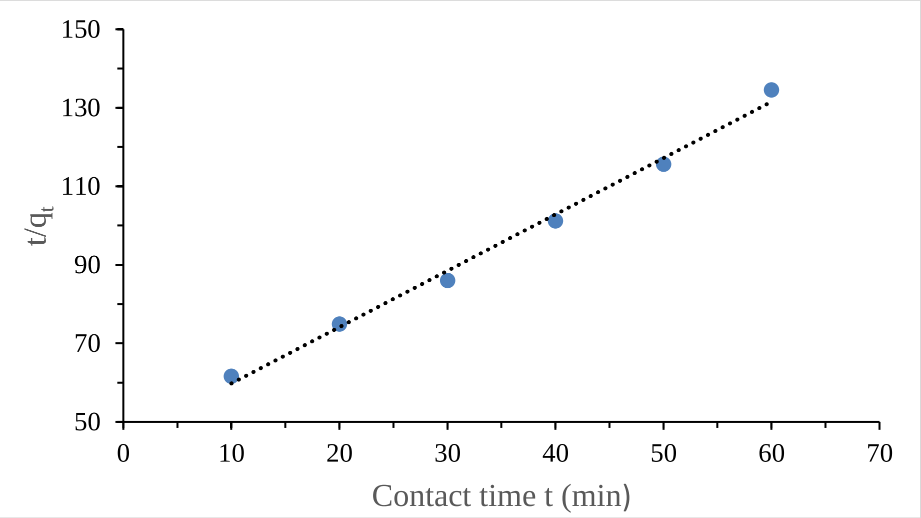


Figure 4.7 Pseudo-second-order plots of fluoride adsorption kinetics (F^-initial concentration, 10 mg/L; dose, 15 g/L; $pH_{initial,}$ 5; volume of solution, 0.05 L; contact time, 60 min; and shaking speed, 200 rpm)

Intra-particle diffusion

Rate of sorption is frequently used to analyze nature of the rate controlling step and the use of the intra-particle diffusion model has been greatly explored in this regard that represented by Weber and Morris equation. In the model developed by Weber and Morris, the rate of intra-particle diffusion is a function of $t^{0.5}$ and can be defined by Eq. (7) which describes the time evolution of the concentration in adsorbed state, where the rate constant (kp) is obtained from the plot of q_t versus $t^{0.5}$ (Weber and Morris, 1963).

$$q_t = k_p t^{0.5} + C \tag{7}$$

Where C is the intercept and k_p is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$). According to this model, the plot of uptake, q_t, versus the square root of time ($t^{0.5}$) should be linear if intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step (Arami *et al.,* 2008). When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. Previous studies showed that such plots might present a multi-linearity which indicated that two or more steps occurred (Onal *et al.,* 2006). The sorption data indicated that the sorption removal of the fluoride from aqueous phase on to ASB was rather complex process, involving both boundary layer diffusion and intraparticle diffusion.

The intra-particle diffusion rate constant, k_p, value was obtained from the slope of the straight-line portions of plot of q_t versus $t^{0.5}$. The correlation coefficient (R^2) for the intra-particle diffusion model is 0.977 (Table 4.1) for initial fluoride concentration of 10 mg/L. Correspondingly, it was observed that the straight lines did not pass through the origin and this further indicates that the intra-particle diffusion is not the only rate controlling step.

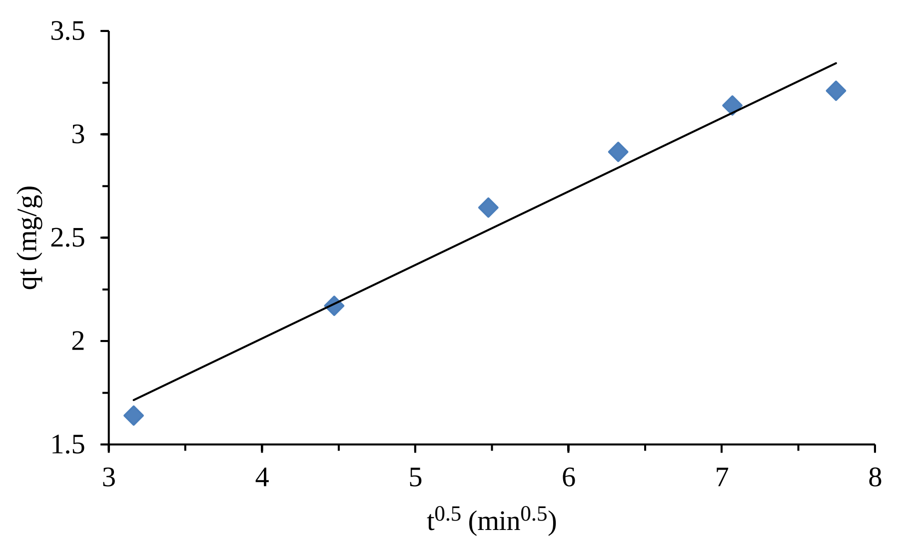


Figure 4.8 Intra particle diffusion plots of fluoride adsorption kinetics (F^{-}initial concentration, 10 mg/L; dose, 15 g/L; $pH_{initial,}$ 5; volume of solution, 0.05 L; contact time, 60 min; and shaking speed, 200 rpm)

Table 4.1 Equilibrium values of kinetic parameters for adsorption of fluoride on Activated Sugarcane Bagasse.

Kinetic Model	Parameters	Value
Pseudo-first Order	$q_{e, cal}$ (mg/g)	0.216
	k_1 (min^{-1})	0.0463
	R^2	0.990
Pseudo-second Order	$q_{e, cal}$ (mg/g)	0.697
	k_2 (g/mg.min)	0.04534
	R^2	0.9933
Intra-particle diffusion	k_p (mg/g.$min^{0.5}$)	0.3555
	C (mg/g)	0.5904
	R^2	0.9774

4.7. Adsorption isotherms

The applicability of the isotherm equation is compared by judging the correlation coefficients R^2. In a view of value of R^2, Langmuir and Freundlich isotherm gives satisfactory fit to the experimental data of fluoride. The results suggest that the fluoride is favorably adsorbed on activated sugarcane bagasse.

Q_{max} (1.226 mg/g) is the maximum amount of adsorption from assumption of Langmuir adsorption isotherm model and R_L (the separation factor) is 0.378 indicating that the equilibrium sorption was favorable and the R^2 value is 0.982. If the value of n lies between one and ten, then it indicates a favorable sorption process (Goldberg, 2005). From the data in Table 4.2, the freundlich isotherm parameter values of 1/n is equal to 0.6051 while n=1.653 indicating that the sorption of F^- onto ASB is favorable and the R^2 value is 0.983 provided that the sorption data can be expressed by the two isotherm models assuming their R^2 value, somehow it fitted well to Freundlich isotherm model.

The values of Langmuir and Freundlich isotherm models graphically presented on Figure 4.9 and the isotherm parameters of both models are given in Table 4.2.

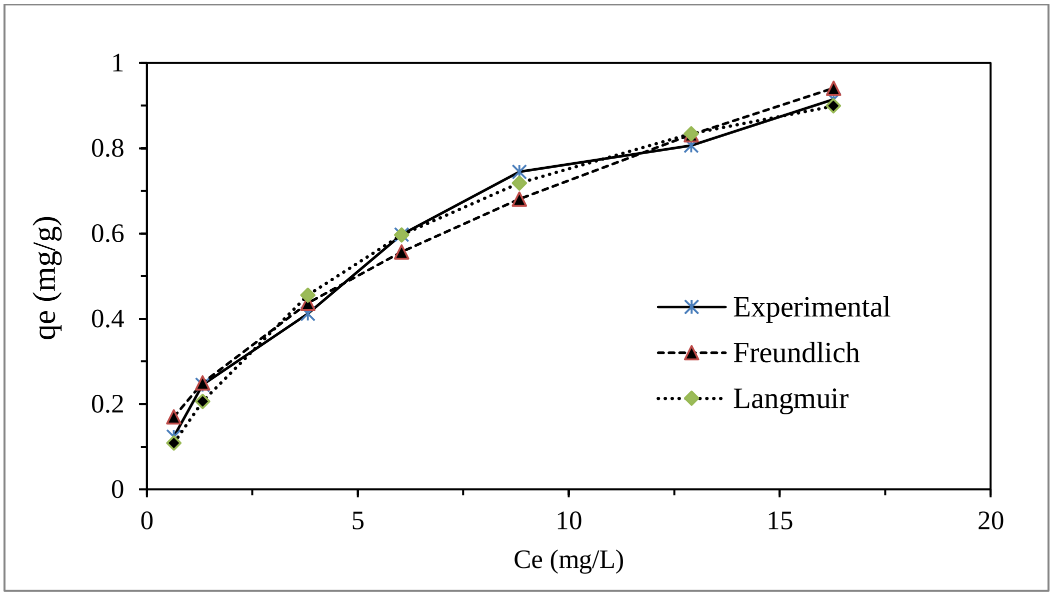


Figure 4.9 Isotherms of the equilibrium adsorption of fluoride on ASB (F^- concentration, 2.5–30 mg/L; dose, 15 g/L; volume of solution, 0.05 L; grain size, < 0.3 mm; $pH_{initial}$, ~5; shaking speed, 200 rpm; and contact time, 60 min)

Table 4.2 Equilibrium parameters of Langmuir and Freundlich isotherms models for adsorption of fluoride on Activated Sugarcane Bagasse (Biochar).

Isotherm Model	Parameter	Values
Langmuir	Q_{max} (mg/g)	1.226
	b (L/mg)	0.163
	R_L	0.379
	R^2	0.982
Freundlich	K_f (mg/g) (L/mg)$^{1/n}$	0.184
	n	1.653
	1/n	0.605
	R^2	0.983

4.8. Real water sample analysis

Real water samples of natural groundwater containing 16.75 mg/L fluoride was collected from Main Campus (Kolo Ber) of Jimma University, Ethiopia. Some of the physicochemical properties of the real water sample was analyzed based on standard procedures and presented in Table 4.3.

Table 4.3 Physicochemical properties of real water sample

Parameter	Value (mg/L)	Parameter	Value (mg/L)
Alkalinity	630	Fluoride	16.75
Total hardness	40	Chloride	5.82
Ca hardness	23	Nitrate	0.113
Mg hardness	17	Phosphate	0.143
pH	7.45		

Defluoridation of the ground water sample was carried out in duplicate with and without adjusting the pH of the water samples and using equilibrium batch adsorption study of the synthetic one (i.e. 15 g/L dose, 60 min contact time, 200 rpm shaking speed, pH 5 for the adjusted one and 16.75 mg/L initial concentration of the sample). Fluoride concentration of well

16.75mg/L was reduced to 8.95 mg/L without the pH adjustment. Considering the WHO optimum fluoride concentration guide line in drinking water further treatments is required once again to reduce 8.95 mg/L fluoride concentration to below the permissible limit of 1.5 mg/L. When the pH of the sample is readjusted to pH 5 the fluoride concentration was reduced from the original 16.75 mg/L to 5.62 mg/L. Though better removal was obtained when the pH is adjusted still further treatments is required to bring down 5.62 mg/L fluoride concentration to the permissible level of 1.5 mg/L. Therefore, multistage removal system is required for the attainment of the required drinking water guide line for fluoride. Which is similar situation for the removal of fluoride using Natural and Activated Coal adsorbents (Regassa *et al.*, 2016).

Table 4.4 Comparison of the defluoridation capacity of different sorbents

Adsorbents	pH	Adsorption Capacity (mg/g)	Reference
Chemically treated Banana peel	6.0	1.340	Aash, (2014)
Chemically treated Groundnut shell	7.0	1.498	Aash, (2014)
Chemically treated Sweet lemon peel	4.0	0.744	Aash, (2014)
Fe^{3+} activated quartz	6.0	1.16	Fan, *et al.* (2003)
Hydroxyapatite	7.5	3.12	Mourabet *et al.* (2012)
Chemically treated tea leaves	6.0	0.253	Jenish *et al.*, (2011)
ASB	5.0	1.226	This study

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

This study demonstrated the adsorption efficiency of activated sugar bagasse can be used for fluoride removal from synthetic aqueous solution and natural groundwater. The equilibrium shaking speed was obtained at 200 rpm. The optimum pH of the solution was achieved at 5 and above pH 7 removal capacities and removal efficiency decreased. The equilibrium adsorption time was achieved within 60 min. The optimum dose for equilibrium fluoride removal was 15 g/L. With increasing the initial fluoride concentration, the removal efficiency of optimum adsorbent dose decreases. The kinetics data of the adsorption of fluoride followed second order models. The intra-particle diffusion plot indicated that intra-particle diffusion is not the only rate controlling step. The equilibrium fluoride adsorption data followed Freundlich isotherm model. The fluoride concentration of the natural groundwater (16.75 mg/L) was reduced to 8.95 mg/L (~ 46.6%) without pH adjustment while it reduced to 5.62 (~ 66.5%) when the pH is adjusted to 5 and the optimum ASB dose is 15 mg/L.

6.2. Recommendations

- As SB is broadly available and demonstrate reasonable sorption capacity it can be used for the sorption removal of F^-.
- Enough attention should be given to defluoridation of water using locally available bisorbents.
- Further investigation such as common ion effect, regeneration, column adsorption, characterization of adsorbents, and analysis of water quality of the defluoridated water as per the WHO guidelines of drinking water is important for practical implementation.

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ANNEX I

BATCH EXPERIMENTS PROCEDURE

(Ali and Gupta, 2007)

Conversion of reactive materials into adsorbents

1. Collect selected material and sieve to remove other particles such as stone, soil, paper etc.
2. Wash with distilled H_2O and dry in an oven at 100^0C for about 2 h.
3. Carbonize organic precursors by heating to 400–800^0C for 5 –24 h.
4. Treat with hydrogen peroxide at 60^0C for 24 h to remove adhered organic matter.
5. Wash with distilled H_2O three times to remove hydrogen peroxide and dry in an oven at 100^0C for ~ 2 h.
6. Heat to 500^0C in a furnace for 6 –12 h to activate the adsorbent.
7. Determine density, porosity and ignition loss by the usual methods
8. Establish the stability of the adsorbent by suspending in distilled H_2O, HCl and NaOH (0.1 to 1.0 M) for about 1–2 h.
9. Establish mineral and crystal structure by X-ray diffractometry and Scanning electron microscope (SEM), using published methods
10. Carry out elemental analysis by chemical methods, as described
11. Collect adsorbent of different particle sizes by sieving and keep in vacuum desiccators. At this stage, the adsorbent is ready for water purification.

    Batch experiments
12. Use a 50-mL Erlenmeyer flask to carry out batch experiments in a thermostatic shaking water bath. Take a known amount of pollutant in 10–25 mL H_2O and add a dose of adsorbent. The dose of adsorbent depends on the type of adsorbent and adsorbate. However, a suggested starting point is 0.5 g/L. Alter the pH of the solution using HCl or NaOH.
13. Agitate flask mechanically in a water bath at desired temperature. Normally temperature is fixed between 25 and 35^0C for 1–3 h.
14. Repeat Steps 12–13 to optimize concentration of pollutant, pH, adsorbent dose, temperature and contact time after varying their values.
15. Centrifuge or filter the mixture and determine the concentration of pollutant in the aqueous phase.

16. Calculate the amount of pollutant adsorbed from the aqueous solution by determining the equilibrium concentration in solution. Kinetic studies

17. Set up 50-ml Erlenmeyer flasks containing various amounts of standard solutions of pollutant and shake in a thermostatic shaking water bath.

18. Add a known amount of adsorbent to each flask.

19. Allow flasks to agitate mechanically in the water bath at a constant temperature. Contact time, temperature and other conditions should be selected based on preliminary experiments.

20. Centrifuge the mixture at pre-decided time intervals and analyze the concentration of pollutant in the supernatant. Adsorbent particle size is an important variable in deciding centrifugation timings. Normally, this varies from 30 to 60 min at 5,000–100,000g.

21. Determine the equilibrium concentration (Ce) and time to reach equilibrium.

22. Calculate thermodynamic parameters as detailed in the introduction and run adsorption models.

ANNEX II

All laboratory analysis results

Table 5 Effect of dose on Fluoride adsorption removal

Dose (g/L)	Co (10 mg/L)				A (%)	pH	
	Ce (mg/L)			q_e (mg/g)			
	Trial 1	Trial 2	Aveg.			pH_i	pH_f
2	4.82	4.88	4.85	0.129	51.5	3.02	5.02
4	4.09	4.17	4.13	0.073	58.7	2.98	5.11
6	3.31	3.18	3.245	0.056	67.6	2.99	5.13
8	2.91	2.99	2.95	0.044	70.5	3.05	5.17
10	2.57	2.47	2.52	0.037	74.8	3.07	5.27
15	1.98	2.04	2.01	0.027	79.9	3.05	5.29
20	1.92	1.86	1.89	0.020	81.1	3.01	5.33
25	1.69	1.71	1.7	0.017	83.0	2.99	5.39

Table 6 Effect of pH on Fluoride adsorption removal

pH_i	Co (10 mg/L)				A (%)	pH_f
	Ce (mg/L)			qe (mg/g)		
	Trial 1	Trial 2	Aveg.			
3.01	2.41	2.37	2.39	0.19025	76.1	5.15
4.97	2.59	2.57	2.58	0.1855	74.2	5.25
6.05	2.72	2.61	2.665	0.183375	73.35	5.53
6.96	3.27	2.91	3.09	0.17275	69.1	6.17
8.98	3.95	3.83	3.89	0.15275	61.1	7.56
10.99	5.97	5.83	5.9	0.1025	41	9.84

Table 7 Effect of shaking speed on Fluoride adsorption removal

Shaking speed (rpm)	Co (10 mg/L)				A (%)	pH	
	Ce (mg/L)			q_e (mg/g)			
	Trial 1	Trial 2	Aveg.			pH_i	pH_f
100	4.47	4.11	4.29	2.855	57.1	5.05	5.12
150	3.62	3.23	3.425	3.2875	65.75	5.07	5.22
200	3.33	3.25	3.29	3.355	67.1	5.03	5.15
250	5.96	5.12	5.54	2.23	44.6	5.01	5.19

Table 8 Effect of contact time on Fluoride adsorption removal

Contact time (min)	Co (10 mg/L)				A (%)	pH	
	Ce (mg/L)			qe (mg/g)			
	Trial 1	Trial 2	Aveg.			pHi	pHf
10	6.75	6.69	6.72	0.218667	32.8	3.04	5.13
20	5.62	5.7	5.66	0.289333	43.4	3.01	5.12
30	4.67	4.75	4.71	0.352667	52.9	3.07	5.23
40	4.21	4.13	4.17	0.388667	58.3	2.98	5.13
50	3.75	3.69	3.72	0.418667	62.8	3.05	5.21
60	3.55	3.61	3.58	0.428	64.2	3.01	5.17
90	3.56	3.48	3.52	0.432	64.8	2.97	5.06
120	3.43	3.49	3.46	0.436	65.4	3.02	5.11
180	3.25	3.29	3.27	0.448667	67.3	3.01	5.09

Table 9 Important parameters from adsorption isotherm models

Initial fluoride con. (mg/L)	Ce (mg/L)	q_e (mg/g)	A (%)	Langmuir Isotherm			Freundlich Isotherm	
				q_e, cal	SE[1]	R_L	q_e, cal	SE[1]
2.5	0.64	0.124	74.40	0.1085	0.000239280	0.9054	0.1699	0.002108994
5	1.33	0.245	73.50	0.2060	0.001520634	0.8221	0.2497	0.000022007
10	3.82	0.412	61.80	0.4558	0.001920413	0.6158	0.4371	0.000631646
15	6.04	0.597	59.73	0.5972	0.000000024	0.5034	0.5570	0.001627437
20	8.83	0.745	55.85	0.7183	0.000696083	0.4095	0.6809	0.004067697
25	12.91	0.806	48.38	0.8339	0.000759192	0.3218	0.8322	0.000669893
30	16.28	0.915	45.73	0.8989	0.000249416	0.2733	0.9410	0.000694541
SSE[2]					0.005385042			0.009822215

[1] Sum Error

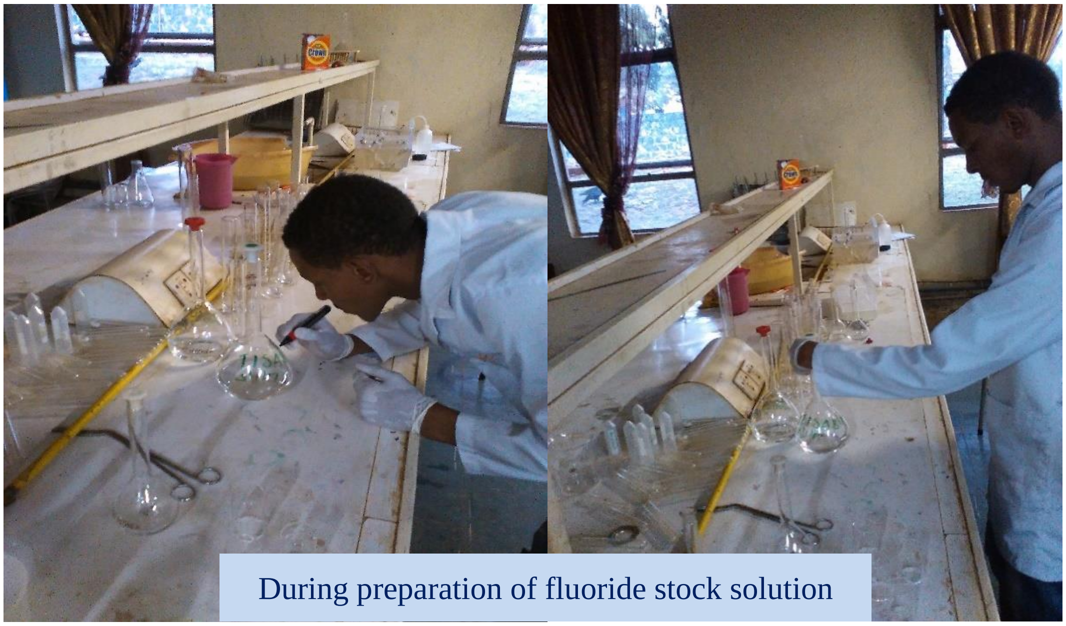
[2] Sum of Square Errors

Photos taken during laboratory work

Crushing and sieving of SB

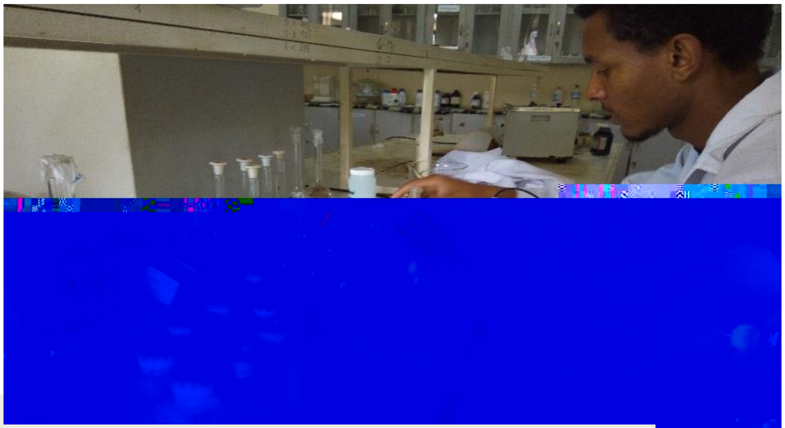
After sieving of SB through 0.3mm sieve

Biochar of SB



During preparation of fluoride stock solution

SB activation in an oven



During preparation of solution for shaking

During Fluoride determination by FISE

Muffle furnace

Washing of the adsorbent