



ALUMINIUM AMENDED ACTIVATED BAMBOO CHARCOAL FOR
FLUORIDE REMOVAL FROM DRINKING WATER

Gizachew Wendimu Kifle

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This is to certify that the thesis prepared by Gizachew Wendimu Kifle, entitled: *Aluminium Amended Activated Bamboo Charcoal for Fluoride Removal from Drinking Water* and submitted in partial fulfillment of the requirements for the Degree of Master of Science in Environmental Science complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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Abstract

The purpose of this study was to investigate the adsorption potential of aluminium amended activated bamboo charcoal (AAABC) for defluoridation of drinking water using batch adsorption experiments. The preparation of activated bamboo charcoal (ABC) was optimized using different activation chemicals (H_3PO_4 and $\text{AlCl}_3/\text{FeCl}_3$) and at different calcination temperature (400-600 °C). The preparation of the adsorbent (AAABC) was then carried out by varying the ratio of aluminium hydro(oxide) (AO) to activated bamboo charcoal (1:1, 1:2, 1:3, 1:4, 2:1 and 4:1). X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) images were used to characterize the solid adsorbent. The specific surface area (SSA) was determined by nitrogen adsorption method at -196.2 °C. The point of zero charge (PZC) was measured by potentiometric mass titrations technique. The concentrations of total acidic and basic groups on AAABC surface were determined from NaOH (0.05 M) and HCl (0.05 M) uptake respectively by acid-base titration. The effect of adsorption parameters such as adsorbent dose, contact time, initial fluoride concentration, solution pH and the presence of interfering co-existing anions on adsorption of fluoride onto AAABC were investigated. The adsorption isotherms and kinetics models were used to determine adsorption parameters. The performance of AAABC was also evaluated in terms of potential for regeneration using different eluent (NaOH) concentrations (0.1, 1 and 5 %) at different time interval (30 and 60 min).

The results obtained from the optimization experiment showed that the adsorbent (AAABC) in which the ABC was impregnated in $\text{AlCl}_3/\text{FeCl}_3$ solution and treated at 400 °C showed higher fluoride uptake capacity. The 1:1 ratio of AO to ABC has also showed higher fluoride uptake capacity after 48 hrs. agitation time. The characterization results showed that inorganic particles were dispersed on the surface of carbon as shown by SEM images and EDS spectra. The main elements found by EDS were carbon, oxygen, aluminium, iron, sodium, and sulfur. Fluoride was associated with the AO particles in the pore spaces of ABC after adsorption. Most peaks from XRD diffractogram correspond to $\text{Ca}_3\text{Al}_2\text{O}_6$. The SSA was reduced from 80.5 to 3.7 m^2/g , when the ABC was impregnated with AO, indicating that the AO particles might cover the surface or pore spaces found in ABC. The PZC of AAABC was found to be 9.6 and the surface acidic and basic groups were found to be 0.75 and 0.125 mmol/g respectively. The rate of adsorption was fairly rapid and maximum fluoride uptake (around 90 %) was attained within 3 hrs. contact time

with optimum adsorbent dose of 0.8 g/L and an initial fluoride concentration of 10 mg/L. Maximum adsorption occurred at a pH range from 5-9 at an initial fluoride concentration of 10 mg/L. It was also observed that the presence of certain co-existing anions (sulfate and chloride) have negligible effect on removal of fluoride, while bicarbonate anion showed significant effect. The adsorption data were well fitted to the Langmuir isotherm model with a maximum adsorption capacity of 21.1 mg/g. The kinetic studies showed that the adsorption of fluoride by AAABC obeys a pseudo-second-order rate equation with an average rate constant of 9.4×10^{-2} g/min·mg. The adsorbed fluoride could be easily desorbed (85.71 %) by treating the exhausted adsorbent with 0.1 % NaOH.

Due to its high adsorption capacity compared to commercially available aluminium hydroxide-based adsorbents for fluoride removal, AAABC is a highly promising material for defluoridation of drinking water.

Key words: Fluoride, bamboo waste, activated charcoal, adsorption, aluminium hydro(oxide).

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List of Acronyms

AA	Activated Alumina
AAABC	Aluminium-Amended Activated Bamboo Charcoal
AC	Activated Charcoal
BDAT	Best Demonstrated Available Technology
DCs	Developing Countries
ED	Electro Dialysis
FTIR	Fourier Transform Infrared
HMOCA	Hydrous Manganese Oxide Coated Alumina
IE	Ion-Exchange
MAAA	Magnesia-Amended Activated Alumina
MER	Main Ethiopian Rift Valley
MOCA	Manganese Oxide-Coated Alumina
NF	Nano-Filtration
POE	Point-Of-Entry
POU	Point-Of-Use
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solid
THA	Treated Hydrated Alumina
UF	Ultra-Filtration
UHA	Untreated Hydrated Alumina
UNICEF	United Nations International Children's Emergency Fund
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

1. Introduction

1.1. Occurrence of fluoride in ground water

Fluorine is the most reactive and electronegative non-metal which almost never occurs in nature in its elemental state. It is the 13th most abundant element found in the earth's crust (Koritnig, 1951). It usually occurs in rocks and soil in a wide variety of minerals such as fluorspar (fluorite) (CaF_2), cryolite (Na_3AlF_6), apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), and topaz $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$ (Buxton and Shernoff, 1999; WHO, 1994; Hamilton et al., 1982). Fluoride contamination in groundwater has been recognized as one of the serious problems worldwide (Amini et al., 2008).

Environmental pollution caused by fluoride might come naturally or anthropogenic. Fluoride found in minerals and geochemical deposits is generally released into surface and groundwater sources by weathering. Fluorine and its compounds are broadly used in various industries; elemental fluorine is necessary in the preparation of many fluoride compounds, which play an important role in semiconductors, fertilizers, production of high purity graphite, electrolysis of alumina and in nuclear applications. Effluents containing fluorine/fluoride are generated in industries using fluorine or its compounds as a raw material (de la Puente et al., 1997).

The other viewpoint is that fluoride is recognized as essential in the human diet. Maintaining fluoride concentrations of 1 mg/L in the dietary intake can prevent particularly skeletal and dental problems. However, when the fluoride concentration is above this level, it affects the metabolism of elements such as Ca, P in human body and leads to bone diseases (fluorosis), mottling of teeth and lesions of the endocrine glands, thyroid, liver and other organs (Cengeloğlu et al., 2002).

1.2. Health effects

Lack of access to an improved source of drinking water is a global health issue affecting 780 million people worldwide (WHO and UNICEF, 2012). Not considered in this statistics are an estimated 200 million people who are exposed to groundwater containing fluoride concentrations above the World Health Organization (WHO) guideline value of 1.5 mg/L (Amini et al., 2008; WHO, 2011). Elevated fluoride concentrations occur in numerous groundwater globally, including areas of India, China, and the Rift Valley of Africa which includes the Main Ethiopian

Rift Valley (MER) (Amini et al., 2008; Fawell et al., 2006; Fewtrell et al., 2006; Rango et al., 2010, 2012). Many water sources in Ethiopia contain elevated fluoride concentrations up to 26 mg/L (Kloos and Tekle-Haimanot, 1999). According to estimates of the Ethiopian Ministry of Water, Irrigation and Energy, more than 11 million people in the Ethiopian Rift Valley rely on drinking water contaminated by fluoride (Tekle-Haimanot, 2005). Above 40 % of deep and shallow wells are contaminated and over 80 % of children suffering from different degrees of dental fluorosis and skeletal fluorosis is increasing, mainly among older people (Tekle-Haimanot et al., 2006).

Fluoride, being a highly electronegative ion, has an extraordinary tendency to get attracted by positively charged ions like calcium. Hence, the effect of fluoride on mineralized tissues like bone and teeth leading to developmental alterations is of clinical significance as they have the highest amount of calcium and thus attract the maximum amount of fluoride that gets deposited as calcium-fluorapatite crystals. Tooth enamel is composed principally of crystalline hydroxyapatite. Under normal conditions, when fluoride is present in the water supply, most of the ingested fluoride ions get incorporated into the apatite crystal lattice of calciferous tissue enamel during its formation. The hydroxyl ion gets substituted by fluoride ion because fluorapatite is more stable than hydroxyapatite. Thus, a large amount of fluoride gets bound in these tissues and only a small amount is excreted. The most common health problems associated with excess fluoride in drinking water are dental and skeletal fluorosis. Endemic fluorosis is known to be global in scope, occurring in all continents and affecting many millions of people. Cases of skeletal fluorosis have been reported all over the world (Hillier et al., 2000, Tsunoda, H. and Tsunoda N., 1986). Dental fluorosis leads to pitting, perforation, and chipping of the teeth, whereas skeletal fluorosis causes severe pains in joints followed by stiffness, which ultimately leads to paralysis. However, recent studies have proved that the health effects of fluoride are not only restricted to dental or skeletal fluorosis but also cause other health problems whether it is acute (muscular and allergic manifestations, gastrointestinal problems) or chronic (osteosclerosis and increased bone density, cancer).

Table 1: Effect of prolonged use of drinking water on human health, related to fluoride content.
(Hillier et al., 2000).

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
> 10.0	Crippling fluorosis

Since the problem of excess fluoride in drinking water becomes a global scenario, there should be mitigation options to cope up with the fluorosis problem.

1.3. Fluorosis mitigation options

1.3.1. Search for alternative sources

If the fluoride concentration in a community's water supply is significantly and consistently beyond the permissible level, it is necessary to consider remedial measures to cope up with the problems of high intake of fluoride. Searching for water with a lower fluoride concentration should be the main choice (Lyengar, 1996).

a) Provision of a new and alternate source of water with acceptable fluoride levels

It may be possible to get a safe water source in the vicinity by drilling a new well and/or drawing the water from different depths, as leaching of fluoride into groundwater is a localized phenomenon. Periodic monitoring is needed though, as mixing of water from different aquifers with different fluoride concentrations can occur.

b) Transporting water from a distant source

This may lead to durable benefits, but initial cost will be high. Such an approach has been implemented in endemic fluorosis areas in few countries. For example in Ethiopia, Wonji/Shoa sugar state was connected to Adama treated surface water supply system dependent on the Awash River (Tekle-Haimanot, 2005).

c) Blending high fluoride with low fluoride water

This mitigation method involves mixing of high and low fluoride containing waters so as to bring the concentration within permissible levels, provided that the low fluoride source is available within reasonable distance and is of acceptable quality with respect to other health standards/parameters.

d) Rainwater harvesting

Individual household-roof rainwater harvesting and container storage of the rain water can provide potable water for families. Harvested surface water run-off can be used to recharge high-fluoride containing groundwater sources.

1.3.2. Defluoridation of water

In some cases when the above techniques could not be applied to maintain the level of fluoride to the acceptable level, defluoridation of drinking water has to be implemented. Defluoridation of drinking water is then available for the community in the way that the central treatment of water at the source or the treatment of water at the point of use/ at the household level. But defluoridation method at community scale is more advantageous than defluoridation at the household level because of cost, accessibility and simplicity.

1.4. Available technologies for fluoride removal

1.4.1. Precipitation/coagulation

In this method, fluoride removal from water is mediated by calcite, $Mg(OH)_2$, $Al(OH)_3$ or $Fe(OH)_3$ floc formation. The principle involved in this technology is that the fluoride ions adsorb on the formed flocs and are then successively removed either simultaneously in succeeding treatment units such as sedimentation, fixed bed or microfiltration unit. A lot of studies have been reported on the use of alum (Mekonen et al., 2001) and lime (Mjengera, and Mkongo, 2003; Shen et al., 2003). In the 70 s, a co-precipitation technique, the so called “Nalgonda technique”, was introduced to the Indian population for fluoride removal from drinking water and also has been tested at pilot scale level in DCs such as Kenya, Senegal and Tanzania. The method involves the addition of alum and lime into water followed by rapid mixing. After some time, the stirring intensity is reduced and this induces floc formation that is subsequently removed by

simple settling. Although precipitation is an economical and a robust technique in the removal of fluoride from water, the technique has been found to suffer from excessive sludge generation and dewatering such sludge has proven to be difficult since the solid size and content are extremely small and low, respectively. Considering the fact that chemical handling is involved in precipitation/coagulation technique, this technique may not be popular with many uneducated groups, especially in LDCs. Therefore, the technique is only suited to centralized water treatment system. In line with the above disadvantages, this technique has not been very attractive to many end users.

1.4.2. Membrane techniques

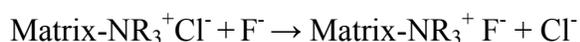
Globally as the quality of drinking water sources gets worse, the outdated water treatment systems need to be modernized. There are many alternative innovative and efficient technologies which are pressure-driven membrane systems such as reverse osmosis (RO), nano-filtration (NF) and ultrafiltration (UF) and electric-driven membrane system such as electro-dialysis (ED).

Production of water of invariable quality, smaller consumption of chemicals, lower consumption of energy, compactness of the installation, possibility to effect full automation of the process, application in both small and larger scale treatment systems as point of entry (POE) and point of use (POU), and simultaneous removal of other dissolved species in water are among the basic advantages over the traditional water treatment systems. Owing partly to the above wholesale advantages, several studies have recently been reported on the use of membranes, in particular NF and RO membranes. Pontie' et al. (2003) and Diawara et al. (2003) have presented various aspects of application of NF to defluoridation of water, while Arora et al. (2004) have studied extensively on the use of RO for the treatment of water containing high level of fluoride under various experimental conditions such as feed composition and pH. They found that up to 95 % of fluoride could be removed from water. At present, the WHO and United States Environmental Protection Agency (USEPA) classify RO as one of the best demonstrated available technology (BDAT). Excitingly, Lhassani et al. (2001) have shown that by optimizing the pressure, selective desalination of fluorinated brackish water by NF is viable and drinking water can be produced at much lower cost than by using RO. Although membrane use has received universal acceptance, a number of limitations has slackened its use in some regions. Fouling arising from feed water

characteristics is a major problem and due to high quantity of water rejection typically between 35 % and 65 %, it is not suitable to regions where water scarcity is observed. Moreover, brine discharge from RO plant is highly concentrated and requires further treatment, which is costly and requires high technology for operation and maintenance. Therefore it does not outfit the developing countries like Ethiopia.

1.4.3. Ion-exchange

Ion-exchange resins have also been evaluated for fluoride removal from drinking water. Fluoride can be removed from water with a strongly basic anion-exchange resin containing quaternary ammonium functional groups. The removal takes place according to the following reaction:



The chloride ions of the resin were replaced by the fluoride ions, in which the process continues until all the sites on the resin are occupied. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt to recharge it with chloride ions replacing the fluoride ions and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electronegativity of the fluoride ions.

1.4.4. Adsorption

Adsorption in water treatment is a vigorous technique for removing water-soluble ions, especially when the ions exist in water at low concentrations. A comprehensive review of the literature reveals that fluoride removal through adsorption onto various materials is most promising in terms of cost of the medium and running costs, ease of operation, adsorption capacity, potential for reuse, number of useful cycles, and possibility of regeneration. Adsorption processes involve the passage of the water through a contact bed where fluoride is removed by ion-exchange or surface chemical reaction with the solid bed matrix. In the past few years, surface adsorption is the most interesting area of research for removing fluoride from water. This method is frequently used by many water treatment plants as it can operate at high flow rates, can produce high quality of water without the generation of sludge, and removes contaminant from water very effectively using materials that are efficient and economical defluoridating agent. Activated alumina, activated carbon, activated alumina-coated silica gel, calcite, activated

saw dust, activated coconut shell carbon-activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent, carbon, defluoron-1, and defluoron-2 are among adsorbent materials reported in the literature (Wang and Reardon, 2001; Thergaonkar and Nawalakhe, 1971; Savinelli and Black, 1958; Rongshu et al., 1985; Padmavathy et al., 2003; Nava et al., 2003; Muthukumaran et al., 1995; Min et al., 1999; Barbier and Mazounie, 1984; Ghorai and Pant, 2004; Kariyanna, 1987).

The most commonly used adsorbents are activated alumina and activated carbon. The adsorption process can remove up to 90 % fluoride and the treatment is very cost-effective. Regeneration is required as effectiveness of the adsorbent for fluoride removal is reduced after each regeneration cycle.

Table 2: Advantages and limitations of available technologies for fluoride removal

Technologies	Advantages	Limitations
Precipitation-coagulation	<ul style="list-style-type: none"> • established method • most widely used method, particularly at the community level 	<ul style="list-style-type: none"> • low treatment efficiency of ~70 % (which means the process cannot be used in cases of high fluoride contamination) • requirement of large dosage of aluminum sulfate, up to 700-1200 mg/L • adverse health effects of dissolved aluminum species in the treated water • requirement of skilled manpower (hence the technique is not suitable for rural areas where the fluoride problem is more severe) • low solubility of

		precipitating agents which does not allow complete removal of fluoride, and poor settling characteristics of the precipitate
Membrane techniques	<ul style="list-style-type: none"> • highly effective technique • no chemicals are required • no interference by other ions • Works under a wide pH range. 	<ul style="list-style-type: none"> • skilled labor required • relatively higher cost • may not be suitable for water with high salinity and TDS (total dissolved solids) • RO systems produce concentrated brine discharges that must be disposed off safely • RO systems also results in significant water loss and are not suitable for arid regions • ED process is energy intensive and hence is not suitable for rural applications
Ion-exchange	<ul style="list-style-type: none"> • removes up to 90-95 % fluoride • retains the taste and color of water intact 	<ul style="list-style-type: none"> • presence of SO_4^{2-}, PO_4^{3-}, HCO_3^-, etc. results in competition • relatively higher cost • treated water sometimes has a low pH and high levels of chloride
Adsorption	<ul style="list-style-type: none"> • locally available adsorbent 	<ul style="list-style-type: none"> • process is dependent on pH

	materials <ul style="list-style-type: none"> • high efficiency • cost effective. 	<ul style="list-style-type: none"> • presence of SO_4^{2-}, PO_4^{3-}, HCO_3^-, etc. results in ionic competition • regeneration is required • disposal of fluoride-laden material.
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1.5. Rationale of the study

The defluoridation methods commercially available and used by industrialized countries are adsorption by activated alumina, reverse osmosis, electro-dialysis and ion-exchange. These methods require more technical support for operation and maintenance also the capital investment cost is very high. Hence, the need to find locally-available defluoridation media as an alternative method for safe and easy use at both household and small community levels is desirable.

Activated carbon is generally recognized as an effective adsorbent due to its high porosity, large surface area, and high catalytic activity, and is currently widely used for the removal of organic compounds in drinking water. However, activated carbon has a relatively small adsorption capacity as well as an affinity for inorganic pollutants such as fluoride. To enhance adsorption efficacy, the modification of existing carbon-based adsorbents with suitable chemicals has been investigated with promising results, suggesting that the new adsorbents might remove fluoride from aqueous solutions effectively. This is because, fluoride has a strong affinity towards metal ions including Al(III), Fe(III), and La(III). Dispersing a mixture of these metals in a protective matrix would limit the total dissolved solids in treated water, and at the same time would provide high fluoride adsorption capacity. For example, maximum fluoride uptake capacity has been achieved by activated carbon impregnating with aluminum or calcium compounds.

In addition, the operational costs of adsorption are mainly determined by the price of the adsorbent, and thus there is a growing interest in looking for alternative precursors (i.e., wastes) in AC production. Residues generated during production of bamboo furniture are abundant and

not reused in Ethiopia; as a consequence, the activated carbon can be used as low-cost adsorbent or as a support for aluminium oxide for the adsorption of fluoride from drinking water.

A fluoride removal method using aluminium hydro(oxide) (AO) as an adsorbent has been under development in the Chemistry Department of Addis Ababa University (AAU) since 2004. The AO can easily be produced from locally manufactured aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, which is purchased from Awash Melkasa Aluminium Sulfate and Sulfuric Acid Factory, Ethiopia. Laboratory tests have demonstrated a very high removal capacity of about 23.7 mg/g (Shimelis *et al.*, 2006). Studies so far have indicated that the adsorbent has better performance than activated alumina (AA), which is a well-known commercially available material for fluoride removal. The AO technology has also been tested as pilot community defluoridation method in Ethiopian Rift Valley and showed promising results. However, this highly promising adsorbent needs to be combined with AC to reduce the cost of production at large scale and also AC is believed to be suitable for different applications including fluoride removal from drinking water.

1.6. Objectives

1.6.1. General objective

The main aim of this study is to develop low cost, high capacity fluoride removal technology, using aluminum-amended activated bamboo charcoal prepared from bamboo waste.

1.6.2. Specific objectives

The specific objectives of the present study include but not limited to:

- Preparation of activated charcoal from locally available bamboo waste
- preparation of AAABC
- characterize the AAABC using XRD, SEM, EDS, SSA and PZC.
- carrying out the batch adsorption experiments to study the effect of adsorbent dose, contact time, initial fluoride concentration, pH and co-existing anions on fluoride removal by AAABC
- investigate the adsorption isotherm and kinetics using conventional models
- evaluate the regeneration potential of AAABC
- compare the results with similar studies that are currently being published

2. Literature review

2.1. Adsorbent materials

2.1.1. Alumina and aluminum-based adsorbents for defluoridation of water

2.1.1.1. Activated alumina

Activated alumina (AA) has been used as adsorbent of interest and extensively studied for fluoride removal from drinking water. It has a high affinity and selectivity for fluoride. Defluoridation processes based on AA have been used at both community and domestic levels. The term “activation” is used to indicate a change in properties resulting from heating. In general, as a hydrous alumina precursor is heated, water is driven off leaving a porous solid structure of activated alumina. Farrah et al. (1987) studied the interaction of fluoride ion with amorphous $\text{Al}(\text{OH})_3$, gibbsite and alumina (Al_2O_3) over a wide pH range (3-8) and F^- concentrations (0.1-1.0 mM). It was found that at $\text{pH} < 6$ and total F:Al ratios > 2.5 , most of the amorphous $\text{Al}(\text{OH})_3$ gel dissolved through the formation of AlF_x complexes. At lower F:Al ratios, some solid persisted in the pH 4-7 region and strongly adsorbed F^- from solution. It was also observed that maximum uptake of F^- occurs in the pH range of 5.5-6.5 (up to 9 mol/kg). At lower pH, fluoride uptake decreased due to the preferential formation of AlF_x soluble species; at higher pH, OH^- displaced F^- from the solid and the amount of F^- adsorbed or converted to complexes declined rapidly towards zero between pH 6 and 8. At a fixed pH (between 5 and 7.5), fluoride uptake varied in accordance with Langmuir model (maximum capacity ~ 1 mol/kg). The amount of substrate converted into AlF_x complexes in acid media increased with decreasing pH and increasing initial fluoride concentration.

Ghorai and Pant (2004) concluded that removal of fluoride was the result of ion-exchange as well as adsorption, which follows both Freundlich and Langmuir isotherms (Ghorai and Pant, 2004; Ghorai and Pant, 2005). AA has a great capacity for fluoride adsorption, which is dependent upon the crystalline form, activation process, solution pH, and alkalinity. Shimelis et al. (2006) also showed the importance of activation by comparing untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) obtained from hydrolysis of locally manufactured aluminium sulfate.

The use of activated alumina in a continuous-flow system was reported to be an economical and efficient method for defluoridating water supplies (Ghorai and Pant, 2004), and an adsorption capacity of 1.45 mg/g at pH 7 can be achieved. The greatest disadvantage of fluoride removal by activated alumina is that the optimum fluoride removal capacity occurs only at a pH value of the solution below 6.0, which strongly limits the practical applications of the AA. The authors observed that adsorption of fluoride was retarded in acidic solutions because of the electrostatic repulsion and when equilibrium solution pH was greater than 7, the fluoride adsorption by alumina decreased due to the electrostatic repulsion of fluoride ions by the negatively charged surface of alumina and the competition for active sites by excessive amounts of hydroxide ions. In addition interference due to the presence of other anions/cations has been reported to affect fluoride removal capacities of AA (Li et al., 2001).

Ghorai and Pant (2004) investigated the removal of fluoride using activated alumina (AA) in batch and continuous experiments. An adsorption capacity of 1.45 mg/g was obtained at pH 7. The percentage of fluoride removal increased in the pH range from 4 to 7 and subsequently decreased. At $\text{pH} > 7$ silicates and hydroxyl ions were well-thought-out to compete strongly with F^- ions for alumina exchange sites, whereas, at $\text{pH} < 7$, the soluble alumino-fluoro complexes were formed which in return accounts for the presence of aluminum ions in the treated water. Early saturation and lower percentage fluoride removal was observed at higher flow rates and at higher concentrations. There was a minimal decrease in the adsorption capacity after each regeneration cycle. Regeneration procedure resulted in 85 % efficiency with the grade of AA studied. A loss of 5 % in adsorption capacity of AA was observed after five cycles.

2.1.1.2. Modified aluminium based adsorbents

Alumina plus iron oxide

When aluminium and iron(III) hydroxides are co-precipitated from a chloride mixture in equimolar quantities using ammonia, the resulting mixed hydroxide, after aging and drying, is a better adsorbent for fluoride than either aluminium hydroxide or iron(III) hydroxide (Biswas et al., 2007).

Data obtained from Fourier transform infrared (FTIR) spectra indicate the presence of the Fe-O-Al bond. Scanning electron microscopy (SEM) showed an almost irregular surface morphology with high porosity, indicative of a high surface area. The monolayer adsorption capacity of the mixed hydroxide, derived from Langmuir isotherms, was greater than for the pure hydroxides.

Chubar et al. (2005) studied the anion adsorption capacity of an adsorbent precipitated from equimolar aluminium and iron (III) chloride by addition of ammonia. The anions investigated were fluoride, chloride, bromide and bromate. Fluoride was the most strongly adsorbed at 88 mg F⁻/g of adsorbent at pH 4.

Kamble et al. (2010) reported the effectiveness of alkoxide-origin alumina, γ -alumina containing small amounts of Fe₂O₃ and SiO₂ as well as activated carbon in its pores, for defluoridation of drinking water. The maximum fluoride removal efficiency was observed in the pH range of 5-7. Co-existing anions such as carbonate, bicarbonate and sulfate significantly reduced the fluoride sorption due to the change in solution pH and competition for active sorption sites. The reason for increased adsorption by the alkoxide-origin alumina was attributed to the increased electropositivity and the small hydrophobicity retained on the alkoxide origin alumina. The breakthrough adsorption capacity was found to be strongly dependent on the feed flow rate, inlet fluoride concentration and bed height.

Alumina plus manganese dioxide

In order to improve the adsorption efficiency of activated alumina, researchers have also modified the alumina surface. Maliyekkal et al. (2006) reported that manganese oxide-coated alumina (MOCA) was able to make fluoride concentrations down to the permissible limit of 1.5 mg/L for drinking water and was faster-acting than activated alumina and had a greater fluoride load capacity (2.85 mg/g compared with 1.08 mg/g for activated alumina). The MOCA was effectively regenerated using 2.5 % NaOH as eluent. Tripathy and Raichur (2008) found that manganese dioxide-coated activated alumina could bring fluoride concentration down to 0.2 mg/L when the initial concentration of fluoride in water is 10 mg/L.

Teng et al. (2009) investigated the sorption efficiency of a novel hydrous-manganese-oxide-coated alumina (HMOCA) by coating hydrous manganese oxide onto alumina surface through a

redox process and used it for defluoridation. The manganese oxides were amorphous and manganese existed mainly in +IV oxidation state. The prepared adsorbent could reduce fluoride concentration from 6.0 to 0.45 mg/L at an initial pH of 5.2 ± 0.05 , while the fluoride removal efficiency was 45 % for the virgin activated alumina under the same condition. The optimum initial pH range of fluoride adsorption by HMOCA was 4.0-6.0 with fluoride removal efficiency higher than 95 %. The presence of bicarbonate, sulfate, and phosphate showed negative influence on the adsorption of fluoride. The adsorbed fluoride could be desorbed by alkali solution.

Alumina plus magnesium oxide

Recently Maliyekkal et al. (2008) considered a magnesia-amended activated alumina (MAAA) prepared by impregnating alumina with magnesium hydroxide and calcining it at 450 °C. MAAA adsorbed fluoride from drinking water more effectively than activated alumina. More than 95 % removal of fluoride (10 mg/L) was achieved within 3 hr. of contact time at neutral pH, bringing concentration down to only 0.5 mg/L. Sorption of fluoride on to MAAA was found to be pH-dependent which decrease at higher pH. An optimum fluoride removal was observed in the pH range of 5.0-7.5. The maximum adsorption capacity for fluoride was 10.12 mg/g in the fluoride concentration range of 5-150 mg/L. Most of the co-existing anions found in the natural water source studied had negligible effect on fluoride sorption by MAAA. However, higher concentrations of bicarbonate and sulfate reduced the fluoride adsorption capacity.

2.1.2. Calcium-based adsorbents

Calcium has a good affinity for fluoride anion and it has been used for fluoride removal in different fields. Wide-ranging research has also been carried out for the removal of fluoride using various calcium salts. Fan et al. (2003) considered the fluoride adsorption on a wide range of minerals including fluorite, calcite, quartz and iron-activated quartz. Their fluoride uptake capacities were also compared.

Turner et al. (2005) studied the sorption of fluoride using crushed limestone in batch experiments and surface-sensitive techniques from solutions having fluoride concentration of 3 to ~ 2100 mg/L. With the help of surface-sensitive techniques, they were able to confirm that a combination of surface adsorption and precipitation reactions removed fluoride from aqueous

systems such that the degree of removal being dependent on calcite surface area. The results proved that fluoride adsorption occurred immediately over the entire calcite surface with fluoride precipitating at step edges and kinks, where dissolved Ca^{2+} concentration was highest.

Performance of activated lime and ordinary quick lime were also evaluated for fluoride removal from aqueous solutions (Islam and Patel, 2007). At optimum condition the percentage removal of fluoride was 80.6 % when artificial initial fluoride concentration was 50 mg/L. The Langmuir maximum adsorption capacity of activated quick lime was 16.67 mg/g. Different anions reduced the fluoride adsorption in the order of $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{NO}_3^-$.

Johnson et al. (2011) have assessed the technical performance, user acceptance and optimal institutional setting of bone char-based community and household filters for sustainable implementation of fluoride removal in Ethiopia. The bone char has an average adsorption capacity of about 1.2 before treated water exceeds 1.5 mg F⁻/L. Bhargava and Killedar (1992) have studied the fluoride adsorption on fishbone char. The shortcomings of bone char in developing countries include: social unacceptability, religious issue, cost, unreliable supply of animal bones and insufficient effectiveness to reduce fluoride concentration to the desired level. For instance, bone char materials are not acceptable in some parts of Ethiopia for cultural and religious reasons.

2.1.3. Carbon-based adsorbents

Some researchers have also used carbon as an adsorbent for fluoride removal. Granular activated carbon was coated with manganese oxides and used for fluoride removal from water and showed maximum adsorption capacity (Ma et al., 2009). Its adsorption capacity was three times higher than the uncoated granular activated carbon. At pH 3, maximum fluoride adsorption was observed. Carbons loaded with specific chemical moieties were prepared from pecan nut shells employing a natural modifying agent obtained from egg shell, which is rich in calcium, for the selective adsorption of fluoride from water. Results showed that carbons obtained from pecan nut shells modified with a calcium solution extracted from egg shells were more effective for fluoride removal than those using the nut shell precursor as such (Montoya et al., 2012).

Continuous down flow adsorption mode at room temperature was also adopted to fluoride sorption in drinking water using zirconium impregnated activated charcoals by Janardhana et al (2007). Fluoride adsorption capacity of impregnated activated charcoals was 3-5 times higher to that of plain activated charcoal. Zirconium ion impregnated coconut fiber charcoal (ZICFC) which has large surface area showed maximum fluoride removal. ZICFC was found effective for 21 L (8.0 mg F⁻/L) test solution and 6 litre (2.47 mg F⁻/L) tap water. Regeneration of ZICFC was conducted by elution with 0.02 M NaOH solution.

Amorphous and highly porous charcoal adsorbents that contain dispersed aluminum and iron oxides have been synthesized by impregnating wood with salt solutions (Eric et al 2010). The adsorbents exhibited the best efficiency with a fluoride sorption capacity of 13.64 mg/g. More than 92 % removal of fluoride was achieved within 24 hr. from a 10 mg/L solution at neutral pH.

2.1.4. Other metal oxides/hydroxides/oxyhydroxides, mixed metal oxides, metal-impregnated oxides as sorbents for defluoridation of water

Various researchers also developed synthetic adsorbents using two or multi-metal oxides/hydroxides for fluoride removal. Defluoridation by an inorganic cerium based adsorbent (CTA) was studied (Zhongzhi et al., 2004). The prepared CTA showed appreciable adsorption capacity for fluoride. The adsorption isotherm data followed Freundlich isotherm, and low pH favoured fluoride removal. The authors also investigated fluoride removal mechanism and found that hydroxyl group of CTA adsorbent played an important role in fluoride removal. The metal oxyhydroxides have surface oxygen which differs in the number of coordinating metal ions to facilitate the adsorption of different cations and anions. This property of oxide minerals was considered as an advantage for fluoride removal by Mohapatra et al. (2004). It was suggested by the authors that various oxyhydroxides could also provide a viable cost-effective alternative to activated alumina. Refractory grade bauxite (RGB), feed bauxite (FB), manganese ore, and hydrated oxides of manganese ores (WAD) were taken as test adsorbents for fluoride removal from aqueous solutions. Preliminary experiments showed that RGB had high fluoride removal efficiency compared to the other three adsorbents. The percentage of fluoride adsorption onto RGB was found to increase with pH up to 5.5 but decreased with further increase in pH. As RGB contains mainly oxides of aluminium and iron and these oxides in aqueous medium would be

hydroxylated to develop a surface charge, thus, adsorption of fluoride by oxide species was modelled as a two-step ligand exchange reaction. The adsorption process was observed to be exothermic, as the adsorption efficiencies decreased with increase of temperature.

Sol-gel method was employed to obtain $\text{CeO}_2\text{-TiO}_2\text{/SiO}_2$ surface composites and further used to determine its potential for fluoride removal by Xiuru et al. (1998). The surface composite exhibited an adsorption capacity of 21.4 mg/g for fluoride. The potential of fluoride removal by magnesia-amended silicon dioxide granules (MAS) was investigated by Zhu et al. (2009). The authors performed the modification of silicon dioxide by wet impregnation with magnesium chloride solution. The porous structure and high surface area of the modified granules made them suitable for adsorption of fluoride. Maximum fluoride adsorption was found in pH range between 3 and 4 and defluoridation decreased sharply as pH increased above 10. The decrease of defluoridation was explained by the change in surface charge of the adsorbent. The maximum defluoridation capacity was reported as 12.6 mg/g at pH 3. The reduction of fluoride adsorption was observed in the order: bicarbonate > sulfate > phosphate. The reduction in fluoride removal in presence of bicarbonate and sulfate was attributed to the competition from these ions for active adsorption sites or due to the change in pH or combination of these two. To increase the fluoride adsorption capacity of iron (III) oxide from the contaminated water, Biswas et al. (2009) incorporated tin(IV), a cation with high positive charge, into the lattice structure of iron(III) oxide and used as an adsorbent for the removal of fluoride from the aqueous phase. The fluoride adsorption capacity of synthetic iron (III)-tin (IV) mixed oxide (HITMO) was nearly constant in the pH range 5.0-7.5 which was presumably due to the neutral or near neutral surface of the solid. The Langmuir model described the equilibrium data well with the capacity of 10.50 mg/g. The mean free energy of adsorption (EDR) value suggested that fluoride removal mechanism by HITMO was mainly governed by anion-exchange. Bicarbonate was the only competing anion which showed an adverse effect on fluoride removal. The solution pH 13.0 could regenerate 1.0 g fluoride-rich adsorbent up to a level of 75%. Two gram HITMO per litre of the fluoride-doped (2.97 mg/L) natural water reduced fluoride level below 1.5 mg/L.

The same workers also prepared synthetic hydrous iron (III)-chromium (III) bimetal mixed oxide (HICMO) (Biswas et al., 2010) and tested for fluoride removal from water. Maximum fluoride

removal was observed at initial pH 3.0, which was attributed to the strong affinity of fluoride for the positive surface charge or replacement of surface hydroxide ion with fluoride of HICMO (pHzpc 6.5). The fluoride removal decreased in the range of pH 3-5 which was explained due to the decrease of positive surface charge density or ligand exchange capacity of HICMO. The adsorption capacity between initial pH 5.0-7.0 was nearly same, which is apparently due to the neutral or near neutral surface of the solid as the analyzed final pH values were 6.4. The rapid decline of fluoride removal above pH 7.0 was described as the result of competition of fluoride with hydroxyl ions for the secondary adsorption sphere where the Na^+ (available in solution) would be at the primary adsorption sphere on the solid surface. The Langmuir monolayer adsorption capacity for fluoride was found to be 16.34 mg/g. The competing ions were found to show negative influence on sorptive removal of fluoride. The 0.5 M NaOH solution was found effective in desorbing 91% of the adsorbed fluoride from the HICMO. The same workers also synthesized hydrated iron (III)-aluminium (III)-chromium (III) ternary mixed oxide (HIACMO) and investigated its potential for fluoride removal (Biswas et al., 2010). Fluoride adsorption was found to be pH sensitive and optimum pH (initial) was between 4.0 and 7.0. Less fluoride adsorption at pH 3.0 was attributed to slight solubility loss of the adsorbent. At $\text{pH} < 5.50$, the positive surface of the adsorbent ($\text{pHPZC} = 5.5-5.7$) was explained to be adsorb fluoride with electrostatic force of attraction or by exchange of hydroxyl ion on the solid surface. The equilibrium data fitted well to the Langmuir isotherm model from which the monolayer adsorption capacity estimated was 31.889 mg/g. Regeneration of fluoride adsorbed material with 0.5 M NaOH solution indicated the reversibility of reaction Xu et al. (2001) prepared cerium (IV) oxide coated on SiMCM-41 ((Ce)SiMCM-41) by using the wetness impregnation-coprecipitation method for the removal of fluoride from water. The adsorption capacity of fluoride on the adsorbent increased with increasing Ce/Si ratio, and the maximum removal was obtained for Ce/Si = 1/30. The Langmuir adsorption capacity of (Ce)SiMCM-41 for fluoride was observed to be 6.02 mmol/g. The adsorption mechanism was explained by the anion-exchange between the hydroxyl groups existing on the surface of (Ce)SiMCM-41 and fluoride ions.

Rare earth metals have restricted use in drinking water clean-up as they are expensive and the optimum pH is in the acidic range. Mixing rare earth metals with cheaper metals or loading rare

earth metals on support materials has been found to be an economic way to reduce the use of expensive rare earth metals, and at the same time to achieve high fluoride adsorption capacity. Liu et al. (2010) prepared Al-Ce hybrid adsorbent through the co-precipitation method and evaluated its performance for fluoride removal. The SEM and XRD results revealed that the hybrid adsorbent was of amorphous structure with some aggregated nanoparticles. The maximum adsorption capacity of the Al-Ce adsorbent for fluoride was 91.4 mg/g at 25°C. The adsorption of fluoride on the adsorbent was fast, and the maximum adsorption capacity was achieved at about pH 6. The higher adsorption capacity at lower solution pH was related to the surface charge of the Al-Ce adsorbent. The adsorbent was effective in fluoride removal from aqueous solution via electrostatic interaction due to the high zero point of potential (9.6). FTIR analysis and zeta potential measurement confirmed that the hydroxyl and the protonated hydroxyl groups on the adsorbent surface were involved in the fluoride adsorption at high and low solution pHs, respectively. Wu et al. (2007) developed a Fe-Al-Ce trimetal oxide adsorbent with a relatively high pHzpc and tested its potential for fluoride removal. The adsorbent was reported to maintain relatively stable fluoride adsorption performance at calcination temperatures lower than 600°C. A high fluoride adsorption capacity (178 mg/g) was acquired under an equilibrium fluoride concentration of 84.5 mg/L, adsorbent dose of 150 mg/L and pH 7.0. The adsorbent showed a considerably high adsorption capacity over a relatively wide pH range of 5.5-7.0, pH_{zpc} of the adsorbent being 7.5. The pHPZC played an important role in fluoride removal. At pH > 7.5, the zeta potentials were negative and further were observed to decrease with pH increase, which tended to repel the fluoride ions via coulombic repulsion. This accounted for the first factor for the decrease of fluoride removal at higher pH. The other factor was considered to be the competition between hydroxyl ions and fluoride on the active adsorption sites. The amount of fluoride adsorbed was also found to decrease with the decrease of pH from 6.0 to 4.0 in spite of the increase of the zeta potential which was attributed to the formation of hydrofluoric acid, which reduced the coulombic attraction between fluoride and the adsorbent surface. The existence of heterogeneous active sites on the adsorbent surface was confirmed by the effect of competitive anions as fluoride adsorption was partially inhibited by high concentrations of phosphate or arsenate, whereas fluoride removal was not affected by the presence of chloride and sulfate, and was only influenced by nitrate when NO³⁻-N concentration exceeded 50 mg/L. A high desorption efficiency of 97% was achieved by treating fluoride

loaded Fe-Al-Ce oxide with NaOH solution at pH 12.2. The column experiment was also conducted at an initial fluoride concentration of 5.5 mg/L, and pH of 5.8, and 2240 bed volumes were treated with the effluent fluoride under 1.0 mg/L.

Sujana et al. (2009) conducted defluoridation studies using amorphous iron and aluminium hydroxides with different molar ratios. The compositions (Fe:Al molar ratio) of the oxides were varied as 1:0, 3:1, 2:1, 1:1 and 0:1. The optimum pH for fluoride adsorption was found to be 4-5 for the oxide sorbents having molar ratio: 1:0, 3:1 and 2:1, whereas it was in the range of 4.0-7.5 for 1:1 and 0:1 and was attributed to both specific and nonspecific adsorption on the sorbent surfaces. All samples exhibited high Langmuir adsorption capacities and the oxide adsorbent with molar ratio 1 showed maximum adsorption capacity of 91.7 mg/g. Adsorption and desorption studies were also conducted to gain an insight into the adsorption mechanism on Fe/Al hydroxides surface by Sujana and Anand (2010). XRD results indicated the formation of new complexes on the fluoride sorbed adsorbent surface. Concentration of other anions such as PO_4^{3-} , SO_4^{2-} and arsenate had an adverse effect on fluoride removal efficiency of adsorbent. A maximum regeneration of 80.5 % was obtained with 0.5 M NaOH.

3. Materials and Methods

3.1. Optimization and preparation of activated charcoal (AC)

To prepare the best adsorbent material, different parameters were investigated and optimized. First to choose the activating chemical, bamboo precursor was immersed in 28 % H_3PO_4 in a 2:1 acid to bamboo ratio for 1 hr. Then the bamboo was separated from the solution and dehydrated in an oven overnight at 105 °C. Next, the dry bamboo was kept for further thermal treatment. In addition, the bamboo precursors were also treated with $\text{AlCl}_3/\text{FeCl}_3$ mixture as they were impregnated with a boiling mixture of 1 M AlCl_3 and 1 M FeCl_3 aqueous solution for 90 min. After heating, the samples were immersed in the aqueous solution for 2 hrs. The impregnated wood was removed from the solution, then dried in air for 2 hrs. and later in an oven at 105 °C for 24 hrs.

Both the impregnated dried samples were placed on a crucible and heated at different temperature (400, 500 and 600 °C) for 1 hr. The carbonization process was carried out in the absence of air. The resulting samples were washed with distilled water, dried and ground to particle size of less than 0.25 mm and stored for further coating and analysis.

3.2. Preparation of the adsorbent (AAABC)

Aluminium amended activated bamboo charcoal (AAABC) was prepared as follows. Bamboo waste discarded from the production of bamboo furniture was cut into pieces approximately 1 x 1 cm^2 in size. It was washed with distilled water and dried at 105 °C for 12 hr. The bamboo precursor was immersed in a boiling mixture of 1M $\text{FeCl}_3/\text{AlCl}_3$ and heated for 90 min. After heating, the sample remained immersed in the aqueous solution for 2 hr. Next the impregnated bamboo was removed, dried in an open air for 2 hrs. and dehydrated in an oven overnight at 105 °C. The dried bamboo then was put on a crucible dish placed in a muffle furnace and heated to 400, 500 & 600 °C for 1hr. After heating, sample was cooled, washed with hot then cold distilled water until pH value of the filtrate become steady and then dried. The resulting sample was ground to particle size <0.35 mm for further amendment process.

The prepared activated carbon was soaked in the AO solution in a 1:1 ratio of AO: AC for 2 days and the mixture was stirred continuously to ensure thorough mixing and the resulting lower pH

(about 3) was adjusted to pH 7 using 2 M NaOH. Finally, the mixture was filtered and then dried in an oven at 105 °C then calcined at 300 °C for 1 hr. and kept for further analysis and characterization. The AO adsorbent was prepared by dissolving locally available aluminium sulfate (100 g) into 500 mL of deionized water, while stirring with a magnetic stirrer until complete dissolution as described elsewhere (Mulugeta et al., 2014).

The performance of activated carbon prepared from bamboo waste in the laboratory was also compared with different commercially available activated carbon which is made in China and England. Both granular and powdered AC were tested for sorption, under similar condition. Additionally the contact time of the AO/AC mixture was varied at different time intervals, ranging from 1-5 days and its performance was investigated.

3.3. Characterization of the Adsorbents

X-ray diffraction (XRD) analysis of adsorbents was done with a Rigaku Ultima IV powder X-ray diffractometer with Cu K α radiation and Bragg-Brentano optics. McCrone micronizing mill was used for crushing, grinding, and homogenizing the samples for XRD analysis. Samples were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) using a Zeiss Neon SEM operating at 10 kV.

Specific surface area (SSA) was determined using BET analysis using a Quantachrome Autosorb Automated Gas Sorption System with a Beckman Coulter SA-3100 Surface Area Analyzer and N₂ adsorption. The point of zero charge (PZC) was measured by potentiometric mass titrations technique (Bourikas et al., 2003). PZC was identified as the common intersection point (CIP) of the potentiometric curve of the blank solution with the corresponding curves of the impregnating suspensions containing 0.5, 1.0, and 1.5 g of the adsorbent in electrolytic solution (50 mL of 0.03 M NaNO₃). The experiment was performed, under a N₂ atmosphere and the aqueous suspensions were equilibrated for 1 hr to reach an equilibrium pH value. Small amount of 1 M NaOH was added to make the pH around 10 and recorded as initial pH after 15 min. Then the solid suspensions were titrated by 0.1 M HNO₃, using 665 Dosimat (Metrohm, Switzerland). The pH of each suspension was then measured at 2 min time interval using a digital pH meter standardized by buffers (WTW Inolab pH/ION Level 2, Germany).

The concentration of total acidic and basic groups on AAABC surface was determined from NaOH and HCl uptake, respectively. 100 mg of AAABC samples were placed in 50 mL of 0.05 M NaOH or 0.05 M HCl. Sealed beakers that contained samples or blanks were shaken for 24 hr. and filtered. Then 10 mL of each filtrate were titrated with 0.05 M of either NaOH or HCl solution. The difference between the NaOH and HCl consumption by the blank and samples was calculated and translated to the equivalent acid or base content per gram of the solid adsorbent. (Eric et al., 2010)

3.4. Batch adsorption studies of AAABC

Batch experiments were conducted in 500 mL Erlenmeyer flask under continuous mixing condition with magnetic stirrers at room temperature (23 ± 2 °C). A sample was taken timely as required, filtered and analyzed for residual fluoride concentrations. The defluoridation capacity and the fluoride removal efficiency at a given time under specified conditions were determined based upon the measurement of liquid phase concentration.

The percent adsorption efficiency and the defluoridation capacity at a given contact time for the selected adsorbent was determined using the following equations:

$$\% \text{ Efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100 \dots\dots\dots (1)$$

$$\text{Defluoridation capacity (mg F}^-/\text{g)} = \frac{(C_0 - C_t)}{m} * V \dots\dots\dots (2)$$

Where, C_0 = initial F^- concentration

C_t = F^- concentration at time t

m = mass of adsorbent in g/L

V = volume of the solution in L

3.4.1. Effect of dose and contact time

To investigate the effect of dose and contact time of AAABC, experimental investigations were carried out at different dosages of 0.4, 0.8, 1.0, 1.6, 2.0 and 2.5 g/ L of adsorbent with initial fluoride concentration of 10 mg/L. The dosage range was selected based on initial preliminary screening experiments.

3.4.2. Effect of initial concentration

To investigate the effect of initial concentration, experiments were conducted at various fluoride concentrations ranging from 5 to 40 mg/L at constant adsorbent dose.

3.4.3. Effect of solution pH

The effect of initial solution pH (3-11) on fluoride adsorption was evaluated by making a series of 10 mg/L fluoride solution at an adsorbent dosage 0.8 g/L, the initial solution pH was adjusted using 0.1 M HCl and 0.1 M NaOH to the desired value.

3.4.4. Effect of co-existing anions

To investigate the selectivity of AAABC for fluoride in the presence of anions most commonly found in water, including SO_4^{2-} , Cl^- and HCO_3^- , the amounts of fluoride adsorbed by 0.4 g of the AAABC from 500 mL of fluoride solutions containing anions at a concentration ranging from 100-500 mg/L of each anion were determined. Samples were withdrawn after 3 hr., filtered and analyzed for residual fluoride concentrations.

3.4.5. Adsorption isotherm

The adsorption isotherm experiments were conducted using an adsorbent dose of 0.8 g/L and varying initial fluoride concentrations within the range between 5 and 40 mg/L.

3.4.6 Adsorption kinetics

The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order and pseudo-second-order reaction mechanisms. Adsorption kinetics was determined using constant surface loading of 12.5 mg/g (0.4, 0.8 and 1.6 g/L of adsorbent) for the corresponding fluoride concentration of 5, 10 and 20 mg/L respectively.

3.5. Desorption studies

To investigate desorption of fluoride from exhausted adsorbent, the adsorbent (AAABC) at 0.8 g/L dose was subjected to adsorption for 180 min (equilibrium time) in 500 mL of 10 mg/L fluoride solution. Then, the solution was filtered and the concentration of fluoride in the filtrate was measured to determine the amount of fluoride on the adsorbent (Maliyekkal et al., 2006).

The exhausted adsorbent was conditioned in 50 mL of 0.1, 1 and 5 % NaOH solution. Samples were taken after 30 and 60 min and concentration of fluoride was determined from which the elution potential of the eluent be calculated.

4. Results and discussions

4.1. Comparison of fluoride removal efficiency of different materials

The adsorbents used were (1) Granular AC, (2) Powdered AC, (3) Powdered AO, (4) Powdered AAABC, (5) China AC, (6) England AC, (7) China ACAO and (8) England ACAO. The fluoride removal efficiency of these adsorbents is shown in Figure 1.

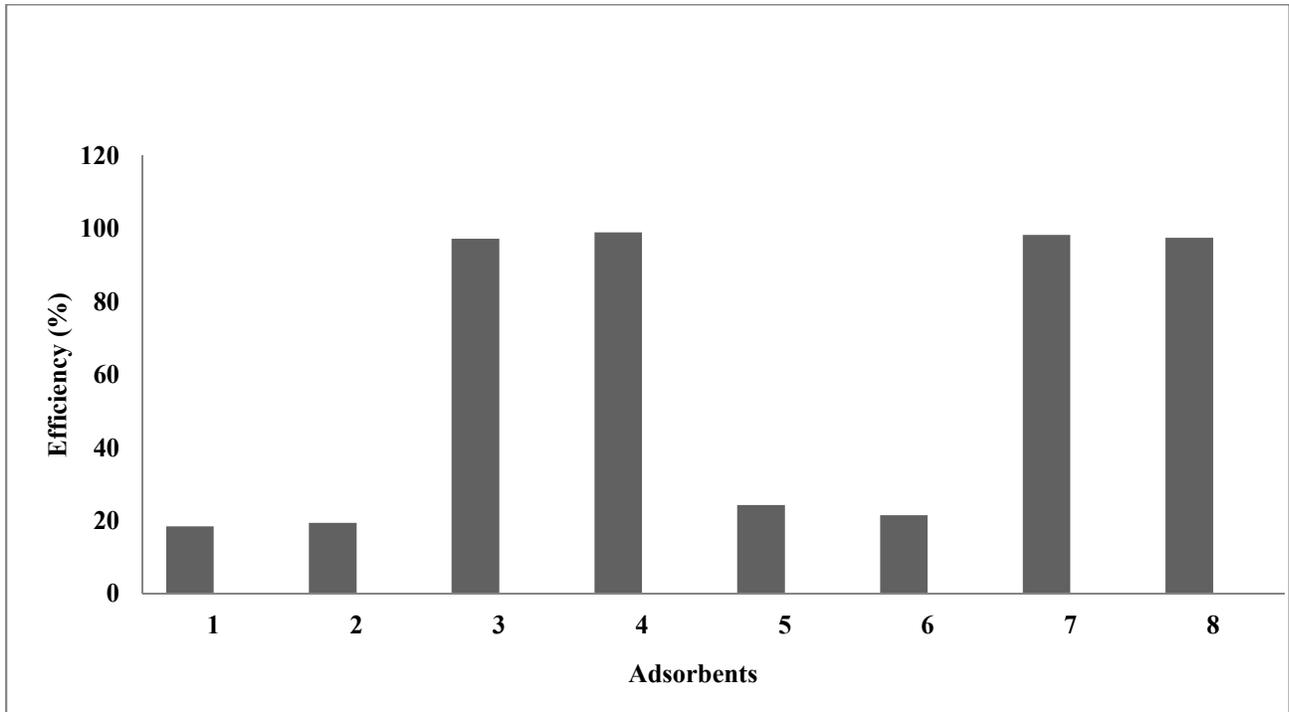


Figure 1: Comparison of fluoride removal efficiency of different materials (adsorbent dose = 1.6 g/L, initial fluoride concentration = 10 mg/L, contact time = 180 min)

As it can be seen from Figure 1, fluoride removal efficiency of powdered AAABC is much higher than that of other adsorbents used in this study. The more finely divided and more porous adsorbents would be expected to yield more adsorption per unit weight of adsorbent. Thus powdered AAABC may exhibit much more active sites for adsorption and fluoride has a greater affinity towards aluminium. Moreover, the prepared activated carbon when coated with AO showed improved fluoride removal, than the commercial one. This might be attributed to the contribution of activating chemicals used during activation process which certainly caused by the activation method, which sometimes results in different surface characteristics (Ferhan and Ozgur, 2011).

4.2. Optimization of the adsorbents

4.2.1. Chemical and thermal activation of ABC

In order to improve the adsorption capacity of the 1:1 ratio adsorbent, an investigation was done by varying the agitation time of AO/AC mixture from 1-5 days. The calcination temperature of ABC was also carried out at different temperature (400-600 °C). The chemical activation of ABC was done by treating the precursor, waste bamboo, with H_3PO_4 .

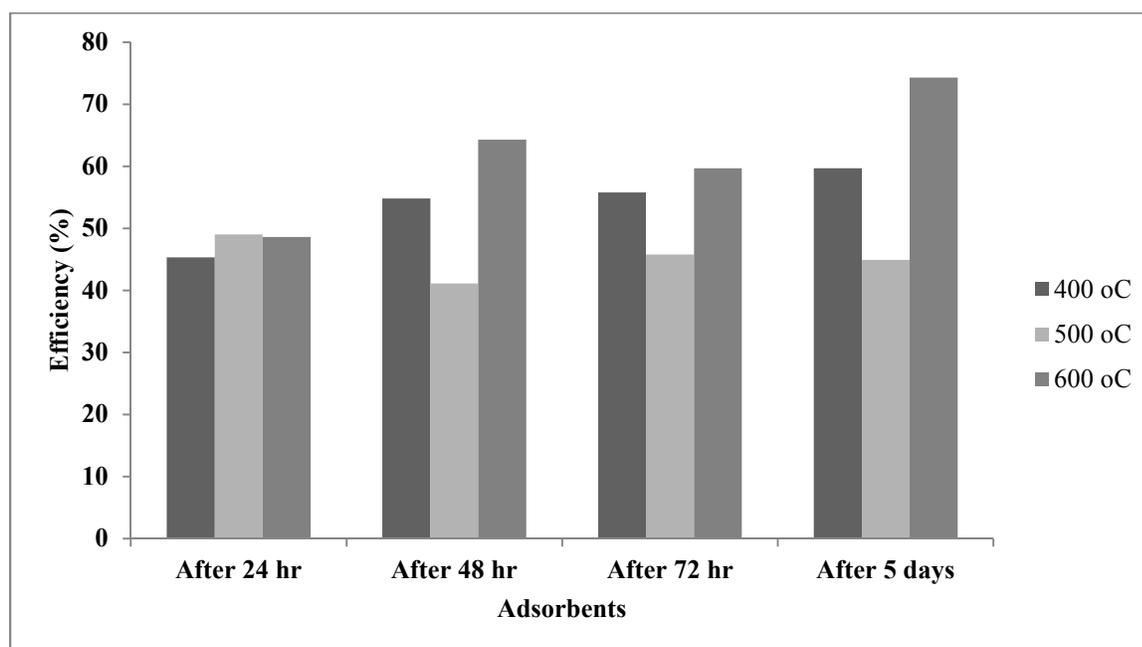


Figure 2: Effect of thermal treatment and agitation time on fluoride removal efficiency of AAABC (activation chemical H_3PO_4 , adsorbent dose = 1.6 g/L, initial fluoride concentration = 10 mg/L).

The best removal efficiency (about 74 %) was obtained by calcinating the ABC at 600 °C and retaining the AO/AC mixture for 5 days. The reason for better fluoride removal might be due to the availability of porous structure of the AC and the proper incorporation of AO in to the pore. Another type of AC was prepared by treating the AC precursor, waste bamboo, with $AlCl_3/FeCl_3$, at different temperature and varying the agitation time of AO/AC in a 1:1 ratio.

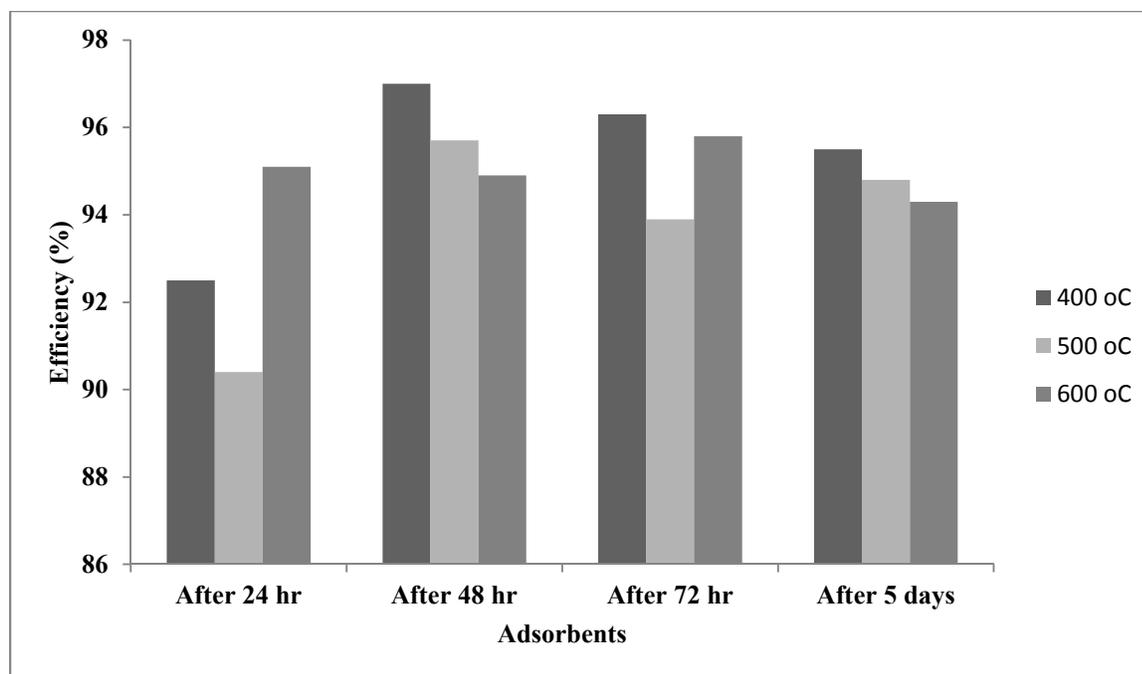


Figure 3: Effect of thermal treatment and agitation time on fluoride removal efficiency of AAABC (activation chemical $\text{AlCl}_3/\text{FeCl}_3$, adsorbent dose = 1.6 g/L, initial fluoride concentration = 10 mg/L).

As can be seen from Figure 3, the fluoride removal efficiency reaches maximum at 400 °C after 48 hr. agitation time of the AO/AC mixture. This might be due to the proper impregnation of Al/Fe oxides in to the wood which makes the wood structure to be highly porous and additionally the incidence of the metal ions occurs. These occurrence of multivalent ions and porous structure, boost the sorption efficiency of AC produced at 400 °C and makes it to be selected as the best adsorbent for further study. The decrease in removal efficiency was observed at higher temperature. This could be resulted from the increment of the temperature which leads to deterioration of the proper structure of the AC (Eric et al., 2010).

On the other hand, the fluoride removal efficiency of ABC prepared by chemical activation was compared. As it was shown in figure 3 and 4, the fluoride removal efficiency of ABC prepared by $\text{AlCl}_3/\text{FeCl}_3$ activation becomes greater. This can be attributed to the greater affinity of fluoride anion towards aluminium and iron (Ferhan and Ozgur, 2011).

4.2.2. Optimization of the ratio of AO to ABC

In order to select the optimum ratio of AO:AC the adsorbents were tested by varying the proportion of AO.

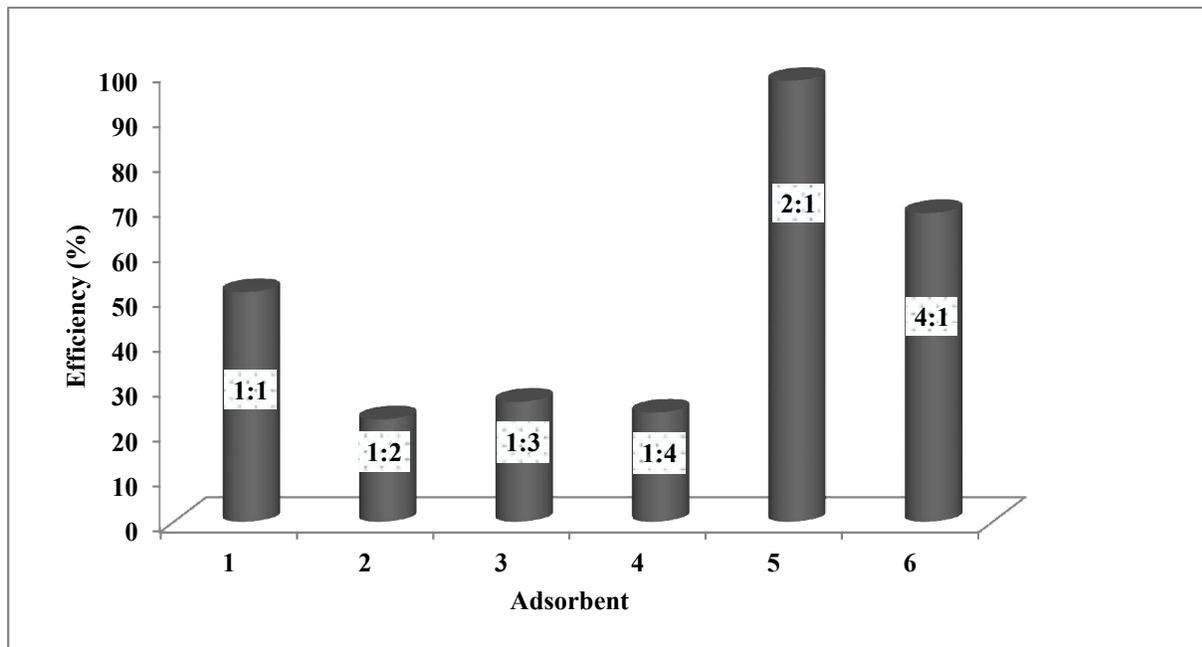


Figure 4: Effect of the proportion of AO on fluoride removal efficiency of AAABC (adsorbent dose = 1.6 g/L, initial fluoride concentration = 10 mg/L, contact time = 180 min).

From Figure 4 it can be seen that the percentage fluoride removal is lower at the lower proportion of AO. This shows the fluoride adsorption capacity of AC can be improved by increasing the amount of AO. The ratio of AO: AC that showed best result was a 2: 1. But, since the aim of this study is to reduce the chemical consumption, the amount of AO should be reduced.

4.3. Characterization of AAABC

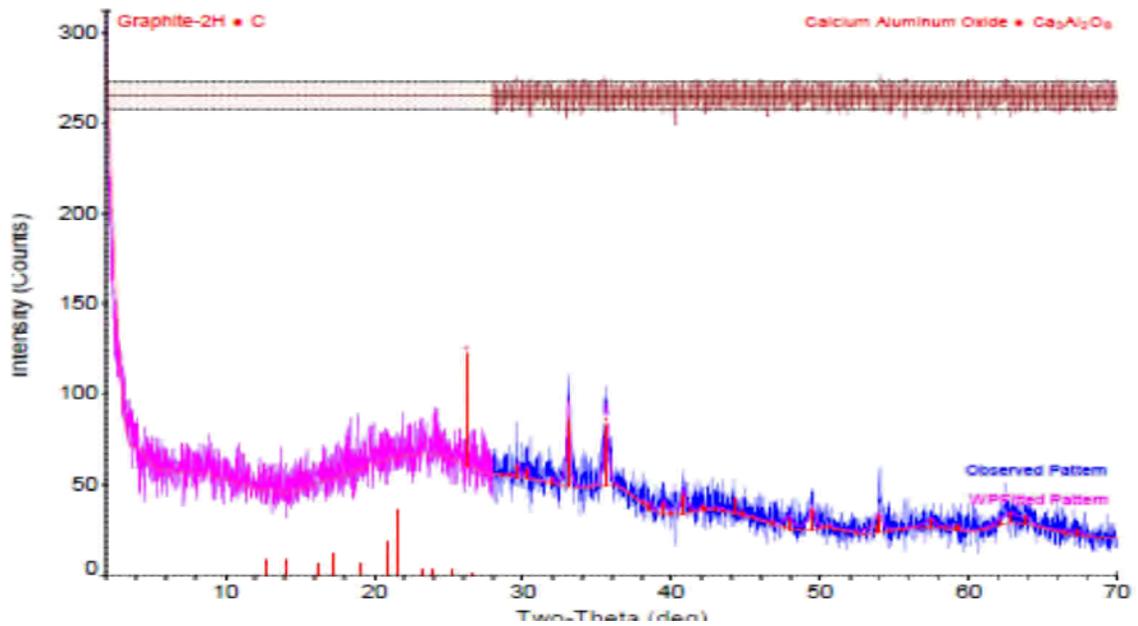


Figure 5: X-ray diffractogram of AAABC

The XRD diffractogram pattern of AAABC is shown in Figure 5. The adsorbent is mainly amorphous and most peaks from XRD diffractogram corresponds to $\text{Ca}_3\text{Al}_2\text{O}_6$. It is known that amorphous materials have good adsorbent properties due to their high specific surface area and more active sites on their surfaces.

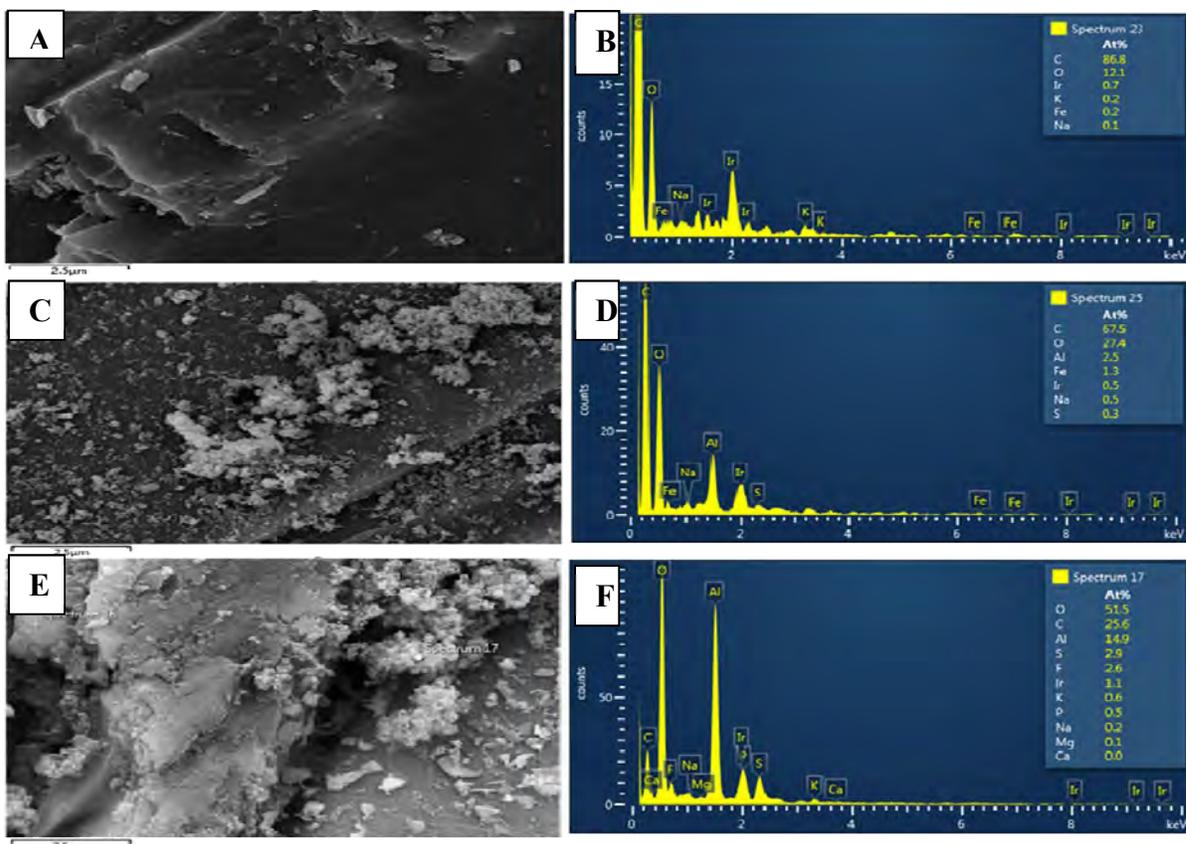


Figure 6: SEM and EDS of ABC (a,b), AAABC/before adsorption (c,d) and AAABC/after adsorption (e,f).

As can be seen from Figure 6, the matrix carbon has the expected porous structure (Figure 6a). An irregular repartition of particles on the surface of carbon is observed. These particles were attributed to the formation of an inorganic layer on the charcoal during the wood carbonization. Since wood has an anisotropic structure, it is not surprising that the wood impregnation was not a uniform step leading to a similar repartition of these particles on the charcoals. The EDS spectrum of Figure 6b shows the presence of C, O, Fe and Na elements in the activated charcoals.

The results shown in figure 6c indicate that inorganic particles were dispersed on the surface of carbon. Apart from the presence of some elements, there is also formation of aluminum and fluoride elements on the adsorbent surface. This indicates the successful impregnation of

aluminum on to ABC. Figure 6 e and f showed a localized chemical composition of AAABC, and it can be concluded that fluoride is associated with the AO particles in the pore spaces.

The SSA was reduced from 80.5 to 3.7 m²/g, when the ABC was impregnated with AO, indicating that the AO particles might cover the surface or pore spaces found in ABC.

The results of the acid-base titration to determine acidic and basic active sites are shown in Table 3. The analysis of these data provided evidence that upon aluminum amendment, the concentration of the total acidic sites increased than basic sites. Thus, it was reasonable to assume that fluoride was adsorbed to acidic sites on the aluminum-amended carbon.

Table 3: Surface acidity and basicity of AAABC

Acidic (mmol/g)	Basic (mmol/g)	PZC
0.75	0.125	9.6

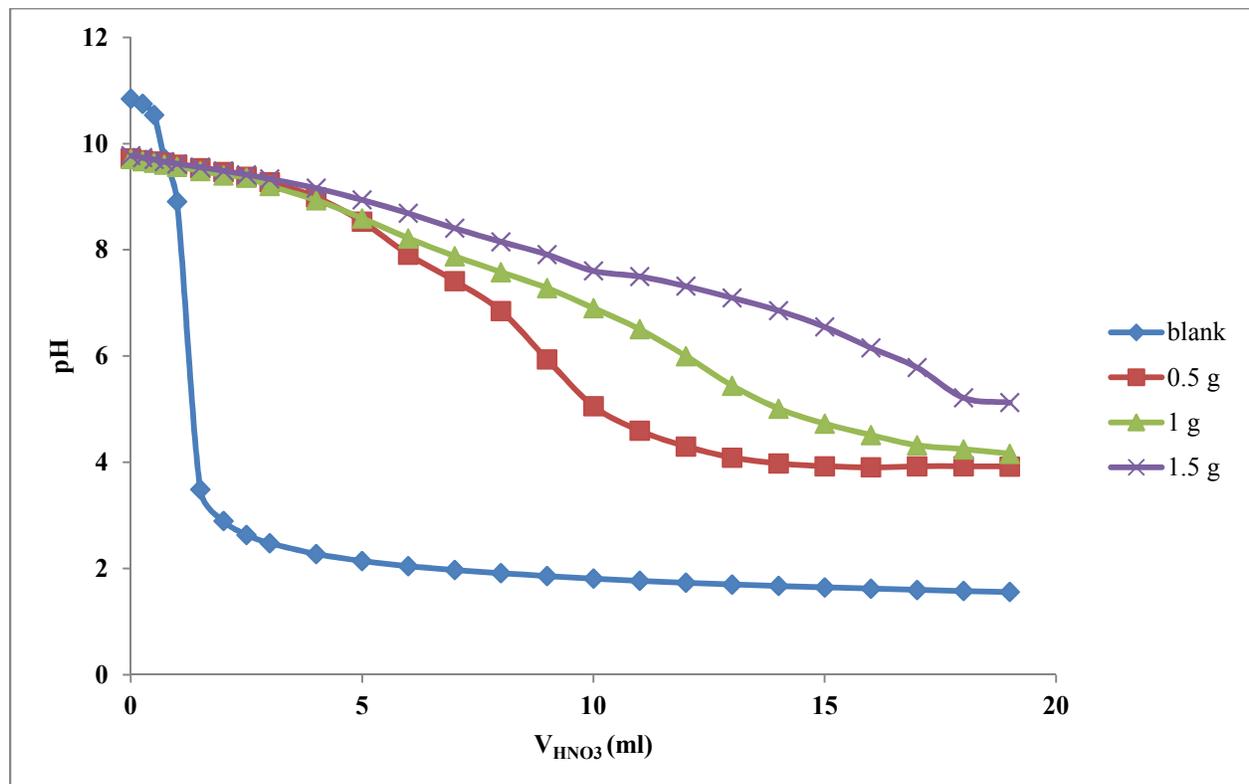


Figure 7: Point of zero charge (PZC) of AAABC.

The point of zero charge pH (PZC) of AAABC, i.e. the pH for which the net surface charge is zero, is determined using a procedure mentioned under section 3.3. From Figure 7 the pH (PZC) of AAABC was found to be 9.6 and thus the surface charge of the AAABC is positively charged below pH 9.6. It thus indicates that below the pH 9.6 the water donates more protons than hydroxide groups, and so the adsorbent surface is positively charged (attracting anions). Conversely, in the event of pH is higher than 9.6 the surface would be negatively charged (attracting cations /repelling anions). Higher is the pH of the solution than 9.6, higher is the electrostatic repulsion between surface and adsorbate fluoride anions. So, as the pH of the solution increases to 9.6, the number of positively charged sites increases and favors the adsorption of fluoride due to electrostatic attraction. This idea coincides with the results obtained from the effect of initial pH of the solution (Alemu et al., 2014).

4.4. Batch adsorption studies

4.4.1. Effect of adsorption parameters onto fluoride removal by the adsorbents

4.4.1.1. Effect of dose and contact time

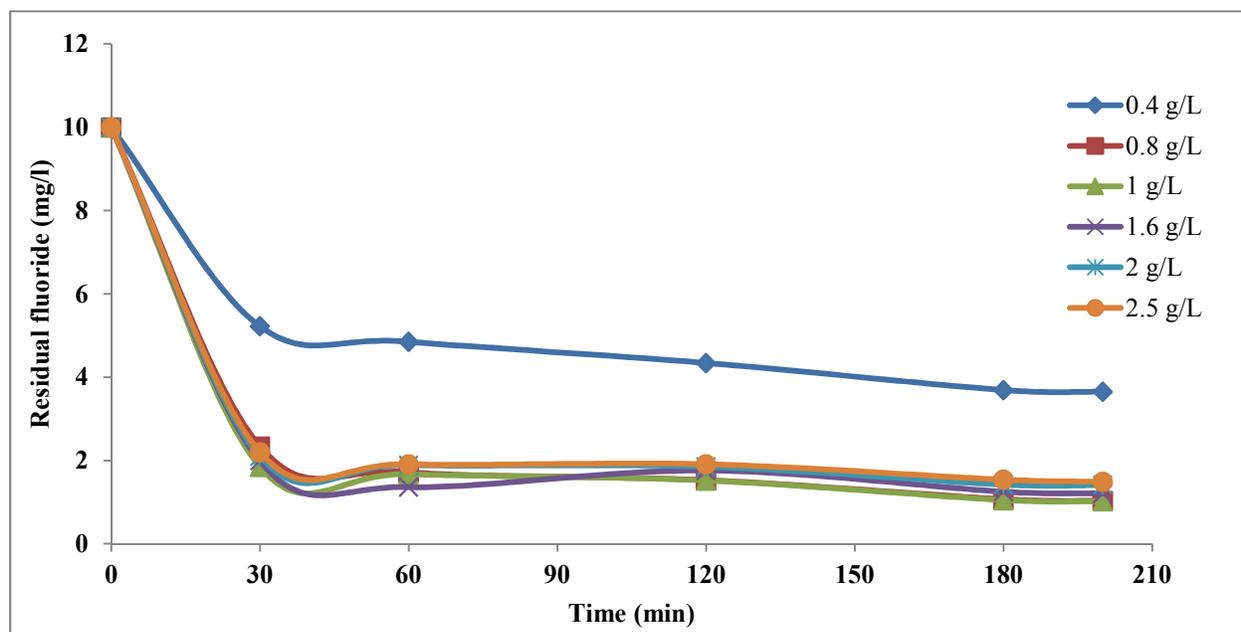


Figure 8: Effect of contact time on the adsorption of fluoride on AAABC (Initial F^- conc. 10 mg/L)

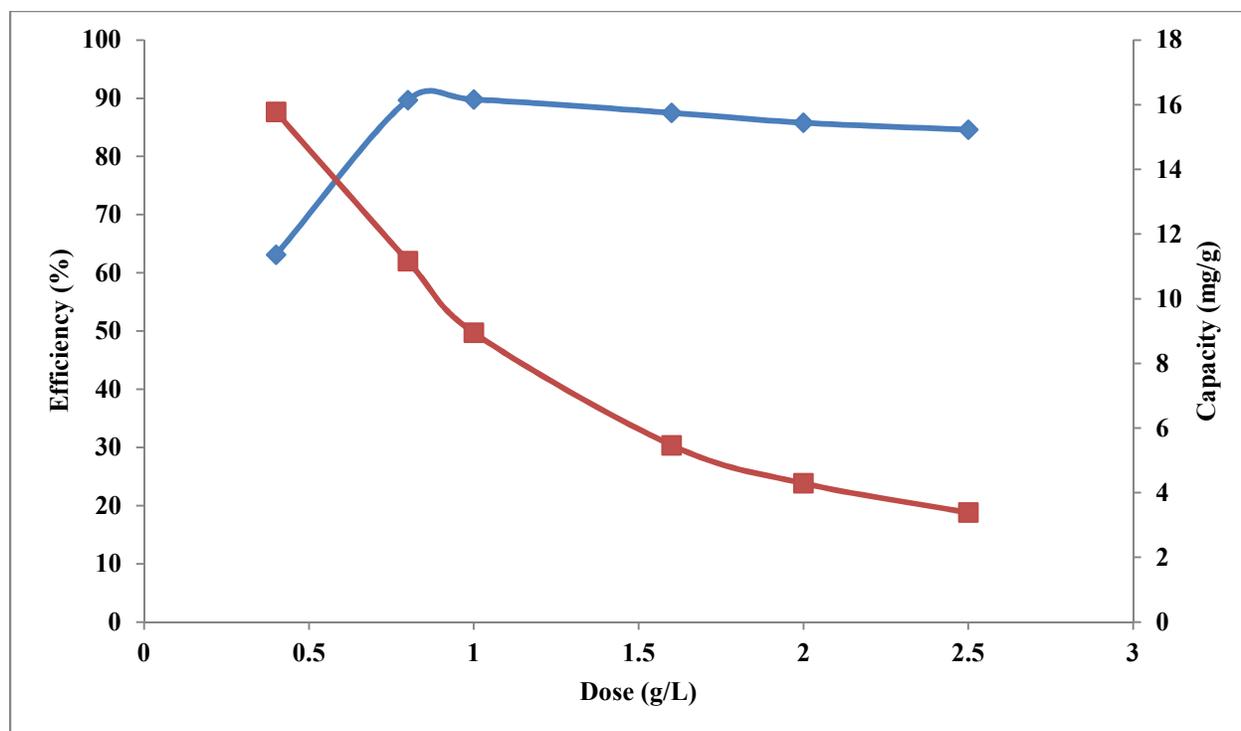


Figure 9: Effect of adsorbent dosage on adsorption of fluoride on AAABC.

The effect of adsorbent dose on fluoride uptake capacity and efficiency is shown in Figure 9. It can be seen that the fluoride removal markedly increased up to adsorbent dose of 1.0 g/L due to increase in adsorbent/fluoride ratio, however further increase in adsorbent dose does not show any appreciable improvement in fluoride removal. This may be because of the very low equilibrium concentration of fluoride, i.e. driving force responsible for adsorption becomes negligible. As observed from Figure 8 rapid increase in adsorption with increase in time was obtained within the first thirty minutes after which the rate of adsorption become slower up to 180 minutes. After 180 minutes contact time there was no visible change of residual F^- concentration i.e. equilibrium was attained. The fast uptake capacity obtained at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The slow and insignificant adsorption observed as time progresses is due to the fact that every adsorbent has a limited number of active sites which becomes occupied with time. Generally, in order to select the optimum dose of the adsorbent material, both the efficiency and capacity of the adsorbent should be considered. Thus, 0.8 g/L of adsorbent dose

corresponding to the capacity of about 11.2 mg F⁻/g of adsorbent and 3 hr. contact time were considered as an optimum dose and contact time for further experiments (Shimelis et al., 2006).

4.4.1.2. Effect of initial fluoride concentration

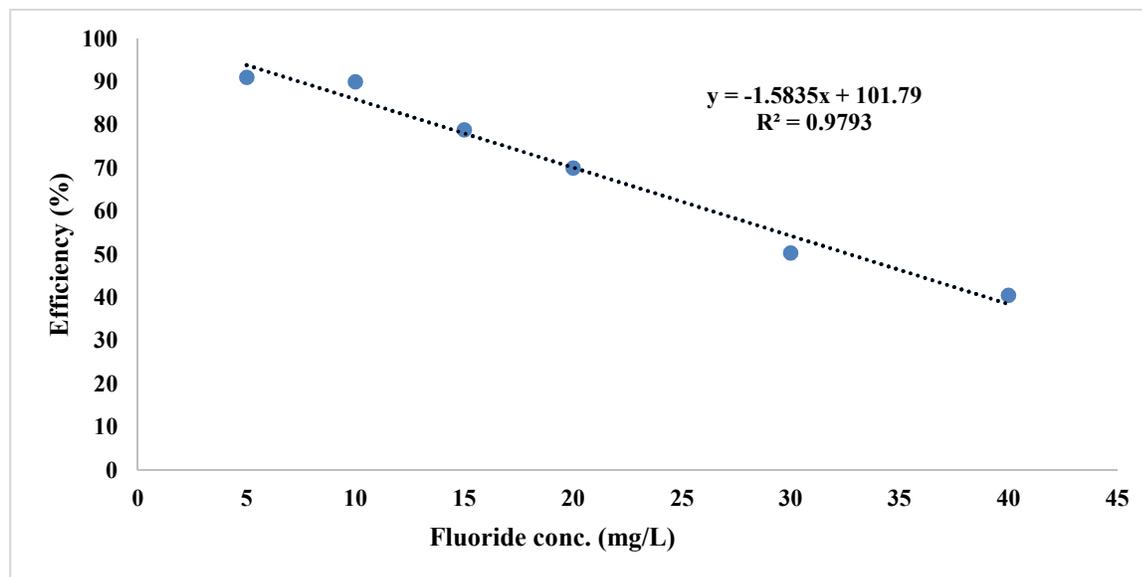


Figure 10: Effect of initial fluoride concentration on removal efficiency by AAABC (dose=0.8 g/L, contact time=180 min).

The effects of initial fluoride concentration on the fluoride removal efficiency were studied by varying the fluoride concentrations from 5 to 40 mg/L, since the fluoride contaminated areas in Ethiopia have in this range, at constant AAABC dose of 0.8 g/L and contact time of 3 hr.

As shown in Figure 10, the efficiency increases with decreasing initial fluoride concentration at the initial stage of adsorption. It can be observed that the adsorption of fluoride from water is relatively more rapid at lower initial concentrations. Thus the initial fluoride concentration had an influence on the equilibrium sorption time, and significant fluoride removal efficiency (more than 90 %) was observed when the initial fluoride was less than or equal to 10 mg/L for a contact time of 3 hr. However, adsorption of more concentrated fluoride solution approached equilibrium slowly. At low fluoride concentrations, the ratio of surface active sites to fluoride ions is high. Hence fluoride ions can occupy the active sites of the adsorbent surface. From Figure 10, at a

high fluoride concentration, the efficiency of the adsorbents for fluoride uptake drops due to the saturation of active sites on the adsorbent surfaces as supported by Eric et al., 2010.

4.4.1.3. Effect of solution pH

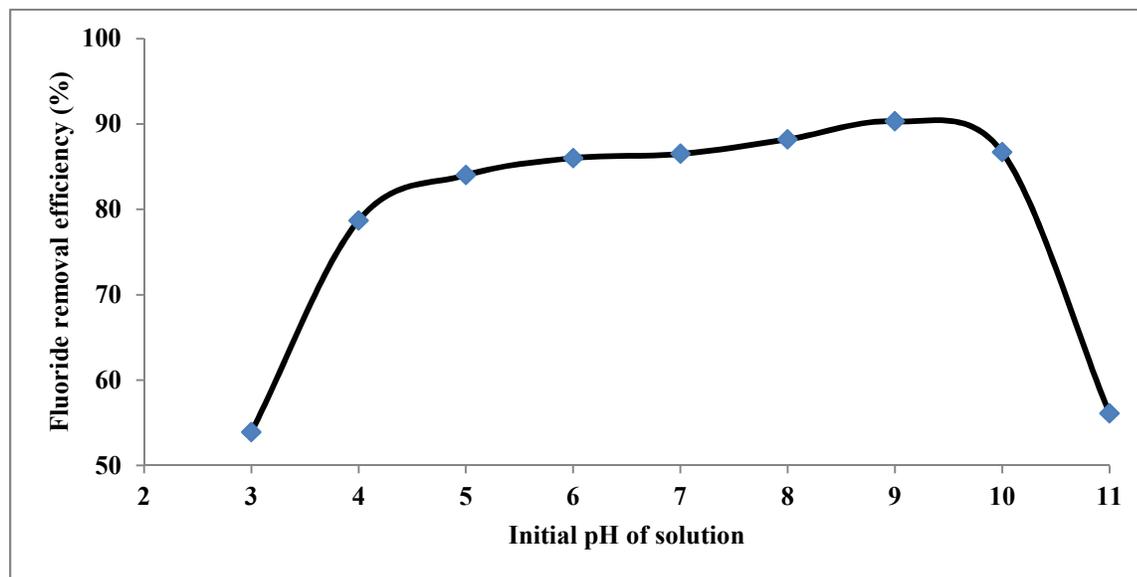


Figure 11: Effect of initial pH on fluoride removal efficiency by AAABC (dose=0.8 g/L, contact time = 180 min).

Figure 11 shows the influence of initial solution pH on the fluoride removal efficiency of the adsorbent. It is marked that the percentage of fluoride removal increases as the pH of the solution increases from of 3-9 and reaches maximum at pH = 9.0. Further increase in the solution pH from 9-11 decreases the fluoride removal efficiency and it becomes significant after pH of 9. The fluoride adsorption capacity of this medium is more enhanced in the pH range from 5 to 9, which is more suitable for practical applications and makes it possible to avoid pH adjustment with the associated cost and operational difficulties, especially if it is to be used in remote areas of developing countries. This is consistent with the work of (Parida et al., 2009; Wang et al., 2008). This can be attributed to the development of positive sites at the surface of the adsorbent and also due to the electrostatic attraction between the positively charged aluminum and iron oxide surface and the fluoride anions. The decrease in the fluoride removal below pH 5 is possibly due to the protonation of the fluoride ion and formation of weakly ionized hydrofluoric acid. On the other hand, at a pH above 9, fluoride removal efficiency decreases possibly due to the surface

acquires negative charge in alkaline pH and hence there is repulsion between the negatively charged surface and fluoride also there will be stronger competition from hydroxide ions (Eric et al., 2010).

4.4.1.4. Effect of co-existing anions

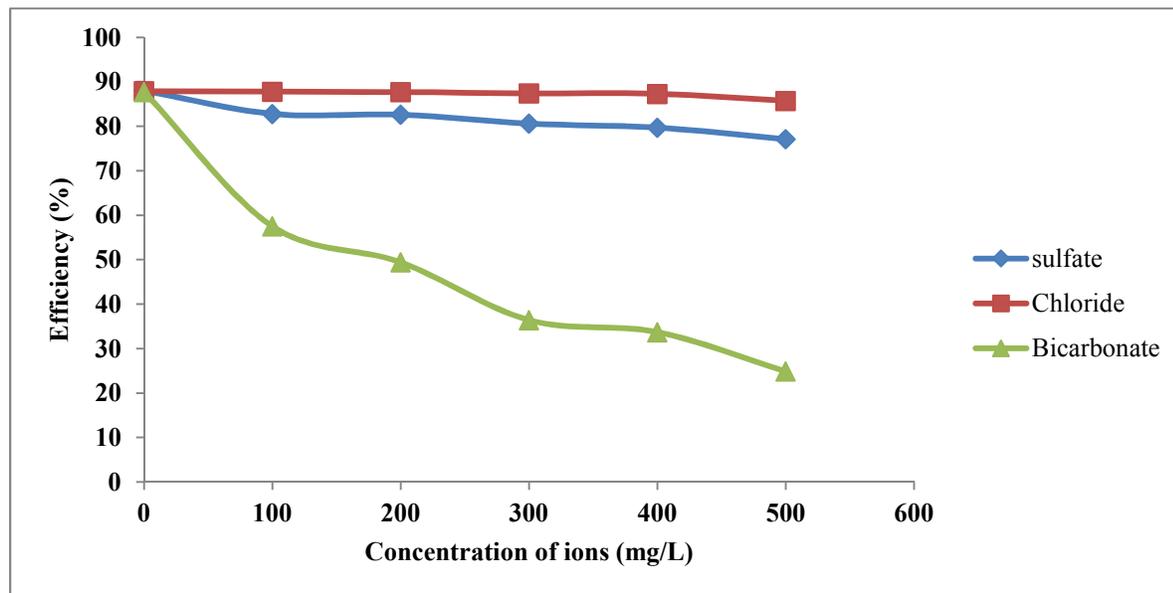


Figure 12: Fluoride removal efficiency of AAABC at various concentrations of sulfate, chloride and bicarbonate ions (adsorbent dose = 0.8 g/L, initial F^- conc. = 10 mg/L and contact time = 180 min).

Groundwater may contain several other co-existing anions along with fluoride, which may compete with fluoride for the active sorption sites of the adsorbent. However, the studies conducted so far are with distilled water spiked with fluoride, where the existence of other ions is negligible. Hence, it is important to study the effect of co-existing anions on fluoride sorption onto AAABC for evaluating the suitability of AAABC for field applications. This study assessed fluoride adsorption behavior in the presence of salt solutions of sulfate, chloride, and bicarbonate, independently with different concentrations ranging from 0-500 mg/L, at an initial fluoride concentration of 10 mg/L. Figure 12 shows the effect of various co-existing anions of different concentrations on fluoride sorption by AAABC. It was observed that in the absence of co-existing anions the fluoride removal efficiency of AAABC was around 90 %. The results also show that Cl^- and SO_4^{2-} have no substantial effect on fluoride adsorption. The increase of sulfate

ions on the feed solution leads to the decrease of the removal rate of fluoride ions than the chloride ion does. It is noticed that the divalent and trivalent anions have more effect than monovalent anions on adsorption capacity, similar results were observed in the literature for fluoride adsorption by Li/Al-LDHs (Zhang et al., 2012). This may be due to a high negative charge density of ions which were easily absorbed by the layer positive charge. The competitive anions were introduced on the surface of AAABC, which can provide less adsorption sites for fluoride and reduced the adsorption capacity.

On the other hand, it was observed that higher level of bicarbonate ion continue to depress the fluoride sorption than the remaining anions tested. This decrease in fluoride sorption might be attributed to the rise in pH of the test solution and/or the surface acquires negative charge in alkaline pH and hence there is repulsion between the negatively charged surface and fluoride. This idea was also supported by the work done by G. Karthikeyan et al., (2007) which showed that chloride and sulfate ions have very little effect on the fluoride removal capacity of activated alumina, whereas bicarbonate ions affected the defluoridation capacity of the adsorbent very much. Presence of bicarbonate had detrimental effect on sorption of fluoride and the removal efficiency was reduced drastically.

4.4.2. Adsorption isotherms of fluoride adsorption onto AAABC

In order to evaluate the relationship between the amount of adsorbed fluoride and the residual fluoride, three well known isotherm models have been tested in this study, namely Freundlich, Langmuir and Dubinin-Radushkevich.

4.4.2.1. Langmuir adsorption isotherms

Langmuir sorption isotherm assumes the monolayer coverage on a structurally homogeneous surface of the adsorbent. The Langmuir isotherm model can be represented in the form

$$\frac{C_e}{q_e} = b \frac{1}{q_m} + \frac{C_e}{q_m} \dots\dots\dots (3)$$

Where C_e is the equilibrium fluoride concentration (mg/L), q_e the amount of fluoride adsorbed per unit mass of the adsorbent at equilibrium (mg/g), q_m the monolayer adsorption capacity of the adsorbent (AAABC) (mg/g), b the Langmuir constant related to the affinity of the binding sites.

The values of Langmuir constants b and q_m can be calculated by from the slope and intercept of the linear plot of C_e/q_e versus C_e .

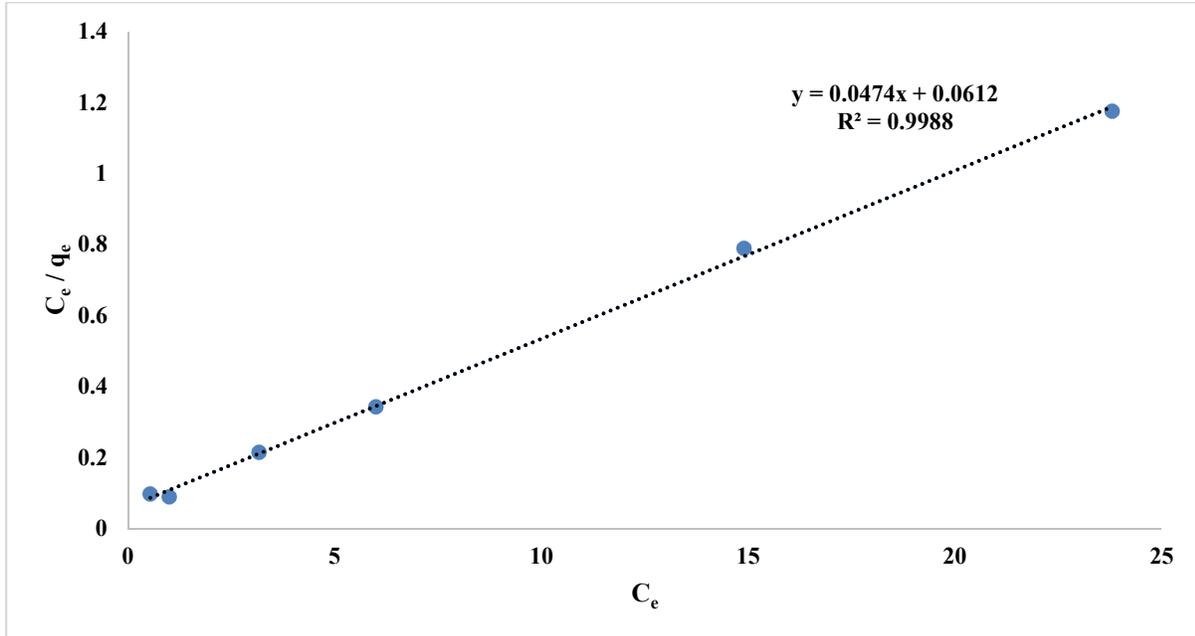


Figure 13: Langmuir isotherms of adsorption of fluoride on AAABC.

4.4.2.2. Freundlich adsorption isotherms

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Adamson and Gast, 1997). Comparing with the Langmuir isotherm, the Freundlich isotherm does not have much limitation, i.e., it can deal with both homogeneous and heterogeneous surfaces, and both physical and chemical adsorption. Especially, this model frequently succeeds in depicting the adsorption behavior of organic compounds and reactive matters. The Freundlich isotherm is expressed as

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \dots\dots\dots (4)$$

Where C_e is the equilibrium fluoride concentration (mg/L), q_e the amount of fluoride adsorbed per unit mass of the adsorbent at equilibrium (mg/g), K (mg/g) and n the Freundlich constants

related to adsorption capacity and intensity. These constants can be calculated from the slope and intercept of the linear plot between $\log q_e$ and $\log C_e$.

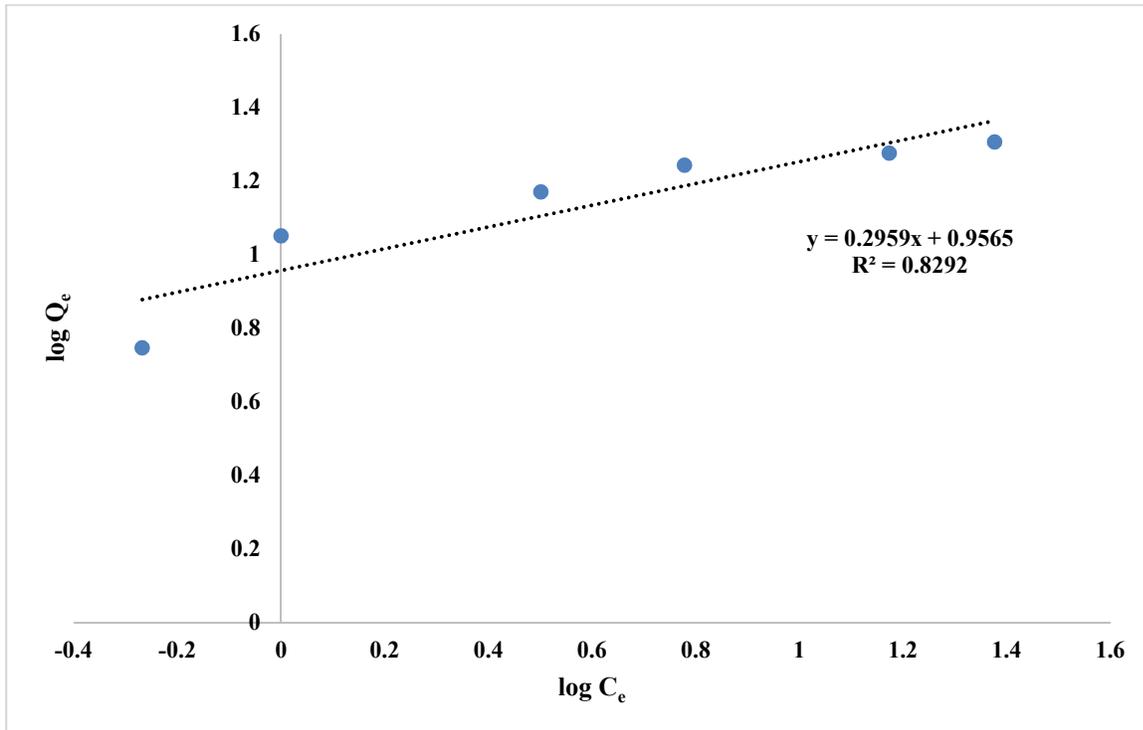


Figure 14: Freundlich isotherms of adsorption of fluoride on AAABC.

4.4.2.3. Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich isotherm is an empirical model initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism. It is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions, with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity). The linear form of Dubinin-Radushkevich isotherm can be written as

$$\ln q_e = \ln q_s - K_{ad} \varepsilon^2 \dots \dots \dots (5)$$

Where q_e = amount of adsorbate in the adsorbent at equilibrium (mg/g);

q_s = theoretical isotherm saturation capacity (mg/g);

K_{ad} = Dubinin-Radushkevich isotherm constant (mol^2/kJ^2)

ε can be correlated as:

$$\varepsilon = RT \ln [1 + 1/C_e] \dots\dots\dots (6)$$

Where R, T and C_e are the gas constant (8.314 J/mol.K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L) respectively. K_{ad} is related to the free energy of sorption/mole of the sorbate as it migrates to the surface of the adsorbent from infinite from infinite distance in the solution. The apparent energy of adsorption from Dubinin-Radushkevich model can be computed using the relationship:

$$E = \frac{1}{\sqrt{2K_{ad}}} \dots\dots\dots (7)$$

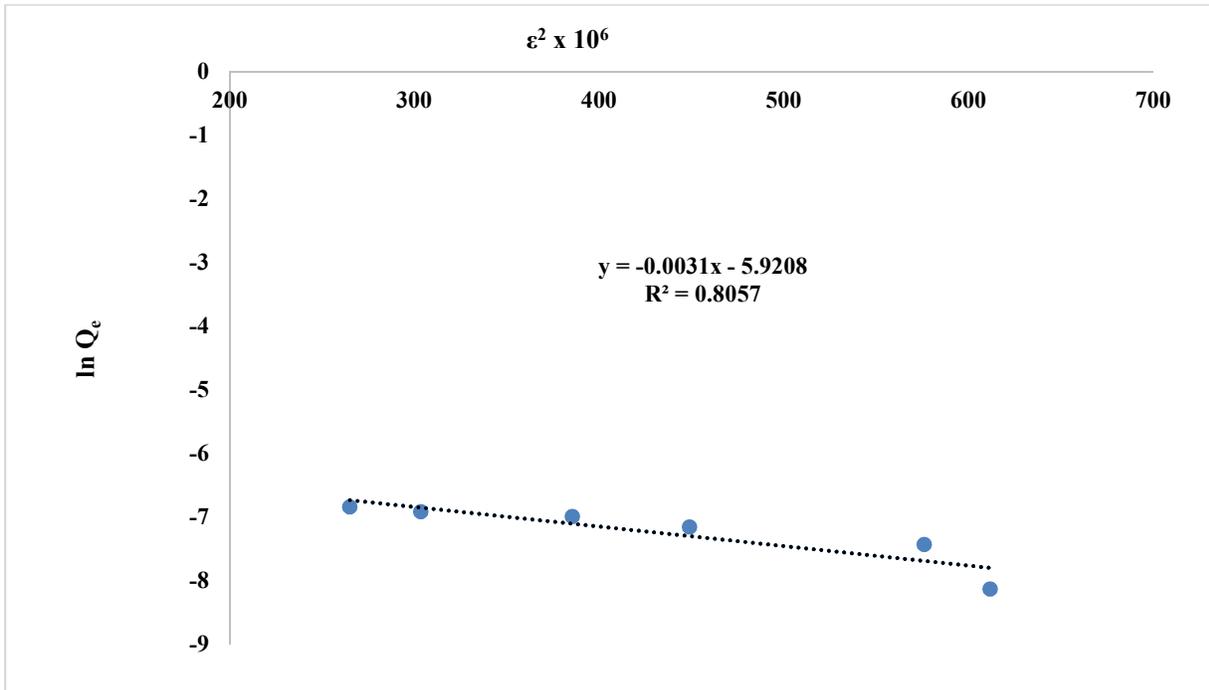


Figure 15: Dubinin-Radushkevich isotherms of adsorption of fluoride on AAABC.

Table 4: Linear isotherm equations and parameters

Isotherms	Linear		
Langmuir	Parameters		
	q_m (mg/g)	b (L/mg)	R^2
	21	0.06	0.9988
Freundlich	Parameters		
	K_F (mg/g)	n	R^2
	9	3	0.8292
Dubinin-Radushkevich (D-R)	Parameters		
	q_s (mg/g)	E (kJ/mol)	R^2
	2.68E-3	12.7	0.8057

Therefore, from the above table, it was observed that the correlation coefficient value for the linear form of Langmuir is higher ($R^2 = 0.9988$) than Freundlich (0.8292) and Dubinin-Radushkevich (0.8057) isotherms. Thus, from the values' of correlation coefficient Langmuir isotherm model was found to be the best representative of adsorption of fluoride by AAABC. The Langmuir equation was chosen for the estimation of maximum adsorption capacity. The maximum adsorption capacity (q_{max}) was found to be 21.1 mg/g.

4.4.3. Adsorption Kinetics of fluoride adsorption on to AAABC

In order to evaluate the adsorption kinetics, constant surface loading of 12.5 mg/g (0.4, 0.8 and 1.6 g/L adsorbents for the corresponding fluoride concentration of 5, 10 and 20 mg/L respectively were subjected to sorption under similar conditions. The experimental results are shown in Fig. 16.

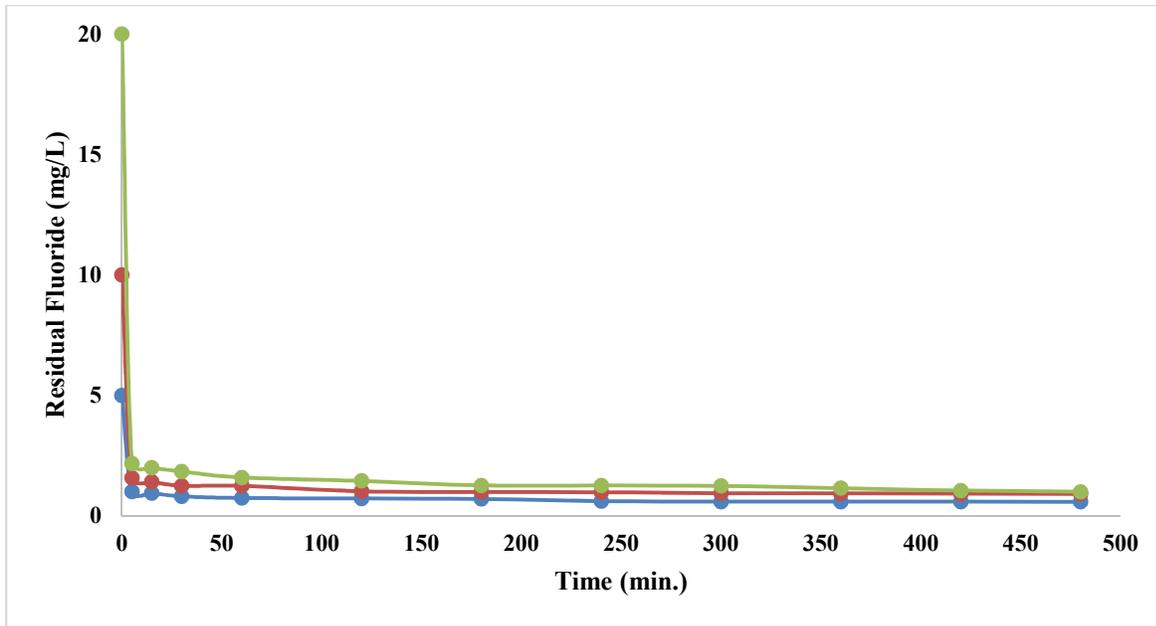


Figure 16: Adsorption kinetics of fluoride at constant surface loading of 12.5 mg/g.

The initial rapid fluoride removal is presumably due to the instantaneous utilization of the most readily available active sites on the outer surface of AAABC by fluoride ions and slower adsorption at the later stage may be due to a gradual diffusion of fluoride ions into the interior surface of the porous adsorbent for adherence. The kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid-solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. Two fluoride removal kinetic models, pseudo-first-order (not shown) and pseudo-second-order models, were studied by using the data obtained from the fluoride removal on AAABC at different time intervals. The experimental data was applied to the pseudo-second-order kinetic model Equation (Lagergren & Svenska, 1898):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots (8)$$

Where,

q_e and q_t are amount of adsorbed fluoride at equilibrium and any time t (mg/g), respectively, k_2 is the rate constant ($\text{g mg}^{-1}\text{min}^{-1}$), t is the stirring time (min), K_2 can be determined by plotting $\frac{t}{q_t}$ against t based on equation 8.

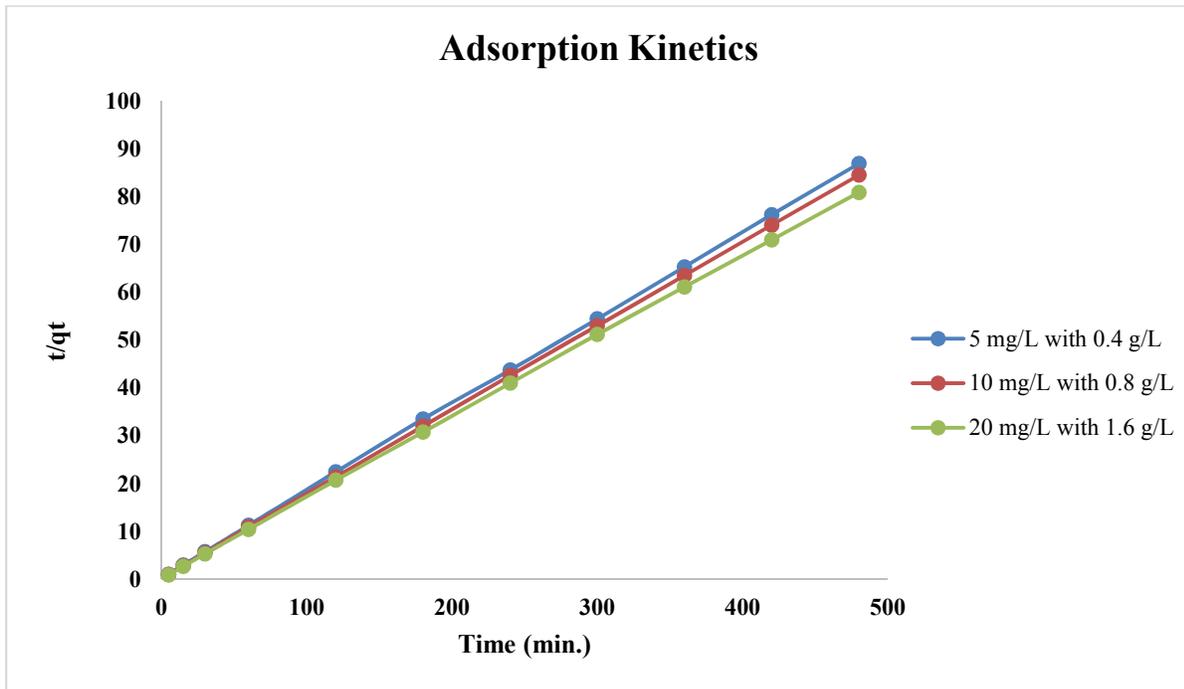


Figure 17: Pseudo-second-order plot of fluoride removal kinetics on adsorbents of different dose.

It can be seen in Figure 17 that in all the three cases, initially the rate of adsorption of fluoride is high during the first 5 minutes. Beyond that, the rate decreases with time, as the liquid phase concentration decreased. We can also observe that the time to reach equilibrium seems shorter as the concentration becomes lower.

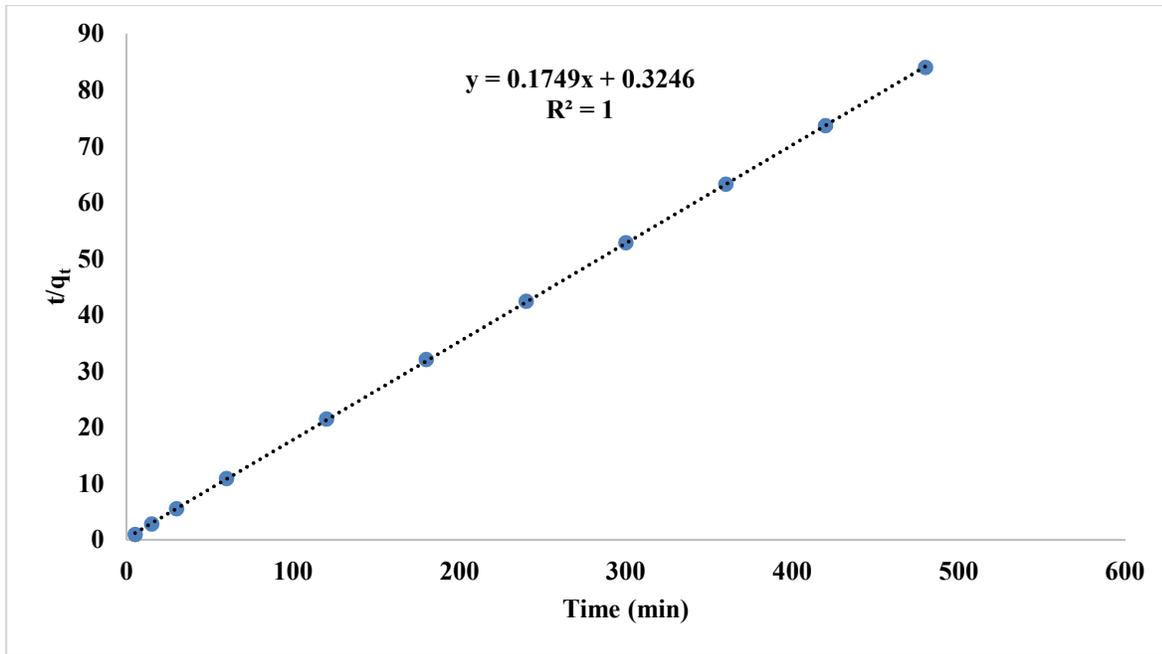


Figure 18: Average pseudo-second-order plot of adsorption kinetics.

Table 5: Pseudo-second-order rate constants, rate equations and correlation coefficients and their averages for the three different initial fluoride concentrations.

F⁻ conc. and adsorbent dose	K₂ (g min⁻¹ mg⁻¹)	Rate equation	R²
5 mg/L with 0.4 g/L	7.7064 x 10 ⁻²	t/q _t = 0.1804x + 0.4223	0.9999
10 mg/L with 0.8 g/L	12.2453 x 10 ⁻²	t/q _t = 0.1757x + 0.2521	1.0000
20 mg/L with 1.6 g/L	9.4862 x 10 ⁻²	t/q _t = 0.1685x + 0.2993	0.9999
Average	9.4055 x 10 ⁻²	t/q _t = 0.1749x + 0.3246	1.0000

Based on the above results, it can be concluded that the reaction rate is well described by pseudo-second-order reaction rate model.

4.4.4. Intraparticle diffusion

The rate-limiting step is the key factor to be determined in the adsorption process to understand the overall mechanism for sorption. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting an intraparticle diffusion plot. According to Weber and Morris, an intraparticle diffusion coefficient K_i is given by the equation:

$$q_t = k_i t^{1/2} \dots\dots\dots (9)$$

Where q_t is the amount adsorbed (mg/g), k_i is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$).

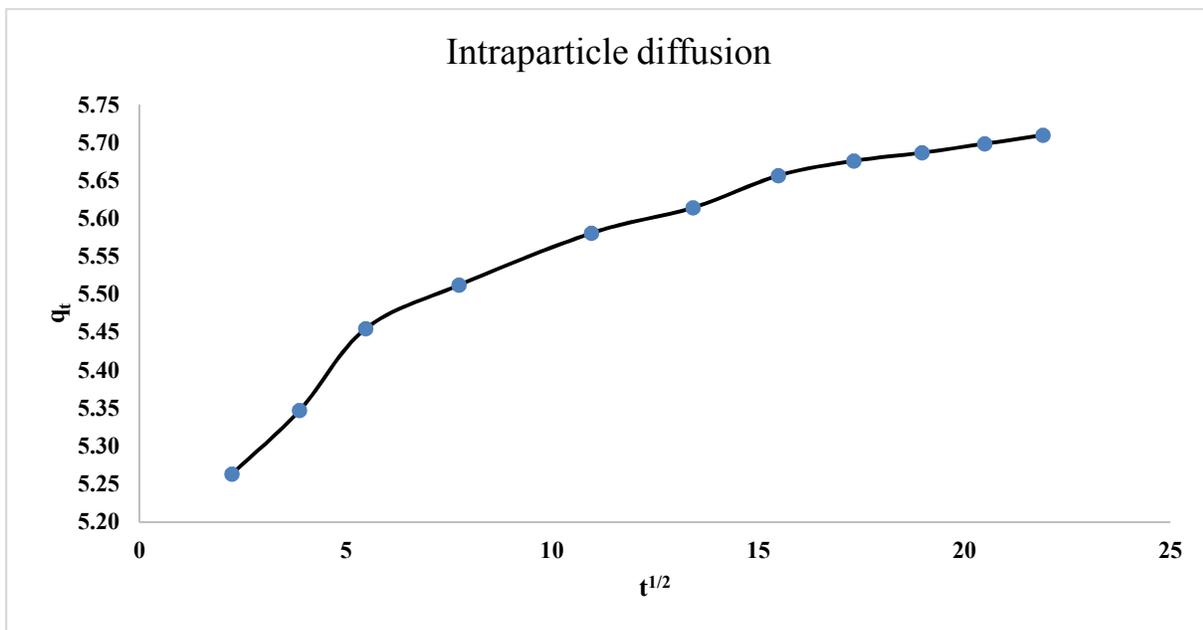


Figure 19: Adsorption capacity, q_t (mg/g) as a function of square root of time ($\text{min}^{1/2}$).

Figure 19 shows the amount of fluoride adsorbed (q_t) versus the square root of time ($t^{1/2}$). If plot of q_t versus $t^{1/2}$ gives a straight line that pass through the origin, then it suggests that the intraparticle diffusion contributes predominantly in the rate-determining step (Namasivayam and Yamuna, 1995). However, if the data reveal multi-linear regions, it is expected that other mechanisms are also involved along with intra-particle diffusion.

Three different regions can be identified in Figure 19. The first, sharp portion of the curve corresponds to the external surface adsorption stage or instantaneous adsorption stage. The

second portion of the curve indicates the intraparticle diffusion, which is predominant rate-controlling process. Under this condition, the diffusive transport of fluoride ions occurs through the internal pores of the adsorbent. When the bulk fluoride concentration gets low, the third region becomes dominant. In this model, the adsorbent is treated as being surrounded by a boundary layer film of water molecules through which the fluoride ions must diffuse prior to adsorption. Linear portion of the curve does not pass through the origin, which indicates the complex nature of the adsorption process. This unusual behavior is possibly due to the heterogeneous nature of the adsorbent. Therefore, the adsorption of fluoride on to AAABC is influenced by both surface reactions as well as intraparticle diffusion effects.

4.5. Desorption studies

After adsorption, the exhausted adsorbent was treated with 0.1, 1 and 5 % NaOH solution. The results of elution of fluoride under various concentrations of NaOH and different conditioning durations are indicated in Figure 20.

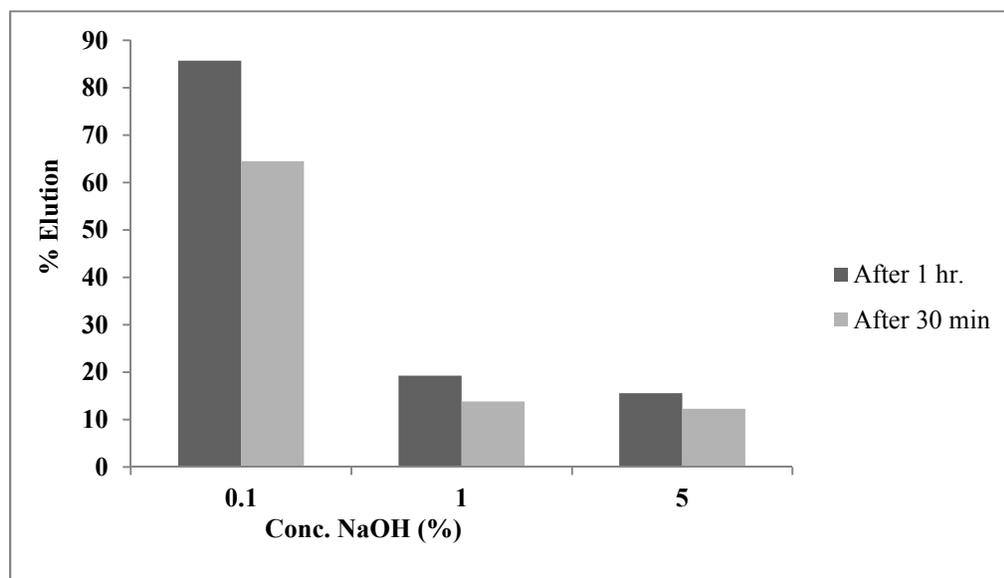


Figure 20: Percentage of fluoride eluted with different concentrations of NaOH (Adsorbent dose = 0.8 g/L, initial fluoride concentration = 10 mg/L).

It can be seen from the result of Figure 20 that desorption was highest in 1 % NaOH after 1 hr (85.71 %). The displacement of adsorbed fluoride from the solid surface seems a faster process

as compared to the adsorption. About 85.71 % of fluoride was desorbed after 1 hr. Although the result indicates the possibility of increased desorption as the contact time increases, further study will be required to optimize desorption process for the efficient utilization of the adsorbent.

The regenerated adsorbent was investigated for its readsorption capacity to assess its reuse potential in order to assess its effectiveness. It was found that the adsorption efficiency drops to 82 % during the second cycle, suggesting that the adsorbent can be reused. Based on the results of desorption and readsorption, it can be concluded that regeneration and reuse is promising if the conditions are optimized over extra studies.

4.6. Fluoride adsorption mechanism

The multiple spectroscopic techniques used here together with potentiometric mass titrations provided valuable information regarding the fluoride adsorption process in AAABC. From the SEM and EDS spectra it can be concluded that there is attraction of fluoride towards aluminium by means of electrostatic adsorption and strong Lewis acid-base interaction.

As pointed out earlier, the PZC of the AAABC was 9.6 indicating that at pH lower than 9.6 the predominant surface groups were acidic whereas at pH greater than 9.6 the predominant groups were basic. At pH below the PZC the fluoride in solution was attracted to the activated alumina surface by the electrostatic forces because the surface was positively charged.

Another point of view goes to the result obtained from the Dubinin-Radushkevich isotherm model. The mean free energy, E value becomes 12.7 KJ/mol. This was indicative of ion exchange mechanism.

The results obtained from the kinetic studies reveal the presence of intraparticle diffusion, which is predominant rate-controlling process. Therefore, the adsorption of fluoride on to AAABC is influenced by both surface reactions as well as intraparticle diffusion effects.

4.7. Comparison of adsorption capacity of different adsorbents

Comparison of adsorption capacity of different adsorbents is essential to evaluate their relative performance. Therefor the adsorption capacity of some adsorbents which have been examined in a batch mode experiment was clearly seen. The optimum contact time required for the maximum adsorption of fluoride was also compared and was indicated in Table 6. Both the adsorption capacity and contact time for AAABC is greater than the other adsorbents except for AlOOH.

Table 6: Comparison of adsorption capacity of different adsorbents

Adsorbents	Adsorption capacity (mg/g)	Equilibrium time (hr.)	References
Activated alumina (grade: A-25)	1.78	6	Ghorai and Pant, 2005
Activated alumina (grade: AD101-F)	0.415	10	Maliyekkal et al., 2006
AlOOH	23.70	1	Beneberu et al., 2006
MOCA	1.10	3	Maliyekkal et al., 2006
Zirconium Impregnated coconut shell carbon	6.41	6	Sathish et al., 2007
Al and Fe dispersed in porous granular ceramics	1.79	48	Chen et al., 2011
KMnO ₄ modified carbon	15.9	3	Daifullah et al., 2007
AAABC	21	3	Present study

5. Conclusion and recommendations

The present study has shown that Aluminium amended activated bamboo charcoal prepared from waste bamboo can be employed as effective and low cost adsorbent for the removal of fluoride from aqueous solution. The AAABC which was pre-treated by $\text{AlCl}_3/\text{FeCl}_3$ at $400\text{ }^\circ\text{C}$ showed higher fluoride uptake capacity for defluoridation of drinking water as compared to other adsorbents. The uptake of fluoride in pH range from 5-9 was higher and decreases with increasing pH. The equilibrium adsorption data fitted well in Langmuir isotherm model. It was also observed that the presence of certain co-existing anions (sulfate, chloride) have negligible effect on removal of fluoride, while bicarbonate anion shows deleterious effect. The rate of adsorption was fairly rapid and maximum fluoride uptake was attained within 3 hr. Therefore, AAABC is a promising low-cost adsorbent for defluoridation of drinking water.

However, the adsorbent needs to be tested under continuous mode (column operations) for its fluoride removal potential. It would also be worthwhile to further investigate the optimization of regeneration study and need to be conducted in more detail to recover the adsorbent and thereby enhancing the economic feasibility of the process.

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