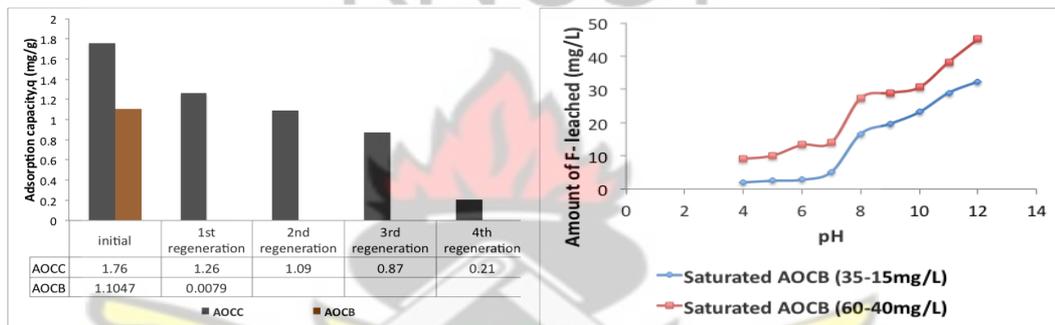


**Kwame Nkrumah University of Science and Technology, Kumasi-Ghana**



Regeneration and disposal of Aluminium oxide coated media (AOCM) used for defluoridation of drinking water.

Catherine Agyarewa Oduro

MSc. Thesis

August, 2012

Kwame Nkrumah University of  
Science and Technology



**Regeneration and disposal of Aluminium Oxide Coated Media (AOCM)  
used for defluoridation of drinking water**

By

**Catherine Agyarewa Oduro, BSc. (Hons)**

KNUST

A Thesis submitted to the Department of Civil Engineering, Kwame Nkrumah

University of Science and Technology

in partial fulfillment of the requirement for the degree of

**MASTER OF SCIENCE**

in

Water Supply and Environmental Sanitation

College of Engineering



August, 2012

**Certification**

I hereby declare that this submission is my own work towards the MSc. and that, to the best of my knowledge it contains no material previously published by another person or material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

KNUST

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(Head of Dept., Civil Engineering)

Signature

Date

**Dedication**

To the Most Gracious God, my family especially my husband and all loved ones

KNUST



### **Acknowledgement**

I am grateful to the Almighty God for His endless mercies and grace bestowed on me through out my study period.

To my supervisors Dr. Richard Buamah of Kwame Nkrumah University of Science and Technology (KNUST), Prof. Branislav Petrusevski and Mr. Abdulai Salifu both of UNESCO-IHE, I say thank you and may the Almighty God bless you exceedingly and abundantly for your assistance and advice.

My work in the laboratory would not have been easier without the assistance of the laboratory technicians Mr. Kingsley Osei-Bonsu (EQE-Civil Engineering Department), Mr. Washington (Chemistry Department) and Mr. Antwi (EQE Lab) to them I say thank you.

To all my friends and course mates, I say it was fun getting to know you all and really appreciative for their company.

I would also like to show my appreciation to my husband, Peter Akwasi Sarpong, my friend Perpetual Yirenkyiwaa as well as my lovely Family for their support and assistance both physically and spiritually through out my studies. God should replenish all you lost in thousand folds.

## ABSTRACT

Fluoride contamination of groundwater has been observed to be prevalent in the northern part of Ghana. Although several methods have been established to be efficient in removing fluoride from ground water the adsorption method is the most popular because of the simplicity of the adsorption units and availability of viable adsorbents locally. Among these viable locally available adsorbents are High Aluminium Bauxite Ore (HABO) and charcoal. Although these adsorbents are viable there is the need to boost their adsorption capacities.

It has been proven that coating these adsorbents with aluminium greatly enhance their adsorption capacities since fluoride ions have high affinity for such multivalent metals due to their electronegativity and small ionic size.

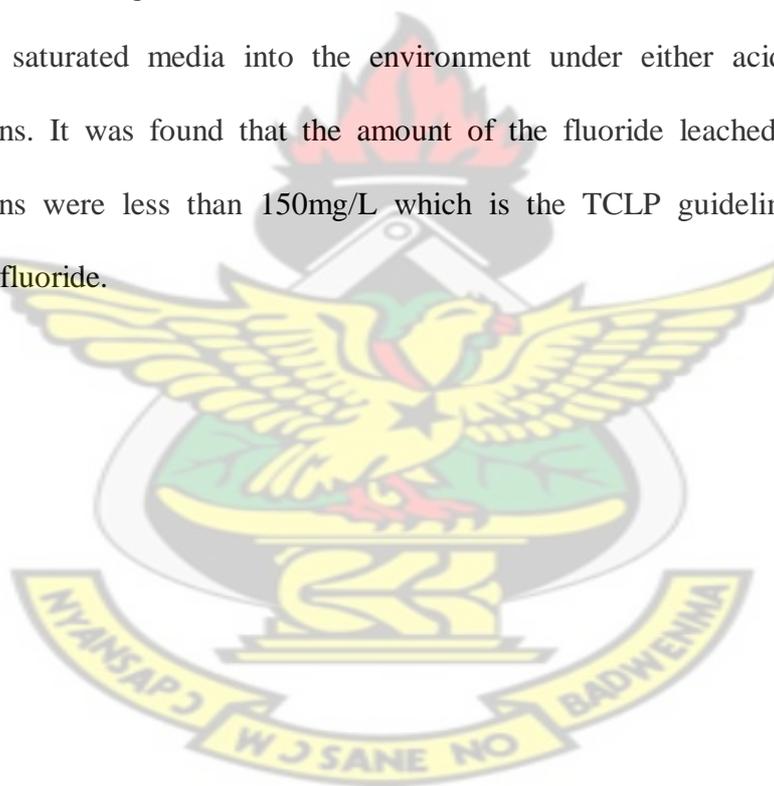
Upon using these media (AOCC and AOCCB) for defluoridation they get exhausted and need to be replaced. The cost of replacement could be expensive and their disposal could pose a challenge to the environment. In order to reduce the cost, regeneration of the adsorbents have been proposed as an acceptable solution.

This study focused on boosting the adsorption capacities and regenerating the Aluminium Oxide Coated Media (AOCCM) by recoating with aluminium oxide when exhausted. The effect of disposal of the exhausted saturated media and its toxicity on the environment was investigated.

The recoating of the AOCC restored the capacity although the capacity reduced averagely by approximately 20% with each successive regeneration. The amount of the aluminium coated onto the media was directly proportional to the

adsorption capacity of the media. The mode of removal of the fluoride was basically chemisorption. The AOCC has an adsorption capacity about 1.5 times that of the AOCCB. The high adsorption capacity of the AOCC may be attributed to the high porosity of the charcoal hence resulting in more Al being coated onto it. The Al coating was considered stable under pH range of 5 to 8 at a temperature of 28°C, hence will not leach and contaminate the water.

Using the Toxicity Classification leaching procedure (TCLP) and the pH dependent leaching test it was established that, it will be safe to dispose the fluoride saturated media into the environment under either acidic or basic conditions. It was found that the amount of the fluoride leached under both conditions were less than 150mg/L which is the TCLP guideline value for leached fluoride.



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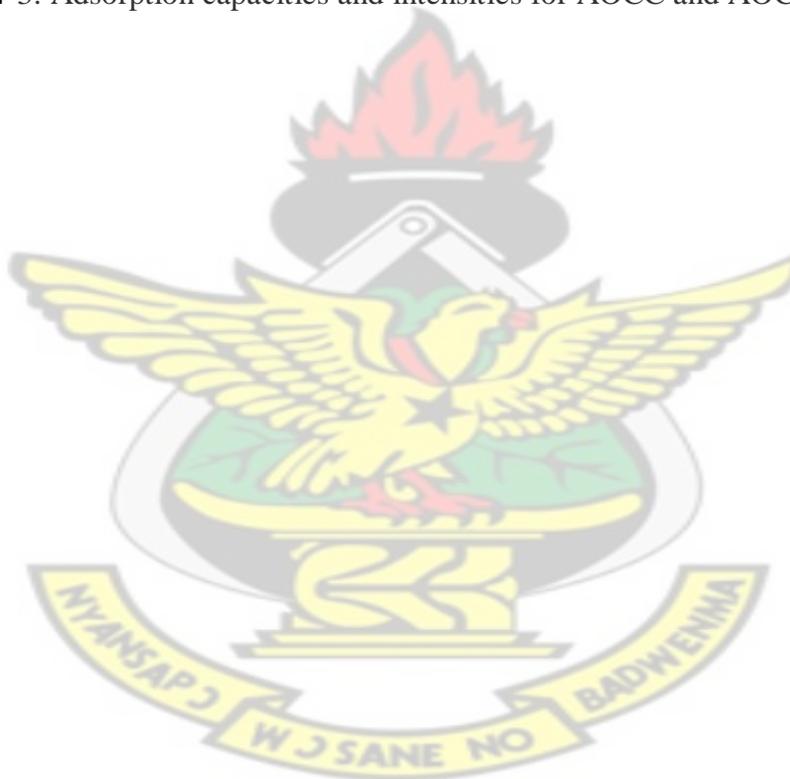
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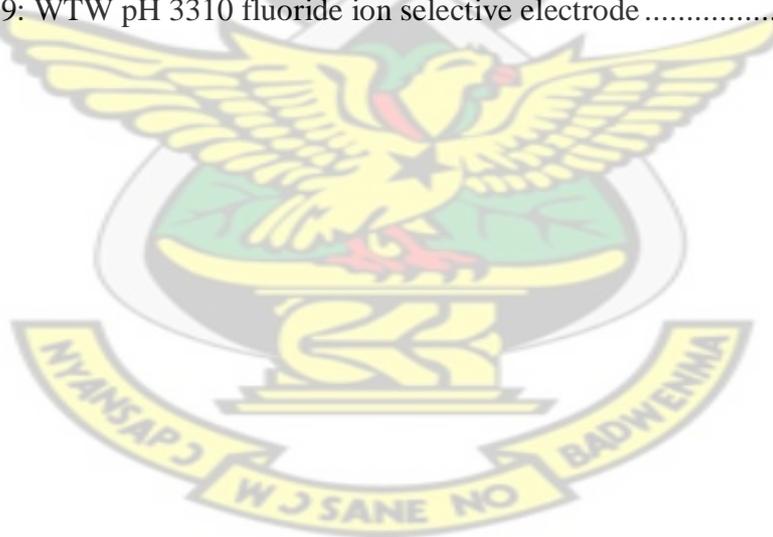
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### List of Acronyms

AOCB	Aluminium Oxide Coated Bauxite
AOCC	Aluminium Oxide Coated Charcoal
AOCM	Aluminium Oxide Coated Media
CWSA	Community Water and Sanitation Agency
EDX	Energy Dispersive X-ray
GNA	Ghana News Agency
HABO	High Aluminium Bauxite Ore
HFBO	High Iron Bauxite Ore
ISE	Ion- Selective Electrode
ISFR	The International Society for Fluoride Research
NORST	Northern Region Small Towns Water and Sanitation Project
SHABC	Soft-Hard Acid Base Concept
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Classification Leaching Procedure
TISAB	Total Ionic Strength Adjustment Buffer
WHO	World Health Organization
XRF	X-ray Fluorescence

## CHAPTER ONE

### 1.0 Introduction

#### 1.1 Background Information

Uncontaminated water is rare and is not readily available to all. Most deprived sections of the society ingest contaminated water, which usually have detrimental effect on their health. These contaminants may originate from natural sources or anthropogenic activities. Fluorine is the most highly reactive element of the halogen family. It is found in seawater, bone and teeth mainly as fluoride ion in trace quantities.

Fluoride is widely distributed in the geological environment and ends up in ground waters by percolation of water through fluoride-rich rocks such as granite, basalt and shale. Also various industrial activities such as quarry for building and road materials also contribute to the fluoride contamination of groundwater to a great extent beside the natural geological sources for fluoride enrichment in groundwater.

Most fluoride associated with monovalent cations such as NaF and KF are water-soluble, while those formed with divalent cations such as  $\text{CaF}_2$  and  $\text{PbF}_2$  are generally insoluble. High level of fluoride in aqueous solution is a worldwide problem. Many people from Africa including Ghana have been suffering from fluoride poisoning for centuries.

Fluoride is considered to be more toxic than lead but less toxic than arsenic and is an accumulative toxin. Fluoride's significance is twofold: Fluoride taken at concentration levels less than 0.5 mg/l may result in lack of protection against dental

caries, especially for children, whilst ingestion of high concentrations between 1.5–4.0 mg/l may cause a disease called dental fluorosis. The mottling and modification of the dental enamel to produce yellow and brown stains on the teeth characterize this disease. Some studies (Mcharo 1986; WHO 1984) have also reported that long-term exposure to levels between 4–6 mg/l of fluoride can also result in skeletal fluorosis, which is also characterized by severe pain and stiffness of the backbone. The International Society for Fluoride Research (ISFR) has reported studies associating fluoride with the rising rates of Down's syndrome, chronic fatigue syndrome and sleep disorder. According to the World Health Organization (WHO) guidelines, the upper limit of fluoride concentration in drinking water is 1.5mg/L.

Due to the aforementioned problems caused by the ingestion of high concentration of fluoride there is always the need to reduce high fluoride concentrations in water to acceptable levels. Existing methods established for effective defluoridation of water include the following: adsorption, ion exchange, precipitation, Nano-filtration and electro dialysis. Among these methods, adsorption has been found to supersede the other techniques for fluoride removal based on initial cost, flexibility and simplicity of design, and ease of operation and maintenance.

Studies have been conducted on a large number of adsorbents for the removal of fluoride ions, including activated alumina, calcite, fly ash, charcoal and pumice. Although these materials are readily available their removal efficiencies are normally not desirable, hence the need for the enhancement of their adsorption capacities.

Coating the natural adsorbents with aluminum hydroxide may offer the required improvement by making the surface of the adsorbent more electro positive, facilitating colloidal adsorption. Some research shows that aluminium oxides and

hydroxide coated media is effective in removal of contaminants such as bacteria, Selenium IV and Selenium VI from water (Chen et al., 1998; Kuan et al., 1998). According to Modestus (2009), aluminium oxide coated pumice is capable of reducing fluoride of concentration 5.3mgF-/L to 0.7mgF-/L which is below the WHO recommended concentration.

### 1.2 Problem Definition

According to literature regeneration of exhausted Aluminium Oxide Coated Media (AOCM) is usually done by cleansing the media with a 0.01M solution of sodium hydroxide (NaOH) for 12hours. The hydroxide ion then displaces the fluoride ion from the surface of the adsorbent. The adsorbent is then rinsed with distilled water. A 0.05M sulfuric acid is passed through the media to neutralize residual caustic after the rinse step. The problem associated with this method is the disposal of the fluoride in the regenerant waste and exhausted materials that are not economically viable to be regenerated. Disposal of these wastes can reintroduce the fluoride into the environment. Also according to Nan Chen *et al* (2010), the adsorption capacity of the adsorbent reduces substantially after regenerating using the above-mentioned method. This may be attributed to the gradual dissolution of the coatings from the surface during the vigorous washing of the adsorbent.

### 1.3 Justification

Although the natural absorbents: charcoal and bauxite may be readily available and inexpensive, the cost of transporting to site may be very expensive.

In order to make a cost effective and user-friendly process, the exhausted media is recoated with aluminium hydroxide. This will in effect reduce the cost of transporting fresh adsorbent to site upon exhaustion and also reduce the exploitation

of limited natural resources to an appreciable level.

The method of regenerating exhausted media by surface coating the media with aluminium oxide seeks to protect the environment from fluoride re-contamination. In that, unlike the regeneration method, which involves the rinsing of the media with NaOH solution, this method will not re-introduce the adsorbed fluoride into the environment in form of regenerant waste.

#### 1.4 Objective

The overall objective of this study is to determine the feasibility of regeneration of exhausted AOCM and its classification for safe disposal after saturation.

#### **Specific Objectives**

The following are the specific objectives to be achieved by this study:

- To determine the effectiveness of the regeneration process based upon the amount of Aluminium adsorbed onto the media
- To assess the fluoride removal performance of the regenerated media using batch adsorption experiments.
- To assess the level of leaching of Aluminium from the regenerated material into water.
- To characterize fluoride- saturated AOCM that allows its classification into hazardous, non hazardous and inert for safe disposal.

#### **1.5 Scope of work**

This research study is a bench scale test; it is to investigate the feasibility of restoring the adsorption capacity of exhausted media by recoating with Aluminium oxide and classifying the waste generated in the regeneration and adsorption processes for safe disposal. For purpose of this study, model water was prepared to simulate the

existing groundwater quality in the northern Ghana where the fluoride problem is prevalent.

This water quality information was obtained from a preliminary study done by Buamah and Dapilah (unpublished) in 2008. The information obtained from that preliminary study confirmed previous groundwater quality survey done by Community Water and Sanitation Agency (CWSA). The duration for that investigation was six (6) months.

Northern Ghana as used in this study comprises the Northern, Upper East and Upper West regions of Ghana.

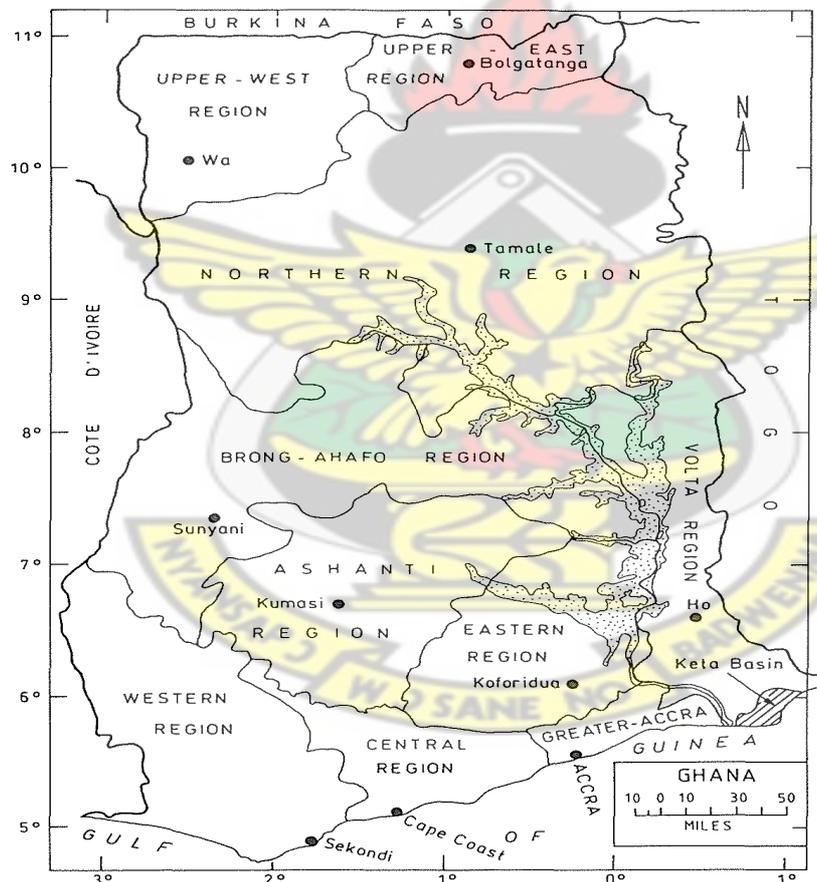


Figure 1 -1: Regional map of Ghana

## CHAPTER TWO

### 2.0 Literature Review

#### 2.1 Water occurrence in Ghana

According to Water and Sanitation Monitoring Platform (WSMP) Ghana, 2009 the potable water coverage in Ghana is about 57% for rural areas and 80% for urban centers although Ghana is well endowed with fresh water resources. The distribution of the available fresh water resources is not uniform throughout the country and changes significantly annually and seasonally. The southwestern part is highly endowed than the Northern and Coastal regions. Conversely, the availability of water is dwindling due to some factors such as rainfall variability (partly due to climate change), rapid population growth, increased environmental degradation and pollution of water bodies (Dwamena-Boateng *et al.*, 2011).

##### 2.1.1 Geology and Groundwater

Groundwater occurrence in Ghana is associated with 3 main geological formations. These are the basement complex, comprising crystalline igneous and metamorphic rocks; the consolidated sedimentary formations underlying the Volta basin (including the limestone horizon); and the Mesozoic and Cenozoic sedimentary rocks. The basement complex and the Voltain formation cover 54 percent and 45 percent of the country respectively. The remaining 1 percent consists of Mesozoic and Cenozoic sediments (Smedley *et al.*, 1995)

According to Kortatsi (1994), groundwater in Ghana is less prone to pollution and has been a major source of water supply to rural communities without the reach of treated water supply systems. Groundwater is usually extracted in Ghana using hand-

dug wells and boreholes (Plates 2-1 and 2-2 respectively). The various groundwater development programmes in Ghana have resulted in the construction of more than 10,000 boreholes nationwide (Kortatsi, 1994).

The percentage of successful boreholes in the Upper East Region is considerably high (93.8%) compared to 60.9% and 90.8% from the Northern and the Upper West regions respectively (Antwi *et al*, 2011). The drilling success depends mainly on the yield of the well or the quality of groundwater.

The dominant controls on fluoride occurrence in groundwater are climate and geology. The regions of Ghana most vulnerable to high fluoride concentrations and its associated dental and skeletal fluorosis are the arid zones of the north and areas where bedrock geology is dominated by granite. The Upper Regions of Ghana are therefore considered to be the most likely areas to experience potential problems.

According to Atipoka (2008), the Bongo district in northern Ghana had 335 boreholes in all the seven Area Councils but 35 of these boreholes are capped due to high fluoride content. These 35-capped boreholes were mostly underlain by granite.

Marked variations in fluoride concentration with depth have been observed in ground waters from the problem areas of Bolgatanga; shallow ground waters and dug wells had significantly lower concentrations than tube well waters this Smedley (1995) explained was as a result of dilution by recent recharge.



Plate 2 -1: Hand dug well



Plate 2 -2: Borehole with hand pump

### 2.1.3 Water Use and Fluoride contamination

The major consumptive water uses in Ghana are water supply, irrigation and livestock watering. Domestic and industrial urban water supplies are based predominantly on surface water, either impounded behind small dams or diverted by weirs in rivers. Water supplies in rural areas, on the other hand, are obtained almost exclusively from groundwater sources.

Generally the ground water on which the rural areas especially those in northern Ghana rely mostly for potable water is characterized by high fluoride concentrations exceeding the World Health Organization (WHO) recommended maximum fluoride concentration of 1.5mg/l. Fluoride concentration beyond this limit can give rise to skeletal or dental fluorosis.

Concentrations of fluoride in excess of 1.5 mg/l (up to 3.8 mg/l) have been observed in Bolgatanga and Sekoti in close association with granitic rock types (Smedley *et al.*, 1995). More recent works conducted in the upper regions of Ghana according to Antwi *et al.*, 2011 recorded fluoride concentration of 20.6mg/L in ground waters.

GNA (2011) also reported that the Northern Region Small Towns Water and Sanitation Project (NORST) was finding it difficult to provide boreholes to some communities in the Yendi Municipality due to high fluoride content in 12 boreholes drilled so far.

From figure 2-1 it can be observed that areas under-lying by granitic rocks in the northern Ghana are prone to fluoride contamination. Contrary ground waters in granitic rocks of the southwest plateau are considered to be less at risk because of higher rainfall and its diluting effect on groundwater compositions according to Dwamena-Boateng *et al.*, 2011.

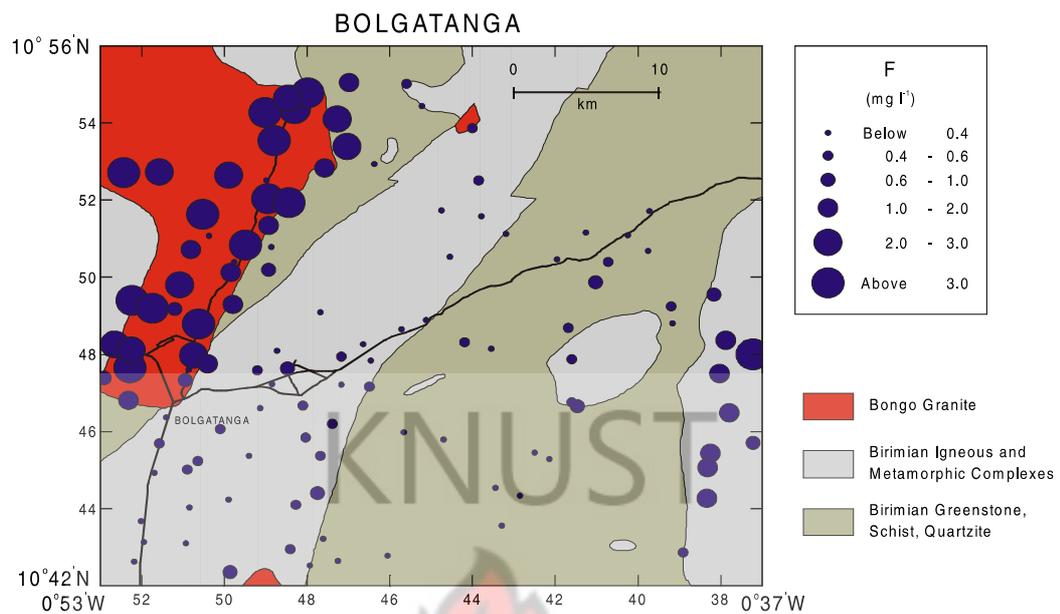


Figure 2-1: Geological map of the Bolgatanga area showing distribution of fluoride in groundwater (Smedley *et al.*, 1995)

## 2.2 Health effects of fluoride

Although fluoride has positive effects on teeth at low concentrations in drinking water, there is no data indicating the minimum nutritional requirement of the element. Excessive exposure to fluoride in drinking water or in combination with fluoride from other sources can result in several health problems. These vary from mild dental fluorosis (plate 2-3) to crippling skeletal fluorosis (plate 2-4) depending on the level and period of exposure (Fawell *et al.*, 2006). According to Shorma *et al.*, (2004), the water intake of people living in the tropics is higher than those living in temperate region. In effect of this although the level of fluoride in ingested water may be similar or same the effect of the fluoride will be higher in the Tropics than in the temperate regions.

Shorma *et al.*, 2004 also reported that the ingestion of fluoride is not only through the

drinking of water but also the eating of some food such as fish and other seafood. High levels of fluoride present in concentrations up 4mg/l were related with dental fluorosis as shown in plate 2-3 (yellowish or brownish stains or mottling of the enamel) while low levels of fluoride less than 0.5 mg/l were associated with high level of dental decay (Edmunds and Smedley, 1996). Additionally poor nutritional status is also an important contributory factor to the latter.

Skeletal fluorosis is known to occur in different part of the world, which result due to high exposure to fluoride (>4mg/l). In its early stages this disease manifests as osteosclerosis, involving the hardening and calcification of bone. This causes pain, stiffness and even irregular bone growth. In its advanced stages, crippling skeletal fluorosis involves severe bone deformation as shown in plate 2-4 and this symptom is irreversible. Ingestion of concentrations greater than 100mg/l can result in growth retardation, kidney changes or even the ultimate, which is death.

Duah (2002) also added that according to a Dental Health Service Survey conducted in 1993 for 1558 students in the Bongo District, 62% of the students (966 students) were suffering dental fluorosis. According to Antwi *et al.*, 2011 although the people of Bongo are aware of the health impact of consuming excessive concentrations of fluoride some communities are unable to stop drinking from fluoride contaminated wells. This is due to non-existence of alternative sources of safe drinking water. The prevalence rate of dental fluorosis among school children has been estimated at 33% in Bongo and surrounding communities (Atipoka, 2008).

Table 2- 1: Concentrations of fluoride in drinking water and its related health effects [Source: Mjengera and Mkongo, 2009; Fawell et al., 2006]

Concentration in mg/L	Health Effect
< 0.5	Dental caries
0.5 - 1.5	Promotes dental health/good bone development
1.5 - 4	Dental fluorosis (Mottled enamel)
> 4	Dental/skeletal fluorosis
>10	Crippling fluorosis
> 50	Thyroid changes
>100	Growth retardation
>120	Kidney changes
> 250	Death



Plate 2 -3: - Dental fluorosis



Plate 2 -4: - Skeletal fluorosis

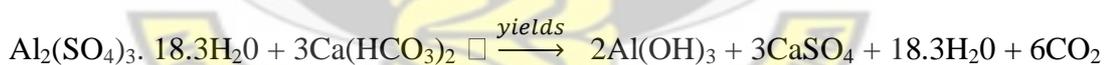
### 2.3 Defluoridation Methods

Numerous defluoridation technologies have been established, however only a few have shown to be promising for field application. A good defluoridation technology, it should ideally use locally available cheap material having an excellent potential for fluoride removal, versatile and additionally simple for field application (table 2-2). According to the IRC technical paper series 40, defluoridation techniques can be classified into four namely:

- Chemical additive methods
- Contact precipitation
- Ion exchange
- Adsorption

### 2.3.1 Chemical Treatment

In this treatment, mostly chemical agents (coagulants) are used to destabilize the fluoride particles in solution. The coagulants promote the aggregation of the molecules aided by mixing and flocculation. The succeeding insoluble fluoride precipitates are then removed by sedimentation and filtration (Benefield *et al.*, 1982). The precipitation of fluoride in water using aluminium sulphate and lime for correction of pH, which is popularly called the Nalgonda technology, is one of the chemical additive methods. Although it is a well-tested technique a large amount of Alum is required and moreover the disposal of the sludge formed is usually problematic. Again if the alum dose is not adhered to based on the fluoride concentration there is a possibility of excess aluminium contamination of the water. Alum upon coming into contact with water reacts with the alkalinity in the water to produce insoluble aluminium hydroxide. The fluoride is hence removed by adsorption onto the aluminium hydroxide precipitates and the resultant flocs formed are mostly separated from the water by sedimentation and or filtration (Benefield *et al.*, 1982). Resultant Alum Reaction is as below:

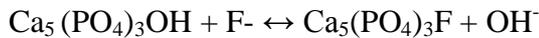


### 2.3.2 Contact Precipitation

According to Fawell *et al.* (2006), contact precipitation is a technique by which the addition of calcium and phosphate compounds to the water does the defluoridation. The water is then brought in contact with an already saturated bone charcoal medium. In solutions containing calcium, phosphate and fluoride, the precipitation of calcium fluoride and/or fluorapatite is theoretically feasible, but practically difficult due to slow reaction kinetics. It has recently been reported that the precipitation is

easily catalysed in a contact bed that acts as a filter for the precipitate (Dahi, 1996).

The expected reaction is as follows:



### **Advantages**

- Locally available, cheap raw material (animal bones)
- High sorption capacity
- Fast reaction time (less than 30 min)
- No additional chemicals are needed for the treatment process
- Filtered water mostly is neutral in taste and colour

### **Disadvantages**

- Limited acceptability of animal bones as filter material for drinking water
- Initial investments and experience needed to set up bone char production
- Maintenance and regular monitoring necessary - if filter is saturated it needs to be regenerated or replaced

### **2.3.3 Ion Exchange**

From studies conducted by Smith and Smith (1937) it was established that caustic and acid treated bone material was capable of reducing fluoride concentration in drinking water very effectively from 3.5 to less than 0.2 mg/l. The removal mechanism employed was the exchange of the carbon radical with the fluoride ions. Maier (1953) also confirmed this principle when he conducted a study on the defluoridation of drinking water using "Bone Char". The study indicated that the principle of this method was the exchange of carbonate ion of the bone char with fluoride ion present in the water. Bone char according to the study could be

regenerated with NaOH to remove bound fluoride after exhaustion and can be reused.

Conversely an investigation conducted by Bellack (1971) indicated the non-practicability of using bone char to remove fluoride from arsenic rich waters. This he attributed to the fact that the arsenic competes with fluoride and the normal caustic- regeneration process cannot strip the arsenic off. Consequently reducing the fluoride exchange capacity of the bone char even after regeneration.

Thomson and Mc Garvey (1953) was among the first to report that the fluoride exchange capacity of a resin was affected by the presence of other anions.

#### **2.3.4 Adsorption**

Crittenden *et al.* (2005) define adsorption as a mass transfer process, which a constituent in the liquid/gas phase is accumulated on solid/liquid phase and separated from its original environment. This process results in the creation of a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent.

The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction. Adsorption is applied in many physical, biological and chemical systems. It is widely used at both industrial and domestic levels. This phenomenon can also be used to remove contaminants such as fluoride, arsenic, and iron and so on from drinking water.

Many studies have been done in search of adsorbents adequate for the removal of fluoride from drinking water. These include charcoal and bauxite (Mwampashi, 2011), neem seeds and zeolite (Asare-Mensah, 2011).

***Adsorption onto virgin charcoal and Aluminium Oxide Coated Charcoal (AOCC)***

Charcoal is the dark grey residue consisting of carbon, and any remaining ash, obtained by removing water and other volatile constituents from animal and vegetation substances. The slow pyrolysis of wood or other substances in the absence of oxygen usually result in the formation of charcoal. The presence of ash usually makes charcoal an impure carbon. The resulting soft, brittle, lightweight, black, porous material resembles coal.

Although charcoal has high adsorption capacity for fluoride its capacity is not adequate to meet the WHO required guideline value. According to a research work done by Mwampashi, 2011: model water with a fluoride concentration of 5.3mg/L was treated with a 10g/L each of virgin and aluminium oxide coated charcoal (AOCC). It was observed that the AOCC had a higher adsorption capacity than the virgin charcoal as can be seen in figure 2.2 below. This high adsorption capacity of the AOCC was attributed to the presence of the Aluminium on the media, which has high affinity for fluoride. Again from the kinetics it was also observed that the fluoride adsorption in the first four hours was very rapid but was relatively slowed afterwards. The rapid adsorption was attributed to the initial availability of active sites on the surface of the charcoal. The reduced rate of adsorption was however related to the saturation of its active sites or the fluoride ions diffusing into intrapores of the charcoal media.

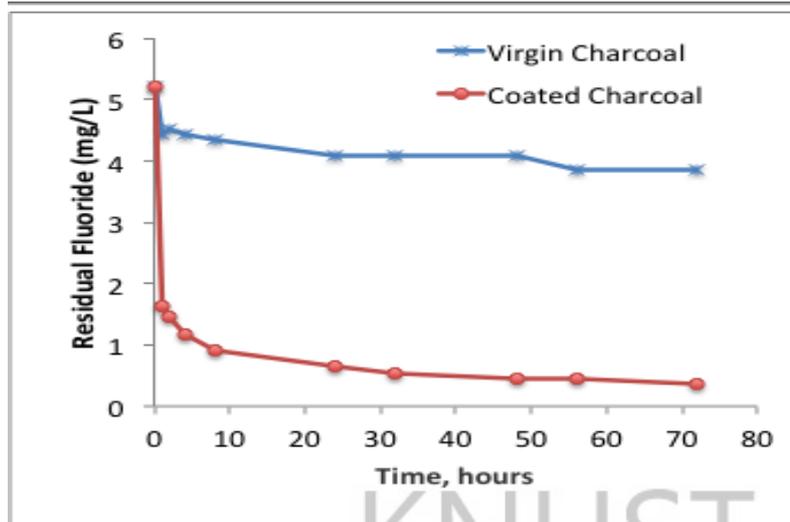


Figure 2-2: Kinetic of fluoride removal by 10g/L virgin and coated charcoal adsorbents from model water at room temperature and pH 7 (Mwampashi, 2011)

### ***Adsorption onto virgin bauxite and AOCB***

Fluoride ion due to its high electronegativity and small ionic size is classified as a hard base, which has a strong affinity for multivalent metal ions including Al (III) and Fe (III).  $Fe^{3+}$  and  $Al^{3+}$  ions have good affinity for fluoride anions, because of the hard-hard combination, in agreement with the soft-hard acid base (SHAB) concept.

In Ghana, there are basically two types of bauxite available namely: High Aluminium Bauxite Ore (HABO) and High Iron Bauxite Ore (HFBO). According to a study made by Asare Mensah, 2011 the fluoride adsorption capacity for HABO is greater than that of HFBO.

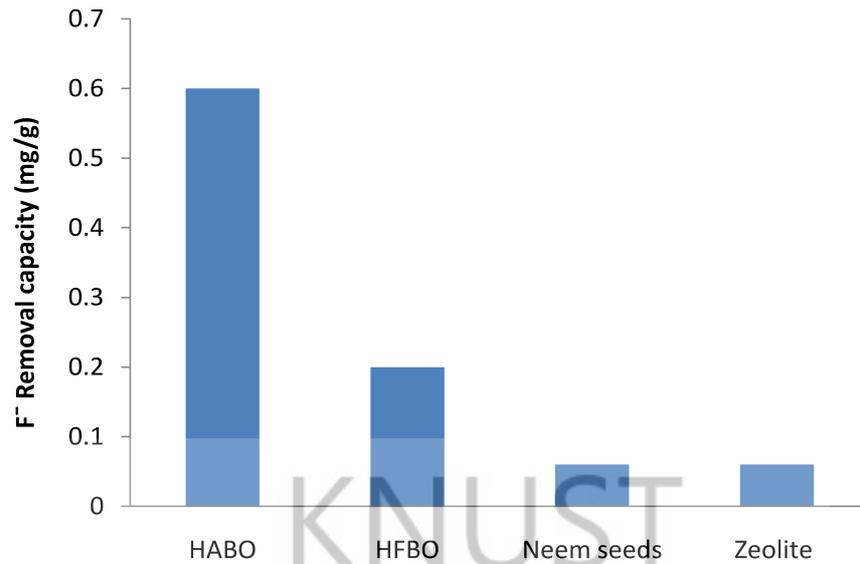


Figure 2-3: Fluoride removal capacities for some selected media (Asare Mensah, 2011)

Asare Mensah (2011) characterized the HABO from Awaso as being crystalline comprising basically of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5$ ) and gibbsite ( $\text{Al}(\text{OH})_3$ ) from the X-ray diffraction (XRD) analysis conducted (figure 2-4).

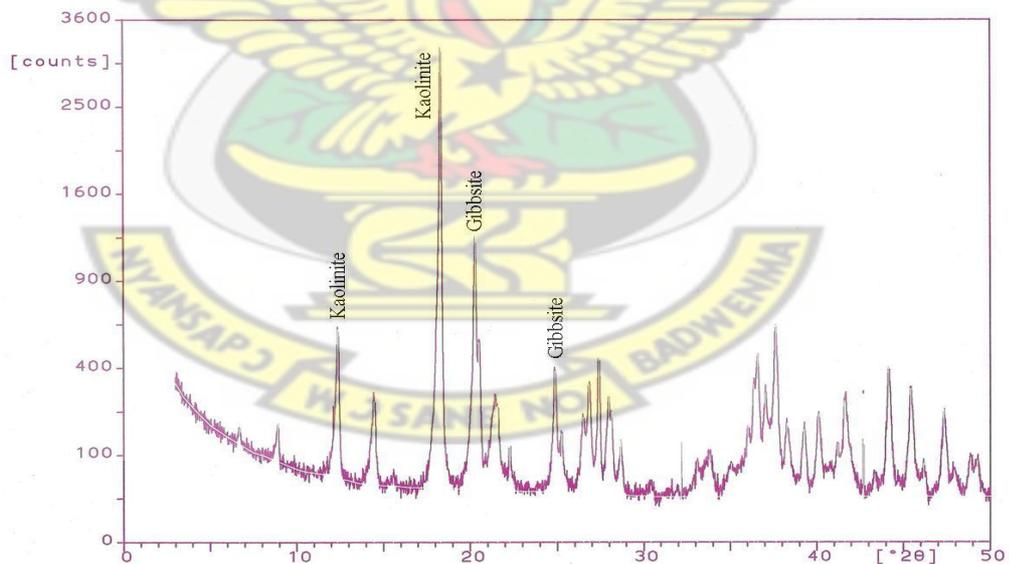


Figure 2- 4: XRD spectra of HABO (Asare Mensah, 2011)

Furthermore from the Energy Dispersive X-ray (EDX) and X-ray Fluorescence (XRF) analysis that were made, it was discovered that the elements that were

predominant on the surface of the HABO were C, O, Al, Si, Ti and Fe (figure 2-5).

The presence of the Ti on the surface of the HABO also makes it possible for the formation of Fluorotitanate complexes, which can decrease its fluoride adsorption capacity.

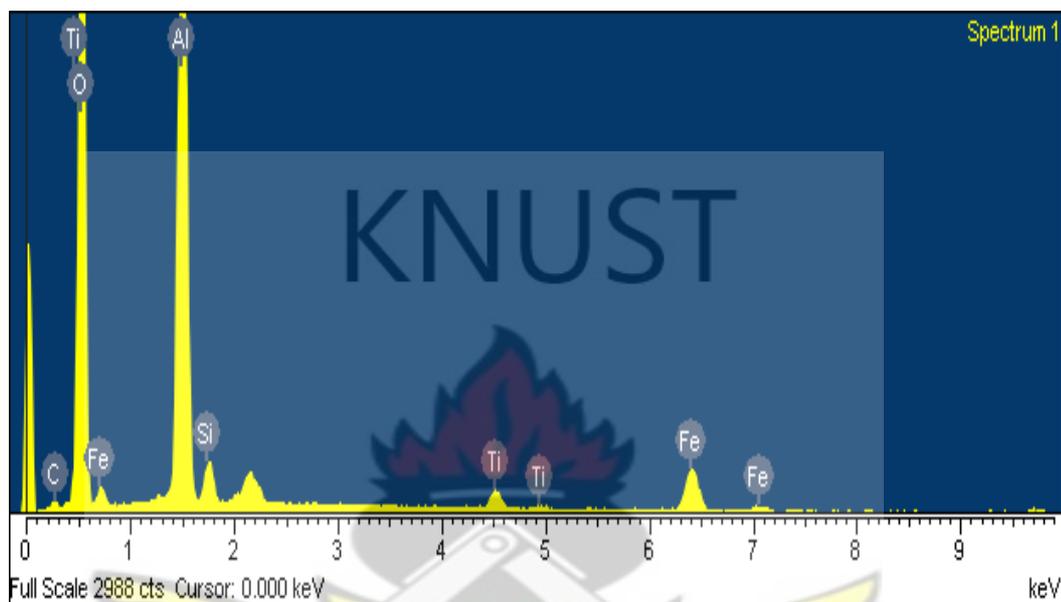


Figure 2 5: EDX spectrum of HABO

Table 2- 2: Treatment options for Defluoridation (Solsona, 1985)

Method	Capacity/ dose	Working pH	Interference	Advantages	Disadvantages
Aluminium sulphate	150 mg/mg F	Ambient	--	Well known Process	Sludge produced low pH of treated water
Lime Softening	30 mg/mg F	Ambient	--	Well known process	Sludge produced high pH of treated water
Alum & Lime (Nalgonda Technique)	(150 mg alum + 7mg lime)/mg F	Ambient	--	Low technology	Sludge produced High chemical dose
Bone	900 g F/ cum	Ambient	Arsenic	Locally Available	Loss of material, Taste problems
Bone char	1000 g F/ cum	Ambient	--	Locally Available	Control of raw water pH
Activated Carbon	Variable	<3.0	Many	--	pH changes before and after treatment
Carbon prepared from agricultural waste like rice husk, coffee waste etc.	300 mg/kg	7	--	Locally Available	Required treatment with KOH
Defluoron-2	350 g F/ cum	7	Alkalinity	--	Steep decline in capacity with

					alkalinity
Activated Alumina	2000-4000 g F/cum	5	Alkalinity	Effective, simple in application	
Electro dialysis	High	Ambient	Turbidity	Can remove other ions used with high salinity	Requires skilled operators, costly, not much used
Reverse osmosis	High	Ambient	Turbidity	"	"

### 2.3.5 Fluoride Measurement

The determination of fluoride in water is primarily done using calorimetric, potentiometric, and titrimetric and chromatographic methods. Potentiometric method that employs the use of an ion- selective electrode (ISE) is the most widely used in that calorimetric, titrimetric and chromatographic methods are expensive and time consuming. ISEs are simple to use, amply sensitive, selective and accurate (Fouskaki, 2003). Fluoride concentrations in water far below the WHO guideline value can be measured using this method.

Sample preparation is very crucial for accurate quantification of fluoride since only free fluoride ion is measured (Fawell *et al.*, 2006). ISEs measure the potential across the reference and the sensing electrodes from which the concentration of analytes in solution is determined. The fluoride electrode, which is a solid-state electrode, employs an inorganic salt crystal as the ion selective membrane. The crystal used is LaF<sub>3</sub> doped with Eu<sup>2+</sup>. The filling solution or the electrolyte is a solution of 0.1 M NaF and 0.1 M NaCl. Doping LaF<sub>3</sub> with EuF<sub>2</sub> creates anion vacancies within the crystal. As adjacent fluoride ions migrate into the vacancy, a potential difference is created and is recorded on a meter as potential. The fluoride electrode has a response to changes in fluoride ion concentration from about 10<sup>-6</sup> - 1 M. Hydroxyl ions (OH<sup>-</sup>) are the only interfering species. As a result, Total Ionic Strength Adjustment Buffer (TISAB) containing glacial acetic acid, Cyclohexane-1-2diaminetetra acetic acid, NaOH and NaCl is used to adjust samples and standards to the same ionic strength

and pH so that the fluoride activity coefficient is constant in all solutions. The pH of the buffer is about 5.5, where interference by  $\text{OH}^-$  is zero and there is little conversion of  $\text{F}^-$  to HF. Citrate also forms stable complexes with  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  to prevent these ions from binding with  $\text{F}^-$ . To use the electrode to determine the fluoride concentration in an unknown sample, a standard curve should be prepared by plotting the concentration of fluoride against measured potential (Harris, 2003).

## 2.4 Aluminium Oxide Coating on HABO and Charcoal

### 2.4.1 Optimum coating cycle

Mwampashi, 2011 reported that the amount of aluminium that can be coated onto the HABO and the charcoal does not increase significantly after the second coating cycle. In coating of HABO and charcoal it will be more economical to coat only twice (figures 2-6 and 2-7 respectively).

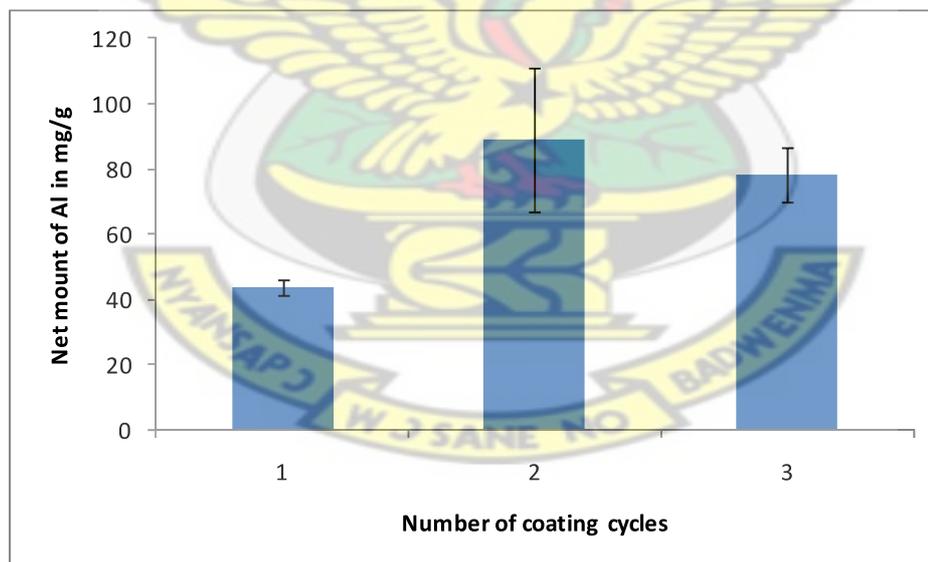


Figure 2-6: Amount of Al coated onto the HABO for three coating cycles

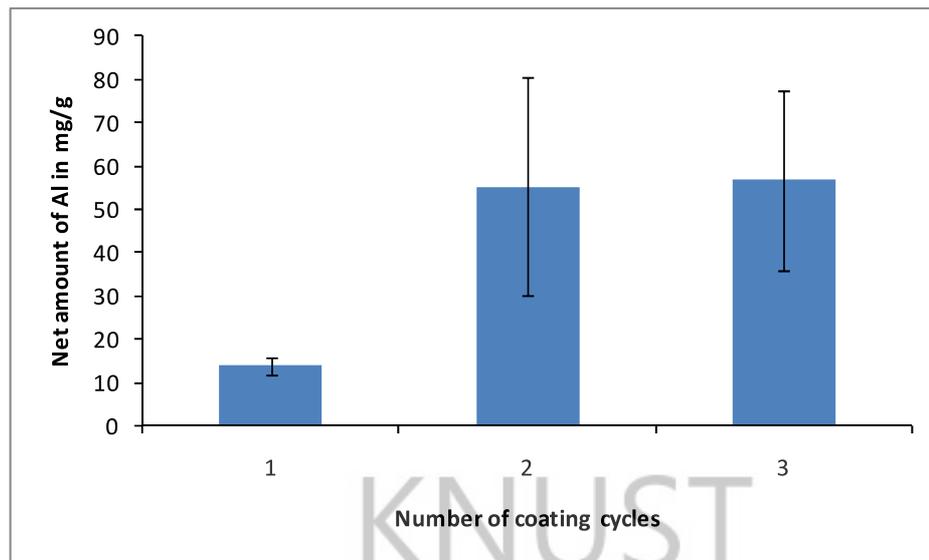


Figure 2 7: Amount of Al coated onto the charcoal for three coating cycles

### 2.4.2 Coating pH

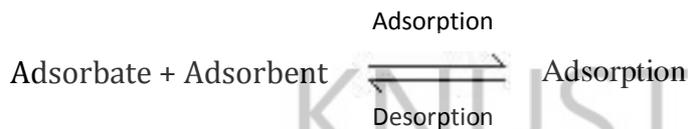
Adsorption is usually critically affected by pH, the higher the pH the lower the adsorption. According to Mwampashi (2011) Aluminium sulphate solutions normally have a pH range of 1.8-2. Fortunately this pH is very low and in order not to introduce more chemicals in the form of acid it was more appropriate to do the coating of the media at this said pH range.

### 2.5 Adsorption Models

Adsorption is the net accumulation of a chemical species at the interface between a solid phase and an aqueous solution phase, leading to a loss from the solution phase. Graphs known as adsorption isotherms are usually used to study the process of adsorption. Adsorption models indicate the equilibrium surface concentration of adsorbate on adsorbent in relation to concentration of adsorbate in the solution at given temperature. It is presented in different mathematical forms. Some are simplified picture of adsorption and desorption while other are purely empirical and

tend to correlate to experimental data in simple equations with two or at most three empirical parameters.

There are many mathematical relationships (model) that can be used to describe the adsorption data, but the most commonly used are Langmuir and Freundlich isotherms and Brunauer, Emmett and Teller (BET) (Faust and Aly, 1998).



### 2.5.1 Freundlich Adsorption Isotherm

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known Freundlich Isotherm.

As per Freundlich adsorption equation,  $q_e = kC_e^{1/n}$

Where,

$q_e$  - is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)

$k$  - is the adsorption capacity (mg/g)

$C_e$  - equilibrium concentration of adsorbate in bulk solution (mg/l)

$n$  - is a measure of the adsorption intensity.

Taking log of both sides of equation, the below equation will be obtained:

$$\log q_e = \log k + \frac{1}{n} \log C_e$$

The equation above is comparable with equation of straight line,

$y = m x + c$  where,  $m$  represents slope of the line and  $c$  represents intercept on y-axis.

Plotting a graph between  $\log (q)$  and  $\log C_e$ , we will get a straight line with value of slope equal to  $1/n$  and  $\log k$  as y-axis intercept.

### 2.5.2 Langmuir Adsorption Isotherm

In 1916, Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm and it holds for single layer adsorption. This isotherm was based on the assumptions that the surface containing the adsorbing sites is perfectly flat with no corrugations with all adsorptive sites being equivalent. Additionally, each site can hold at most one molecule of the adsorbate and there are no interactions between the adsorbed molecules.

Linearization of the Langmuir adsorption equation,  $q_e = \frac{b q_m C_e}{1 + b C_e}$  takes the form

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{b q_m C_e}$$

Where  $q_e$ - is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g),  $b$ -Langmuir isotherm constant,  $q_m$ - Maximum adsorption capacity (g/g),  $C_e$ - Equilibrium concentration of adsorbate in bulk solution (mg/l).

### 2.5.3 BET adsorption Isotherm

BET Theory established by Brunauer, Emmett and Teller explained that multilayer formation is the true picture of physical adsorption rather than the single layer adsorption predicted by Langmuir. The proposed equation is as follows:

$$\frac{q_e}{q_m} = \frac{B C_e}{(C_e - C_s)[1 + (B - 1)(C_e/C_s)]}$$

Where

B- is a dimensionless constant

$C_s$ – saturation concentration of the adsorbate

$C_e$  -Equilibrium concentration of adsorbate in bulk solution (mg/l)

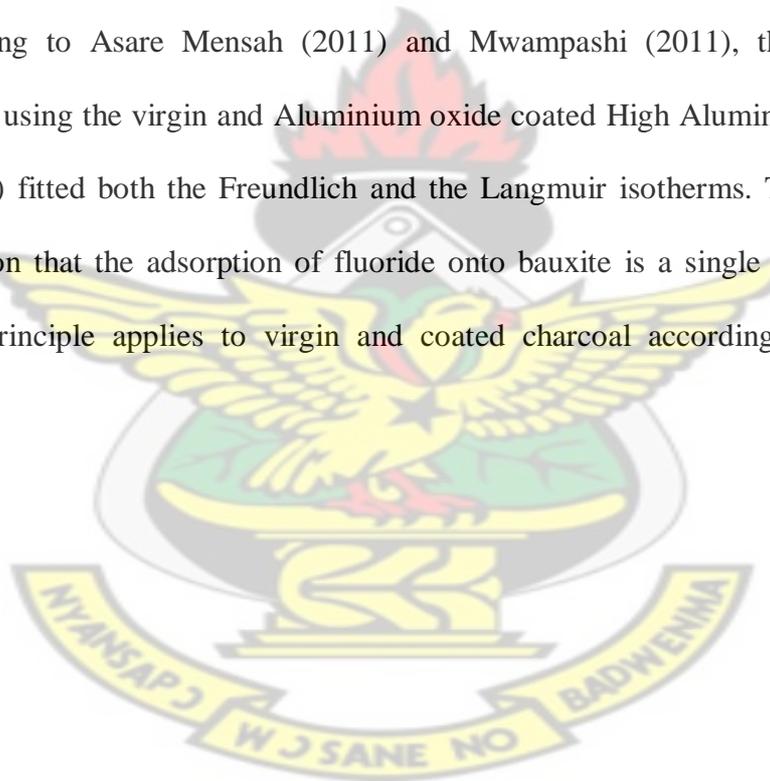
$Q_e$ - is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)

$q_m$ - Maximum adsorption capacity (g/g)

Upon linearizing this above stated equation the following will be obtained:

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{Bq_m} + \frac{B - 1}{Bq_m} \frac{C_e}{C_s}$$

According to Asare Mensah (2011) and Mwampashi (2011), the adsorption of fluoride using the virgin and Aluminium oxide coated High Aluminium Bauxite Ore (HABO) fitted both the Freundlich and the Langmuir isotherms. This was then an indication that the adsorption of fluoride onto bauxite is a single layer adsorption. Same principle applies to virgin and coated charcoal according to Mwampashi (2011).



## 2.6 Adsorption Kinetic models

### 2.6.1 Pseudo-first order kinetic model

Lagergren in 1898 established a first-order rate equation to describe the kinetic process of liquid-solid adsorption phase of oxalic acid and malonic acid onto charcoal. This is considered to be the earliest model relating to the adsorption rate based on the adsorption capacity. It can be presented as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Where:  $q_e$  and  $q_t$  (mg/g) are the adsorption capacities at equilibrium and time  $t$  (hours), respectively.  $k_{p1}$  ( $\text{hour}^{-1}$ ) is the pseudo-first-order rate constant for the kinetic model.

According to Ho (2004), upon integrating and linearising the above equation with the boundary conditions  $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$  the equation below was obtained.

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

### 2.6.2 Pseudo-second order kinetic model

Ho and Ofomaja (2005) reported that the adsorption of lead ion onto palm kernel fiber followed the pseudo-second order rate law. It was therefore predicted that the rate of the reaction was not dependent on the concentration of the adsorbate but rather on the available adsorptive sites on the adsorbent. Additionally the model also suggests that the mode of adsorption is more chemisorption than physisorption. The reaction order and rate constants are determined by experiments.

The rate expression for this model can be written as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Where,

$K_2$ - is the rate constant of sorption (g/(mg min))

$q_e$  - the amount of adsorbate adsorbed at equilibrium (mg/g),

$q_t$  - is the amount of adsorbate adsorbed on the surface of the adsorbent at any time  $t$  (mg/g).

$t$ - time (hours)

The linearized form of the above equation is:

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

The adsorption rate constant ( $k_2$ ) and adsorption capacity can be estimated when a graph of  $t/q_t$  against  $t$  is plotted.

According to Asare Mensah (2011) and Mwampashi (2011) the kinetics for the adsorption of fluoride onto High Aluminium Bauxite Ore (HABO) and Charcoal fitted better the pseudo second order model than the pseudo first order model. This then was an indication that the adsorption capacity of the media played a significant role in the rate of the defluoridation and also the adsorption could be described as chemisorption.

### 2.6.3 Intra-particle diffusion kinetic model

Weber and Morris in 1962 developed the first intra- particle diffusion model. According to this model, the fractional approach to equilibrium varies according to a function of  $(D_t/r^2)^{0.5}$ , where  $D_t$  is the diffusion coefficient in the media and  $r$  the particle radius. From this function the initial rate of intra-particle diffusion can be calculated by linearizing the curve,  $q_t = f(t^{0.5})$ .

where  $q_t$  is the amount of adsorption time  $t$  (hour) (mg/L) ,  $f$  is the rate constant of

intra-particle diffusion (mg/g).hour and t is time in hours.

Urono and Tachikawa (1991) also proposed a model, which considered the adsorption rate to be independent of the stirring speed and external diffusion being negligible relative to the low overall sorption rate.

The model has the following equation:

$$f(q_t/q_m) = -[\log(1 - (q_t/q_m)^2)] = \frac{4\pi^2 Dt}{2.3d^2}$$

Where  $q_t$  and  $q_m$  are the solute concentration in the solid at t and at equilibrium, d is the particle diameter and D is the diffusion coefficient in the solid ( $m^2.s^{-1}$ ).

Qin Li *et al.*, 2006, reported that if the relation plots of  $q_t$  and  $t^{1/2}$  do not go through origin then the adsorption of the adsorbate on the adsorbent is not controlled by intra-particle diffusion.

## 2.7 Regeneration

When the adsorption capacity of an adsorbent reduces drastically and it is unable to adsorb any more adsorbate, such adsorbent can be said to be exhausted. Regeneration is a process of restoring the adsorption capacity of the adsorbent in order to be put to use again. According to Jacobsen and Dahi (2007) there are various methods that can be applied to restore the adsorption capacities of adsorbents these include: regenerating using 1% alkaline solution, the main principle underlying this method is the ion exchange between the fluoride ions and the hydroxyl ions.

Additionally another potential regenerating method is the surface coating. From the study conducted by Christoffersen *et al.* (2007) recoating the surface with hydroxyapatite makes the bone char media behave like a fresh media able to adsorb

new amount of fluoride. This was found out to work for several cycles although the capacities declined successively (figure2-8).

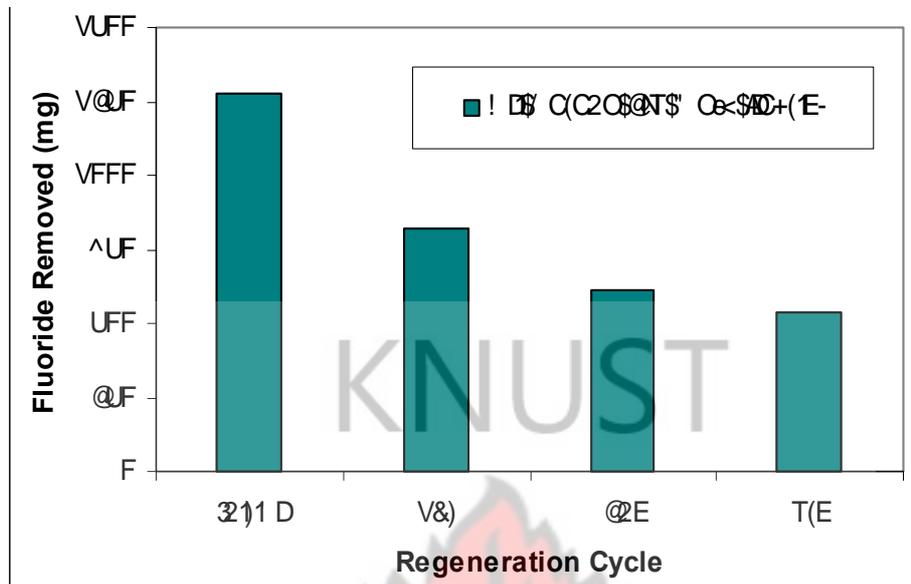


Figure 2.8: Fluoride adsorption capacity of Activated Alumina after 3 regeneration cycles (Christoffersen *et al.*, 2007)

### 2.8 Establishing the regeneration efficiency through Al extraction test

The Aluminium extraction test is conducted to know the amount of Aluminium coated onto the media before and after the regeneration. This is to establish the efficiency of the regeneration. Due to fluoride having high affinity for multivalent metals such as Aluminium: the higher the amount of Al coated onto the media the greater its adsorption capacity will be (Tchomgui-Kamga, *et al.*, 2009). According to Mwampashi (2011) the adsorption efficiency of bauxite and charcoal coated twice is better than that coated once because more Aluminium tends to be coated onto the media. Nevertheless coating more than twice does not increase the amount of Al coated onto the media.

## **2.9 Aluminium leaching test**

This is a test conducted to ascertain the stability of the Aluminium coated onto the media. This is to ensure that no or little amount of Aluminium leach into the drinking water after treatment since ingestion of high concentration of Aluminium can be detrimental to the human health (Alzheimer disease).

According to Mwampashi (2011), Aluminium leaches mostly from AOCC when pH is below 5.5 and above 7. AOCB on the other hand has a least leach when pH is between 6.5-7. A maximum of 0.05mg/L and 0.057mg/L of Al leached from the AOCB and AOCC respectively. This concentration leached was less than the recommended WHO guideline value of 0.2mg/L. This then indicated that treating water with the AOCC and AOCB does not poison the water upon treatment.

## **2.10 Fluoride leaching test**

A leaching test is an established procedure, which is used to determine the readiness of contaminants (inorganic, organic or radionuclides) to mobilize out of a solid phase into a liquid phase. The main purpose of the leaching test is to know the amount of the contaminant, which will be present in the leachate when disposed at a landfill site. It is therefore assumed that if the contaminant does not leach from the waste then its disposal will not cause any threat to groundwater. Redox, pH, dissolved organic matter and biological activity usually affect the leaching process.

According to literature several laboratory leaching test have been documented. These various test do not differ from one another that much, so there is no need adopting all at the same time.

The American Society for Testing and Materials (ASTM) have developed standard leaching tests which use alternate leaching fluids with very little additional

difference in the test methodology. The American Environmental Protection Agency (AEPA) has one regulatory test for the classification of solid wastes under The Resource Conservation and Recovery Act (RCRA): the Toxicity Classification Leaching Procedure (TCLP) (Method 1311). AEPA also has the Synthetic Precipitation Leaching Procedure (SPLP) (Method 1312).

The TCLP is expected to simulate leaching of solid wastes placed in a municipal landfill, while the SPLP is designed to simulate a mono-disposal situation. The TCLP and SPLP have been widely used to generate leachate concentrations for all types of solids for both inorganic and organic constituents.

#### **2.10.1 Synthetic Precipitation Leaching Procedure (SPLP)**

The Synthetic Precipitation Leaching Procedure (SPLP) procedure is applicable for materials where the leaching potential due to normal rainfall is to be determined. The SPLP is useful in situations where a determination must be made if a potentially contaminated material left in situ will leach toxic substances when exposed to normal weathering. A solution of acetic acid was used to simulate the landfill leachate whereas a solution of nitric and sulfuric acids was used to simulate the acid rains resulting from airborne nitric and sulfuric oxides.

#### **2.10.2 Toxicity Leaching Classification Procedure (TCLP)**

The Toxicity Leaching Classification Procedure (TCLP) was developed to estimate the mobility of specific inorganic and organic contaminants that are destined for disposal in municipal landfills. With this method, soaking the solid waste into a simulating landfill leachate does the extraction of the supposed contaminant. The TCLP assumes that the waste will be disposed off together with organic waste at the

landfill. As a result of this Acetic acid was chosen as the extraction fluid because it is the major component of typical municipal landfill where organic waste are disposed at the landfill site.

Two leaching liquids are normally used for the extraction test according to ASTM method 1311, composition of both extraction fluids are elaborated below.

*Extraction fluid 1:* Compose of 5.7 mL glacial  $\text{CH}_3\text{CH}_2\text{OOH}$  and 64.3 mL of 1N NaOH diluted to a volume of 1 liter. When correctly prepared, the pH of this fluid will be  $4.93 \pm 0.05$ .

*Extraction fluid 2:* A 5.7 mL glacial  $\text{CH}_3\text{CH}_2\text{OOH}$  diluted to a volume of 1 liter with distilled water. When correctly prepared, the pH of this fluid will be  $2.88 \pm 0.05$ . When the pH recorded after soaking 5g of the sample in distilled and stirred vigorously for 5 minutes is less than 5 then extraction fluid 1 is used. Otherwise 3.5ml 1N of HCl is added, heated for 10 minutes at a temperature of  $50^\circ\text{C}$  and made to cool to room temperature. Extraction fluid 1 is used when the pH is now less than 5 if not extraction fluid 2 is used.

A schematic diagram of the processes involved in the TCLP is elaborated below (figures 2-10a and 2-10b).

The weight of the appropriate extraction fluid to be used is 20 times the weight of the sample taken.

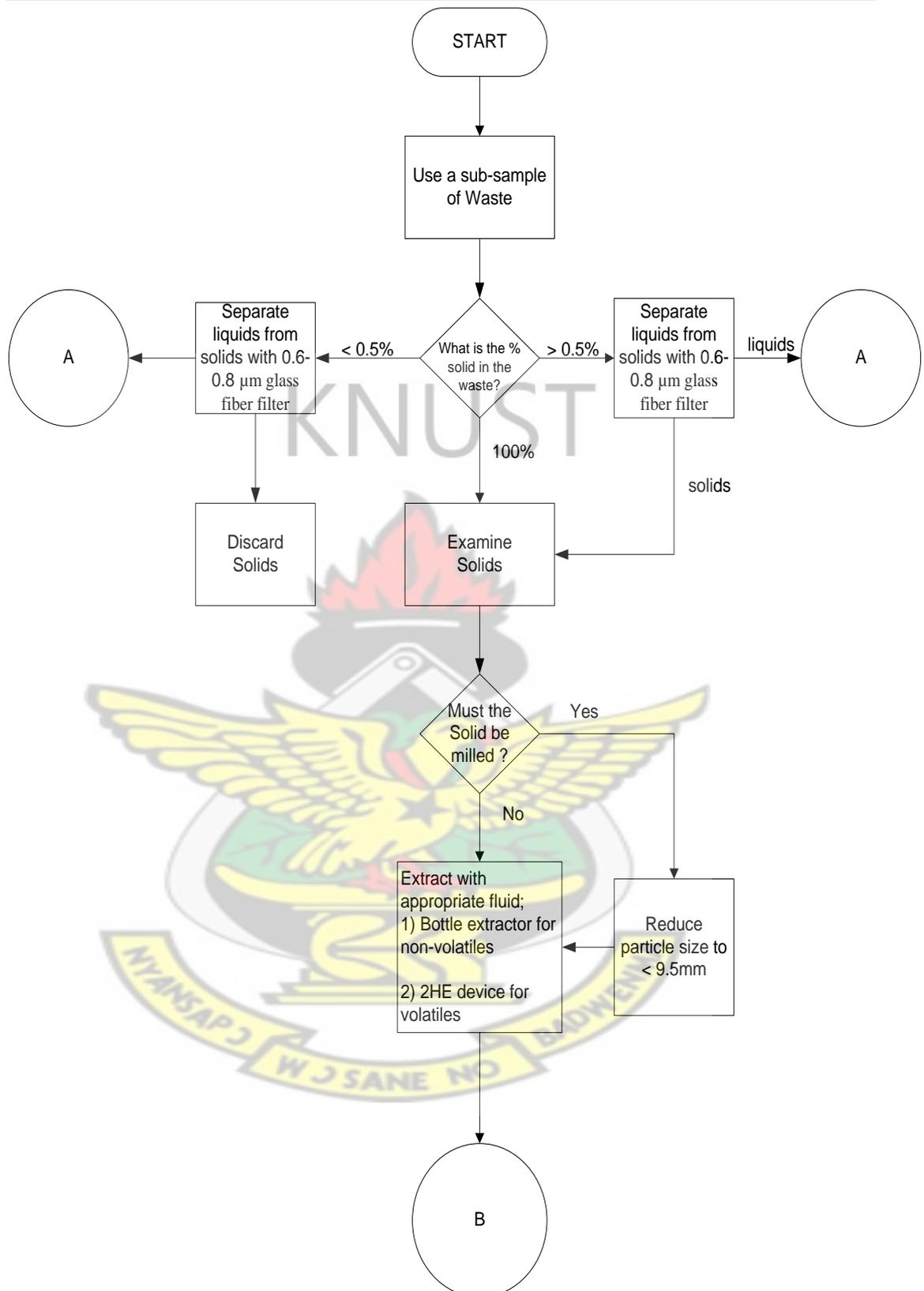


Figure 2 9: Schematic diagram for the performance of the TCLP test

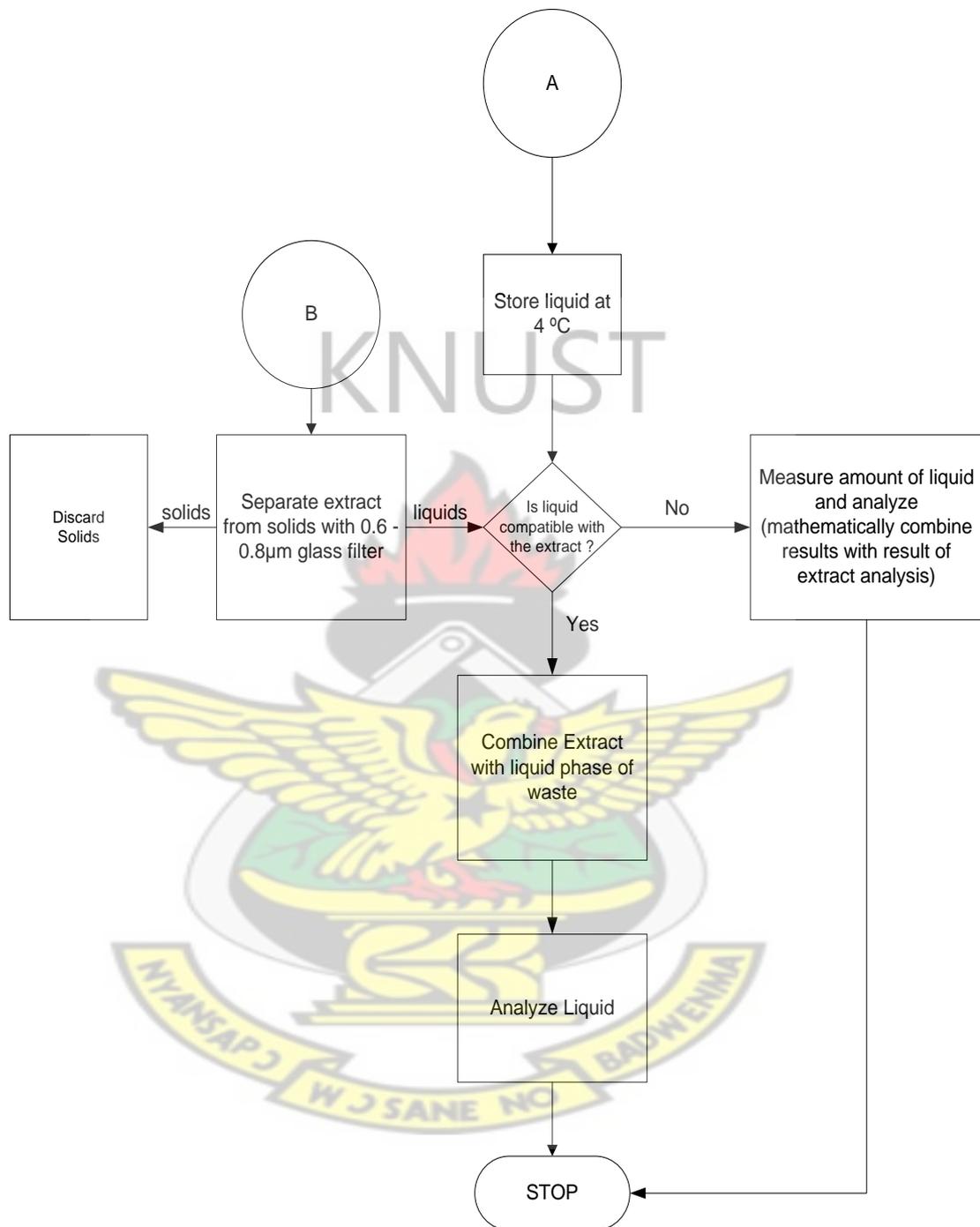
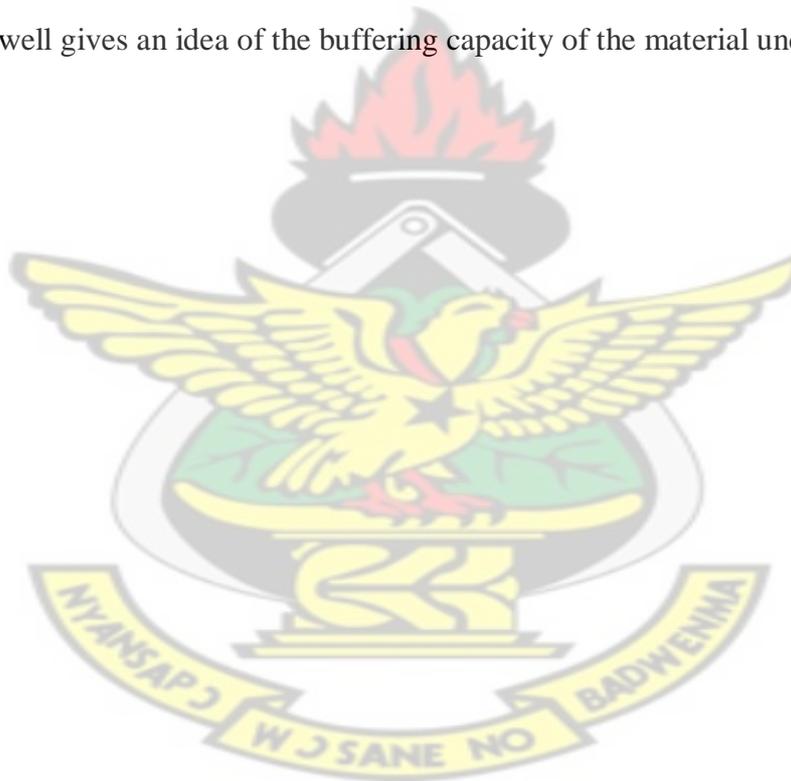


Figure 2 10:Schematic diagram for the performance of the TCLP test

### 2.10.3 pH dependent leaching test

There are more than 50 leaching tests identified worldwide. There is no need adopting all for the characterization of waste since most of the tests are similar.

The pH dependent leaching test however is considered as a generic characterization test due to its agreement with most leaching tests hence most of these leaching tests can be linked with it. The pH dependent leaching test is a European standard (CEN, 2003a, method 1313) that determines the leaching characteristics of granular materials under varying pH conditions. pH range from 2 to 13 is usually used. The test as well gives an idea of the buffering capacity of the material under study.



### **3.0 Research Methodology and Procedures**

#### **3.1 Introduction**

This chapter covers the outcomes of the desk study made as well as the procedures followed to obtain the desired laboratory results. The chemicals as well as the apparatus required in performing each of these experiment are mentioned in this chapter. All chemicals used throughout this study were of analytical grade.

#### **3.2 Laboratory Experiment**

The laboratory experiment included the preparation of the model water, Total Ionic Strength Adjustment Buffer (TISAB), determination of fluoride concentration and coating of Charcoal and HABO. Aluminium leaching and aluminium extraction tests were both conducted to establish the efficiency of the regeneration procedure as well as the stability of the Al coated onto the media.

##### **3.2.1 Preparation of model water**

Model was prepared mimicking the ground water quality in the northern part of Ghana. The model water was prepared using tap water from the Civil Engineering Environmental Quality Engineering (EQE) laboratory. The quality of the tap water was tested and the necessary adjustment made to get the required ground water quality (Table 3.1).

Table 3 1: Water quality of ground water from Northern Ghana (Buamah and Dapilah, 2008)

Parameters	Ground water quality	Parameters	Ground water quality
Alkalinity	137-171	Phosphate	
pH	6.9-7.5	Fluoride	3.97-4.6
Calcium	16-44	Nitrate	16.84-29.5
Magnesium	5.6-17	Nitrite	25
Iron (Total)	0.001-0.004	Sodium	22-28
Chloride	4.63-6.26	Potassium	1.3-1.5
Sulphate	28.6-34.7	Aluminium	0.002-0.049
Manganese	0.003-0.004	Silica	49.2-74.87

### 3.2.2 Preparation of TISAB

A Total Ionic Strength Adjustment Buffer (TISAB) is a buffer solution, which increases and stabilizes the ionic strength of a solution. In potentiometric measurements including ion selective electrodes, this is very important since the activity of the ion instead of its concentration is measured. The TISAB basically is to mask other ions present in solution, which can interfere with the measurement and also releases all Fluoride ions into solution in order to increase the accuracy of the measurement.

#### *Apparatus*

- 1L beaker
- Magnetic Stirrer
- pH meter
- Measuring cylinder
- Measuring scale

#### *Reagents*

- Demineralized water
- Glacial Acetic Acid

- Sodium Chloride (NaCl)
- Cyclohexane-1-2-Diaminetetra Acetic Acid (CDTA)
- Sodium hydroxide (NaOH)

#### ***Procedure***

- 500ml demineralized water was placed in a 1L beaker containing 57ml glacial acetic acid
- 58g NaCl and 4g CDTA was then added to the beaker
- The mixture was stirred to dissolve all its content and placed in a cool water bath after which 125ml of 6M solution of NaOH was added slowly until the pH was constant between 5.3-5.5

#### **3.2.3 Preparation of Adsorbents**

Although there are other locally available viable media the charcoal and HABO were selected for this work due to its availability, relative cheapness and their high adsorption capacity. As per the recommended particle size for Rapid Sand Filter (RSF) these media were crushed and sieved to particle sizes ranging from 0.8-1.12mm. Both samples were washed thoroughly with demineralized water to remove dust and any foreign materials before coating was done.



**Plate 3-1:** 0.8-1.12 mm particle size for Bauxite and Charcoal

### 3.2.4 Determination of media porosity

Porosity ( $\phi$ ) is the fraction of the total media volume that is taken up by the pore space. Thus, it is a single-value quantification of the amount of space available to fluid within a specific body of soil. Being simply a fraction of total volume,  $\phi$  can range between 0 and 1

#### *Apparatus*

- Measuring cylinder and water
- Weighing scale

#### *Procedure*

- A known volume of the cleaned media was taken
- The volume of water was then added to the media just to saturate it
- The mass of the saturated media less the dry mass of the media, divided by the density of water, gives the volume of water. This divided by the original sample volume gives porosity.

$$V_p = \frac{(W_{sat} - W_{dry})}{\rho_w}$$

$$\phi = \frac{V_p}{V_b}$$

Where:

$W_{sat}$ - Weight of saturated media

$W_{dry}$ - Weight of clean dry media

$\phi$ - Porosity

$V_p$ -Pore volume

$V_b$ -Volume of dry media

$\rho_w$ - Density of water (1000kg/m<sup>3</sup>)

### 3.2.5 Coating of Media

Although from the Literature reviewed the virgin HABO and charcoal had some adsorption capacity for the removal of fluoride this was maximized by coating with Aluminium oxide. Also it was observed that double coating of both media was optimal therefore each media was coated twice each following the procedure elaborated below.

#### *Apparatus*

- A stainless steel basin
- Mechanical stirrer
- Stop clock
- Trays

#### *Reagents*

- Aluminium sulphate-hexa-deca-hydrate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ )
- Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ )
- Distilled water

#### *Procedure*

- 1.8kg and 0.5kg of the HABO and Charcoal respectively were weighed and soaked in 3L of 0.5M  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  solution in the stainless steel basin. This is to ensure that there is no reaction with the basin.
- Using a mechanical stirrer the mixture was stirred at a speed of 120rpm. This was to enhance the mass transfer of the Aluminium onto the media
- The stirring was allowed for 30minutes after which the mixture was made to stand for an extra 30minutes

- The excess solution was then decanted after the 30minutes elapsed and was air-dried for 2days in aluminium trays with plastic lining.
- The dried sample was then re-soaked in a 3M NH<sub>4</sub>OH solution. The NH<sub>4</sub>OH was to neutralize the Alum solution leading to the formation of the aluminium oxide coating.
- The excess solution was decanted after 10minutes and was again air - dried for 2 days.
- Since the optimal coating cycles has been established to be twice the second coating was done following the same procedure as mentioned above.
- The expected reaction for the coating is as follows:



**Plate 3- 2:** Mechanical stirring of Charcoal and HABO in Alum solution at speed of 120rpm



**Plate 3- 3:** Air-drying of coated HABO and Charcoal at room temperature

### 3.2.6 Aluminium Extraction Test

The test was performed to establish the efficiency of the coating of the media. The Aluminium is the main element that does the removal of the fluoride since it is a trivalent metal and fluoride due to its electronegativity has high affinity for it.

#### *Apparatus*

- Hot plate
- Conical flasks, 125mL
- 100mL Volumetric flask

#### *Reagents*

- Nitric Acid (HNO<sub>3</sub>)
- Demineralized water

#### *Procedure*

- 5mL of the sample was transferred into a 125mL conical flask
- 50mL of solution consisting of 10ml HNO<sub>3</sub> and 40mL of demineralized water was added to the sample.
- The mixture was slow boiled at a temperature of 200°C till 10mL of the solution remained and was allowed to cool.
- The remaining 10mL solution was transferred into a 100ml volumetric flask and was topped with demineralized water to the etched mark.
- Samples were then taken for Aluminium measurements.



**Plate 3- 4:** Boiling of media in nitric acid for the extraction of Al from AOCM



**Plate 3- 5:** Aluminium extract to be measured

### 3.2.7 Aluminium Leaching Test

This leaching test was done to check the stability of the Aluminium on the media, since the ingestion of Al in excess of 0.3mg/L recommended by the WHO can cause Alzheimer disease. There was therefore the need to check Al stability in order not to re-contaminant the drinking water after treatment.

#### *Apparatus*

- PE bottles
- Weighing scale

#### *Reagents*

- Sodium Carbonate ( $\text{NaCO}_3$ )
- Hydrochloric acid (HCl)
- Sodium hydroxide (NaOH)

### ***Procedure***

- Five bottles for each AOCC and AOCB. The bottles were filled with 50mL of demineralized water.
- The demineralized waters were buffered with  $\text{NaCO}_3$  and pH were corrected using HCl and or NaOH
- The leaching test was conducted for the coated charcoal at pHs 5,5.5, 6, 7,8 and that of the coated bauxite was at pHs 6, 6.5, 7,7.5, 8
- The bottle and its contents were shaken thoroughly and were made to stay for 24 hours. Afterwards the water was sampled using syringes and was tested for the amount of Al that has leached into solution.



Plate 3- 6: Bottles with media soaked in water at different pH

### **3.2.8 Batch Adsorption Test**

The batch adsorption test was performed to establish whether the fluoride removal capacities of the adsorbents were restored by the regeneration and also whether or not the adsorption capacities dwindle or increased with the regeneration.

### ***Apparatus***

- 1L beaker
- Jar test Apparatus
- 25 $\mu\text{m}$  cellulose acetate filter

**Reagents**

- NaOH
- HCl

**Procedure**

- The batch adsorption test was performed using the freshly coated media as well as the regenerated media
- Six beakers each containing 1L of varied concentration of fluoride solution was used with pH adjusted to 7 using NaOH and or HCl
- 12g of the freshly coated media was added to the model water and stirred continuously at a speed of 150rpm using the jar test apparatus.
- Samples were taken using syringes and were immediately filtered through a 25 $\mu$ m cellulose acetate filter. This filtration was to stop any further reaction between the adsorbent and adsorbate.
- Sampling was done for 5 days at predetermined intervals



Plate 3- 7: Setup for the Batch adsorption for both AOCC and AOCCB

### 3.2.9 Toxicity Classification Leaching Procedure (TCLP)

The TCLP was adopted because in Ghana indiscriminate disposal at landfill sites are the predominant practice. Therefore this test was used to determine the effect of organic waste on the leaching characteristic of the saturated AOCM.

#### *Apparatus*

- Extraction bottles (PP bottles)
- Shaker
- Hot plate
- Magnetic stirrer
- pH meter
- 500ml beaker and glass cover
- Membrane filters

#### *Reagents*

- Glacial Acetic acid ( $\text{CH}_3\text{CH}_2\text{OOH}$ )
- Hydrochloric acid (HCl)
- Sodium Hydroxide (NaOH)
- Distilled water

#### *Procedure*

- The appropriate extraction fluid to be used was determined by first soaking 5g of the saturated AOCB in 96.5 ml of distilled water in a 500ml beaker with a glass cover and stirred vigorously using a magnetic stirrer for 5minutes. A pH of 6.55 greater than 5 was recorded. 3.5ml 1N HCl was then added and boiled at a temperature of 50°C for 10minutes and made to cool to room temperature. The new pH measured was 1.56, which was less than 5;

hence the extraction fluid 1 which is a solution of glacial acetic acid ( $\text{CH}_3\text{CH}_2\text{OOH}$ ) and NaOH was used.

- 10g of the saturated AOCB were taken and the weight of the extraction fluid used was 20 times this weight (200g), which was equivalent to 185ml.
- The extraction fluid together with the sample was kept in a 500ml PE bottle sealed with Teflon tape and kept on a shaker
- The speed of the shaker was 300rpm and lasted for 18 hours. After which the leachate was filtered using 0.25 $\mu\text{m}$  membrane filter and the fluoride concentration in the leachate measured.

### 3.2.10 pH Dependent Leaching Test

The pH dependent leaching test was adopted together with the TCLP test because the latter simulate only acidic condition. This study wanted to ascertain the safety of disposing the waste in either basic or acidic conditions. This was necessitated by the fact that fluoride tends to leach more in basic conditions than acidic conditions.

#### *Apparatus*

- Bottles made of polyethylene (PE) or polypropylene (PP)
- 0.45 $\mu\text{m}$  membrane filters
- pH meter
- Shaker

#### *Reagents*

- Nitric acid (0.1-14.4M)
- Sodium Hydroxide, NaOH (0.1-5M)
- Distilled water with pH greater than 5 but less than 7 and conductivity <0.5ms/m

*Procedure*

- The test was conducted over a pH range of 4-12 with both limits included
- The leachant was prepared from distilled water and acid or base according to the acid or base required to attain the relevant pH
- A liquid-solid ratio of 10(ml/g) was used. A dry solid mass of 2g for each pH value was used hence the volume of the leachant was estimated to be 20ml
- The leachant was divided into three (6.7ml). The first fraction was added to the PE bottle containing the dry solids at time 0; the second fraction was then added after 30minures and finally the last fraction was added after 2 hours had elapsed.
- Each bottle was closed and agitated using the shaker between each addition of the leachant
- pH after 4hours, 44 hours and 48hours were measured and recorded
- The fluoride leached into the leachant was measured after 48 hours



Plate 3- 8: Setup for pH dependent leaching test

### 3.3 Analytical Methods

#### 3.3.1 Standardization of fluoride measurement

A stock fluoride solution of concentration 1000mg/L was prepared by dissolving 2.21g of NaF salt into 1L of distilled water. Series of solutions with known concentrations were then prepared from the stock solution (1mg/L, 5mg/L, 10mg/L, 25mg/L, 50mg/L and 100mg/L). Using the WTW 3310 fluoride meter the potentials of these standard solutions were found. A graph was then plotted with the measured potentials as the ordinate and the fluoride concentrations as the abscissa and with the help of the linear regression model a linear equation was established. This equation was therefore used to estimate all concentration after measuring their potentials.

#### 3.3.2 Fluoride measurement

In order to establish whether or not the regeneration is efficient and the number of regeneration cycles that will be ideal to ensure efficient fluoride removal and the fluoride concentrations in tested water samples should be monitored.

#### *Apparatus*

- Sampling bottles
- Pipette
- Syringes
- 25 $\mu$ m cellulose acetate filter
- Fluoride selective electrode (WTW pH 3310)
- Demineralized water

#### *Reagent*

- Total Ionic Strength Adjustment Buffer (TISAB)

**Procedure**

- 1mL of the sample water was measured using the pipette and 1mL of the TISAB was added
- Sample bottle was covered and shaken in order to mix the two thoroughly
- With the help of the WTW pH 3310 meter and a predetermined standard equation the fluoride concentration of the sampled water was measured.



Plate 3- 9: WTW pH 3310 fluoride ion selective electrode

**Determination of Adsorption Isotherm**

Adsorption isotherms can be established either using fixed amount of media and varying initial concentrations of the adsorbate or a fixed initial adsorbate concentration and varying amount of media. The former was used for this study.

The amount of the fluoride adsorbed per unit mass of the AOCC and AOCCB at equilibrium was calculated using the equation below:

$$q_e = \frac{(C_i - C_e)V}{m}$$

Where:  $q_e$ - amount of fluoride adsorbed per unit mass of media (mg/g)

$C_i$  = Initial fluoride concentration (mg/L)

$m$  = Mass of adsorbent (g)

$C_e$  = Fluoride concentration at equilibrium (mg/L)

$V$  = Volume of the solution used (L)

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

#### 4.1 Introduction

This study was undertaken to establish the possibility of regenerating exhausted Aluminium oxide coated media (charcoal and HABO) by recoating with the Aluminium oxide. This chapter therefore presents the data and the findings that were made under the study. Batch adsorption tests were conducted to ascertain the adsorption capacities of both the freshly coated as well as the regenerated media. Additionally the batch adsorption tests were also used to exhaust the media making them adequate for regeneration.

The amount of aluminium coated onto the media and the stability of the aluminium on the media are also discussed in this chapter.

#### 4.2 Standardization

As mentioned in chapter three the WTW 3310 fluoride meter used in this study was standardised by preparing a standard graph (figure 4-1) from which an equation was established to estimate the fluoride concentration in every sample taken during the batch adsorption tests upon measuring their corresponding ionic potentials.

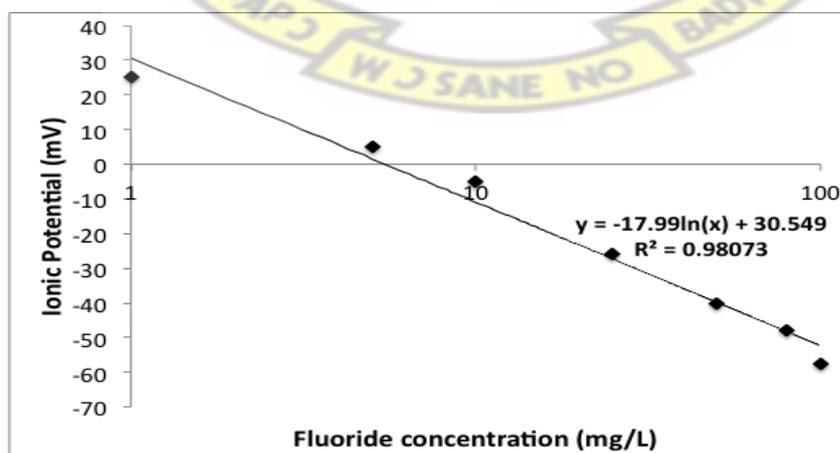


Figure 4- 1 Standard curve for estimation of fluoride concentration

### 4.3 Porosity of media

From the volumetric porosity tests conducted on the AOCC and AOCB it was observed that the porosity of the AOCC (0.73) was about three times greater than that of the AOCB (0.2).

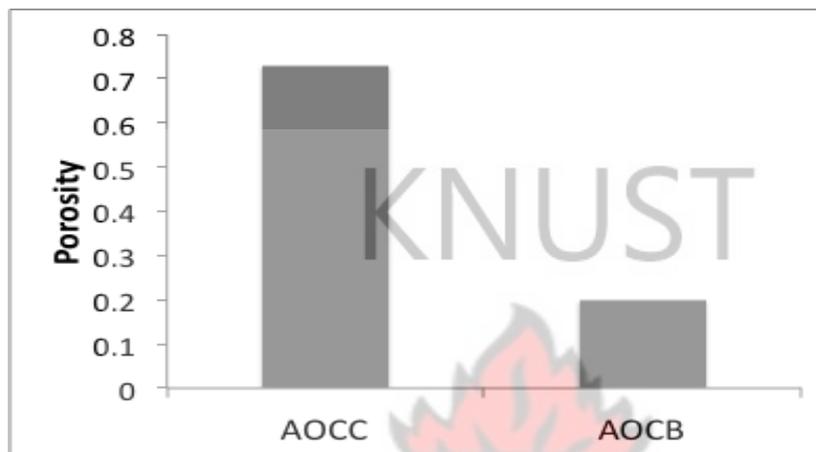


Figure 4- 2: Porosity of AOCC and AOCB

### 4.4 Batch Equilibrium and Exhaustion Studies

Batch studies were conducted to determine the equilibrium adsorption isotherms using both the freshly coated media as well as the regenerated media. Four regeneration cycles were conducted for the AOCC and one for the AOCB. The media were perceived to be exhausted when it reaches equilibrium and no further appreciable amount of fluoride was adsorbed.

A fixed known mass of the AOCB (12g and 10g for the freshly coated and 1<sup>st</sup> regenerated AOCB respectively) and the AOCC (12g, 10g, 8g, 6g and 4g) for the freshly coated, 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> regenerated AOCC respectively) were used for the batch adsorption tests. The mass of adsorbent used for the batch adsorption tests were always 2g less that of the previous test, this was to get enough samples for the Aluminium extraction as well as the Aluminum leaching tests after a regeneration cycle.

Varied initial fluoride concentrations were used for each batch adsorption test, this was to enable the estimation of the adsorption capacities of the freshly coated and regenerated media. A preliminary study was conducted using fluoride concentrations of 7.5mg/L, 6mg/L, 4.5mg/L, 3.5mg/L, 2.5mg/L for both AOCC and AOCB in order to cover both the upper and lower limits of the average fluoride concentrations in the ground waters in Northern Ghana; 3.97mg/L- 4.6 mg/L established from a survey conducted by Buamah and Dapilah (unpublished) in 2008.

For this preliminary study, monitoring was conducted for 5days after which the fluoride concentrations in the model water were below detectable limits however equilibrium could not be attained (Figures 4-3 and 4-4). The media was found to be taking longer time to reach equilibrium and time being a limitation in this study; the initial fluoride concentrations were increased to 60mg/L, 55mg/L, 50mg/L, 45mg/L and 40mg/L for both AOCC and AOCB.

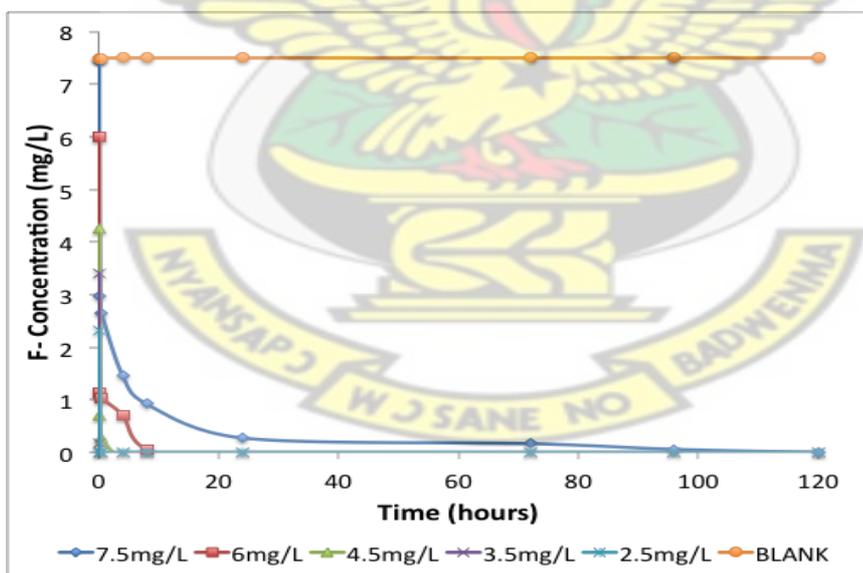


Figure 4-3: Fluoride removal using AOCB, initial  $F^-$  concentration of 7.5mg/L-2.5mg/L and media dose of 12g/L

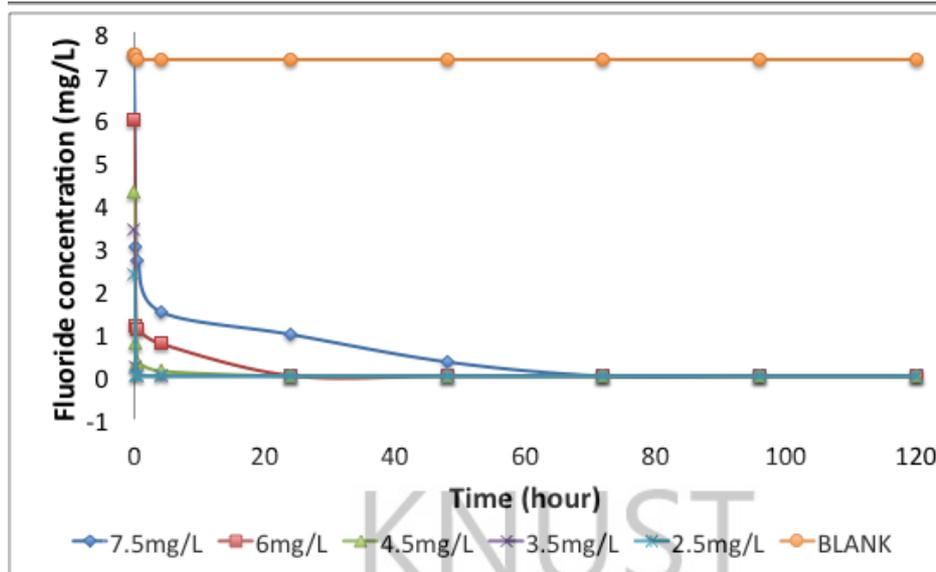


Figure 4- 4: Fluoride removal using AOCC, initial  $F^-$  concentration of 7.5mg/L -2.5mg/L and adsorbent dose of 12g/L

All studies were conducted at room temperature of 28°C and pH 7 since the average pH of the ground waters in northern according to Buamah and Dapilah, (unpublished) 2008 was established to be 7. Additionally, Waheed and Attar (2008) also affirmed pH 7 as the optimal pH for the adsorption of fluoride onto alumina, which has similar characteristics as the AOCC and AOCCB.

The pH was monitored to ensure that it remained constant since a preliminary study performed indicated that there was the tendency of the adsorbed fluoride to leach back into solution upon increase in the pH as can be seen in figure 4-5. Likewise, Karthikeyan and Elango (2007); Karthikeyan *et al.* (2004) also confirmed that in alkaline pH range hydroxide ions compete with fluoride ions for adsorptive sites thereby lowering the removal of fluoride ions.

1L model water with fluoride concentrations of 35mg/L and 60mg/L seeded with no media were used as the control for the batch adsorption test for the AOCCB and AOCC respectively.

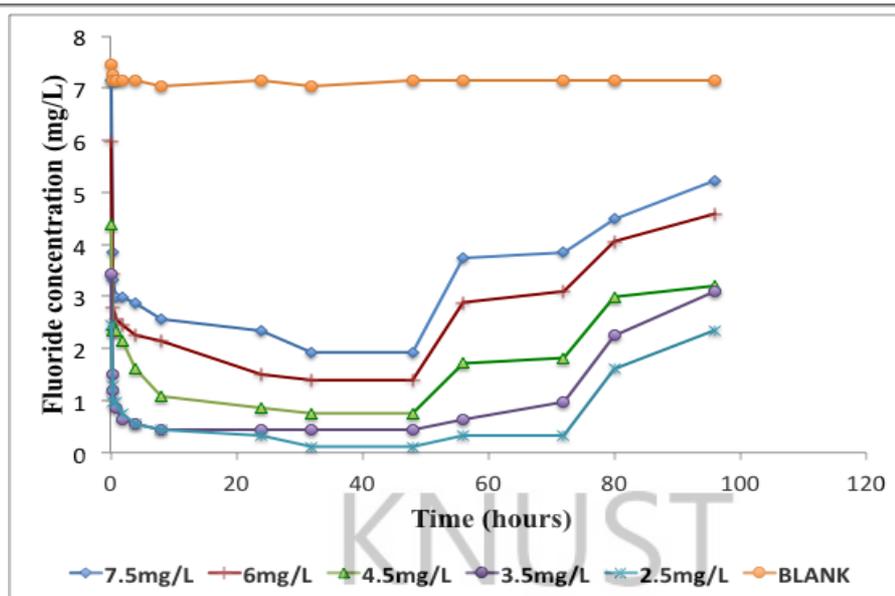
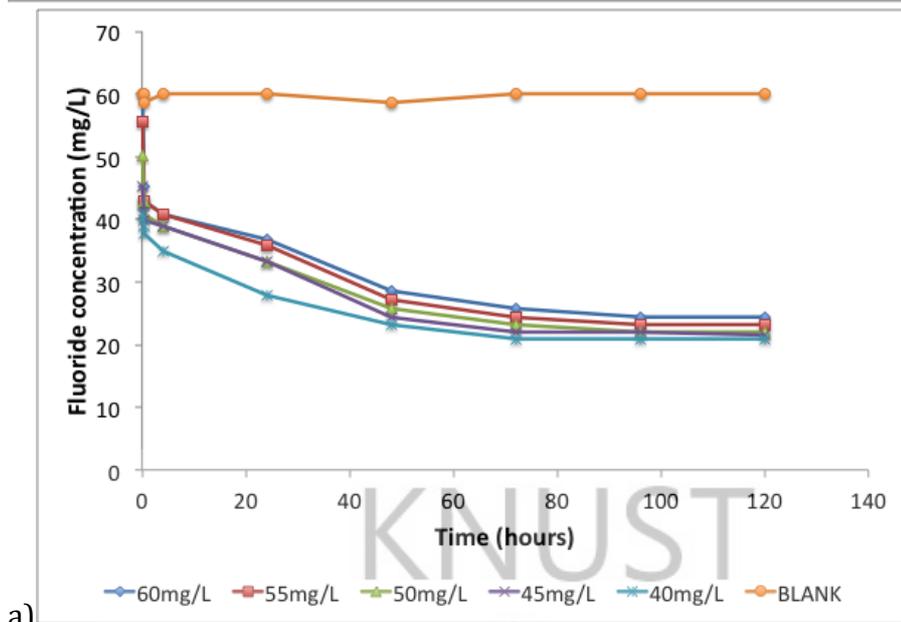


Figure 4- 5: Fluoride leaching into solution after 48hours when pH increased from 7 to 9.2. Adsorbent- AOCB, initial F<sup>-</sup> concentration of 7.5mg/L -2.5mg/L and adsorbent dose of 12g/L

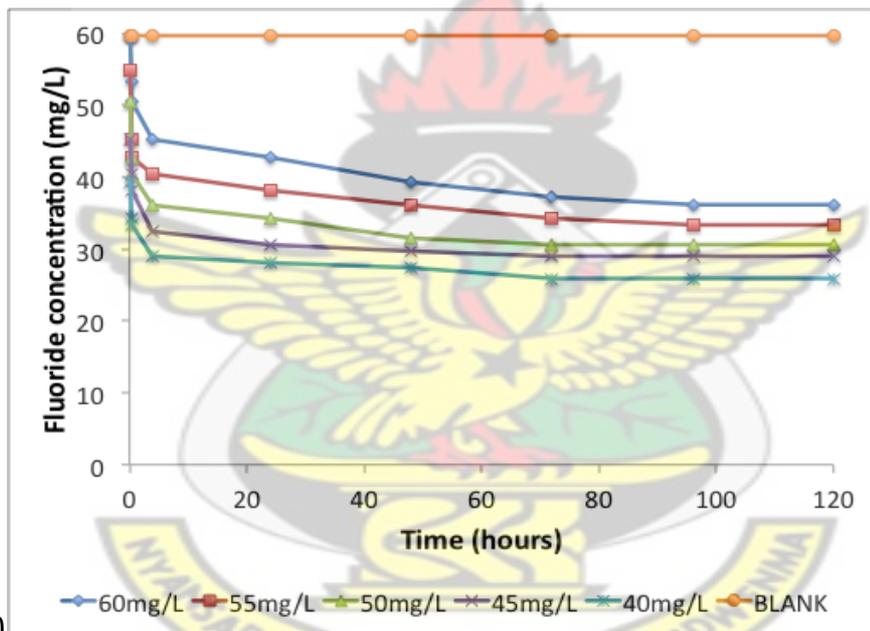
It was therefore observed that the equilibrium time for both media was 3days but monitoring was conducted till the fifth day to ascertain the exhaustion of the media. Hence all batch adsorption tests were observed to take about 120hours (5days) averagely to reach equilibrium (figures 4-6 and 4-7 for AOCB and AOCC respectively).

In the absence of any documented concentration that can be used to exhaust the media further studies were conducted using initial fluoride concentrations of 60mg/L, 55mg/L, 50mg/L, 45mg/L and 40mg/L for the for both media (figures 4-6 and 4-7).

Higher concentrations were selected because AOCC had higher adsorption capacity hence required higher concentration for it to reach exhaustion. The media together with the water were stirred using the jar test apparatus at a speed of 120rpm. This was to ensure a better mass transfer of the adsorbate (F<sup>-</sup>) onto the media.



a)



b)

Figure 4-6: F<sup>-</sup> removal using AOCB. (a) Non-regenerated AOCB (b) 1<sup>st</sup> regenerated AOCB

Regeneration and disposal of AOCC used for defluoridation of drinking water

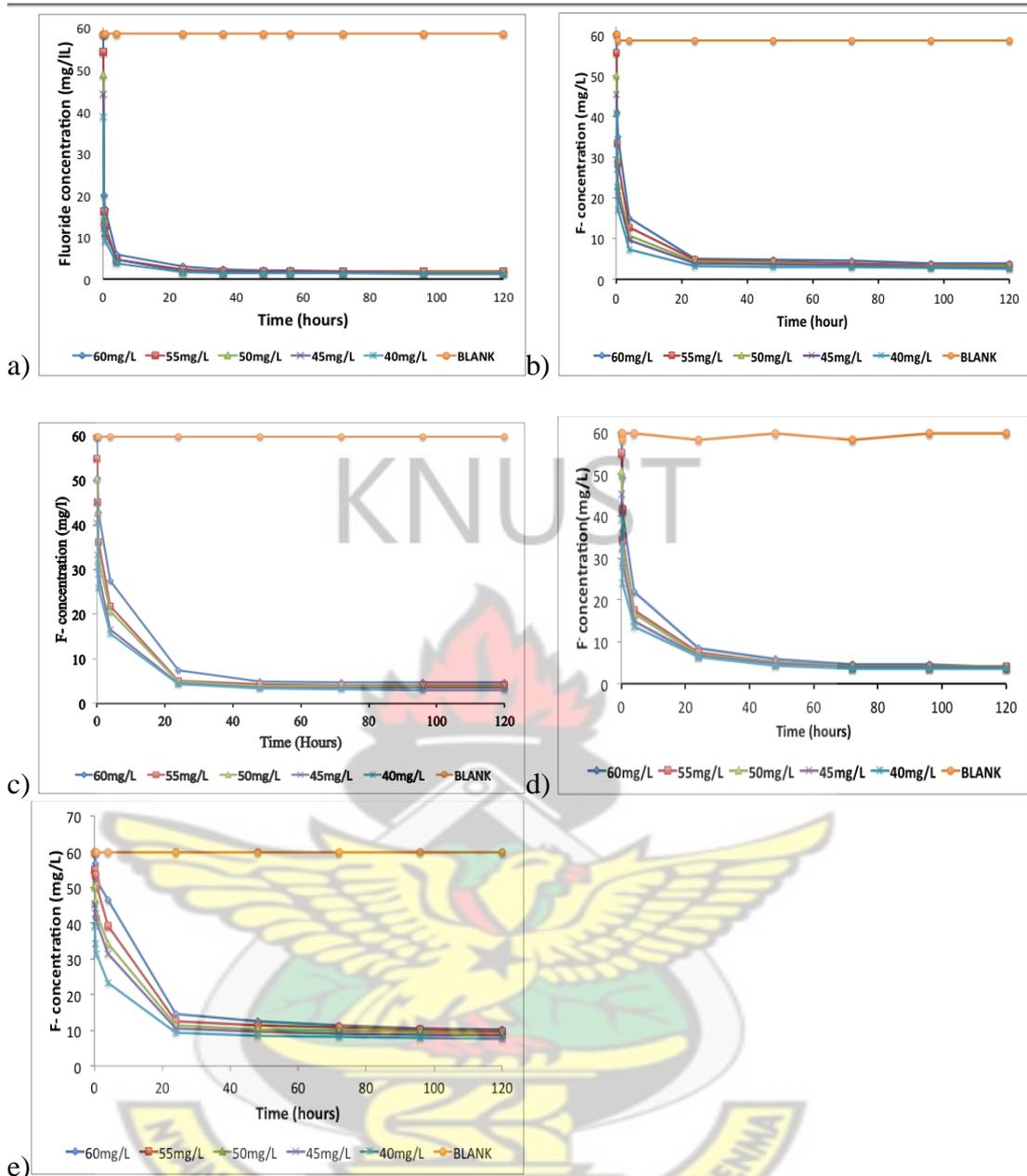


Figure 4-7: F<sup>-</sup> removal using AOCC (a) Non-regenerated AOCC (b) 1<sup>st</sup> regenerated AOCC (c) 2<sup>nd</sup> regenerated AOCC (d) 3<sup>rd</sup> regenerated AOCC (e) 4<sup>th</sup> regenerated AOCC

With initial fluoride concentrations of 60mg/L - 40mg/L the AOCC was saturated after the first regeneration (putting the media to use once); the removal efficiency was less than 50% (figure 4-8) and the adsorption capacity reduced from 1.1mg/g to 0.008mg/g (figure 4-9). The abrupt reduction in the adsorption capacity after the first

regeneration was an indication that regenerating the AOCB by recoating with Aluminium oxide was not feasible.

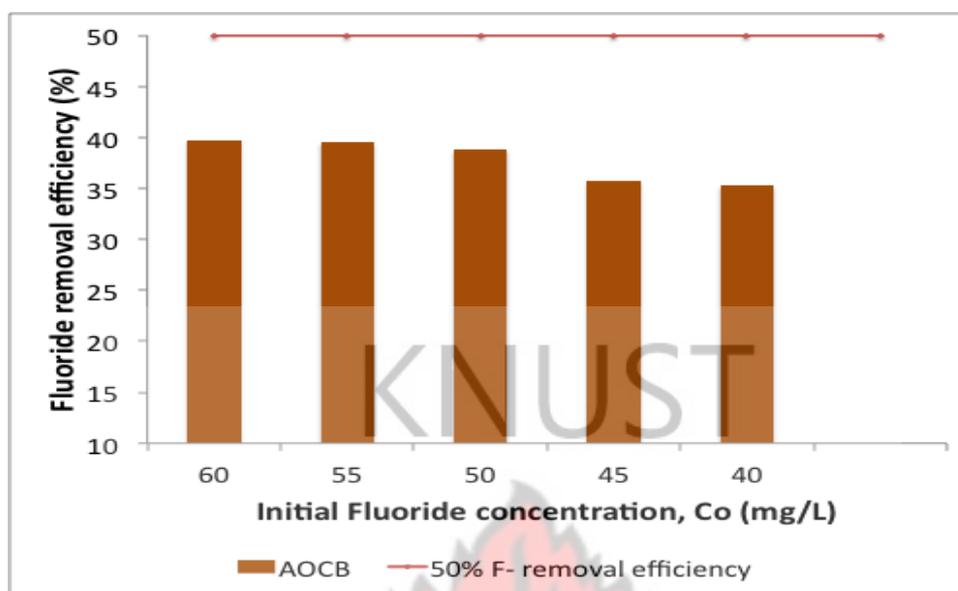


Figure 4- 8: Fluoride saturated AOCB - removal efficiency less than 50%

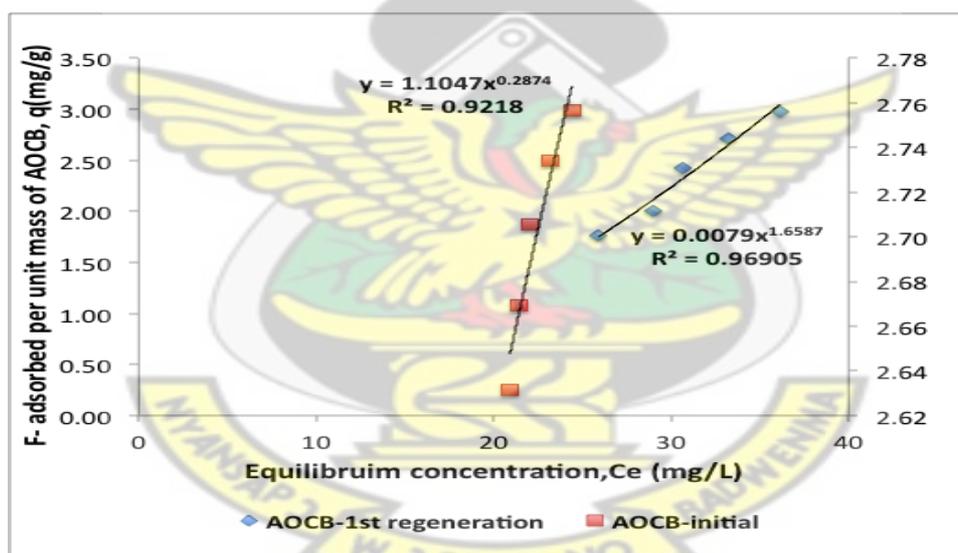


Figure 4- 9: Fluoride removal capacities of AOCB before and after first regeneration using initial F- concentration of 60mg/L-40mg/L

#### 4.5 Effect of initial fluoride concentration on the rate of Fluoride removal

This study confirmed the observation made by Malakootian *et al.* (2011) that initial fluoride concentration influences the amount of adsorbate adsorbed per unit mass of the adsorbent, q (mg/g). As illustrated in figure 4-10, the result obtained showed that

$q$  increased with increasing initial fluoride concentration for both AOCC and AOCB.

This could be due to the increment of the driving force of the concentration gradient resulting in more F<sup>-</sup> being adsorbed per unit mass of the media.

Even though same initial concentrations were used for both media, AOCC had higher  $q$  values compared to those of the AOCB, this could be attributed to the fact the AOCC had a higher adsorption capacity.

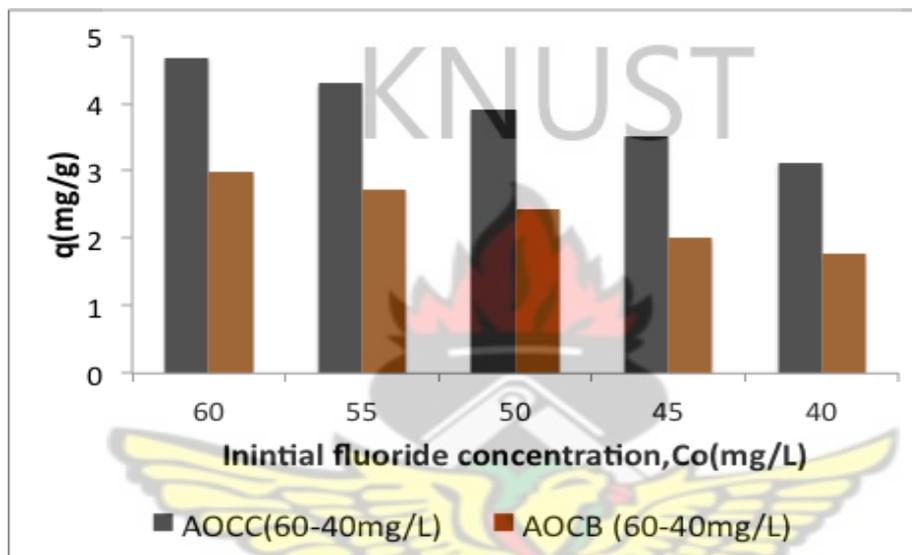


Figure 4-10: Effect of initial fluoride concentration ( $C_0$ ) on  $q$  (contact time 120 hours, 12g/L AOCC and 12g/L AOCB at pH 7 and room temperature)

## 4.6 Adsorption kinetics

### 4.6.1 Pseudo First and Second Order Kinetic Models

From the equilibrium and exhaustion studies, it was observed that the higher the initial fluoride concentration the higher the amount of the fluoride adsorbed per unit mass of adsorbent (AOCC and AOCB). The kinetics of the adsorption was therefore studied to verify whether or not the initial fluoride concentration was the rate-determining step for the removal of the fluoride. The adsorption kinetic studies were done for both AOCC and AOCB using fluoride concentration of 60mg/L and adsorbent dosage of 12g/L. The adsorption process was monitored for a 5day period

within which samples were taken at predetermined time intervals. All studies were done at room temperature of 28°C and neutral pH.

The pseudo first and second order kinetic models were used to estimate the kinetic rates and the mechanisms of adsorption of fluoride onto the AOCC and AOCB.

From figure 4-11, it was observed that co-relation coefficients,  $R^2$  of 0.96 and 0.95 were obtained for the pseudo first order kinetic model for AOCC and AOCB respectively. These were lesser than the  $R^2$  values obtained for AOCC (1.00) and AOCB (0.99) using the pseudo second order kinetic model.

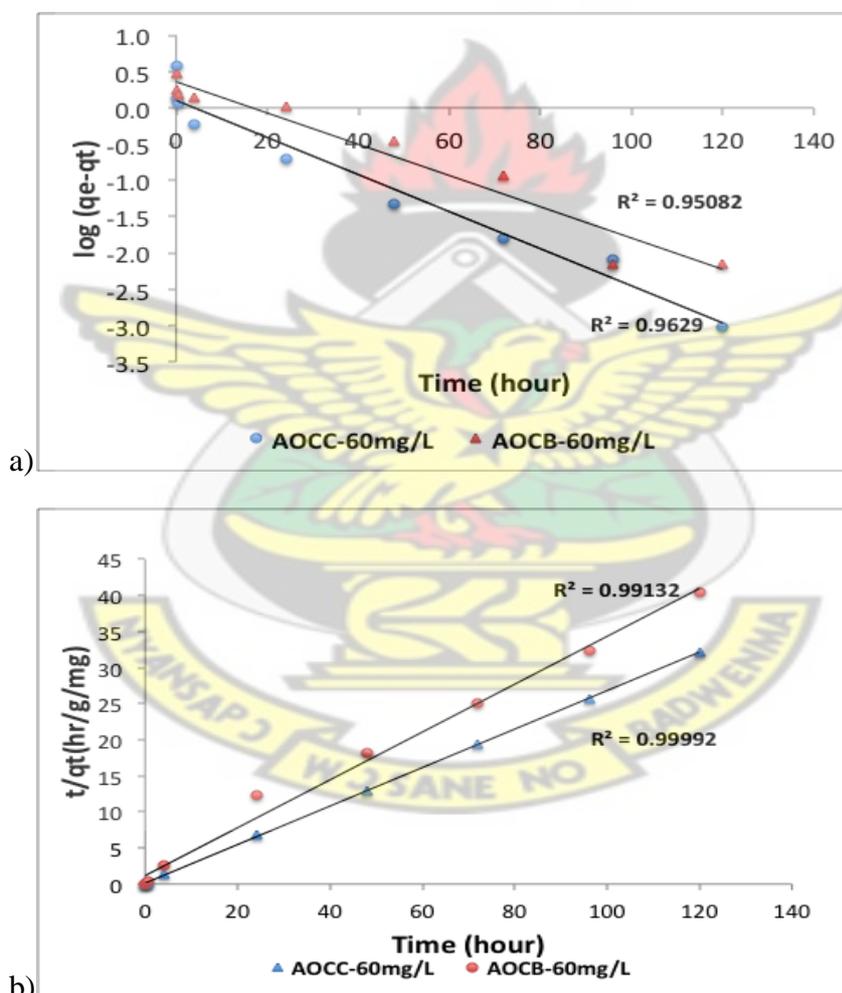


Figure 4-11: Kinetic models for AOCC and AOCB: (a) Pseudo first-order model (b) Pseudo second-order model.

This was therefore an indication that the adsorption of fluoride onto AOCC and AOCCB was not a first order reaction but rather followed the pseudo second-order kinetics. According to Ho and McKay (1998), if the pseudo second-order kinetic model holds true: that is if a linear relationship is obtained for the plot of  $t/(q_t)$  against  $t$  (Figure 4-11b), then it can be assumed that the  $F^-$  removal mechanism may be chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

Therefore with the  $R^2$  values and the linearity of the graphs obtained for both media from this study (figure 4-11), it was concluded that the Pseudo second order adsorption mechanism is predominant and that the adsorption of fluoride onto AOCC and AOCCB is more likely to be a chemisorption process, thus there is a chemical bond between the fluoride ions and the aluminium coated onto the media.

Ho and Ofomaja (2005) also suggested that if the pseudo second-order equation is more pertinent, then rate of adsorption of the fluoride onto both media was affected by availability of adsorptive sites on the surface of adsorbent (AOCC and AOCCB) rather than fluoride concentration in the bulk solution. The constants for the pseudo first and second-order kinetics models are presented in Table 4-1.

Table 4 -1: Kinetic models' constants

Kinetic model	Linear form	Media	Constant	Value
Pseudo First-order	$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$	AOCC (60mg/L)	$K_1$ (L/hr.)	0.059
			$q_e$ (mg/g)	1.27
		AOCCB (60mg/L)	$K_1$ (L/hr.)	0.050
			$q_e$ (mg/g)	2.29
Pseudo Second-order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t$	AOCC (60mg/L)	$K_2$ (L/hr.)	0.55
			$q_e$ (mg/g)	3.75
		AOCCB (60mg/L)	$K_2$ (L/hr.)	0.09
			$q_e$ (mg/g)	3.02

#### 4.6.2 Intra-particle diffusion kinetic model

It was observed that the intra-particle diffusion modeling of fluoride adsorption on both the AOCC and AOCCB were not linear over the whole observation period of 120hours (figure 4-12).

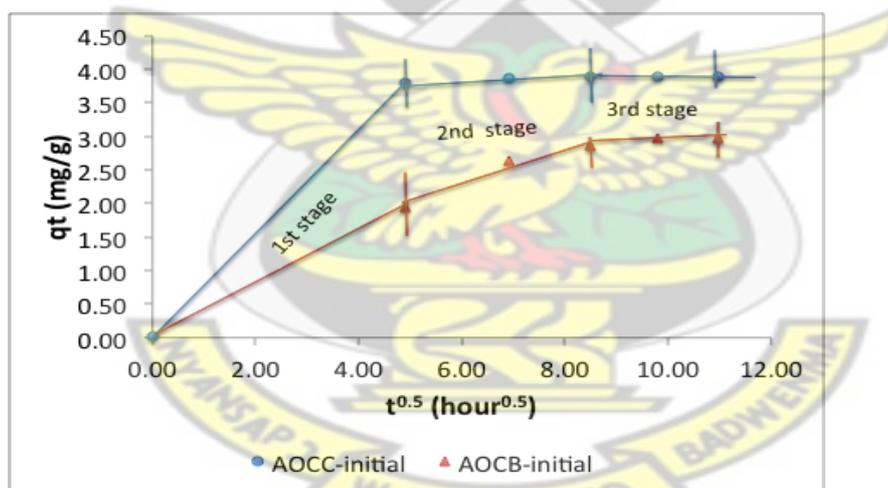


Figure 4-12: Intra-particle diffusion kinetic model using AOCC and AOCCB with F-concentration of 60mg/L at pH 7 and room temperature

The graphs were found to be in three sections, with the initial parts being linear followed by intermediate linear portions and finally plateau portions.

The adsorption processes by AOCC and AOCCB were similar. The first portion being the linear part, which span for the first 24hours for both media, is described as the

external surface adsorption phase. The second stage is the intra-particle diffusion process attained between the 24<sup>th</sup> and 72<sup>nd</sup> hours. The last step is the equilibrium adsorption process, which begins from where the second phase ended (figure 4-12). The fluoride ions were rapidly adsorbed on the external surface of the adsorbents and slowly transported into the interior of the particles and then finally retained within the pores of the AOCC and AOCB. Additionally the intra-particle diffusion rate constants,  $k_i$  calculated from the slopes of the plots from the second stage of figure 4-12 were 3.58 and 0.61 mg/g h<sup>0.5</sup> for the AOCC and AOCB respectively. The AOCC had a higher diffusion rate because of its high porosity (0.73) as compared to AOCB (0.2).

#### **4.7 Equilibrium studies and Adsorption capacity**

In order to determine the feasibility of regenerating the AOCC and AOCB media by recoating with aluminium oxide, a batch adsorption study was conducted to estimate the adsorption capacities of the media before and after the regeneration. Adsorbent dosages of 12g/L and fluoride concentrations of 40-60mg/L were used for this study. The test was conducted at room temperature of 28°C and pH7±0.05. The Freundlich and the Langmuir adsorption isotherms were used to estimate the adsorption capacities of the media.

##### **4.7.1 Freundlich Isotherm against Langmuir Isotherm**

From this study, the AOCC recorded a co-relation coefficient ( $R^2$ ) of 0.979 and 0.986 for Freundlich and Langmuir isotherms respectively (figure 4-13). Similarly AOCB also had a  $R^2$  value of 0.922 and 0.929 for Freundlich and Langmuir models respectively. Hence it was observed that the data for both AOCC and AOCB fitted both the Langmuir and the Freundlich isotherms.

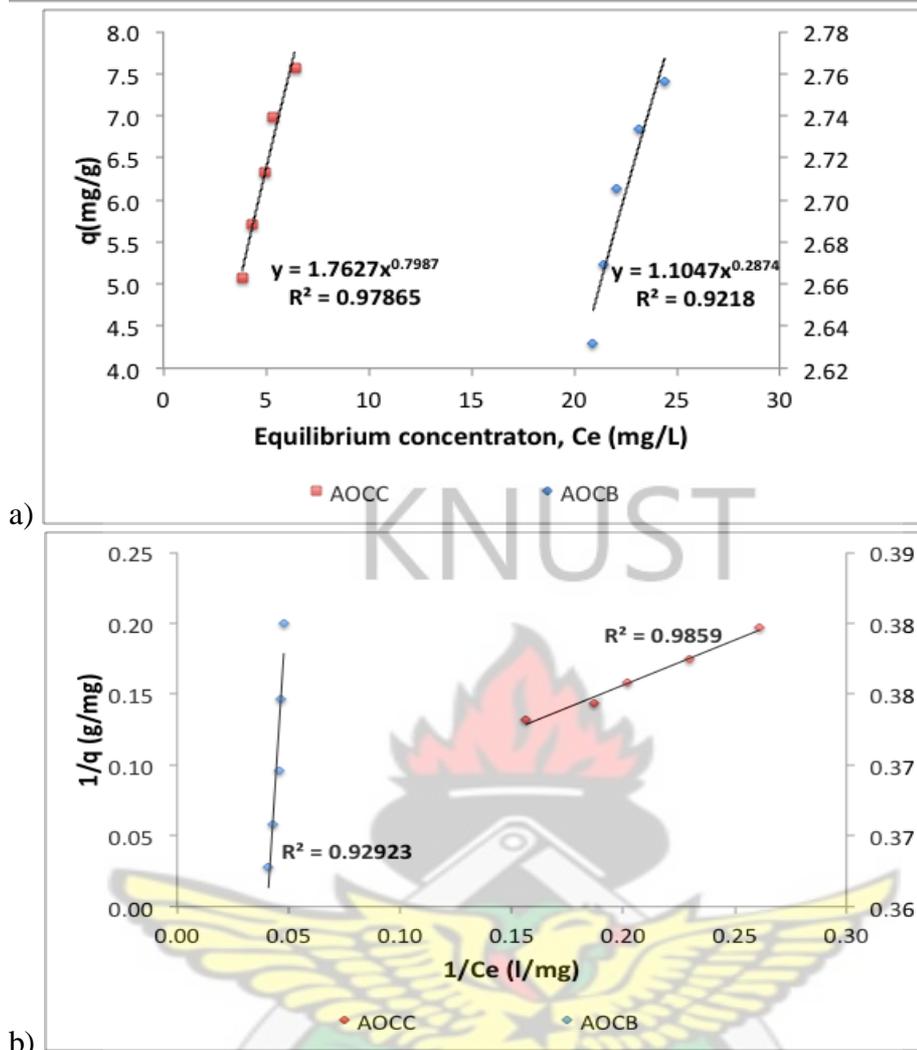


Figure 4-13: Adsorption isotherms for AOCC and AOCCB: (a) Freundlich isotherm (b) Langmuir isotherm

From the adsorption capacities and values of constants obtained from both models presented in Table 4-2, it was observed that the models confirmed each other. Using the Freundlich model the adsorption capacity of the AOCC was observed to be about 1.5times greater than that of AOCCB. A similar observation was made from the Langmuir model, which recorded a maximum adsorption capacity of 34.247mg/g for AOCC as against 3.828mg/g for AOCCB. This was attributed to some extent to the high porosity (0.73) of the AOCC, since that may have contributed to more aluminium being coated onto it (Figure 4-14) and consequently more fluoride being adsorbed.

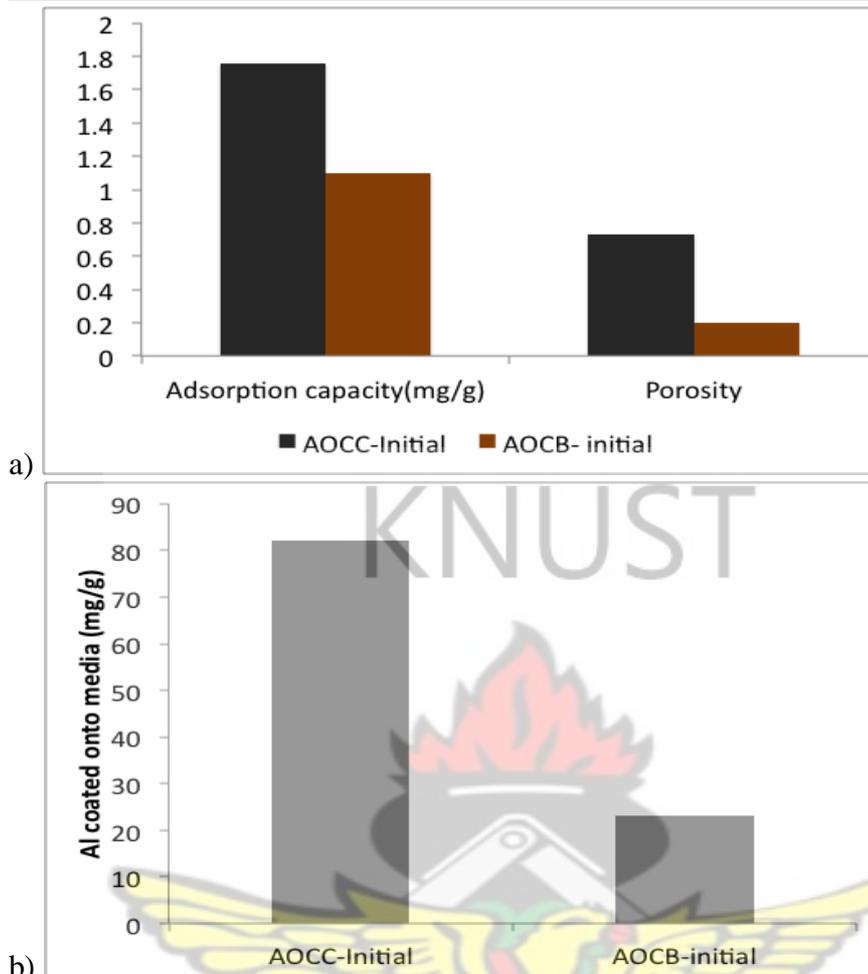


Figure 4-14: Effect of media porosity on (a) Adsorption capacity and (b) amount of Aluminium coated onto media

Table 4-2: Isotherm constants

Isotherm	Linear form	Media	Constant	Value
Freundlich	$q_e = kC_e^{1/n}$	AOCC	K (mg/g)	1.7627
			1/n	0.7987
		AOCCB	K (mg/g)	1.1047
			1/n	0.2874
Langmuir	$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m C_e}$	AOCC	$q_m$ (mg/g)	34.247
			b	0.0459
		AOCCB	$q_m$ (mg/g)	3.828
			b	0.41

The electronegativity and small ionic size of fluoride make it likely to have high affinity for multivalent metals including Aluminium. Hence the amount of

aluminium coated onto the media may therefore have a direct bearing on their adsorption capacity. Based on this, the observation made from the study that the amount of aluminium coated onto the media was directly proportional to the adsorption capacity of the media; thus the higher the amount of aluminium coated onto the media the higher its adsorption capacity can be justified (figure 4-14).

#### 4.8 Recoating and Regeneration

The media upon exhaustion (attaining equilibrium) was regenerated to restore its capacity by recoating the media with aluminium oxide.

It was observed that although the regeneration restored the adsorption capacity of the AOCC, the capacities and the intensities reduced subsequently with each regeneration cycle (Table 4-3).

Table 4-3: Adsorption capacities and intensities for AOCC and AOCCB

Media	Adsorption capacity, K (mg/g)	Adsorption intensity, n
AOCC-initial	1.76	1.2520
AOCC-1st regeneration	1.26	1.0161
AOCC-2nd regeneration	1.09	0.9374
AOCC-3rd regeneration	0.87	0.6710
AOCC-4th regeneration	0.21	0.6261
AOCCB-initial	1.105	2.3375
AOCCB-1st regeneration	0.0079	1.4736

Bigger values of the adsorption intensity, n indicate a better adsorption mechanism and the formation of relatively stronger bonds between the adsorbent and the adsorbate. AOCCB recording higher adsorption intensity values than AOCC, to some extent indicate that, under same conditions the fluoride adsorbed onto AOCC will have a higher tendency to leach than that of the AOCCB.

From figure 4-15, it was observed that there was a drastic drop in the adsorption capacity for AOCC after the third regeneration. This may be an indication that regenerating after the third regeneration cycle was not efficient hence media can be replaced after three regeneration cycles.

On the other hand, it was observed that regenerating the AOCB by recoating was not successful since the capacity reduced from 1.1 to 0.0079mg/g, which was almost negligible after the first regeneration (figure 4-15).

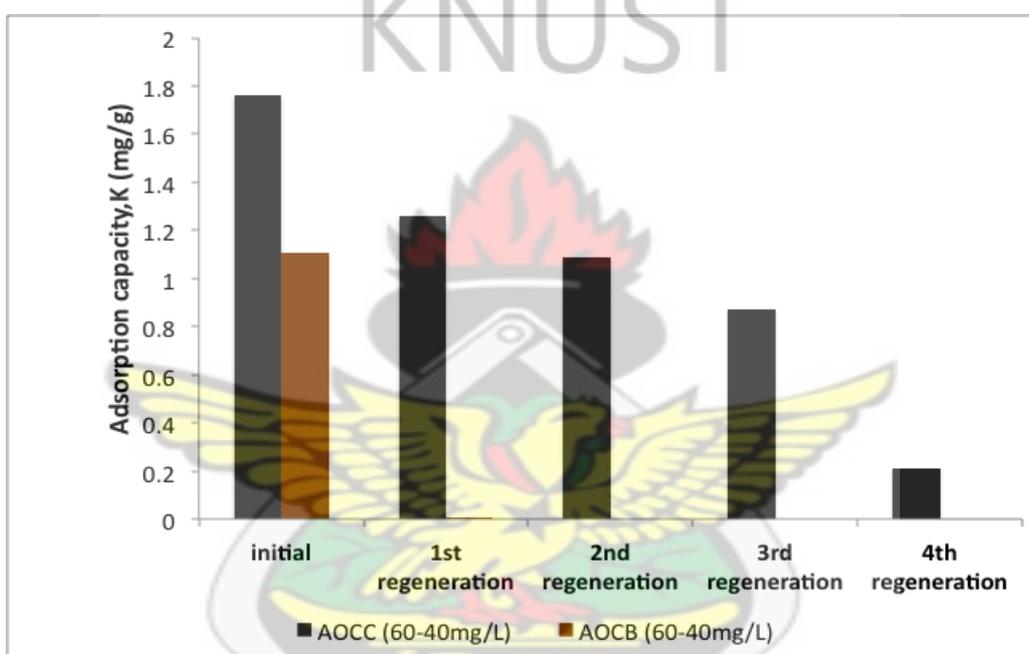


Figure 4-15: Fluoride adsorption capacity of AOCB and AOCC after 1 and 4 respective regeneration cycle using initial fluoride concentrations of 60-40mg/L.

#### 4.9 Aluminium Extraction Test

The Aluminium extraction test was conducted to know the amount of Aluminium coated onto the media before and after the regeneration. This was to establish the efficiency of the regeneration.

From this study, it was observed that under the conditions applied the amount of aluminium coated onto both media decreased with successive regeneration as seen in figure 4-16. This may be related to the reduction in the available adsorptive sites on the media.

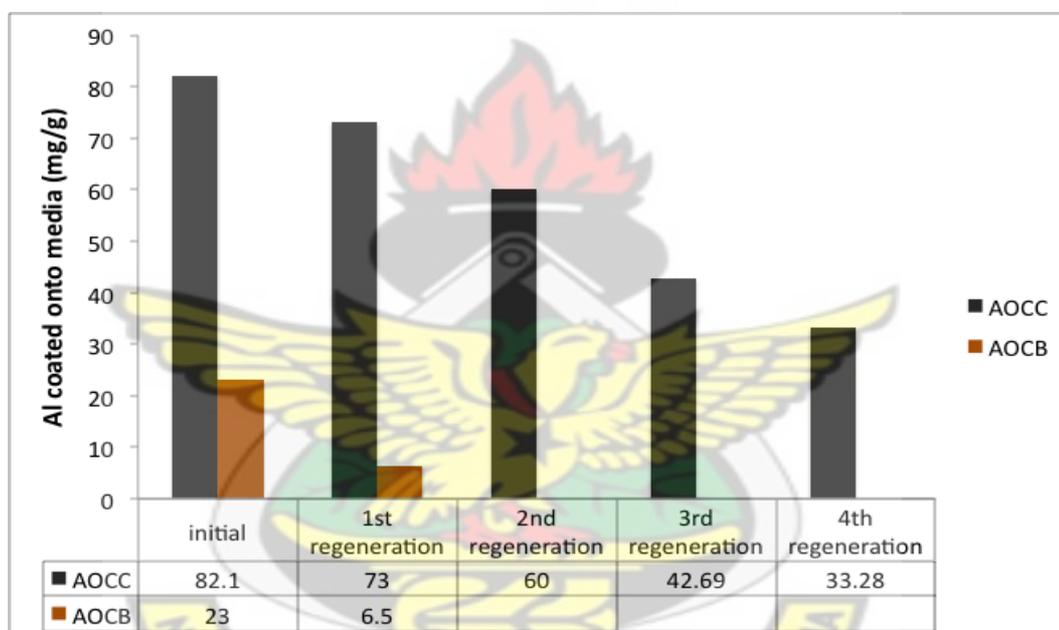


Figure 4-16: Amount of Al coated onto AOCC and AOCB before and after regeneration

Since the Al bonds with the already adsorbed fluoride, the number of the adsorptive sites available on the coated AOCC and AOCB tend to decrease. This was supported by the adsorption intensity values recorded from the Freundlich isotherm (Table 4-3), which decreased with increasing regeneration cycle.

This therefore explains the reduction in the adsorption capacities as well, since fluoride has a high affinity for Aluminium. As established earlier, the fluoride

removal mechanism is basically chemisorption hence the higher the Al coated onto the media the greater the amount of fluoride that will be removed. Consequently, the media with most Aluminium coated onto it will have the highest adsorption capacity as well. This will however require an EDX or XRF analysis to confirm whether or not the reduction in the amount of Al adsorbed was actually due to the reduction in the available adsorptive sites on the media.

#### 4.10 Aluminium leaching test

The stability of the aluminium coated onto the media was determined using the aluminium-leaching test. From this study, it was established that the minimum amount of Al leached for both AOCC and AOCB occurred at pH 5 and the maximum occurring at after pH 7 (figure 4-17). The maximum amount of Al leached were 0.026mg/L and 0.047mg/L for AOCC and AOCB respectively (figure 4-17).

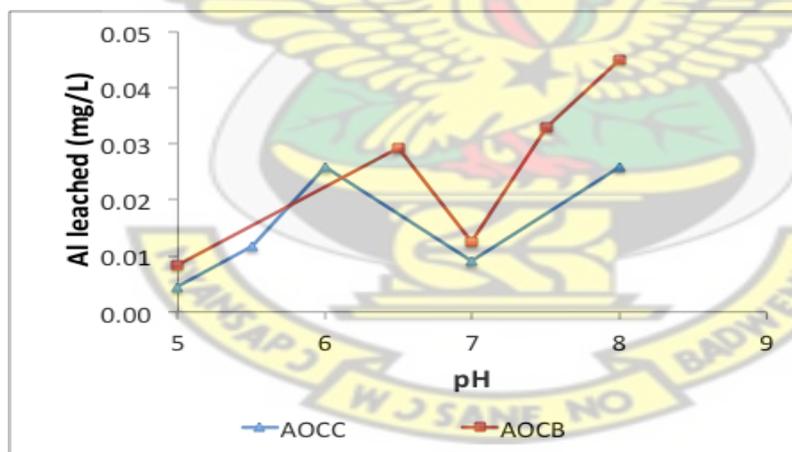


Figure 4-17: Al leached from AOCB and AOCC at pH 5-8

Both amounts were less than the WHO guideline value of 0.2mg/L for Aluminium in drinking water; this was therefore an indication that the AOCC and AOCB were stable and do not contaminate the water upon treatment. Although AOCB had higher adsorption intensity than AOCC, it recorded a higher leached Al concentration. This

could be due to the high intra-particle adsorption of the Al in the case of the AOCC.

From figure 4-18, it was observed that the amount of Al leached from both AOCCB and AOCC increased with increasing regeneration cycle. This can therefore be attributed to the reduction in the adsorption intensity after successive regeneration though it is not confirmatory. An EDX or XRF analysis needs to be done for confirmation. Again from figure 4-18 it was observed that the amount of Al leached was minimal at lower pH and increased drastically after pH 7 meaning there is reduction in the amount of Al adsorbing the fluoride from solution. This therefore can confirm the high adsorption of fluoride in acidic pH and leaching of fluoride at pH greater than 7 for both AOCC and AOCCB.

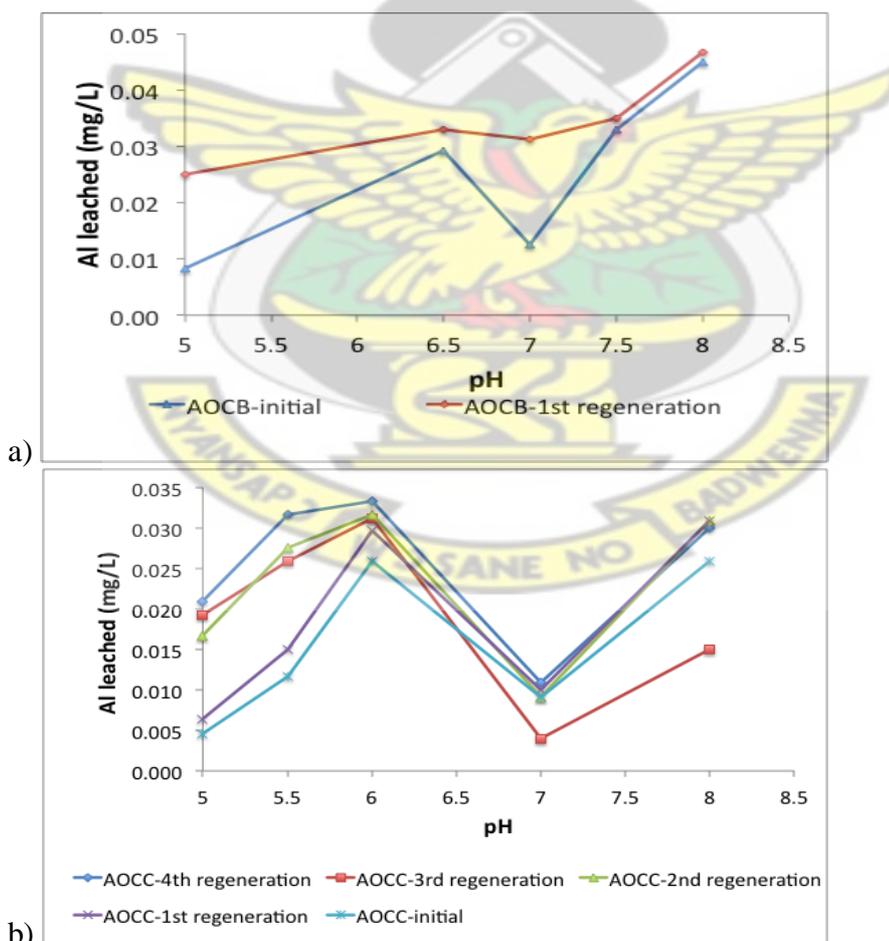


Figure 4-18: Amount of Al leached from (a) AOCCB (b) AOCC at pH 5-8

The amount of aluminium leached into solution for the regenerated media; both AOCC and AOCB are also less than the WHO guideline value and followed the same trend as the initial AOCC and AOCB respectively. Hence the regenerated materials were also considered stable.

#### **4.11 Toxicity Classification Leaching Procedure (TCLP)**

The TCLP is a protocol devised to classify waste into hazardous and non-hazardous for disposal at landfill sites.

The TCLP was therefore adopted to classify the completely exhausted media into hazardous and non-hazardous for safe disposal. Completely exhausted media used in this study refers to the media that can no longer be regenerated; such a media is fluoride saturated.

To saturate the AOCB, initial fluoride concentrations of 40-60mg/L were used for 10days. The adsorption capacity of the AOCB was observed to have dropped from an initial value of 1.1 to 0.0079mg/g, indicating that the fluoride removal capacity of the media has fallen below an efficiency of 50% (figure 4-19). Although the fluoride removal efficiency for AOCC was greater than 50% after the 4<sup>th</sup> regeneration, it was deemed completely exhausted and was to be disposed off because of the drastic reduction in the adsorption capacity after the 3<sup>rd</sup> regeneration (0.8mg/g to 0.2mg/g) (figure 4-15). In this situation both media were deemed saturated and thus ready to be disposed off.

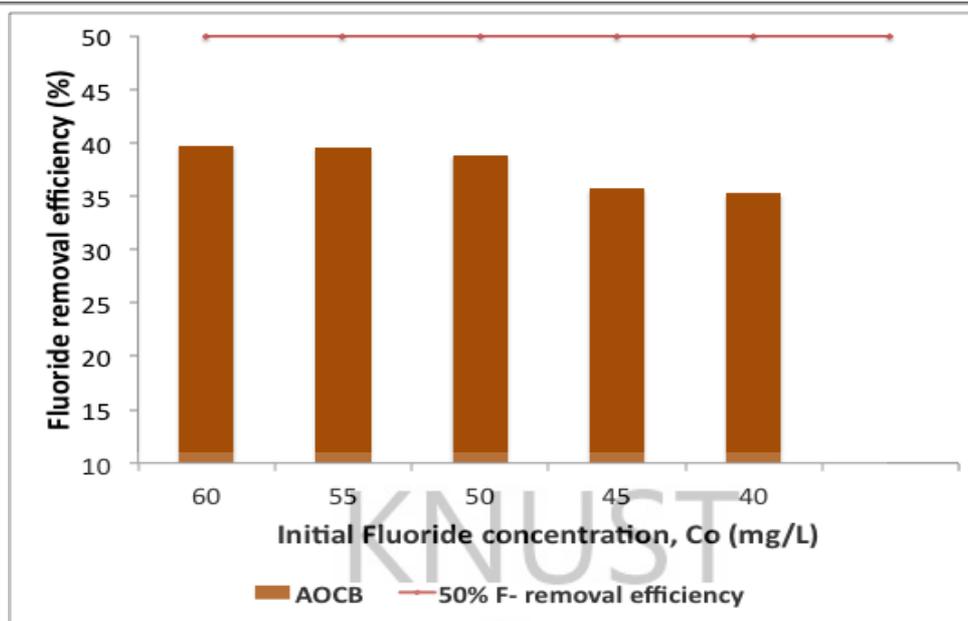


Figure 4-19: Saturated AOCB

According to the TCLP protocol fluoride saturated waste material is declared non hazardous for disposal when the concentration of the fluoride leached after the TCLP is less than 150mg/L. On the other hand if the  $F^-$  leached is in excess of 150mg/L then it will be harmful when reintroduced into the environment, and hence must be treated as hazardous waste.

From the TCLP conducted, a fluoride concentration of 22mg/L and 18mg/L were recorded for the saturated AOCB and AOCC respectively. Since the concentrations of the  $F^-$  leached are below the guideline value of 150mg/L it was concluded that the saturated AOCB and AOCC could be safely disposed off at the landfill site without re-contaminating the groundwater resources or being harmful to the environment.

#### 4.12 pH Dependent Leaching Test

The pH dependent leaching test was adopted together with the TCLP to simulate disposal of the saturated media in basic or acidic conditions. Fluoride tends to leach more under basic conditions than acidic conditions. Since the pH dependent leaching test is a generic leaching test, the results obtained were compared to the guideline

value from the TCLP test in order to establish whether or not the disposal of the saturated media will be safe to the environment.

A pH range of 4-12 was chosen for this test. An estimated fluoride concentration of approximately 313mg/L and 418mg/L were adsorbed by the AOCB and AOCC respectively after saturation. It was observed that the amount of fluoride leached increased with increasing pH as shown in figure 4-20. Correspondingly the greatest amount of fluoride leached from both AOCB and AOCC were 45.17mg/L and 33.26mg/L respectively which were observed at pH 12. Approximately maximum of 20% and 8% of the total adsorbed fluoride by respective AOCB and AOCC were leached (figure 4-21).

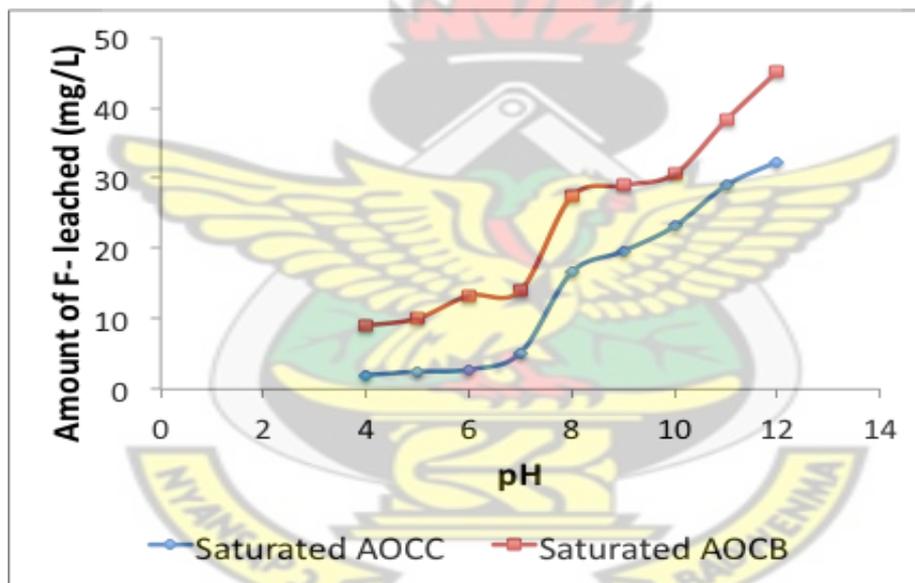


Figure 4-20: Fluoride leached from saturated AOCB and AOCC at pH 4-12

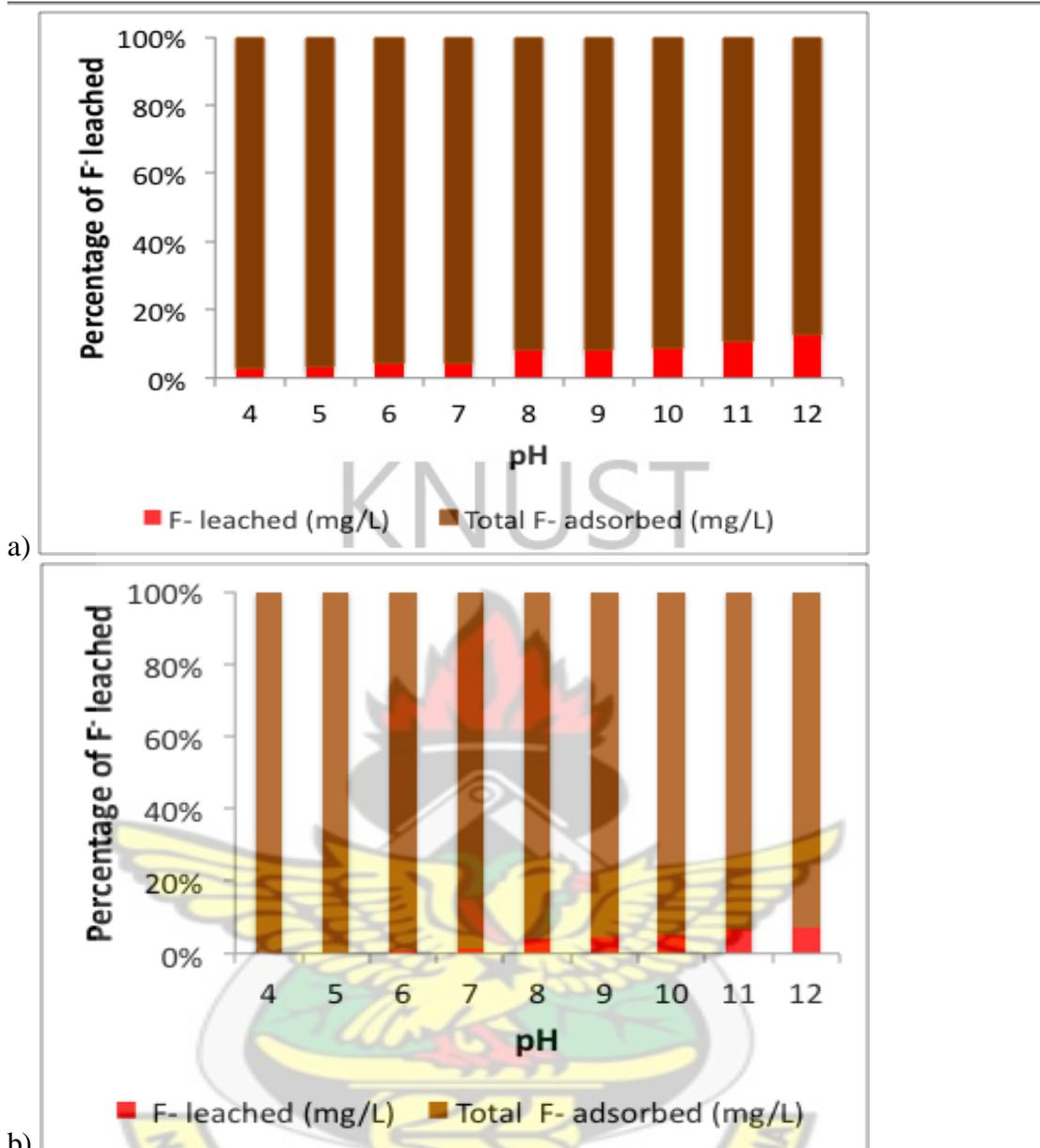


Figure 4-21:Percentage of Fluoride leached at pH 4-12 (a) AOCB (b) AOCC

However, the highest recorded amounts of fluoride leached from both AOCC and AOCB were less than the TCLP guideline value of 150mg/L hence it was again concluded that the saturated AOCB and AOCC were safe to be disposed into the environment under both acidic and basic conditions.

#### **4.13 Regenerating by NaOH against regenerating by surface coating**

According to Mandal and Mayadevi (2009), a possible way of regenerating as-synthesized Zn/Al/Cl anionic clay media used for defluoridation of drinking water was by rinsing the media with a 0.01M NaOH solution. The  $\text{OH}^-$  displaces the adsorbed  $\text{F}^-$  into solution. The initial adsorption capacity of the as-synthesized media was determined to be 0.11mg/g for an initial fluoride concentration of 0.52mg/L. A total of five feasible regenerations were recorded. Mandal and Mayadevi (2009) reported a 73% restoration of the initial adsorption capacity after the 5<sup>th</sup> regeneration whereas a 45% restoration of adsorption capacity of AOCC was recorded in this study after three cycles of surface coating regenerations. Although the regeneration by rinsing media with NaOH was more efficient than the Aluminium oxide surface coating regeneration the disposal of the fluoride rich regenerant waste was said to be problematic. Improper disposal of the regenerant waste can re-introduce the fluoride into the environment, which can be dreadful eventually. In terms of protecting the environment the aluminium oxide surface coating regeneration was considered a better option than regenerating the media by rinsing the media with NaOH solution.

## CHAPTER FIVE

### 5.0 CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusions

From the study conducted it can be concluded that:

Recoating of exhausted AOCC with aluminium oxide in order to regenerate it was successful and feasible empirically with three possible regeneration cycles unlike the AOCB.

The fluoride adsorption capacity of the AOCC was restored after regeneration, however successive regenerations led to gradual reduction in the fluoride adsorption capacity

The fluoride removal mechanism of both AOCC and AOCB is basically chemisorption

The aluminium coated onto all exhausted media was stable and did not leach into solution.

It is safe to dispose off both fluorides saturated AOCB and AOCC at landfill sites under both acidic and basic conditions.

AOCC has a higher adsorption capacity than AOCB

#### 5.2 Recommendations

- Economic analysis of the coating should be done to determine when it is economically feasible to regenerate the media
- The synergetic effect of the ions present in the water on the stability of the Aluminium coated onto the media should be studied.

- EDX or XRD analysis of both AOCC and AOCCB should be conducted to confirm the reduction of the adsorptive sites on the media after regeneration.

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**Appendix 1: Results for batch adsorption studies**

(a) Table showing measured potentials and corresponding concentrations using AOCC-initial at pH 7

AOCC-initial											
Time (hours)	0	0.25	0.5	4	24	36	48	56	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)										
BLANK	-37	-37	-36.5	-37	-37	-36.5	-37	-37	-36.5	-37	-37
60	-37	-16	-12.5	8	20.5	25.5	28	28	30	30	30
55	-35.5	-12	-7.5	12	26	29.5	31	31	31.5	31.5	31.5
50	-33.5	-10	-5	12.5	29.5	32	33	33	33.5	33.5	33.5
45	-31.5	-9	-4.5	12.5	30.5	33	33.5	33.5	34	34	34
40	-29	-6.5	-1	16	33	36	36	36	36.5	36.5	36.5
F- concentration (mg/L)	Fluoride concentration (mg/L)										
BLANK	58.57	58.57	57.08	58.57	58.57	57.08	58.57	58.57	57.08	58.57	58.57
60	58.57	19.87	16.60	5.78	3.04	2.35	2.06	2.06	1.86	1.86	1.86
55	54.21	16.18	12.83	4.70	2.29	1.91	1.77	1.77	1.72	1.72	1.72
50	48.91	14.59	11.28	4.58	1.91	1.68	1.60	1.60	1.56	1.56	1.56
45	44.13	13.86	11.00	4.58	1.82	1.60	1.56	1.56	1.52	1.52	1.52
40	38.80	12.19	9.18	3.83	1.60	1.37	1.37	1.37	1.33	1.33	1.33

(b) Table showing measured potentials and corresponding concentrations using AOCC-first regeneration at pH 7

AOCC-First Regeneration									
Time (hours)	0	0.25	0.5	4	24	48	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)								
BLANK	-37.5	-37.5	-37	-37	-37	-37	-37	-37	-37
60	-37.5	-30	-27	-10.5	11	12	12.5	15.5	16
55	-36	-26	-23	-7.5	12	13	16	17.5	18
50	-34	-24	-19	-4	14	15	18	19	20
45	-32	-22	-16.5	-2	16	17	18.5	20.5	22
40	-30	-18.5	-13	3.5	19	20.5	21.5	23	24
F- concentration (mg/L)	Fluoride concentration (mg/L)								
BLANK	60.09	60.09	58.57	58.57	58.57	58.57	58.57	58.57	58.57
60	60.09	40.85	35.00	14.97	4.95	4.70	4.58	3.93	3.83
55	55.63	33.25	28.49	12.83	4.70	4.47	3.83	3.54	3.45
50	50.19	30.00	23.19	10.72	4.24	4.03	3.45	3.28	3.12
45	45.28	27.06	20.39	9.67	3.83	3.64	3.37	3.04	2.81
40	40.85	22.60	17.03	7.28	3.28	3.04	2.88	2.67	2.54

(c) Table showing measured potentials and corresponding concentrations using AOCC-second regeneration at pH 7

AOCC-Second Regeneration									
Time (hours)	0	0.25	0.5	4	24	48	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)								
BLANK	-43	-43	-42.5	-43	-42	-43	-43	-42	-43
60	-43	-40	-37	-29	-5.5	2	2.5	2.5	2.5
55	-41.5	-38	-34	-25	1	4	5	5	5
50	-40	-37	-32	-24	2	6	6	6	6
45	-38	-32.5	-30	-20	3	8	8	8	8
40	-36	-31	-28	-19	4	9	10	10.5	11
F- concentration (mg/L)	Fluoride concentration (mg/L)								
BLANK	59.64	59.64	58.01	59.64	56.42	59.64	59.64	56.42	59.64
60	59.64	50.48	42.73	27.39	7.42	4.89	4.75	4.75	4.75
55	54.87	45.17	36.16	21.93	5.17	4.37	4.14	4.14	4.14
50	50.48	42.73	32.36	20.74	4.89	3.91	3.91	3.91	3.91
45	45.17	33.27	28.95	16.61	4.62	3.50	3.50	3.50	3.50
40	40.42	30.61	25.91	15.71	4.37	3.31	3.13	3.05	2.96

(d) Table showing measured potentials and corresponding concentrations using AOCC-third regeneration at pH 7

AOCC-Third Regeneration									
Time (hours)	0	0.25	0.5	4	24	48	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)								
BLANK	-43	-42.5	-43	-43	-42.5	-43	-42.5	-43	-43
60	-43	-39.5	-36	-25	-8	-1.5	3	3	6.5
55	-41.5	-36.5	-33	-21	-5.5	1	5	5	5
50	-40	-34.5	-32	-20	-4	1.5	6	6	6
40	-38	-32	-30	-18	-3.5	2	6.5	6.5	6.5
45	-35.5	-29.5	-26.5	-16.5	-3	4	7.5	7.5	7.5
F- concentration (mg/L)	Fluoride concentration (mg/L)								
BLANK	59.64	58.01	59.64	59.64	58.01	59.64	58.01	59.64	59.64
60	59.64	49.10	40.42	21.93	8.52	5.94	4.62	4.62	3.81
55	54.87	41.55	34.21	17.56	7.42	5.17	4.14	4.14	4.14
50	50.48	37.18	32.36	16.61	6.82	5.03	3.91	3.91	3.91
45	45.17	32.36	28.95	14.86	6.64	4.89	3.81	3.81	3.81
40	39.31	28.16	23.83	13.67	6.46	4.37	3.60	3.60	3.60

(e) Table showing measured potentials and corresponding concentrations using AOCC-fourth regeneration at pH 7

AOCC-Fourth Regeneration									
Time (hours)	0	0.25	0.5	4	24	48	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)								
BLANK	-43	-43	-43	-43	-42.50	-43.00	-42.5	-43	-43
60	-43	-42	-40.5	-38.50	-17.5	-15	-13	-11.5	-11
55	-41.5	-41	-40	-35.5	-15	-13	-12	-11	-10
50	-40	-38.5	-37	-33	-13	-11	-10.5	-10	-9
40	-38	-37	-36	-31.5	-11.5	-10	-9	-8.5	-8
45	-35.5	-33	-31.5	-26	-9.5	-8	-7	-6.5	-6
F- concentration (mg/L)	Fluoride concentration (mg/L)								
BLANK	59.64	59.64	59.64	59.64	58.01	59.64	58.01	59.64	59.64
60	59.64	56.42	51.90	46.44	14.45	12.58	11.25	10.35	10.07
55	54.87	53.36	50.48	39.31	12.58	11.25	10.65	10.07	9.53
50	50.48	46.44	42.73	34.21	11.25	10.07	9.79	9.53	9.01
45	45.17	42.73	40.42	31.47	10.35	9.53	9.01	8.76	8.52
40	39.31	34.21	31.47	23.18	9.26	8.52	8.06	7.84	7.63

(f) Table showing measured potentials and corresponding concentrations using AOCB-initial at pH 7

AOCB-Initial									
Time (hours)	0	0.25	0.5	4	24	48	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)								
BLANK	-33.5	-33	-33.5	-33.5	-33.5	-33	-33.5	-33.5	-33.5
35	-33.5	-32	-29.5	-25.5	-16.5	-15	-14.5	-12.5	-12.5
30	-30.5	-26	-24.5	-21.5	-13	-10	-9.5	-7.5	-7.5
25	-27	-21	-20	-16.5	-8	-4	-3.5	-1	-1
20	-23	-16	-12.5	-11	-2.5	3	4	5	5
15	-18	-9	-7	-4.5	5.5	12	14	15	15
F- concentration (mg/L)	Fluoride concentration (mg/L)								
BLANK	35.17	34.21	35.17	35.17	35.17	34.21	35.17	35.17	35.17
35	35.17	32.36	28.16	22.55	13.67	12.58	12.23	10.95	10.95
30	29.77	23.18	21.33	18.05	11.25	9.53	9.26	8.29	8.29
25	24.51	17.56	16.61	13.67	8.52	6.82	6.64	5.78	5.78
20	19.62	13.30	10.95	10.07	6.28	4.62	4.37	4.14	4.14
15	14.86	9.01	8.06	7.02	4.02	2.80	2.51	2.37	2.37

(g) Table showing measured potentials and corresponding concentrations using AOCB-first regeneration at pH 7

AOCB-First Regeneration									
Time (hours)	0	0.25	0.5	4	24	48	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)								
BLANK	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5
35	-33.5	-31.0	-30.0	-26.0	-22.0	-17.0	-16.0	-15.0	-15.0
30	-30.5	-27	-26	-23	-18.5	-13	-12	-11	-11
25	-27	-22.5	-21	-19	-14.5	-10	-9	-8	-8
20	-23	-17	-16	-14	-9	-3	-2	-1	-1
15	-18	-10	-9	-5.5	-3.5	2	3	4	4
F- concentration (mg/L)	Fluoride concentration (mg/L)								
BLANK	35.17	35.17	35.17	35.17	35.17	35.17	35.17	35.17	35.17
35	35.17	30.61	28.95	23.18	18.56	14.06	13.30	12.58	12.58
30	29.77	24.51	23.18	19.62	15.28	11.25	10.65	10.07	10.07
25	24.51	19.08	17.56	15.71	12.23	9.53	9.01	8.52	8.52
20	19.62	14.06	13.30	11.90	9.01	6.46	6.11	5.78	5.78
15	14.86	9.53	9.01	7.42	6.64	4.89	4.62	4.37	4.37

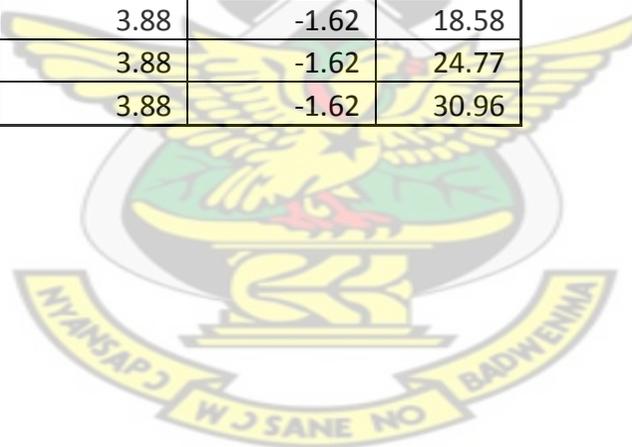
(h) Table showing measured potentials and corresponding concentrations using AOCB-second regeneration at pH 7

AOCB-2nd Regeneration									
Time (hours)	0	0.25	0.5	4	24	48	72	96	120
F- concentration (mg/L)	Ionic Potential (mV)								
BLANK									
35	-33.5	-33	-32.5	-32	-27	-26	-24	-23.5	-23.5
30	-30.5	-30	-30	-29	-25	-23.5	-22	-20.5	-20.5
25	-27	-26	-26	-24	-21	-20	-18.5	-18.5	-18.5
20	-23	-22	-22	-19	-17	-15	-14	-14	-14
15	-18	-16	-15	-11.5	-10	-9.5	-9	-9	-9
F- concentration (mg/L)	Fluoride concentration (mg/L)								
BLANK	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5	-33.5
35	35.17	34.21	33.27	32.36	24.51	23.18	20.74	20.17	20.17
30	29.77	28.95	28.95	27.39	21.93	20.17	18.56	17.08	17.08
25	24.51	23.18	23.18	20.74	17.56	16.61	15.28	15.28	15.28
20	19.62	18.56	18.56	15.71	14.06	12.58	11.90	11.90	11.90
15	14.86	13.30	12.58	10.35	9.53	9.26	9.01	9.01	9.01

**Appendix 2: Results for Kinetic Models**

(a) Table showing data for Lagergren model and pseudo second-order kinetics model at pH 7 using initial AOCC

Time (hour)	60mg/L-AOCC Initial			
	Fluoride Concentration (mg/L)	qt	log(qe-qt)	t/qt
0	58.57	0.10	0.58	0.00
0.25	19.87	2.68	0.09	0.09
0.5	16.60	2.89	0.00	0.17
4	5.78	3.61	-0.54	1.11
24	3.04	3.80	-0.99	6.32
48	2.06	3.86	-1.42	12.43
72	1.86	3.88	-1.62	18.58
96	1.86	3.88	-1.62	24.77
120	1.86	3.88	-1.62	30.96



(b) Table showing data for Lagergren model and pseudo second-order kinetics model at pH 7 using initial AOCB

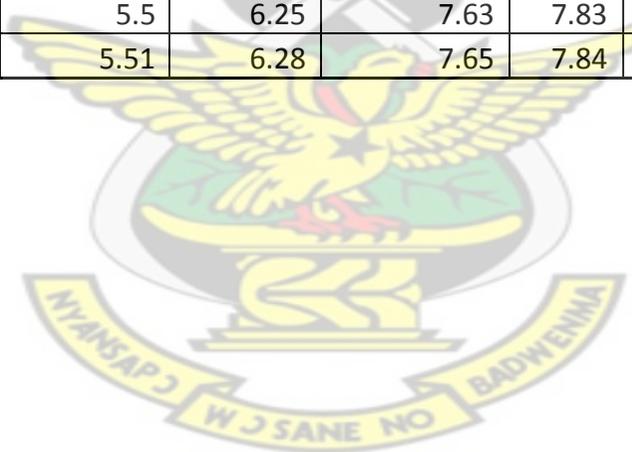
Time (hour)	60mg/L-AOCB Initial			
	Fluoride Concentration (mg/L)	qt	log(qe-qt)	t/qt
0	35.17	0.00	0.31	0.00
0.25	32.36	0.23	0.25	0.40
0.5	28.16	0.58	0.16	0.30
4	22.55	1.05	-0.01	1.05
24	13.67	1.79	-0.64	3.53
48	12.58	1.88	-0.86	6.60
72	12.23	1.91	-0.96	9.72
96	10.95	2.02	-2.89	12.27
120	10.95	2.02	-2.89	15.34



**Appendix 3: Results for pH dependent leaching test**

j) Table showing data for pH dependent leaching test for saturated AOCB

	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12
Dry mass of the test portion (g)	2	2	2	2	2	2	2	2	2
Acid concentration (M)	12	12	12	12	12	12	12	12	12
Base concentration (M)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Leachant volume (ml)	20	20	20	20	20	20	20	20	20
pH at to+4hours	4.03	5.02	6.08	7.02	8.05	9.01	10.03	11.07	12.00
pH at to+44hours	4.66	5.5	6.25	7.63	7.83	8.35	9.94	10.82	12.25
pH at to+48hours	4.66	5.51	6.28	7.65	7.84	8.36	9.94	10.85	12.25



k) Table showing data for pH dependent leaching test for saturated AOCC

	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	pH 11	pH 12
Dry mass of the test portion (g)	2	2	2	2	2	2	2	2	2
Acid concentration (M)	12	12	12	12	12	12	12	12	12
Base concentration (M)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Leachant volume (ml)	20	20	20	20	20	20	20	20	20
pH at to+4hours	4.01	5.03	6.05	7.02	8.01	9.01	10.03	11.04	12.00
pH at to+44hours	4.32	5.18	6.22	7.43	7.55	9.12	9.98	10.97	12.26
pH at to+48hours	4.32	5.18	6.22	7.44	7.56	9.12	9.98	10.99	12.27

