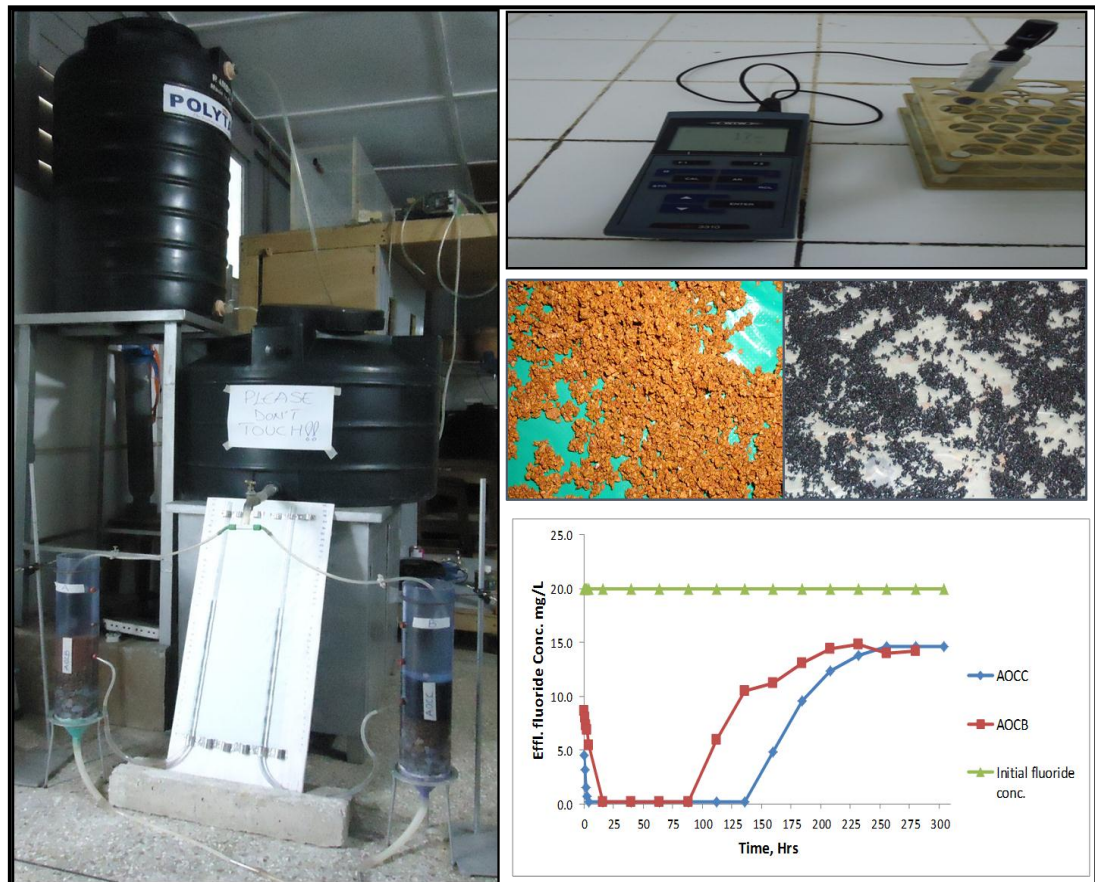




**Pilot Column Studies on Adsorption of Fluoride onto Coated High Aluminium
Bauxite Ore (HABO) and Charcoal**

Mahamud Hamid Sidik

MSc. Thesis

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Kwame Nkrumah University of
Science and Technology



**Pilot Column Studies on Adsorption of Fluoride onto Coated High Aluminium
Content Bauxite Ore (HABO) and Charcoal**

By

Mahamud Hamid Sidik, BSc. (Hons.)

A Thesis submitted to the Department of Civil Engineering
Kwame Nkrumah University of Science and
Technology
in partial fulfilment of the requirements for the degree

MASTER OF SCIENCE

in

Water Supply and Environmental Sanitation

Faculty of Civil and Geomatic Engineering,

College of Engineering

July, 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.

Mahamud Hamid Sidik		
(PG 4777410)	Signature	Date

Certified by:

Dr. R. Buamah		
(Principal Supervisor)	Signature	Date

Certified by:

Prof. M. Salifu		
(Head of Dept., Civil Engineering)	Signature	Date

Dedication

To the Most High God, my wife, best friend (Osman Sahanun), and family

Abstract

The quality of drinking water is important for public safety and quality of life. Fluoride contamination in drinking water due to natural and anthropogenic activities has been recognized as one of the major problems worldwide imposing serious threat to human health. Fluoride concentrations in drinking water above 1.5 mg /L may be detrimental to human health.

The three Northern regions of Ghana (Upper East, Upper West and Northern region) are noted for the high concentration ($>1.5\text{mg/L}$) of fluoride in underground water bodies. Finding a sustainable and cost effective adsorbent to reduce the fluoride concentration in the drinking water before being used has become a major challenge for researchers.

In this study, fluoride removal behaviour of aluminium oxide coated bauxite (AOCB), aluminium oxide coated bauxite (AOCB), and regenerated exhausted media were investigated. The study also examined the adsorption of inorganic anions (sulphate, nitrate and bicarbonate) from the model water by using the virgin media (bauxite and charcoal) and the coated media (AOCB and AOCC). Pilot column studies were conducted using the mentioned media a sampling episode that span over the period of the filter run times.

AOCC was effective in reducing initial fluoride concentration of 20mg/L in the model to fluoride levels below 1.5mg/L from 1 hour to 132 hours of filter run time with adsorption capacity of $0.006\text{gF}^-/\text{g}$ sorbent. AOCB on its part reduced the fluoride concentration of 20mg/L to values below 1.5mg/L for up to 72 hours with adsorption capacity of $0.001\text{gF}^-/\text{g}$ sorbent. The first generation re-coat gave rise to an increased fluoride removal potential. Subsequent recoating did not improve the fluoride removal capacity. The water quality experiments showed that AOCB and AOCC leached sulphate into the treated water above the initial sulphate concentration used (32mg/L) in the model water. However the sulphate concentration in the treated water was below the WHO guideline value of 250mg/L . The virgin media (bauxite and charcoal) and coated media (AOCB and AOCC) were effective in reducing the initial bicarbonate and nitrate concentrations to acceptable levels.

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List of Abbreviations and symbols

AA	Activated Alumina
AOCB	Aluminium Oxide Coated Bauxite
AOCC	Aluminium Oxide Coated Charcoal
AOCM	Aluminium Oxide Coated Media
AWWA	American Water Works Association
CC	Calcium Chloride
CWSA	Community Water and Sanitation Agency
EDX	Energy Dispersive X-ray
F ⁻	Fluoride
HABO	High Al Content Bauxite Ore
MSP	Mono-Sodium Phosphate
MWCO	Molecular Weight Cut-Off
MF	Micro-Filtration
NR	Northern Region
RO	Reverse Osmosis
TISAB	Total Ionic Strength Adjustment Buffer
UNESCO	United Nations Educational, Scientific and Cultural Organization
UF	Ultrafiltration
W.H.O	World Health Organisation
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

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1. INTRODUCTION

1.1 Background

Fluoride (F⁻) contamination in groundwater has been recognized as one of the serious problems worldwide. Fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO), in addition to arsenic and nitrate, which cause large-scale health problems. Elevated fluoride concentrations in the groundwater occur in various parts of the world. Fluoride is widely distributed in the geological environment and generally released into the groundwater by slow dissolution of fluorine-containing rocks (Amit et al., 2011). The WHO recommended health based guideline for fluoride in drinking water is 1.5 mg/L (WHO, 2008).

Fluoride is an ion of the chemical element fluorine which is among the member of halogen group. Fluoride is an important micronutrient in human beings for the calcification of dental enamel and bone formation, when present in low concentration (Mandal et al., 2009). Fluoride element is essential as well as detrimental for the dental and skeletal growth of human beings. Deposited fluoride contaminations are found in water mostly due to natural processes (e.g., geochemical reactions and volcanic emissions) and industrial activities (e.g., semiconductor, electroplating, steel and fertilizer industries) (Nan Chen et al., 2011). Due to its high electronegativity and small ionic size, the fluoride ion is classified as a hard base, which has a strong affinity towards metal ions including Al⁺³ and Fe⁺³.

In Ghana, the most affected regions are the Upper West, Upper East and Northern Regions. Bongo district in the Upper East Region of Ghana is noted for the high concentration of fluoride in its underground water bodies of which the people depend

so much on to meet their drinking water needs. As a result of this, most people in the endemic areas suffer from dental fluorosis (Antwi et al., 2011). Naturally occurring fluoride in water is usually derived from the solvent action of water on the rocks and soils of the earth's crust. Fluoride concentration in natural waters, especially underground water largely depends, among other things, on the solubility of fluoride-containing mineral in the underground water and the porosity of the rocks and soil through which the water passes. Geologically, the Upper Regions of Ghana are underlain mainly by Precambrian granite rocks composed largely of granites, granodiorites and gneiss. In Ghana, high fluoride levels ($>1.5\text{mg/l}$) in groundwater have been recorded in Bongo and surrounding communities (Atipoka, 2009)

Victims show signs of lowliness as they shy away from their visitors to whom they are unable to return a welcome smile because of the bad state of their teeth. Currently, the district has 35 wet boreholes drilled but capped due to high fluoride contamination with level ranging between 1.7 and 4.0 mg/L (Atipoka, 2009).

Several treatment technologies based on the principle of precipitation, ion exchange, membrane and adsorption processes have been proposed and tested for removal of excess fluoride from drinking water before consumption. Among these technologies, adsorption continues to be an effective and most extensively studied process for its simplicity and easy operation. Activated alumina has been widely used as adsorbent in such processes. In recent years, many studies have been carried out for the investigation and development of new, locally available and cost effective fluoride sorbents using various synthetic and naturally occurring materials. Notably among these, alum-impregnated activated alumina (AIAA), red mud, clay (Mandal and Mayadevi, 2009), bauxite and charcoal (Mwampashi, 2011), zeolites (Onyango,

2004), have shown potential to fluoride adsorption from drinking water but are yet to get wide spread acceptability.

Bauxite ores, abundantly available in many parts of India, usually contain oxides of Al, Fe, and Si. The titanium content in the bauxite ore depends upon the geological process which controlled the development of bauxite (Das et al., 2005). In Ghana, bauxite ores rich in Aluminium oxide are available at Awaso in the Western region (Asare, 2011).

1.2 Problem Statement

Fluoride in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested. Fluoride is beneficial especially to young children below eight years of age when present within permissible limits of 1.0-1.5mg/L for calcification of dental enamel. Excess fluorides in drinking water cause dental fluorosis and/or skeletal fluorosis (Srimurali, 1998). High level of fluoride beyond the allowable limits recommended by WHO was recorded in ground water in the Bongo district of Upper East region of Ghana causing fluorosis, a disease of bones and teeth. The district has 35 wet boreholes drilled but capped due to high fluoride contamination with level ranging between 1.7 and 4.0 mg/L. In 1995, a survey was conducted by the Ghana Health Service in Bongo to study the number of children of school going age with dental fluorosis. The outcome of the survey indicated that about 33% of the schoolchildren in the district suffered from dental fluorosis (Atipoka, 2009).

Fluoride removal techniques commonly used require high level of skills to operate, generate larger amount of sludge and brine, high investment, operation and maintenance cost. Due to the constraint in terms of cost and productions of waste the application of these technologies need to be replaced with low cost technology.

1.3 Justification

Most rural communities affected by high levels of fluoride in their drinking waters have low income so they cannot afford the expenses of applying high cost technologies to remove fluoride from water. This research would therefore facilitate the design and construction of pilot filters using short columns to study the practical applications of adsorption using aluminium oxide coated charcoal and bauxite as low cost adsorbents. The development of a low-cost fluoride removal filter would increase affordability and subsequently reduce the incidence of dental fluorosis in fluoride endemic communities as well as improve the socio-economic status of such communities.

Consequently, boreholes that have been capped for several years due to the high levels of fluoride could be put back into operation to service their communities. This will contribute to the effort being made by Ghana to achieve the goal of the National Water Policy of “achieving sustainable development, management and use of Ghana's water resources to improve health and livelihoods, reduce vulnerability while assuring good governance for present and future generations”.

1.4 Study Objectives

The goal of this research is to investigate the fluoride removal potentials of aluminium oxide coated bauxite (AOCB) and Aluminium oxide coated Charcoal (AOCC)

The specific objectives of the research are:

- i. To design and construct a pilot filter using short columns with improved fluoride removal adsorbent
- ii. To evaluate the fluoride adsorption potential of AOCB and AOCC using the short column adsorption experiment.
- iii. To evaluate the fluoride adsorption performance of regenerated AOCB and AOCC using the short column adsorption experiment.
- iv. To determine the water quality of the treated water

1.5 Scope of study

Laboratory scale short column adsorption experiment would be set up to investigate the fluoride removal capacities of AOCB and AOCC for this study. The model water will be prepared in the KNUST Civil engineering (water) laboratory by simulating the existing water quality in Northern Ghana. The water quality information to be used will be obtained from a preliminary study done by Buamah and Dapilah (unpublished) in 2008. The information obtained from the preliminary study confirms previous groundwater quality survey done by CWSA. Northern Ghana as used in this thesis comprises of the Northern region, Upper East region and Upper West region of Ghana.

2. LITERATURE REVIEW

2.1 Groundwater availability

A geological investigation conducted in Ghana by the British Geological Survey in 1995, revealed that groundwater flow is mostly restricted to joints and fractures within the crystalline rock formations. Borehole yields are therefore often limited. In Ghana (parts of the south-west), a dense layer of weathered material overlies the crystalline basement and provides potential for increased groundwater storage. This weathered layer can be in excess of 100 m thick in places, though is more typically in the range 1-70 m thick (Asomaning, 1992). Groundwater supplies may be higher in the minor sedimentary deposits of the coastal basins. In the tropical southern part of the country, handpump tubewells and dug wells are in common usage. In the arid north of Ghana, where surface water is more scarce, water supply is dominantly from tubewells and dug wells (Smedley, et al., 1995).

2.2 Groundwater quality

Geology plays an important role in the determination of groundwater quality and potential water-quality problems. As Ghana is dominated by crystalline silicate rocks and weathered derivatives (regolith), groundwater is mainly of low salinity and commonly acidic in composition ($\text{pH} < 6.5$), with low values of total hardness. Exceptions occur in areas of limestone (parts of the south-east) and along the coastal margin where hardness and pH values are higher and where seawater intrusion of the coastal aquifers may increase groundwater salinity. Minor occurrences of saline groundwater have also been noted in isolated boreholes in rocks of the Voltaian Basin. The principal groundwater-quality problem observed in Ghana is high iron concentrations, seen in many groundwater supplies. The most serious direct health problems related to drinking water are considered to be from fluoride excess and

iodine deficiency which have been noted in parts of the Upper Regions of northern Ghana. In the gold-belt zone of Ghana, nearly 290 well water samples from three regions namely Ashanti, Western and Brong-Ahafo, were analyzed for the presence of arsenic and manganese. It was reported that 5-12% of sampled wells had arsenic levels exceeding the $10\mu\text{gl}^{-1}$ -WHO provisional guideline value (Buamah et al., 2008)

Table 1- 1: Summary of potential groundwater quality in Ghana

Determinant	Potential Problem	Geology	Location
Iron (Fe)	Excess, often significant	All aquifers	Many locations
Manganese (Mn)	Excess	All aquifers	Several locations
Fluoride (F)	Excess (up to 4 mg/l)	Granites and some Birimian rocks	Upper Regions
Iodine (I)	Deficiency (less than 0.005 mg/l)	Birimian rocks, granites, Voltaian	Northern Ghana (especially Upper Regions)
Arsenic (As)	Excess (>0.01 mg/l)	Birimian sediments, Birimian volcanics and Tarkwaian formation	Especially south-west Ghana (gold belt)

(Source: British Geological Survey, 1995)

2.3 Occurrence of fluoride in the environment

Fluorine is the lightest member of the halogen group and is the most reactive of all chemical elements. Fluorine does not occur in the element state in the environment however it acquires a negative charge to form fluoride. Fluorides are found at significant levels in a wide variety of minerals, including fluorspar, rock phosphate, Cryolite, apatite and mica (Fawell et al., 2006). Fluoride is widely distributed in the geological environment and generally released into the groundwater by slow dissolution of fluorine-containing rocks (Abe et al., 2004). Besides the natural geological sources for fluoride enrichment in groundwater, various industries are also

contributing to fluoride pollution to a great extent in the environment (Reardon and Wang, 2000)

2.3.1. Chemistry of fluoride

The element fluorine was discovered in 1886 by Moissan. A fluoride ion is the ionic form of fluorine. Fluoride belongs to group 7 of the periodic table. It has an atomic number 9 and an oxidation number -1 and an electron affinity of $83.5 \pm 2 \text{ kcal/g-atom}$. Fluoride forms binary compounds with other elements or radical. Examples of common fluoride compounds include hydrofluoric acid (HF), and sodium fluoride (NaF).

Fluoride is the 13th most abundant element found in the earth's crust. According to Schuiling (1989) fluorine is a pale yellow, highly corrosive, poisonous gaseous element. It is the most electronegative and most reactive of all the elements. Due to its high electronegativity it has a powerful attraction for electrons and able to attack all elements except oxygen and nitrogen (Hem, 2005).

Free fluorine is characterized by pungent odour and it is strongly irritant and very corrosive. It has been observed that low calcium and high bicarbonate alkalinity favour high fluoride content in groundwater (Meenakshi et al., 2006). The chemical properties and fluoride release rate of a material depend on the pH of the solution on which the material is exposed. It occurs in the sedimentary and igneous rocks and associated with volcanic activities and with thermal water with high pH. There are several minerals known for their fluoride content but the major minerals which contain fluoride are mentioned below.

Table 2- 1: Fluoride bearing minerals

Mineral	Chemical formula	% fluorine
Sellaite	MgF ₂	61
Villiamite	NaF	55
Fluorite (fluoraspars)	CaF ₂	49
Cryolite	Na ₃ AlF ₆	45
Bastnaesite	(Ce,La)(CO ₃)F	9
Fluorapatite	Ca ₃ (PO ₄) ₃ F	34

[Source: Rao, 2003]

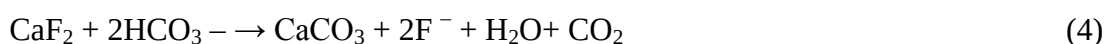
Fluoride forms very strong bonds with carbon which make it resistant to be attacked or destroyed by chemical and biological processes and can be substitute for hydrogen atoms and hydroxyl ions in molecules. Fluorine is the most electronegative non-metal with an oxidation potential greater than ozone. The occurrence of carbonates in the soil zones is due to CO₂ formed from the weathering of country rocks.

Equation 2- 1: Combination of Carbon dioxide with rain water to form Carbonates



Equation 2- 2: Weathered rocks and CaF₂ precipitating Calcium Carbonate

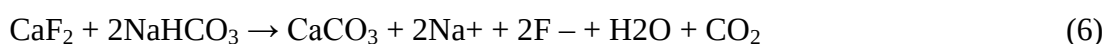
Alkaline water can mobilize F⁻ from soils,



Equation 2- 3: Dissociation of Fluoride from fluorine-containing minerals as:



Equation 2- 4: The dissolution activity of fluoride in the presence of excessive sodium bicarbonates in ground water



2.3.2 Fluoride occurrence in groundwater

Widespread occurrence of fluoride in groundwater more than the prescribed limit has caused multidimensional health problems (Yakun, et al., 2011). Fluoride (F⁻) contamination in groundwater has been recognized as one of the serious problems worldwide (Amit, et al., 2011). Higher fluoride concentrations in the groundwater occur in various parts of the world. Fluoride generally released into the groundwater by slow dissolution of fluorine-containing rocks (Banks, et al., 1995). A number of minerals, e.g., fluorite, biotites, topaz, and their corresponding host rocks such as granite, basalt, syenite, and shale, contain fluoride that can be released into the groundwater (Apambire, et al., 1997).

The dominant controls on fluoride occurrence in groundwater are climate and geology. The regions of Ghana most vulnerable to high fluoride concentrations (and associated dental 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.

Concentrations of fluoride in excess of 1.5 mg/l (up to 20 mg/l) have been observed in Bolgatanga and Sekoti (Upper East Region, Fig 2-1) in close association with granitic rock types (Smedley et al., 1995). Occurrence of dental fluorosis is common in these areas. Groundwaters in granitic rocks of the south-west plateau are considered to be less at risk because of higher rainfall and its diluting effect on groundwater compositions. Marked variations in fluoride concentration with depth were observed in groundwaters from the problem areas of Bolgatanga (e.g. the Bongo Granite, Fig 2-1).

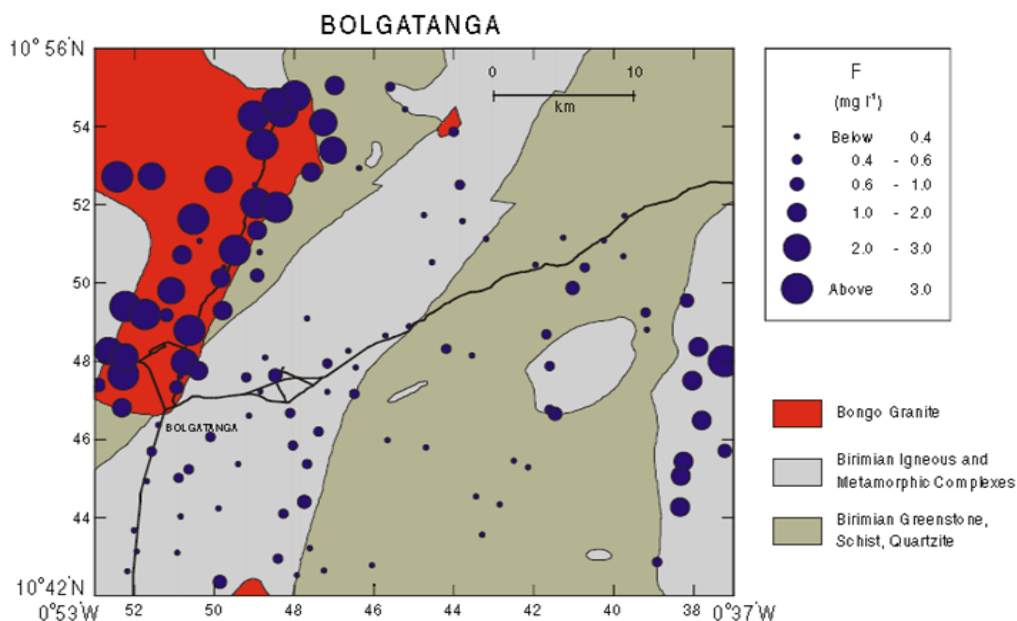


Figure 2- 1: Geological Map of Upper East Region (Northern Ghana)

2.4 Fluoride in humans and health effects

2.4.1 Fluoride intake and metabolism

Small amounts of fluoride in ingested water are usually considered to have a beneficial effect on the rate of occurrence of dental caries, particularly among children (Mahramanlioglu et al., 2002). On the contrary, excess intake of fluoride leads to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder (Chinoy, 1991 and Harrison, 2005). Following ingestion, the gastro-intestinal tract is the earliest and most commonly affected organ system. Fluoride can also interfere with a number of enzymes disrupting oxidative phosphorylation, glycolysis, coagulation, and neurotransmission (Islam and Patel, 2011).

When water containing fluoride is consumed, some fluoride (about 50 percent) is retained by fluids in the mouth and is incorporated onto the teeth by surface uptake (topical effect). The rest (about 50 percent) enters the stomach, where it is rapidly adsorbed by diffusion through the stomach walls and intestine. Fluoride enters the blood plasma and is rapidly distributed to all parts of the body, including the teeth (systemic effect). Because of the systemic effect, the fluoride ion is able to pass freely through all cell walls and is available to all organs and tissues of the body. Distributed in this fashion, the fluoride ion is available to all skeletal structures of the body in which it may be retained and stored in proportions that generally increase with age and intake. Bones, teeth, and other parts of the skeleton tend to attract and retain fluoride. Soft tissues do not retain fluoride (Raymond, 1999).

2.4.2 Absorption

Fluoride toxicity may occur by several pathways. Approximately 75–90 per cent of ingested fluoride is absorbed. In an acidic stomach, fluoride is converted into hydrogen fluoride (HF) and up to about 40 per cent of the ingested fluoride is absorbed from the stomach as HF. High stomach pH decreases gastric absorption by decreasing the concentration uptake of HF (WHO, 2006; Fawell et al., 2006). Fluoride not absorbed in the stomach is absorbed in the intestine and is unaffected by pH at this site (Whitford, 1997). While ingested, fluoride initially acts locally on the intestinal mucosa; it can later form hydrofluoric acid in the stomach, which leads to gastro-intestinal irritation or corrosive effects (Islam and Patel, 2011).

Once absorbed into the blood, fluoride readily distributes throughout the body. In infants, about 80 to 90 per cent of the absorbed fluoride is retained but in adults this level falls to about 60 per cent. Fluoride crosses the placenta and is found in mothers' milk at low levels essentially equal to those in blood (WHO, 1996).

2.4.3 Acute and chronic effects

It is apparent that fluorides have the ability to interfere with the functions of the brain (US National Research Council, 2006). Long term exposure of water fluoride levels greater than 1.5 mg/l were significantly associated with higher rates of mental retardation (IQ <70) and borderline intelligence (IQ 70-79). In endemic fluorosis areas, drinking water fluoride levels greater than 1.0 mg/L may adversely affect the development of children's intelligence (Xiang et al., 2003).

According to the National Toxicology Program, the majority of evidence from laboratory 'in vitro' studies indicates that fluoride is a mutagen (a compound that can cause genetic damage). It is generally accepted that if a substance can induce genetic damage there is a heightened risk that it could cause cancer as well (<http://www.fluoridealert.org/health/cancer>).

When bone turnover occurs, the potential exists for immune system cells and stem cells to be exposed to concentrations of fluoride in the interstitial fluids of bone that are higher than would be found in serum. Patients who live in a community where the drinking water naturally contains fluoride at 4 mg/L have all accumulated fluoride in their skeletal systems and potentially have very high fluoride concentrations in their bones. The bone marrow is where immune cells develop and that could affect humoral immunity and the production of antibodies to foreign chemicals (US National Research Council, 2006)

The kidneys are responsible for ridding the body of ingested fluoride, and thereby preventing the buildup of toxic levels (> 1.5 mg/L) of fluoride in the body. In healthy adults, the kidneys are able to excrete approximately 50% of an ingested dose of fluoride. However, in adults with kidney disease the kidneys may excrete as little as 10 to 20% of an ingested dose - thus increasing the body burden of fluoride and increasing an individual's susceptibility to fluoride poisoning (e.g. renal osteodystrophy) (<http://www.fluoridealert.org/health/kidneys>).

The pineal gland is a small gland located between the two hemispheres of the brain that regulates the production of the hormone melatonin. Melatonin is a hormone that helps regulate the onset of puberty and helps protect the body from cell damage caused by free radicals. The soft tissue of the adult pineal gland contains more fluoride than any other soft tissue in the body - a level of fluoride (~ 300 ppm) capable of inhibiting enzymes. The pineal gland also contains hard tissue (hydroxyapatite crystals), and this hard tissue accumulates more fluoride (up to 21,000 ppm) than any other hard tissue in the body (e.g. teeth and bone). ([http://www.fluoridealert.org/health/pineal gland](http://www.fluoridealert.org/health/pineal%20gland))

Fluoride affects normal endocrine function or response; the effects of the fluoride-induced changes vary in degree and kind in different individuals. Fluoride is therefore an endocrine disruptor in the broad sense of altering normal endocrine function. In humans, effects on thyroid function were associated with fluoride exposures of 0.05-0.13 mg/kg/day when iodine intake was adequate and 0.01-0.03 mg/kg/day when iodine intake was inadequate (US National Research Council, 2006)

2.4.4 Dental effects

Dental fluorosis is defined as a hypomineralisation of the enamel characterised by greater surface and subsurface porosity than in normal enamel as a result of excess fluoride intake during the period of enamel formation (Browne et al., 2005).

It has been confirmed that there is significant positive relationship between fluoride intake by water and the prevalence of dental fluorosis (WHO, 2006). The recommended level of fluoride in drinking-water, associated with the maximum level of dental caries protection and minimum level of dental fluorosis, is considered to be approximately 1 ppm (WHO, 2006).

Low levels of fluoride exposure in drinking water have negative effects on children's intelligence and dental health. The results of an investigation carried out by Søggaard, et al., 1995 also confirmed the dose-response relationships between fluoride concentrations and IQ scores as well as dental fluorosis condition.

Exposure to fluoride that is above optimal levels during enamel formation may induce appearance of dental fluorosis (Pendrys, 2000). In a study conducted by Mandic, 2010, the teeth of the schoolchildren were assessed for fluorosis, using Dean's criteria and according to the WHO guidelines (WHO, 1987).

Criteria for Dean's fluorosis index are described as follows (Dean, 1942). Normal (0): the enamel represents the usual translucent semivitriform type of structure, and the surface is smooth, glossy, and usually of a pale creamy white color. Questionable (1): the enamel discloses slight aberrations from the translucency of normal enamel, ranging from a few white flecks to occasional white spots.

Very mild (2): small opaque, paper-white areas scattered irregularly over the tooth but not involving as much as 25% of the tooth surface. Frequently included in this classification are teeth showing no more than about 1–2 mm of white opacity at the tip of the summit of the cusps of the bicuspid or second molars. Mild (3): The white opaque areas in the enamel of the teeth are more extensive but do not involve as much as 50% of the tooth. Moderate (4): all enamel surfaces of the teeth are affected, and the surfaces subject to attrition show wear. Brown stain is frequently a disfiguring feature. Severe (5): includes teeth formerly classified as “moderately severe and severe.” All enamel surfaces are affected and hypoplasia is so marked that the general form of the tooth may be affected (WHO, 1987).

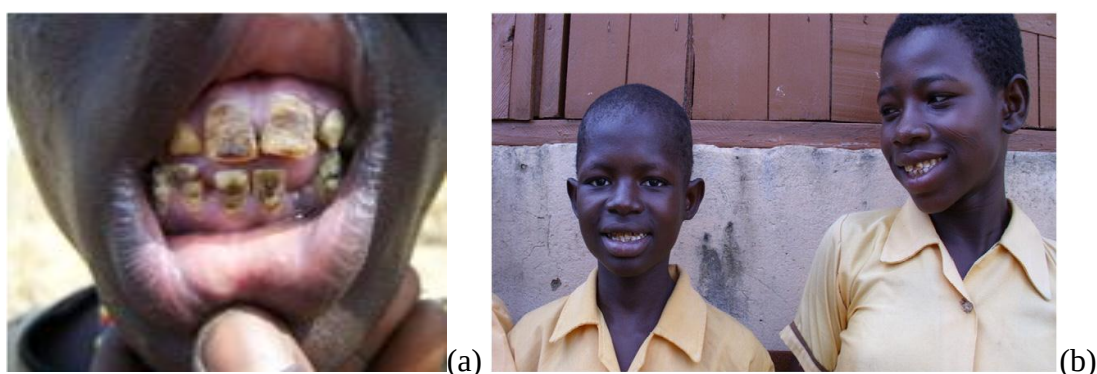


Figure 2- 2: Dental fluorosis in Bongo district (Antwi et al., 2011)

2.4.5 Skeletal Fluorosis

In humans, fluoride has been shown to increase bone formation to a larger extent in trabecular bone than cortical bone and therefore, to exert a greater response in the axial than the appendicular skeleton. Additionally, studies showed that the peripheral effects of fluoride were most pronounced in the weight-bearing bones. Fluoride has a possible detrimental effect on bone quality (Søgaard et al., 1995).

Skeletal fluorosis affects children as well as adults. It does not easily manifest until the disease attains an advanced stage. Fluoride mainly gets deposited in the joints of neck, knee, pelvic and shoulder bones and makes it difficult to move or walk. The symptoms of skeletal fluorosis are similar to spondylitis or arthritis. Early symptoms include sporadic pain, back stiffness, burning like sensation, pricking and tingling in the limbs, muscle weakness, chronic fatigue, abnormal calcium deposits in bones and ligaments. The advanced stage is osteoporosis in long bones and bony outgrowths may occur. Vertebrae may fuse together and eventually the victim may be crippled. It may even lead to a rare bone cancer; osteosarcoma and finally spine, major joints, muscles and nervous system get damaged (Meenakshi et al., 2006).



Figure 2- 3: Severe cases of skeletal fluorosis

2.5 Fluoride-Containing Products

The success of fluoride in controlling dental caries has led to the production of fluoride-containing products including toothpaste, mouth washes and professionally applied gels or varnishes (Browne et al., 2005).

Surface waters generally do not contain more than 0.3 mg/L of fluoride unless they are polluted from external sources. Though drinking water is the major contributor (75–90% of daily intake), other sources of fluoride poisoning are food, industrial exposure, drugs, cosmetics, etc. (Meenakshi et al., 2004). Fluoridated toothpaste now occupies over 95% of the toothpaste market. It has led to a marked decrease in caries in all countries. EU guidelines state that fluoride toothpastes sold over the counter should contain no more than 1500 ppm. It has been noted that an increasing number of infants and very young children ((before 18 months to 2 years when baby molars appear in the mouth) have tended to swallow toothpaste and this is likely to be contributing to the increasing level of enamel fluorosis (Browne et al., 2005).



Figure 2- 4: Toothpaste containing; (a) no fluoride and (b) contains (1450ppm) fluoride

2.6 Fluoride Determination

Accurate determination of fluoride has increased in importance with the growth of the practice of fluoridation of water supplies as a public health measure. Maintenance of an optimal fluoride concentration is essential in maintaining effectiveness and safety of the fluoridation process.

The electrode method is suitable for fluoride concentrations from 0.1 to more than 10 mg/L. Adding the buffer (TISAB) frees the electrode of most interferences. The fluoride electrode is an ion-selective sensor. The key element in the fluoride electrode is the laser-type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations. The fluoride electrode measures the ion activity of fluoride in the solution rather than concentration. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complexing species. Adding an appropriate buffer provides a nearly uniform ionic strength background, adjusts pH, and breaks up complexes so that, in effect, the electrode measures concentration.

The SPADNS colorimetric method has analytical range of 0 to 1.40 mg/L with virtually instantaneous colour development. Colour determinations are made photometrically, using either a filter photometer or spectrometer. A curve developed from standards is used for determining the fluoride concentration of a sample. Fluoride also may be determined by the automated complex-one method. Ion chromatography may be an acceptable method if weaker eluents are used to separate fluoride from interfering peaks (Greenberg, et al., 1992).

2.7 Fluoride removal technologies

The most commonly used methods for the defluoridation of water are adsorption, ion exchange, precipitation, and electrodialysis. Among these methods, adsorption is the most widely used method for the removal of fluoride from water. Several techniques have been developed for removal of fluoride from drinking water by adsorption and precipitation processes. The existing fluoride removal techniques include precipitation, membrane filtration and ion exchange or adsorption based processes.

A wide variety of adsorbents, such as activated alumina, bone charcoal, zeolites, bauxite, clay etc. have been tested for defluoridation of water.

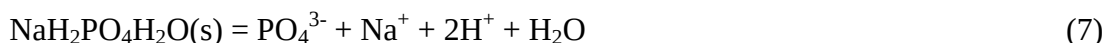
2.7.1 Precipitation

Contact precipitation is a technique by which fluoride is removed from the water through addition of calcium and phosphate compounds and then bringing the water 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 impossible due to slow reaction kinetics. In contact precipitation there is no sludge and no saturation of the bed, only the accumulation of the precipitate in the bed. Using calcium chloride (CC) and sodium dihydrogenphosphate or “monosodium phosphate” (MSP) chemicals. The following equations illustrate the removal of fluoride using precipitation (Fawell *et al.*, 2006).

Equation 2- 5: Dissolution of Calcium Chloride (CC)



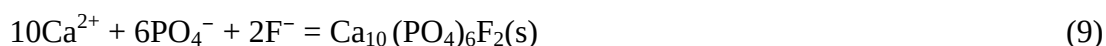
Equation 2- 6: Dissolution of monosodium phosphate (MSP):



Equation 2- 7: Precipitation of calcium fluoride



Equation 2- 8: Precipitation of fluorapatite

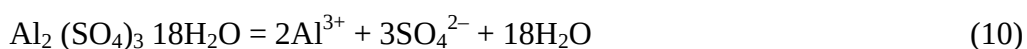


Too short contact time would reduce the removal capacity and increase the escape of chemicals in the treated water. Too long contact time may result in precipitation of calcium phosphates in the upper parts of the filter bed, thus also reducing the removal efficiency. The optimum contact time is not yet known but contact times of 20 to 30 minutes have been shown to produce excellent operation (Fawell et al., 2006).

2.7.2 Nalgonda

The process is aluminium sulfate based coagulation-flocculation sedimentation, where the dosage is designed to ensure fluoride removal from the water. Aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, is dissolved and added to the water under efficient stirring in order to ensure initial complete mixing. Aluminium hydroxide micro-flocs are produced rapidly and gathered into larger easily settling flocs. Thereafter the mixture is allowed to settle. During this flocculation process many kinds of micro-particles and negatively charged ions including fluoride are partially removed by electrostatic attachment to the flocs. The following equations illustrate the removal (Fawell *et al.*, 2006).

Equation 2- 9: Alum dissolution



Equation 2- 10: Aluminium precipitation (Acidic)



Equation 2- 11: pH adjustment



A much larger dosage of aluminium sulfate is normally required in the defluoridation process. As the aluminium sulfate solution is acidic, simultaneous addition of lime is often needed to ensure neutral pH in the treated water and complete precipitation of aluminium. Discarding the sludge from the Nalgonda process is often thought of as a serious environmental health problem. The sludge is quite toxic because it contains the removed fluoride in a concentrated form (Fawell et al., 2006).

2.7.3 Membrane filtration processes

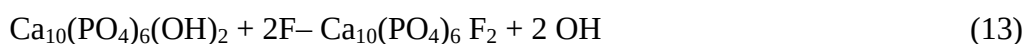
Membrane filtration is generally considered to include both micro-filtration (MF) and ultrafiltration (UF). Microfiltration ranges in size from approximately 0.05 μm to 1.0 μm . Ultrafiltration is expressed in terms of molecular weight cut-off (MWCO), and ranges from 1,000 MWCO for a very tight UF membrane to approximately 500,000 MWCO for a very open UF membrane. There is some overlap between these two ranges, so a membrane with a pore size that might be considered to be a loose UF membrane might also be considered to be a tight MF membrane depending on the industry. For comparison, a 100,000 MWCO membrane has a pore size of about 0.01 μm . Membrane sizes are usually nominal. A generally accepted definition is that a membrane with a given pore size or MWCO would be expected to remove 90% of material of this size. The largest pores in these membranes would be expected to be larger than the nominal pore size. The pore size variation depends on the membrane type and manufacturing process (Antonio, 2000).

2.8 Fluoride removal by different adsorbents

2.8.1 Bone Charcoal

Bone charcoal is a blackish, permeable, coarse material. The major components of bone charcoal are calcium phosphate 57–80 per cent, calcium carbonate 6–10 per cent, and activated carbon 7–10 per cent.

In contact with water the bone charcoal is able, to a limited extent, to absorb a wide range of pollutants such as colour, taste and odour components. Moreover, bone charcoal has the specific ability to adsorb fluoride from water. This is believed to be due to its chemical composition, mainly as hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, where one or both the hydroxyl-groups can be replaced with fluoride. The principal reaction is hydroxyl-fluoride exchange of apatite (Fawell et al., 2006):



The preparation of bone charcoal is crucial to optimize its properties as a defluoridation agent and as a water purifier. Bone charcoal is prepared by heating ground bone in retorts or in pots stacked in a furnace resembling a potter's kiln at temperatures ranging from 400 to 500 °C without or with only limited admission of atmospheric oxygen. Ground bone is prepared by degreasing, boiling, washing and drying, prior to grinding and sieving (Jacobsen and Dahi, 1998 cited in Fawell et al., 2006).

It is feasible to regenerate bone charcoal saturated with fluoride. The used bone charcoal is regenerated with 1000cm^3 of 0.01M NaOH solution for 12 hours, filtered and washed with distilled water till the washing was neutral (Mandal and Mayadevi, 2009). Regeneration is probably only cost effective at a large-scale water works level or in the case of a shortage of the medium. At village-community and household levels, it may be environmentally acceptable to use the saturated bone charcoal as a fertilizer and soil conditioner (Fawell et al., 2006).

Bone charcoal is the oldest known water defluoridation agent. It was used in USA in the 1940s through to the 1960s, when bone charcoal was commercially widely available because of its large scale use in the sugar industry (AWWA, 1971).

Today bone charcoal defluoridation at waterworks has been replaced by the use of ion-exchange resins and activated alumina. At a domestic level, bone charcoal defluoridation seems to work well in Thailand and Africa, but so far there is no experience of wide scale implementation (Fawell et al., 2006).

One of the constraints of bone charcoal defluoridation is related to religious beliefs in some societies and communities that any use of animal bones is unacceptable. In such cases the use of bone charcoal must be avoided. From a scientific point of view all types of bones are equally good as raw materials for bone charcoal, but in such circumstances the problem would be solved through production of bone charcoal in accordance with local acceptability and ensuring that this is widely known in the community (Fawell et al., 2006).

2.8.2 Activated Alumina

Activated alumina is manufactured from aluminium hydroxide by dehydroxylating it in a way that produces a highly porous material; this material can have a surface area significantly over 200 square meters/g. The compound is used as a desiccant (to keep things dry by absorbing water from the air) and as a filter of fluoride, arsenic and selenium in drinking water. It is made of aluminium oxide (alumina; Al_2O_3), the same chemical substance as sapphire and rubies (but without the impurities that give those gems their color). It has a very high surface-area-to-weight ratio. That means it has a lot of very small pores, almost like tunnels, that run throughout it.

When water passes through a packed column of activated alumina, pollutants and other components in the water are adsorbed onto the surface of the grains (Fawell et al., 2006).

Activated alumina, when used as a fluoride filter, can be regenerated by a solution of lye (sodium_hydroxide; NaOH), sulfuric acid (H_2SO_4), or alum ($KAl(SO_4)_2$). Regeneration of the saturated alumina is carried out by exposing the medium to 4 per cent caustic soda (NaOH) either in batch or by flow through the column. Residual caustic soda is then washed out and the medium is neutralized with a 2 per cent sulfuric acid rinse. During this process about 5–10 per cent of the alumina is lost, and the capacity of the remaining medium is reduced by 30–40 per cent. After 3–4 regenerations the medium has to be replaced. Regeneration may result in the presence of aluminium at a concentration greater than 0.2 mg/l if the pH is not readjusted to normal (Fawell et al., 2006).

2.8.3 Clay

Clay is an earthy sedimentary material composed mainly of fine particles of hydrous aluminium silicates and other minerals and impurities (Fawell et al., 2006). The main components of common clay and shale are illite and chlorite. Illite is also a component of ball clays. Illite closely resembles micas, but it has less substitution of aluminium for silicon and/or partial replacement of potassium ions between the unit layers by other cations, such as hydrogen, magnesium, and calcium (WHO, 2005). Clay is fine-textured, plastic when moist and retains its shape when dried. Both clay powder and fired clay are capable of sorption of fluoride as well as other pollutants from water (Fawell et al., 2006).

2.8.4 Bauxite

Bauxite is an aluminium ore and is the main source of aluminium. This form of rock consists mostly of the minerals gibbsite $\text{Al}(\text{OH})_3$, boehmite $\gamma\text{-AlO}(\text{OH})$, and diaspore $\alpha\text{-AlO}(\text{OH})$, in a mixture with the two iron oxides goethite and hematite, the clay mineral kaolinite, and small amounts of anatase TiO_2 . Lateritic bauxites (silicate bauxites) are distinguished from karst bauxite ores (carbonate bauxites). The lateritic bauxites are found mostly in the countries of the tropics. Bauxite introduces traces of aluminium in the water whereas gypsum increases the sulphate content of the water beyond WHO recommendations (Thole, 2005).

The high Al content bauxite ore (HABO) was characterised using several techniques. The thermal stability of the adsorbent was analysed using the Perkin Elmer Thermogravimetric Analyser. The mineralogy and crystallinity of the adsorbents were characterised by X-ray diffraction (XRD). The diffraction patterns were recorded on a Philips PW 1710 X-ray powder diffractometer over a 2θ range of 3° to 50° . The elemental composition of the adsorbent was also determined by using X-ray fluorescence (XRF) and Energy Dispersive X-ray (EDX) spectrometry analysis (Asare, 2011).

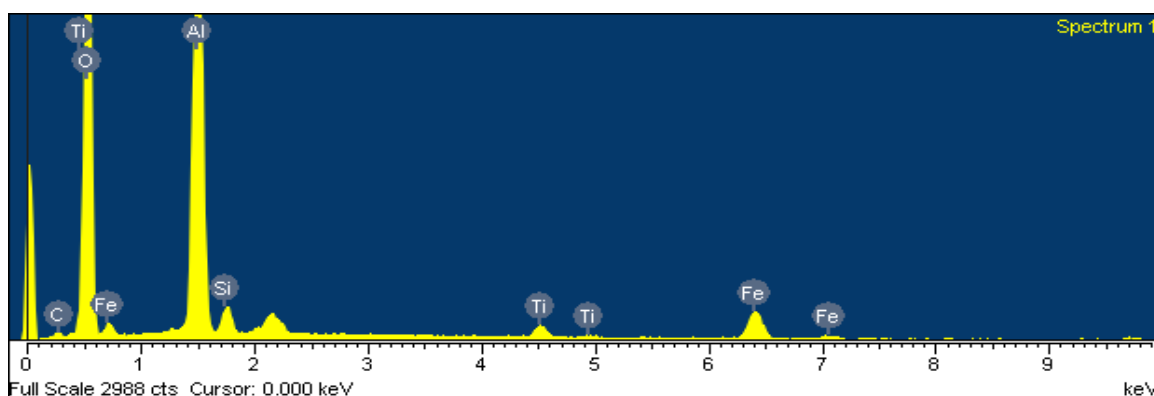


Figure 2- 5: EDX spectrum of HABO (Source: Asare, 20011)

Table: 2-5. Elemental Composition of HABO (Source: Asare, 2011)

Element	Symbol	Atomic no.	Abundance (%)	
			EDX	XRF
Carbon	C	6	3.5	
Oxygen	O	8	63.59	
Aluminium	Al	13	24.88	>32.38
Silicon	Si	14	1.66	2.684
Titanium	Ti	22	1.12	2.234
Iron	Fe	26	5.24	7.145

2.8.5 Charcoal

Charcoal is a traditional term for char obtained from wood, peat, coal or some related natural organic materials. This solid product is obtained by carbonization, a process by which solid residue with increase content of element carbon are formed from organic material (Pastor-Villagas et al., 2005). Charcoal has a macropore structure. The macropore is more rudimentary in the case of Holm oak charcoal. Macropores play a very important role in any adsorption process. They serve as a passage for adsorbate to the micropore. The equivalent surface area for charcoal is 387 m²/g which is relatively higher compare to other char products prepared in laboratory scale (Pastor-Villagas et al., 2005).

The rate of fluoride adsorption on the media (charcoal) is time dependent and able to reduce fluoride in the model water from 5.3 mg/L to below the WHO standard of 1.5 mg/L within 2 hours. Aluminium oxide coated charcoal has high fluoride removal rate compared to virgin charcoal (Mwampashi, 2011). 8 mg/L aluminium oxide coated pumice, Moringa oleifera and chitosan were observed to take 8 hours to reduce 5.3 mg/L of fluoride to required standard (Modestus, 2009).

2.9 The adsorption process

Adsorption is a physical or chemical process which involves the accumulation or concentration of a chemical species (adsorbate) at the interface between a solid phase and a liquid phase in comparison to the bulk of the solution. The process can occur between any of these two phases: liquid-liquid, gas-solid, gas-liquid and liquid-solid. The material being concentrated or adsorbed is adsorbate and the adsorbing phase is termed as adsorbent. The bonding is usually temporary and is accomplished by ionic, ligand, dipole, hydrogen, or Van der Waal's bonds (Yong et al., 1999).

2.9.1 Factors that affect adsorption

2.9.1.1 Nature of adsorbent

The efficiency of adsorption depends on physicochemical properties, mainly surface area, porosity and particle size of adsorbents.

Generally, the rate of adsorption will increase as the particle size decreases, as the process step of diffusion to the adsorbent surface should be enhanced by the smaller particles. Note that another critical aspect of rate of adsorption is the pore size distribution, and development of "transport pores" within the particle that allow effective migration of contaminants to the point of adsorption. As the particle size of the adsorbent increases, the fluoride removal capacity of the adsorbent decreases. The decrease of the removal percentage is attributed to the insufficient active sites on the adsorbent occupied by the fluoride ions, as the more fluoride ions in solution the more active sites are engaged (Gao et al., 2009).

2.9.1.2 Nature of adsorbate

Adsorption in aqueous solution is influenced by several adsorbate properties such as solubility, molecular weight, size of the adsorbate molecule, and ionic radii. Other ions in solution affect the solubility of a substance (Warren and Mark, 2005).

Solubility is the most significant property affecting the adsorptive capacity. Higher solubility indicates a strong solute-solvent interaction. Increase in adsorption is then due to the increase in hydrophobicity and the decrease in solubility with the increase in the chain length. In other words, the increase in the side chain length increases the hydrophobicity of the molecule, which results in greater adsorption

2.9.1.3 Effect of pH

Generally the pH is an important variable affecting defluoridation since hydrogen and hydroxide ions are adsorbed relatively strongly. In acidic pH range, high quantity of particles is adsorbed because the positively charged adsorbent attracts fluoride ions electrostatically. In the alkaline pH range it is well known that the hydroxide ions compete effectively with the fluoride ions leading to a lower defluoridation in this range. The defluoridation efficiency increases with the increase in the dose of the adsorbent and contact time, but decreases with increasing the initial fluoride concentration and the pH of aqueous solution (Gao et al., 2009). Zero point of charge is a concept in physical chemistry relating to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero. In other words, is (usually) the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface (Yuxin et al., 2011).

2.9.1.4 Effect of contact time

As contact time increases, percentage removal also increases initially, but then gradually approaches a more or less constant value, denoting attainment of equilibrium. The time to reach equilibrium appears to be independent of initial fluoride concentration in the range of 5–20 mg/L (Das et al., 2005). Decrease of the

contact time will result in premature breakthrough to occur, thus reducing the service time of the bed (Jusoh et al., 2007).

2.9.1.5 Effect of flow rate

Slower flow rate produces higher empty bed contact time (EBCT) and the adsorbate takes longer time to diffuse onto the solid phase of the adsorbing media. The shape of the breakthrough curves produced from slower flow rates was more approximate to the ideal breakthrough curve. Therefore for faster flow rates, the breakthrough curve obtained deviates more from the ideal breakthrough curve and thus results in a larger root mean square error value (Jusoh et al., 2007).

2.9.1.6 Temperature

In the process of sorption there is always loss of degrees of freedom of the solute in passing from the dissolved state to the adsorbed state (Modestus, 2009). In general, there is a smooth and continuous change in all of the physicochemical properties of an adsorbent according to the temperature used during defluoridation (Del Cul et al., 2000). Adsorption increases continuously with increasing temperature. The adsorption of fluoride onto an adsorbent is exothermic in nature (Gao et al., 2009). There is a slow increase in the surface area and micro-porosity for higher temperature fluorinated charcoals (Del Cul et al., 2000). Calcination at different temperatures leads to surface modifications, structural transformations, and loss of structural water molecules which ultimately affect the adsorption of fluoride ions (Das et al., 2005).

2.9.2 Adsorption equilibrium isotherms

The Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the adsorption of component from liquid phase onto a solid phase.

In adsorption modeling, the distribution of adsorbate between the two phases (the bulk solution and the adsorbent) is often described in terms of isotherms. The presentation of amount of solute adsorbed per unit of adsorbent (q) as a function of the equilibrium concentration of the solute in the bulk solution (C_e), at a constant temperature, is called the adsorption isotherm, $q = f(C_e)$ (Saroj, 2007). Analysis of the equilibrium data is important to develop an equation which accurately represents the adsorption process and which could be used for design purposes. Several models have been published in the literatures to describe the experimental data of adsorption equilibrium. Among them, the Langmuir and the Freundlich models are the most frequently employed (Gao et al., 2009).

2.9.2.1 Langmuir Isotherm

The Langmuir equation is valid for monolayer adsorption onto a surface with finite number of identical sites, and is one of the most popular isotherm models due to its simplicity and its good agreement with experimental data (Gao et al., 2009).

Equation 2- 12: The Langmuir isotherm equation:

$$q = Q_o b \frac{C_e}{1 + b C_e} \quad (14)$$

Where C_e is the equilibrium fluoride concentration (mg/L), Q is the amount adsorbed per unit mass of the adsorbent at equilibrium (mg/g), Q_o is the monolayer adsorption capacity of the adsorbent (mg/g), and b is the Langmuir constants related to the energy (L/mg).

The Langmuir equation can be rearranged as follows:

$$\frac{1}{q} = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e} \quad (15)$$

These constants can be evaluated from the intercept and the slope of the plot of $1/Q$ versus $1/C_e$.

2.9.2.2 Freundlich Isotherm

The Freundlich model is empirical in nature which assumes the adsorption on heterogeneous surface (Gao et al., 2009). The equation can be written as:

Equation 2- 13: Freundlich Isotherm equation

$$q = K C_e^{1/n} \quad (16)$$

Where C_e is the equilibrium fluoride concentration (mg/L), q is the amount adsorbed per unit mass of the adsorbent at equilibrium (mg/g), K is the empirical constant of Freundlich isotherm (L/mg), and n is the empirical parameter related to the intensity of adsorption.

The Freundlich equation can be rearranged as follows:

$$\ln q = \ln k + \ln \frac{C_e}{n} \quad (17)$$

The Freundlich model's K and n are calculated from the slope and intercept of the plot of $\ln Q$ versus $\ln C_e$.

2.9.3 Adsorption kinetics models

The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order and pseudo second-order mechanisms (Fan et al., 2003).

Equation 2- 14: Pseudo-first-order rate equation

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (18)$$

Equation 2- 15: The integrated pseudo-first-order rate equation:

$$\log(q_s - q_t) = \log q_s - k_1 t \quad (19)$$

Equation 2- 16: Pseudo-second-order adsorption

$$\frac{dq_t}{dt} = k_2 (q_s - q_t)^2 \quad (20)$$

$$\frac{d(q_s - q_t)}{(q_s - q_t)^2} = -k_2 dt \quad (21)$$

Integrating at boundary conditions ($t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$) gives;

$$\frac{1}{(q_s - q_t)} = \frac{1}{q_s} + k_2 t \quad (22)$$

$$\frac{t}{q_t} = \frac{1}{k_2} \frac{1}{q_s^2} + \frac{1}{q_s} \quad (23)$$

Where q_s and q_t are the amount of adsorbed fluoride at equilibrium and any time t (mg/g solid material), k_1 (min^{-1}) and k_2 ($\text{gm g}^{-1} \text{min}^{-1}$) are the equilibrium rate constant of first- and second-order sorption respectively, and t is the shaken time (min). k_1 can be calculated according to the linear plot of $\log(q_s - q_t)$ Versus t : A larger adsorption rate constant k_1 usually represents a quicker adsorption rate (Fan et al., 2003).

2.9.4 Hydraulics of Column filtration

With accumulation of impurities, head loss gradually increases until the filter is backwashed (Viessman and Hammer, 2005). Several equations have been developed to describe the flow of water through a porous medium (Carman, 1937). Iwasaki (1937) developed relationships describing the performance of deep bed filters. According to Iwasaki (1937), the removal of a substance within a filter reduces in depth in relation to the concentration of the substance in water. From Iwasaki equation, the following assumptions are made; filter bed is clean from impurities, filter bed is uniform with depth and the amount of impurities C_0 is reduced to C at depth (L).

Equation 2- 17: Iwasaki's equation for water quality improvement

$$\frac{dC}{dL} = -\lambda C \quad (24)$$

Where

C = Concentration of adsorbate

L = Filter depth (m)

λ = Filter coefficient (m^{-1})

$$\frac{dC}{C} = -\lambda dL \quad (25)$$

Integrating both sides: using $C = C_0$ and $L = 0$

$$\ln C - \ln C_0 = -\lambda L \quad (26)$$

$$C/C_0 = e^{-\lambda L} \quad (27)$$

In most cases, the equations for the flow of clean water through a porous medium are derived from a consideration of Darcy-Weisbach equation for flow in a closed conduit and dimensional analysis (Metcalf and Eddy, 2004).

Equation 2- 18: Darcy-Weisbach equation

$$h_L = \frac{fLV^2}{2Dg} \quad (28)$$

Where

h_L = head loss, m

L = pipe Length, m

D = pipe diameter, m

F = friction factor

V = Flow velocity, m/s

g = acceleration due to gravity

The friction factor is related to the Reynolds number and the relative roughness of the pipe. The finer particles give the highest removal but the filter will clog faster. One has to apply a filter bed as uniform as possible to prevent rapid clogging. With a certain type of filter material different measurements can be used to determine the specific properties of the medium. According to Carman-Kozeny a linear relationship exists between the head loss of the clean bed and the laminar flow velocity.

Equation 2- 19: Carman-Kozeny equation for head loss

$$\Delta H = 180 \frac{v}{g} \frac{(1-P)^2}{P^3} \frac{V}{d_h^2} L \quad (29)$$

Where

ΔH = Head loss,	(m)
ν = kinematic viscosity,	(m ² /s)
g = gravity acceleration,	(m/s ²)
P = porosity,	(-)
V = velocity,	(m/s)
d_h = hydraulic diameter of adsorbent medium,	(m)
L = Bed height,	(m)

3. RESEARCH METHODOLOGY AND PROCEDURES

3.1 Introduction

This chapter describes the laboratory experiments and experimental setups used to work towards the achievement of the main objective. The laboratory experiment was mainly short-column adsorption experiment.

3.2 Desk study

Relevant literature was reviewed on fluoride removal processes and column adsorption. Data obtained from these laboratory experiments were processed and analysed to make meaningful deductions.

3.3 Laboratory experiments

3.3.1 Preparation of adsorbents

In the present study bauxite (HABO), the geomaterial, obtained from Awaso District, Western region, Ghana, was used as a low-cost adsorbent. The second low-cost material used was charcoal.

The boulders of bauxite were washed with water to remove dirt. It was then dried, crushed and milled into smaller sizes. The crushed bauxite was then sieved through standard sieves to obtain the desired particle size ranges (0.8 – 1.12mm and 1.7 – 2.26mm). 2kg of the 0.8-1.12mm and 1.7-2.26mm particle size ranges were weighed and coated with aluminium sulphate, then ammonia hydroxide solutions to increase the adsorption capacity of the media (HABO).

The raw charcoal material was also washed, dried, crushed and milled into similar particle sizes (0.8 – 1.12mm and 1.7 – 2.26mm). 0.6kg (600g) of the 0.8-1.12mm and 1.7-2.26mm particle size ranges were also weighed and coated as in HABO.

3.3.2 Preparation of aluminium oxide coated adsorbents

The coated adsorbents that were used in this research are aluminium oxide coated Bauxite and aluminium oxide coated charcoal. The Aluminium oxide coated adsorbents were prepared according to the standard coating method developed by Truesdail et al., 1998.

The graded bauxite and charcoal (0.8-1.12mm diameter) were coated with aluminium oxide to enhance the adsorption of fluoride according to the following procedure. The aluminium oxide coating onto the virgin adsorbents was done in a two-step process. In the first step, sufficient amount of 0.5M of $\text{Al}_2(\text{SO}_4)_3$ solution was added to completely soak each batch of virgin bauxite (about 5kg) and virgin charcoal (about 2kg) in an aluminium basin and the pH taken after 5-10mins. The content in the basin was mixed using a mechanical stirrer at a speed of 100rpm for 30mins and allowed to stand for another 30mins. The excess solution was drained and the samples (bauxite and charcoal) thoroughly air-dried. In the second step, the dried samples were neutralized with 3M ammonium hydroxide solution for 10mins and air-dried to complete one coating cycle. This coating cycle was repeated a second time for both bauxite and charcoal in order to increase the amount of Al coating. The dried coated bauxite and charcoal were sieved and rinsed vigorously with deionized water to remove any loosely bound aluminium oxides and separate granular aluminium oxide coated media from any precipitate. The washed samples (coated bauxite and coated charcoal) were air-dried again and stored for use.

The expected reaction for the process is;



3.3.3 Regeneration of exhausted media

The aluminium oxide coated media (coated bauxite and coated charcoal) were used for fluoride adsorption until exhaustion in the designed and constructed short column adsorption filters.

Regeneration was done by re-coating aluminium onto the exhausted media using the same method as described for the coating of aluminium oxide onto virgin materials (bauxite and charcoal). The regenerated bauxite and charcoal were used for the short column adsorption experiments to determine the fluoride removal capacity. The regeneration-fluoride adsorption cycle was repeated 2 times in order to determine the optimum recoating cycle.

3.3.4 Standardization

Series of standard solutions of concentrations; 0.5, 1.0, 1.5, 2, 4, 8, 12, 16, 20 and 24mg/L were prepared from a 1000 mg/L stock fluoride solution. Using a WTW F 800 fluoride meter, the potentials of the standard solutions were determined. This was done by mixing samples of treated water with total ionic strength adjustment buffer (TISAB) in a ratio of 1:1. The TISAB regulated the ionic strength of samples and standard solutions. The TISAB also adjusted the pH and prevents interferences by polyvalent cations such as Fe^{3+} , Al^{3+} and Si^{3+} which could precipitate with fluoride and decrease the concentration of free fluoride in the solution. A graph of measured potentials versus fluoride concentrations was drawn and using the linear regression model, a linear equation was established for the relation as shown in Fig 3-1

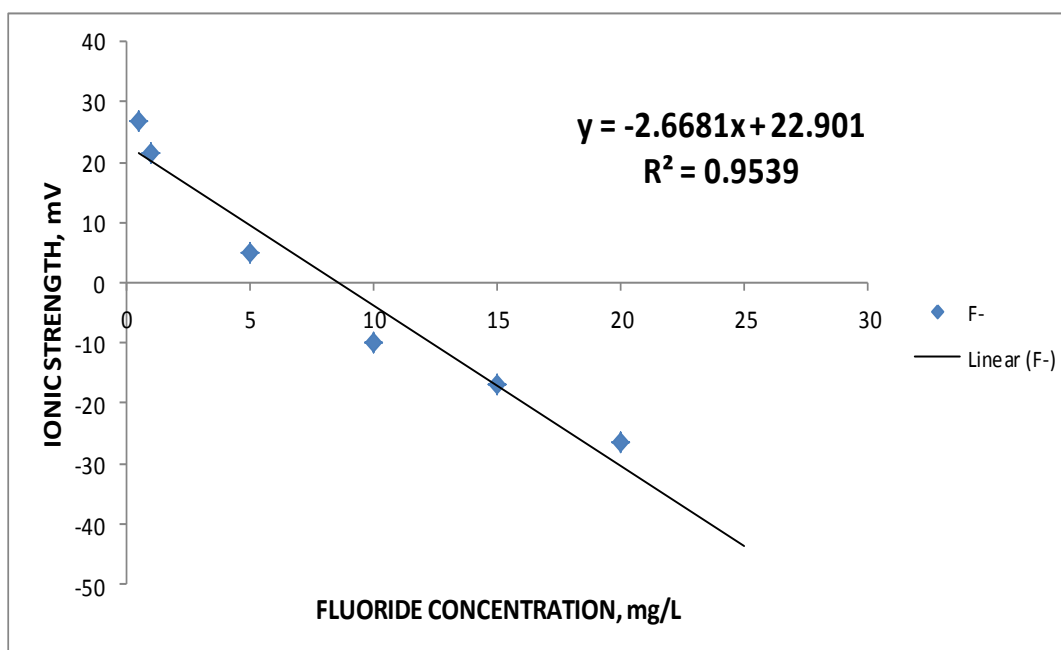


Figure 3- 1: Standard curve for fluoride measurement

3.3.5 Preparation of model water

The model water used in the experiments was prepared using tap water spiked with the following chemicals; calcium sulphate (9.406mg/L), calcium hydroxide (16.344mg/L), Iron Sulphate (0.0124mg/L), manganese sulphate (0.0106mg/L), sodium nitrate (31.546mg/L), sodium nitrite (37.49mg/L), sodium bicarbonate (50.95mg/L), and sodium fluoride (20mg/L). A mechanical stirrer was mounted over the tank to stir the model water evenly with the spiked chemicals to mimic the water quality of wells from Northern Ghana (Table 3-1). A sample (1ml) of the model water and an equal volume of TISAB were mixed. The ionic strength of the mixture was determined using a WTW 3310 fluoride meter. The potential (18mV) correlated to a fluoride concentration of 7.5mgF⁻/L which is the model water fluoride concentration.

The model water pH (7.05) recorded after mixing was within the pH range (6.9 – 7.5) of Northern Ghana water. The initial fluoride concentration for the second column experiment was 20mg/L.

Table 3- 1: Water quality of wells from Northern Ghana

pH	6.9 – 7.5	Mg ²⁺ (mg/l)	5.6 – 17
Alkalinity (mg/l)	137 – 171	Na ⁺ (mg/l)	22 – 28
SO ₄ ²⁻ (mg/l)	28.6 – 34.7	K ⁺ (mg/l)	1.3 – 1.5
Cl ⁻ (mg/l)	4.63 – 6.26	Fe ²⁺ (mg/l)	0.001 – 0.004
NO ₂ ⁻ (mg/l)	25	Mn ²⁺ (mg/l)	0.003 – 0.004
NO ₃ ⁻ (mg/l)	16.84 – 29.5	Al ³⁺ (mg/l)	0.002 – 0.049
F ⁻ (mg/l)	3.97 – 4.6	SiO ₂ (mg/l)	49.2 – 74.87
Ca ²⁺ (mg/l)	16 – 44	Sr (mg/l)	0.36 – 1.3

Source: (Buamah and Dapilah, 2008)

3.3.6 Fluoride measurement

The fluoride concentration was measured by using ions selective coupled to pH meter model WTW pH3310 as shown in Figure 3-1. The potentials of sample solutions were determined by adding 1ml of TISAB to 1ml of treated water sample (mixture ratio of 1:1). Using the initially derived standard curve/ equation, the concentration of fluoride in sampled solutions was calculated.



Figure 3- 2: Fluoride meter (Model No. WTW, pH 3310)

Removal Efficiency

The efficiency of fluoride removal by the adsorbents at a given sampling period was calculated using the equation:

$$R = \frac{C_i - C_t}{C_i} \times 100 \quad (30)$$

R = removal efficiency at time, t (%)

C_t = fluoride concentration in solution at time, t (mg/L)

C_i = initial fluoride concentration (mg/L)

Removal Capacity

The amount of fluoride adsorbed per unit mass of adsorbent, q_e (mg/g), at equilibrium was calculated by using the formula below:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (31)$$

C_i = Initial fluoride concentration (mg/L)

m = Mass of adsorbent (g)

C_e = Fluoride concentration at equilibrium (mg/L)

V = Volume of solution (L)

3.3.7 Continuous-flow column adsorption experiment

Column studies were carried out in two columns made of transparent Perspex of 10cm internal diameter (ID), 0.5cm thickness and 50cm length. The bottom of the column was filled with supporting materials (pebbles) to a depth of 15cm. The adsorbent media is introduced on top of the supporting material to a depth of 10cm. A height of 15cm is allowed above the adsorbent media for the supernatant of influent aqueous fluoride solution and 5cm height for free board. To maintain a constant flow through the filter column, an overhead tank (300L) was used to transport the model water using gravity into the constant head tank. This was done to ensure that the change in the height of the liquid level in the constant head tank was negligible during the experiment. Due to the negligible change in the height of the liquid level the flow rate remained constant. The influent model water was allowed to flow through the bed at constant flow rate (13ml/min) for column A (AOCB) and B (AOCC), in a down-flow manner. Treated water samples were collected every hour for four (4) hours, then 24 hours thereafter at the outflow of the columns. These samples were collected into 14-ml graduated polypylene tubes and capped. All the experiments were carried out at room temperature. The effluent solution was collected at different time intervals and the concentration of the fluoride in the effluent solution was monitored by WTW 3310 fluoride ion selective electrode.

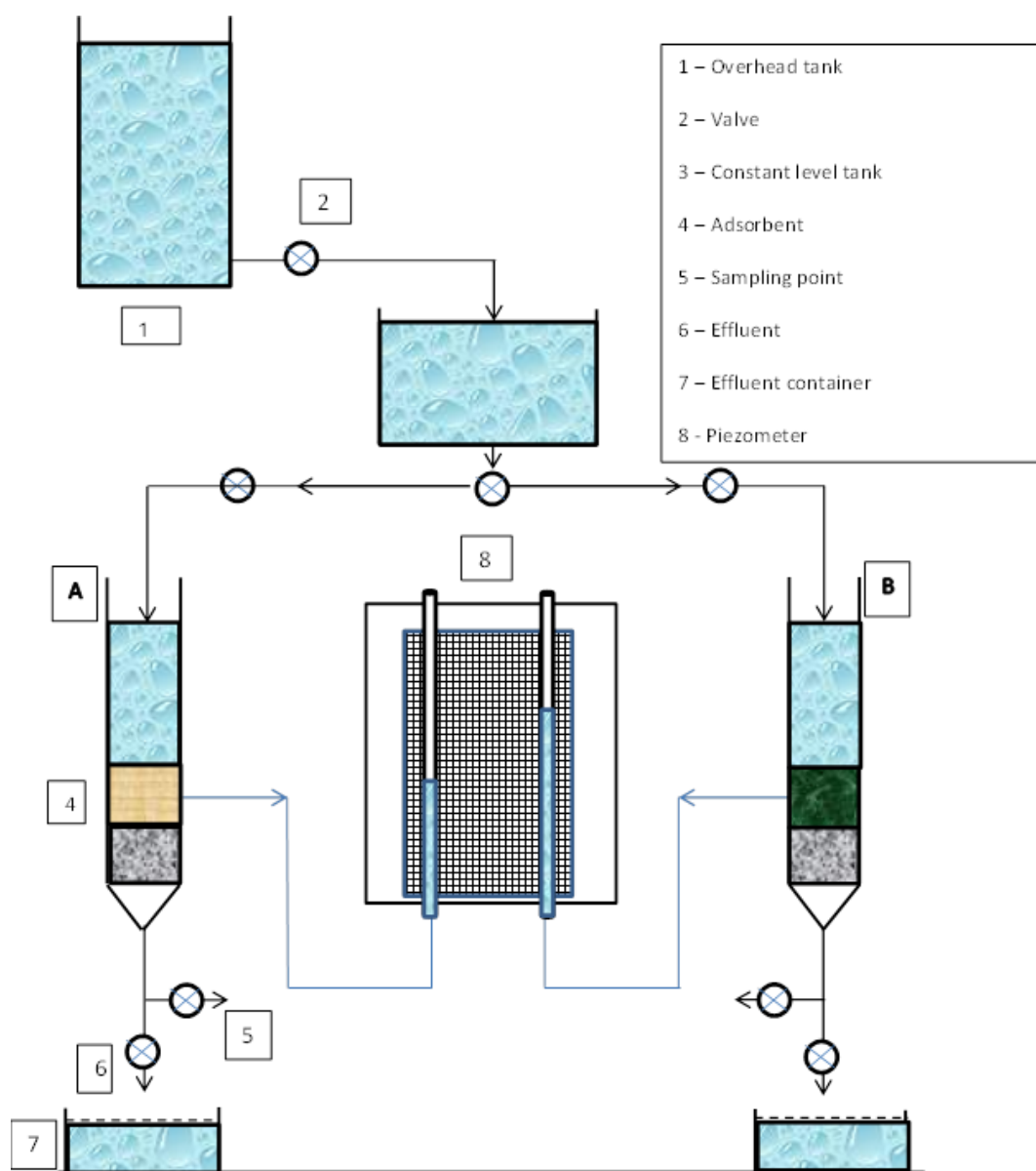


Figure 3- 3: Schematic diagram of column adsorption experiment



Figure 3- 4: Column adsorption experiment setup for AOCB and AOCC

4. RESULTS AND DISCUSSIONS

This research was conducted to study the fluoride removal performance of AOCB and AOCC under continuous flow conditions in a designed and constructed short column adsorption experiment. In this chapter, the results obtained in applying regenerated exhausted AOCB and AOCC in the short columns experiments are reported.

4.1 Standardization

The fluoride meter used in this research was standardized by preparing fluoride standard curves using various standard fluoride solutions and measuring their corresponding potentials (Figure 4-1). The standard curve (Figure 4-1) was used to determine the fluoride concentration for the various samples taken in the pilot column tests.

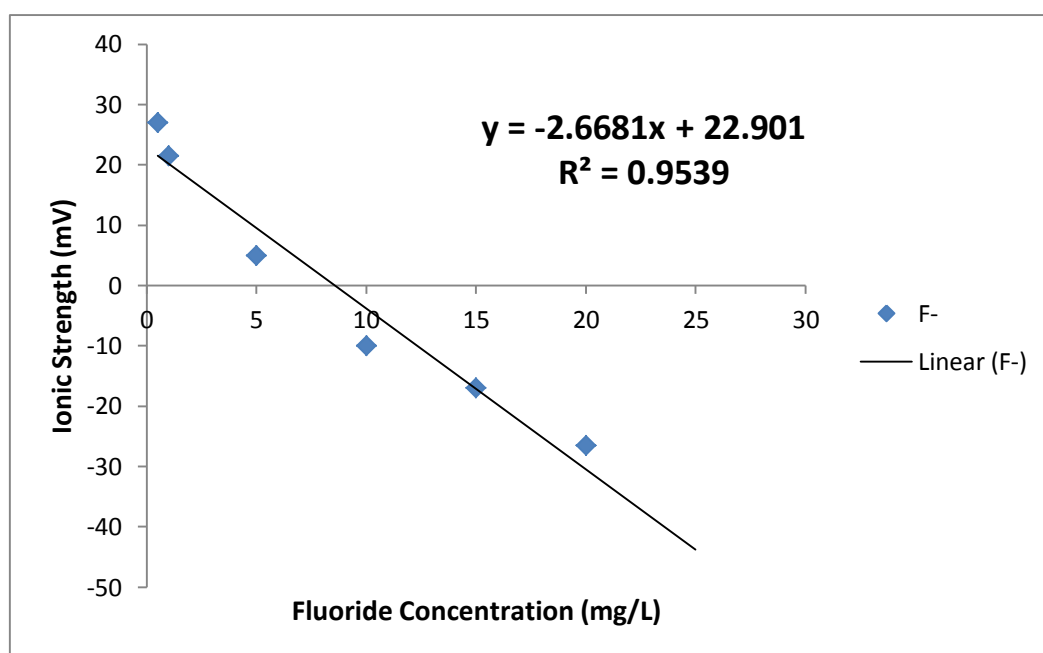


Figure 4- 1: Standard Curve for Fluoride Measurement

4.2 Pilot column adsorption experiments using aluminium oxide coated media (AOCM)

The fluoride adsorption studies were carried out in the designed and constructed short column filter having AOCM. All column adsorption experiments were performed under the same operational parameters; initial fluoride concentration of 20mg/L, pH of 7.0, flow rate of 13ml/min and an adsorbent bed depth of 10cm.

4.2.1. The fluoride removal potential of AOCB and AOCC

The study of fluoride adsorption by coated bauxite and coated charcoal was carried out to compare the fluoride removal process, capacity and trends of coated bauxite and coated charcoal. For this experiment an influent solution with a fixed F^- concentration of 20mg/L was applied

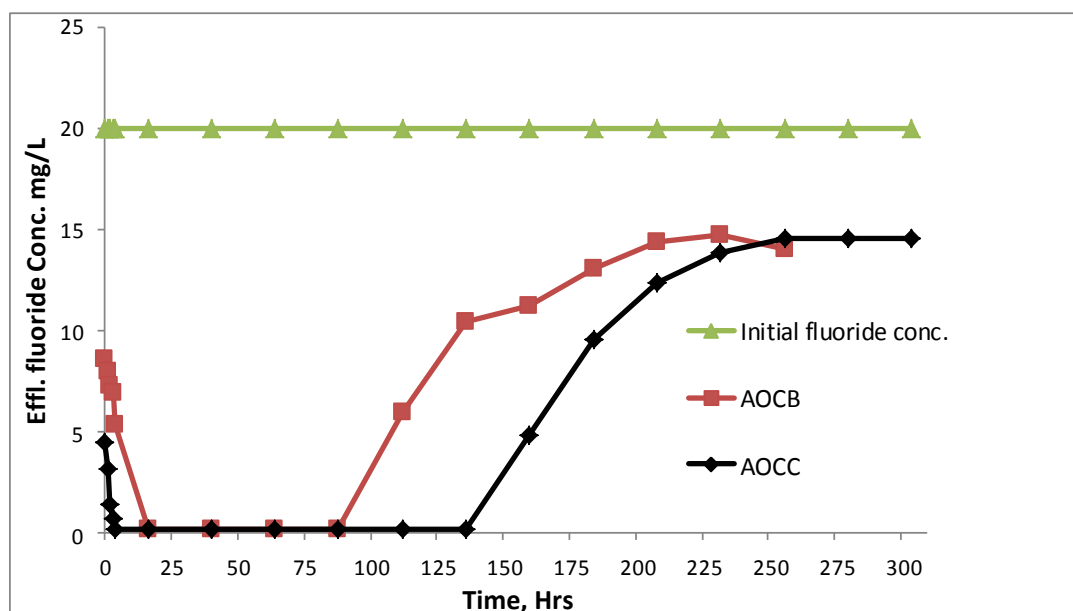


Figure 4- 2: Comparing the effect of contact time on the adsorption of fluoride onto coated AOCB and AOCC

It was observed from Fig 4-2, that aluminium oxide coated charcoal (AOCC) showed high fluoride removal compared to aluminium oxide coated bauxite (AOCB).

From figure 4-2, it is seen that both AOCB and AOCC went through an initial short “ripening” or lag phase before (in the case of AOCC, 4hours and 16hours for AOCB) their peak fluoride removal performance was attained. This peak performance manifested when the media removed all the fluoride that was in the incoming influent. The continuous flow of influent through the media probably exhausted adsorptive sites on the surface of the adsorbents, hence the gradual increase of fluoride concentration in the effluents. From Fig 4-2, it is seen that the adsorption of fluoride onto AOCB and AOCC followed a three-step process, a rapid initial adsorption followed by a period of slower uptake of fluoride and finally no significant uptake. The first step may be attributed to the instantaneous utilization of the most readily available active sites on the adsorbent surface (bulk diffusion). Second step, exhibiting additional adsorption is attributed to the diffusion of the adsorbate (fluoride ions) across the boundary layer to the exterior surface of the adsorbent particles. The fluoride ions at the exterior surface of the adsorbent particles are transported into the interior surface of the adsorbent via pores on the exterior surface (pore diffusion or intra-particle diffusion). The last stage is an equilibrium stage.

From Fig 4-2, it is found in the “ripening” or lag phase that the mass of fluoride ions (F^-) adsorbed increased in the range of 0.03 mg/g (78% removal efficiency) to 0.2 mg/g (99% removal efficiency) for a period of 4hours in the case of AOCC whereas in AOCB, the mass of F^- adsorbed increased in the range of 0.01 mg/g (57% removal efficiency) to 0.18 mg/g (99% removal efficiency) within 16hours contact time.

The faster removal of fluoride by AOCC may be due to the availability of a larger area of binding sites at the exterior surface of AOCC compared to AOCB. The second step of constant fluoride uptake (Fig 4-2) indicates that AOCC and AOCB attained peak performance of fluoride removal. AOCC recorded a maximum adsorption capacity of 1.05 mg/g (99% removal efficiency) within 132hours (about 6days) whereas AOCB attained a peak fluoride adsorption capacity of 0.18 mg/g (99% removal efficiency) within 72hours (about 3 days). It is observed that AOCC (1.05mg/g) adsorbed 0.87mg/g of fluoride more than AOCB (0.18mg/g). It is also observed that AOCC has a longer filter run time (6 days) than AOCB (3 days). AOCC is therefore a more practical choice of adsorbent for application in fluoride removal, particularly for groundwater treatment in rural communities. The increase in fluoride adsorption and longer filter run time by AOCC has significant practical importance as it may ensure higher efficiency and economy. At the equilibrium stage, the effluent fluoride concentration increased until it attained the breakthrough concentration of 10mg/L ($\geq 50\%$ of the initial fluoride concentration). From Fig 4-2, the adsorption capacity of both media declined at the equilibrium stage. The fluoride removal capacity of AOCC decreased from 1.05mg/g (99% removal efficiency) to 0.41mg/g (38% removal efficiency) within 72hours whereas the fluoride removal capacity AOCB declined from 0.18mg/g (99% removal efficiency) to 0.08mg/g (44% removal efficiency) within 72hours (breakthrough time where 50% of initial F-concentration is achieved).

4.2.2 Pilot column adsorption experiment: using regenerated AOCC and AOCB

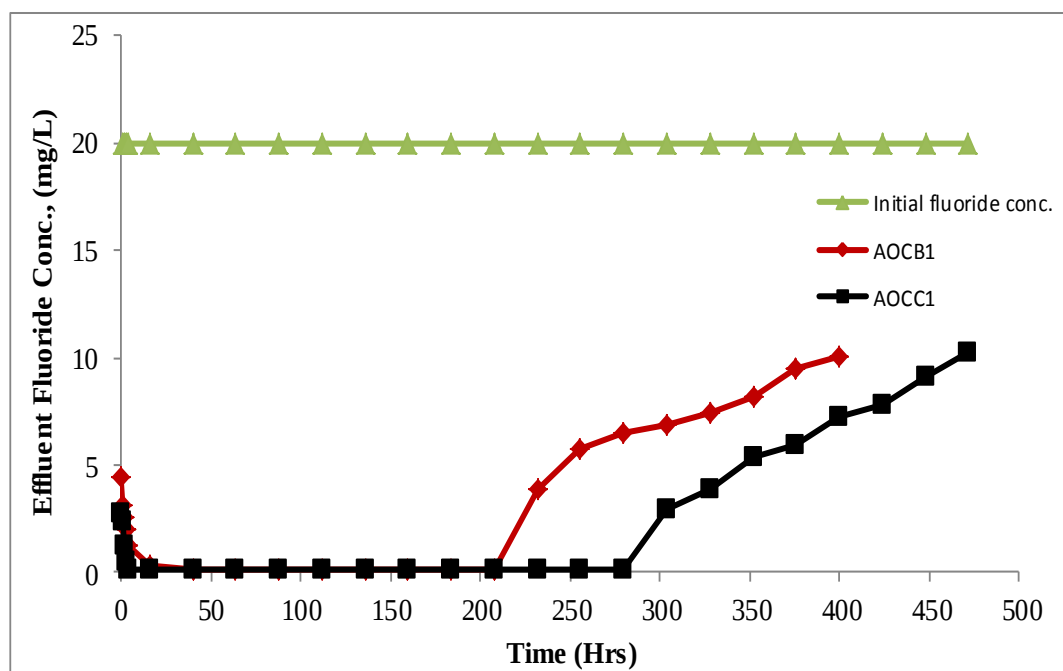


Figure 4- 3: Comparing the effect of contact time on adsorption of fluoride onto aluminium oxide coated charcoal (AOCC1) and recoated aluminium coated bauxite (AOCB1)

The aluminium oxide coated media (coated bauxite and coated charcoal) are used for fluoride adsorption until exhaustion in the pilot column filters. Regeneration is performed by recoating aluminium onto the exhausted media using the same method as described for the coating of aluminium oxide onto virgin materials (bauxite and charcoal). The regenerated bauxite (AOCB1) and regenerated charcoal (AOCC1) are used for the pilot column adsorption experiments to increase the fluoride removal capacity of the media. From Fig 4-3, the effluent fluoride concentrations at the exhaustion points for AOCC and ACOB are 12.3mg/L (0.41mg/g adsorption capacity) and 11.21mg/g (0.08mg/g adsorption capacity) respectively. The effect of regeneration on the adsorption of fluoride from water (initial fluoride concentration of 20mg/L) is investigated at different contact times onto the recoated media (AOCB1 and AOCC1) and the results presented in Fig 4-3.

Similar to Fig 4-2, it is clear from Fig 4-3, that the adsorption of fluoride onto AOCB1 and AOCC1 follows a three-step process, a rapid initial adsorption followed by a period of slower uptake of fluoride. From Fig 4-3, the peak performance (100% removal efficiency) by AOCC1 is attained within 4hours (Effluent F^- concentration = 0.1mg/L; adsorption capacity = 0.18mg/g). However, AOCB1 attained peak performance (100% removal efficiency) within 40 hours (Effluent F^- concentration = 0.1mg/L; adsorption capacity = 0.37mg/g). AOCC1 has a filter run time of 157hours (7days), effluent F^- concentration of 0.1mg/L, 12.3mg/g adsorption capacity and 100% removal efficiency. In the case of AOCB1, the filter run time is observed to be 108hours (5days) at an effluent F^- concentration of 0.1mg/L, 3.22mg/g adsorption capacity and 100% removal efficiency. The rapid adsorption (within 4hrs) of all fluoride by AOCC1 and the longer filter run time (20days) makes it more economical in the treatment of groundwater for rural communities than AOCB1. The increase in fluoride removal could probably be due to the recoating of aluminium oxide onto AOCC (AOCC1) and AOCB (AOCB1).

The adsorption of fluoride ions onto AOCC1 and AOCB1 is usually characterised by either external mass transfer (boundary layer diffusion) or intra-particle diffusion or both. The mechanism of fluoride ion removal from groundwater (aqueous phase) by adsorption is assumed to consist of four steps: migration of the fluoride ions from the bulk solution to the surface of the adsorbent (AOCC1 and AOCB1), diffusion through the boundary layer to the exterior surface of the adsorbent, adsorption at active sites and intra-particle diffusion into the interior of the adsorbent. Since adsorption is a surface phenomenon, the rate of adsorption is directly related to the increase of surface area of the adsorbent or the number of readily available active sites on the adsorbent.

4.2.3 Pilot column adsorption experiment: comparing the effluent fluoride concentration for the 2nd regeneration (re-coated) AOCC1 and AOCB1

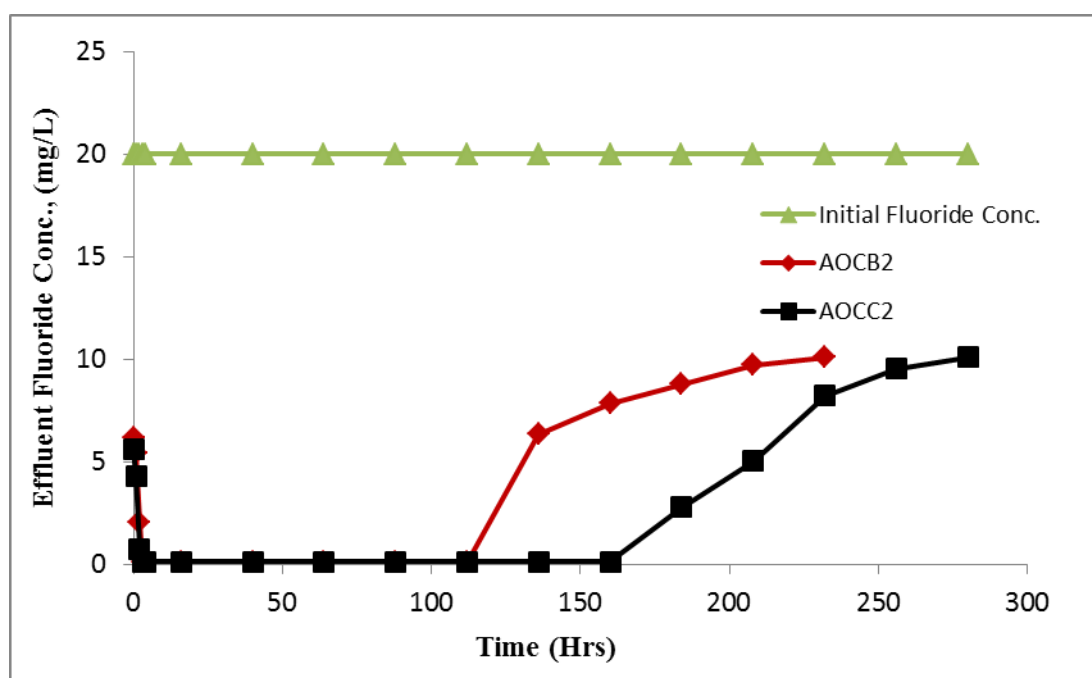


Figure 4- 4: Comparing the effect of contact time on the adsorption of fluoride onto recoated AOCC and AOCB

The exhausted media from the second pilot column experiment (AOCB1 and AOCC1) are recoated with aluminium oxide. The Aluminium oxide coated adsorbents (AOCB2 and AOCC2) were prepared according to the standard coating method developed by Truesdail et al., 1998. The results obtained from the pilot column experiment are presented in Fig 4-4.

Comparing the results obtained from the second recoating episode of AOCC and AOCB, it was evident that fluoride was rapidly adsorbed onto both recoated AOCC2 and AOCB2 (Figure 4-4).

The maximum fluoride removal was reached at 3 hours for the recoated AOCC and recoated AOCB. This was an indication that the fluoride removal efficiency was

100% after 3 hours of operation. After 3 hours, the rate of fluoride removal remained constant until the increase of fluoride in the effluent (Figure 4-4).

From Fig 4-4, it is observed that similar adsorption behaviour is manifested as in the case of Fig 4-2 and Fig 4-3. An initial rapid “ripening” or lag phase (within 3hrs) of AOCC2 and AOCB2 produced effluent F^- concentrations of 0.1mg/L (F^- removal capacity= 0.13mg/g; removal efficiency = 100%) and 0.1mg/L (F^- removal capacity= 0.05mg/g; removal efficiency = 100%) respectively. The effluent F^- concentration at the exhaustion of AOCC2 and AOCB2 are 10.1mg/L (F^- removal capacity= 6.13mg/g; removal efficiency = 50%) and 10.1mg/L (F^- removal capacity= 1.76mg/g; removal efficiency = 50%).

The coating episode 3 (AOCB and AOCC) of aluminium oxide could not increase the fluoride adsorption capacity of exhausted AOCB1 and AOCC1 (Table 4-1) probably due to the complete occupation of all adsorptive sites on AOCB1 and AOCC1 by the initial coating of aluminium ions (Al^{3+}). The existing Al^{3+} attached to the active sites may be strongly bonded to the surfaces and therefore leave little or no active sites for new Al^{3+} to occupy.

4.2.4 Pilot column adsorption experiments: comparing the effect of filter run time per coating episode of Bauxite

The run time of filters play significant role in practical application, particularly in the treatment of groundwater for rural communities. Filters with longer run times are efficient and economically attractive to low income users to treat fluoride contaminated water. The effect of coating aluminium oxide on adsorbents (coating episodes) is studied and the results presented in Fig 4-5 and Fig 4-6 below.

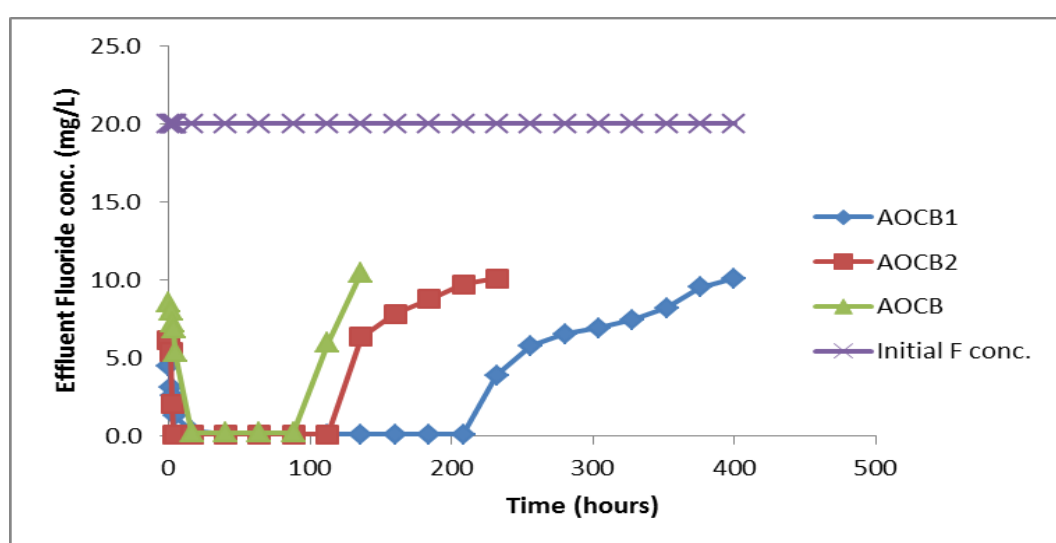


Figure 4- 5: Effect of coating episode of high aluminium content bauxite ore (HABO) on filter run time.

The filter run-time of the pilot column is the period of time (hours or days) within which all fluoride ions in the influent are remove (100% removal efficiency). The filter is seen to perform at its peak during the run-time.

From Fig 4-5, it is observed that the filter run-times of the coated and recoated adsorbents followed this order; AOCB1 (168hrs) > AOCB2 (109hrs) > AOCB (72hrs). It is obvious from this order that coating episode2 (AOCB1) has the longest filter run-time, followed by coating episode 3 (AOCB2) and finally the first coating episode (AOCB). The percentage (%) increase in filter run-time of AOCB1 from coating episode 1 (AOCB) is 133.3% and AOCB2 is 50% (Table 4-1).

Table 4- 1: Percentage (%) increase in run time per coating episode

Coating Episode (Adsorbent)	Filter Run-Time, FRT (hours)	Increase in FRT (hours) from Episode1	% Increase per coating Episode
AOCB 1 (Episode 2)	168	96	133.3
AOCB 2 (Episode3)	108	36	50
AOCB (Episode1)	72	0	0

4.2.5 Pilot column adsorption experiment: comparing the effect of filter run time per coating episode of charcoal

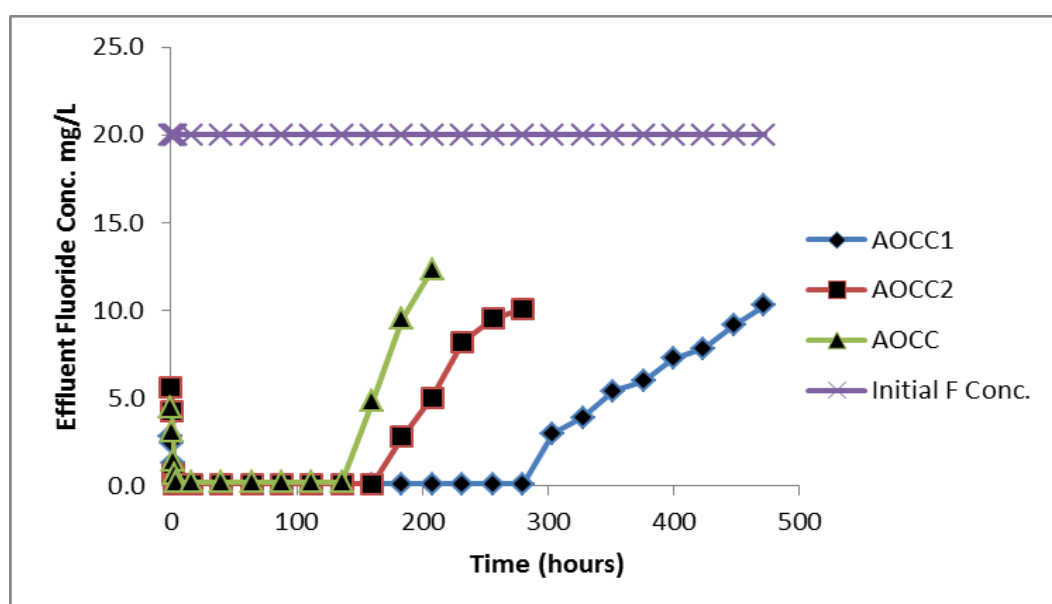


Figure 4- 6: Effect of coating episode of Charcoal on filter run time.

It is evident from Fig 4-6, that the coating episode 2 (AOCC1) showed the highest increase in filter run-time than coating episode 3 (AOCC2) and coating episode 1 (AOCC). Similar to Fig 4-5, the order of filter run time increase is; AOCC1 (276hrs) > AOCC2 (157hrs) > AOCC (132hrs).

The percentage (%) increase in filter run-time of AOCC1 from coating episode 1 (AOCC) is 109.1% and AOCC2 is 18.9% (Table 4-1).

Table 4- 2: Percentage (%) increase in run time per coating episode

Coating Episode (Adsorbent)	Filter Run-Time, FRT (hours)	Increase in FRT (hours) from Episode1	% Increase per coating Episode
AOCC 1 (Episode 2)	276	144	109.1
AOCC 2 (Episode3)	157	325	18.9
AOCC (Episode1)	132	0	0

4.2.6 Column adsorption experiment: Comparing the effluent fluoride concentrations for AOCC, AOCB, 1st and 2nd regeneration (re-coating) of AOCC and AOCB

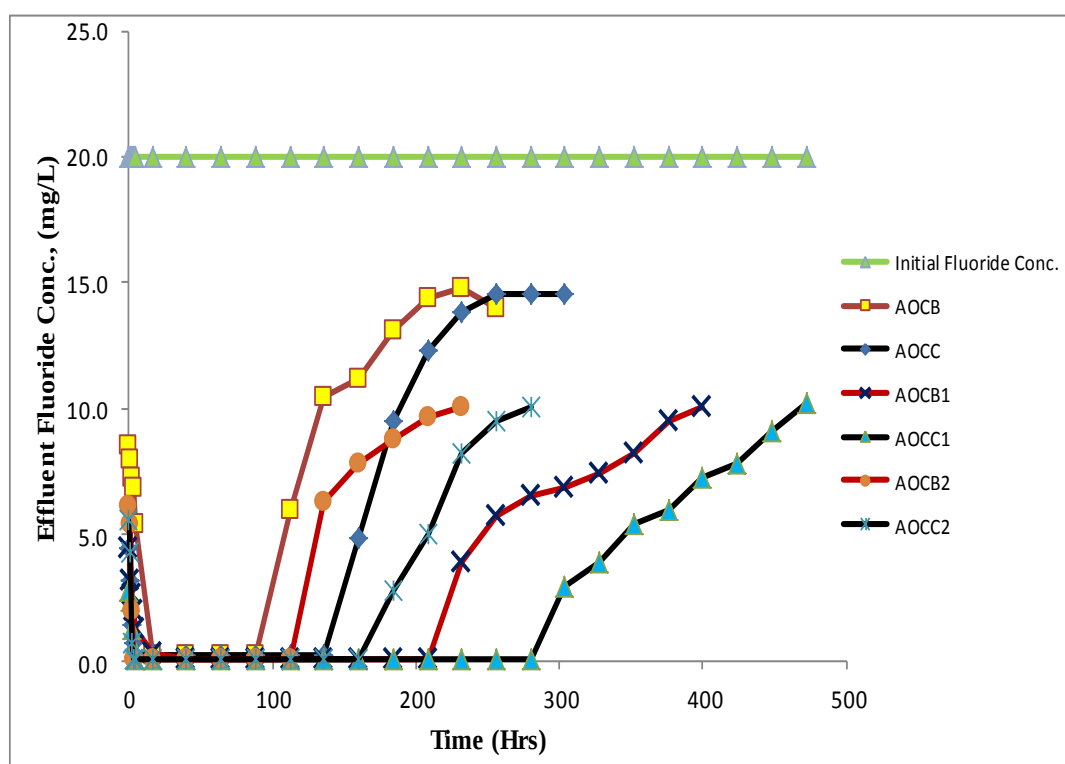


Figure 4- 7: Comparing the effect of contact time on the adsorption of fluoride per coating episode

Comparing the experimental results from Fig 4-5, it was observed that after 2 hours of the initial period of fluoride adsorption, AOCC2, AOCC1 and AOCC rapidly reduced the initial influent fluoride concentration from 20mg/L to 0.7mg/L (96% removal efficiency), 1.3mg/L (94% removal efficiency) and 1.5mg/L (93% removal efficiency) respectively. The effluent fluoride concentration range (0.7 – 1.5mg/L) agrees with the WHO guide (0.5 – 1.5mg/L). In practice, a minimum of 2hrs of contact time is required to reduce fluoride concentration in groundwater to recommended levels. From the above observation, it could be deduced that the adsorption of fluoride increased with the coating of aluminium oxide onto charcoal. For the filter operation using AOCB2 (3hrs of contact time), AOCB1 (4hrs of contact time) and AOCB (16hrs of contact time) the initial fluoride concentration, 20mg/L is reduced to 0.1mg/L, 1.3mg/L and 0.2mg/L respectively. It is seen that 0.1, 1.3 and 0.2mg/L have fluoride levels below the WHO guideline value (1.5mg/L).

4.2.7 Graph of maximum adsorption capacity of bauxite coating episodes

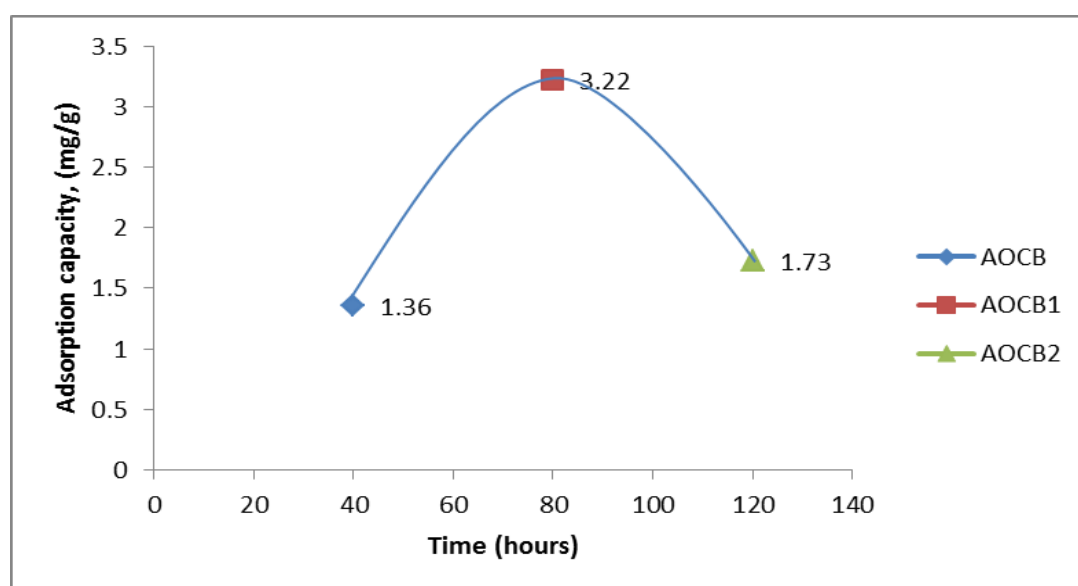


Figure 4- 8: Comparing adsorption capacities of bauxite (HABO) coating episodes

The significant practical importance of the AOCCM is the improvement of water quality (remove all fluoride ions) for a longer period of time and at low costs.

All the fluoride ions are removed from the influent (100% removal efficiency) when the filter attains peak performance.

The high fluoride adsorption capacity of AOCCB1 seen in Fig 4-8 could be associated with the recoating of aluminium oxide on AOCB. The recoating of aluminium oxide on the AOCB could probably increase the attraction of more aluminium ions (Al^{3+}) onto the surface.

4.2.8 Graph of maximum adsorption capacity of charcoal coating episodes

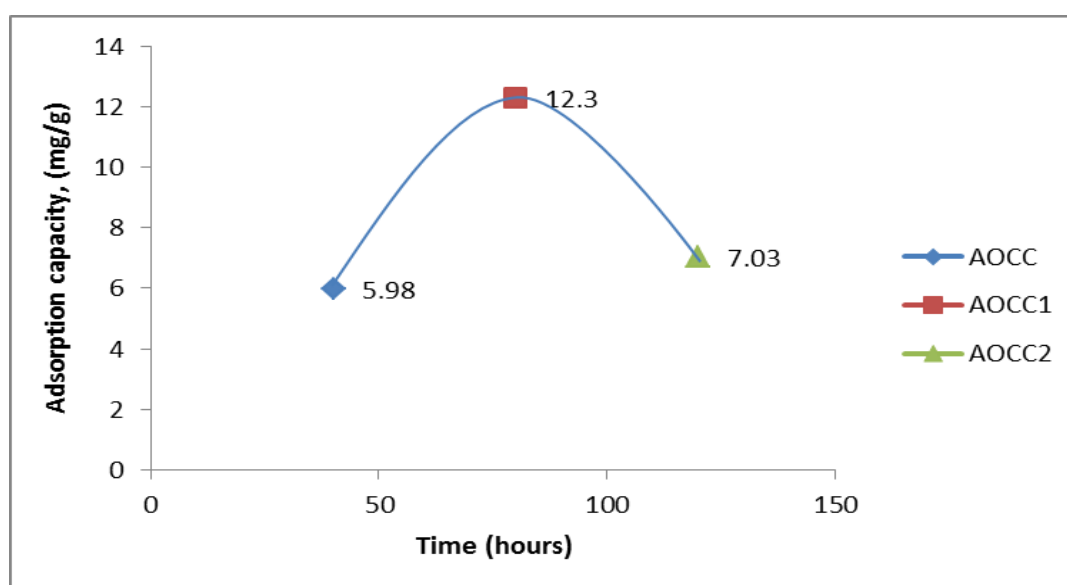


Figure 4- 9: Comparing adsorption capacities of Charcoal coating episodes

The coating episode 2 (AOCCB1 and AOCC1) of virgin bauxite (HABO) has shown higher levels of fluoride uptake than coating episode 1 (AOCCB and AOCC) and coating episode 3 (AOCCB2 and AOCC2).

This trend of adsorption suggests that, two coating cycles are required to optimize the fluoride adsorption capacities of virgin bauxite (0.8 – 1.12mm particle size) and virgin charcoal (0.8 – 1.12mm particle size).

From Fig 4-9, the high adsorption capacity of AOCC1 (12.3mg/L) could be associated with the recoating of aluminium oxide and the combined binding effect of existing and recoated aluminium ions occupying the exterior and interior surface of AOCC1 on incoming fluoride ions.

Table 4- 3: Summary of the adsorption capacities of adsorbents

Adsorbent	Mass of Adsorbent (g)	Filter Run Time (hour)	Total Volume Treated (L)	Total mass of fluoride removed (g)	Capacity of adsorbent in filter bed (gF-/g)
AOCB	1002	72	56.16	1.123	0.001
AOCC	353	132	102.96	2.059	0.006
AOCB1	997	168	131.04	2.621	0.003
AOCC1	344	276	215.28	4.306	0.013
AOCB2	985	108	84.24	1.685	0.002
AOCC2	331	157	122.46	2.449	0.007

4.3 Water quality analysis of treated water from pilot column experiments

The reduction of ionic contaminants in water to acceptable levels is important to water quality. Treated water from the pilot column experiments was tested and analysed for ions, namely; bicarbonate (HCO_3^-), nitrate (NO_3^-), and sulphate (SO_4^{2-}).

4.3.1. Comparing the effect of adsorbents on sulphate concentration in treated water from pilot column experiments

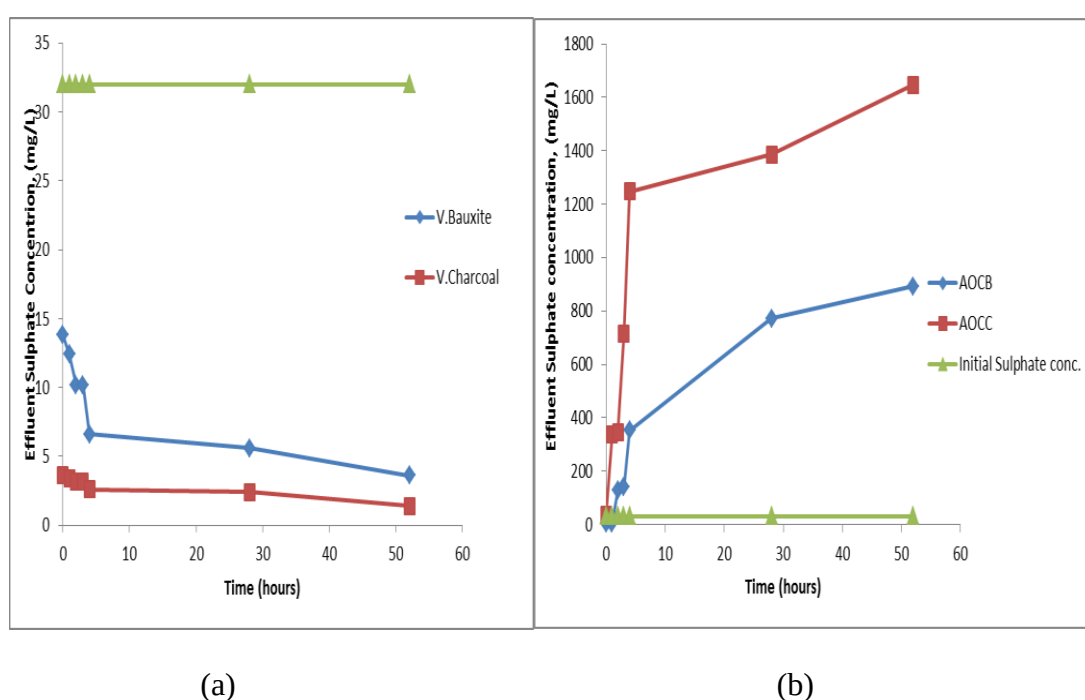


Figure 4- 10: Effect of contact time on removal of sulphate by different adsorbents

The adsorption of aqueous anions, such as sulphate (SO_4^{2-}) is important in the reduction of toxic species in drinking water. The results of sulphate ion concentration in treated water are presented in Fig 4-10.

From Fig 4-10, it is seen that, the initial sulphate concentrations measured in the effluent solutions were high ($>500\text{mg/L}$) in the case of AOCB and AOCC. The increase in initial sulphate concentration could be attributed to the dissociation and

leaching of sulphate ions (SO_4^{2-}) from aluminium oxide coating ($\text{Al}_2(\text{SO}_4)_3$). Physically, if the sulphate ion (SO_4^{2-}) is not tightly held in the aluminium oxide coating, it may easily be desorbed by water.

The removal of sulphate is probably connected to the physical and chemical properties of the media used in the pilot column filter systems. From Fig 4-10(a), virgin bauxite and virgin charcoal appear more attractive for use as filter media to remove excess sulphate than AOCB and AOCC. Virgin charcoal appears more attractive than virgin bauxite probably due to its high cation-exchange ability, high selectivity towards SO_4^{2-} .

The mechanism of adsorption of sulphate on the adsorbents is assumed to be a two-step process. Initially, sulphate ions migrate from the bulk solution to the boundary layer of the adsorbent by diffusion. The sulphate ions (SO_4^{2-}) surrounding the boundary layer are transported to the electrically charged surface (positive) of the adsorbent.

It is observed from Fig 4-10, that the effluent sulphate ion concentrations are reduced to 1.4mg/L (virgin charcoal), 3.6mg/L (virgin bauxite), 4mg/L (AOCB) and 36mg/L (AOCC) within 48hrs of contact time. The concentrations of sulphate ions (SO_4^{2-}) present in the treated effluent are less than the WHO guide (Table 4-3)

4.3.2. Comparing the effect of adsorbent adsorption on Nitrate concentration in treated water from pilot column experiments

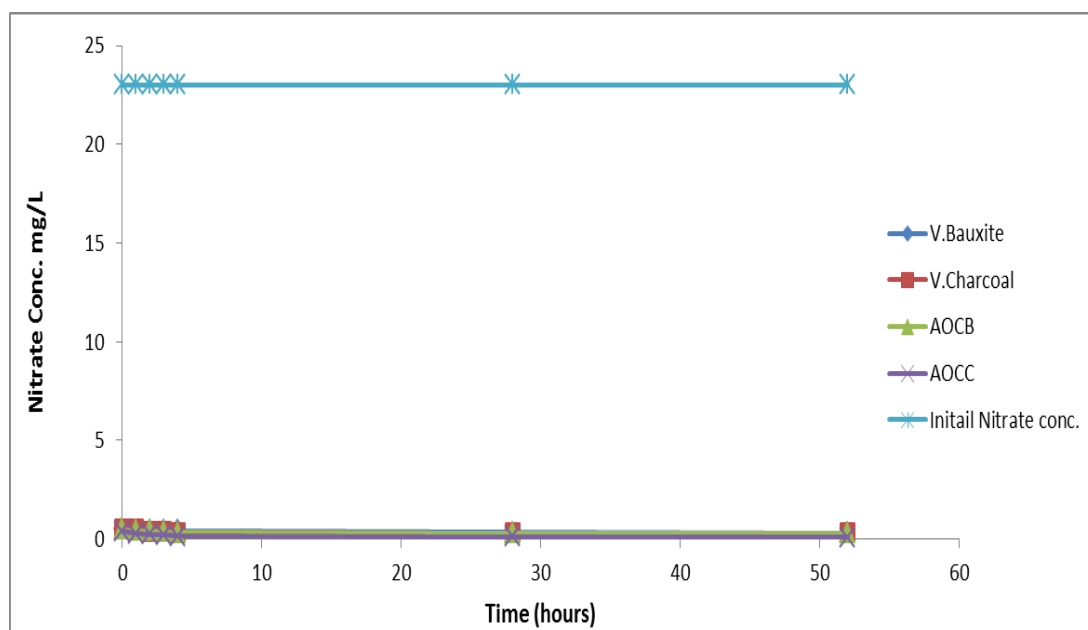


Figure 4- 11: Effect of contact time on the removal of nitrate by different adsorbents

The adsorption of nitrate onto different adsorbents (virgin bauxite, virgin charcoal, AOCB and AOCC) was studied by performing pilot column experiments for a period of 48 hours. Samples of the effluent solution were tested for nitrates. The results obtained show that the adsorbents have effect on the concentration of nitrate in treated effluents (Fig 4-12).

It was observed that the results obtained (nitrate concentration) by the pilot column experiment reduced (below 1mg/L) within the 48 hour contact time. The removal of nitrate was very high for adsorbents (Fig 4-12). The reason for the increase in removal of nitrate by the adsorbents may probably be associated with the porous oxides of aluminium coated on the surface. The aluminium (Al^{3+}) present in the aluminium oxide coating may have reacted with almost all incoming nitrate (NO_3^-).

4.3.3. Comparing the effect of adsorbent adsorption on bicarbonate concentration in treated water from pilot column experiments.

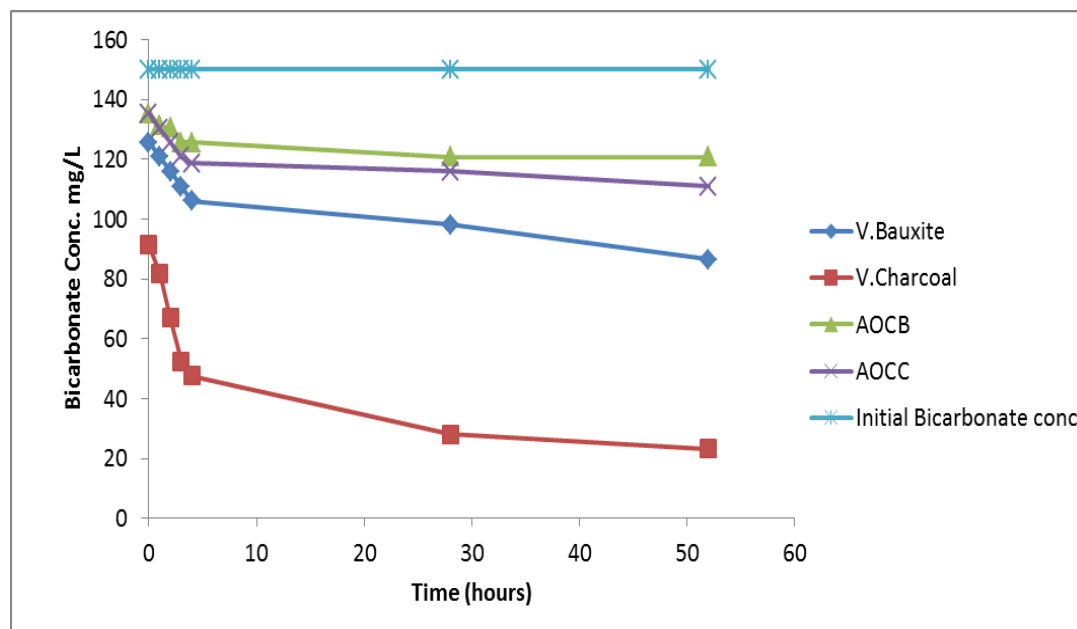


Figure 4- 12: Effect of contact time on removal of bicarbonate by different adsorbents

The removal of bicarbonate (HCO_3^-) by different adsorbents (virgin bauxite, virgin charcoal, AOCB and AOCC) was performed by pilot column experiments for 48hrs. Samples of treated effluent solutions were collected and tested to determine the concentration of (HCO_3^-) present in the effluent. The HCO_3^- concentration test was performed by using the alkalinity test (titration). The results obtained show that the adsorbents have reduced the concentration of HCO_3^- (Fig 4-13).

The high bicarbonate uptake by virgin charcoal in Fig 4-13, is probably due to the availability of active sites on charcoal surfaces, whereas the observed low adsorption by AOCB (relative to virgin charcoal) could be due to the saturation of active site or gradual diffusion of bicarbonate ions inside the AOCB. The mechanism of

bicarbonate adsorption is probably associated with the reaction of carbon dioxide (CO_2) with ionic species on the surface of the adsorbents (i.e. H^+ , Oxygen etc.).

Table 4- 4: Water quality data of treated water

		Effluent Parameter Concentration, Avg $\pm$ std (mg/L)						
Parameter	Model Water, mg/L	V. Bauxite	V.Charcoal	AOCB	AOCC	Standard (mg/L)		
	Influent (mg/L)	Effluent	Effluent	Effluent	Effluent	WHO	EC	NL
Bicarbonate (HCO_3^-)	150	109.12 ± 13	55.89 ± 26	127.10 ± 6	122.47 ± 8			>60
Nitrate (NO_3^-)	23	0.42 ± 0.07	0.38 ± 0.08	0.38 ± 0.08	0.21 ± 0.11	50		
Sulphate (SO_4^{2-})	32	8.91 ± 3.74	2.83 ± 0.76	327.71 ± 365.11	816.29 ± 615.10	250		150
Phosphate (PO_4^{2-})	0	0.19 ± 0.22	0.29 ± 0.26	0.11 ± 0.10	0.13 ± 0.13	3	6.5	6

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the pilot column studies conducted the following conclusions were drawn.

- 1) Both the Aluminium oxide coated bauxite (AOCB) and Aluminium oxide coated charcoal (AOCC) were effective adsorbent for the adsorption of fluoride from drinking water. Their porosity, high surface area and effective capacity for fluoride removal made them potential media to be used in the purification of fluoride contaminated waters.
- 2) In the short column experiments, the AOCB and the AOCC treated 56.16L and 102.96L respectively with adsorption capacities of $0.001\text{gF}^-/\text{g}$ and $0.006\text{gF}^-/\text{g}$ respectively.
- 3) Regeneration of exhausted media by coating with Aluminium sulphate and Ammonium hydroxide restored their fluoride (F^-) removal capacity.
- 4) The first generation re-coating of the exhausted adsorbents resulted in an increase in their fluoride removal potential and the adsorbents filter run times. However subsequent recoating gave rise to reduced fluoride removal potential.
- 5) The regenerated AOCC performed better than the regenerated AOCB, in the removal of fluoride.
- 6) Virgin and regenerated adsorbents (AOCB and AOCC) were found to be effective for the removal of nitrate, sulphate and bicarbonate.

5.2 Recommendations

- X-ray Diffraction (XRD) and Energy Dispersive X-ray (EDX) analysis should be performed to investigate the molecular structure and adsorption phenomenon within the pores of the exhausted and regenerated media.
- Construct a filter that will be applied to one of the capped boreholes in the northern Ghana to see how other environmental and hydraulic factors will affect the fluoride removal process.

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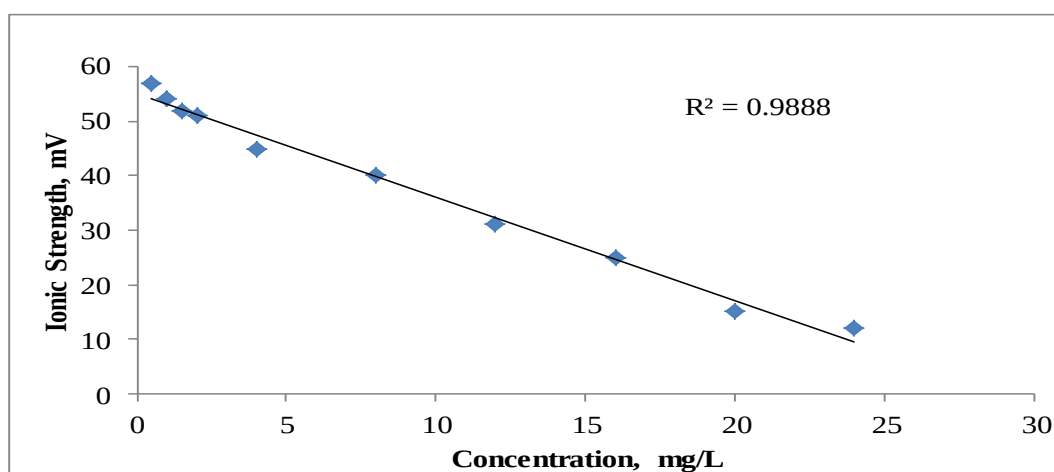
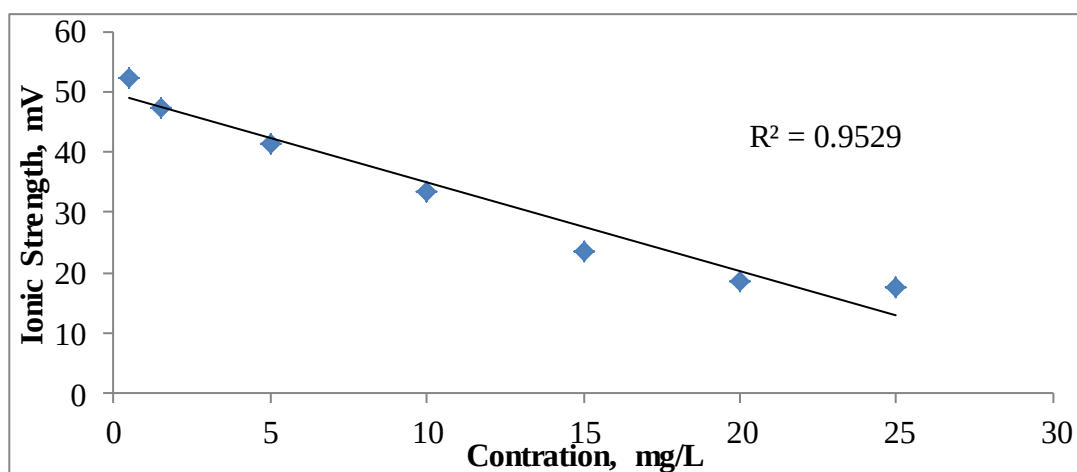
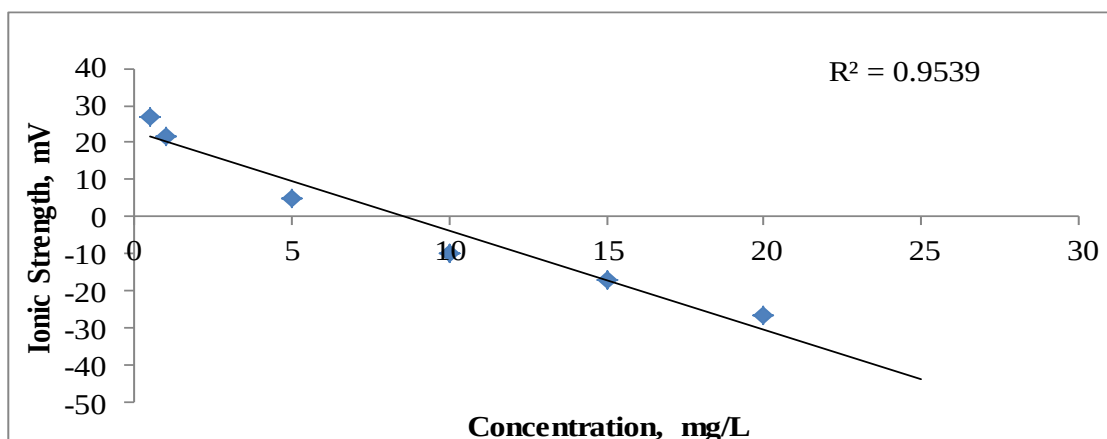
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APPENDICES

Appendix 1: Standard Curves used for fluoride determination



Appendix 2: Results of pilot column experiments using AOCC at; initial flow rate, $F_i=20\text{mg/L}$, $\text{pH}=7$, Bed depth, $H=10\text{cm}$

i Pilot column experiment: results for AOCB and AOCC

TIME(HR)	AOCC	AOCB	AOCC	AOCB	AOCC	AOCB	AOCC	AOCB
	Fluoride Concentration mg/L	Fluoride Concentration mg/L	F-adsorption	F-adsorption	Removal Efficiency %	Removal Efficiency %	Treated Effl. Volume, L	Treated Effl. Volume, L
0	4.5	8.6	0.00	0.00	78	57	0	0
1	3.1	8.0	0.04	0.01	84	60	0.78	0.78
2	1.5	7.3	0.08	0.02	93	64	1.56	1.56
3	0.7	6.9	0.13	0.03	96	66	2.34	2.34
4	0.1	5.4	0.18	0.05	100	73	3.12	3.12
16	0.1	0.1	0.70	0.25	100	100	12.48	12.48
40	0.1	0.1	1.76	0.62	100	100	31.2	31.2
64	0.1	0.1	2.81	0.99	100	100	49.92	49.92
88	0.1	0.1	3.87	1.36	100	100	68.64	68.64
112	0.1	6.0	4.92	1.22	100	70	87.36	87.36
136	0.1	10.5	5.98	1.01	100	48	106.08	106.08
160	4.8	11.21	5.36	1.09	76	44	124.8	124.8
184	9.5	13.1	4.26	0.99	52	35	143.52	143.52
208	12.3	14.4	3.52	0.91	38	28	162.24	162.24
232	13.8	14.8	3.16	0.94	31	26	180.96	180.96
256	14.6	14.0	3.06	1.19	27	30	199.68	199.68
280	14.6		3.35		27		218.4	
304	14.6		3.64		27		237.12	

TIME(HR)	AOCC1	AOCB1	AOCC1	AOCB1	AOCC1	AOCB1	AOCB1	AOCC1
			F-adsorption	F-adsorption	Removal Efficiency	Removal Efficiency	Treated Effluent volume, L	Treated Effluent volume, L
0	2.8	4.5	0.00	0.00	86	78	0	0
1	2.4	3.1	0.04	0.01	88	84	0.78	0.78
2	1.3	2.6	0.08	0.03	94	87	1.56	1.56
3	0.5	2.0	0.13	0.04	97	90	2.34	2.34
4	0.1	1.3	0.18	0.06	100	94	3.12	3.12
16	0.1	0.3	0.70	0.24	100	98	12.48	12.48
40	0.1	0.1	1.76	0.62	100	100	31.2	31.2
64	0.1	0.1	2.81	0.99	100	100	49.92	49.92
88	0.1	0.1	3.87	1.36	100	100	68.64	68.64
112	0.1	0.1	4.92	1.73	100	100	87.36	87.36
136	0.1	0.1	5.98	2.11	100	100	106.08	106.08
160	0.1	0.1	7.03	2.48	100	100	124.8	124.8
184	0.1	0.1	8.08	2.85	100	100	143.52	143.52
208	0.1	0.1	9.14	3.22	100	100	162.24	162.24
232	0.1	3.9	10.19	2.91	100	81	180.96	180.96
256	0.1	5.8	11.25	2.83	100	71	199.68	199.68
280	0.1	6.5	12.30	2.94	100	67	218.4	218.4
304	3.0	6.9	11.44	3.10	85	66	237.12	237.12
328	3.9	7.5	11.66	3.20	81	63	255.84	255.84
352	5.4	8.2	11.35	3.23	73	59	274.56	274.56
376	6.0	9.5	11.66	3.07	70	52	293.28	293.28
400	7.3	10.1	11.24	3.09	64	50	312	312
424	7.8		11.39		61			330.72
448	9.1		10.74		54			349.44
472	10.3		10.14		49			368.16

ii Pilot column experiment: results for AOCB1 and AOCC1

iii Pilot column experiment: results for AOCB2 and AOCC2

TIME(HR)	AOCC2	AOCB2		AOCC2 F- adsorption	AOCB2 F- adsorption	AOCC2 Removal Efficiency	AOCB2 Removal Efficiency	AOCB2 pH	AOCC2 pH	AOCC2 vol (L)	AOCB2 vol(L)
0	5.6	6.1	20	0.00	0.00	72	69	5.37	7.25	0	0
1	4.3	5.4	20	0.03	0.01	79	73	4.95	7.24	0.78	0.78
2	0.7	2.0	20	0.09	0.03	96	90	4.76	7.20	1.56	1.56
3	0.1	0.1	20	0.13	0.05	100	100	4.59	7.20	2.34	2.34
4	0.1	0.1	20	0.18	0.06	100	100	4.76	7.10	3.12	3.12
16	0.1	0.1	20	0.70	0.25	100	100	5.36	7.01	12.48	12.48
40	0.1	0.1	20	1.76	0.62	100	100	4.84	6.81	31.2	31.2
64	0.1	0.1	20	2.81	0.99	100	100	6.32	6.73	49.92	49.92
88	0.1	0.1	20	3.87	1.36	100	100	6.81	6.48	68.64	68.64
112	0.1	0.1	20	4.92	1.73	100	100	7.27	6.37	87.36	87.36
136	0.1	6.3	20	5.98	1.45	100	68	7.13	6.34	106.08	106.08
160	0.1	7.8	20	7.03	1.52	100	61	7.17	6.20	124.8	124.8
184	2.8	8.8	20	7.00	1.61	86	56	7.30	6.16	143.52	143.52
208	5.0	9.7	20	6.88	1.67	75	51	7.30	6.00	162.24	162.24
232	8.2	10.1	20	6.04	1.79	59	50	7.69		180.96	180.96
256	9.5		20	5.92		52		7.41		199.68	
280	10.1		20	6.13		50		7.34		218.4	

Appendix 3: Results of comparing the effect of filter run time per coating
episode of adsorbents

- i Table of filter run-time effect per coating episode of AOCB, AOCB1 and AOCB2

Time (hours)	Effluent Fluoride Conc. Mg/L			% increase in run time
	AOCB	AOCB1	AOCB2	
0	8.6	4.5	6.1	0
1	8.0	3.1	5.4	0.25
2	7.3	2.6	2.0	0.5
3	6.9	2.0	0.1	0.75
4	5.4	1.3	0.1	1
16	0.2	0.3	0.1	4
40	0.2	0.1	0.1	10
64	0.2	0.1	0.1	16
88	0.2	0.1	0.1	22
112	6.0	0.1	0.1	28
136	10.5	0.1	6.3	34
160		0.1	7.8	40
184		0.1	8.8	46
208		0.1	9.7	52
232		3.9	10.1	58
256		5.8		64
280		6.5		70
304		6.9		76
328		7.5		82
352		8.2		88
376		9.5		94
400		10.1		100

ii Table of filter run-time effect per coating episode of AOCC, AOCC1 and AOCC2

Time (hours)	Effluent Fluoride Conc. Mg/L			% increase in run time
	AOCC	AOCC1	AOCC2	
0	4.5	2.8	5.6	0
1	3.1	2.4	4.3	0
2	1.5	1.3	0.7	0
3	0.7	0.5	0.1	1
4	0.2	0.1	0.1	1
16	0.2	0.1	0.1	3
40	0.2	0.1	0.1	8
64	0.2	0.1	0.1	14
88	0.2	0.1	0.1	19
112	0.2	0.1	0.1	24
136	0.2	0.1	0.1	29
160	4.8	0.1	0.1	34
184	9.5	0.1	2.8	39
208	12.3	0.1	5.0	44
232		0.1	8.2	49
256		0.1	9.5	54
280		0.1	10.1	59
304		3.0		64
328		3.9		69
352		5.4		75
376		6.0		80
400		7.3		85
424		7.8		90
448		9.1		95
472		10.3		100

Appendix 4: Pilot column experiments: Water quality analysis of treated water

i Results of Sulphate (SO_4^{2-}) removal by adsorbents

Contact time (hours)	ADSORBENTS			
	Virgin bauxite	Virgin Charcoal	AOCB	AOCC
0	13.8	3.6	892	1646
1	12.4	3.4	772	1386
2	10.2	3.2	352	1248
3	10.2	3.2	140	716
4	6.6	2.6	128	344
24	5.6	2.4	6	338
48	3.6	1.4	4	36

ii Results of Phosphate (PO_4^{2-}) removal by adsorbents

Contact time (hours)	ADSORBENTS			
	Virgin bauxite	Virgin Charcoal	AOCB	AOCC
0	0.664	0.813	0.315	0.314
1	0.245	0.454	0.14	0.314
2	0.19	0.28	0.071	0.071
3	0.071	0.175	0.071	0.071
4	0.071	0.14	0.071	0.071
24	0.071	0.1	0.035	0.035
48	0.035	0.098	0.035	0.035

iii Results of Nitrate (NO_3^-) removal by adsorbents

Contact time (hours)	ADSORBENTS			
	Virgin bauxite	Virgin Charcoal	AOCB	AOCC
0	0.54	0.5	0.49	0.4
1	0.46	0.49	0.43	0.26
2	0.45	0.38	0.43	0.23
3	0.44	0.36	0.37	0.2
4	0.42	0.34	0.33	0.16
24	0.34	0.32	0.3	0.12
48	0.32	0.3	0.29	0.08

iv Results of Bicarbonate (HCO_3^-) removal by adsorbents

Contact time (hours)	ADSORBENTS			
	Virgin bauxite	Virgin Charcoal	AOCB	AOCC
0	125.6	91.44	135.36	135.36
1	120.72	81.68	131.25	130.16
2	115.84	67.04	130.48	125.6
3	110.84	52.4	125.6	120.72
4	106.08	47.52	125.6	118.63
24	98.2	28	120.72	115.84
48	86.56	23.12	120.72	110.96

Appendix 5: Results of fluoride measurement for pilot column experiments

- i Table showing measured potentials and corresponding fluoride concentrations using AOCC

Time(Hour)	Ionic Strength (mV)			Fluoride Concentration mg/L
	1	2	Average	
0	11	11	11	4.5
1	15	14	14.5	3.1
2	19	19	19	1.5
3	21	21	21	0.7
4	24	24	24	0.0
16	36	35	35.5	0.0
40	38	37	37.5	0.0
64	40	40	40	0.0
88	42	42	42	0.0
112	42	42	42	0.0
136	36	36	36	0.0
160	10	10	10	4.8
184	-2	-3	-2.5	9.5
208	-10	-10	-10	12.3
232	-14	-14	-14	13.8
256	-16	-16	-16	14.6
280	-16	-16	-16	14.6
304	-16	-16	-16	14.6

- ii Table showing measured potentials and corresponding fluoride concentrations using regenerated AOCB

Time(Hour)	Ionic Strength (mV)			Fluoride Concentration mg/L
	1	2	Average	
0	11	11	11	4.5
1	15	14	14.5	3.1
2	16	16	16	2.6
3	18	17	17.5	2.0
4	19	20	19.5	1.3
16	22	22	22	0.3
40	35	35	35	-4.5
64	49	49	49	-9.8
88	51	50	50.5	-10.3
112	48	48	48	-9.4
136	48	47	47.5	-9.2
160	46	46	46	-8.7
184	34	35	34.5	-4.3
208	31	30	30.5	-2.8
232	8	6	7	6.0

iii Table showing measured potentials and corresponding fluoride concentrations using regenerated AOCC

TIME(Hour)	Ionic Strength (mV)			Fluoride Concentration mg/L
	1	2	Average	
0	15	16	15.5	2.8
1	16	17	16.5	2.4
2	20	19	19.5	1.3
3	22	21	21.5	0.5
4	24	23	23.5	-0.2
16	40	40	40	-6.4
40	46	46	46	-8.7
64	52	52	52	-10.9
88	53	52	52.5	-11.1
112	52	52	52	-10.9
136	54	53	53.5	-11.5
160	50	49	49.5	-10.0
184	51	50	50.5	-10.3
208	48	49	48.5	-9.6
232	47	52	49.5	-10.0
256	44	45	44.5	-8.1
280	40	41	40.5	-6.6
304	9	9	9	5.2

iv Table showing measured potentials and corresponding fluoride concentrations using regenerated AOCB

Time(HR)	Ionic Strength (mV)			Fluoride Concentratio
	1	2	Average	
0	7	6	6.5	6.1
1	8	9	8.5	5.4
2	17	18	17.5	2.0
3	25	25	25	0.0
4	27	26	26.5	0.0
18	39	40	39.5	0.0
42	46	46	46	0.0
66	46	46	46	0.0
90	46	46	46	0.0
114	24	23	23.5	0.0
138	6	6	6	6.3

- v Table showing measured potentials and corresponding fluoride concentrations using regenerated AOCC

Time(HR)	Ionic Strength (mV)			Fluoride Concentration mg/L
	1	2	Average	
0	8	8	8	5.6
1	12	11	11.5	4.3
2	21	21	21	0.7
3	29	29	29	0.0
4	33	33	33	0.0
18	48	48	48	0.0
42	49	48	48.5	0.0
66	51	52	51.5	0.0
90	47	53	50	0.0
114	48	53	50.5	0.0
138	41	43	42	0.0
162	23	23	23	0.0
186	16	15	15.5	2.8
210	10	9	9.5	5.0