KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,

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Removal of Chemical Contaminants from Drinking Water using Local Adsorbents in

Column Filters

by

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DECLARATION

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.

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DEDICATION

This work is dedicated to the Almighty God, my wonderful parents, loving husband

and beautiful Nkunim Okyere Ampong.

ACKNOWLEDGEMENT

ABSTRACT

Good drinking water is essential in ensuring the health of consumers. It also enhances the quality of life of the populace. The presence of chemical contaminants like Fluoride, Nitrates, Nitrites, Iron and Manganese are naturally occurring in water sources and Phosphates, often introduced by human activities have both health and environmental effects at high concentrations in drinking water. This study targeted the removal of the above mentioned contaminants using locally synthesized adsorbents; Aluminium Oxide Coated Charcoal (AOCC), Iron Oxide Coated Sand (IOCS) and Surfactant Modified Zeolite (SMZ). The adsorbents were characterized using the Xray Diffraction (XRD), Scanned Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) techniques. The adsorbent media were used in column experiments and effluent sampling was done at different times during the experimental run time. The effluent samples were then analysed to ascertain their concentrations using appropriate techniques. The model water used was prepared by simulating the groundwater quality of Northern Ghana along with the WHO guideline values of the contaminants in drinking water. The column experiment results showed that AOCC was highly effective in the removal of anionic contaminants except Phosphate. The AOCC removal capacities were as follows; Fluoride recorded a removal capacity of 0.6 mg/g; 23.4 mg/g Nitrate and 1.2 mg/g Nitrite. SMZ also had better removal capacity with Phosphate contaminant. SMZ recorded a removal capacity of 0.2 mg/g. IOCS adsorbent was highly effective in the removal of cationic contaminants in the column experiments. Removal capacities recorded were 0.089 mg/g and 0.073 mg/g for Iron and Manganese respectively. AOCC was a better adsorbent in the removal of Fluoride, Nitrate and Nitrite than the SMZ. SMZ was better at removing phosphate than that of the AOCC. IOCS on the other hand was an effective adsorbent in cationic contaminant (Iron and Manganese) removal. The characterization results confirmed the adsorbents

as AOCC, SMZ and IOCS. Properties such as mineralogy, morphology and elemental

compositions were obtained.

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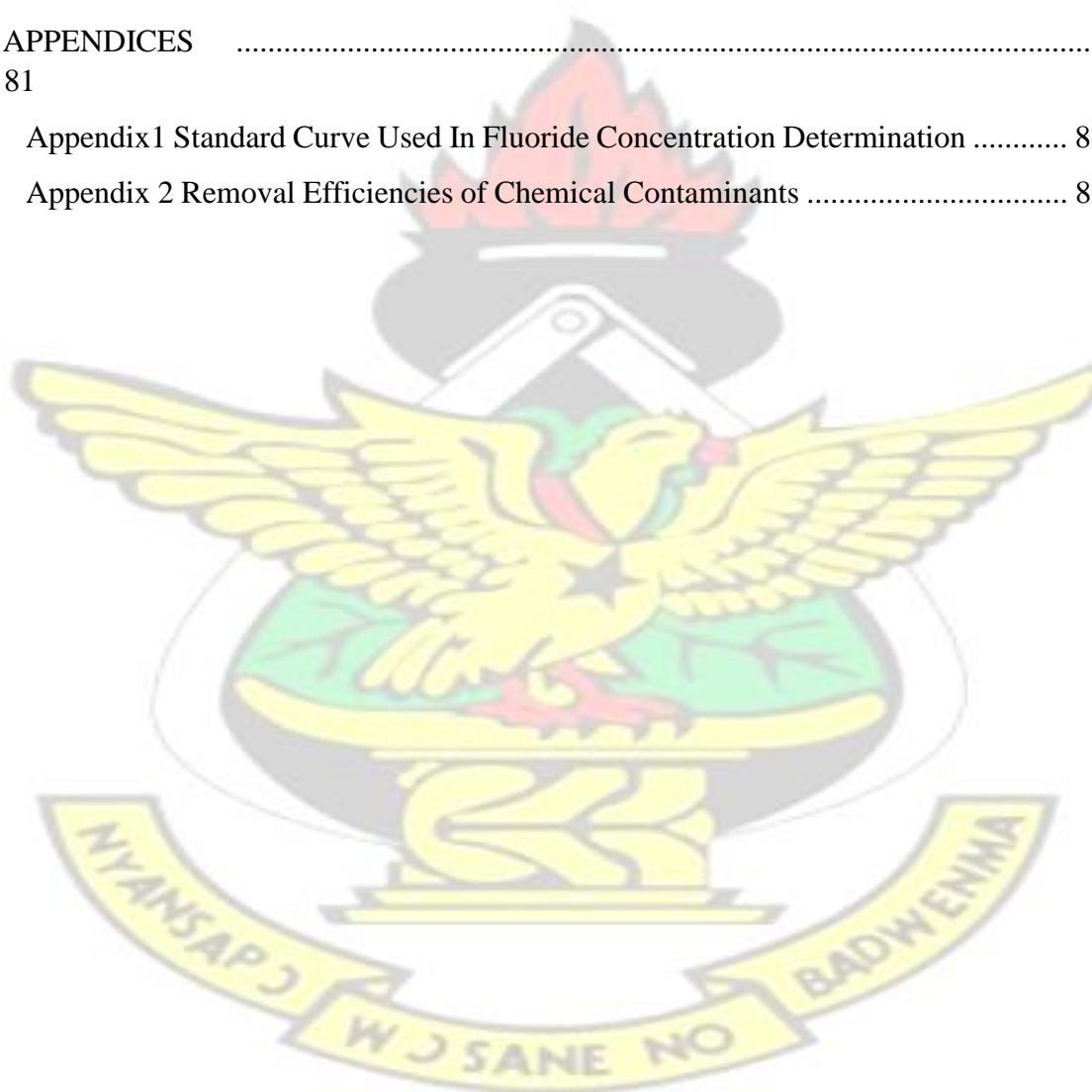# LIST OF
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LIST OF ABBREVIATIONS

ADP	Adenosine Diphosphate
ATP	Adenosine Triphosphate
AOCC	Aluminium Oxide Coated Charcoal
AAS	Atomic Absorption Spectrometry
DNA	Deoxyribonucleic Acid
EDX	Energy Dispersive X-ray Analysis
EPA	Environmental Protection Agency
F^-	Fluoride
HDTMA-Br	Hexadecyltrimethylammonium bromide
HF	Hydrogen Fluoride
IPCS	International Programme on Chemical Safety
IZA	International Zeolite Association
Fe	Iron
IOCS	Iron Oxide Coated Sand
Mn	Manganese
NO_3^{2-}	Nitrate
NO_3^-	Nitrite
PO_4^{3-}	Phosphate
RNA	Ribonucleic Acid
SEM	Scanning Electron Microscopy
Si/Al	Silica Alumina ratio
Na-LSX	Sodium Low Silica X
SMZ	Surfactant Modified Zeolite
UNESCO	United Nations Educational Scientific and Cultural Organization
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WWC	World Water Council
XRD	X- Ray Diffraction

CHAPTER 1:

INTRODUCTION

1.1 Background

In order for life to exist and be sustained on earth, it is imperative that there is constant supply of water. Living things require and are contingent upon water to execute composite processes of biochemical activities that occur in biological systems of living organisms to help maintain life on earth. Of all the materials that are contained in the surface of the earth, water makes up about 70% of it. Aside air that is taken-up by human or animals for breathing, water is one of the elements of much significance to man. Despite the fact that water takes up 70% of the surface of earth, fresh water occupies only 2.5% of the total volume, with the remaining being takenup by salt water (UNESCO, 2003). In 2005, the World Water Council (WWC), as cited by Danquah (2010) reported that, just 0.3% of the 3% fresh water is found in rivers and lakes with the rest remaining frozen. This puts forward that mankind has relatively small amount of fresh water resources on which daily activities thrive.

Water treatment in urban areas often goes through the conventional treatment schemes which involve aeration, coagulation and flocculation, sedimentation, deep bed filtration, disinfection water conditioning among others. Due to the large number of people being catered for by these treatment plants, the cost of operation and maintenance are more bearable than the provision of these same facilities in the low populated rural and peri-urban areas. Efforts are also made to ensure the water produced for distribution and consumption has met the health-based recommended guidelines to ensure the wellbeing of consumers.

In rural areas of most developing countries, the treatment of drinking water is often faced with the issue of financial constraint which prevents the usage of conventional

treatment schemes in the provision of potable water. The point-of-use system is generally the treatment scheme employed in order to make potable water available to inhabitants in such areas. The inability of the point-of-use system to go through as many steps as that of the conventional water treatment along with poor maintenance culture has led to the presence of contaminants like fluoride, Iron, Nitrates and Nitrites in drinking water making it unwholesome for consumption. An ample number of serious health issues may be found to exist due to the contamination of the water resource by chemicals. In the rural and peri-urban localities, some chronic consequences may be possible, where the excess application of agricultural chemicals has contributed to substantial levels of pesticides in water sources. Nitrate and nitrite occurrence in water may be consequence of application of fertilizers beyond normal limits, the slow passage of wastewater as well as other organic waste substances into both surface and groundwater. In spite of the fact that consequences may be hard to determine among populations of human, contaminations like that may present human health risks. Contact to high levels of naturally occurring fluoride may result in teeth blotching and in serious conditions, fluorosis of the human skeleton as well as crippling. Drinking water which contains Arsenic over a long period of time can result in cancer of the skin, lung, bladder, and kidney cancer, and also changes in pigmentation, unusual thickening of the skin which is known as hyperkeratosis, disorders of the nervous system, weakness of the muscles, loss of appetite, and nausea. This is different from acute intoxication, which generally result in vomiting, oesophageal and abdominal pain, and bloody diarrhea, popularly known as "rice water" diarrhea (Mohan and Pittman , 2007; Gautam *et al.*, 2014).

1.2 Problem Statement

Water is crucial for the sustenance of life on earth, for divers purposes and in divers ways drinking-water should be worthy for usage by human and for all normal domestic

utilization (Gorchev and Ozolins, 1984). Due to anthropogenic activities, the available water sources in Northern Ghana face with one form of pollution or another. Due to the low flow of surface water from prolonged dry season, inhabitants rely greatly on groundwater. However, fluoride concentrations exceeding the WHO recommended level of 1.5 mg/L have been recorded in the groundwater underlying the Upper regions of Ghana (Anku *et al*., 2008). Along with Fluoride are other naturally occurring chemicals like Nitrate, Nitrite, Iron, Manganese, Calcium are also present in groundwater.

Chemical substances with more potential to be found and be very hazardous to the health of human should be considered to be of greater priority for risk management than those regarded less likely to be found in drinking-water and to have lower health hazards (Fawell and Kingston, 2007). Some of the chemicals present in drinking water that are likely to cause problems to consumers include Iron, Manganese, Phosphate, Nitrates, Nitrites and Fluoride. However the existing removal methods of these chemicals from drinking water advanced technologies, highly skilled personnel needed to operate, coupled with high capital and operating cost make these methods less suitable for rural communities. Affordability, sustainability and versatility are thus major problems associated with most contaminant removal technologies.

There is therefore the need to conduct further research into methods through which the levels of chemical contaminants present in drinking water will be reduced to meet required standard level for the well being of consumers.

1.3 Justification

This research would make possible the selection of an appropriate adsorbent media for the development of filters for removal of fluoride and other chemical contaminants in the groundwater from the Northern part of Ghana to a recommended health and

aesthetic levels. The Filter Development Team in the Civil Engineering Department of Kwame Nkrumah University of Science and Technology (KNUST) has come up with three adsorbents. These are, Aluminium Oxide Coated Charcoal (AOCC), Iron Oxide Coated Sand (IOCS), and Zeolite Na- LSX (Raw and Surfactant modified).

Previous works (Sidik, 2012 and Donkor, 2014) done employed the use of AOCC, Aluminium Oxide Coated Bauxite (AOCB) and Zeolite Na- LSX in fluoride removal from drinking water using column and batch experiments respectively. This work continues with the addition of five more contaminants (Nitrate, Nitrite, Phosphate, Iron and Manganese) in column experiments using AOCC, SMZ and IOCS

adsorbents. These adsorbents will be used in the construction of filters for the reduction of the afore mentioned contaminants and ensure their removal from drinking water.

1.4 Research Objectives

Objectives to be achieved in this research are outlined as follows;

1.4.1 Overall Objective

To assess the extent to which fabricated adsorbents filters are able to remove some chemical contaminants from drinking water.

1.4.2 Specific Objectives

- To fabricate Aluminium Oxide Coated Charcoal (AOCC), Iron Oxide Coated Sand (IOCS) and Surfactant Modified Zeolite (SMZ) using locally available raw materials.
- To characterize the prepared Aluminium Oxide Coated Charcoal (AOCC), Iron Oxide Coated Sand (IOCS)and Surfactant Modified Zeolite (SMZ) adsorbents using XRD, SEM and EDX analysis.

- To determine the efficiencies of the fabricated adsorbents in short column experiments for the removal of Fluoride, Nitrates, Nitrites, Phosphates, Iron and Manganese from drinking water.

CHAPTER 2:

LITERATURE REVIEW

2.1 Water Accessibility

Water demand refers to the volume of water that is required for effective functioning. This can be further broken down into three categories; industrial, domestic and recreational. In the case of water for domestic purposes, a number of factors are looked at during the provision process; the standard of living, economic status, educational level, culture and religion of users. These criteria cover only a small percentage of the population (often the rich and affluent in the society) who have access to clean and potable water while the rest of the populace are left with irregular supply of water and in most cases have to travel long distances to get water.

2.1.1 Coverage

The percentage of a population that has access to a recognizable water supply system is known as water coverage. The two main bodies Ghana Water Company Limited (GWCL) and Community Water and Sanitation Agency (CWSA) responsible for the provision of water to the populace are functioning below their expected level of coverage due to a number of reasons. In rural areas, account of coverage of 57% in 2009 was done by the CWSA. It ranged from as high as 77% in Upper West to as low as 41% in Western. Nevertheless, 76.6% of the rural population were with sustainable access to an improved water source according to the 2008 Demographic and Health, Survey (IRC and Aguaconsult,2011). Be as it may, the rate of coverage does not highlight the story wholly. A more precise view of the sustainability of services is determined by evaluating the functionality of the systems. Yet it is very hard to obtain numbers on their functionality, even though Figures are different and change from 90% when considering boreholes under project that were all the same working in villages

that were surveyed (Bakalian and Wakeman, 2009) to 58% of water points demanding to be fixed in a survey in the northern Ghana (IRC and Aguaconsult, 2011). According to Dwamena-Boateng and Larmie (2011), water availability is fast dwindling due to natural and anthropogenic factors like rainfall variability, fast population growth, increasing environmental degradation and water source pollutions.

2.1.2 Geology and groundwater quality

Ghana is dominated by crystalline silicate rocks and weathered derivatives, leading to groundwater with low salinity, low total hardness values and acidic pH (< 6.5). However, in the south–eastern and coastal areas, there is the exception of this condition. The major groundwater quality problem observed in Ghana is high iron concentrations, evident in many groundwater supplies. High fluoride concentrations have resulted in serious direct health related problems especially in the Northern and

Upper regions of Ghana (Buamah *et al*., 2008)

2.2 Chemical Contaminants Present in Drinking Water

Naturally occurring chemical substances were mostly present in water used for drinking. These are as a result of the water striking rocks or establishing contact with rocks and or soil and hence the consequences of the geological setting, which include climate. On the other hand, the chemical constitution of water used for drinking purposes as well relies on the polluting consequences of industry, human settlements, agricultural activities and water treatment and distribution (Olivares and Uauy, 2004).

2.2.1 Fluoride

Among members of the halogen chemical group, Fluorine is the lightest of all. It is therefore very reactive of all chemical substances and present in the environment as fluorine. On the scale of electronegativity, Fluorine is the most electronegative among all the elements (Fawell *et al.*, 2004; Fawell *et al*., 2006). In all natural waters, Fluorine

is present at some concentration. Fluoride is found in all natural waters at some concentration. Water from the sea generally made of about 1 mg l^{-1} although water with rivers and lakes as their source normally present concentrations of less than 0.5 mg l^{-1}. With ground waters, nevertheless, low or high concentrations of fluoride can be seen, and this may be due to the type of the rocks and the presence of fluoride-bearing minerals. The solubility of Fluorite ions determines the concentrations of Fluorine in water, so that when calcium occurs at 40 mg l^{-1}, it should be limited to 3.1 mg l^{-1} (Fawell *et al*., 2004)

In another perspective, it is when calcium is absent in solution that allows for stabilizing higher concentrations of fluoride. In ground water obtained from calciumpoor aquifers, concentrations of fluoride are seen to be high, as well as places that usually have fluoride-bearing minerals. In groundwater where there is exchange of cations of sodium for calcium, an increase in the density of Fluoride may also be recorded (Edmunds and Smedley, 1996).

2.2.1.1 Fluoride Effects on Life

Fluoride is among the few chemicals substances that have been established to present substantial consequences in people as a result drinking water contaminated with it. At the right concentration, Fluoride presents effects that promote healthy teeth development, when it occurs in drinking-water. However, when a person is exposed to excess amount in their domestic water for drinking purposes, or in combination with exposure to other sources of fluoride, it can lead to a many health issues. Some of the adverse health consequences may range from mild dental fluorosis to crippling skeletal fluorosis when the level and length of exposure is increased unreasonably. In many locations of the world, the skeletal crippling can significantly lead to morbidity (Fawell *et al*., 2006). According to Slooff *et al*., (1988), the geographic location is a significant factor when considering quantity of fluoride exposed to on daily basis. For

instance, in the Netherlands, it is therefore estimated that the total intake of fluoride on daily basis is 1.4–6.0 mg. About 80-85% of fluoride consumption appears to come from food. For drinking water, it appears 0.03-0.68 mg of fluoride is consumed daily. The total consumption for children through food and water is reduced due to lower food and water intake. The consumption of food and water compared to weight of the body is higher. Yet it can be increased further by swallowing of toothpaste or fluoride tablets up to 3.5 mg of fluoride daily (Fawell *et al*., 2004).

On the average, some 75 to 90% of fluoride that is taken in through drinking or other means is taken up the tissues of the body. When the stomach environment is acidic, fluoride is changed over to hydrogen fluoride (HF), which makes up about 40% of fluoride taken in and thus is taken up by the body tissues from the stomach in the form of HF. When the pH of the stomach gastric content is high, the absorption rate of the gastric is reduced by cutting down on the concentration uptake of hydrogen fluoride. The fluoride content which is not taken up in the stomach yet in the intestine is not influenced by the pH at this site. Compared to the quantity of fluoride taken in, substances like calcium, magnesium and aluminium, which make up cations of high concentrations which form insoluble complexes with fluoride, can substantially reduce the absorption of gastrointestinal fluoride. Fluoride is easily disseminated throughout the body immediately it is taken up by the blood, with almost 99% of the body load of fluoride held in calcium rich areas including bone and teeth dentine and enamel. Here, the fluoride is integrated into the crystal lattice. Between 80 to 90% of fluoride take into the body is retained in infant. However, in adults, the quantity falls to about 60%. In breast-feeding mothers, fluoride is observed to move across the placenta and into the breast milk of the mother. Here, the amount found is essentially similar to those found in the blood (Fawell *et al*., 2006).

The guideline value of 1.5 mg/l of intake of fluoride may have to be change altered in countries or localities where it is realized that the quantity exposed to inhabitants through feeding is greater than or equal to 6 mg per day. It would therefore be suitable to take into consideration setting a standard or local guidepost at a density below 1.5 mg per litre (Fawell *et al*., 2004).

2.2.2 Nitrates and Nitrites

Nitrate and nitrite are ions that occur naturally in the environment and form part of the nitrogen cycle. For oxygenated systems, nitrate ion (NO_3^-) is the stable form of combined nitrogen. Even though nitrate is chemically unreactive, it can be broken down by the action of microbes. The nitrite ion (NO_2^-) on the other hand comprises of nitrogen in a relatively unstable oxidation state (WHO, 2011). As a result of the stability of the nitrate ion, it is relatively common in nature compared to the nitrite. Almost all salts of nitrate and nitrite dissolve readily in water, and it is seen as a whitish powder when it precipitates in water. Nitrates and nitrites do not pass off into vapour and therefore are probable to stay in water until it is utilized by plants or other organisms. Ammonium nitrate is absorbed by bacteria, and in conditions where oxygen is absent, the breakdown of nitrate occurs fastest.

Nitrates are easy to move from one place to the other in soil. It is therefore highly possible for them to move into ground water because they are readily soluble in water and are not easily retained by soil (USEPA, 2007). In the presence of oxygen, nitrate can spread gradually in relatively large amounts into the aquifer. This is usually observed in areas where there is little or no plant materials growing around to absorb the nitrate, hence the net movement of the water in the soil is toward the aquifer in a downward manner. In the soil, denitrification or the breakdown of nitrogen substances takes place just to a small degree, as well as in the rocks-forming aquifers. In the absence of oxygen, nitrate may be broken down almost entirely to nitrogen. Also

significant to determine the fate of nitrate in the soil are the following: presence water tables, quantity of rainwater, presence of other organic material and other physicochemical properties (WHO, 2011).

For small-community water supplies, a more suitable and generally appropriate means of cutting down on the quantities of nitrite and nitrate present in water is not particularly defined. In shielding off sources of water from being tainted, well thoughtful approaches should be put in place, especially where the use of agricultural fertilizers or wastewater and sewage discharges are the main source of contamination. In water reservoirs, the activity of algae can be employed to cut down on the quantities of nitrate substantially. At the bottom silt layer, this can however be assisted by the activities of denitrifying bacteria in the bottom silt layer (Gorchev and Ozolins, 1984).

2.2.2.1 Human Exposure to Nitrates and Nitrites

Normal haemoglobin can be altered by nitrate, especially in bottle-fed infants to form methaemoglobin. Haemoglobin is the chemical substance in the red blood cell responsible for oxygen transport from the lungs to the body tissues. Usually, of the total amount of haemoglobin in the body, methaemoglobin accounts for less than 2.5% (Division of Public health, 2010). The activities of nitrates tend to increase the level of methaemoglobin, which in turn cuts down on the blood's ability to supply body cells with oxygen. One of the prime health issues to bottle-fed babies is nitrate where the risk of developing methaemoglobinaemia, which is commonly known as "blue-baby syndrome", is increased as a result of the rise in the concentration of nitrates above 50 mg/L. When nitrite is present, the health risk is increased because, nitrite is a much more powerful methaemoglobin agent than nitrate, and also by the presence of microbial contamination, which can result in gastric infections in infants (Thompson *et al.,* 2007). The bluish tint of the lips, ears and nose in slight cases is as a result of oxygen

starvation, known as "blue-baby syndrome" in infants (Division of Public Health, 2010).

Infants are particularly prone to the consequences of nitrates in water used for drinking purposes and this is as a result of their low blood level and high pH of their stomach content, which enhance the process of changing nitrate over to nitrite (Division of public health, 2010; Ungureanu andUngurasu, 2011). This is of a double significance, which is if the water is used in making their formula as well. For the pregnant women, the risk of nitrate exposure is also more. This is due their levels of methaemoglobin being generally on the high side of around 10%, particularly during pregnancy. The typical rise of this substance in pregnant women indicates that their system is just tolerable to less exposure to nitrate than when they are not pregnant. Almost all the nitrite and nitrate inspired or consumed, are removed quickly by the urinary system. Only isolated cases of cancer caused by nitrite and nitrate have been accounted for, even though the disease is in existence. However, the potency of these chemical substances to cause cancer is still being investigated (Division of public health, 2010).

2.2.2.2 Nitrates and Nitrites in Water Sources

The nature of soil, depth of the underground water, climate and the practice of irrigation are contributing factors that determine how often and the point or degree to which nitrate moves into ground and surface water (Sumner and McLaughlin, 1996).

Even though the concentration of nitrate can attain high levels in the environment due to agricultural and refuse dump run-offs or contamination with human or animal wastes, the concentration is normally low, between 0 – 8 mg/l. With the climatic changes, the concentration of nitrate usually changes with season and may rise as a result of feeding rivers with nitrate-rich aquifers (Gorchev and Ozolins, 1984). Due to agricultural practices like the excess utilization of inorganic nitrogenous fertilizers and manures,

nitrate can be found in surface water as well as groundwater. Nitrate found in ground and surface waters can also result from wastewater treatment and as well as from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks. Along distribution pipes, nitrites can also occur chemically by the activities of Nitrosomonas bacteria. This happens during the stagnation of nitratecontaining and oxygen-poor drinking-water in galvanized steel pipes. Also if chloramination is employed as residual disinfectant and the activity is not well manned (WHO, 2011).

2.2.2.3 Nitrate and Nitrite Guideline Values

The guideline established to regulate the amount of nitrate intake has set a value for nitrate of 50 mg/l and this is based on the grounds of epidemiology to control infant methaemoglobinaemia, which results from short-term exposure and it ensures bottlefed infants are protected, eventually, other groups in the population. The consequences of this are further made more difficult by contamination resulting from microorganisms. Afterwards, microbial contamination and gastrointestinal infection can significantly increase the risk for this population group (WHO, 2011). In the event where water being used for bottle-fed infant have nitrate levels near the guideline value, efforts should be made to ensure that water is microbiologically safe in order to lower the risk of methaemoglobinaemia occurring.

The guideline established to regulate the amount of nitrite intake has set a value for nitrite of 3 mg/l and this is based on the grounds human data, which indicate that amounts of nitrite that results lead to the development of infant methaemoglobinaemia is between 0.4 to about 200 mg/kg of the human body weight. In using the minimum level of the range, a body weight of 5 kg for an infant and an intake of drinking-water of three-forth (0.75) of a litre, a guideline value of 3 mg/l, which is a rounded Figure can be obtained (WHO, 2011).

2.2.3 Manganese

For human beings as well as other animals, the element Manganese is very essential. It is however found to occur naturally in many sources of food. The most significant state of oxidation of manganese which is beneficial for the environment and life of living organisms are Mn^{2+}, Mn^{4+} and Mn^{7+}. The element occurs naturally in the most ground and surface waters, especially in conditions where oxygen concentration is very low or absent (anaerobic).These sources of natural water are thus the most important reservoirs for drinking water. In most cases, the exposure to manganese which is of major significance is the one which usually comes from food (WHO, 2006). Many kinds of food are known to contain manganese. Among these varieties of food are many nuts, grains, fruits, legumes, tea, leafy vegetables, infant formulas, as well as some meat and fish. Food samples are where the element manganese is mostly found in the general population (USEPA, 2004). Some negative health consequences may however result from inappropriate consumption or overdose. In humans and other mammals, the lack of manganese or its insufficiency is apparently rare, and this because manganese can be found in many common foods. In investigations where animals were kept on manganese-deficient diet Animals experimentally maintained on manganese-deficient diets show marred growth, abnormalities in skeletal development, reproductive deficits, ataxia of the newborn and defects in lipid and carbohydrate metabolism (USEPA, 2004).

2.2.3.1 Effects of Manganese Exposure

Manganese is a very important element that plays a vital role in ensuring that body functioning of both humans and animals are executed properly, because it is needed for many cellular enzymes, which include manganese superoxide dismutase and pyruvate carboxylase. It can also be used to activate many other enzymes such as kinases, decarboxylases, transferases as well as hydrolases (Cotruvo *et al*., 2011). The

consequences of the inspiration of manganese have been well reported in people who are constantly in contact or exposed to higher levels at work stations. The condition of where a person is sickened with manganese is referred to as "manganism". Manganism is as a result of exposure to elevated levels of dusts or fumes of manganese with characteristic features similar to that of Parkinson's disease, thus referred to as "Parkinson-like syndrome". The symptoms of manganism include the following: anorexia, weakness, apathy, muscle pain, slow speech, emotionless "masklike" facial expression, slow, clumsy movement of the limbs and monotonous tone of voice (USEPA, 2004; Cotruvo *et al.*, 2011).

Surface water does not contain much manganese due to the fact that oxygen-rich water causes the mineral to settle out as sediments (Lemley *et al.*, 2005).

Due to the constant metabolic equilibrium maintained by humans and other vertebrates over manganese, the metallic element is normally not regarded poisonous especially when taken during feeding (WHO, 2011). The problem are however encountered when certain concentrations of manganese is found in water pipelines and fixtures. In high concentrations of more than 0.1 mg for every 1000 ml, ionic form of the element gives an unattractive and unwanted taste to drinkables and soils plumbing fixtures and laundry. In a solution where compounds of Mn^{2+} undergo oxidation, the precipitation of manganese leads to troubles of encrustations. However, when manganese is found in concentrations as low as 0.02 mg/l, it may cause coating of water pipes that may be cast off as black precipitations. In some countries including the United States, secondary standards provide 0.05 mg/l for manganese, above which issues of discoloration can occur (USEPA, 2004). It should be understood that drinking-water containing manganese could be liable to objection or cause disapproval by users when the metal element is put in water mains and leads to water decolorisation. Although the minimum

concentration may vary from place to place, a concentration less than 0.05 mg/l is generally approved (Cotruvo *et al*., 2011).

2.2.3.2 Manganese Adsorption

Investigations recently conducted indicates that substantial variations exist in the quantity of manganese that are taken in over different exposed routes, with inspired ones being taken in quickly and to a greater degree than ingested manganese. By means of the skin, only a small amount of manganese is allow to enter the body. Taking in manganese through the process of inhalation, intra-tracheal instillation, or intravenous infusion avoid the control processes of the gastrointestinal tract. Depending on the particle size, in-take of manganese by means of inhalation takes different forms, hence the smaller the particle, the higher the chance of arriving at the lower airways. This way, they can be taken in easily while particles with larger sizes make their way into the upper airways where through the process of mucociliary activities, they are moved to the throat which eventually ends up in the gastrointestinal tract (USEPA, 2004).

2.2.3.3 Manganese Excretion

Through faeces, a chunk of manganese is eliminated, with the urinary system helping remove only a smaller portion between 0.1 and 2% of the entire manganese absorbed. Manganese remove by means of passing faeces or found in faeces comprises of manganese excreted in bile as well as dietary manganese. The removal of this metallic element is biphasic in humans, having half-lives of 13 and 37days. Also contributing factors of excretion includes sweat, hair and the milk of lactating (USEPA, 2004; Cotruvo *et al*., 2011).

2.2.4 Iron

Among all the elemental substances, iron is the one found or present in greater quantities in the crust of the Earth. It occurs in natural fresh waters in quantities

between 0.5 and 50 mg per litre. It may as well occur in drinking water due to the utilization of iron coagulants or steel corrosion in addition to cast iron pipes when water is being distributed.

2.2.4.1 Iron Exposure and Excretion

In the nutrition system of humans, iron is of great importance. Depending on the factors such as age, sex, status of a person's physiology, the minimum required amount of iron for a day is determined, and this is found to be about 10 – 50 mg per day (Fawell *et al.,* 1996). Iron is a very important substance which is required in small amounts in the body of living organisms. The absorption of iron mostly takes place in the duodenum and upper part of the jejunum. Depending on a person's status of iron in his/her body, their absorption varies and it is controlled in such a way that the person's body does not store excess amount of iron than it can hold. Generally, in adult males and females, the complete iron composition of the body is normally about 50 mg/kg for males and between 34 – 42 mg/kg for females. Present in the largest divide is in the form of haemoglobin, myoglobin and haem-containing enzymes. The second major store in the body is found as ferritin and haemosiderin, which usually occur in the spleen, bone marrow, striate muscle and liver. The rate at which iron is lost from the body in males is known to be small around 1mg per day and this is primarily as a result of exfoliation of cells. In all, about two-thirds of total loss is known to take place in the gastrointestinal tract with the remaining occurring in the skin. Through urine or sweat, the loss of iron is insignificant. However, in female adults, more blood of about 15-70 mg is lost through menstrual blood each month (Fawell *et al.*, 1996).

2.2.4.2 Iron recommended values

In 1958, the standards established internationally by the World Health Organization for regulating the amount of chemicals found in drinking water proposed that when the

concentration of iron reaches levels greater than 1 mg / litre, the suitability of the water to be used as drinking material is considerably impaired. International measures set in the 1963 and 1971 ensured that an amount of 1 mg/ litre be maintained as the uttermost concentration that is permitted. In the first publication that announced the maiden guidelines for drinking water in 1984, the concentration of 0.3 mg per litre was established as the guideline value. This concentration value was reached as the middle way between the two extreme concentrations resulting from the usage of iron in the treatment of water and the iron employed because of aesthetic considerations. In the 1993 guideline, there was no guideline value for iron in drinking water that was due to health considerations. However, as a precaution against the excessive bioaccumulation of iron in the body, a guideline concentration value of 2 mg/litre was acknowledged. This was obtained from PMTDI instituted in 1983 by JECFA. Above a concentration level of 0.3 mg per litre, iron soils washable materials and plumbing fixtures. Taste-wise, an iron concentration below 0.3 mg per litre is normally not capable of being perceived. Furthermore, concentrations between 1 and 3 mg per litres can be satisfactory for people drinking anaerobic well water (Fawell *et al*., 1996).

2.2.5 Phosphate

Phosphorous is the eleventh most common mineral in the crust of earth, constituting roughly 0.1% by weight (Summer and McLaughlin, 1996). It is found in nature mostly in the form of Phosphates (PO_4^-). Excluding small quantities of volcanic phosphate emissions, compounds of phosphate that occur on the Earth surface do not evaporate readily at normal temperatures and pressures. Their movement in the atmosphere mainly takes place in the form of dust particles or aerosols. Comparing the atmospheric flux rate of phosphate compounds that occur on the earth surface with those that occur in surface water, it appears to be slow (Hutchinson, 1957).

2.2.5.1 Phosphate exposure

Phosphate (PO_4^-) as a nutrient element is very important for all forms of life. In the living cell, phosphate performs a very significant role in the formation of deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine diphosphate (ADP), and adenosine triphosphate (ATP) (Hutchinson, 1957; Hardoyo *et al.*, 1994; Kotoski, 1997). Phosphorus is one of the most essential components of the body that is needed for the sustenance of life. In freshwater and marine systems, phosphorus occurs in either a dissolved state or state of distinct particles. Included in the later state are amorphous phosphorus, living and dead plankton, as well as precipitates of phosphorus absorbed to particulates. In the former state, organic phosphorus removed as waste excreta from organisms, inorganic phosphorus, as well as macromolecular colloidal phosphorus are examples of forms in which phosphorus may occur (Kotoski, 1997).

2.2.5.2 Phosphate in Humans

Phosphorous in the form of calcium phosphate, otherwise calcium hydroxyapatite, is a structural constituent of an animal bone. Compared to calcium, phosphorus occurs in a mass ratio of one is to two. In totality, the skeletal system of the body takes up 85% of the entire phosphorus present in the body. Some of the essential functions of the element is structural, hence as a structural component of cell membrane phospholipids. It is also imperative for the production and storage of energy in the body, phosphorylation of numerous enzymes, hormones and molecule that are employed in cell signaling; also support in the maintenance of a normal acid-base equilibrium of the body. The lack of phosphorus or its presence in insignificant quantities is not common at the population level, even though it has been found in underdeveloped or premature babies who are taking breast milk exclusively as well as in patients taking aluminum hydroxide with antacids over long periods of time. The consequences of lack of phosphorus is muscle weakness, malaise, mass loss and pain (Olivares and Uauy, 2005). Based on a number of factorial approach, the right amount needed by children

and teenagers or grown-ups can be determined. Among these approaches are body growth with regards to bone and soft tissue formation, potency of absorption and removal of waste by the urinary system. With adults the right amount taken in depends on association between the individual's dietary consumption inorganic phosphorus present in their serum. It has been declared by the European

Commission's Scientific Committee for Food that phosphorus intakes that is equivalent to the usage of calcium on the basis of molarity for determining the requirement of phosphorus be used (Olivares and Uauy, 2005).

2.3 Contaminant Removal Technologies

The ultimate aim of any water treatment procedure is to obtain healthy water that is free of chemical and pathogenic substances that contaminate it, as well as have turbidity removed to the lowest minimum level in a more cost-effective and practical fashion possible. A lot of technologies which have been engineered perform best in demand-specific circumstances. The demand is either of mass-volume or of massflow (Ray and Jain, 2011). Some of these treatment methods have been successful in the removal of contaminants from very low to significant levels. However, the cost, efficiency and availability of these processes have led to further options being looked into. Some known removal technologies include; precipitation, membrane separation processes, ion exchange, micro and nanofiltration, reverse osmosis and adsorption.

2.3.1 Precipitation

Precipitation processes employs the addition of chemicals like calcium and aluminium salts to precipitate the fluoride ion out of solution (Feenstra *et al*., 2007). Chemical precipitation can remove dissolved and suspended solids from a wastewater via sedimentation through the addition of chemicals to alter the physicochemical state of the solids. Over the years, a number of different substances have been used as

precipitants. The most commonly used inorganic chemicals in chemical precipitation include aluminium chloride, calcium hydroxide (lime) and ferric chloride (Metcalf and Eddy, 2003). Chemical precipitations are often used to reduce the levels of TSS, BOD, and phosphorus in water.

2.3.2 Membrane Separation Processes

The process of membrane filtration is merely the filtration of water through a sieve or semi-semi-permeable layer in such a way that molecules of water are permitted to go through while restraining the passage of bacteria, chemicals and viruses. The procedural steps employed in the membrane technology ranges from the utilization of a sand-filled T-shirt fed by gravity to highly advanced pressurized systems using nano-technology to actively prevent microbes from entering or passing through (Ray and Jain, 2011). For each individual processes of the membrane technology, there is a particular water treatment function that it is best suited for. Some examples are of very low pressure processes and these include the microfiltration (MF) and ultra filtration (UF). These more efficiently get rid of particles and microorganisms. The process of reverse osmosis (RO) efficiently deals with the removal of salt from brackish water and seawater. It therefore takes away natural organic matter and artificially synthesised organic and inorganic chemical substances. To soften water by removing calcium and magnesium ions, the nanofiltration process is employed (Cheremisinoff, 2002).

2.3.3 Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion from a solution is substituted for a charged ion with similar characteristics that is attached to an immobile solid particle. Such particles that are involve in the exchange are either inorganic Zeolite that occur naturally or organic resins that are artificially synthesized. Recently, the latter is common and often used and this is as a result of certain features that can be

adjusted to carry out specific applications. In an ion exchange that involves organic resin, the constituent polyelectrolytes which is of high molecular weight is used to exchange their movable ions for ions with similar charge that occur in the same medium as the polyelectrolyte. Because specific number of mobile ion sites present on each resin, there is a maximum quantity of exchange per unit of resin that can occur at a given time. In the industrial sense, metal plating is a kind of technology that is most familiar to the technology identified in ion exchange. After each process bath, water is used to clean the surface of the parts in metal plating process. To maintain quality standards, the level of dissolved solids in the rinse water must be regulated. Fresh water added to the rinse tank accomplishes this purpose, and the overflow water is treated to remove pollutants and then discharged. As the metal salts, acids, and bases used in metal finishing are primarily inorganic compounds, they are ionized in water and could be removed by contact with ion exchange resins. In a water deionization process, the resins exchange hydrogen ions (H+) for the positively charged ions (such as nickel. copper, and sodium).and hydroxyl ions (OH-) for negatively charged sulphates, chromates and chlorides. Because the quantity of H+ ions and OH -ions is balanced, the result of the ion exchange treatment is relatively pure, neutral water. Ion exchange technology is applied in many other industry sectors, including the petroleum and chemical industries, as well as general wastewater treatment applications. The technology is most often compared to reverse osmosis, since both technologies are often aimed at similar objectives.

(Cheremisinoff, 2002)

2.3.4 Micro and Nanofiltrations

The nanofiltration (NF) process softens water by removing calcium and magnesium ions while Microfiltration membranes are mostly used to achieve very low turbid effluents with very little variance in treated water quality. Because bacteria and many

other microorganisms are also removed, such membrane disinfection might avoid the need for chlorine and subsequent dechlorination. Metal salts of iron or aluminum may also be added to enhance membrane performance. For example, iron or aluminum coagulants may be added to precipitate otherwise soluble species such as phosphorus and arsenic as well as improving the removal of viral particles. Coagulation of colloidal materials may also increase the effective size of particles applied to membranes and increase permeate flux by

1) Reducing foulant penetration into membrane pores,

2) Forming a more porous cake on the membrane surface,

3) Decreasing the accumulation of materials on the membrane due to particle size effects of particle transport,

4) Improving the back-flushing characteristics of the membrane

In this regard, the process appears to be as effective as chlorination for the removal of coliforms from secondary waste effluent. A key advantage is the ability to filter and disinfect in a single step without the need for subsequent dechlorination. Preliminary results indicate that coagulation pre-treatment in conjunction with membrane microfiltration can be used to reduce phosphorus concentrations as well (Cheremisinoff, 2002).

2.3.5 Reverse Osmosis (RO)

Reverse osmosis is a means for separating dissolved solids from water molecules in aqueous solutions as a result of the membranes being composed of special polymers which allow water molecules to pass through while holding back most other types of molecules; since true "pores" do not exist in the membrane, suspended solids are also retained by super filtration In an actual reverse osmosis system, operating in a continuous-flow process, feed water to be treated or desalinated is circulated through

an input passage of the cell, separated from the output product water passageway by the membrane The feed stream is split into two fractions - a purified portion called the product water (or permeate) and a smaller portion called the concentrate' containing most of the impurities in the feed stream. At the far end of the feed-water passage, the concentration (dewatered) reject stream exits from the cell. After permeating the membrane, the product (fresh-water) flow is collected. The percentage of product water obtained from the feed stream is termed the recovery, typically around 75 percent (Cheremisinoff, 2002).

Major problems inherent in general applications of RO systems have to do with

(1) The presence of particulate and colloidal matter in feed water,

(2) Precipitation of soluble salts, and

(3) Physical and chemical makeup of the feed water.

All RO membranes can become clogged, some more readily than others. This problem is most severe for spiral-wound and hollow-fibre modules, especially when submicron and colloidal particles enter the unit (larger particulate matter can be easily removed by standard filtration methods).

2.3.6 Adsorption

Adsorption is the process by which liquid or gaseous molecules are concentrated on a solid surface (Cheremisinoff, 2002). Surface adsorption to a solid falls into two broad categories; physisorption and chemisorption. Physisorption is a non-specific loose binding of the adsorbate to the solid via Van der Waals type interactions while Chemisorption involves a more specific binding of the adsorbate to the solid. Adsorption is caused by London Dispersion Forces, a type of Van der Waals Force which exists between molecules. The force acts in a similar way to gravitational forces between planets. London Dispersion Forces are extremely short ranged and therefore

sensitive to the distance between the carbon surface and the adsorbate molecule. They are also additives, meaning the adsorption force is the sum of all interactions between all the atoms. The short range and additive nature of these forces results in activated carbon having the strongest physical adsorption forces of any material known to mankind. All compounds are adsorbable to some extent. In general, the adsorbability of a compound increases with

(1) Increasing molecular weight,

(2) A higher number of functional groups such as double bonds or halogen compounds,

(3) Increasing polarisability of the molecule (Cheremisinoff, 2002).

2.3.6.1 Factors Affecting Adsorption

2.3.6.1.1 Temperature

Adsorption reactions are normally exothermic: thus the extent of adsorption generally increases with decreasing temperature. Changes in enthalpy for adsorption are usually of the order of those for condensation or crystallization reactions, thus small variations in temperature tend not to alter the adsorption process in waste treatment to a significant extent (Weber Jr. , 1974). Physisorption which can give rise to multilayered adsorption is possible is easily disrupted by increasing temperatures. Chemisorption on the other hand, involves a more specific binding of the adsorbate to the solid. It is a process that is more akin to a chemical reaction and hence, only monolayer adsorption is possible (Sime, 2013). The difference between physical and chemisorption is typified by the behaviour of nitrogen on iron. At the temperature of liquid nitrogen, -190 $^{\circ}$C, nitrogen is adsorbed physically on iron as nitrogen molecules, N_2. The amount of N_2 adsorbed decreases rapidly as the temperature rises.

At room temperature iron does not adsorb nitrogen at all. At high temperatures, ~500 °C, nitrogen is chemisorbed on the iron surface as nitrogen atoms (Castellan, 1983).

2.3.6.1.2 Adsorbent properties

The property that is possessed by the adsorbent is very important in determining the extent of adsorption of the adsorbate in question. Using Activated Carbon, an important adsorbent as an example, investigations have revealed that the most characteristic physical property of activated carbon is its extremely large surface area, which is comprised mainly of surfaces bordering inner pore spaces. The surface area of active carbon can be greater than 1000 m^2/g (Cheremisinoff, 2002). Relative to the small geometric area of the granules or particles of this material, the large total area requires the existence of a considerable internal surface which can be provided only by small capillaries. In explaining many observed relationships associated with adsorption of materials from solution by carbon, it is essential to consider the physical structure of the adsorbent because the size and arrangement of the capillaries (micropores: 10-30 Å) and channels or interstices (macropores: 30- 100000 Å) appear to play a significant role in adsorption processes (Weber Jr. , 1974).

2.3.6.1.3 Surface Area

Extent of adsorption is generally proportional to specific surface area, (specific surface area being that portion of the total surface available for adsorption.) If the mechanism of uptake is one of adsorption on external sites of a non-porous adsorbent, the rate should vary reciprocally with the first power of the diameter. This holds also for porous adsorbents when the rate is controlled by an external resistance, i.e. 'film transport'. Conversely, for cases in which intra-particle transport controls, the variation should be with the reciprocal of a higher power of the particle diameter

(Weber Jr. , 1974). The amount and distribution of pores play key roles in determining how well contaminants are filtered. The best filtration occurs when pores are barely

large enough to admit the contaminant molecule. Because contaminants come in all different sizes, they are attracted differently depending on pore size of the filter (Cheremisinoff, 2002).

2.4 Adsorption theory

Surface adsorption to a solid falls into two broad categories; Physisorption and Chemisorption. Physisorption is a non-specific loose binding of the adsorbate to the solid via van der Waals type interactions. Multilayered adsorption is possible and it is easily disrupted by increasing temperatures. Chemisorption involves a more specific binding of the adsorbate to the solid. It is a process that is more akin to a chemical reaction and hence, only monolayer adsorption is possible (Sime, 2013). In the endeavour to explore novel adsorbents in accessing an ideal adsorption system, it is essential to establish the most appropriate adsorption equilibrium correlation (Srivastava *et al*., 2006), this is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorbent behaviour for different adsorbent systems (or for varied experimental conditions) (Foo and Hameed, 2009). In the perspective, equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems (Thompson *et al.,* 2001; El-Khaiary, 2008; Foo and Hameed, 2009)

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with

the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (Foo and Hameed, 2009).

2.5 Low- cost Adsorbents

2.5.1 Zeolites

Zeolites are crystalline solid structures composed of silicon, aluminium and oxygen that form a framework with cavities and channels for cations, water and/or small molecules to reside. Zeolites are mostly also referred to as molecular sieves. Many of them occur naturally as minerals, and are extensively mined in many parts of the world finding applications in various fields of endeavour. On the other hand, most of zeolites have been made synthetically; some of them made for commercial use while others are created by scientists to study their chemistry. Even though several materials with zeolite framework structures are being synthesized, only 191 zeolite framework types have been approved by the International Zeolite Association (IZA) Structure Commission (IZA-SC) (Peskov, 2010).

2. 5.1.1 Zeolite used in this study

Zeolite LSX is in the faujasite (FAU) family with a structure containing double 6 rings linked through sodalite cages that generate supercages with pore diameters of

7.4 Å (Khemthong *et al*., 2007). The typical Si/Al ratio of LSX is in the range of 1 - 1.5. It belongs to the space group F3m and has a large number of extra-framework cations. LSX can be synthesized from a variety of silica sources including natural clay such as kaolinite, oil shale ash, and commercial silicates (Khemthong *et al*., 2007).

Natural zeolites are recognized as efficient adsorbents for cationic pollutants. In order to increase the ability of zeolites to eliminate anionic pollutants in water, it is relevant to modify their surface with modifiers. Vujakovic *et al*., (2003) mentioned the need to modify the negative charge in the crystal structure of minerals like zeolite, bentonite,

kaolinite, among others, by using long chain organic cation- surfactants make them suitable for anion adsorption. The zeolite produced was thus modified with Hexdecyltrimethyl ammonium Bromide (HDTMA-Br). The process helped to combine the sorption properties of the zeolites with the ability to sorb anionic species or contaminants from drinking water (Shoumkova, 2011).

2.5.1.2 Zeolite Applications

Zeolites have been used in the adsorption a variety of materials. These include applications in drying, purification and separation. Increases in environmental focused issues have led to the applications hydrophobic molecular sieves, highly siliceous Y zeolite and silicalite of zeolite (Kulprathipanja, 2010). According to Kwakye- Awuah (2008), the porous structure of zeolites can be used to "sieve" molecules having certain dimensions and allow them to enter the pores.

2.5.2 Iron Oxide Coated Media

The hydrated surface of oxides (silica sand and lOCS) can adsorb different cations and anions existing in the water. The degree of adsorption or surface complexation rests on the type and density of the adsorption sites available and the nature of the adsorbing ion. A cation can associate with a surface as an inner-sphere or outer-sphere complex, depending on whether a chemical bond between the metal and the electrondonating oxygen ions is formed or if a cation of opposite charge gets closer to the surface groups at a critical distance.

In the case of an outer-sphere complex, as with the solute ion pairs, the cation and the base are separated by one or more water molecules. Furthermore, ions may be in the diffuse swarm of the electric double layer. A simple method of distinguishing between inner-sphere and outer-sphere complexes is to assess the effect of ionic strength on the surface complex formation equilibria. A strong dependence of ionic strength is typical for an outer-sphere complex. Furthermore, outer-sphere complexes involve

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electrostatic bonding mechanisms and therefore are less stable than inner surface complexes, which necessarily involve appreciable covalent bonding along with ionic bonding (Sharma, 2001).

Earlier researches by Adekoya 1995; Amoateng 1996 and Ibrahim 1997, showed that water quality improves, filter ripening time reduces, and filter run time increases when iron (II) ions are removed via adsorption onto filter media, compared when iron (III) are removed as flocs. Ibrahim (1997) reported that iron oxide coated sand has much higher efficiency for iron removal compared to new sand. Further, it was found that once the coating is developed, the filter media could give a higher efficiency even at lower pH. Sharma (1997) found that likened to new filter sand, iron oxide coated sand has very high capacity for iron (ll) adsorption. There is thus the possibility of improving efficiency of iron removal in the filter by maximising the adsorption of iron (II) onto iron oxide coated media. Adsorption of iron (ll) onto iron oxide coated media could be the primary iron removal method for treating anoxic groundwater and an attractive alternative to the conventional oxidation-flocs formation method. With the adsorption-oxidation mechanism, the head loss is likely to be very low because the iron forms a coating on the filter media, rather than a floc which would normally block the filter pore. Thus, the filter runs could be longer and the backwash water requirement and volume of the sludge reduced. Under this mechanism, it is likely that filters could be run at higher filtration rates as head loss development is not a limitation. Hence, considerable savings are likely in the capital, and operation and maintenance (O&M) costs (Sharma, 2001).

CHAPTER 3:

MATERIALS AND METHODS

3.1 Introduction

The chapter gives the laboratory experiments and protocols used to arrive at the set objectives of this thesis. Laboratory tests were all done using column adsorption experiments to determine the removal of contaminants from drinking water.

3.2 Desk Study

Various Literatures related to the area of contaminant removal and column adsorption were reviewed to establish the relevant processes involved in adsorption. Data obtained from laboratory experimentations were also analysed.

3.3 Fabrication of Adsorbents

The adsorbents that are to be assessed in the removal of contaminants from drinking water were obtained from locally acquired materials. These adsorbents were produced using the following protocols;

3.3.1 Preparation of Zeolite

The procedures used in preparing both raw and surfactant modified Zeolite are outlined below;

3.3.1.1 Raw zeolite

Kaolin was used as the aluminosilicate source in the preparation of Zeolite Na-LSX. The Kaolin sample, which was obtained from Wassa clay, has high silicon and aluminium contents and usually dissolves to form Zeolite when alkaline conditions prevail (Shoumkova, 2011). A known mass of kaolin was then calcinated in the furnace for about two (2) hours at a temperature of 600°C. Metakaolin was thus produced. This product is a more reactive form of the kaolin. The sample was then combined with

sodium hydroxide through the process of alkaline fusion by putting the combined product in the furnace at a temperature of 600°C for an hour after which the sample was ground and water added to form slurry. The slurry was crystallized in an oven at 80°C for twenty-four (24) hours after which the crystallized product was quenched. The sample was filtered with distilled water in order to ensure a near neutral pH. The prepared zeolite is shown in plate 3-1.

3.3.1.2 Surfactant Modified Zeolite (SMZ)

The produced SMZ, as shown in plate 3-2 was prepared using a concentration of 5 mg/l surfactant solution in the modification process. A calculated volume of the surfactant solution was added to a mass of the Zeolite in a ratio 100 ml: 1g. The combined solution was mixed for 24 hours at a speed of 100 rpm. The solution was then filtered till the foamy filtrate resulting from the action of the surfactant was no more in the effluent.
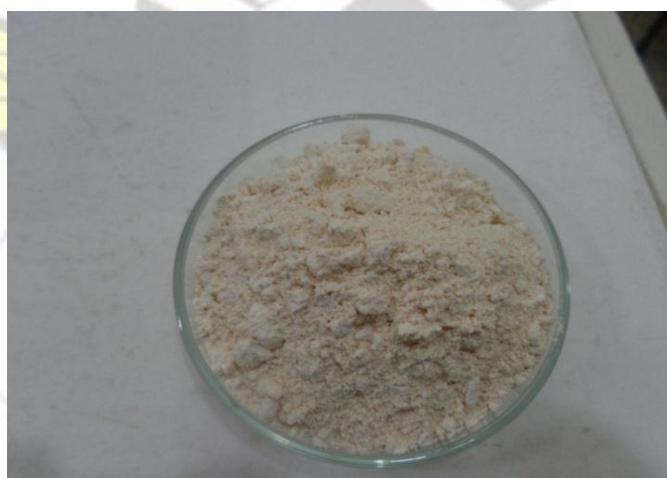
Plate 3-1 Raw Zeolite
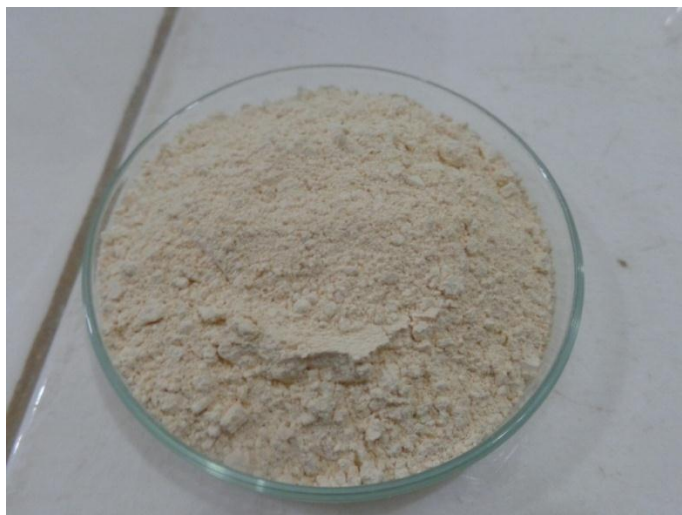
Plate 3-2 Surfactant Modified Zeolite

3.3.2 Preparation of Iron Oxide Coated Sand

The sand used in the coating process was obtained from river sand. The sand grains were washed to rid it of dirt and debris. It was then dried and sieved using standard sieve sizes to get the desired grain diameters of 0.6 mm.

The preparation process further continued with the soaking in batches of the sand in HCl solution for 24 hours after which it was air dried. The sand was then soaked in NaOH solution for another 24 hours and air dried. A total of five (5) kilograms of sand were prepared. The soaking of the sand grains in acid and later base was done to get rid of any contaminant attached to the grains that couldn't be removed by the washing with water. The coating process of the sand grains was done with a combination of Ferrous (II) sulphate ($FeSO_4.7H_2O$), Sodium Hydroxide (NaOH) and Sodium bicarbonate ($NaHCO_3$) solutions. The solutions were combined at a pH of 5 to make certain the conversation of the ferrous oxide to ferric oxide just as the solution gets onto the sand grains. Plate 3-3 is a sample of the produced IOCS adsorbent.
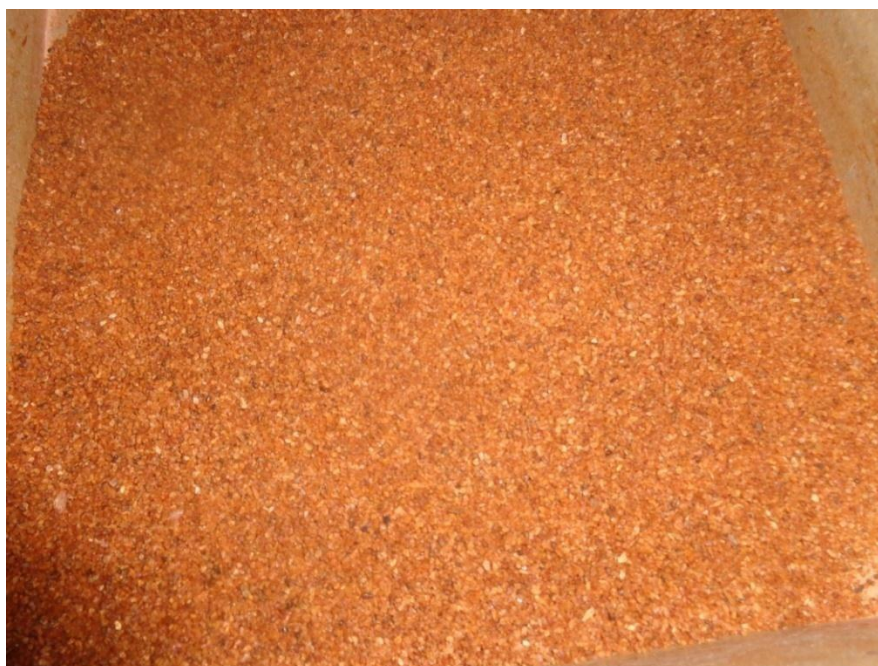
Plate 3-3 Prepared Iron Oxide Coated Sand

3.3.3 Aluminium Oxide Coated Charcoal

Plate 3-4 is an image of the coated charcoal. The charcoal used in the preparation of the Aluminium Oxide Coated Charcoal (AOCC) was washed and graded to a range of 0.8-1.12mm diameter. The virgin charcoal of specific mass was soaked in 0.5M of $Al_2(SO_4^3)$ in an aluminium basin. The pH of the solution was taken after 10 minutes. The mixture was continuously stirred with a mechanical stirrer at a speed of 100 rpm for 30 minutes and allowed to stand for another half hour. The excess solution was drained and the charcoal air-dried. The charcoal was then by first neutralizing them with 3M Ammonium Hydroxide solution for 10 minutes and air-dried to complete one coating cycle. The coating process was repeated to ensure as much Aluminium coating as possible. The dried sample was sieved and vigorously rinsed with deionised water in order to rid any loosely bound aluminium oxides and also to separate granular aluminium oxide coated media from any precipitate. The washed sample was the air-dried and stored for use (Sadik, 2012).

Plate 3-4 Aluminum Oxide Coated Charcoal

3.4 Characterization of Adsorbents

The adsorbents used in the experimental process were characterized using a number of techniques. Their thermal stability was analyzed using the Perkin Elmer Thermogravimetric Analyzer. All three adsorbents had their mineralogy and crystallinity determined by the use of X-ray Diffraction (XRD). The morphology of each adsorbent was also determined with the help of the Scanned Electron Microscope (SEM) while the Energy Dispersive X-ray (EDX) and X-ray fluorescence (XRF) gave the individual elements that make up the adsorbents

Phase identification was performed by XRD as well as phase purity determined. During this activity, the adsorbent sample is subjected to an x-ray beam ray. The intensity of the emergent rays is recorded as a function of the deflection angle. The distance between the crystal cells was determined. The XRD patterns were identified by comparing them with reference diffractograms (Von-Kiti, 2012).

For the EDX analysis, the sample was bombarded by the SEM's beam. The relative abundance of the emitted x-rays versus their energy was measured by the EDX detector.

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The energy as determined from the voltage measurement for each incident ray was sent to a computer display and further data evaluation.

Samples were then rinsed with distilled water and transported to an inductive couple plasma which is a high temperature zone. The samples were heated to different states to produce characteristic optical emissions. These emissions were separated based on their respective wavelengths and their intensities were measured. The intensities are known to be proportional to the concentration of analytes in the aqueous sample to obtain the elemental composition.

For thermogravimetric analysis, the sample was subjected to heat for a specific time. The thermally activated sample events were recorded and expressed as weight loss or weight change for the given time. SEM was used to determine the morphology of the zeolites. The size of zeolites studied with this apparatus was between 20nm and 20µm. A beam of incident electrons in an electron column was generated from the SEM. An SEM image was created as the electron beam scanned the surface of the zeolite sample creating a pattern on the detector (Von-Kiti, 2012).

3.5 Model Water Preparation

The model water used in the experiments was prepared using the groundwater quality of Northern Ghana as a guideline, shown in table 3-1. Distilled water was spiked of with Sodium Fluoride (NaF), Sodium Bicarbonate ($NaHCO_3$), Sodium Nitrate ($NaNO_3$), Sodium Nitrite ($NaNO_2$), Dipotassium Hydrogen Orthophosphate (K_2HPO_4), Ferrous Sulphate ($FeSO_4.7H_2O$) and Manganese Sulphate hydrated ($MnSO_4.H_2O$) to prepare individual contaminant solutions.

Table 3-1: Groundwater quality of Northern Ghana

pH	6.9-7.5	Mg^{2+}	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)	397-4.6	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)

3.6 Continuous Flow Adsorption Experiments

The column experiments, shown in plates 3-5 (a and b) and 3-6 were carried out in glass columns of length of 198 mm, internal diameter of 48 mm and thickness of 2 mm. The columns were first lined with a supporting media of washed sand grains (1mm diameter) to a depth of 35 mm. The adsorbents were added to the supporting media to a depth of 65 mm. A room of 40 mm was left above the adsorbent to allow for the supernatant of the model water and 30 mm for free board.

In order to ensure constant flow through of the model water through the columns, an overhead gallon was placed on an elevated platform to flow by gravity into the constant head gallon feeding the columns. The flow rate of the influent was 13 ml/min for all columns of the AOCC adsorbent. In the case of SMZ, its influent flow rate started from 8 ml/min. The effluents from the columns were sampled at given time intervals for the first hour, then the second, fourth, eighth, twenty fourth hours. Samples were then taken after every twenty-four hours for the five (5) days. All experiments were conducted under room temperature. The effluent samplings were done at different time intervals and the necessary analytical method applied to determine the concentrations of the contaminant under investigation were used.

Plate 3-5a Adsorption Column set ups for AOCC

Plate 3-5b Adsorption Column set ups for AOCC

Plate3-6 SMZ Setup with Stirrer Used in Contaminant Removal

3.7 Contaminant Measurements

The contaminants that were assessed include Fluoride, Nitrate Nitrite Iron Manganese and Phosphate.

3.7.1 Fluoride Measurement

A number of standard solutions were prepared from a 1000 mg/l stock fluoride solution. The potentiometric method, which involved the use of the ion selective electrode, was used. The WTW F 800 fluoride meter was used in measuring the potentials of the standard solutions. Equal volumes (1:1 ratio) of the fluoride solution and Total Ionic Strength Adjustment Buffer (TISAB) were mixed. Fluoride ion activity relies on the

solutions total ionic strength and pH, and on fluoride complex species. Adding an suitable buffer provides a nearly uniform ionic strength background, adjusts the pH, and breaks up complexes so that the electrode measures concentration (Fawell *et al*., 2006; Sun *et al*.,2011). The values obtained from the measured potentials were used in the plotting of a standard curve of potentials verses fluoride concentrations. The linear regression model was used to determine the linear equation of the graph.

The fluoride concentrations of the water samples were obtained by measuring the potentials using the WTW F 800 fluoride meter. The water samples were mixed with TISAB in a 1:1 ratio. Using the initially derived standard curve/ equation, the concentration of fluoride in sampled solutions was calculated

3.7.2 Nitrate, Nitrite and Phosphate Measurement

Nitrates, nitrites and phosphate were measured using a Hach DR 3900 spectrophotometer, shown in plate 3-7. The equipment is self-calibrating, thus requires no calibration curve. The procedure required a volume of ten (10) millilitre (ml) of the effluent into a sample cell. Powdered pillow containing the reagent for the measurement of the needed contaminant and allowed to stand for some the allocated time for a specific chemical. After that, prepared sample is put in the Spectrophotometer and the corresponding value read.

Plate 3-7. Hach Spectrophotometer used in Contaminant Concentration Measurements

3.7.3 Iron and Manganese Measurements

Atomic Absorption Spectroscopy (AAS) is a technique for determining the concentration of a particular metal element within a sample/ material. This technique makes use of a flame to atomize the sample; however, atomizers such as a graphite furnace can also be utilized.

In the most common implementation of AAS, a liquid sample containing the metal analyte is aspirated into an air-acetylene flame, causing evaporation of the solvent and vaporization of the free metal atoms. This process is known as atomization (*www.phy.ohiou.edu/~small/AAS.pdf)*

Light of a suitable wavelength for a particular element is shone through the flame, and some of this light is absorbed by the atoms of the sample. The amount of light absorbed is proportional to the concentration of the element in the solution, and hence in the original object. Measurements are made separately for each element of interest in order to achieve a complete analysis of an object. This makes the technique relatively slow to use. However, the equipment is highly sensitive and can measure trace elements

down to the part per million level, as well as measure elements present in minor and major quantities. The electronic energy levels for atoms are very specific for the element. As a result, the absorption of quantized energy from a monochromatic light beam of the appropriate wavelength can give selective information about the identity and amount of elements (normally metals) in a sample. In AAS, solutions containing metal ions are aspirated into a flame in which they are converted to a free atom vapour. A monochromatic light source is directed through the flame, and the amount of radiation of a specific energy is detected. In this way, the amount of metal present in the original sample can be determined. The AAS is a very sensitive technique for the determination of metals, and is used routinely in environmental work, for example, the determination of Iron and Manganese in natural waters, soils or paints. The analyte concentration is often determined from the amount of absorption.

3.8 Contaminant Removal Efficiency and Capacity

3.8.1 Removal Efficiency

The efficiency of contaminant removal in the experimental set up was calculated using the equation below;

$$R = \frac{Ci - Ct}{Ci} * 100$$ ……………… (eqn. 3.1)

R = removal efficiency at time, t (%)

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

C_i = initial contaminant concentration (mg/l)

3.8.2 Removal Capacity

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

$$q_e = \frac{(c_i - c_e)V}{m} \qquad \ldots\ldots\ldots\ldots\ldots \qquad \text{(eqn. 3.2)}$$

C_i = Initial contaminant solution concentration (mg/l) m

= Mass of adsorbent (g)

C_e = Contaminant effluent concentration at equilibrium (mg/l)

V = Volume of effluent solution (L)

CHAPTER 4:

RESULTS AND DISCUSSION

4.1 Introduction

The chapter presents analyses of the results obtained from the column experiments conducted to determine the adsorption performance of AOCC, SMZ and IOCS in the removal of six chemical contaminants namely Fluoride, Nitrate, Nitrite, Phosphate, Iron and Manganese from water.

4.2 Fabrication of Adsorbents

The three adsorbents (AOCC, SMZ and IOCS) used in conducting the column adsorption experiments were fabricated using existing protocols and locally acquired materials.

4.3 Characterization Results of Adsorbents

Results obtained from the characterisation of the adsorbents that were subsequently used in the contaminants removal are discussed below. All characterisation tests were conducted in University of Wolverhampton, United Kingdom.

4.3.1 Aluminium Oxide Coated Charcoal (AOCC)

The XRD, SEM and EDX test results for AOCC are discussed below with appropriate illustrations

4.3.1.1 X-Ray Diffraction (XRD)

The X-Ray Diffraction pattern (figure 4-1) was done to determine the mineralogy and crystallinity of the adsorbent under consideration. The peaks indicate minerals present in the adsorbent while the base gives an insight in to the crystallinity and purity of the adsorbent. The AOCC sample showed distinct peaks conforming to a highly crystalline sample. The main crystalline phase in the XRD of AOCC adsorbent is Calcite, making

up 99.7% of the adsorbent. The calcite is a major component of charcoal and with its known properties, will aid in the adsorption of contaminants from drinking water. The presence of this compound was validated by the EDX which showed calcium, carbon and oxygen peaks.
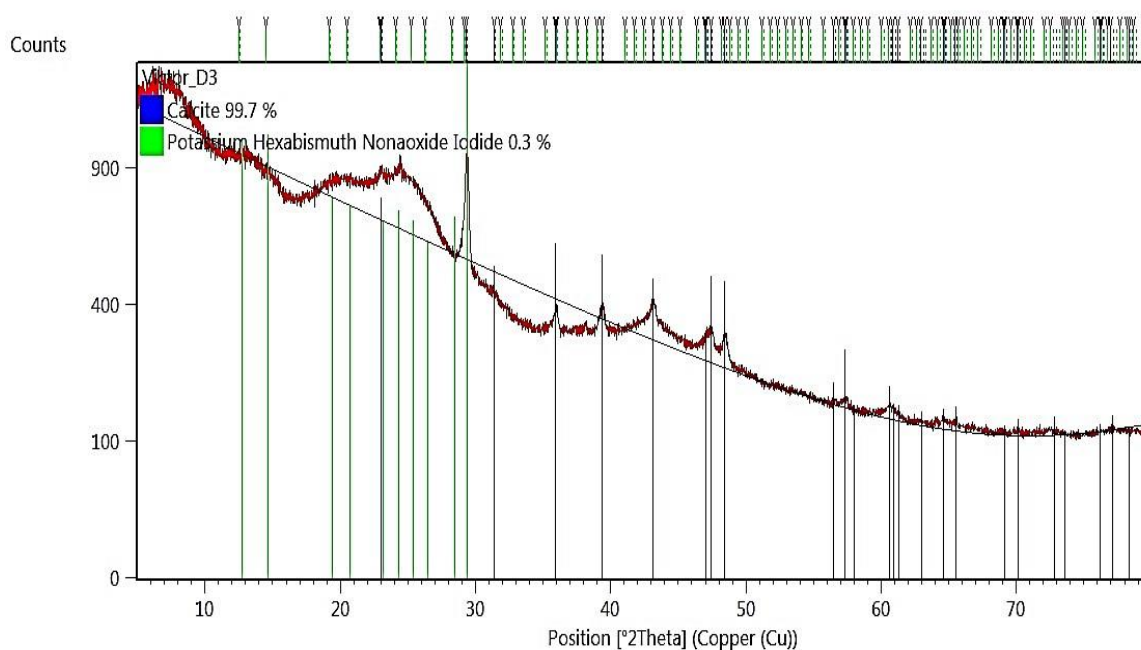
Figure 4-1 XRD of AOCC Adsorbent

4.3.1.2 Scanned Electron Microscopy (SEM) of AOCC

The SEM gives an image of the morphology of the adsorbent under study. SEM of the AOCC adsorbent is shown in Figure 4.2. The charcoal morphology portrayed a fibrous-like appearance. The image showed that charcoal has a large surface area with numerous pore spaces. Figure 4.2 B shows the SEM of charcoal from Bennett *et al*., (2004). Both images show abundant pore spaces and large surface area, properties that are relevant in most adsorbents. This porous quality is expected to aid in the adsorption process. Both SEM images were taken using an equal scale of 10μm.
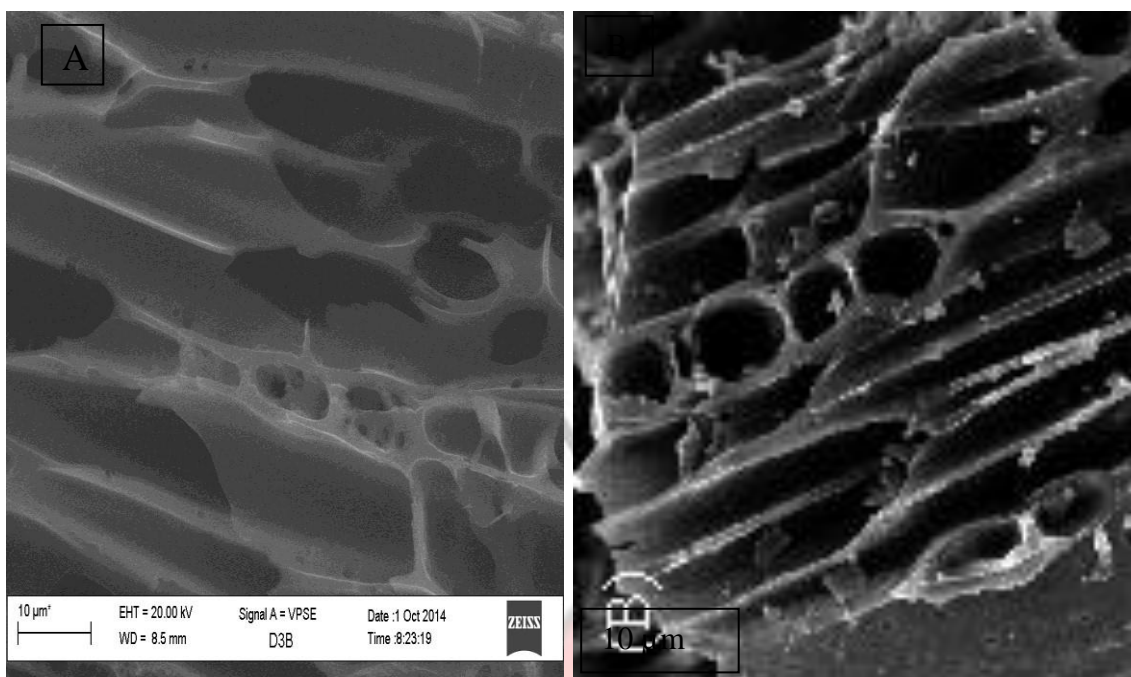
Figure 4-2 SEM image showing the porous nature of (A) Aluminium Oxide Coated
Charcoal (AOCC) and (B) Charcoal (Bennett *et al.* (2004))

4.3.1.3 Energy Dispersive X-ray (EDX) of AOCC

The EDX analysis is done to determine the elemental composition of an adsorbent. The intensity of each peak conforms to the quantity of element present. The EDX spectrum of Figure 4-3 shows several elements (Ca, C, and Al) occurring within a narrow range of the spectrum. However, the breakdown of percentage weights gives their actual weight in the adsorbent. The percentage weight compositions of the elements are showed in Table 4-1.

The EDX spectrum of AOCC reveals Aluminium and Oxygen of comparable weighting. This confirms that the process of aluminium Oxide coating onto charcoal surface was effective. The Aluminium Oxide is expected to facilitate the adsorption process. Calcium carbonate (Calcite), a major component of charcoal, was highly represented. Traces of other elements like Potassium, Sodium and Sulphur are also visible in the EDX diagram as interlayer ions.
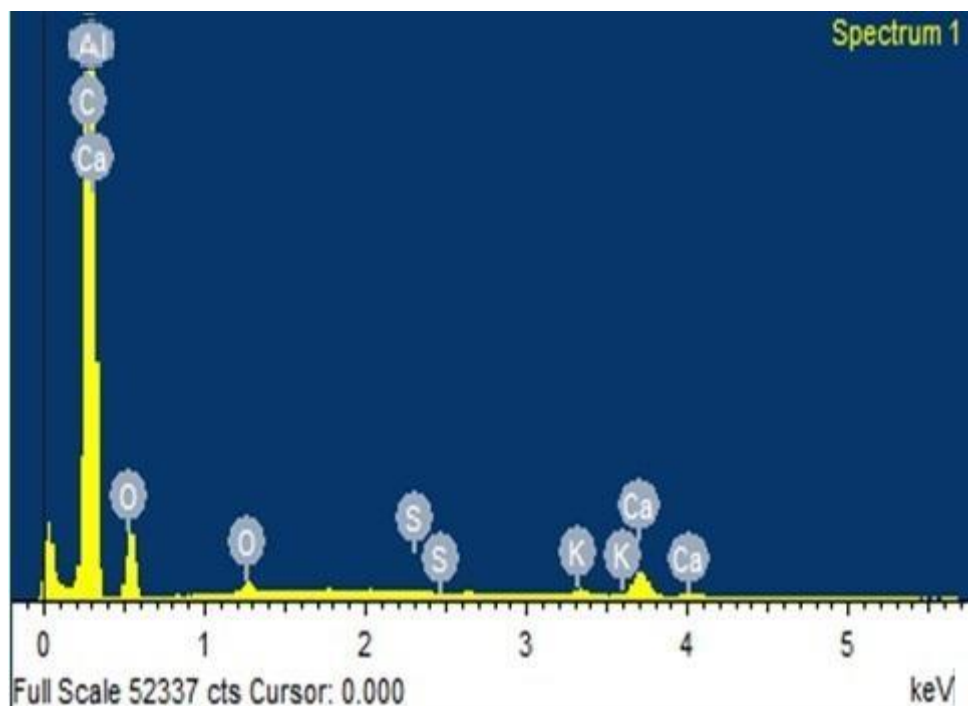
Figure 4-3 EDX of AOCC showing the constituent elements

Table 4-1 Elemental composition of AOCC

Element	Weight %
C	34.27
O	28.06
Al	26.31
Ca	11.01
K	0.17
Na	0.12
S	0.06
Total %weight	100.00

4.3.2 Iron Oxide Coated Sand (IOCS)

In the section below, the XRD, SEM and EDX test results of the IOCS adsorbent have

been presented.

4.3.2.1 X-ray Diffraction (XRD)

The XRD Pattern of the IOCS adsorbent shown in figure 4-4 gives the mineralogy and crystalline nature of the adsorbent. Major mineral that occurred in the XRD was Quartz, a major component of sand. Quartz made up 96.2% of the adsorbent. The presence of the iron oxide is expected to aid in the adsorption process.
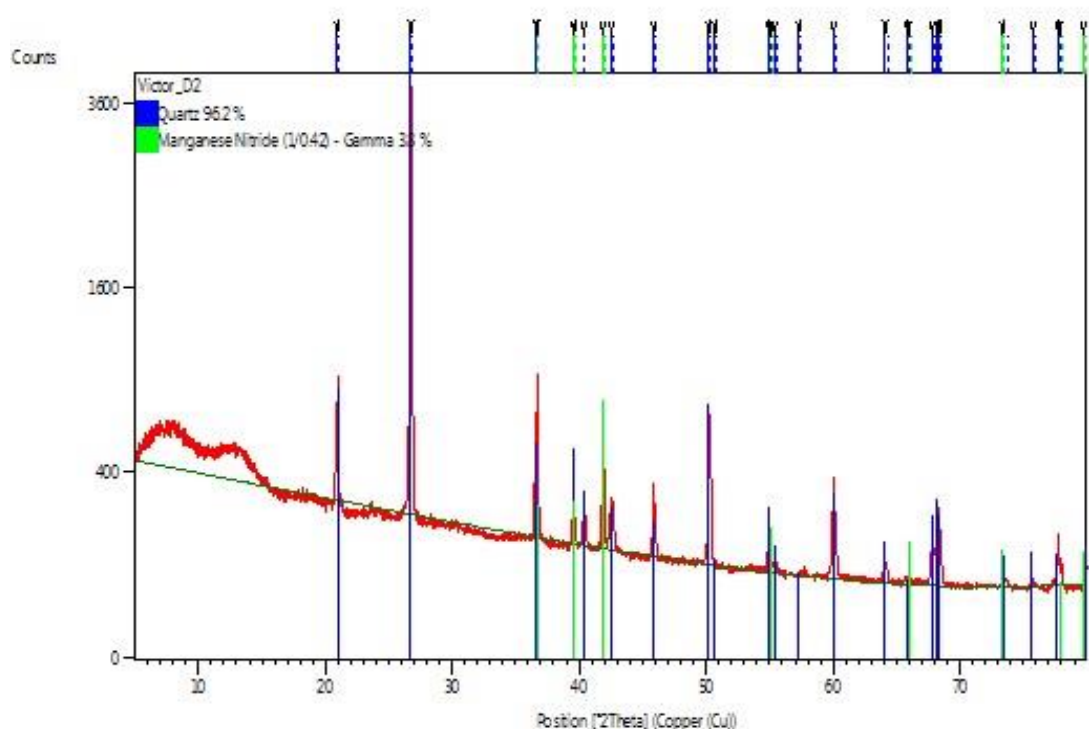
Figure 4-4 XRD of IOCS Adsorbent

4.3.2.2 Scanned Electron Microscopy (SEM) of IOCS

The SEM Image of the IOCS adsorbent as shown in figure 4-5 gave an insight into the coating of iron oxide onto the sand grains. Although there is no clear cut morphology for the IOCS sample, it corresponds to SEM images of IOCS by Sharma (2001). The SEM image depicts the adsorbent as being amorphous. However, the coating process is expected to increase porosity. This will help in the adsorption of the adsorbate onto the adsorbent.
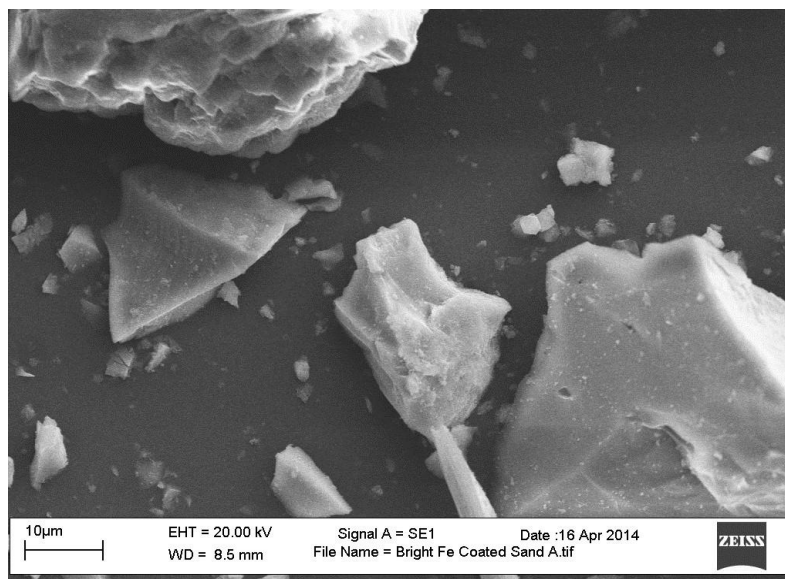
Figure 4-5 SEM Image of IOCS Adsorbent

4.3.2.3 Energy Dispersive X-ray (EDX) of IOCS

The EDX spectrum (figure 4-6) revealed that Silicon and Oxygen were the two major elements in the adsorbent. The EDX results obtained shows that iron features prominently in the coating onto the sand grains. The presence of iron in the IOCS was high in terms of percentage weights (11%). The coating formed a third of the silica content, which is the highest element, even though the coating was done a three times. The percentage weight of the elements in the adsorbent is shown in Table 4- 2.

Compared to the EDX results presented by Sharma (2001), where the IOCS was obtained from groundwater treatment plants, iron and oxygen had high percentage weight values. Sharma (2001) obtained his results because the sand grains were used in water treatment plants for Iron removal from groundwater. From his work, the sand grains had been coated many times with varying concentrations of iron oxide. The iron oxide coating for this work was done in three complete coating cycles. The aim was to achieve an effective coating to enhance contaminants removal from drinking water. Traces of other elements like sulphur, sodium, potassium and aluminum were also visible in the EDX diagram as interlayer ions.
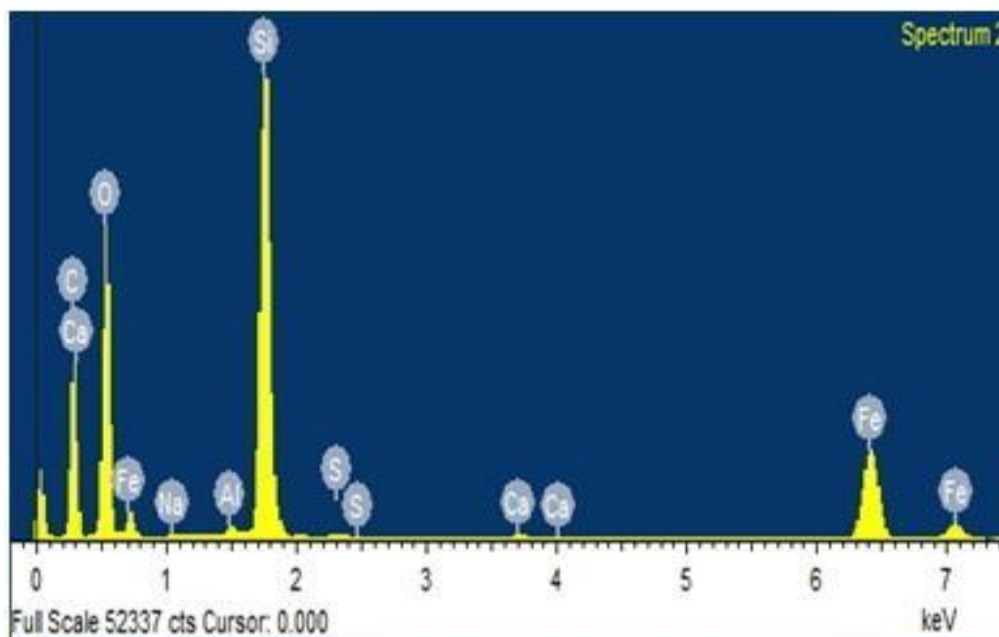
Figure 4-6 EDX of IOCS Adsorbent

Table 4-2 Percentage Elemental composition of IOCS

Element	Weight %
Si	31.36
O	20.66
C	16.26
Ca	14.28
Fe	11.27
S	2.02
Na	2.20
K	1.0
Al	0.95
Total %weight	100.00

4.3.3 Zeolite Na-LSX

The characterization results for SMZ are presented as follows;

4.3.3.1 X-ray Diffraction (XRD)

The XRD's of both raw and modified Zeolite were compared with that of a standard XRD of Zeolite Na-LSX (Figure 4-7). The peaks in the XRD pattern of the unmodified and modified Zeolite occur at the same points as observed in the standard Zeolite Na-LSX diagram, thus confirming that it is zeolite. The modified zeolite also has similar peaks occurring at the same point as that of the unmodified zeolite. Peaks of the raw zeolite are more distinct than those of the SMZs. The peaks of the SMZ however appear

shorter than those of the raw (unmodified) zeolite. This result indicates that the modification did not have an effect on the crystal structure of the zeolite but rather coated the surface of the zeolite (Malekian *et al.*, 2011)
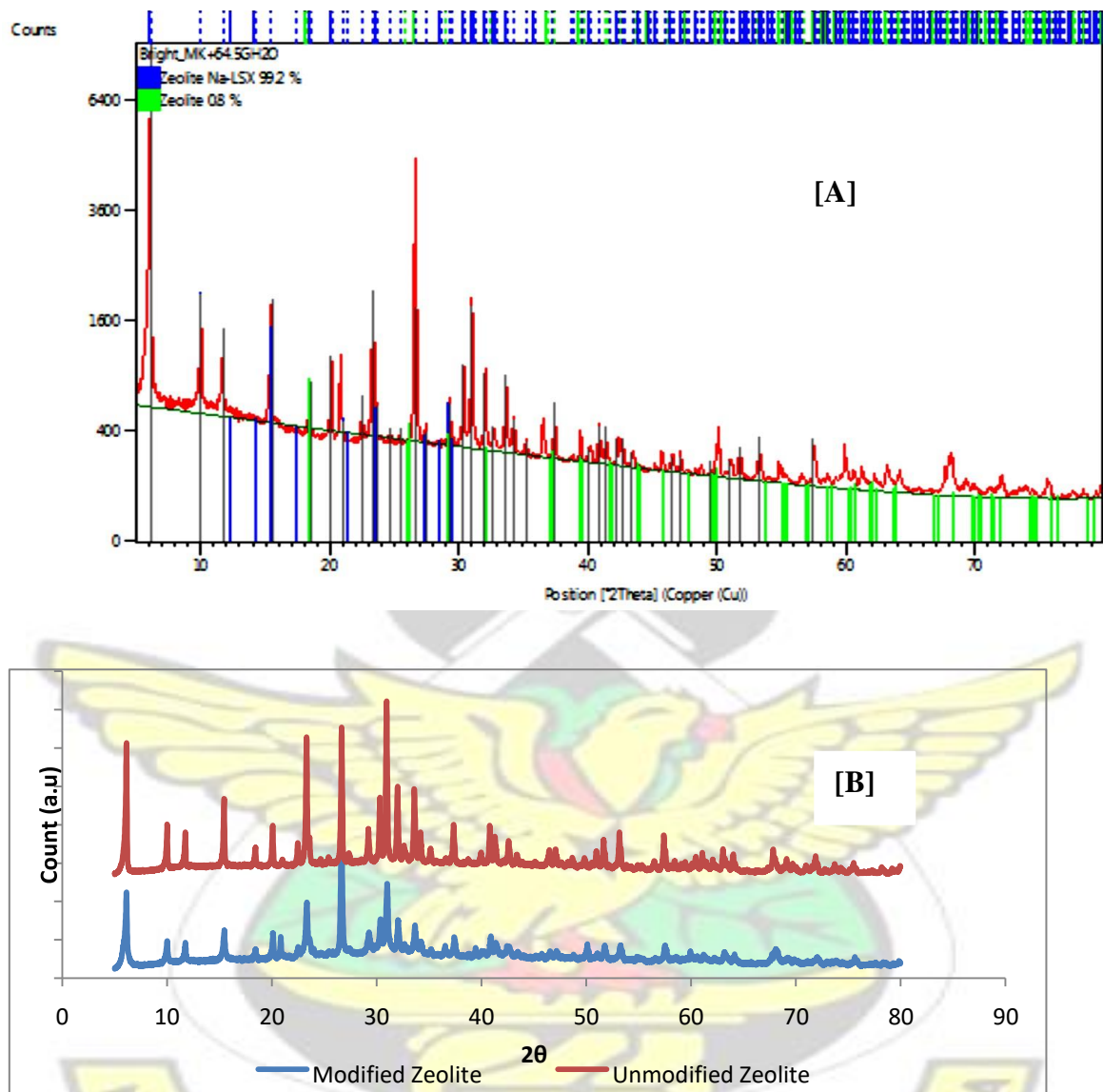
Figure 4-7: (A) XRD of standard Zeolite Na-LSX (B) XRD of Unmodified and Surfactant Modified Zeolite (SMZ)

4.3.3.2 Scanned Electron Microscopy (SEM) of Raw and Modified Zeolite SEM images show the morphology of samples under consideration. In the case of the synthesized Zeolite Na-LSX (figure 4-8), the image revealed an octahedral morphology of the zeolite similar to that in literature. The SEM of the modified zeolite showed a similar image, Figure 4.8b. However, the image of the raw Zeolite appeared more as

distinct or single units while that of the modified Zeolite show highly clustered molecules. This is an indication that the modification process did not affect the structure or shape of the zeolite. Results obtained confirm research works conducted by Ozdemir and Piskin (2013) and Hui *et al*., (2014). The clustered appearance in the SEM image of the modified Zeolite is expected to aid in the adsorption of anions from solution during the experimental phase.
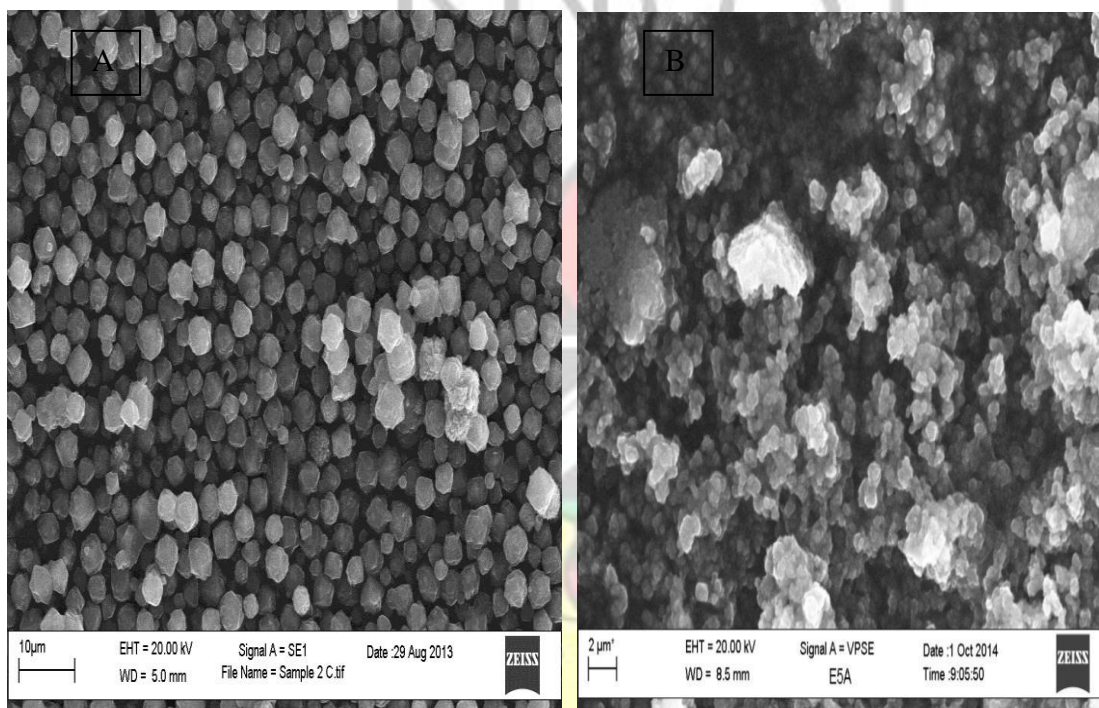
Figure 4-8 SEM image of (A) unmodified Zeolite Na- LSX (B) HDTMA- Br modified Zeolite Na- LSX

4.3.3.3 Energy Dispersive X-ray (EDX) of Zeolite Na-LSX

The elemental composition of the adsorbent is shown by their percentage weights in Table 4-3 below. From the table, it is evident that the Aluminium oxide and Silica, which are major components of Zeolite, are represented in the EDX of the Zeolite adsorbent. The pattern, shown in figure 4-9 confirms that the adsorbent is certainly Zeolite.
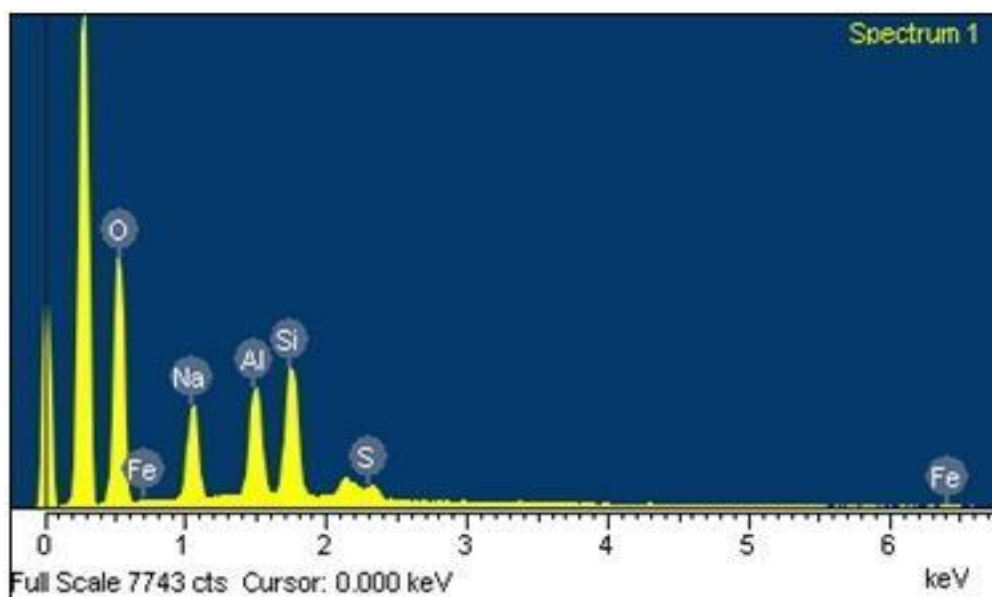
Figure 4-9 EDX Spectrum of Zeolite Na-LSX

Table 4-3 Percentage Elemental Composition of Zeolite Na- LSX

Element	Weight %
O	59.31
Na	14.55
Al	10.56
Si	13.39
S	1.81
Fe	0.39
Total Weight %	**100.00**

4.4 Column Adsorption Results

4.4.1 Standardization of fluoride meter

The fluoride meter used for the study was standardized by drawing fluoride standard curves using of various standard fluoride solutions and measuring their corresponding potentials. The standard curve (Figure 4-10) was used to determine the fluoride concentration for the various samples taken from the column experimental set ups.
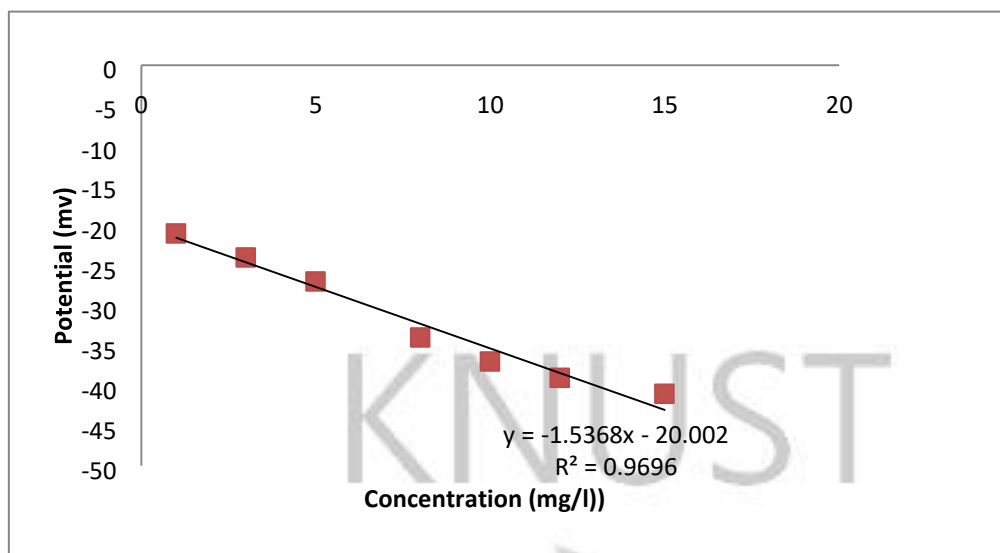
Fig. 4-10: Standard Curve for Fluoride Concentration Measurements

4.4.2 Column Adsorption for Fluoride Removal

Figure 4-11 shows the column experiments of AOCC and SMZ to remove fluoride from solution. The experiment was conducted with an initial fluoride concentration of 5 mg/l, 150 mg/l of bicarbonate solution and a pH of 5.5 ± 0.2.
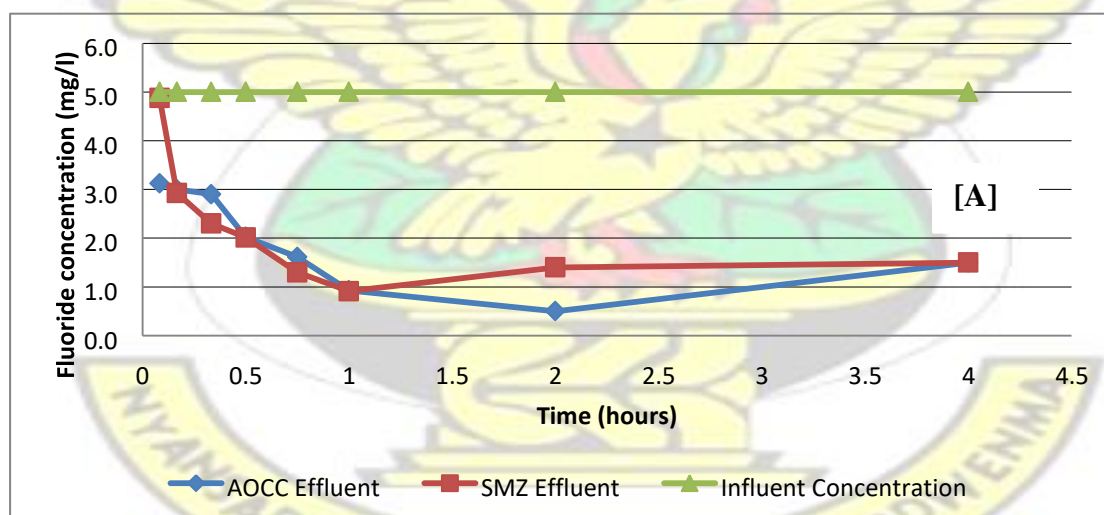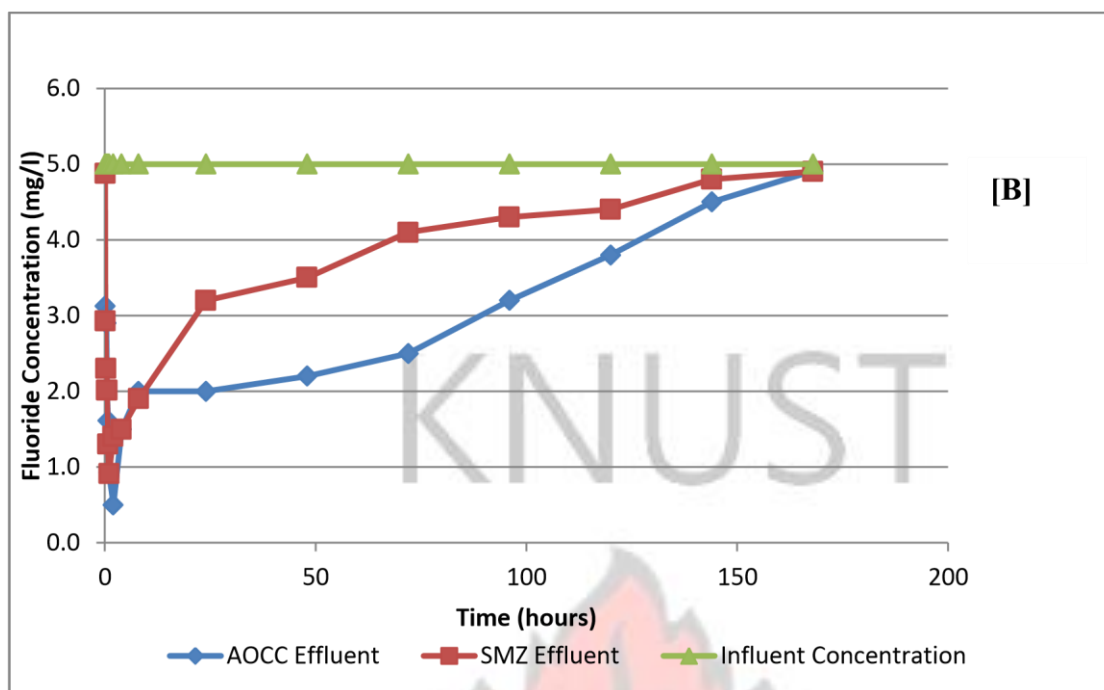
Figure 4-11 Short and Long Term adsorption of fluoride onto AOCC and SMZ.

Initial fluoride concentration: (5mg/l), $[HCO_3^-]$: (150 mg/l), pH: $5.5 \pm \mathbf{0.2}$

The Figure 4-11(A) shows the short term performance of AOCC and SMZ adsorbents in the column experiments. This was observed in the first four hours of running the columns. During this time, significant removal of fluoride ions from solution. The F ion removal increases as column run time progressed. By the end of the first hour SMZ had its highest fluoride removal efficiency of 81.8 % while the removal efficiency of 90 % for AOCC happened after the second hour. Fluoride removal efficiency of AOCC reduced from 90% to 70% and SMZ and 81.8% to 70.5 % respectively to attain a concentration of 1.5 mg/l by the end of the four hours. Despite the reduction in adsorption that took place, the percentage removal that was recorded for F ions in effluent solution still met the WHO guideline value of 1.5 mg/l allowed for drinking water.

Due to the continuous flow of influent through the media, there is a gradual decrease in the rate of fluoride adsorption onto the adsorptive sites of the Aluminium Oxide Coated

Charcoal (AOCC) and Surfactant Modified Zeolite (SMZ). This is seen in the long term graph of Figure 4-11(B). The decrease in adsorption is probably due to the exhaustion of adsorptive sites on the media owing to the large volume of influent solution that had passed through the media or the increase in pH of the influent solution resulting in fluoride to remain in solution. The fluoride removal of AOCC adsorbent showed higher removal efficiency compared to that of SMZ. AOCC had a higher removal than that of the SMZ probably due to the availability of the numerous pores in the charcoal as compared to that of the SMZ.

The graph also gave insight into the filter run time of the columns. The fluoride removal rate followed the Iwasaki curve, there is an initial ripening stage where minimal contaminant is removed from the filter column. It is then followed by a time where removal is at its highest and then the exhaustion of adsorptive sites on the adsorbent, leading to the effluent concentration increasing to that of the influent concentration. This implies that, In the case of AOCC, a filter run time of 8 hours was recorded. Using a flow rate of 13ml/min implied that, a volume of 6.2 l of water was treated during the filter run time and a fluoride removal capacity of 0.6 mg/g of the adsorbent was achieved. SMZ adsorbent also followed a similar trend of adsorption as that of the AOCC. A total volume of 1.92 l of water was treated by the filter column having a filter run time of 4 hours. At the end of the filter run time, a mass of 0.168 mg Fluoride had been removed per the mass of adsorbent used.

A study conducted by Emmanuel *et al,* (2008) compared the effectiveness of commercially produced activated carbon (CAC) and indigenously produced activated carbon (IPAC). Their research showed that the IPAC adsorbent gave a better fluoride removal than the CAC. Thus AOCC, also indigenously produced stands as an effective adsorbent given the characteristic of charcoal coupled with modification using the trivalent ion Al^{3+}. Onyango *et al*., (2005,2006) as cited by Mohapatra *et al*., (2009)

worked at modifying low silica zeolites with trivalent Aluminium ions and the adsorption of fluoride from solution by the modified zeolites was at reducing fluoride concentration below WHO recommended values than the adsorption of unmodified zeolite.

4.4.3 Column Adsorption for Nitrate Removal

The graph Figure 4-12 shows results of nitrate adsorption onto AOCC and SMZ at room temperature. Nitrate removal curve in Figure 4-12 shows both media underwent gradual adsorption at the start of the experiment before reaching the adsorption peak where the highest concentration of nitrate was removed. The nitrate removal curve for AOCC shows higher removal efficiency than that of SMZ.

Using the groundwater quality of Northern Ghana as a guide, a concentration of 100 mg/l of nitrate solution was used in running the column experiments in anticipation of an extreme case of groundwater contamination.

The short term graph for nitrate adsorption gives clear insight into the adsorption process of SMZ. The concentration of nitrate solution is reduced to the WHO guideline value from 20 minutes of running the column till the end of 4 hours. The adsorption of the AOCC on the other hand did not get to the guideline value until the second hour of running the column.
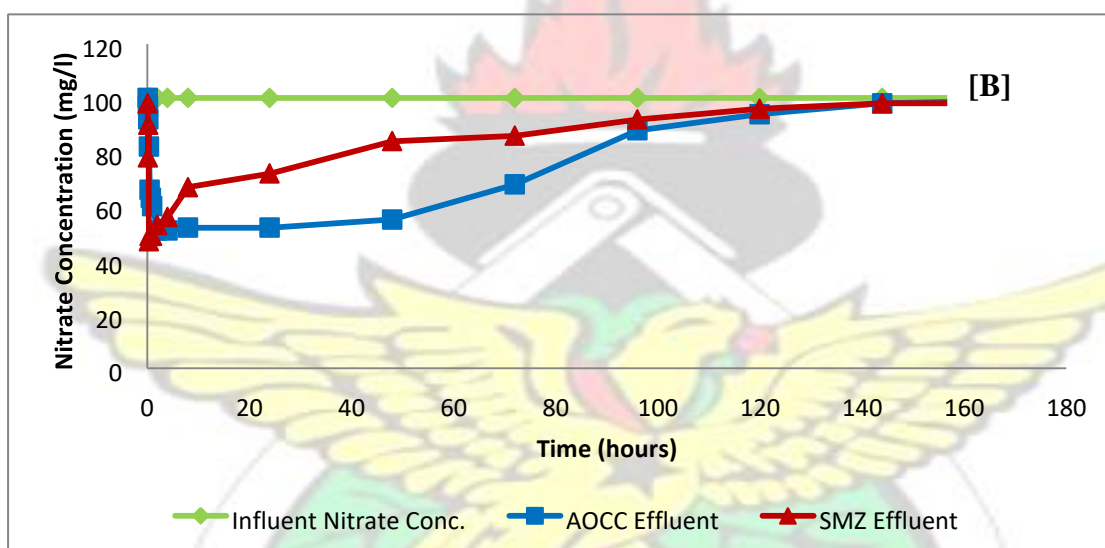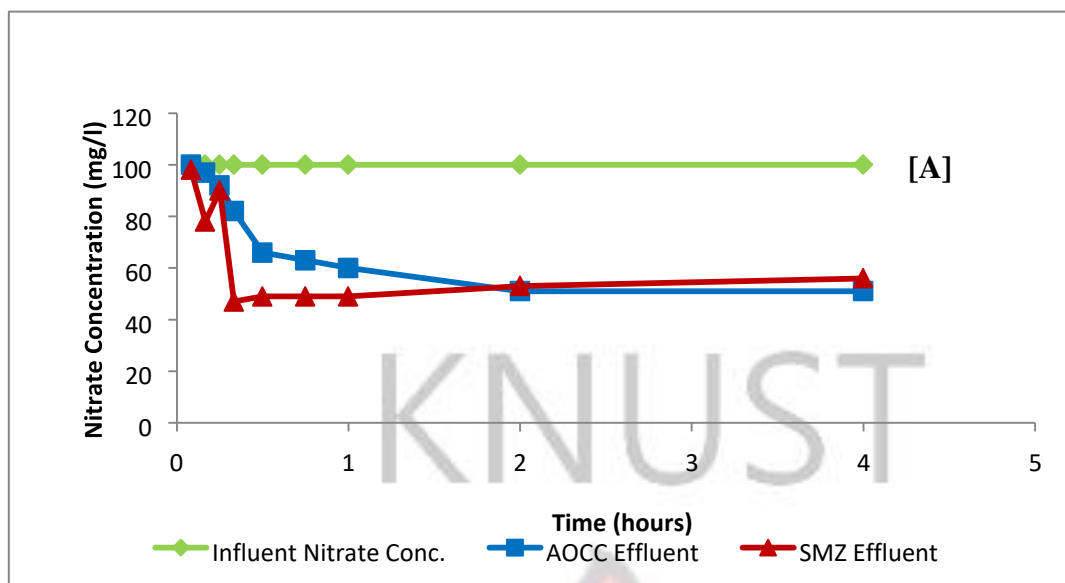
Figure 4-12 Short (A) and Long (B) Term adsorption of nitrate onto AOCC and SMZ.

Influent nitrate concentration: 100mg/l, pH: 7.5$\pm$ **0. 2**

On the whole, AOCC adsorption curve showed higher nitrate removal. At the start of the filter run, the amount of nitrate removed from the influent solution of 100 mg/l [NO_3^-] was minimal, that is 3% removal efficiency in 10 minutes. However, as the experiment progressed, the removal efficiency of the AOCC adsorbent increased. By the first hour, 40% of the nitrate concentration had been reduced from the influent solution.

The highest nitrate removal for AOCC was observed between 2-24 hours of running the filter columns, making the AOCC the adsorbent with the higher filter run time of 24 hours. In relation to nitrate removal, the SMZ had higher removal efficiency but with relatively shorter filter run time compared to that of the AOCC.

The adsorption of nitrate onto AOCC and SMZ adsorbents in this graph followed a step-wise process. Initial rapid adsorptions took place followed by a slower uptake and finally equilibrium. The initial nitrate adsorption can be attributed to the readily available adsorptive site on the adsorbents. The uptake is attributed to the diffusion of the adsorbate across the boundary layer to the exterior surface of the adsorbent particles. Secondly, secondary adsorption follows where there is the transportation of the nitrate ions from the exterior into the interior surface of the adsorbent. Equilibrium is established resulting from the exhaustion of adsorptive sites in the case of both adsorbents when the concentration of influent solution is almost the same as the effluent solution.

The trivalent charge of the aluminium oxide coating on the AOCC adsorbent media is probably responsible for the adsorption of more nitrates from solution compared to that of HDTMA-Br with a monovalent charge on the SMZ. AOCC had a better contaminant removal than that of SMZ. A total of 18.7 l of water was treated by AOCC during the filter run time of 24 hours. With a flow rate of 13 ml/min, a mass of 23.4 mg/g of nitrate was removed from the influent solution per mass of adsorbent used in the column experiment. In the case of SMZ, a total of 1.9 l of water was treated with the filter run time of 4 hours using a flow rate of 8 ml/min. A mass of 2.5 mg of nitrate was removed per gram of SMZ adsorbent used in the column experiment. By the end of the filter run time, a mass of 97.9 mg of nitrate was removed by the 40 g mass of SMZ.

Previous work investigated by (Kinoshita and Mihara, 2010) indicates that treated activated carbon with CaCl2 was a better adsorbent at removing Nitrate from water than untreated activated carbon. Hanafi and Azeema (2016) using activated carbon from rice straw (RS), observed that oxidized RS gave the best Nitrate removal from solutions compared to the action of other adsorbents including SMZ with between 100-200% HDTMA loadings. Rodriguez (2012), in removing Nitrate from aqueous solution had straw char being the best removal of nitrate than Lucerne char and charcoal. Thus, the Aluminium Oxide modification of Charcoal goes a long way in increasing its sorption abilities.

4.4.4 Column Adsorption for Nitrite and Phosphate Removal

The graphs in Figure 4-13 illustrate nitrite and phosphate adsorption using AOCC and SMZ adsorbents under room temperature conditions with an initial concentration of 10 mg/l and 5 mg/l for nitrite and phosphate respectively and a pH of 6.5 $\pm$0.3. Both adsorbents showed high contaminant removal from the influent solution. The graphs compare the effect of contact time on the removal of Nitrite and Phosphate using AOCC and SMZ.
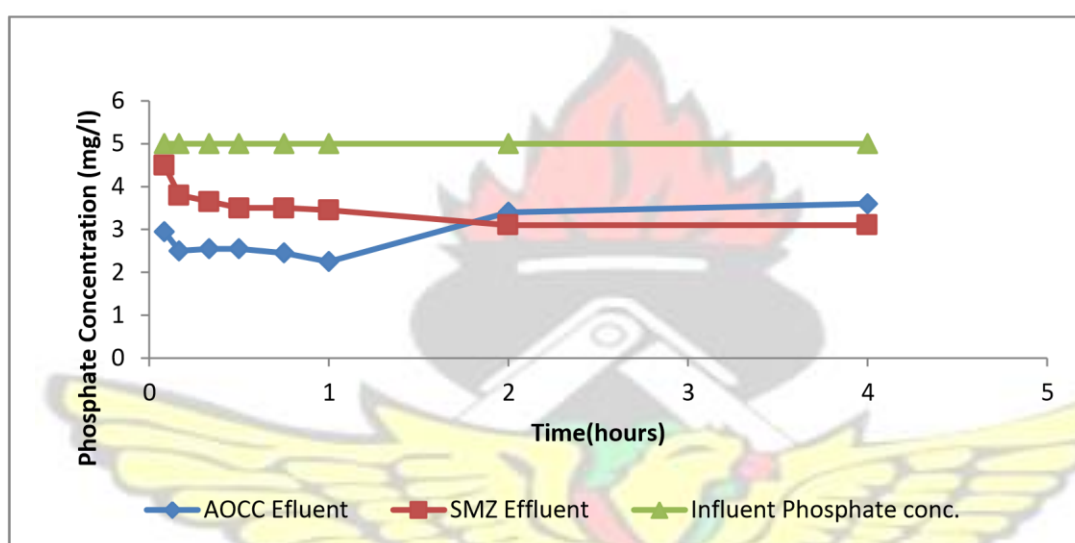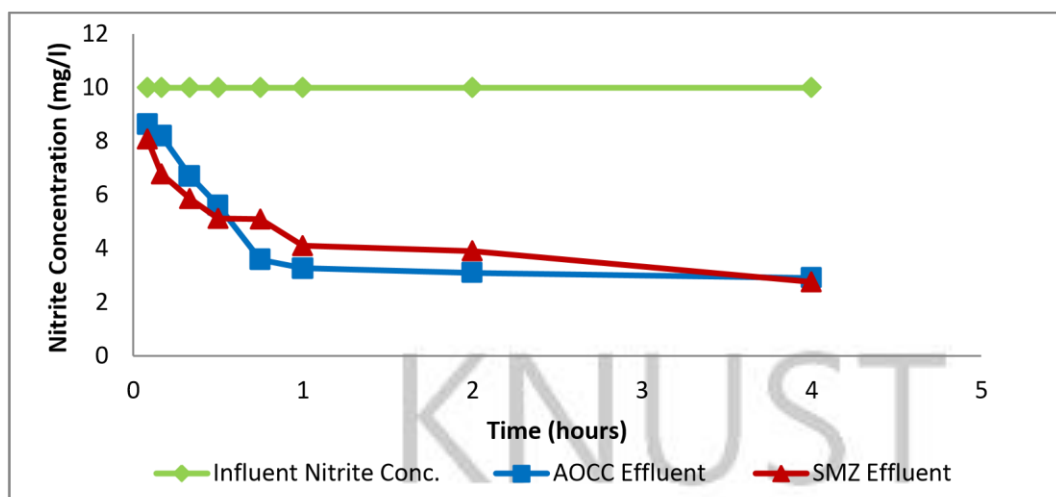
Figure 4-13: Short term adsorption of Nitrite and Phosphate onto AOCC and SMZ.

Influent Contaminant concentration: 10mg/l (NO_2) and 5mg/l (PO_4^{3-}), pH: 6.5±0.3

The short term graphs for both contaminants show fast contaminant removal. SMZ is seen to give a faster removal of the nitrite contaminants while the AOCC gave a faster phosphate removal. These curves, however, have shorter filter run times compared to their other adsorbent. By the end of the 4 hours, effluent concentration of both contaminants were almost as WHO and EPA-Ghana guideline values of 3 mg/l and 2 mg/l for Nitrite and Phosphate respectively.
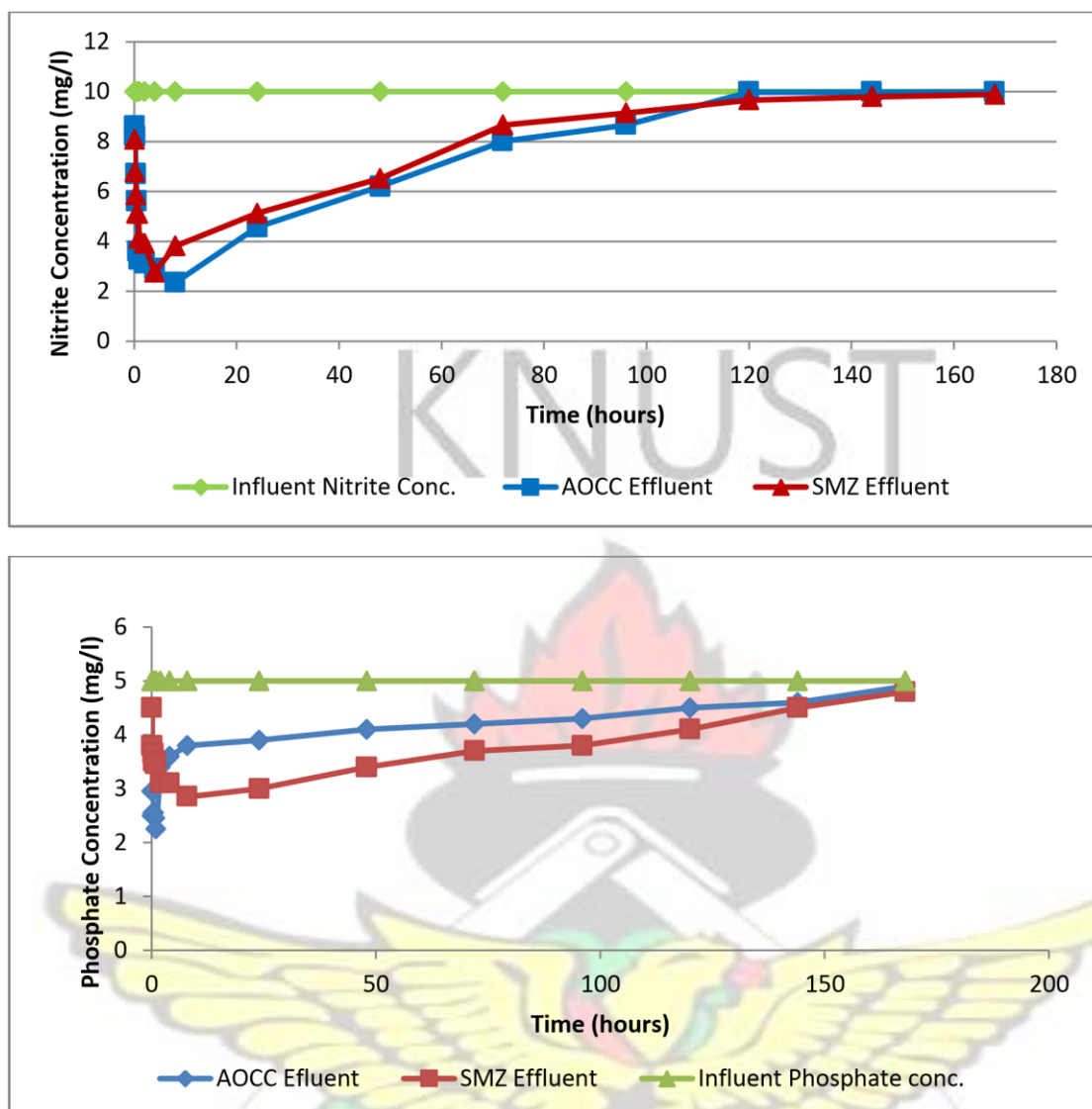
Figure 4-14: Effect of contact time on Nitrite and Phosphate adsorption onto AOCC and SMZ. Influent concentration: 10 mg/l (NO_2^-) and 5 mg/l (PO_4^{3-}), pH: 6.5±0.3

Both adsorbents went through a gradual contaminant removal phase (except for AOCC in phosphate removal) until the peak of their adsorptions took place. An inverse relationship is seen to exist between the adsorbents in term of the one with a better performance for the contaminants. By the end of the column experiments, AOCC performed better in Nitrite removal whilst SMZ did better for Phosphate contaminant.

In the AOCC curve for nitrite, the removal started quite slowly from the beginning of running the filter columns and picked up in the 45th minute, where a removal efficiency

of 64.1% was recorded. This process increased gradually through the experiment until the highest removal peak of 76.6% was recorded at the end of eight (8) hours. The AOCC adsorbent showed higher nitrite removal in terms of having a longer filter run time and removal efficiency compared to that of the SMZ adsorbent.

The SMZ curve for phosphate removal gave an initial removal efficiency of 10%. This increased till the highest efficiency (43%) was recorded after 8 hours of running the columns. The concentration of effluent obtained after the highest phosphate removal (2.85 mg/l) was higher than the EPA – Ghana recommended guideline value for effluent wastewater of 2 mg/l. A continuous decrease in removal efficiency is seen till the end of the filter run time where the lowest efficiency of 4% was recorded. The volume of water treated by the adsorbent by the end of the filter run time was 3.84 l. The AOCC column experiment gave the highest removal efficiency leading to an effluent concentration of 2.25 mg/l but the short filter run time prevents less water from being treated, hence SMZ was selected as the better adsorbent.

The initial fast removal adsorption that took place can be attributed to the readily available sites on the AOCC adsorbent while the SMZ took a longer time due to the limited adsorption area within which the influent had ample contact with the adsorbent. Work done by Guan et al., (2009) as cited by Shoumkova (2011) used low calcium zeolite and saturated it with Na^+, $Mg^{2+,}$ Ca^{2+}, Al^{3+}, and Fe^{3+} ions. Fe and Al showed complete removal of phosphate while Na^+ zeolite had the lowest phosphate removal. The results obtained in the phosphate removal confirm their results as SMZ had its least contaminant removal with phosphate.

Insight into the filter run time of the columns is clearly seen from the graphs. Contaminant removal using both adsorbents followed the Iwasaki curve. An initial ripening stage where minimal contaminant is removed from the filter column, followed by a time where removal is at its highest and then the exhaustion of adsorptive sites on

the adsorbents leading to an increase in effluent solution concentration. In the case of AOCC, Flow rate of 13 ml/min was used. Filter run times of 8 and 2 hours were recorded for nitrite and phosphate respectively. This led to the treatment of 6.24 l and 1.56 l of water during which time a nitrite and phosphate removal capacity of 1.20 mg/g and 0.11 mg/g for the AOCC adsorbent were attained. AOCC adsorbent removed 48 mg of nitrite and 4.4 mg phosphate from solution.

The SMZ, following the same adsorption trend as that of the AOCC had a total volume of 1.92 l (NO_2^-) and 3.84 l (PO_4^{3-}) of water treated with a filter run time of 4 and 8 hours respectively. At the end of the run time, a mass of 0.35 mg NO_2^- had been removed per mass of adsorbent used while 0.21 mg/g was recorded for phosphate. The end of the filter run time led to the removal of 14 mg NO_2^- by the 40g of SMZ.

Nitrite removal results obtained by Hanafi and Azeema (2016) gave oxidized rice straw (activated carbon) as an effective adsorbent compared to adsorbents including SMZ with 100-200 % HDTMA loadings.

4.4.5 Column Adsorption for Iron Removal

The Figure 4-15 shows the adsorption of iron onto Iron oxide coated sand adsorbent over a twelve-hour period. The experiment was conducted at room temperature, with initial Iron concentration of 0.5 mg/l. The concentration of solution was used with the ground water quality of Northern Ghana international standards as a guide. Iron concentration in the water is very low, the highest being 0.004 mg/l, far below the aesthetics based US-EPA guideline value of 0.3 mg/l.

The graph in Figure 4-15 below shows the adsorption of iron ions onto IOCS adsorbent. From literature, O'Connor (1971) and Anderson *et al*. (1973), iron oxide coated media is observed to play an important role in the oxidation and removal of iron. The iron

removal capacity increases as the already adsorbed iron serve as 'catalyst' for the adsorption of further iron (II) ions.
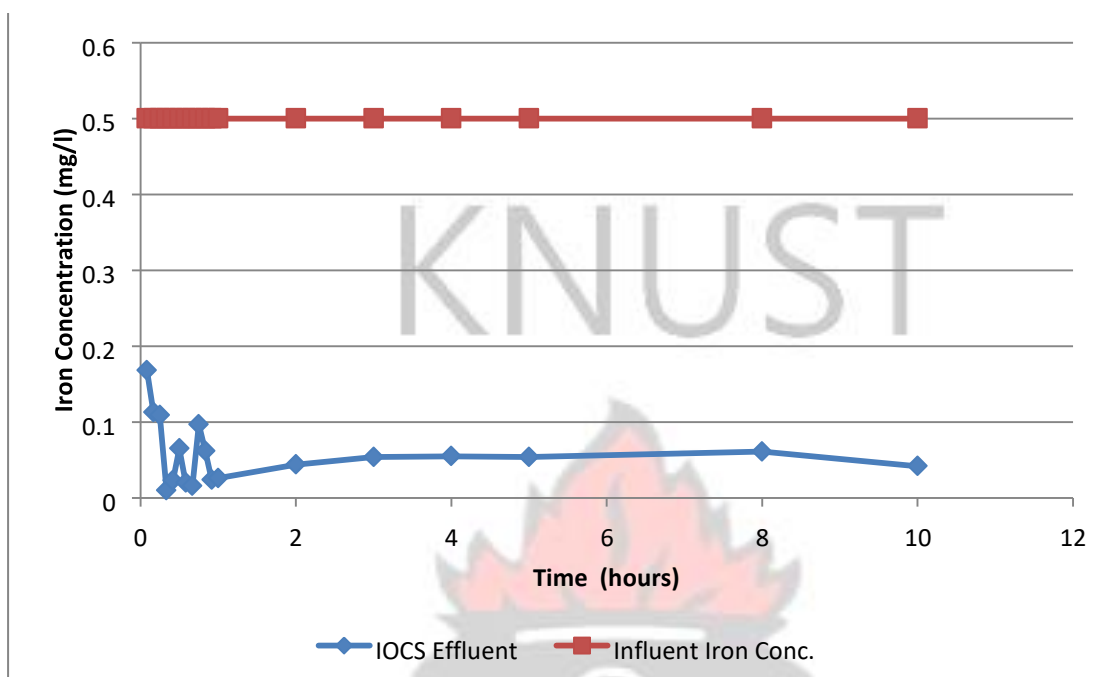
Figure 4-15: Effect of contact time on Iron removal with IOCS adsorbent. Influent

Iron conc.: 0.5mg/l, pH: 6.3$\pm$. **02**

Cox (1964) as cited by Sharma (2001) calls it 'catalytic iron removal' because the iron removal rate increases with the formation of coating as the previously retained iron oxide acts as the "catalyst" for further iron removal.

The ripening phase of the media in the experiment took place by the first twenty (20) minutes of running the filter after which the highest adsorption of iron is seen. The end of this duration gave the adsorption peak with the highest concentration of iron removal from the column.

The initial rapid adsorption can be attributed to the 'catalytic' effect of the iron oxide coated adsorbent, leading to the oxidation of the iron in solution onto the adsorbent. Secondly, the fluctuating uptake is also attributed mainly to the effect of pH on the adsorption process. The slight difference in pH during the running of the column

resulted in the oxidation of some of the iron ions in solution without getting adsorbed onto the adsorbent media.

The removal efficiency of the column set up for iron was evident right from the onset of the run time. By the end of the first twenty minutes of running the column, there was seen a 98% removal of iron ions from the influent solution which reduced to about 94.8% by the first hour. The removal efficiencies that followed wavered between 91.2-87.8% till the end of the filter run time. The ability of the media to remove iron at such efficiency is due to the uniformity of the coating on the sand and also the low guideline value for iron concentration in drinking water.

Due to the low concentration of initial iron concentration, there is very significant removal of iron from solution. All results obtained from the sampling times were well below the WHO recommended guideline value. A total of 7.8 l of water was treated by the column experiment and a removal capacity of 0.09 mg/g of IOCS adsorbent used.

4.4.6 Column Adsorption for Manganese Removal

The graph shows the adsorption of Mn^{2+} ions onto IOCS adsorbent. The experiment was conducted at room temperature with an initial Mn concentration of 0.4 mg/l.

The adsorption of manganese onto the IOCS adsorbent media shows a very fast ripening time which took place within the first five (5) minutes of running the filter column. This duration gave the adsorption peak at which point the highest concentration of manganese removal from the column was recorded.
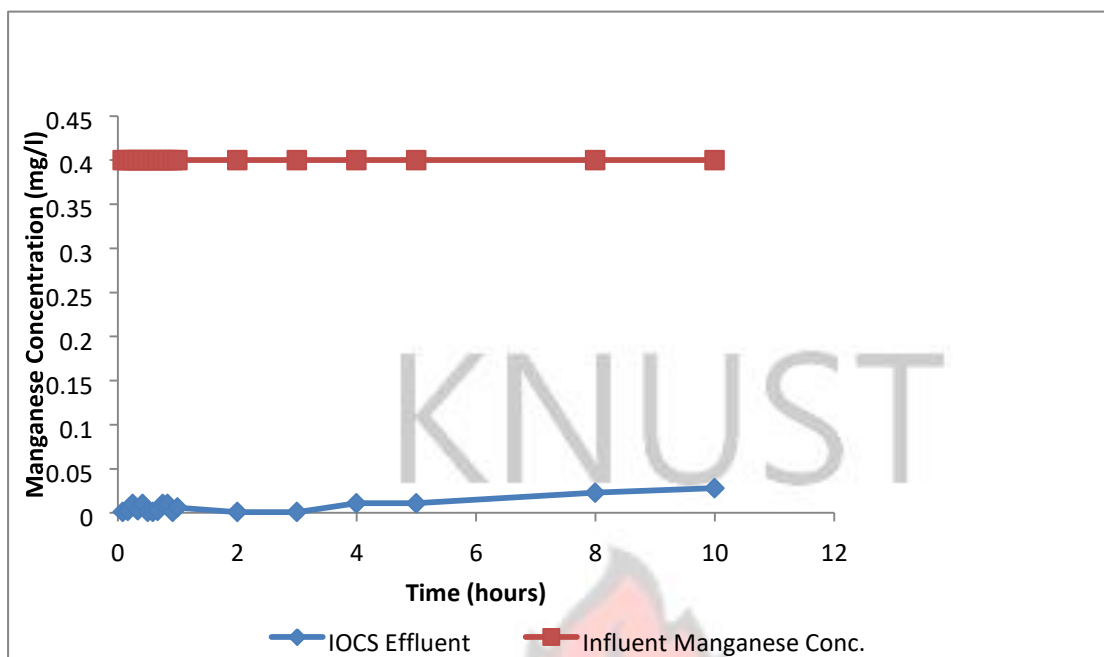
Figure 4-16: Effect of Time on the Removal of Manganese with IOCS Influent

Manganese conc.: 0.4 (mg/l), pH: 6.5±0.2

The catalytic nature of the adsorbent is believed to have caused the fast adsorption of the manganese ions in the influent solution. With both Iron and Manganese are found together in nature, treatment for iron removal can also be applied for manganese (Properzi, 2010). Since the Mn^{2+}ions, have the same oxidation state as that of Fe^{2+}, they were quickly adsorbed onto the IOCS media.

The adsorption of manganese onto the IOCS adsorbent media followed a step wise process. This started with an initial rapid adsorption followed by fluctuating uptake of manganese ions into the effluent solution. However, the fluctuation observed was not significant as the concentration of manganese effluent solutions obtained were below the concentration of 0.1 mg/l that could either affect pipelines, plumbing fixtures or humans as cited by USEPA (2004).

The removal efficiency of the column set up for manganese was evident right from the onset of the run time. By the end of the first five minutes of running the column, there

was a 99.75% removal of manganese ions from the influent solution which reduced to about 97.5% by the 50th minute. The removal efficiencies that followed wavered between 99-97% till the lowest efficiency values of (94.255 and 93%) were recorded in the last two hours of the filter run time.

The use of a relatively low concentration of influent manganese solution along with the effectiveness of the adsorbent media led to the high removal efficiency of manganese ions in the experiment. In the calculation of the removal capacity of contaminant by the IOCS adsorbent, it was realized that a removal capacity of 0.073 mg of Mn^{2+} ions were removed per mass of adsorbent utilized. Due to their similarity in valence, MOCS (Manganese Oxide Coated Sand) when used by Ndungutse (2014) in the removal of Manganese yielded very high manganese adsorption under aerobic conditions.

CHAPTER 5:

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The following conclusions have been drawn from the results that were obtained in this study;

- The three adsorbents, AOCC, SMZ and IOCS were fabricated successfully using locally acquired raw materials.

- The adsorbents characterization using the XRD, SEM and EDX tests were done. XRD results revealed AOCC to be dominantly Calcite (99.7%), IOCS had 96.2% of the adsorbent being Quartz and finally SMZ exhibited Zeolite Na-LSX as the mineral with 99.2% composition.

- SEM results on the adsorbents depicted the highly porous nature of the AOCC adsorbent for easy adsorption of the contaminants and having an amorphous structure; IOCS gave a complex structure with evidence of iron coating while an octahedral morphology for SMZ.

- The major elements in AOCC were Ca, C, O and Al; Si, O, C, Ca and Fe were the major elements in IOCS and lastly, SMZ had O, Na, Al and Si showed in the EDX results as major elements in the adsorbent.

- The adsorbents produced served as effective material for the removal of F^-, NO_3^-, NO_2^-, PO_4^-, Fe^{2+} and Mn^{2+} ions from drinking water in order to meet WHO guideline values of 1.5 mg/l, 50 mg/l ,3 mg/l ,2 mg/l 0.3 mg/l and 0.1 mg/l respectively.

- AOCC and SMZ were applied in column experiments for the removal of the tested anionic contaminants

- Results from the column experiments showed that the AOCC adsorbent performed better than that of the SMZ in the removal of the tested anionic contaminants except for Phosphates.

- Volumes of contaminant solutions treated by the end of the filter run time for AOCC were Fluoride (6.24 L), Nitrate (18.72 L), Nitrite (6.24 L), Phosphate (3.84 L).

- Removal capacities calculated for the AOCC adsorbent in anionic contaminants are 0.564 mg/g, 0.612 mg/g and 1.195 mg/g for Fluoride, Nitrate and Nitrite respectively. SMZ had a removal capacity of 0.206 mg/g for Phosphate.

- The IOCS adsorbent was used in the removal of cationic contaminant (Iron and Manganese). The adsorbent was very effective in their removal to levels far below recommended guideline values

- With a filter run time of 10 hours, total volume of 7.8 L for each contaminant solutions. Removal capacities of 0.089 mg/g and 0.073 mg/g for Iron and Manganese respectively were recorded.

5.2 Recommendations

- Characterization of exhausted adsorbent should be conducted the changes in the mineralogy, morphology and elemental composition of the AOCC, SMZ and IOCS.

- The AOCC and SMZ adsorbents can be regenerated to determine further usage of the adsorbents in adsorption of anionic contaminants from drinking water.

- Column experiments can be done to analyze the synergetic effects of anionic and cationic contaminants in the column adsorption process.

- Column experiments combining the tested adsorbents should be conducted to determine the efficiency of the media in removing the tested contaminants.

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APPENDICES

Appendix1 Standard Curve Used in Fluoride Concentration Determination

$y = -1.5368x - 20.002$
$R^2 = 0.9696$
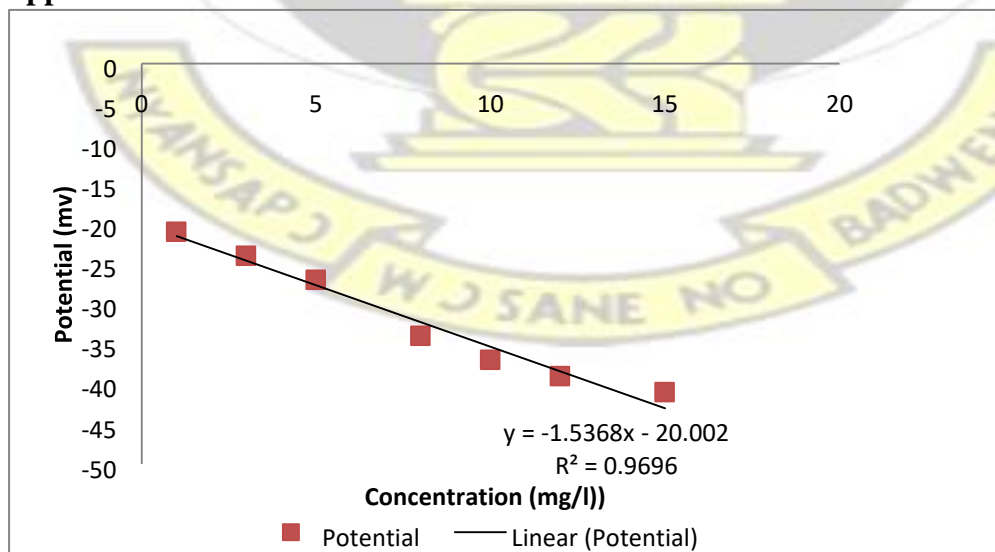
Appendix 2 Removal Efficiencies of Chemical Contaminants

i.   Fluoride Column Experiment Results

TIME(hours)	Fluoride conc. (AOCC)	Removal eff. (%)	Fluoride conc. (SMZ)	Removal eff. (%)
0.083333	3.1	37.53	4.9	2.42
0.166667	3.0	40.00	2.9	41.46
0.333333	2.9	42.00	2.3	54.00
0.5	2.0	59.49	2.0	59.68
0.75	1.6	67.73	1.3	74.00
1	0.9	81.46	0.9	81.81
2	0.5	90.00	1.4	72.02
4	1.1	78.00	1.5	70.00
8	1.5	70.00	1.9	62.00
24	2.0	60.00	3.2	36.00
48	2.2	56.00	3.5	30.00
72	2.5	50.00	4.1	18.00
96	3.2	36.00	4.3	14.00
120	3.8	24.00	4.4	12.00
144	4.5	10.00	4.8	4.00
168	4.9	1.83	4.9	2.00

ii.   Nitrate Column Experiment Results

TIME(hours)	Nitrate conc. (AOCC)	Removal eff. (%)	Nitrate conc. (SMZ)	Removal eff. (%)
0.083333	100	0	98	2
0.166667	97	3	78	22
0.333333	92	8	90	10
0.5	82	18	47	53
0.75	66	34	49	51
1	63	37	49	51
2	60	40	49	51
4	51	49	53	47
8	51	49	56	44
24	52	48	67	33
48	52	48	72	28
72	55	45	84	16
96	68	32	86	14
120	88	12	92	8
144	94	6	96	4
168	98	2	98	2

iii.   Nitrite Column Experiment Results

TIME(hours)	Nitrite Conc. (AOCC)	Removal eff. (%)	Nitrite Conc. (SMZ)	Removal eff. (%)
0.083333	8.63	13.7	8.08	19.2
0.166667	8.21	17.9	6.78	32.2
0.333333	6.71	32.9	5.86	41.4
0.5	5.61	43.9	5.12	48.8
0.75	3.59	64.1	5.1	49
1	3.27	67.3	4.11	58.9
2	3.1	69	3.91	60.9
4	2.91	70.9	2.76	72.4
8	2.34	76.6	3.81	61.9
24	4.56	54.4	5.12	48.8
48	6.21	37.9	6.54	34.6
72	8.01	19.9	8.66	13.4
96	8.66	13.4	9.14	8.6
120	9.98	0.2	9.66	3.4
144	9.98	0.2	9.79	2.1
168	9.99	0.1	9.88	1.2

iv.   Phosphate Column Experiment Results

TIME(hours)	Phosphate Conc. (AOCC)	Removal eff. (%)	Phosphate Conc. (SMZ)	Removal eff. (%)
0.083333	2.95	41	4.5	10
0.166667	2.5	50	3.8	24
0.333333	2.55	49	3.65	27
0.5	2.55	49	3.5	30
0.75	2.45	51	3.5	30
1	2.25	55	3.45	31
2	3.4	32	3.1	38
4	3.6	28	3.1	38
8	3.8	24	2.85	43
24	3.9	22	3	40
48	4.1	18	3.4	32
72	4.2	16	3.7	26
96	4.3	14	3.8	24
120	4.5	10	4.1	18
144	4.6	8	4.5	10
168	4.9	2	4.8	4

v.   IOCS results for Iron and Manganese column experiments

Time (hours)	Iron Conc.	Removal eff. (%)	Manganese Conc.	Removal eff. (%)
0.083333	0.168	66.4	0.001	99.75
0.166667	0.113	77.4	0.002	99.5
0.25	0.109	78.2	0.01	97.5
0.333333	0.01	98	0.003	99.25
0.416667	0.023	95.4	0.01	97.5
0.5	0.065	87	0.001	99.75
0.583333	0.02	96	0.001	99.75
0.666667	0.016	96.8	0.002	99.5
0.75	0.097	80.6	0.01	97.5
0.833333	0.062	87.6	0.01	97.5
0.916667	0.024	95.2	0.001	99.75
1	0.026	94.8	0.006	98.5
2	0.044	91.2	0.001	99.75
3	0.054	89.2	0.001	99.75
4	0.083	83.4	0.011	97.25
5	0.054	89.2	0.011	97.25
8	0.061	87.8	0.023	94.25
10	0.042	91.6	0.028	93