JIMMA UNIVERSITY

JIMMA INISTITUTE OF TECHNOLOGY

SCHOOL OF GRADUATE STUDY

FACULTY OF CIVIL AND ENVIRONMENLAL ENGINEERING

ENVIRONMENTAL ENGINEERING MASTERS PROGRAM

Sorptive removal of Arsenic from aqueous solution using activated carbon produced from coffee husk

By

Bona Getane (MSc.)

A Thesis submitted to Jimma University, Jimma Institute of Technology, Faculty of Civil and Environmental Engineering, Environmental Engineering Chair in Partial fulfillment of the requirements for the Degree of Masters of Science in Environmental Engineering.

February, 2019

Jimma, Ethiopia

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DECLARATIONS

I, Bona Getane, hereby declare that the thesis, entitled "Sorptive removal of Arsenic from aqueous solution using activated carbon produced from coffee husk", is entirely my original work. To the best of my knowledge, the work has not been presented for the award of MSc. degree or any other degree either in Jimma University or any other Universities. Thorough acknowledgment has been given where reference has been made to the work of others.

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Name (Internal examiner)   Signature   Date

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Name (Chair)   Signature   Date

ABSTRACT

Nowadays, arsenic removal from water is a major problem in many parts of the world. As recent studies document, groundwater from Ethiopian rift valley is also under the risk of arsenic contamination. Exposure to high level of Arsenic have been shown to cause acute health effects such as nausea, vomiting and abdominal pain. Long-term exposure to Arsenic is known to increase the risk of chronic diseases such as lung, skin, kidney, urinary and bladder cancers. The general objective of this study was to investigate removal of arsenic from aqueous solution by adsorption using activated carbon derived from coffee husk. In this study, batch adsorption experiments were conducted to examine the As (III) adsorption capacity of chemically activated coffee husk as the function of contact time, pH of the solution, initial Arsenic concentration, adsorbent dose, agitating speed, adsorbent particle size and desorption study parameters were investigated. The study showed that adsorption capacity increased with increasing time and equilibrium time reached 60 min maximum adsorption percentage was 56%. The adsorption of As was greatly dependent on pH of the solution. Generally, adsorption was remained that with increasing solution pH percent removal also increased. The amount adsorbed and percentage removal of As (III) was increased from 0.75 to 1.68 mg/g and 24.95% to 56% respectively as the amount of activated carbon was increased from 0.5 to 4 g. As initial As (III) concentration increases As (III) removal efficiency decreased from 79.8(%) to 43.9(%).The equilibrium adsorption data were better represented by the Freundlich isotherm ($R^2 = 0.9649$). The adsorption kinetics data of As adsorption followed well the pseudo-first order equation with the correlation coefficient $R^2 = 0.96$ and $K_f = 0.087$. The desorption experiment done using alkaline solution of 0.1M and 0.3 M of NaOH and desorption capacity was increased from 52.5% and 71.4% respectively. Thus chemically activated coffee husk could be used as a media for removal of arsenic from aqueous solution and the spent CACH can be regenerated and reused as desorption study reveals.

Key words: Activated carbon; Adsorption; Arsenic; Coffee husk; desorption; Removal

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ACRONYMS

As	Arsenic
ERV	Ethiopian Rift Valley
HDPE	High Density Polyethylene
US EPA	United States Environmental Protection Agency
WHO	World Health Organization
CH	Coffee Husk
MCL	Maximum Contamination Level
BAT	Best Available Technology
As (III)	Arsenite
As (V)	Arsenate
CACH	Chemically Activated Coffee Husk
POU	Point Of Use
AA	Activated Aluminia
POE	Point-Of-Entry
IBS	Iron Based Sorbent
PPB	Parts Per Billion
MF	Membrane Filteration
UF	Ultra Filteration
RO	Reverse Osmosis
NF	Nano Filteration
RPM	Rotation Per Minute

CHAPTER ONE

INTRODUCTION

1.1 Background

Arsenic (atomic number 33) is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the Earth's crust, 14th in the seawater, and 12th in the human body (Mohan and Pittman, 2007). It is a silver-grey brittle crystalline solid with atomic weight 74.9; specific gravity 5.73, melting point 817 ∘C at 28 atm, boiling point 613 ∘C and vapor pressure 1mm Hg at 372 ∘C (Mohan and Pittman, 2007). As an ultra-trace nutrient, arsenic deficiency leads to inhibited growth, although beyond its necessary level it causes toxic effect on plants, animals, and human beings (Mondal *et al*., 2017).

Arsenic is a natural component of the earth crust and is found in air, water, soil as a metalloid in the form of chemical compounds. It is very mobile in the environment and its mobility largely depends on the parent mineral form, oxidation state, and mobilization mechanisms (Nicomel *et al.,* 2016). In terms of oxidation state, arsenic can exist in four forms and among arsenic species, the most prevalent forms, which are commonly found in water, are the inorganic arsenite and arsenate in +3 and +5 oxidation states depending upon the relevant redox condition (Nicomel *et al.,* 2016).

Arsenic is one of the most toxic heavy metals which can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits (Benhima *et al.,* 2008). Even though exposure to arsenic can be through ingestion of arsenic-contaminated water or food and contact with arsenic-contaminated air, reports have shown that elevated levels of arsenic in drinking water primarily contribute to human arsenic toxicity in the world (Nicomel *et al.,* 2016).

The potential sources of arsenic contamination in water resources are either anthropogenic (i.e., gold mining, non-ferrous smelting, petroleum-refining, combustion of fossil fuel in power plants and the use of arsenical pesticides and herbicides, etc.) and or natural (i.e., weathering reactions, biological activity and volcanic emissions, etc.) (Akin *et al*., 2011).

The occurrence of arsenic in natural waters, mainly in groundwater, is a worldwide problem. Arsenic pollution has been reported in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India

(Mohan and Pittman, 2007; Akin *et al*., 2011). Although Groundwater from the Ethiopian Rift Valley is known to contain high levels of fluoride, yet, recent studies have also documented As concentrations in drinking water of the area is above the WHO limit of 10 p.p.b. (Merola *et al.,* 2014). Since groundwater is used for drinking water supply and arsenic removal is then of unquestionable importance.

As studies shows that, there are several methods for remediation of As contaminated waters, and presently available techniques for As removal from water involve oxidation, adsorption ion exchange, membrane technologies and coagulation-flocculation. Most of the available removal techniques are more efficient for arsenate than arsenite and treatment technologies are believed to be more effective by using a two-step approach: initial oxidation from arsenite to arsenate then removal of arsenate (Yoon *et al*., 2017; Viera *et al*., 2017).

Among available technologies, adsorption has been reported as the most widely used technique for arsenic removal due to its several advantages including relatively high arsenic removal efficiencies, easy operation, and handling, cost-effectiveness, and no sludge production (Mohan and Pittman, 2007; Chiban *et al.,* 2011).

Many adsorbent media have been in use, among which activated carbon (AC) is widely used for adsorption treatment process. Activated carbons are versatile adsorbents with a wide range of uses in so many sectors basically due to the large surface area that confers a high capacity for holding chemicals from gases or liquids. It is widely used for adsorption and removal of pollutants from gaseous and liquid phases. It has also several applications in medical, industrial and pharmaceutical processes (Zhou *et al*., 2015).

Granular or powdered activated carbon is the most widely used adsorbent but their use is usually limited due to their high cost .These constraints have caused the search for alternative methods that would be efficient for arsenic sequestering. Such a possibility offers a method that uses sorbents of biological origin.

But recently, the search for new effective biosorbents involving removal of arsenic from wastewater has directed attention and natural sorbents are searched among many vegetable and waste materials from food and agricultural industry. These materials can be considered as low cost adsorbents and require little processing and abundant in nature. For the past few years, the focus of the research was to use cheap materials as potential adsorbents and the

processes developed so far are based on exploring those natural adsorbent, which can improve economic and bring cost effectiveness (Chiban *et al.,* 2011).

Coffee husk used as an adsorbent in this study is one of the agricultural by products or wastes obtained from coffee processing operation. It is an abundant material on a large scale in many Regions of Ethiopian. The existence of huge amount of coffee production indicates the likely increase in quantities of coffee husk residue from processing units which contains cellulosic and lignocellulosic wastes which have long been recognized as raw materials for the preparation of activated carbon (Berhe *et al*., 2015).

1.2 Statement of the problem

Arsenic is known to be highly toxic to all life forms and classified as group one human carcinogenic substance. It is a non-biodegradable substance therefore it cannot be destroyed when released and will accumulate with time.

Recently, many studies have been conducted regarding the environmental fate and behavior of arsenic due to several arsenic pollution cases worldwide and the hazards associated with these. Even though, exposure to arsenic can be through ingestion of arsenic-contaminated water or food and contact with arsenic-contaminated air, reports have shown that elevated levels of arsenic in drinking water primarily contribute to human arsenic toxicity in the world. Arsenic (As) exposure is a global phenomenon; millions consume drinking water with As concentration exceeding the WHO recommended guideline of 10 p.p.b.

High levels of As exposure have been shown to cause acute health effects such as nausea, vomiting, abdominal pain, profuse diarrhea, renal failure, and shock, whereas long-term exposure to relatively lower levels of As is known to increase the risk of chronic diseases such as lung, skin, kidney, urinary, bladder cancers, cardiovascular diseases, peripheral neuropathies, and diabetes.

Although Groundwater from the Ethiopian Rift Valley is known to contain high levels of fluoride, yet, recent studies have also documented As concentrations in drinking water above the WHO limit of 10 p.p.b. (Merola *et al.,* 2014).

Even though there are so many conventional technologies of arsenic removal, many of them are expensive, demand large energy and also need skilled manpower and hence not easily applicable in developing countries; except adsorption technology which is considered as the best water treatment method due to its universal nature, inexpensiveness and ease of

operation and also applicable to remove soluble and insoluble organic pollutants. But what matter is finding best adsorbent which overcome problem stated above. Many adsorbent media have been introduced to be used in water treatment processes. There is a great need of the removal of pollutants from water by using low cost adsorbents at pilot and industrial scales.

However, yet low cost and locally available adsorbents have to be investigated and employed. A current problem faced coffee fruit' processing is that the generation of an excessive amount of wastes during the fruit processing. For environmental and ecological reasons, the innocuous disposal of these wastes has become immensely important. The conversion of coffee husk to activated carbon provides an innovative, environmentally safe, and economically feasible solution to the problem of waste management at coffee bean processing firms. In this study, chemically activated coffee husk which is an agricultural waste was used as an adsorbent to remove arsenic from aqueous solutions and from drinking water under different experimental conditions.

1.3 Objectives

1.3.1 General Objective

The main objective of this study was to investigate arsenic removal from aqueous solution using activated carbon derived from coffee husk.

1.3.2 Specific Objectives.

The following specific objectives were addressed during the study:

1. To characterize adsorbent derived from coffee husk.
2. To measure the effect of initial concentration of solution, solution pH, adsorbent dose, contact time, shaker speed and adsorbent particle size on the adsorptive removal efficiency.
3. To predict the adsorption process with isotherm and kinetics models.
4. To investigate the desorption capacity of adsorbent.

1.4 Research questions

1. What are the major characteristics adsorbent derived from coffee husk?
2. What affect does the initial concentration of solution, solution pH, adsorbent dose, contact time, shaker speed and adsorbent particle size on Arsenic removal?
3. Which adsorption isotherm and kinetic model best fits the experimental data?
4. What are the factors that affect desorption capacity of coffee husk based adsorbent?

1.5 Significance of the study

The finding of this study will redound to the benefit of the huge society regarding access to improved drinking water free from arsenic pollutant. Since arsenic is known to be highly toxic to all life forms its removal from water is an important issue. Although there are so many conventional technologies of arsenic removal such as coagulation followed by precipitation, lime softening, membrane separation and ion exchange, which are not cost-effective and suitable, especially for developing countries like Ethiopia. Now a day, the adsorption process is getting the best preference over other treatment processes because of its low cost, local availability, environmentally friendly, high removal efficiency. On the other hand, although many adsorbents are available, providing low-cost and locally available adsorbent with high adsorption capacities that can be easily prepared from agricultural waste (coffee husk) will reduce pollution due to disposal of coffee husk. Also this finding of the study will initiate other scholars to use the application of agricultural waste in water treatment scheme. In addition, it will indicate management option for agricultural waste like coffee husk produced from coffee processing operation.

1.6 Scope of the study

In this study, coffee husk was used as a raw material to prepare adsorbent using chemical process to produce the activated carbon. The experiments were carried out in an airtight electric furnace for activation process. This study was focused on removal of arsenic from water using low cost, abundant and locally available material which can be generated from Agricultural wastes.

1.7 Limitation of the study

Real sample is not used in the experimental analysis because of finding direct determined arsenic concentration from ground water is difficult. For example different well may have different arsenic concentration. Instead of this determined fresh arsenic stock solution was prepared and used in the adsorption test.

CHAPTER TWO

LITERATUREREVIEW

2.1 Nature and Occurrence of arsenic

Arsenic (As) is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites (Chiban *et al.,* 2011). Elemental arsenic is yellow or metallic gray in color, very brittle, and not soluble in water, and it has a semi-metallic crystalline structure (Ayanda *et al*., 2017; Chiban *et al.,* 2011).

Table 1 physical properties of arsenic (Youngran Jeong, 2005).

Atomic symbol	As
Classification	Metalloid
Color	Gray
Crystal structure	Rhombohedra
Density @ 293K	5.72 g/cm^3
Atomic mass	74.9216
Atomic number	33
Electronic configuration	[As] $4s^23d^{10}4p^3$
Oxidation state	5, 3, 0, -3
Atomic radius	125 pm
Melting point	~817ºC
Boiling point	603ºC

Total arsenic is the sum of both particulate arsenic and soluble arsenic. Inorganic form of soluble arsenic in natural waters usually occurs as trivalent arsenite or pentavalent arsenate. Under anaerobic conditions, groundwater normally contains arsenite. Arsenite is readily oxidized to arsenate in aerobic water at pH values above 7.0. Conversely, arsenate can be reduced to arsenite at low pH values (Feenstra *et al.,* 2007).

Arsenic combined with carbon and hydrogen is referred to as organic arsenic and it is found in marine animals and plants such as seaweed. Inorganic arsenic exists in four main oxidation states, of which +3 [As (III)] and +5 [As (V)] are the most common (Yaqub *et al*., 2016).

The existence of arsenic in a specific oxidation state in the hydrosphere depends on various environmental factors such as reduction-oxidation reactions, pH conditions, general hydrochemistry, microbial activity, and other ionic distribution states. But the concentration of arsenic species mainly depends on redox potential and pH (Youngran, 2005).

Natural sources of arsenic are related to various types of rocks and to geothermal activity. Industrial activities, especially mining, can also contribute to an increased arsenic concentration in groundwater (Feenstra *et al.,* 2007). A review of the sources and behaviour of arsenic in natural waters is given by Smedley and Kinniburgh (2002).The most common As minerals are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment. The greatest concentrations of these minerals occur in mineralized areas and are found in close association with the transition metals (Chiban *et al.,* 2011). Though not a major component arsenic is also often present in varying concentrations in other common rock-forming minerals.

Since the chemistry of arsenic follows closely that of sulphur, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite is the most abundant. Arsenic may also present in the crystal structure of many other sulphide minerals as a substitute for sulphur (Chiban *et al.,* 2011).

According to Smedley and Kinniburgh (2002), arsenic concentrations in ground or surface water vary from 0.01 to more than 500,000 µg/L depending on the physical and hydrogeological environment.

Arsenic contamination of ground waters is now termed as global environmental issue and the countries like Bangladesh, India, USA, Canada, China, Mexico, Taiwan, etc. are affected greatly having large aquifers with higher concentrations of arsenic (over 50µg/L) (Youngran, 2005; Yaqub *et al.,*2016).

Nowadays, ground water of ERV contains arsenic concentration above the WHO limit of 10 p.p.b. according to recent studies. In terms of exposure and bioaccumulation from drinking water examination has been made by monitoring human keratin in the form of toenails. However, the study was aimed in analysis of detection and bio-accumulation, and of the total number of wells tested, 53% had As level above the WHO maximum contamination level of 10 p.p.b. (Merola *et al.,* 2014).
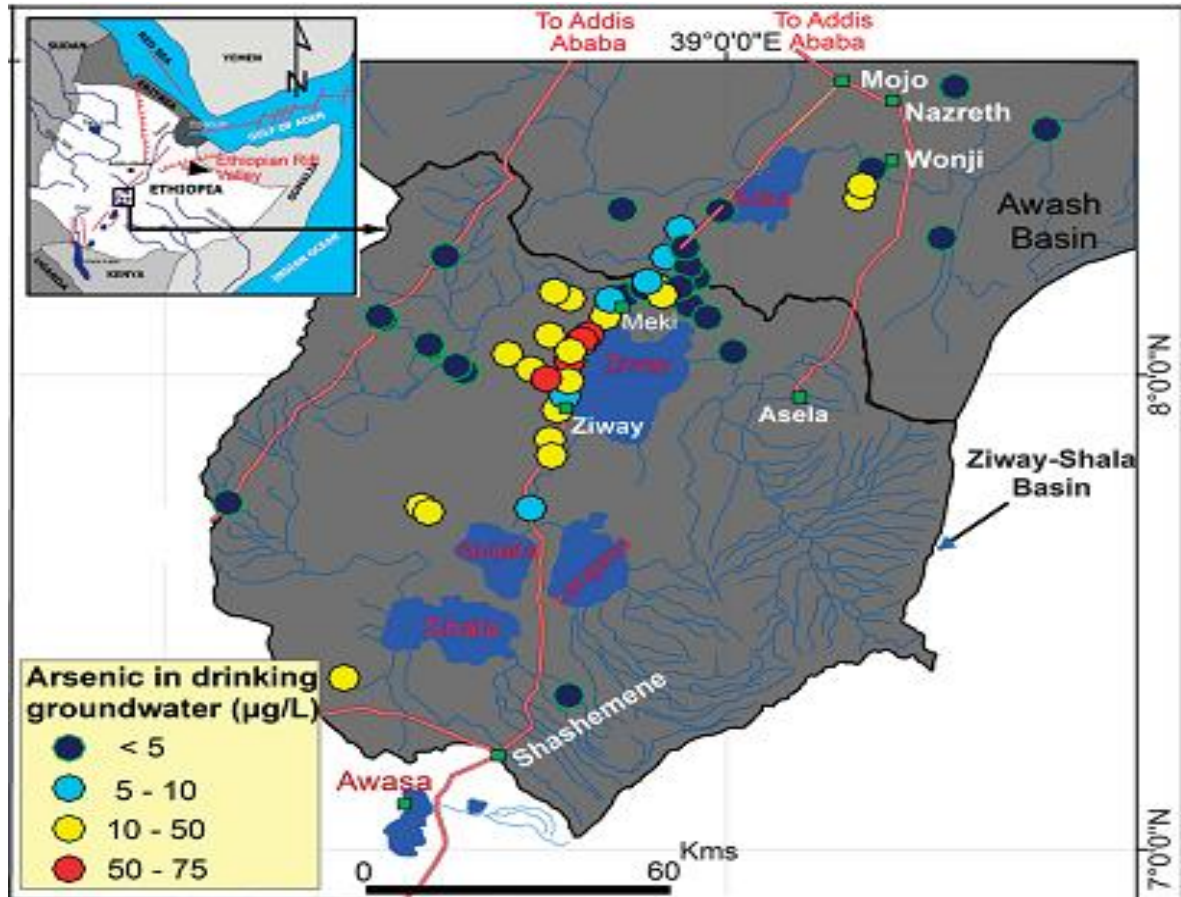
Figure 2. 1 Location of drinking water wells in ERV and the spatial distribution of their arsenic concentration. (Merola *et al*., 2014).

2.2 Environmental transport and distribution of Arsenic

Arsenic is released into the atmosphere from fossil-fuel combustion power plants, smelter operations, burning vegetation, volcanism, and other high-temperature based processes. These particles are dispersed by the wind and are returned to the earth by wet or dry deposition. (Youngran, 2005). In addition, arsines are known to release as biomethylate arsenics, from many activities of microorganisms (bacteria, molds, and yeasts) and animals present in soils or sediments, which on oxidation in the air reconvert to both volatile (e.g., methylarsines) and nonvolatile (e.g., methylarsonic acid and dimethylarsinic acid) arsenic compounds and settle back to the ground (Bentley and Chasteen, 2002).

Furthermore, wind and water erosion weathers away rocks and soils, resulting in the transportation of these arsenic compounds. Many arsenic compounds tend to adsorb to soils, which on leaching usually results in transportation over short distances within soils. It was reported that soil erosion and leaching could contribute to $612 * 10^8$ and $2380 * 10^8$

g/year or total arsenic, respectively in the dissolved and suspended forms received by the oceans (Tiwari and Lee *et al*., 2012).

Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts (Mohan and Pittman, 2007).
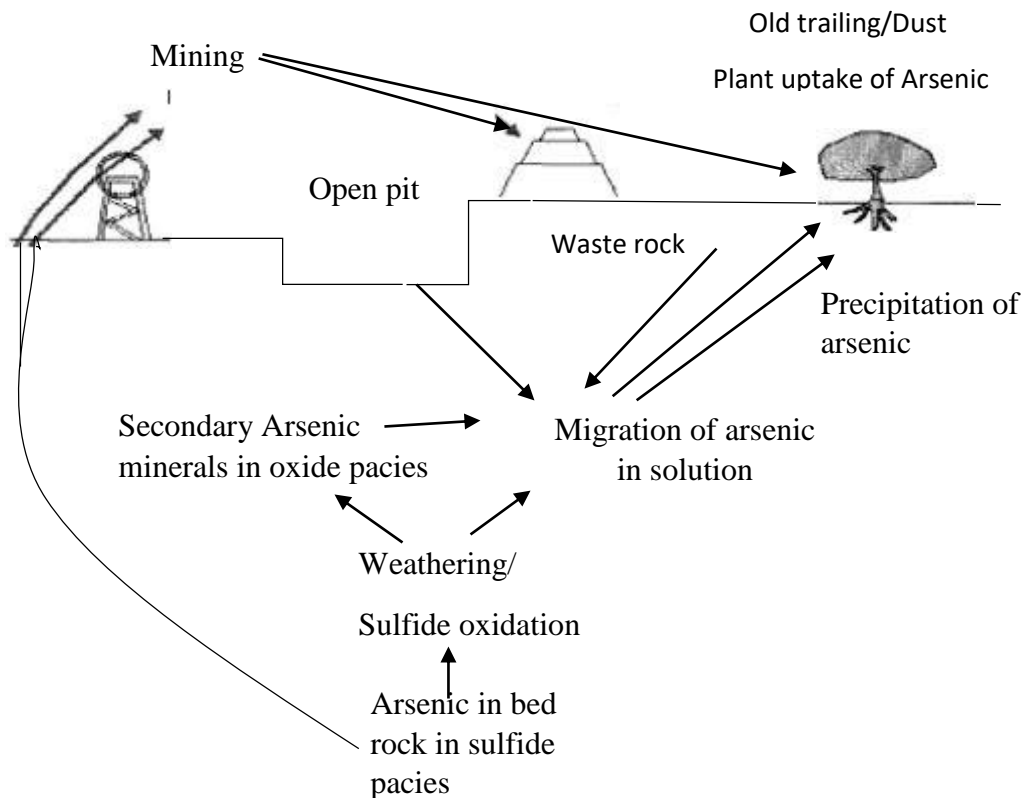
Figure 2. 2 Arsenic cycle in mining environment (Youngran, 2005)

2.3 Arsenic related Health effects

In general, organic metal compounds such as tin, mercury, and lead (simple methylated species) tend to be more harmful than the respective inorganic species. However, inorganic arsenic compounds are known to be 100 times more toxic than organic arsenic compounds (Ferguson and Gavis, 1972; Prange and Jantzen, 1995).

Arsenic toxicity is of two types, acute and sub-acute. The main sources of acute arsenic poisoning are contaminated food or drink (Youngran, 2005). The symptoms of acute arsenic poisoning include burning sensation and dryness of mouth and throat, muscular cramps, projectile vomiting, and diarrhea.

The symptoms of sub-acute arsenic poisoning mainly link to cardiovascular, pulmonary, immunological, and neurological effects. Long term exposure causes loss of hair, brittle nails, and darkened skin exfoliation. Specifically, long-term exposure to arsenic-contaminated water causes various diseases such as cardiovascular diseases and conjunctivitis (Youngran, 2005).

According to many researchers revealed that the relationship of arsenic to cancers of the bladder, lungs, kidney, nasal passages, liver, and prostate, as well as to skin cancer and black foot disease. According to several researchers' reports that high concentrations of arsenic in drinking water lead to an increase in stillbirths and spontaneous abortions (Smith *et al*., 1992).

2.4 Techniques for Removal of arsenic

2.4.1 Mitigation Techniques

Problematic arsenic levels in drinking water can be removed using different methods. The selection of the most appropriate method for a particular water system should be based on feasibility issues, system constraints, and costs. Following are treatment approaches (EPA 2002):

2.4.1.1 Switching to Alternative source

Abandonment of the problematic source(s) and switching to other source(s) within the system or purchasing from a neighboring system. Systems with multiple sources that do not all have arsenic problems should first analyze whether they can meet the standard without installing treatment; systems located near other systems may wish to investigate purchasing finished water.

2.4.1.2 Blending (dilution sysem)

The combination of multiple water sources to produce a stream with an arsenic concentration below the MCL. Blending is a viable mitigation strategy for conservative inorganic substances, such as arsenic. Blending involves mixing waters from two or more different sources prior to distribution. At its simplest, a high arsenic source (with arsenic levels above the MCL) and a low arsenic source (with arsenic levels below the MCL) are fed into a combined header. Blending should be a second choice for systems (EPA, 2002).
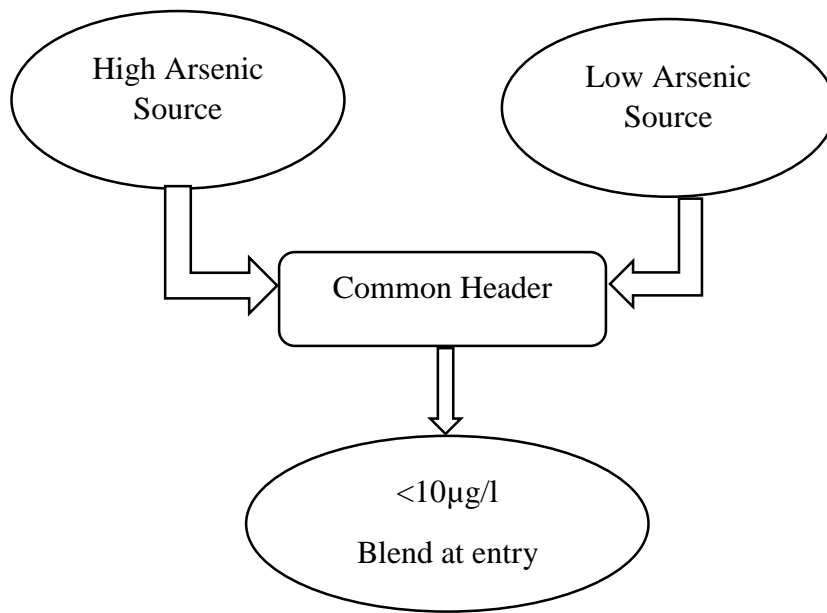
Figure 2. 3 Schematic of Arsenic blending

2.4.1.3 Centralized treatment method

The processing of a high arsenic water stream to reduce the arsenic concentration to below the MCL. Centralized treatment can be used to treat the full stream of influent water, or it can be used for side-stream treatment, which is the centralized treatment of a portion of the high arsenic water stream and subsequent blending of this stream back with the untreated portion to produce a water that meets the MCL. Centralized arsenic treatment can be produced either by modifying an existing treatment technology or by installing new treatment equipment (EPA, 2002).

2.4.1.4 Point of use (POU) treatment

Only the water to be used for human consumption is treated at the utility at a point after the water exits the distribution system (e.g., at a household faucet). POU devices are particularly attractive for removing contaminants that pose only an ingestion risk, as is the case with arsenic. This is because a very small fraction of the total water supplied to a given household is ultimately consumed. In most cases, the POU unit is plumbed in at the kitchen sink (the device will have its own faucet) (EPA, 2003). The primary advantage of employing POU treatment in a small system is reduced capital and treatment costs, relative to centralized treatment. On the downside, however, these programs generally incur higher administrative and monitoring costs to make sure that all units are functioning properly.

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Previous studies have suggested that POU programs are an economically viable alternative to centralized treatment for systems serving roughly 50-500 people (EPA, 2003).

Most POU devices do not address the issue of pre-oxidation. While RO may remove As(III) to acceptable standards, sorptive processes such as AA or IBS will probably not. In this case, water systems may need to conduct centralized chlorine treatment to convert As(III) to As(V). There is also a concern that even with centralized pre-oxidation, anoxic conditions could exist in the distribution system that allow As(V) to reduce back to As(III). Depending on the extent of reduction, this could be detrimental to a POU program (EPA, 2003). The primary criteria for selecting an appropriate POU treatment device are arsenic removal performance and cost.

2.4.2 Techniques for Removal of arsenic

Various common treatment technologies have been used for removal of arsenic from drinking water. Chemistry and composition of arsenic-contaminated water are the major factors determining the removal of arsenic (Mohan and Pittman, 2007; Akin *et al*., 2011). Recently, the presence of dissolved arsenic in drinking water has emerged as a problem of global magnitude. Promulgation of new maximum contaminant levels (MCL) by the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO) has resulted in a demand for more efficient arsenate ions removal technologies (Harisha *et al*., 2009).

The new MCL of 10 ppb for arsenic publicized by US EPA has led researchers to improve newer treatment techniques for more effective arsenic removal from drinking water.

The US EPA suggested the criteria for the best available technology (BAT) as follows:

✓ The capability of achieving a high removal efficiency
✓ A history of full-scale operation
✓ General geographic applicability
✓ Reasonable cost based on large and metropolitan water systems
✓ Reasonable service life
✓ Compatibility with other water treatment processes
✓ The ability to bring all of the water in a system into compliance (US EPA, 2001; Youngran, 2005).

In general, some of presently available technologies that can be used for the removal of arsenic from water summarized in figure below:
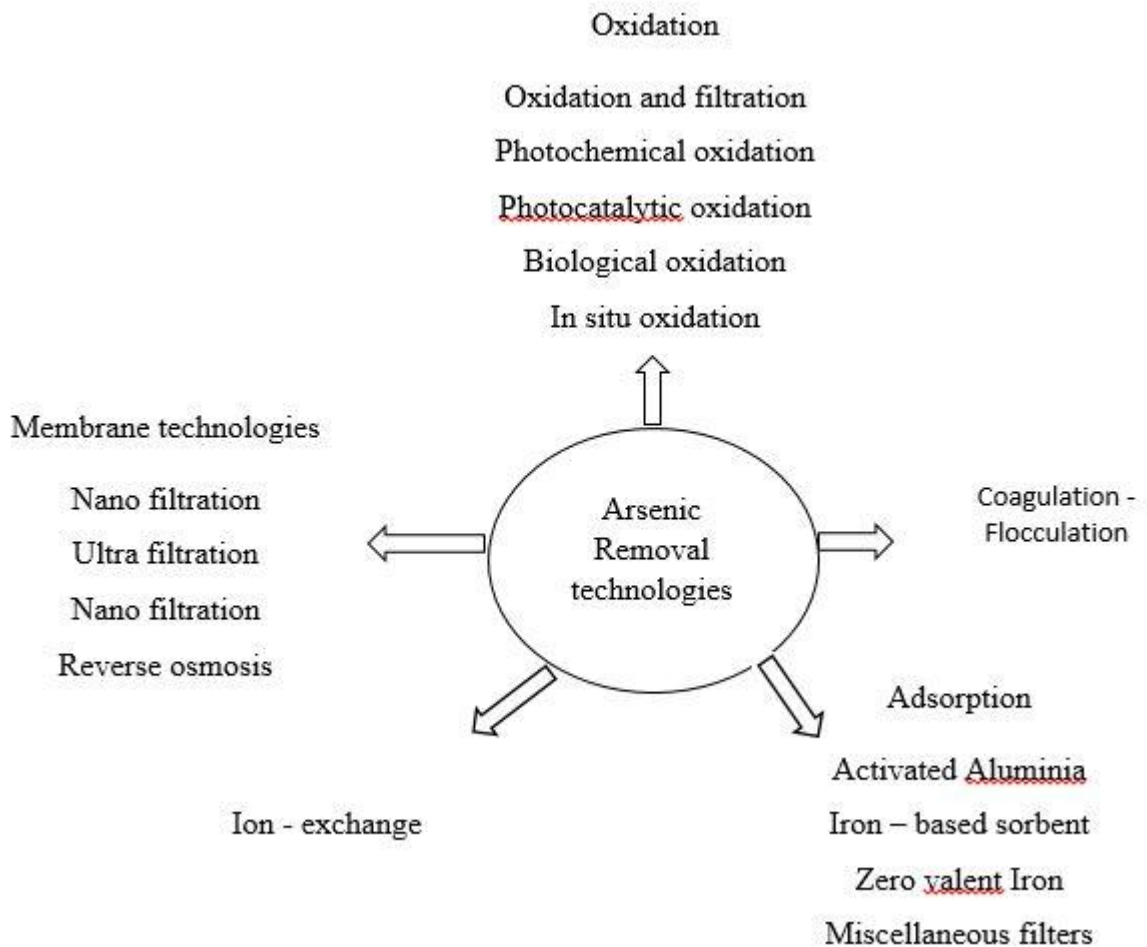
Figure 2. 1 Various techniques used for the removal of arsenic from water (Nicomel *et al*., 2016).

2.4.2.1 Oxidation Techniques

Oxidation involves the conversion of soluble arsenite to arsenate. This alone does not remove arsenic from the solution, thus, a removal technique, such as adsorption, coagulation, or ion exchange must follow (Johnston and Heijnen, 2015).

 In developing countries, atmospheric oxygen, hypochlorite, and permanganate are the most commonly used oxidants. Oxidation of arsenite with oxygen is a very slow process, which can take hours or weeks to complete (Nicomel *et al.,* 2016).

On the other hand, chemicals, such as chlorine, ozone, and permanganate, can rapidly oxidize As (III) to As (V). However, despite this enhanced oxidation, interfering substances

present in water need to be considered in selecting the proper oxidant as these substances can greatly affect and dictate the kinetics of As (III) oxidation (Singh *et al*., 2015). Thus, to efficiently remove arsenic from a solution by oxidation, oxidants should be selected carefully. Moreover, all cited disadvantages of oxidation alone make it a less competent method for arsenic removal (Nicomel *et al.,* 2016).

2.4.2.2 Coagulation-Flocculation method

Coagulation and flocculation are among the most employed and documented techniques for arsenic removal from water (Singh *et al*., 2015). In coagulation, positively charged coagulants (e.g. Aluminum sulphate (Al_2 $(SO_4)_3$), ferric chloride ($FeCl_3$) reduce the negative charge of colloids, thereby making the particles collide and get larger.

Flocculation involves the addition of an anionic flocculant that causes bridging or charge neutralization between the formed larger particles leading to the formation of flocs. During these processes, dissolved arsenic is transformed by the chemicals into an insoluble solid, which undergoes precipitation later (Mondal *et al*., 2013).

The major drawback of coagulation-flocculation is the production of high amounts of arsenic-concentrated sludge (Singh *et al*., 2015). The management of this sludge is necessary so as to prevent the consequence of secondary pollution of the environment and treatment of sludge is expensive. These limitations make this process less feasible, especially in field conditions (Mondal *et al*., 2013).

2.4.2.3 Membrane Technologies

Membrane separation technologies are attractive arsenic treatment processes for small water systems. They can address numerous water quality problems while maintaining simplicity and ease of operation (EPA, 2003). In view of drinking water production, membrane filtration is a technique that can be used for the removal of arsenic and other contaminants from water. A driving force, such as pressure difference between the feed and the permeate sides, is needed to transport the water through the membrane (Van der Bruggen *et al*., 2003).

Generally, there are two categories of pressure-driven membrane filtrations:

(i) Low-pressure membrane processes, such as microfiltration (MF) and ultrafiltration (UF); and (ii) high-pressure membrane processes, such as reverse osmosis (RO) and nanofiltration (NF) (Shih, M, 2005; Mondal *et al*., 2013).

Using membranes with pore sizes between 0.1 and 10 μm, MF alone cannot be used to remove dissolved arsenic species from arsenic-contaminated water (Singh *et al*., 2015). Thus, the particle size of arsenic-bearing species must be increased prior to MF; the most popular processes for this being coagulation and flocculation.

PH of the water and the presence of other ions are major factors affecting the efficiency of this arsenic immobilization. This can be a disadvantage of this technique especially when dealing with arsenite removal as this arsenic form has a neutral charge in the pH range of 4–10. In the same way as MF, UF alone is not an effective technique for the treatment of arsenic-contaminated water due to large membrane pores (Shih, 2005).

Both NF and RO are suitable for the removal from water of dissolved compounds with a molecular weight above 300 g/mol. These techniques can significantly reduce the dissolved arsenic level in water given that the feed is free from suspended solids and that arsenic is preferably present as arsenate (Nicomel *et al.,* 2016). RO units have a much larger retention spectrum, and can be used as stand-alone arsenic treatment under most water quality conditions. Figure 2.5 provides a block flow diagram for a typical RO membrane process (EPA, 2003).
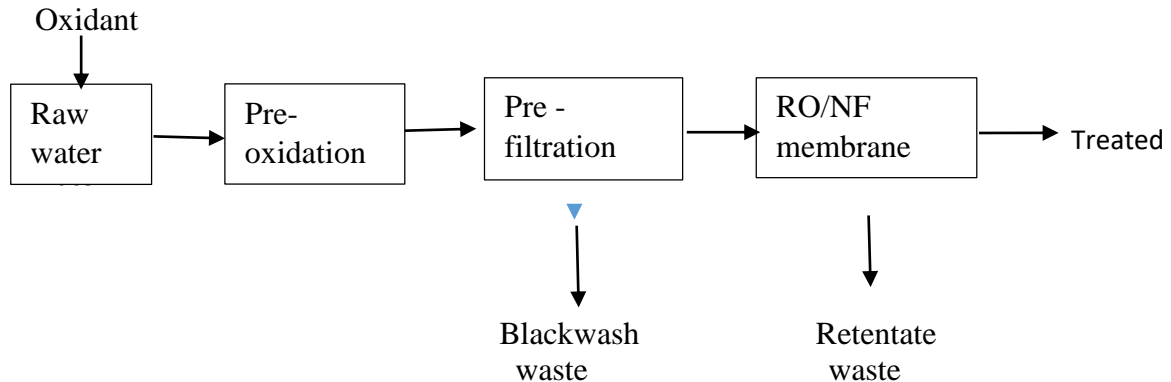
Figure 2.5 RO membrane flow diagram

According to findings of Uddin *et al.,* who indicated that without oxidation of arsenite to arsenate, NF cannot comply with the MCL of arsenic in drinking water. The same is the case for RO, as shown in several studies (Brandhuber. P and Amy 1998).

2.4.2.4 Ion exchange method

Ion exchange is a physical or chemical process in which ions held electrostatically on the surface of a solid phase are exchanged for ions of similar charge in a solution. It is a reversible interchange where there is no permanent change in the structure of the solid

(Chiban *et al.,* 2012). The solid is typically a synthetic anion exchange resin, which is used to remove particular contaminants of concern. Ion exchange is commonly used in drinking water treatment for softening (that is removal of calcium, magnesium etc. in exchange of sodium) as well as removing nitrate, arsenate, selenate etc. from municipal water (Clifford, 1999). Arsenic removal is accomplished by continuously passing water under pressure through one or more columns packed with exchange resin. Figure 2.6 (EPA, 2003) shows a typical process flow diagram for ion exchange.

Oxidant

| Raw water | → | Pre-oxidation | → | Pre - filtration | → | Ion Exchange | → | Treated |

Blackwash   waste   regenerant
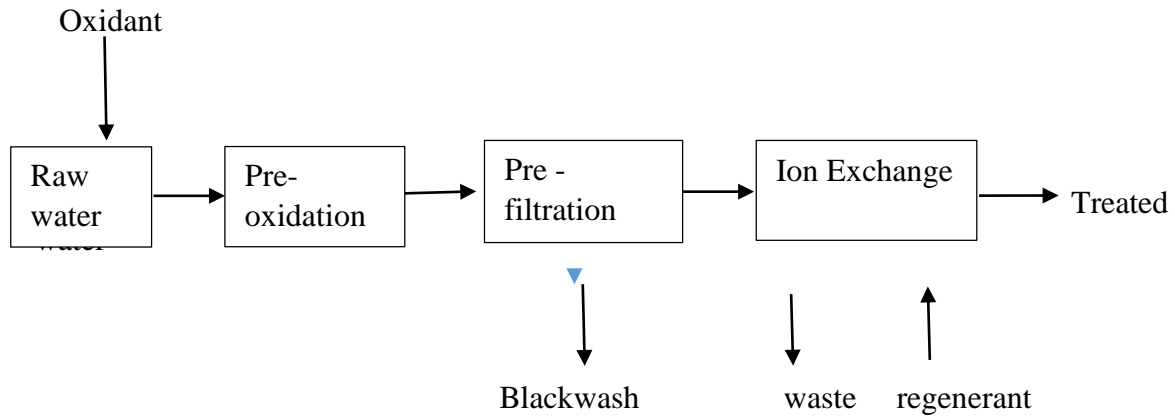
Figure 2.6 Ion exchange process flow diagram

For arsenic removal, an ion exchange resin, usually loaded with chloride ions at the "exchange sites", is placed in vessels. The effect of the presence of sulphate, competition with other anions, is an important factor to ion exchanger treatment of arsenic. Sulphate levers can limit the applicability of ion-exchanger as arsenic treatment. Due to its higher treatment cost compared to conventional treatment technologies, ion exchange application is limited primarily to small-to-medium-scale. Other factors affecting the use of the ion exchange process include contact time and spent regenerant disposal (Chiban *et al.,* 2012).

2.4.2.5 Adsorption Technology

Adsorption phenomena have been known for a very long time. And can be utilized as a treatment process to remove highly undesirable compounds from feed water (Youngran, 2005). It is a process that uses solids such as activated carbon, metal hydrides and synthetic resins for removing substances from either gaseous or liquid solutions. The adsorbing surface is called the adsorbent while the adsorbed substance is called the adsorbate. The chemical equilibrium which represents the adsorption of molecules on a surface is as follows:

$$A + B \rightleftharpoons AB \qquad (1)$$

Where, A is the adsorbate, B is the adsorbent and AB is the product of the adsorption process. Adsorption phenomena are operative in most natural physical, biological, and chemical systems (Chiban *et al.,* 2012).

Basically, substances are separated from one phase followed by their accumulation at the surface of another. This process is driven mainly by van der Waals forces and electrostatic forces between the adsorbate molecules and the adsorbent surface atoms (Nicomel *et al.,* 2016). So it is important to characterize first the adsorbent surface properties (e.g., surface area, porosity) before being used for adsorption (Choong *et al*., 2007).

For adsorption of compounds on activated carbon, which is a reversible reaction, molecules continue to accumulate on the surface of the carbon until the rate of the forward reaction (adsorption process) is equal to the rate of the backward reaction (desorption process). At this point, equilibrium state is attained and no further accumulation of the adsorbate on the adsorbent surface occurs. Hence, adsorption stops. This equilibrium state enables relationship known as adsorption isotherm (Atkins, 1997).

Based on the energy associated with adsorption and the type of bond responsible for the adherence of the adsorbate on the adsorbent, adsorption process can be classified into physical and chemical adsorption.

- **Physical Adsorption (Physisorption)**

This is a weak form of interaction between an adsorbent and adsorbate molecules. The forces involved are similar to vander Waal's forces and the heat evolved during the exothermic adsorption reaction is low (usually of the same magnitude as the enthalpy of condensation, < 42KJ/mol). This amount of energy can be adsorbed as vibrations of the lattice and dissipated as thermal motion. Because of the energy requirements for the process, equilibrium between the solid surface and the gas molecules is usually easily attained and is readily reversible. The amount of physisorption decreases rapidly as temperature is raised and is generally very small above the critical temperature of the adsorbed specie. Due to the weak force involved in physisorption, the activation energy is low, not more than 42kJ/mol. The rate of physisorption is very high but the process is non-specific. Generally, the process of physical adsorption begins as an adsorbate molecule is transported from the bulk adsorbate phase to the surface of the adsorbent. Next, the molecule then diffuses into the pore and then physically bonds with the surface. Heat is usually evolved, making adsorption an exothermic process. In the first step, the bulk adsorbate stream must be intimately mixed with the adsorbent to promote good contact

between the two components. In the second and third stages, the concentration gradient between the amount of adsorbate present in the bulk adsorbate stream and that within the micro pore provides the driving force for adsorption.

- **Chemical Adsorption (Chemisorption)**

This type of adsorption is one in which chemical bond is formed between the adsorbate and the adsorbent. The chemical bond involved is usually covalent bond and the adsorbent tends to find sites that will maximize its co-ordination number with the substrate. Chemisorption is specific and involves forces which are stronger than those associated with physisorption. Hence, the heat of adsorption in this case is high and is of the same order as heat of reaction.

This process requires generally high temperature and is often irreversible. Unlike physisorption, in which multilayer coverage is possible, chemisorption does not exceed monolayer coverage. This is because the valence force holding the molecules on the adsorbent surface diminishes rapidly with distance. Generally, chemical adsorption is linked to the porosity and surface chemistry of the carbon, since chemisorption is associated with the number of active sites and carbon surface.

Chemisorption is of two kinds; activated and non-activated chemisorption. In activated chemisorption, high activation energy is involved and the rate varies with temperature according to the finite activation energy (between 8.4 -83.7kJ/mol) in the Arrhenius equation (2) given below (Aksu, 2002).

$$K = Ae(-\frac{E}{RT}) \qquad\qquad (2)$$

Where:

K - The rate of reaction.

A - Proportionality constant.

E- Activation energy.

R- Universal gas constant

T- Absolute temperature. In non-activated chemisorptions, the process occurs very rapidly, hence, the activation energy is low, usually close to zero.

Among available removal technologies, adsorption has been reported as the most widely used technique for arsenic removal due to its several advantages including relatively high arsenic removal efficiencies, easy operation, and handling, cost-effectiveness, and no sludge production (Nicomel *et al.,* 2016).

In addition to the system's conditions, the effectiveness of adsorption in arsenic removal can also be hindered by the type of adsorbent itself (Chiban *et al.,* 2012; Nicomel *et al.,* 2016). Many activated carbons are available but few are selective and are expensive as well. Therefore, the research thirst over the years is leading to find improved and tailor-made materials, which will meet several requirements such as regeneration capability, easy availability, cost effectiveness etc. (Chiban *et al.,* 2012).

2.4.5 Factors affecting adsorption process

The pH of the medium is one of the most critical parameter in the adsorption process of arsenic from aqueous solutions. The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbents (Chiban *et al*., 2011). The standard range of pH in drinking water varies from 6.5 to 8.5, and therefore the investigation of the effect of wide range of pH on arsenic removal is needed. The pH effect on the arsenic adsorption by low-cost adsorbents is dependent on the types of adsorbent.

The contact time of adsorbate and adsorbent has a great importance in batch adsorption experiments, because it depends on the nature of the system used (Chiban *et al.,* 2012).

Among the process parameters frequently investigated in the literature, temperature is also shown to affect adsorption capacity. The thermodynamic parameters present the essential parameters for subsequent engineering evaluation on the ultimate uptake of the adsorbents, and, hopefully, also provide insights to the adsorption mechanisms thus applied for further use in process modification and optimization. Types of adsorbent itself hinders effectiveness of adsorption of arsenic removal in addition to system's condition (Chiban *et al.,* 2012; Nicomel *et al.,* 2016). The amount of a substance that can be adsorbed on activated carbon depends on the nature of the substance and its concentration, the surface structure of the activated carbon and the temperature and pH of the water. For a treatment system with a specific type of carbon and a known substance, there is a relationship between the amount of adsorbed matter per unit of weight of carbon and the equilibrium concentration in the water, when temperature and pH are constant. This relationship is called an isotherm. Agitating speed and adsorbent particle sizes are other major factor that affect adsorption of heavy metals.

Kinetics and Equilibrium Isotherm Models

Adsorption Kinetics

The knowledge of the pollutant adsorption kinetics of materials is of a great importance when dimensioning filters for pollutant removal. The adsorption kinetics is usually determined by batch experiments, monitoring the pollutant concentrations over time until equilibrium in pollutant adsorption is reached. The pseudo-first order and second order kinetic models are used to study the sorption kinetics of pollutants and to quantify the extent of uptake in sorption kinetics. Due to rapid stirring in the batch reactor, ions are transported from aqueous phase to the surface of the adsorbent and subsequently they may diffuse into the interior of the particles if they are porous

Adsorption isotherms

Langmuir and Freundlich models are the most frequently employed for describing the adsorption isotherms from experimental data (Foo & Hameed, 2010). These models can be used to design and optimize an operating procedure. Furthermore, they provide information to predict removal efficiency of solute and an estimation of adsorbent amounts needed to remove solute ions from aqueous solution

2.4.6 Activated carbon and low cost adsorbents

2.4.6.1 Characteristics of Activated Carbon

Activated carbon represents substances with high carbon content which have undergone the process of activation and are extremely versatile adsorbents with major industrial significance. A generalized definition is that activated carbons are nonhazardous, processed, carbonaceous products having a high degree of porosity and an extended inter-particulate surface area.

Hence, they are able to absorb a wide variety of substances and are good adsorbents (Aksu 2002). The ability of active carbon to arrest different molecules at the inner surface makes it a very powerful adsorbent. The adsorption of molecules from solution is strongly dependent on the porous nature of the activated carbon. This arises from the fact that mass transfer through the carbon pores limits the rate at which a carbon can adsorb any species. The pore volume of active carbon usually exceeds 0.2 cm^3/g but in many instances it is greater than 1 cm^3/g.

The single structural factor that results in the adsorptive properties of activated carbon is the extensive pore structure. The pore size distribution depends on the type of raw material

and the conditions of manufacture .The International Union of Pure and Applied Chemistry has classified the pore size of activated carbon as follows; micro pores have dimensions less than 1.6 nm, mesopores have dimensions between 1.6 and 200 nm, while macro pores have dimensions exceeding 200 nm.

2.4.6.1.1 Physical properties of activated carbon

Forms

Activated carbons are available in different forms such as symmetrical pellets, irregularly shaped granules, powder and specialties like pre-formed shapes, example, wool and slurry for coating supports. The major forms of activated carbon are the powdered form, the granular form and the pellets.

Particle size

This property is important due to the fact that adsorption rate varies inversely with particle size. Mathematically, **r α (1/s)**. where **r** is the rate of adsorption and **s** is the particle size. This means that, an increase in particle size will lead to a decrease in adsorption rate while a decrease in particle size will favor high adsorption rate (Lanzetta and Blasi, 1998).

Bulk density

Apparent or bulk density is a measure of the weight of material that can be contained in a given volume under specified conditions. The density does not affect the effectiveness of the activated carbon measured in adsorption per unit weight, but will have an effect on adsorption per unit volume. Higher density provides greater volume activity.

Surface area

Activated carbons have very large surface area, typically ranging from $500 - 3000 m^2/g$. This is an important property of activated carbon as it greatly affects the adsorptive properties of the carbon. Increase in surface area enhances the adsorptive capabilities of activated carbon by exposing a wide surface for physical as well as chemical adsorptions.

Pore structure

The amount and distribution of pores in an adsorbent play key roles in determining how well adsorbates are adsorbed. Practically, the type of raw material and the method of activation are important parameters which may influence the type of porosity. The pore structure of an activated carbon limits the size of the molecules that can be adsorbed on it. Individual pores can vary greatly in size and shape for different adsorbents and even within

the same adsorbent. Pores are usually characterized in terms of their width, meaning the diameter of a cylindrical pore or the distance between two sides of a slit-shaped pore (Lanzetta and Blasi, 1998).

According to International Union of Pure and Applied Chemistry, Pore Classifications based on Pore Width classified into:

Micropores (< ~ 20Å (2nm)), mesopores (between ~ 20 and ~ 500 Å (2 and 50 nm), macropores (> ~500 Å (50 nm)).

The basis for the pore classifications presented above is that each size range corresponds to different adsorption effects, as observed in an adsorption isotherm. Physical adsorption of molecules from gas or liquid onto activated carbon takes place in the pores and usually involves 3 steps:

1. Macro transport: The movement of adsorbate material through the macropore system of the activated carbon
2. Micro transport: The movement of adsorbate material through the mesopore and micro pore system of the activated carbon.
3. Sorption: The physical attachment of adsorbate material in the mesopores and micropores on the surface of activated carbon.

Pore size is a determinant of efficient adsorption. Within the pores exists an adsorption energy potential which emanates from each pore wall. In the case of physical adsorption, these forces closely resemble dispersion (or van der Waals forces). If large enough, this energy of adsorption is able to capture adsorbate molecules as they enter the pore, adhering the molecules to the pore wall (Fisher *et al.,* 2002).

If the proximity of the pore walls causes overlap of the adsorption fields, as in the case of micropores, the result is an increase in the potential for adsorption. So, although some activated carbons may have lower surface areas and total pore volumes, their smaller pore sizes increases their potential for adsorption. This makes small pores prime candidates for removal of low adsorbate concentrations, where the driving force for diffusional transport of the molecule to the surface is minimal (Bridge water, 2007).

The presence of micropores increase the adsorption potentials of carbons over those of nonporous and mesoporous materials. These micropores are responsible for the large

surface area of activated carbon particles created during the activation process. It is in the micropores that adsorption largely takes place.

The interaction potential in micropores is much greater than that in larger pores due to the closeness of the pore walls, resulting in an enhanced adsorption potential. An adsorbate molecule within a micropore is held there by adsorption forces originating from approximately the ten nearest surface atoms. The forces on adsorbate molecules depend on the distance between adsorbate and adsorbent atoms (pore size) (Gaikwad, 2004).

The macropores and large mesopores play an extensive role in the molecular transport process by providing a passage-way to the internal part of the activated carbon into the micropores. They do not contribute substantially to the particle surface area unlike the micropores. Capillary condensation takes place within mesopores, resulting in a hysteresis loop in the adsorption isotherm. In macropores, the pores are so wide that it is almost impossible to map out the isotherm in detail, especially for gaseous adsorbate in which case pressures of the adsorbate would become so close to unity. The more widely the pore sizes are distributed, the more enhanced the adsorptive capacity of the carbon.

2.4.6.1.2 Chemical properties of activated carbon

pH

The pH of an activated carbon is a measure of the surface acidity/basicity of the carbon. This is the pH of a suspension of the activated carbon in distilled water. The numerical values of the pH are affected by the experimental conditions when carrying out the experiment. A carbon pH of 6-8 is acceptable for most application such as sugar decolorization, water treatment, etc. The pH of many of the commercial carbons is due to inorganic components originating from the raw material used or added during the manufacturing process. After activation (with acid) and carbonization, activated carbons are usually washed to bring them to neutral pH.

Moisture content

Generally activated carbons are stored under dry conditions. If not it might adsorb considerable moisture. Actually they may adsorb as much as 25 to 30% moisture and still appear dry. For many purposes, the moisture content does not affect the adsorptive power, but obviously it dilutes the carbon.

Ash content

The total amount of inorganic constituents will vary from one carbon to another depending on the source of materials and from activating agents added during manufacture. Ash content lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regeneration. The inorganic material contained in activated carbon is generally in the range between 2 and 10%.

2.4.6.2 Classification of activated carbon

Activated carbons are complex products which are difficult to classify on the basis of their behavior, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics.

- **Powdered activated carbon (PAC)**

The size of powder activated carbon is less than 100μm in size with an average diameter between 15 and 25 μm. Thus, they present a large internal surface with a small diffusion distance.PAC made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieve. Powdered activated carbons are mainly used in liquid phase adsorption and flue gas treatment. In wastewater treatment, the most common used of powdered activated carbon is in the secondary treatment called powdered activated carbon treatment process.

- **Granular activated carbon (GAC)**

Granular activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system

- **Extruded activated carbon**

Extruded activated carbon combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block with diameters from 0.8 to 130 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

- **Impregnated carbon**

These are porous carbons which have been impregnated with other substances. i.e. it is impregnated with several types of inorganic impregnate cations such as Al, Mn, Zn, Fe, Li, and Ca. They are usually prepared for specific applications in air pollution control especially in museums and galleries. Silver loaded activated carbon is used as an adsorbent for purification of domestic water.

2.4.6.3 Low cost adsorbents

In the adsorption process activated carbon is most popular and widely used adsorbent in waste water treatment throughout the world, but the high prices and regeneration cost of activated carbon limits their large scale use for the removal of inorganic and organic pollutants, and has encouraged researchers to look for low cost adsorbing materials (Bailey *et al*., 1999).

Recently, adsorption of arsenic using natural materials or the wastes products from industrial or agricultural operations has emerged as an option for developing economic and eco-friendly wastewater treatment processes. Numerous low-cost adsorbents have so far been studied for the removal of arsenic from water and wastewater. Dry plants, red mud, fly ash, zeolites, blast furnace slags, hydrotalcites, hydroxides and various bio-adsorbents are few to mention (Chiban *et al.,* 2012).

 Dried plants are natural materials widely available and studied as an alternative adsorbent for different heavy metals. Dry plant leaves of thyme, sage, banana, mint, anise and oleander plants have also been suggested as natural, simple and cheap adsorbent for efficient removal of several metal ions from polluted water (Abu-El-Halawa *et al*., 2003). Also according to (Chiban *et al.,* 2012). Numerous biological materials have been tested for removal of toxic ions from aqueous solutions over the last two decades. However, only a limited number of studies have investigated the use of bioadsorbents e.g., bio-char (Mohan et al., 2007b), methylated yeast biomass (Seki *et al*., 2005), fungal biomass (Say et al., 2003), chicken feathers (Teixeira and Ciminelli, 2005), alginate (Zouboulis and Katsoyiannis, 2002) to remove arsenic from aqueous solution.

It is noteworthy that biological materials represent a potential source of abundant low cost adsorbents and there is no environmental or technical reason which impedes the preparation of adsorbents by using those materials (Chiban *et al.,* 2012). Coffee Husk used as a precursor in this study were the coffee husk that was collected from coffee bean processing firms. Which is a lignocellulossic material that is rich in carbon content. Which is one of

the most pollutant activities in agriculture due to a large amount of waste generated in the process. For each kilogram of processing coffee we have a kilogram of waste (cheap and abundant).

2.4.7 Preparation of Activated Carbon

2.4.7.1 Raw Materials

It has already been stated that essentially any carbonaceous material can potentially be activated. Commercial activated carbons are commonly produced from naturally occurring carbonaceous materials such as coal, wood and peat. Due to the growing need for activated carbons in our society and the high cost of raw materials and production, many researchers have attempted various wastes such as tires resins, agricultural by-products and dried sewage sludge, as raw materials and proposed new production methods for activated carbons with potential applications in many fields. High volumes of agricultural by-products are lingo-cellulosic wastes that may offer inexpensive and renewable sources of activated carbon. This option is particularly attractive since the yearly harvesting and processing of various agricultural crops grown in Ethiopia yields considerable quantities of agricultural by-products. Coffee processing wastes are one of the lingo-cellulosic residues generated in large quantities all over the world because coffee is the second largest traded commodity in the world, after petroleum.

Generally, any carbonaceous material can be suitable to be a good adsorbent but have to meet some requirements for being used commercially:

- ❖ Good availability
- ❖ Low cost
- ❖ The resulting activated carbon satisfies all kind of applications.
- ❖ The main properties of the activated carbons produced from lignocellulossic materials are:
  - High temperature stability
  - Resistance against acid attack
  - Slightly hydrophilic
  - Considerable mechanical strength
  - Low economical cost due to the abundance of the raw material

2.4.7.2 Method of manufacturing

Activated carbons are high surface area materials prepared from various amorphous carbon materials. In principle, the methods for production of activated carbon can be divided into two categories: physical and chemical activation.

The physical activation method involves carbonization of a precursor at elevated temperatures (500 - 900 °C) in an inert atmosphere, followed by activation of the resulting char at high temperatures (800 - 1000 °C) in the presence of a CO_2 or steam atmosphere.

In the chemical activation method, raw material is impregnated with an activating reagent and the impregnated material is heated under an inert atmosphere. The carbonization step and the activation step progress simultaneously in the chemical activation method. Different well-known chemical agents can be used in the chemical activation process and phosphoric acid and zinc chloride are most commonly used as activation reagents. The common feature of all substances used in the chemical activation process is that they are dehydrating agents which influence pyrolytic decomposition and inhibit the formation of tar, thus enhancing the yield of activated carbon (Marsh and Rodriguez-Reinoso, 2006; Reffasa *et al*., 2004)

Generally the advantages of the chemical activation method can be summarized as follows:

- ❖ It uses lower temperatures for pyrolysis;
- ❖ Usually, it can be performed in one step;
- ❖ It produces a much higher yield than physical activation;
- ❖ Very high surface area activated carbons can be obtained;
- ❖ If desired, micro porosity can be well developed, controlled and maintained in a narrow range;
- ❖ There is an important reduction of the mineral matter content.

The literature also mentions some disadvantages of the chemical activation process, such as the corrosiveness of the process and the washing stage (Teng *et al*., 1998). In general, Activated carbons produced by chemical activation generally exhibit a very open structure and bottle shaped, ideal for the adsorption of large molecules.

2.4.7.3 Preparation process

Activated carbon is produced from its precursor material through pyrolysis process. The pyrolysis technology involves heating biomass in an environment restricted of oxygen.

Pyrolysis is a conversion technique in which biomass is transformed to gaseous, liquid and solid products that can be used as improved fuels. Essentially the method consists in heating the biomass in an inert atmosphere up to a certain desired temperature. The process of pyrolysis of organic matter is very complex and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. In this process; thermal decomposition of organic components in biomass starts at 350 °C – 550 °C and goes up to 700 °C – 800 °C in the absence of air/oxygen (Fisher., *et al* 2002). The long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the form of gases, condensable vapors (tars and oils) and solid charcoal under pyrolysis conditions. Rate and extent of decomposition of each of these components depends on the process parameters of the reactor (pyrolysis) temperature; biomass heating rate; pressure; reactor configuration; feedstock; etc.

Figure below shows possible reaction pathways for the pyrolysis of wood biomass. These include three lumped product categories, starting with a first order reaction. Lanzetta and Blasi found that, at the beginning of the pyrolysis (250 °C – 300 °C) process, most of the volatiles are released at a rate 10 times faster than the next step (Lanzetta and Blasi, 1998).

Wood biomass
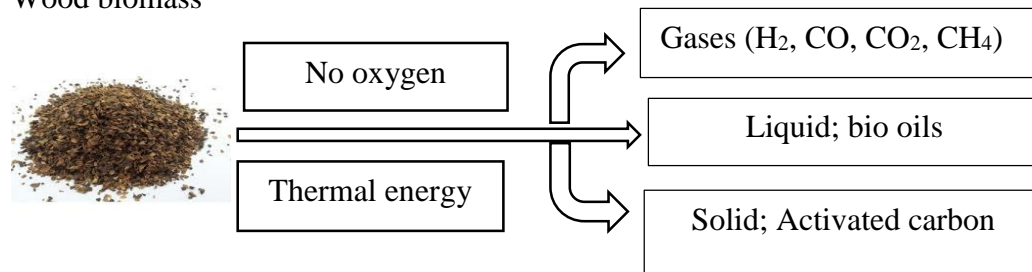
(Lanzetta and Blasi 1998).

Figure 2.5 Representation of the reaction paths for biomass pyrolysis.

The following reactions will occur in a pyrolysis reactor to give those products.

$$3H_{2\ (g)} + CO_{(g)} \leftrightarrow CH_{4\ (g)} + H_2O_{(g)} \tag{3}$$

$$H_2O_{(g)} + CO_{(g)} \leftrightarrow CO_{2\ (g)} + H_{2\ (g)} \tag{4}$$

$$C_{(s)} + 2H_{2\ (g)} \leftrightarrow CH_{4\ (g)} \tag{5}$$

$$C_{(s)} + CO_{2\ (g)} \leftrightarrow 2CO_{(g)} \tag{6}$$

$$C^{(s)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2\ (g)} \tag{7}$$

Where (g) represents for gas and (s) represents for solid.

2.4.7.4 Pyrolysis Classification

Depending on the operating condition, pyrolysis can be classified into three main categories: conventional slow, fast and flash pyrolysis. These differ in process temperature, heating rate, solid residence time, biomass particle size, etc. However, relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters. The range of important operating parameters for pyrolysis processes and the typical product yields obtained by different modes of pyrolysis of wood biomass on a dry basis are given in Table 2.

Table 2 Typical operating parameters and products for pyrolysis processes

Pyrolysis Process	Solid Residence Time(s)	Heating Rate (K/s)	Temperature (K)	Product Yield (%)		
				Oil	Char	Gas
Slow	450 – 550	0.1–1	550-950	30	35	35
Fast	0.5–10	10–200	850-1250	50	20	30
Flash	<0.5	>1000	1050-1300	75	12	13

(Bridgewater *et al*., 2007).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study setting/area and Study period

Laboratory based experimental study was conducted at Jimma University, College of Public Health and Medical Science, Department of Environmental Health science and Technology, which located latitude 7°40′N and longitude of 36°50′E from July 2018 to September 2018 GC.

3.2 Study design

Study design was laboratory based experimental and shown in figure 3.1.
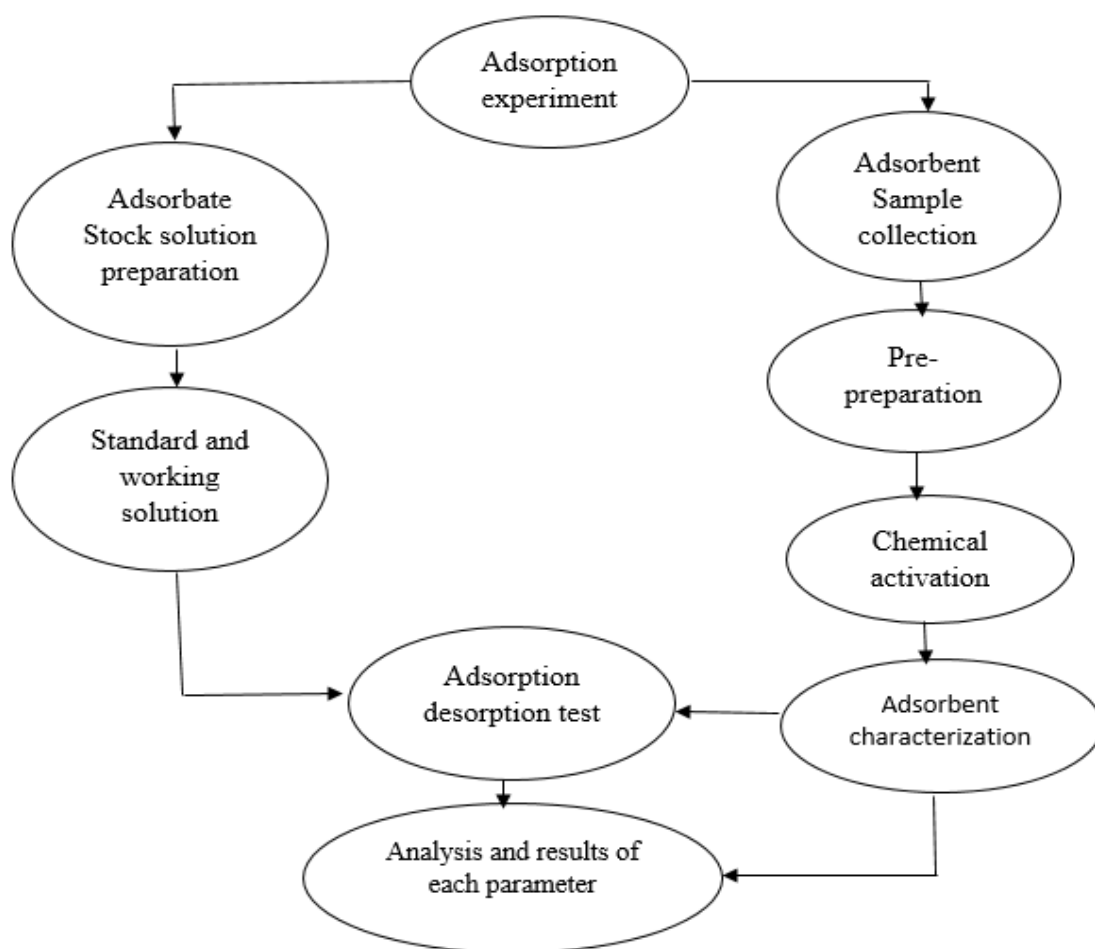

Figure 3.1 Adsorption experiment flow chart

3. 3 Study variables

3.3.1 Independent variables

The independent variables are pH, Contact time, Initial As concentration, shaker speed, Adsorbent particle size and Adsorbent dose**.**

3.3.2 Dependent variable

Activated carbon adsorption capacity.

3.4 Chemicals

Analytical grade chemicals and reagents were used throughout the study. Chemicals such as solution of H_3PO_4, NaOH (0.1 M), and/or HCl (0.1 M), Safranine O, Iodine, Potassium iodide, Thiosulphate solution (0.1 N), Methylene blue and Arsenic trioxide (As_2O_3) were used to produce Arsenic stock solution and deionized water was used for appropriate dilution of stock solution to produce working solution.

3.5 Instruments

Analytical balance (BP110S), Horizontal shaker (Edmund Buhler GmbH, SM – 30 A), plastic bag muffle furnace (Nabertherm Muffle Furnace LT 15/11), mortar, Oven, (GP/150/CLAD/F/VIS/SD/100/DG WAGTECH), pH meter (EN 16-102 WAGTECH pH/ ^{o}C), UV spectro-photometer (DR-5000) and Sieve were used.

3.6. Adsorbent Preparation and Characterization

In this study coffee husk was used as pre cursor. 100 gram of solid residue of the coffee husk was obtained from local coffee processing industry and plastic bag was used as sample container. The coffee husk was washed with distilled water, dried at 110 °C for 24 h in oven to remove moisture, crushed and sieved to obtain particle size pre-determined size using different type of seive. Then dried coffee husk was treated with 45% (w/w) H_3PO_4 (phosphoric acid) solution in a 1:1 mass proportion (phosphoric acid: raw material) and activated at 500 °C for 2 h in furnace (Nabertherm Muffle Furnace LT 15/11). After the activation, the excess H_3PO_4 was washed with hot distilled water until a neutral pH ($\approx$ 7.5) was reached (Lamine *et al*., 2014). The washed activated carbon then dried overnight at 100 °C in an oven then, The dried samples were crushed by hand in a mortar, and separated into four sieve size fractions: silt (<0.075 mm), fine (0.075 – 0.425 mm), medium (0.425 –

2.0 mm), and coarse (2.0 – 4.75 mm) sand size in diameter using the American Society for Testing and Materials (ASTM D 422) weighed and packed in an airtight plastic bag for later use.

3.6.1 Adsorbent Characterization

Determination of Iodine Number

0.5g of produced activated carbon (AC) from each sample was weighed into a beaker and 25ml of standardized iodine solution (0.0216M) was added. The mixture was swirled vigorously for 10 minutes and 20 ml of the clear filtrate was titrated with standardized sodium thiosulphate solution (0.1220M) to a persistence pale yellow color. 5ml of the freshly prepared starch indicator solution was added while titration resumed until a clear solution appeared. The procedure was repeated for two more times. The titration was also repeated with 20ml portion of the standardized iodine (not treated with AC from the precursor) to serve as blank titration

The iodine adsorption number (IAN) was calculated using the following relationship:

$$IAN = \frac{(Wt * Ms(Vb - Vs))}{2Ma} \qquad (8)$$

Where:

W_t is the molecular weight of iodine, M_s is the molarity of the thiosulphate solution (mol/dm^3), V_s is the volume of thiosulphate (cm^3) used for titration of AC aliquot, V_b is the volume of thiosulphate (cm^3) used for blank titration and M_a is the mass of AC (g).

Methylene Blue Number (MB)

MB number determination followed procedure of (American Society for Testing Materials, 2000). MB (0.15g) was weighed and dissolved in 100ml deionized water. The activated carbon samples (0.1g) each were weighed and transferred into 50ml stoppered flask. 10ml MB solution was added from a burette and the mixture shaken for 5 minutes. Once the 10ml solution was decolorized, MB solution was added 1ml at a time until there was no further decolorization. The end point was considered to be reached when the blue color persisted for 5 minutes.

MB adsorbed amount was calculated as given in equation (9):

$$MB \ number \left(\frac{mg}{g}\right) = \frac{15 * V}{10 * m} \qquad (9)$$

Where; V= Volume of the methylene blue solution consumed (ml), m= Mass of activated carbon sample used for the test (g).

Carbon Yield

The total yields were determined after sample processing in terms of raw material mass. The dried weight, Wo of each pre-treated sample was determined using Metler balance and the carbon yield calculated as;

$$Ych = \frac{Wf}{Wi} * 100 \%$$ (10)

Where; Y_{ch} is yield of coffee husk, W_o is dry weight before impregnation and w_f is dry weight of produced coffee husk activated carbon.

Proximate Analysis

Moisture content

Moisture content was determined according to ASTM 2867-99. Each AC sample (2g) was weighed and dried in a furnace continuously. The drying sample was constantly reweighed at a 10 mins interval until a constant weight (W_p) was obtained. The crucible and its content was retrieved and cooled in desiccators. The difference in weight (∂W) was recorded and the moisture content (MC) calculated as

$$Mc = \frac{Wo - Wp}{Wo} * 100$$ (11)

Where; W_0 is weight of Carbon retrieved from the furnace and W_o initial dry weight of the AC sample.

Volatile content and Ash content:

Are the non-combustible residue left after burning samples at 750-800°c for 0.5 h in muffle furnace. Ash content determination was done according to the ASTM D2866-94 method. Dry AC sample (1.0g) was placed in to a porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 1000 °c. The furnace was left on for one hour after which the crucible and its content was transferred to desiccators and allowed to cool. The crucible and content was reweighed and the weight lost was recorded as the ash content of the AC sample (Wash). Then the % ash content (dry basis) and Volatile Content (%) was calculated from the equation;

$$Ash\ cont\ (\%) = \frac{Wash}{Wo} * 100$$ (12)

$$\text{Volatile Content (\%)} = \frac{Wo - Wash}{Wo} * 100 \tag{13}$$

Where Wo is dry weight of activated carbon before ashing.

Fixed Carbon:

Fixed Carbon was determined by assuming that the sulphur content was negligible in all cases the fixed carbon content (FC) was given as:

$$FC = 100\% - MC - VC \tag{14}$$

Where MC= Moisture Content (%) and VC=Volatile Content (%)

pH

The pH were determined according to the method of ASTM D3838-80 as follows; 1.0 g of carbon activated carbon sample was weighed and transferred into a 250 mL beaker and 100 mL of distilled water was added and stirred for1 hour. Samples were allowed to stabilize and then pH measured using an electronic pH/Conductivity meter.

3.7 Preparation of arsenic stock and standard solution

Arsenic was studied under the trivalent (arsenite) and an arsenic (III) stock solution (1000 mg/ L) was prepared by dissolving 1.3200 g of As_2O_3 in distilled water. The initial pH of the arsenic solutions was adjusted using NaOH (0.1 M) and/or HCl (0.1 M) solutions as and when necessary and measured by Cyberscan pH 510 (Eutech) instrument. Deionized water was used for all analytical preparations. All the instruments used for the experimental were calibrated as per recommended by manufacturer. A series of standard working solutions for adsorption experiment was prepared by a stepwise dilution with deionized water from their stock solution (1000 mg/ L).

3.8 Batch adsorption experiments

Sets of batch adsorption experiments were performed in order to investigate the Arsenic adsorption process onto CACH under various experimental conditions. Adsorption experiments were conducted by varying the initial As (III) concentration, adsorbent dose, contact time, solution pH, and agitation speed: mixing desired amount of adsorbate (arsenic containing solution) volume of 100 mL with desired amount of adsorbent (CACH) pouring in 250 mL Erlenmeyer flask. The As (III) containing solution was agitated by a horizontal shaker (SM-30, Edmund Buhler GmbH Germany) at 200 rpm for a desired contact time.

Then each sample was filtered through 0.45µm membrane filter (MN 640 d, No. 46, Blauband, Germany) filter paper prior analysis of the solution. Finally, As concentration of solution was determined using DR-5000 spectrophotometer at wavelength of 602.2 nm. The average of duplicate measurements was reported.

The removal percentage As (%) and Arsenic adsorbed amount per unit mass of adsorbent q (mg/ g) was calculated by a mass balance equation (Eq. (14)) and (Eq. (15)) respectively.

$$\text{As (\%) removal} = \frac{(co - ce)}{co} * 100 \tag{14}$$

$$q = \frac{(Co - Ce)}{m} v \tag{15}$$

Where Co and Ce are As (III) concentration (mg/L) at time 0 and t, respectively, V is the volume of the solution (mL), m is the mass of the activated carbon and q is the amount of As (III) uptake by the adsorbent in mg/g.

3.8.1 Effects of Initial concentration

The effects of initial As (III) concentration was performed by preparing 10 to 100 mg/L As (III) from the stock solution. Then each solution was poured in to Erlenmeyer flasks and mixed for time one hour on horizontal shaker (SM-30, Edmund Buhler GmbH, Germany) shaking speed 200 rpm and keeping other parameters constant. The supernatant solution samples were then filtered with filter paper through 0.45µm membrane filter (MN 640 d, No. 46, Blauband, Germany) for the analysis of percentage removal using equation (14).

3.8.2 Effects of Adsorbent dose

The effect of the adsorbent dose was performed at 20 ^{0}C in Erlenmeyer flasks, stirred on horizontal shaker (SM-30, Edmund Buhler GmbH Germany) at 200 rpm for 60 min contact time. Different masses of the adsorbent (0.5 to 3 g) were thoroughly mixed and treated with As (III) solution.

3.8.3 Effects of contact time

The effect of contact time was performed at 20 ^{0}C in Erlenmeyer flasks containing known g of the adsorbent and As (III) aqueous solution. The flasks were stirred at varied contact time of 10 min to 2 h keeping other parameters at optimum. The supernatant solution samples were then filtered with 0.45-µm filter paper then equilibrium time were determined.

3.8.4 Effect of Solution pH

Solution pH was investigated to determine the optimum pH for maximum adsorptive removal of Arsenic (III). pH of As (III) aqueous solution was maintained at a desired value (pH 2 to 10) by adding 0.1 M NaOH and/or 0.1 M HCl. While maintaining other parameters at their optimum at shaking speed of 200 rpm.

3.8.5 Effect of shaking speed (Agitation time)

Finally, the effect of agitation speed on As (III) adsorption was carried out with a horizontal shaker at room temperature by varying the agitation speed from 100 to 300 rpm while keeping other parameters to their optimum and effects of agitation speed determined.

3.8.6 Effect of adsorbent particle size

The effect of adsorbent particle size on As (III) removal was conducted over the particle size ranged from silt to coarse sand size (subsection 3.6) by keeping other parameters constant.

3.9 Adsorption kinetics and isotherm models

3.9.1 Adsorption kinetics

The knowledge of the pollutant adsorption kinetics of materials is of a great importance when dimensioning filters for pollutant removal. The adsorption kinetics is usually determined by batch experiments, monitoring the pollutant concentrations over time until equilibrium in pollutant adsorption is reached.

The pseudo-first order and second order kinetic models are used to study the sorption kinetics of pollutants and to quantify the extent of uptake in sorption kinetics. To determine kinetic adsorption parameters, the obtained kinetic adsorption data were evaluated by using simple Langergren pseudo-first order equation, pseudo-second order equation (Ho and McKay, 1999) and Intra-particle diffusion models

The pseudo-fist order kinetic model is given by Equation 16.

$$Log\ (qe - qt) = \ \log qe - \frac{Kad}{2.303}\ t \qquad\qquad (16)$$

Where q_t and q_e are the adsorption capacity at time t (mg/g) and at equilibrium, respectively, and kad (min^{-1}) is the pseudo-fist order rate constant of the adsorption. A plot of log (q_e - q_t) versus t should give a straight line if the pseudo-fist order kinetic describes the

adsorption process. Log (q_e-q_t) versus at different time were plotted to calculate the rate constant and coefficient of determination (R^2).

The linearized-integral form of the pseudo second order reaction model is represented by Equation 17 as follows:

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe} t \tag{17}$$

Where $h = kq_e{}^2$ (mg/g/min) and k is the rate constant for pseudo-second order adsorption (g/mg/min). The plot of t/qt versus t should give a straight line if pseudo second order kinetic is applicable and qe, k and h can be determined from the slope and intercept of the plot (Ayanda et *al*., 2013).

Due to rapid stirring in the batch reactor, ions are transported from aqueous phase to the surface of the adsorbent and subsequently they may diffuse into the interior of the particles if they are porous. The intra-particle diffusion can be expressed by the equation 18 (Weber and Morris, 1963) cited in (Alemayehu & Lennartz, 2010; Fufa, *et al*., 2014)

$$qt = Kp\, t^{0.5} + C \tag{18}$$

Where qt is the amount of As (III) adsorbed (mg/g) at a given time t (min); kp [mg/g.min$^{0.5}$)] is the intra-particle diffusion rate constant; and C (mg/g) is the intercept of the intra-particle diffusion model. The plots of q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the diffusion rate constant, k_p.

3.9.2 Adsorption isotherms

One of the most commonly used adsorption model, the Langmuir isotherm can be expressed as;

$$\frac{1}{q} = \frac{1}{qmKl}\frac{1}{ce} + \frac{1}{qm} \tag{19}$$

Where K_L is the Langmuir equilibrium constant (L/mg) that is related to the heat of adsorption and q_m is the maximum monolayer sorption capacity (mg/g).

The Freudlich isotherm model is expressed by Equation 20 as follows.

$$Log\, q = \log kf + \frac{1}{n}\log c \tag{20}$$

where q is the quantity of the solute adsorbed per unit weight of the adsorbent (mg/g), C is the equilibrium concentration of the adsorbing compound (mg/L), and K_F represents the

adsorption capacity (mg/g $(L/mg)^{1/n}$), and n represents the degree of dependence of adsorption on equilibrium concentration.

To identify a suitable these isotherm models for the sorption of As (III) on CACH, The sum of the squares of the errors (SSE) analysis was carried out and mathematically SSE is given by equation 21.

$$SSE = \sum(qe\ cal - qe\ exp)^2 \tag{21}$$

Where qe,calc (milligrams per gram) is the equilibrium capacity obtained by calculation from the model, and qe,exp (milligrams per gram) is the experimental data on the equilibrium capacity. If data from the model are similar to the experimental data, SSE will be a small number; while if they differ, SSE will be a bigger number

3.10 Regeneration of adsorbent

Regeneration of adsorbents is an important process in the water/wastewater treatment to reduce the processing cost, recover adsorbates, and/or explain adsorption mechanism. To investigate the reusability of adsorbent, desorption has been investigated using optimum adsorbent dose to adsorb optimum adsorbate concentration. The adsorbent was separated from the solution by filtration using 0.45μm filter paper and washed gently with distilled water to remove un-adsorbed As (III) on adsorbent surface. The As loaded on AC of coffee husk was dried in an oven at 105^oC for 24 hrs and then soaked and shacked in (0.1 - 0.2 M) NaOH solution. Then, the amount of desorbed As was measured and desorption ratio of As (III) calculated using Eq. (22).

$$\text{Desorption ratio (\%)} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} * (100) \tag{22}$$

3.11 Data Analysis and Quality

At each sets of experiments calibration (standardization) was conducted for analysis. Each batch adsorption experiment was performed in duplicates and the average values were reported to ensure reproducibility and accuracy of the data analysis. Blank and control were used for correction of interference that leached from instruments and adsorbents. Quality control measures for each parameter including calibration with reference samples, blanks and replicate analysis followed throughout the analysis in order to ensure reliable analytical data. The data was analyzed using Microsoft's Excel spreadsheet 2013 and Minitab was used. The data presented using graphical and tabular statistical tools.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Characterization of adsorbent

First, it was found to be important to prepare AC with good adsorptive property and reasonable yield. Iodine and MB number is a fundamental parameter used to characterize activated carbon performance. MB number and iodine sorption capacity have relationship with the pore structure of adsorbents. Because of I_2 is a small molecule with a size of 0.56nm, the iodine sorption capacity is related to the degree of micro and mesopores present in the activated carbon, while MB number indicate the capacity of an adsorbent to adsorb large molecular size species into its macropores. The micropores are responsible for the large surface area of AC particles and are created during the activation process. It is in the micropores that adsorption largely takes place. Increasing surface area and surface active groups cause a rise in iodine and MB adsorption. Thus adsorptive capacity which is indicated by Iodine Number of prepared activated carbon and yield was determined and the study demonstrated that AC with good IN value (386 mg/g) can be prepared from coffee husk at reasonable yield of 54.1(%). The calculated MB value was found to be 306 (mg/g) and pH of finally produced activated carbon was 6.1. The chemical composition and various physical properties of the coffee husk were presented in Table 3. Proximate and ultimate analyses were performed for the raw material. Proximate analysis is one of the thermal analysis techniques in which a physical property is measured with a temperature-programmed variation. In this case, the property measured is the weight. Proximate analysis provides an approach to estimate the content of: moisture, volatile matter, fixed carbon and ash.

Table 3 Analysis of dried coffee husk

Proximate analysis		Ultimate analysis	
Moisture content%	7.32	C%	49.6
Volatile matter %	76.6	H%	6.2
Fixed carbon %	15.6	N%	0.71
Ash	0.68	S%	0.07

From the ultimate analysis of the precursor, coffee husk has a negligible sulfur and low nitrogen content, and high carbon contents. Generally, the composition of ash, fixed carbon, and volatile matter are given on a dry basis. The proximate analyses a presented in Table 3 showed a less amount of moisture, ash and volatile matter, and high value of fixed carbon indicating that high graphitization grade and low amount of functional groups. This in turn shows that the activated carbon can be an excellent raw material for adsorbents to be used in column or fixed-bed reactors. Ash content reduces the overall activity of activated carbon, the lower the ash value therefore the better the activated. Volatile content in AC is mainly due to the presence of non-carbonaceous matters. The elimination of non-carbonaceous matters is controlled by activating agent and temperature. Finding of other researchers agrees with the result of this study. According to Chen *et al,* result of ultimate analysis showed that dry coffee husk includes 46.62 wt% of C, 8.87 wt% of H, 23.90 wt% of O, 5.64 wt% of N and 0.94 wt% of S (Chen *et al*., 2016). Preparing ACs using activating agent, in this study phosphoric acid has strong influence on the pore volume and structure of ACs. Low impregnation ratios led to essentially microporous ACs, whereas at intermediate ratios, ACs with wider pore size distribution (from microporous to mesoporous) were obtained. High impregnation ratios yielded essentially mesoporous carbons with a large surface area and pore volume (Baquero, 2003).

4.2 The effect of initial As (III) concentration

The effect of the initial As (III) concentration on the removal efficiency of As is presented in Figure 4.1 reveals that adsorption efficiency is higher at lower initial arsenic concentration and a slow decrease in arsenic (III) adsorption by CACH were observed with increasing initial arsenic (III) concentration. This is in agreement with the findings from various researchers that suggest the more concentrated solution is the better adsorption (Xu *et al*., 2006). As initial As (III) concentration increase As (III) removal efficiency decreased from 79.8(%) to 43.9(%).This could be explained with the fact that at higher As (III) concentration, the available sites of adsorption becomes fewer and hence the percentage removal of As (III) decreases (Ananta *et al*., 2015). Also this is one of the principles adsorption of adsorption isotherm that is, the site with greater affinity by adsorbate are occupied first followed by other sites with less affinity by adsorbate, until the saturation of the adsorbent (Imyim and Praralimrungsi, 2010; Nsaifabbas and Saeed, 2014).
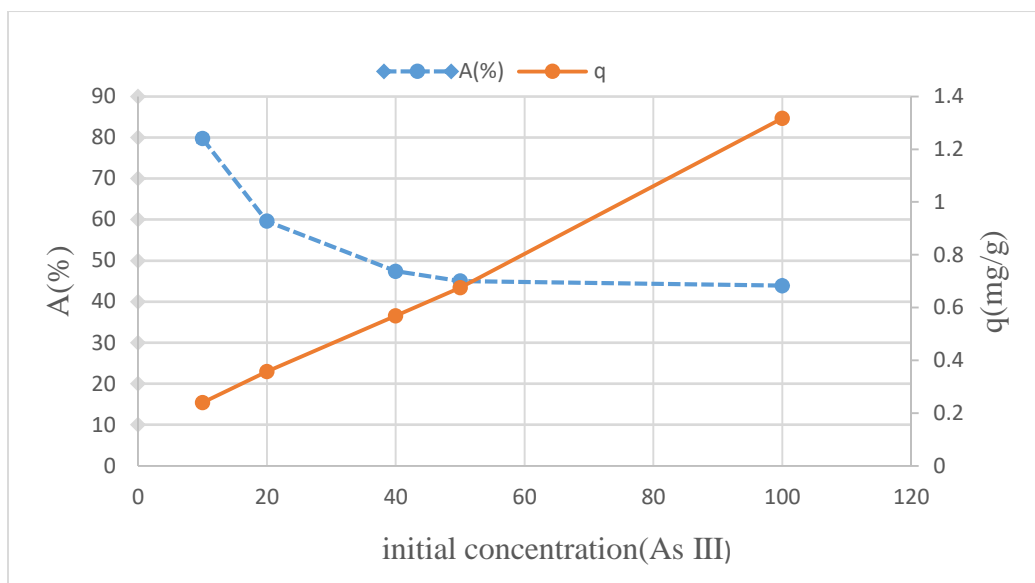
Figure 4. 1 Effect of initial As (III) concentration of the adsorption of As (III) ions on to CACH at contact time 60 min, adsorbent dose 3 g at room temperature and pH 7.4.

4.3 Effects of adsorbent dose.

Different masses of the adsorbent (0.5 to 4g) were thoroughly mixed with As (III) solution maintaining other parameters constant. The experiment for the adsorbent revealed that the removal efficiency of As (III) in a fixed contact time of 60 min increase significantly from 24.95% to 56%. The results obtained (Figure 4.2) showed that as the amount of activated carbon was increased from 0.5 to 4 g, the amount adsorbed and percentage removal of As (III) was increased from 0.75 to 1.68 mg/g and 24.95% to 56% respectively. The adsorbent dose affects the adsorption capacity directly; as the dosage increases, more active sites become available for As (III) ions. The increase in the removal efficiency of arsenic (III) may be attributed to the fact that with the increase in adsorbent dose, available surface for adsorption increases for the solute to be adsorbed (Ananta *et al.,* 2015). It is observed that, after dosage of 3 gm, there was no significant change in percentage of removal of As (III). It may be due to overlapping active sites at higher dosage. So, it seems there was not any appreciable increase in the effective surface area resulting due to the conglomeration of exchanger particles (Sumathi and Alagumuthu, 2014).
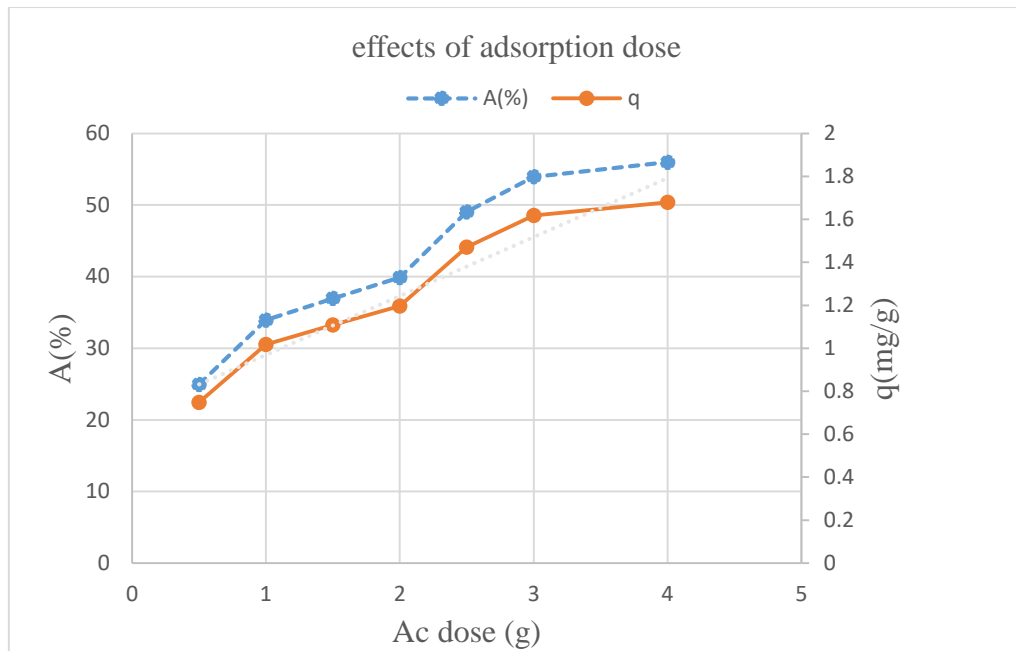
Figure 4.2 Effects of adsorption dose for the adsorption of As (III) solution on to CACH at

(C$_o$ = 100mg/l, contact time 60 min, pH 7.4 and at room temperature)

4.4 Effects of contact time

Effects of contact time of CACH onto arsenic (III) solution was also determined increasing from 10 min to 2 hour keeping other parameters constant. It was observed in Figure 4.3 that as the contact time increases, there was also enhancement in the adsorption of As (III) according to both percentage removal as well as amount adsorbed values. This was due to a larger surface area of the activated carbon being made available with time in contact for the adsorption of As (III). From figure 4.3 the result showed that As (III) removal capacity increased from 0.3 to 1.8 mg/g and the removal percent from 10% to 56% as the contact time increased from 20 to 120 min of agitation speed.

Starting from 10 min to 60 min of contact time the removal percent and capacity showed high increment, whereas from 60 to 120 min showed increment with insignificant change almost constant. The reason may be due to the fact that, initially all adsorbent sites were empty and the arsenic concentration was high. Afterward, the arsenic (III) adsorption capacity of the adsorbent was decreased significantly due to the decrease in available adsorption sites as well as arsenic concentration (Ananta *et al.,* 2015). Therefore 60 min was taken as equilibrium contact time.
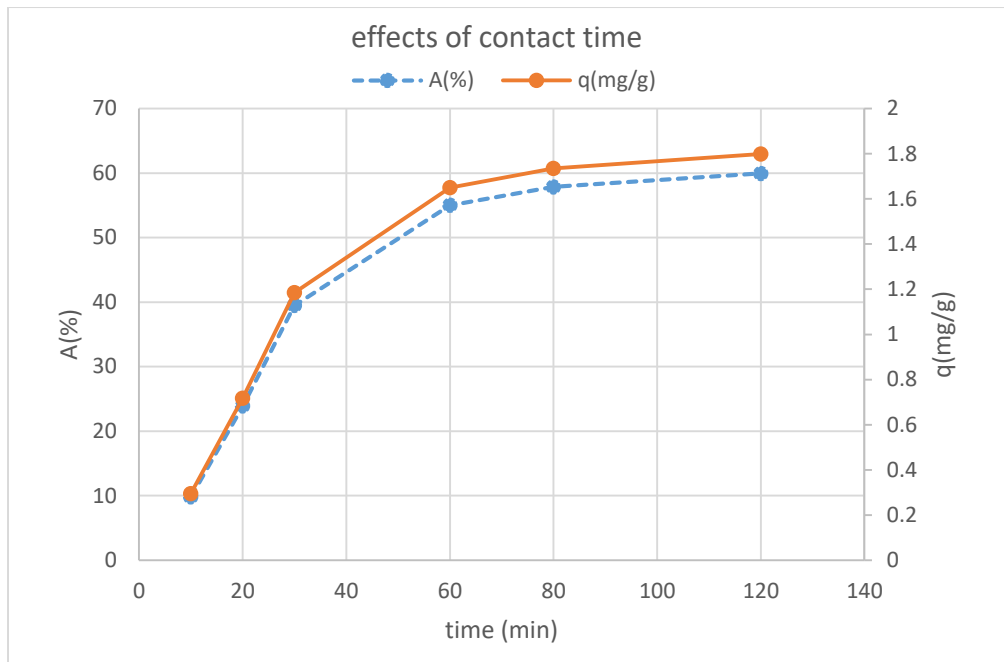
44

Figure 4.3 Effects of contact time for the adsorption on As (III) ions on to CACH at (Co = 100mg/l, 20 °C, pH 7 and 200 rpm).

It can be seen that the adsorption of As is rapid at the initial stage of contact period, but it gradually slowed down until it reached equilibrium. The rapid uptake until it reaches equilibrium due to the presence of a large number of free competent active adsorbing sites available on the surface of the adsorbent. The result shows that the adsorption rate with increasing initial contact time in a given mass of adsorbent is raised and then gradually reaches equilibrium because the adsorbent surface of a given particular mass of adsorbent involve particular site to adsorb As (III) concentration. So, those site would be occupied by adsobate within short period of time due to increasing contact time.

4.5 Effects of solution pH

The effects of pH on the adsorption of As (III) onto the activated carbon was examined for pH values ranging from 2 to 12. Figure 4.4 demonstrated that as the pH of the solution increased from 2 to 12 the percentage of As (III) adsorbed steadily increased, amount of As (III) adsorbed also. The increase in the percentage removal of As (III) from pH 2 to 12 might be due to the decrease in the concentration of H^+ ions (as the solution become less acidic) which initially compete with As (III) ions for binding onto the surface of the activated carbon (Ayanda *et al.*, 2017).
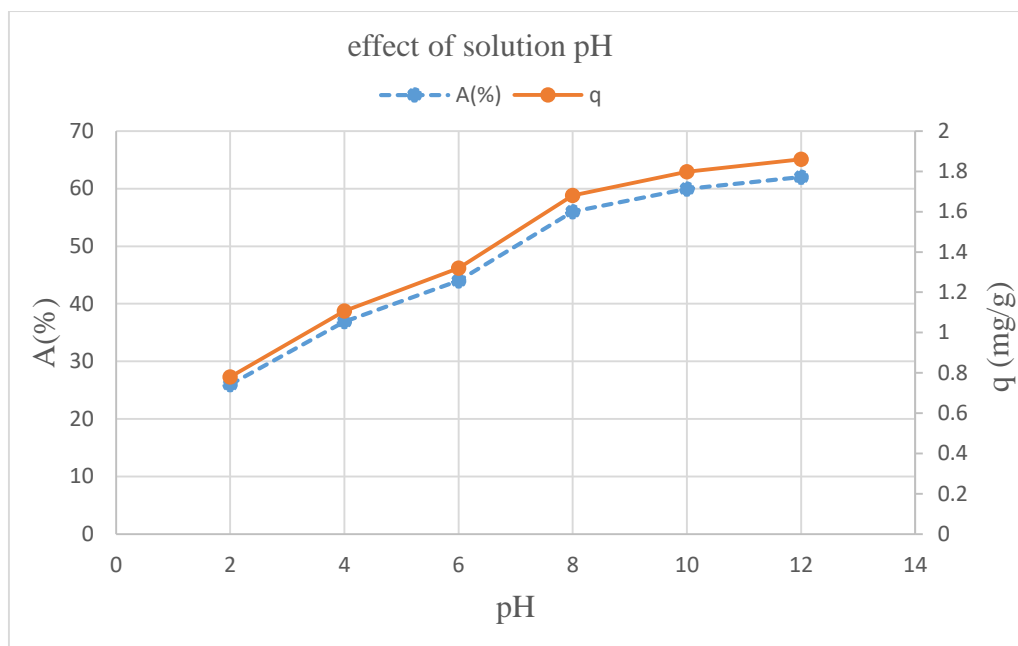
Figure 4.4 effects of solution pH onto As (III) adsorption CACH at (temp 20 °C, shaking speed 200 rpm, C₀ 100mg/l).

4.6 Effect of Agitating speed

Adsorption studies were carried out using horizontal shaker (SM-30, Edmund Buhler GmbH, Germany) at an initial concentration of As (III) 100 mg/L; adsorbent dose (3 g/L) with contact time 60 min and pH 7. Then agitation speed varied from 150 to 250 rpm to determine effect of agitation speed on As removal efficiency. The plot of agitation speed with removal efficiency was shown in figure 4.6. It was observed that the adsorption percentage of As (III) onto the CACH increased with increasing agitation speed reaching maximum of 56% at 200 rpm rotation speed. This is due to dispersal of the adsorbent particle in the aqueous solution which leads to reduced boundary mass transfer and even then it may increase the velocity of particles, so that it increases the percent removal of As (III). Optimum agitation speed confirms usability of all the surface active sites of adsorbent to uptake arsenic. It was an optimum speed of agitation to assure the availability of all the surface binding sites for arsenic uptake. Decreased value of As removal efficiency on CACH after 200 rpm observed as a result of too vigorous agitation rate which causes more As (III) molecule to be desorbed from the adsorbed surface (Berhe *et al*., 2015).
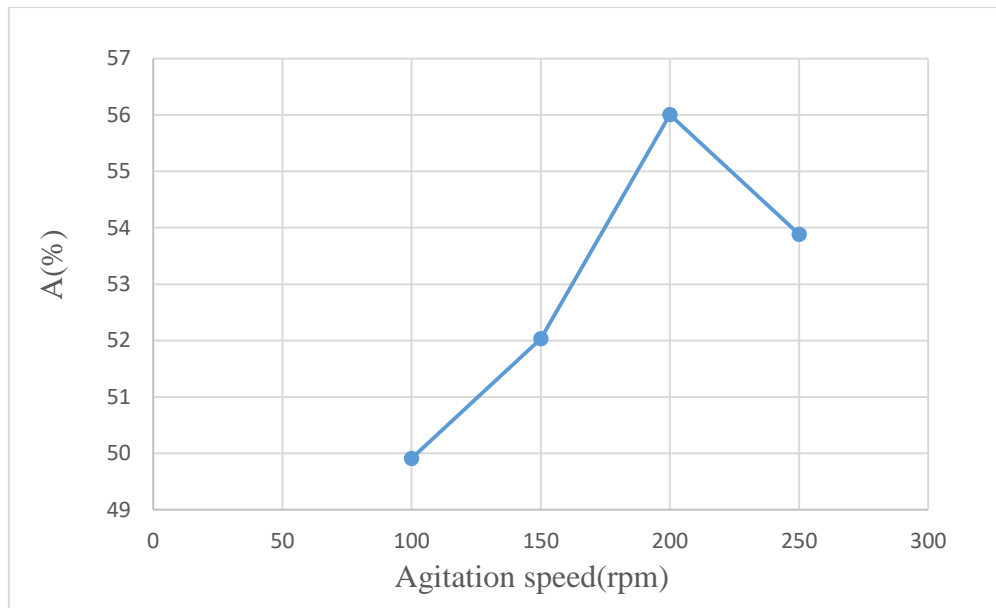
Figure 4.6 Effect of agitating speed on the adsorption of As (III) onto CACH at (Co: 100 mg/L, adsorbent dose: 3 g/L, pH: 6, contact time: 60 min).

During slow agitation speed, shaker did not spread in the solution properly, instead it conglomerated in the solution. thus, beneath the apex layers of adsorbent it hide many active sites so apex layer is only available for adsorption and in this process hidden layers are not present to participate in the adsorption process, since they had no proper contact with As(III).

At higher agitation speed, As (III) particles have not enough time to make a bond with CACH due to random collisions among the participant particle. Approach type of agitation speed pattern was also found by the other researchers (Liu *et al.,* 2012; Mondal et *al.,* 2017).

4.7. Effect of adsorbent particle size

Adsorption studies were carried out using horizontal shaker (SM-30, Edmund Buhler GmbH, Germany) at an initial concentration of As (III) 100 mg/L; adsorbent dose (3 g/L) with contact time 60 min, pH 7 and 200 rpm agitation speed. The results are presented in Fig.4.7 indicated that the percentage of As (III) adsorbed increased with a decrease in particle size of the adsorbent from 4.75 to 0.075 mm (Fig. 4.7)
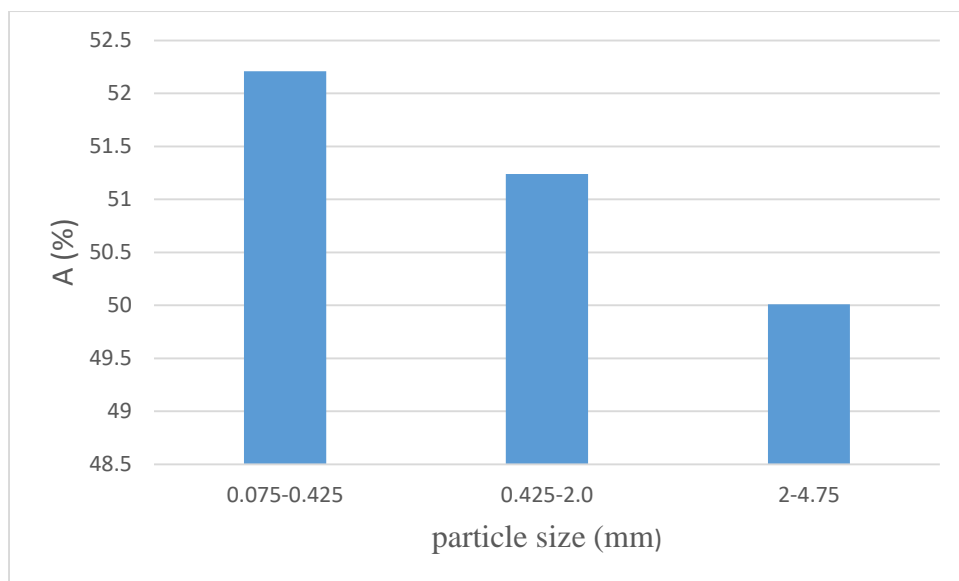
Figure 4.7 Effect of adsorbent dose on adsorption of As (III) onto CACH

The Percent removal of As (III) increased systematically with decreasing particle size. On changing the particle size from 4.75 to 0.075 mm, the percent removed increased from 50.01 to 51.24 and from 51.24 to 52.21 respectively. However, the smallest particle size (< 0.075mm, powder) did not exhibited an enhanced removal that which was attributed to a loss of porosity, and thus of diffusion controlled sorption of Arsenic.

4.8. Adsorption isotherms

Adsorption isotherms describe the distribution of adsorbate between adsorbent and solution when adsorption process reaches the equilibrium, which are an important data to explain the adsorption mechanism. The applicability of the isotherm equation is compared by judging the correlation coefficients R^2. In a view of value of R^2, Langmuir and Freundlich isotherm gives satisfactory fit to the experimental data of Arsenic. The results suggest that the Arsenic is favorably adsorbed on CACH. The isotherm plots of the equilibrium adsorption of As (III) graphically represented in fig 4.8.1 and 4.8.2 for Freundlich and Langmuir respectively and the value of equilibrium constant computed from the isotherm models using non-linear regression using Sum of square error function are given in Table 4.

Table 4 nonlinear isotherm parameters of Langmuir and Freundlich isotherms models for adsorption of Arsenic onto CACH.

Langmuir Isotherm		Freundlich Isotherm	
parameters	value	parameters	value
q_{max}	1.71	K_F	0.19
Kl	0.22	1/n	0.48
R^2	0.78	R^2	0.96
SSE	0.108	SSE	0.0615

From the evaluation of the fitting criteria, it was clear that the Freundlich isotherm demonstrated higher coefficient of determination, $R^2 > 0.96$. This means equilibrium isotherm data set of As adsorption well described by Freundlich isotherm. These facts indicate that the chemical adsorption mechanism may involve in adsorption process of As on CACH and As molecules are adsorbed in the form of homogenous coverage on adsorbents' surface.
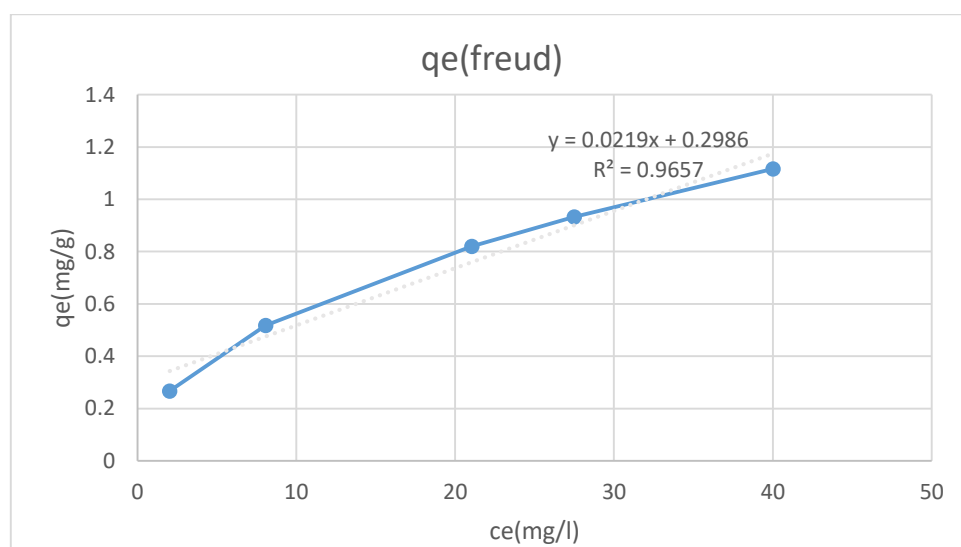
Figure 4.8.1 Freundlich isotherms of CACH for Arsenic adsorption.

For Langmuir model, the adsorption affinity between adsorbate and adsorbent can be described by the separation factor (RL). The adsorption process is irreversible if RL = 0, favorable if 0 < RL < 1, linear if RL=1 and unfavorable if RL > 1. From the plot Qmax (1.71 mg/g) is the maximum amount of adsorption from assumption of Langmuir adsorption isotherm model and *RL* (the separation factor) The calculated value range from

0.17 to 0.02 with decreasing in value at high level of initial concentration indicating that As (III) adsorption on CACH is favorable and the R^2 value is 0.78.

Figure 4.8.2 Langmuir isotherms of CACH for Arsenic adsorption.

From The Langmuir and Freundlich plots presented, showed that the R^2 value of the Langmuir isotherm (0.78) was lower than the Freundlich isotherm (0.96). Hence, As (III) adsorption onto activated carbon follows the Freudlich isotherm.
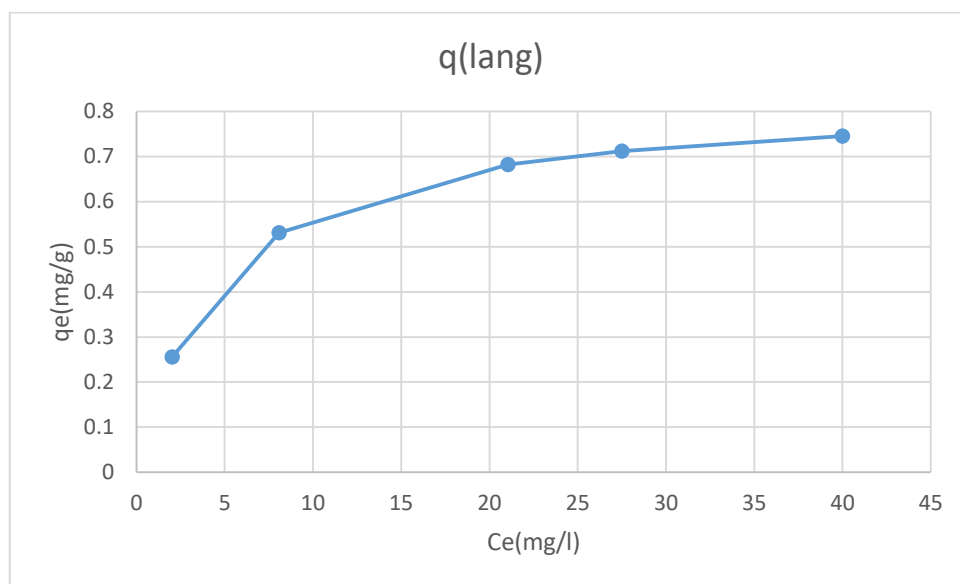
4.9 Adsorption Kinetics

To evaluate the kinetics of the adsorption process, the pseudo-fist order and pseudo-second order models and intra particle diffusion model were tested to interpret the experimental data. The results of fitting the experimental data to the pseudo-first order, pseudo-second order kinetic equations and intra-particle diffusion (represented in Eq. 16, 17, and (Eq. 18) respectively are presented in Table 5. The values of the pseudo-first-order adsorption rate constant k_f (Table 5) are determined using Eq. (16) by plotting log (qe - qt) against t for As (III) adsorption onto the CACH. The result shows that the modeled equilibrium capacity is qe, cal (2.98 mg/g) from the linear plot of pseudo-first order log (qe-qt) versus t and have coefficient of determination $R^2 > 0.96$. Also, the values of the modeled equilibrium capacities, were comparable to the experimental equilibrium capacities.

Table 5 the kinetic parameters and values for adsorption of As (III) onto CACH

Pseudo first order		Pseudo second order		Intra particle Diffusion	
parameter	value	parameter	value	parameter	value
qe_{cal} (mg/g)	2.98	qe_{cal} (mg/g)	2.7	Kp	0.069
Kf[g/(mg.min)]	0.087	Ks [(g/mg.min)]	0.0062	C	3.088
R^2	0.965	R^2	0.8528	R^2	0.97

The linear plots of pseudo-first order, pseudo-second order kinetics and intra particle diffusion model were shown in figure 4.9.1 fig 4.9.2 and fig 4.9.3 respectively. In the linear plot of pseudo-second order, the plots of t/qt versus t were not straight line with coefficient of determination, $R^2 > 0.85$ which is much less than pseudo first order. This suggests that As (III) adsorption onto activated carbon followed the pseudo-first order kinetics and As (III) were adsorbed onto the activated carbon (i.e. CACH) surface via chemical interaction. Thus suggests a reaction whose rate of reaction is determined by the concentration of one chemical species.
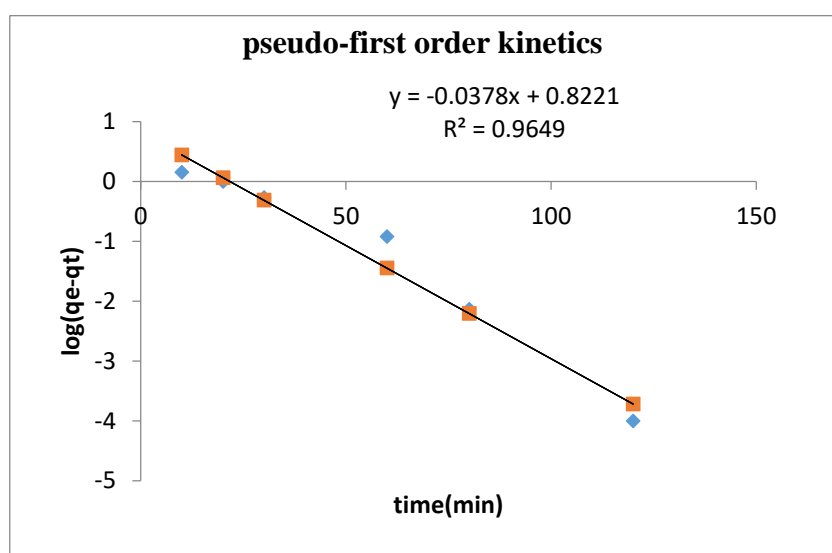
Figure 4.9. 2 Pseudo-first order reactions of the adsorption of As (III) ions onto CACH.
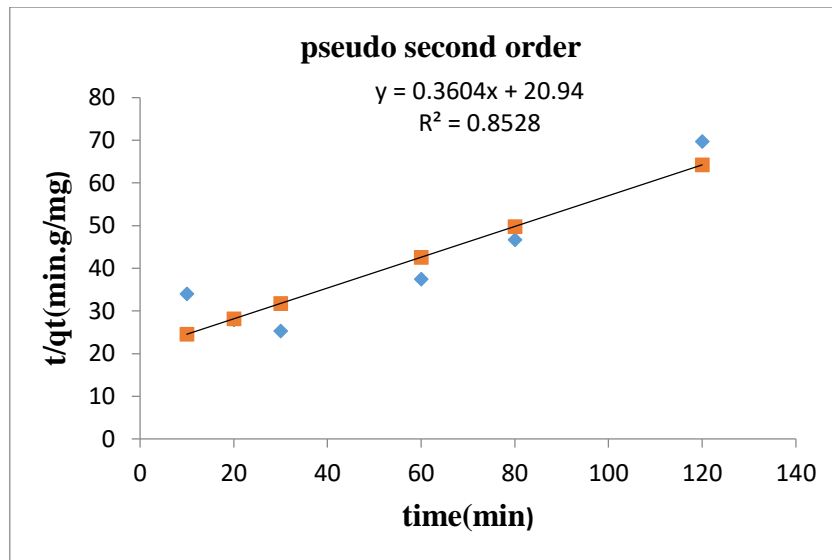
Figure 4.9.3 Pseudo-second order reactions of the adsorption of As (III) ions onto CACH

The intra-particle diffusion model (Eq. 18) based on the theory proposed by Weber and Morris, (1963) was tested to determine if the particles' diffusion is the rate-limiting step for the As (III) adsorption onto CACH. The intra - particle diffusion rate constant (Kp) value estimated from the slope of plot of q_t versus square root of time ($t^{0.5}$) was found to be 0.069 mg/ (g. $min^{0.5}$).
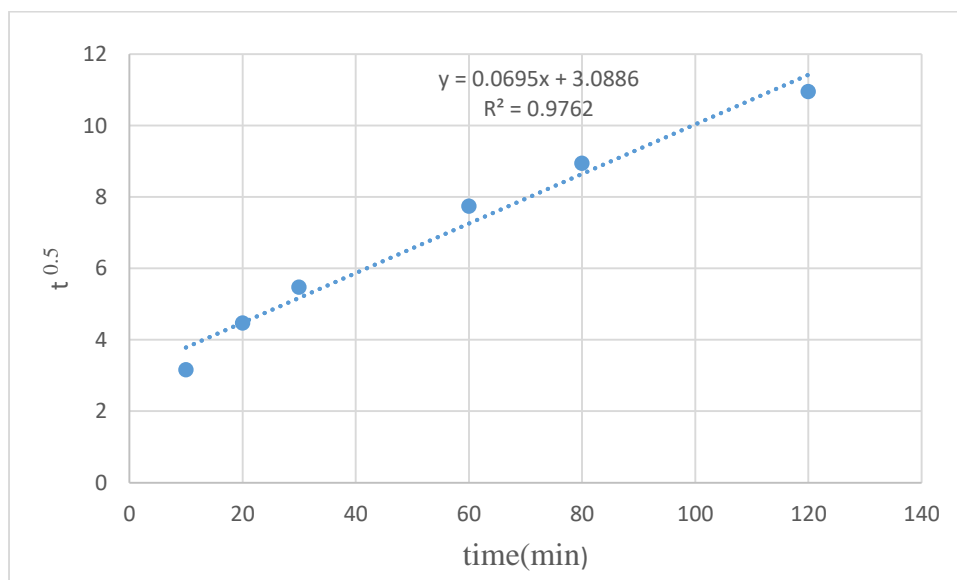
Figure 4.9.3 The intra-particle diffusion model of CACH for Arsenic adsorption

According to Weber and Morris, if intra-particle diffusion is a rate-controlling step, then the plots should be linear and pass through the origin (Weber and Morris 1963 cited in (Kebede, *et al.,* 2014; Fufa, *et al*., 2014)). As shown in Fig. 4.9.3 though the plot is not passing through the origin. These indicates that the Arsenic adsorption onto CACH is a

complex process and this is indicative of some degree of boundary layer control and this shows that the intra-particle diffusion was not the sole rate controlling step, but other kinetic models may control the rate of adsorption.

4.10 Desorption Study

Any adsorbent is economically viable for pollutant removal from aqueous environment if the adsorbent can be regenerated and reused. Desorption study was investigated and batch desorption of As adsorbed was carried out identical experimental conditions of the batch adsorption studies using 100 mL of 0.1 and 0.3 M NaOH solution separately. The experimental results from the desorption study revealed that trend of desorption percentage at different concentration of NaOH is in the 0.1M < 0.3M. Fig 4.10 shows the percentage removal of As (III) desorbed by different concentration of NaOH solution. The result showed that the percentage desorbed or desorption ratio increased from 52.5% to 71.4% as the concentration of NAOH increased from 0.1 to 0.3 in the solution of CACH.
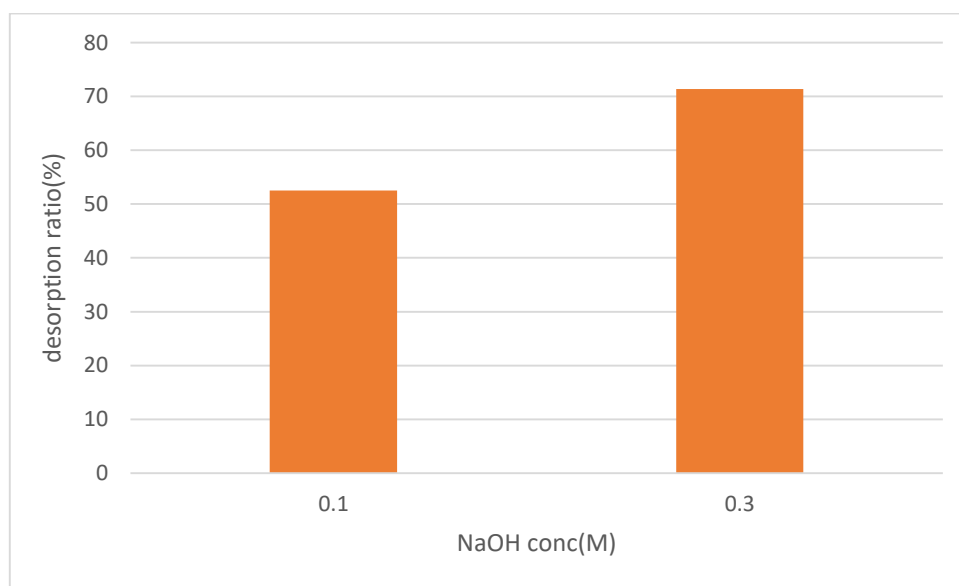

Figure 4.10 desorption ratio As (III) onto CACH (Co: 100mg/l, dose: 3g, contact time: 60 min, at room temperature and pH: 12)

From the study it is revealed that the used CACH can be regenerated satisfactorily and reused for further arsenic (III) removal due to which the process is seems to be cost effective.

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CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUTIONS

Arsenic has become a major challenge around the world due to its harmful effect on animals, human and the environment. Thus sorptive removal of Arsenic using CACH investigated and results of the present study indicated that activated carbon (produced from coffee husk) were capable of removing As (III) from aqueous solutions. From characterization of adsorbent, it can be concluded that activated carbon can be produced at reasonable yield, with good pore volume and surface area; as IN and MB value showed which are direct indicator of adsorption capacity. Although the study parameters such as the initial As (III) concentrations of solution, contact times, adsorbent, particle sizes, pH and shaking speed significantly affected the removal efficiency of As (III). With increasing the initial Arsenic concentration the amounts of Arsenic uptake increase and removal efficiency decrease. As the initial As (III) concentrations of solution increase, removal efficiency decreased from 79.8 (%) to 43.9 (%). The adsorption of As (III) by CACH increased with the increase in contact time, equilibrium time was achieved within 60 minutes contact time. pH of the solution increased from 2 to 12 the percentage of As (III) adsorbed steadily increased, amount of As (III) adsorbed also. The optimum dose for maximum Arsenic removal was 3 g from the study as the amount of dose decrease the removal efficiency also decrease. Optimal agitating speed was reached at 200 r.p.m. The Percent removal of As (III) increased systematically with decreasing particle size from sand size course to silt, the percent removed increased from 50.01 to 51.24 and from 51.24 to 52.21 respectively. Adsorption isotherm of As (III) on the adsorbent most satisfactorily described by Freundlich ($R^2 > 0.96$) than Langmuir isotherm model. As (III) adsorption process onto CACH follows pseudo-first order kinetics with $R^2 > 0.96$. The result of the adsorption-desorption-adsorption cycle showed that As (III) saturated adsorbent can be regenerated using 0.1 M and 0.3 M NaOH solution and the regenerated adsorbent still possessed adsorption capacity for As (III) in solution. Therefore, since coffee husk is widely and locally available, low-cost adsorbent; its utility will be economical and can be viewed as part of a feasible waste management strategy of coffee processing industry area and processed and used as adsorbent. The present finding hopefully reveals that CACH can

be used to purify the aqueous As (III) in drinking water with further investigation for large scale.

5.2 RECOMMENDATIONS

Depending on the current study it is remind that to use an adsorption technology using coffee husk adsorbents for arsenic and other heavy metals. It reveals to be useful for tackling the impacts of high concentrations of As (III) in water.

Further investigation such as:

- Real water based analysis to fully optimize sorptive removal using CACH.
- Investigation of adsorption capacity of the adsorbent under continuous flow conditions.
- For large-scale application, further column experiments needs to be conducted to determine the real adsorption capacity.

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ANNEXE

Experimental Result and Laboratory Pictures

I. Experimental Result

1. Initial Concentration

C_o	A	B	Av	C_o-C_e	A (%)	q
10	2.0563	1.9961	2.0262	7.9738	79.738	0.23921
20	7.981	8.166	8.0735	11.9265	59.6325	0.3578
40	21.201	20.872	21.0365	18.9635	47.4088	0.56891
50	27.532	27.456	27.494	22.506	45.012	0.67518
100	46.221	45.996	46.1085	53.8915	53.8915	1.61675

(Contact time = 60 min, Agitating speed = 200 rpm, CACH dose = 3 gm, pH = 7)

2. Solution pH

PH	A	B	Av	C_o- C_e	A (%)	q
2	74.0325	73.996	74.0143	25.9858	25.9858	0.77957
4	63.211	63.004	63.1075	36.8925	36.8925	1.10678
6	55.998	56.004	56.001	43.999	43.999	1.31997
8	44.012	44.001	44.0065	55.9935	55.9935	1.67981
10	40.221	39.891	40.056	59.944	59.944	1.79832
12	38.018	37.992	38.005	61.995	61.995	1.85985

(Co = 100 mg/L, Agitating speed = 200 rpm, contact time = 60 min, CACH dose = 3 g/L)

3. Contact Time

Co	time(min)	A	B	Av	$C_o - C_e$	A (%)	q_t
100	10	89.251	91.115	90.183	9.817	9.817	0.29451
100	20	75.99	76.201	76.0955	23.9045	23.9045	0.71714
100	30	60.0145	61.005	60.5098	39.4903	39.4903	1.18471
100	60	44.99	45.015	45.0025	54.9975	54.9975	1.64993
100	80	42.3358	41.958	42.1469	57.8531	57.8531	1.73559
100	120	40.112	40.001	40.0565	59.9435	59.9435	1.79831

(Co = 100 mg/L, Agitating speed = 200 rpm, pH = 7, CACH dose = 3 g/L)

4. CACH Dose

Ac dose(g)	A	B	Av	$C_o - C_e$	A (%)	q
0.5	75.122	74.995	75.0585	24.9415	24.9415	0.748245
1	66.014	66.108	66.061	33.939	33.939	1.01817
1.5	62.995	63.094	63.0445	36.9555	36.9555	1.108665
2	60.241	60.011	60.126	39.874	39.874	1.19622
2.5	51.02	50.898	50.959	49.041	49.041	1.47123
3	46.119	46.008	46.0635	53.9365	53.9365	1.618095
4	44.114	43.917	44.0155	55.9845	55.9845	1.679535

(Co = 100 mg/L, Agitating speed = 200 rpm, Contact time = 60 min, pH = 7)

5. Agitating Speed

(rpm)	A	B	Av	Co - C e	A (%)
100	49.585	50.598	50.0915	49.9085	49.9085
150	47.365	48.569	47.967	52.033	52.033
200	44.001	43.991	43.996	56.004	56.004
250	46.224	46.012	46.118	53.882	53.882

(Co = 100 mg/L, Contact time = 60 min, CACH dose = 3 g/L, pH = 7)

6. Equilibrium isotherm model

Experimental	Freundlich		Langmuir		Separation factor
q_e	q_e		q_e		R_l
0.24012	0.266662		0.255909		0.17
0.35502	0.517778		0.531027		0.09
0.57384	0.819938		0.682524		0.04
0.67632	0.932369		0.712247		0.039
1.32012	1.116201		0.745306		0.02
	R^2	0.96	R^2	0.78	
	K_f	0.19	q_m	1.71	

7. Desorption study

Amount adsorbed by adsorbent (mg/g)	Eluent used	Eluent concentration(M)	Amount desorbed(mg/g)	Regeneration ratio (%)
2.1	NaOH	0.1	1.102	66.67
2.1	NaOH	0.3	1.501	90.5

II- Pictures taken during Laboratory work

Figure. 1 untreated coffee husk

Figure. 2 coffee husk treated with H_3PO_4

Figure.3 finally obtained activated carbon

Figure.4 During preparation of stock and working solution

Figure.5 During adsorption test with shaker and filtering spent CACH from the solution