OPTIMISATION AND SURFACE MORPHOLOGICAL ANALYSIS OF ACTIVATED CARBON FROM AGRICULTURAL WASTE PRODUCTS

By

Nyogbe Emmanuel Komla

(10551087)

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DECLARATION

I hereby declare that this thesis is the undertaken of EMMANUEL KOMLA NYOGBE under the supervision of Dr. K. A. DANSO and Dr. ANDREW NYAMFUL both of the School of Nuclear and Allied Sciences (SNAS), University of Ghana (UG).

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EMMANUEL KOMLA NYOGBE

DATE:

…….. ……

DR. K. A. DANSO
(Principal Supervisor)
DATE:

DR. ANDREW NYAMFUL
(Co-Supervisor)
DATE:

DEDICATION

I dedicate this work to my father, Francis Koku Nyogbe for the principles of hard work and excellence he instilled in me. I also dedicate this work to my supervisors, Dr. Andrew Nyamful and Dr. K. A. Danso all of the School of Nuclear and Allied Sciences, University of Ghana for their mentorship.

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LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunaeur-Emmett-Teller
CA	Chemical activation
CGA	Coal-gold agglomeration
CIP	Carbon-in-pulp
CS	Coconut Shell
CS-AC	Coconut shell activated carbon
DOC	Dissolved organic carbon
EAC	Extracted Activated Carbon
ELCD	Evaporative loss control devices
GAC	Granular Activated Carbon
IR_{opt}	Optimum impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
PA	Physical activation
PAC	Powdered Activated Carbon,
PET	Polyethylene terephthalate
PKO	Palm Kernel Oil
PKS	Palm Kernel Shell
PKS-AC	Palm Kernel Shell activated carbon
PO	Palm oil
PVC	Polyvinyl chloride

SDGs	Sustainable Development Goals
SEM	Scanning Electron Microscope
SS	Suspended solids
TEM	Transmission Electron Microscope
T_{opt}	Optimum temperature
t_{opt}	Optimum time

ABSTRACT

Many conventional or agricultural by-products and wastes go unused in Ghana. These wastes find their way into our water bodies and also sometimes become breeding grounds for mosquitoes and other insect pest causing diseases leading to severe health problems. These wastes sometimes are used as fillers in pot-holes which inadvertently blocks drainages during rainfall thereby leading to flooding in flood prone areas. The precursors used in this study to produce activated carbon were palm kernel shell and coconut shell. The produced activated carbon was activated chemically using three different activating agents, acid (H_3PO_4), base (NaOH) and a salt ($CaCl_2$). The maximum yield of activated carbon, 26.3 g (PKS) and 22.9 g (CS), using H_3PO_4 as an activating agent were obtained at 400 ^oC, 1 h carbonisation time and an impregnation ratio of 1.2. Similarly, maximum yield of activated carbon, 22.4 g (PKS) and 17.3 g (CS), using NaOH as an activating agent was also obtained at 500 ^oC, 2.5 h and impregnation ratio of 1.2. Using $CaCl_2$ as activating agent, the maximum yield of activated carbon were 25.5 g (PKS) and 20.8 g (CS), these maximum values corresponded to 400 ^oC, 1 h carbonisation time and an impregnation ratio of 1.2. The H_3PO_4 activated carbons were fairly better in the areas of ash content (7.17 %), moisture content (1.94 %), bulk density (0.65 g/cm^3), pore volume (0.94 ml/g), iodine adsorption (743.02 mg/g) and porosity (0.49). On the other hand, the NaOH activated carbon was also advantageous in terms of carbon content (57.78 %). $CaCl_2$ activated carbons, were also commendable in terms of volatile matter (30.46 %) and electrical conductivity (2130 µS/cm). Scanning Electron Microscopy (SEM) technique was employed to observe the surface physical morphology of the coconut shell and palm kernel shell activated carbons. Prior to chemical activation the surface morphology of the raw

coconut shell compared to the palm kernel shell at a magnification of ×5000 did not show porous surface, while the external surfaces of the chemically activated carbon were rich with cavities.

CHAPTER ONE

1.0 INTRODUCTION

This chapter presents the background to the present study, statement of the research problem, the objectives and the justification for undertaking this research. The chapter also provides the scope and organization of the study.

1.1 Background

Agricultural wastes such as coconut shell and palm kernel shell which are by products of coconut fruit and oil palm respectively, contain a high amount of organic constituents (i.e., cellulose, hemicellulose and lignin) and possess a high-energy content (Tsai *et al.*, 2006; Yahya *et al.*, 2015). Despite the commercial viability of the oil palm and coconut fruit, the fibrous tissue in the form of husk (mesocarp) and woody endocarp surrounding the palm and coconut seed constitute a large quantity of waste in the environment due to improper disposal (Nasri *et al.*, 2014).

On the other hand, productive use of palm kernel shell and coconut shell in Ghana would significantly reduce the amount of waste generated in the environment. A look at the demand in activated carbon, a carbonaceous material with characteristic surface area and highly developed porous structure, for industrial applications, coconut shell and palm kernel shell have been reported to be a viable raw material for activated carbon production (Yalcin and Arol, 2002). This implies that, processing of the tonnes of coconut and palm kernel waste obtained in Ghana into activated carbon could open up a new industry.

Carbonisation of lignin containing materials such as palm kernel shell and coconut shell involves the conversion of the organic matrix into carbon containing residue, thereby

leading to the formation of porous materials with relatively moderate surface area (Sethupathi *et al.*, 2015). Areas of application of the carbon residue include solute adsorption, gas adsorption, air filter in nuclear reactor facilities, precious metal recovery, medical and pharmaceutical applications (Soleimani and Kaghazchi, 2008; Li *et al.*, 2008). Due to the immense quantity of palm kernel and coconut waste available in Ghana, this study seeks to investigate the processing of these raw materials into activated carbon for industrial applications.

Detailed studies carried out by Abbaszadeh *et al.*, (2016) on carbonization of lignocellulosic materials described the physical and chemical processes involved in activated carbon formation. In physical activation, a raw material is first carbonized and then activated with an oxidizing gas such as steam or carbon dioxide to develop internal porosity by gasification reaction at temperatures of about 800-1100 ^{o}C (Nasri *et al.*, 2014).

In chemical activation, prior to carbonization, the carbon precursor is impregnated with certain chemicals, then the precursor is carbonized at relatively lower temperatures of 450-900 ^{o}C. It is believed that the carbonization and activation step proceeds simultaneously with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating materials (Wei and Yushin, 2012). High surface areas and narrow micropore formation using chemical methods has been considered to be advantageous in efficient production of activated carbon (Ioannidou and Zabaniotou, 2007). Typical examples of chemical activating agents used include H_3PO_4, KOH, NaOH, $ZnCl_2$, K_2CO_3, NaCl, Na_2CO_3, H_2SO_4, $KHPO_4$ (Lillo-Ródenas *et al.*, 2003; Ioannidou and Zabaniotou, 2007; Sethupathi *et al.*, 2015).

However, carbonisation temperature, time and impregnation ratio plays a key role in the pyrolytic step towards the formation of activated carbon (Zanzi *et al.*, 2001). Katesa *et al.*, (2013) and Jun *et al.*, (2010) respectively reported that as carbonisation temperature and time increased, the yield of activated carbon decreased which was attributed to large release of volatile matter in the precursor. Rahman *et al.*, (2012) and Yang and Qiu, (2010) also opined that increasing impregnation ratios above 1.0 promotes the evolution of volatiles which leads to the creation of micropores and subsequently to mesopores and probably macropores.

This study focused on palm kernel shell and coconut shell waste collected from the Accra metropolis of Ghana, and its processing into activated carbon using H_3PO_4 and NaOH as activating agent. Carbonisation temperature, time, and impregnation ratio were investigated and discussed. Other physicochemical parameters considered after the carbonisation process included pH, moisture content, volatile matter, ash content, carbon content, bulk density, pore volume, porosity, iodine number and electrical conductivity.

1.2 Problem Statement

Over the years, global environmental issues such as air, water and soil pollution are increasing with developing technology. Industrial wastewater containing organic pollutants, phenol, toxic metal compounds among others are said to have harmful effects on the environment and human health. These toxic chemicals being released onto the surface of the earth flow into water bodies (sea, ponds, lakes, and reservoirs) and pollute ground water in minute quantities by percolation during rainfall (Uzun and Guzel, 2000). Consequently, it is important for toxic compounds to be eliminated from water and waste water.

In the past decade, a lot of research has been done on the production of AC from pyrolysis of coconut shell and palm kernel shell using standard methods, that is, the physical and chemical activation processes. The ability of the two activation methods as probable sorbents for a number of pollutants, heavy metals as well as the recovery of some precious metals have been evaluated hence prompting further attention from researchers in recent times.

With respect to Ghana, agricultural by-products like coconut shell, sugarcane bagasse, palm kernel shell and sawn dust to a large extent go unused and are disposed of as waste. The shell of fruits such as coconut shell and palm kernel shells are very hard materials, a characteristic useful as a substitute precursor for granular activated carbons (Soleimani and Kaghazchi, 2008).

ACs used in the petroleum, gold recovery, food, pharmaceutical, water and waste water treatment industries in Ghana are imported from developed countries such as China, Germany among others at expensive costs (Soleimani and Kaghazchi, 2008). Using agricultural and industrial leftovers provides developing countries like Ghana the opportunity to produce activated charcoal in a cost-effective way.

Since studies using chemical as well as physical activation method in manufacturing AC from carbonaceous material are limited, this research was mainly conducted to examine the performance of manufactured AC using the chemical method. Specifically, this study aimed at preparing highly mesoporous activated charcoal from coconut shell and palm kernel shell which are suitable for adsorbing fairly large molecules.

This study is significant because when the adsorption ability of activated carbon prepared from agricultural products such as coconut shells and kernel shells are studied, it could impact our environment positively in many ways. Some of these are waste water treatment, thorough purification of exhaust and circulating gas in the nuclear industry, filtering gasoline, and recovery of gold in an environmentally friendly way therefore in the long run reduce environmental pollution, morbidity and mortality. Previous studies have identified many types or characteristics of activated charcoal. The need to identify the most efficient and suitable characteristics of activated charcoal is therefore very important.

1.3 Objectives

1.3.1 Main Objective

- To produce activated carbon from two agricultural by-products palm kernel shell and coconut shell, through chemical activation using H_3PO_4, NaOH and $CaCl_2$.

1.3.2 Specific Objectives

- To assess and select suitable agricultural by-products as starting raw material for the production of activated carbon.
- To investigate the effect of impregnation ratio, carbonisation temperature and time on the yield of activated carbon.
- To examine the effect of activating agents on the production of activated carbon; and to select suitable activating agents.

1.4 Justification

In various beverage and food producing industries, ACs are used to purify waste water by removing coloured pigments, odour and also reducing the levels of heavy metals. Edible oil processing companies use ACs in the production of palm oil.

In current gold mining processes, activated carbon, an essential sorbent in industries, is used to extract gold from cyanide solutions. Gold mining firms in Ghana mostly rely on imported ACs for production activities. The demand for efficient procedures for gold recovery by these companies make it imperative to pursue the production of activated carbon locally.

In nuclear industries, the application of activated carbon filter beds are in keeping radioactive gases from the nuclear boiling water reactor turbine condenser. As Ghana makes plans to add nuclear power to its energy generation capacity, purification of exhaust and circulating gases during nuclear power plant operations will be an area of concern. The elimination of these gases can be achieved by activated carbon adsorption and therefore pointing to the need of exploring the production of this adsorbent.

1.5 Scope of the Research

AC in this study was made from CS and PKS by chemical activation. The activating agents used for this study were phosphoric acid (H_3PO_4), sodium hydroxide (NaOH) and calcium chloride ($CaCl_2$) followed by carbonisation. The operating parameters that were studied are carbonisation temperature (400, 500, 600, and 700 ^oC); time (1, 1.5, 2.0 and 2.5 h); and impregnation ratio (0.6, 0.8, 1.0, 1.2).

These parameters were varied respectively for each precursor and the activating agent to establish optimum conditions at which carbon yield was maximum. Sisvar, a statistical software was used to establish the optimum conditions (Ferreira, 2014: Jelihovschi, 2014).

1.6 Organisation of the study

This thesis has five (5) chapters.

Chapter one comprises the research background, the problem statement, objectives of the research and the justification of the study.

Chapter two discusses previous studies in the fields of adsorption and activated carbon and explores related theoretical models. Chapter three describes the preparation of the sample and other processes carried out in the experiment. Chapter four consists of the results and discussion. The results obtained from the experiment were analysed and plausible scientific explanations for the outcomes were given.

Chapter five concludes the study and presents study recommendations based on the results obtained. Recommendations are made for further studies and policy.

CHAPTER TWO

2.0 LITERATURE REVIEW

The chapter gives information about the activated carbon, its applications in industry. It also throws light on the different precursors used in the production of the adsorbent. The chapter also reports on the methods of activation and various physicochemical characterizations in ascertaining the quality of the activated carbon.

2.1 Activated Carbon

The position occupied by the element carbon, with proton number six and four valence electrons capable of multi-bonding, on the Periodic Table is quite unique. It undergoes hybridization to form sp in linear molecules; sp^2 in ring molecules; and sp^3 in tetrahedral molecules like diamond. It has a low atomic mass of 12.011 amu (Marsh and Rodriguez-Reinoso, 2006).

Carbon is an element that was discovered in pre historic times and is ubiquitously present in meteorites, in suns, stars, comets and the atmospheres of numerous planets. This, therefore, makes carbon a significantly stable element, immensely versatile and combining with heteroatoms and other elements to form not less than 1×10^7 organic compounds. Life in its various forms would have been impossible without carbon (Marsh and Rodriguez-Reinoso, 2006).

Carbon matter are distinctive and multipurpose in their function hence have significant application in industry. Activated carbon materials as carbon matter are described by high surface area and modifiable porosity. They are utilized by most technologies such as sensors, environmental protection (regulate SO_x and NO_x emissions from fuel combustion

in automobiles), energy conversion (fuel cells, solar cells), manufacture of fine and bulk chemicals and catalysis, energy storage (super capacitors, batteries, hydrogen sorption) (Viswanathan *et al.*, 2009).

Activated carbon, also referred to as Activated charcoal, Activated Coal or Solid Sponge (Zanzi *et al.*, 2001) has been described in several ways. Soleimani and Kaghazchi, (2008) defined activated carbons as carbonaceous materials with a well-developed porous structure made up of hydrophobic graphene layer surface and hydrophilic surface functional groups. Marsh (1989) explained activated carbon as porous carbon, which has been treated by oxidising gases during or after carbonisation so as to increase porosity. Norlia Baharun (1999) also explained activated carbon as an organic material, primarily made up of a graphitic structure. Benaddi (2000) on the other hand noted that activated carbon is primarily an adsorbent with a large internal pore volume and surface area. Aznar (2011) also added that activated carbon is any porous material formed in the major part of carbon and characterised by a well-developed porosity.

From the definitions above, Activated carbon (AC) is generally used to refer to the class of formless carbon-containing sorbent-material with a high crystal-like form and a fully improved inner pore composition. There is a difference between two types of carbon: graphitisable and non-graphitisable. Anaerobic burning of carbon at around 3000 ^{o}C converts it to graphite. Activated carbons form part of the latter kind - non-graphitisable carbon – which are produced from carbonaceous precursors during carbonisation (Aznar, 2011). A typical structure of activated charcoal is shown in Fig 2.1.

Figure 2.1 Structural representation of activated carbon

AC is a highly spongy substance rendering it favourable for sorption and catalytic use. In addition, it is tasteless, formless, microcrystalline, and a black solid substance which is similar to powdered or granulated charcoal. Being non-graphite means that, activated carbon is not convertible to crystal-like graphite even at high temperatures (e.g. above 3000 ^{o}C) (Adib *et al.*, 2015). Activated carbon has been utilized in industry in the specific areas of petroleum, food, drugs, water treatment, mining, gold recovery and carbon-in-pulp process (Soleimani and Kaghazchi, 2008)

2.1.1 History of activated carbon and areas of application

Usage of activated charcoal dates back in history. The power of certain materials to eliminate colour from dye-containing media has been known for over a century (Pandharipande *et al.*, 2012). Charcoal has been used for filtering water by early Hindus in India before drinking, and carbonised wood was used as a medical adsorbent and filtering agent by the Egyptians in 1500 B.C (Karthikeyan *et al.*, 2008).

In 420 BC, it was recorded that Hippocrates deodourise sores using powdered charcoal. A Swedish chemist named Karl Wilhelm Scheele, pioneered adsorption of gases on charcoal in 1773. Some years later, activated carbons found uses in the sugar industry as a decolourising agent for syrup (Seitkhan, 2015).

Prior to 1880, the variety of carbon that existed was the lampblack which was obtained from smoking flames and served as the only existing writing material. Porous carbons usually acquired by carbonising wood, known as charcoals, were helpful as medicine (e.g. stomach problems), as a deodorizer (soap was non-existent), in gunpowder (ballistics) and in making fireworks. The inception of gas warfare in World War II saw the rise in the use of activated carbon respirators. Its ineffective use could result in death (Marsh and Rodriguez-Reinoso, 2006).

The first part of the 20th century saw the introduction of activated carbon, produced from vegetable material for industrial use in sugar refineries. During World War I, gas masks were used as filters to shield against harmful gases and vapours. Activated carbon in powdered form was first produced in commercial quantities in Europe during the 19th century; using wood as a precursor, in the sugar industry. In the United States, the first synthesis of activated carbon used black ash as raw material, after it was coincidentally revealed that the ash was very effective in decolourising liquids (Khalil *et al.*, 2013).

Activated carbons are inimitable and multi purpose adsorbents, and they are utilized widely for the elimination of odour, colour, taste, and other organic and inorganic impurities from domestic and industrial waste water, solvent recovery, air purification in populated areas, eateries, food processing, and chemical industries. In addition, they have thriving

applications in fields of medicine for detoxification and antibacterial purposes. These varied uses of activated carbon are of importance to most economic sectors. It concerns diverse areas as the food, petroleum, chemical, pharmaceutical, mining, nuclear, automobile, and vacuum industries. Almost four-fifths (~300,000 tonnes per year) of the total active carbon is consumed by liquid-phase applications, and the gas-phase applications consume about 20 percent of the total production (Bansal and Goyal, 2005).

2.1.2 Types of Activated Carbon

Depending on the product dimension and physical characteristics, commercial activated carbon can be classified for general purposes as: Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC), Pelletised Activated Carbon, Extracted Activated Carbon (EAC), Impregnated Carbon, Polymer Coated Carbon (Onyeji and Aboje, 2011). GAC is extensively used as a multipurpose adsorbent in water purification because it can get rid of several pollutants, of which include organic carbon, heavy metals and turbidity (Pollard *et al.*, 1992: Goel *et al.*, 2015). The effectiveness of GAC in removing pollutants using the process of adsorption is as a result of unique characteristics such as its large surface area (500–1500 m^2/g), internal microporosity, different functional groups, low cost, and easy obtainability (Taylor *et al.*, 2010). Though GAC can remove heavy metals, the efficiency with which it removes these metals is dependent on the concentrations of other pollutants in the water, such as suspended solids (SS) and dissolved organic carbon (DOC). Notwithstanding these effects, studies in this area has been limited (Sounthararajah *et al.*, 2015).

PACs are mainly used in liquid phase adsorption, production of industrial chemicals, beverage clarification and flue gas treatment. In wastewater treatment, PACs are most

commonly used during secondary treatment, also referred to as powdered activated carbon treatment process (Amri, 2008). It is also the kind of activated carbon used for mercury control applications (Hung, 2012). PAC has a particle size less than 1.0 mm and an average diameter between 0.15 and 0.25 mm hence they tend to have the largest surface area due to their small particle size.

2.1.3 Activated Carbon and the Nuclear Industry

Nuclear technology comprises of a number of procedures, the more significant being the production of nuclear fuels, processing of spent fuels, and operation of nuclear reactors. Exhaust and circulating gas during nuclear plant operations needs to be purified completely. Separation and purification processes based on adsorption technique play an essential role in the nuclear industry; where activated carbon is often used for the separation of metal ions from solutions, due to its selective adsorption, high radiation stability and high purity (Kütahyalı and Eral, 2004). Due to the fact that many of the separation and purification processes involve noble gases, their removal is best carried out by activated carbon adsorption. For instance, helium, a noble gas, is distributed as gas shield in nuclear reactors, cooled and moderated by heavy water and transports with it deuterium and oxygen formed by radiolysis, thereby preventing the creation of an explosive mixture. During the exchange of fuel elements, argon gets mixed up with the air entering the system. It accrues and changes the normal function of the reactor so that the circulating helium needs to be cleaned intermittently (Bansal and Goyal, 2005).

Bansal and Goyal, (2005), explained the removal of helium form the nuclear reactor as following “contaminated helium is first led to a reactivator in which deuterium and oxygen combine over a catalyst to form heavy water and then pass through an activated carbon bed

cooled in liquid nitrogen. Active carbon adsorbs argon and nitrogen as well as radioactive xenon and krypton that may have leaked into the protective gas from faulty fuel elements. The loaded activated carbon is regenerated by raising its temperature and evacuation. The temperature during regeneration is raised slowly so that the desorbed gases can be separately collected. Helium is collected first and returned to the cycle while the products of radioactive decay are compressed and collected in pressure vessels for disposal. The adsorption on activated carbon in the field of nuclear technology is carried under very specific conditions, and the process is expensive because it is usually carried out at low temperatures and it must take into account the heating of the adsorbent carbon due to the heat of the radioactive decay of the adsorbed species."

Also Billinge *et al.*, (1984), described the elimination of radioactive iodine isotopes from the nuclear plant as "the nuclear fission reaction in nuclear plants also produces radioactive iodine isotopes ^{131}I and ^{133}I, which are present in the coolant release and in the ventilation system both in the elemental form and in the form of its compounds e.g., methyl iodide. Activated carbons impregnated with potassium iodide and similar compounds and with amines including several pyridines have been widely used for the retention of radioactive iodine compounds. These carbons remove very low levels of iodine and its compounds from gas streams with high efficiency, even in the presence of high humidity."

2.1.4 Activated Carbon and the Petroleum Industry

One essential and universally used energy source in the world today is Petroleum. This is because it is available in liquid form and hence can be conveniently stored. Contrastingly, it is environmentally unfriendly as it produces oxides of sulphur, oxides of nitrogen, and carbon monoxide during its refinery processes. These compounds produced are harmful to

humans, animals, vegetable matter and the ecosystem as a whole. Also, the process generates relatively large quantities of wastewater, with different characteristics depending on the process configuration and plant size. Furthermore, gasoline, a derivative of petroleum, contains several types of sulphur compounds, for instance, mercaptans. These compounds could be filtered from gasoline using activated carbons impregnated with 10 to 15% sodium hydroxide. The removal of mercaptans involves adsorption on the carbon surface and a chemical reaction with sodium hydroxide (Bansal and Goyal, 2005). The equation representing the chemical reaction is:

$$RSH + NaOH \rightarrow NaSR + H_2O \quad \ldots\ldots\ldots (1)$$

An increase in the proportion of automobiles in urban centres has dire implications for the availability of clean air. These automobiles produce two types of emissions: those from the by-products of combustion such as CO, CO_2, oxides of nitrogen, sulphur and carbon particles, and those from the evaporation of the fuel itself. Carbon monoxide (CO) is both highly poisonous and the principal constituent of photochemical smog. Some studies have outlined the health effects of short and long duration as well as low and high levels of CO exposure. Being exposed to CO concentration 100 (parts per million) for ten hours results in headache; and 1000 ppm for four hours leads to death. Other effects include heart disease, cancer, low birth weight and neurological damage (Townsend and Maynard, 2002).

Sulphur oxides are formed through the burning of fuels containing sulphur, for instance, some coals and some petroleum-based products. The main product is sulphur dioxide:

$$S \text{ (in fuel)} + O_2 \rightarrow SO_2 \quad \ldots\ldots\ldots (2)$$

Sulphur dioxide is a colorless gas which has a pungent smell. It irritates the eyes, nostrils, throat, hand mouth (Lewis, 2007). Though not hazardous, when it is released into the atmosphere, it reacts with oxygen in the air to form sulphur trioxide:

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3 \quad \ldots\ldots\ldots (3)$$

Sulphur trioxide irritates the respiratory tract. A concentration of 1 volume of SO_3 in a million volumes of air (1 ppm) is enough to cause coughing and choking and further harm the respiratory system. Continuous exposure leads to a high likelihood of suffering from bronchitis. Sulphur trioxide is water soluble. In water, it transforms into sulfuric acid, a strong acid with corrosive ability and ability to destroy many materials. Additionally, Sulphur trioxide can also dissolve easily in rain drops, and fall to the earth as acid rain (Radovic and Schobert, 1997).

Nitrogen oxide is mainly obtained from fuel. NO_x is produced when nitrogen atoms chemically combined with the molecules of the fuel are oxidised during the combustion process to form nitric oxide:

$$2\ N \text{ (in fuel)} + O_2 \rightarrow 2\ NO \ldots\ldots\ldots (4)$$

In addition, thermal NO_x is produced in some combustion processes that operate at such high temperatures that nitrogen molecules in the air are oxidised to nitric oxide:

$$N_2 \text{ (in air)} + O_2 \rightarrow 2\ NO \ldots\ldots\ldots (5)$$

(Air is 79 % N_2 and 21 % O_2.) When the nitric oxide is emitted to the environment, it readily reacts with oxygen in the air to form nitrogen dioxide:

$$2\ NO + O_2 \rightarrow 2\ NO_2 \ldots\ldots\ldots (6)$$

Nitrogen dioxide is a noxious gas that can cause inflammation of the lungs and, at high concentrations, even death. In addition, nitrogen oxides will react further with water and oxygen to form nitric acid:

$$4\ NO_2 + 2\ H_2O + O_2 \rightarrow 4\ HNO_3 \ldots\ldots\ldots\ldots (7)$$

Like sulfuric acid, nitric acid is a very strong acid that easily corrodes or attacks many materials. Nitric acid is also a component of acid rain (Radovic and Schobert, 1997).

Efforts have been made to reduce the pollutant emissions mentioned above by improving upon the working of internal combustion engines in cars; a more efficient system to reduce the amount of emissions from these pollutants. Additionally, by using catalytic converters in efficient internal combustion engines, the harmful exhaust emissions are further reduced. In relation to gasoline or diesel oil, focus has been placed on reducing emissions by fitting activated carbon cylinders called evaporative loss control devices (ELCDs) on vehicles to prevent emissions of volatile petroleum constituents (Derbyshire *et al.*, 2001).

2.1.5 Activated Carbon for Gold Recovery

The use of gold in ancient times was recorded prior to 3400 BC. As a precious metal, it is treasured for its unique colour. In addition, it is highly demanded in the jewellery, high-tech industries and in the area of medicine due to its unique physical and chemical properties (Spitzer and Bertazzoli, 2004). In the past decades, substantial amounts of gold

have been utilized by the electronic industry as a result of its ability to conduct electricity, low contact electrical resistance for inserting connections and outstanding resistance to corrosion (Syed, 2012). As demand for gold increases, it is important that efforts should be focused on optimising gold yield from the gold concentration processes with particular emphasis on recovery from gold tailings (Chingosho *et al.*, 2014). The gold recovery process is only relevant if the cost of recovery is much less than the value of the precious metal (Chingosho et. al., 2014). In addition, technologies that are environmentally friendly and economically viable should be used given the strict regulations on waste disposal and the environment (Syed, 2006). s

According to Cui Zhang, (2008) and Fleming, (1992), mechanical separation, pyro-metallurgical, hydrometallurgical, and bio-hydrometallurgical technologies have been widely used to recover gold from secondary sources. There has been an increase in environmental accidents at various parts of the world during various gold recovery processes using cyanide as leachants. This has resulted in severe pollution of water bodies. In recent times, many processes have been proposed for the recovery of gold from cyanide solutions and pulp in which granular or powdered activated carbon is used as an adsorbent for the gold. Undoubtedly, that which enjoys the greatest prominence at present is the carbon-in-pulp (CIP) process. In this, carbon granules are added directly to the cyanided pulp and moved counter-current to it. The gold-loaded carbon is later recovered by screening (Mcdougall and Hancock, 1982). To overcome the environmental hazards that using cyanide leachants pose, many substituted leaching agents being used are presented in Table 2.2. These solutions are then subjected to separation and purification procedures such as cementation, reduction, adsorption, coagulation, solvent extraction, ion exchange

resin, gravity separation, ionic flotation, emulsion liquid membrane electro-winning and coal-gold agglomeration (CGA). A list of gold recovery agents noted in various studies is presented in Table 2.1 and Table 2.2.

Table 2.1 List of substituted leaching agents of gold

Reagents	**References**
Aqua-regia	Park and Fray, (2009)
Ammoniacal thiosulfate	V. Hung *et al.*, (2010)
Thiourea	Aydin *et al.*, (2016)
Chloride–hypochlorite	Feng and Deventer, (2006)
Acid thiourea	Orgul and Atalay, (2002)
1-Phenyl-2-thio-3-(2-hydroxyethyl) urea	Soo *et al*., (2008)
Aqueous ozone–chloride	Viñals *et al.*, (2006)
Thiourea–thiosulfate	Zhang and Dreisinger, (2002)

Table 2.2 List of gold recovery agent from leaching solutions

Recovery agents	**References**
Cementing	
Magnesium	Karavasteva, (2010)
Copper	Karavasteva, (2010)
Iron	Wang *et al.*, (2007)
Zinc	Navarro *et al.*, (2004)
Aluminum	Lee *et al.*, (1997)
Adsorption	
Bayberry tannin-immobilized mesoporous silica	Huang *et al.*, (2010)
Orange Waste	Kawakita *et al.*, (2009)
Porous carbon of barley straw and rice husk	Chand *et al.*, (2009)
Graphitized carbon black	Park and Fray, (2009)
Lemon peel gel	Parajuli and Kawakita, (2008)
α-Zirconium(IV) Bismonohydrogenphosphate (α -Zrp)	Woźniak *et al.*, (2008)
Mesoporous adsorbents	Fung *et al.*, (2008)
Activated carbon derived from hard shell of apricot stones	Soleimani and Kaghazchi, (2008)
Persimmon peel gel	Parajuli *et al.*, (2007)
Novel lignin-based adsorption gels	Parajuli *et al.*, (2006)
Poly((N-(Hydroxymethyl)methacrylamide)-1-allyl-2-thiourea) hydrogels	Döker *et al.*, (2006)
Flax shive	Cox *et al.*, (2005)
Novel tannin gel	Ogata and Nakano, (2005)
Nanostructure Mn_2O_3	Koyanaka *et al.*, (2005)
Activated carbon	Zhang *et al.*, (2004)
Chitosan derivatives	Arrascue *et al.*, (2003)
Silicon (111) surface	Kinoshita *et al.*, (2003)

2.2 Precursors

Girgis *et al.*, (2002), reported that AC could be formed from both naturally occurring and synthetic of carbonaceous solid precursor. Mostly, materials for activated carbons are normally determined by how readily available they are and low cost. Common examples of commercial raw materials are materials made from parts of plants (e.g. wood, coconut shell, fruit stones and nut kernels) and degraded or coalified plant matter (e.g. peat, lignite and all ranks of coal). AC has been categorised based on its starting material or precursor. The type of precursor determines the quality, characteristics and properties of the resulting activated carbon (Spahis *et al.*, 2008; Mozammel *et al.*, 2002). Preparing AC from botanical waste materials has numerous economic and environmental advantages. Diverse types of AC have been prepared from different waste materials, for instance, conventional wastes (from agriculture and wood industry), as well as non-conventional wastes (from municipal and industrial activities).

2.2.1 Conventional wastes

Conventional wastes refer to waste from agricultural and wood industry (Yahya *et al.*, 2015). They are of low economic value as a result of being plenteous in the environment hence creating significant environmental degradation. Agricultural waste serves as a rich source for AC production as a result of its low ash content and reasonable hardness (Ahmedna *et al.*, 2000); therefore, conversion of agricultural wastes into AC is a promising alternative to solve environmental problems and also to reduce the costs of AC preparation (Dias *et al.*, 2007).

Many studies have focused on the use of several agricultural wastes to produce AC. Most of them emphasize the use of considerably rigid waste material, such as the shells and/or

stones of fruits like nuts, peanuts, olives, dates, almonds, apricots and cherries; however, wastes resulting from the production of cereals such as rice, coffee, soybean, maize and corn as well as olive cakes, sugar cane and sugar beat bagasse, coir pith, oil-palm shell (from oil-palm processing mills) and various seed wastes were already used. The preparation of AC from these materials has been made using both physical and chemical activation. According to a study by Ioannidou and Zabaniotou, (2007) an extensive revision regarding AC preparation from agricultural residues is made and the effects of different parameters regarding activation procedures are presented. The structure of the raw material tends to strongly influence the best parameters needed to obtain a specific AC. It is possible to obtain AC with different pore texture by varying the activation conditions, therefore optimising their production for a specific purpose. High surface areas might be obtained, with values over 2500 m^2g^{-1}.

2.2.1.1 Palm Kernel Shell (PKS)

The origin of Oil Palm had been associated with the tropical rainforest of West Africa but has spread to most of the equatorial tropics of South-East Asia and America (Luangkiattikhun *et al.*, 2008). Most Asian countries, for instance, Malaysia, Indonesia and Thailand export oil palm hence they serve a source of foreign income to them. In the production process of palm oil and palm kernel oil, derived from the oil palm plant, palm oil fibre, effluent, kernel shell and empty fruit bunch are regarded as wastes. Okoroigwe and Saffron, (2012) note that about 0.07 tonnes of palm shell, 0.103 tonnes of palm fibre and 0.012 tonnes of kernel are produced as the solid wastes for every tonne of oil-palm fruit bunch being fed into the palm oil processing plant. The amount of each component

waste generated from palm oil (PO) and Palm Kernel Oil (PKO) processing may be attributed to the type of oil palm species dominant in the quantity being processed.

The two main species of oil palm being cultivated are Dura and Pisifera. Dura is distinguished from Pisifera by its thick shell with thin mesocarp. The Pisifera species is thin shelled with thicker mesocarp. This invariably contributes to the amount of palm oil, palm kernel oil and palm kernel shell that can be obtained from the species. However, improved varieties Dura are being cultivated with the help of advances in plant genetic technology (Okoroigwe and Saffron, 2012). Figure 2.2, shows a heap of palm kernel shells at a factory and dump site near Madina, Accra.

Figure 2. 2 Palm kernel shell factory and dumpsite, Madina

Palm kernel shell is an inexpensive and widely available agricultural by-product in countries such as Ghana, Indonesia and Malaysia. Palm shell has been effectively transformed into a well-developed activated carbon by thermal and chemical activation

combined with carbon dioxide (CO_2) and H_2PO_3 (Adinata *et al.*, 2007). One of the parameters which diff erentiates one material from another is the material composition, that is lignin, cellulose and holocellulose. For instance, lignocellulose based activated carbon has a significant amount of mesopores and macropores as it is composed of lignocellulosic materials that contain comparatively large percentage of lignin content (Daud and Ali, 2004).

2.2.1.2 Coconut Shell (CS)

Coconut shell is a hard and thick bony endocarp material (Babel and Kurniawan, 2004). It has about 21% carbon content and a very low ash content of less than 1.0 wt. %. In addition, its waste product is less harmful compared with activated carbon that is made from raw coal (Katesa *et al.*, 2013). Despite being less harmful, it often presents serious disposal problems for local environments (Babel and Kurniawan, 2004).

Some researchers have reported processing of coconut shells wastes into chars with sufficient densities and high sponginess for treating industrial and municipal wastewaters. The high porosity of the coconut shell is as a result of its composition of functional groups such as carboxylic, hydroxyl, and lactone which have a high attachment to metal ions. In recent decades, diverse forms of AC with superior adsorption ability have been developed. The use of improved activated carbon made from a surface-modified coconut shell would help improve its ability to filter out metal ions, add to its economic value, help reduce waste disposal cost, and most significantly, offer an inexpensive alternative to existing commercial AC (Amuda *et al.*, 2007). Figure 2.3 shows a picture of coconut shells at a dumping site near Dome, Ga-East Municipal, Accra.

Figure 2.3 Coconut shells deposit at Dome, Ga-East Municipal, Accra

2.2.2 Non-conventional wastes

In today's globalized world, increased economic activities have progressively created a pattern of mass production, mass consumption as well as mass deposition (Gao *et al.*, 2005). Hence, there is a build-up of several industrial and consumer pollutants which naturally are difficult to be recycled into other material forms. Therefore, they end up being burnt in dumping sites or buried in landfill sites. The discharge of plastic wastes, such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC), manufacturing wastes, such as oil combustion residues and fabrics, as well as the discharge of tires, sewage, and fertilizers, represents a serious challenge for waste management schemes (Dias *et al.*, 2007). Hence it is important to find alternatives by which such waste materials could be recycled in accordance to ecologically acceptable processes (Hayashi *et al.*, 2005). Using

these non-conventional wastes as a source of carbon for producing AC could be an effective waste management practice, and help produce more affordable AC.

Many studies have been dedicated to the study of how wastes such as plastic wastes, various industrial wastes like fly ashes, pitch, and polymeric residues from factories as well as other wastes such as tires and sewage have been used as raw material to produce AC (Gun'Ko *et. al.*, 2005). As an example, an ion-exchange resin waste might be used to produce AC with different sizes of surface areas and pore volume giving it the added advantage of the ability to apply it for different purposes, that might include aqueous-phase treatments (Gun'Ko *et al.*, 2005). Also, AC could be effectively produced from old newspaper and paper prepared from simulated paper sludge by physical and chemical activation (Okada *et al.*, 2003). Per the nature of many raw materials such as plastics and polymeric materials, manufactured ACs usually take the physical form of AC fibers. Studies also show that raw materials with higher carbon content leads to the production of superior AC which has good texture and prospects to compete with other commercially produced ones (Dias *et al.*, 2007).

2.3 Modes of Preparation

Although organic macromolecular systems can be carbonised to microporous carbons, their porous potential is not maximized as their adsorption capacity, measured as a micropore volume or surface area is too low for commercial use. Hence the need to widen existing porosity to include wider micropores and some mesoporosity (Marsh and Rodriguez-Reinoso, 2006). Additionally, sponginess within the carbon, which is closed to a specific adsorbate, can be opened to allow access to larger adsorbate molecules (Marsh and Rodriguez-Reinoso, 2006).

From this therefore, there are two processes for preparing AC to maximise its adsorption potential; chemical and physical treatment. Applying adequate physical and chemical treatments are responsible for changing the shapes and the sizes of the AC pores. Similarly, the production of AC comprises of two main stages, the carbonisation of the starting material and the activation of the resulting char.

2.3.1 Physical Activation

The objective of activation is to improve the pore structure. The physical or thermal activation is the partial gasification of the char with steam, CO_2 and air at temperatures of about 1100-1250 K. The main change is an increase in pore volume making the crystallites become exposed to the action of the activating agent (oxidising gases) for further development of porosity with increasing burn-off. The oxidising gases employed, steam or CO_2, are reactive agents that react with the raw material and also remove volatile material from the solid (Aznar, 2011).

Figure 2.4 Gradual activation process of carbon during thermal treatment

Figure 2.4 represents the gradual activation process of carbon during the thermal treatment of the activated carbon. The above mentioned process gives rise to the pore creation and increase as some parts of the char structure are reacted faster than the others. As physical activation does not produce waste water as it uses gaseous activation agents, this method

is seen as environmentally friendly. The disadvantage of this process is that, it takes much time and energy for producing microporous activated carbon through physical activation methods. Also, an additional disadvantage is that a large amount of internal carbon mass is removed to obtain well-developed pore structure therefore carbon yields are limited (Viswanathan *et al.*, 2009).

Gasification of a char is mainly carried out with carbon dioxide, steam, or a mixture of both (Marsh and Rodriguez-Reinoso, 2006). Oxygen is not usually used as an activating agent since the carbon-oxygen reaction is highly exothermic hence difficult to control unless very low partial pressures of molecular oxygen are used. The reactions of carbon with carbon dioxide and steam are endothermic hence easy to control (Marsh and Rodriguez-Reinoso, 2006):

$$C + CO_2 \longrightarrow 2CO \qquad \Delta H = +159\ kJmol^{-1} \quad \ldots\ldots\ldots (8)$$

$$C + H_2O \longrightarrow CO + H_2 \qquad \Delta H = +117\ kJmol^{-1} \quad \ldots\ldots\ldots (9)$$

There are varied gasification rates for different forms of carbon such as graphite, coke and chars. For a given temperature, the reactivity with steam is larger than with carbon dioxide. However, when the effect of the activating agent on the development of porosity is analysed, the results do not show a clear leaning, for example, graphite. Many authors have shown that the most significant factors in the gasification process from the point of view of porosity development are:

i. Activating agent
ii. The final burn-off reached

iii. The presence of inorganic impurities that catalyse or inhibit the gasification reaction

2.3.2 Chemical Activation

Chemical activation is the term used to refer to the carbonisation of the precursor which has been mixed with some chemical as calcium chloride or phosphoric acid which restricts the formation of tar; in this way, a carbonised product with a well-developed porosity may be obtained in a single operation. All the agents involved in the chemical activation have a common feature of being dehydrating agents that influence during the pyrolytic decomposition and inhibit the formation of tar increasing the yield of carbon. The yield and properties of activated carbons depend on the impregnation conditions, such as impregnation ratio (weight of activating reagent/ weight of carbon precursor), time of predrying impregnated materials, as well as pyrolysis conditions, such as temperature, soaking time (period of time that the sample and chemical are in contact) and atmosphere. All these process variables vary with the type of carbon precursor and the activating agent. The main impregnation condition is the chemical ratio, one of the most important parameters in the production of activated carbon by chemical activation. As said before, this parameter makes a relation between the agents as a function of the starting material involved. In the preparation of activated carbons, different ratios are studied in order to find out the effect on yield and other properties, though the typical ratios are 2:1 and 4:1. There are two competing mechanisms of pore evolution in the carbon structure. The first one is the micropore formation, which starts with the addition of chemicals into the lignocellulosic structure that seems to be the cause of the formation of micropores, and the second one is the pore widening that is the result of the chemical effects inside the pores;

therefore it starts acting when the chemical ratio is reasonably high. Many studies reported that activated carbons obtained at low impregnation ratios were essentially microporous and when the amount of impregnation agent increases, the activated carbon becomes largely mesoporous.

The pyrolysis temperature is also an important factor that must be studied in detail, depending on the raw material the optimum temperature can vary taking into account the wide range of available temperature. Activation mostly involves a single process and the temperature range commonly used for this process is between 450 to 900 ºC. The ideal pyrolysis temperature for manufacturing activated carbon from lignocellulosic materials is 500 ºC as at this temperature, the maximum development of sponginess is produced. Some research have reported that by increasing the pyrolysis temperature, an increase in the mesopore size corresponds to a decrease in microporosity and after a certain temperature, surface area decreases causing a contraction of the carbon porous structures.

Pyrolysis time refers to the total time that the sample is going to burn off. It is a critical factor that affects the quality of activated carbon. In most studies related to the preparation of activated carbon by chemical activation, the pyrolysis time more often used ranged between an hour and two. Generally, for a soaking time, longer than an hour led to a decrease in both surface area and total pore or micropore volume. There are many different activation agents, but the most studied ones are phosphoric acid, zinc chloride and potassium hydroxide.

2.3.2.1 Phosphoric acid (H_3PO_4)

The mineral acid, phosphoric or orthophosphoric acid, with formula H_3PO_4 works as an acidic catalyst stimulating reactions involving cleavage of bonds and crosslink formation. In combination with organic species it forms phosphate linkages**,** including polyphosphate esters and phosphate that serve as connection between fragments biopolymers (Haimour and Emeish, 2006).

As mentioned earlier, it is one of the most used chemical agent, at temperatures around 450-500 ºC producing high pore volume, even though the carbonization process of the material can be partially complete. The other role H_3PO_4 plays is producing structural alterations and chemical changes at lower temperatures than in thermal treatment without impregnation (Solum *et al.*,1995).

2.3.2.2 Sodium Hydroxide (NaOH)

Activation by NaOH is economical as it produces the highest specific surface area AC material per unit weight. It is also environmentally friendly. Creation of metallic sodium is unavoidable, upon NaOH activation of carbon material. The stoichiometric reaction between the carbon precursor and the activating agent is (Cazorla-Amoros *et al.*, 2003):

$$6NaOH + 2C \longrightarrow 2Na + 3H_2 + 2Na_2CO_3 \quad \text{..... (10)}$$

2.3.2.3 Calcium Chloride ($CaCl_2$)

In the preparation of activated carbon, a commonly used activating agent is the dehydrating agent, Calcium Chloride, $CaCl_2$. This agent was commonly used in the 1980´s specifically for wood wastes in the adsorption of gold but not currently utilized as a result of its role in environmental pollution.

Research by Davidson, (1974), found that reproducible isotherms could be obtained only in the presence of a borate buffer solution when coconut shell carbon was used in the adsorption of $Au(CN)_2$. His work was aimed at studying the effect of the addition of spectator cations for instance calcium ion and sodium ion to the adsorption medium and also the temperature of the carbon retention capacity of gold. To further advance his argument and account for his observations in the experiment he involved the adsorption of the metal dicyanoaurate complex ion-pair $M^{n+}[Au(CN)_2^-]_n$ from solution. He noticed that the ability of M^{n+} to inhibit gold desorption with alkaline carbonate solutions followed the sequence:

$$Ca^{2+} > Mg^{2+} > H^+ > Li^+ > Na^+ > K^+$$

2.4 Adsorption Process

Three interfaces within which liquid phase adsorption occurs are liquid-vapor, liquid-liquid, or liquid-solid. However the liquid-solid interface has much of the attention the reason being that the decolourisation, detoxification and purification of liquids such oils, wine and water have been carried out for centuries using charcoal and active carbons. The development of the pharmaceutical, chemical and food industrieshas vastly increased the different varieties of items that undergo purification by carbons (Bansal and Goyal, 2005).

Adsorption is a physicochemical phenomenon in which a solid, called adsorbent, retain in the walls a certain kind of molecules, called adsorbates, that are contained in a gas or liquid (Rodríguez, 2012). The most employed adsorbents are silica, some synthetic resins and activated carbons. According to Rodríguez, (2012), variables to be considered in a sorption process in relation to the sorbent and the sorbate include, the particle and pore size,

structure, distribution, the affinity of the adsorbate, the specific surface and porosity of the solid, contingent on the chemical properties of the adsorbent surface and lastly, partial pressure or concentration of the adsorbate in the fluid phase, where may be equilibrium established between the adsorbate concentration in the solution and the mass adsorbed per mass unit of the adsorbent using i.e. the Freundlich equation.

Three types of adsorption attributed to the adsorbent-adsorbate attraction are electrical, physical and chemical adsorption. Electrical adsorption is also known as ion exchange since the ions of a substance are present in a high proportion on the surface due to electrostatic attraction. Physical adsorption occurs when the molecule is bound into the interphase usually at low temperatures. For this type of adsorption, activated carbon is used to adsorbed most of the organic compounds from water. Chemical adsorption is a reaction that happens between the adsorbent and the adsorbate due to their chemistry. It is considered strong in the active point of the adsorbent.

In an adsorption process, it is common to have a combination of all the three types. Actually, sometimes it is not easy to differentiate between a physical and chemical adsorption. The union between the adsorbates in the surface of the carbon is mostly caused by the Van der Waals forces, which means, that the activated carbon of apolar nature, will adsorb all the apolar substances depending on the affinity of the chemical surface properties. However, when there are mixtures of gases or substances with different affinity, the concentration of one of the substances will increase on the activated carbon surface, decreasing it in the mixture, until the adsorption-desorption equilibrium is achieved. In that sense, the process studied for evaluating an activated carbon is a term that explains the

adhesion of ions, dissolved solids and all kind of molecules of gas and liquid including biomolecules to a solid surface. That process is explained by the force field created between the surface of the solid where the molecules fill in, the adsorption potentials are enhanced in micropores due to the overlap of the fields from the opposite pore walls and interactions between the adsorbed molecules. Adsorption is a superficial phenomenon, as the high surface area the active carbon could achieve means that higher adsorptive capacity it will have. The surface is an important characteristic of the activated carbon and their typical range is around 500-1000m^2/g (Marsh and Yan, 1984).

Adsorption is usually described in terms of isotherms, which explains the relation of the amount of adsorbate on the adsorbent as a function of its concentration-liquid or pressure-gas at a constant temperature (Pratheesh, 2011). Isotherms usually provide useful information about the adsorption volume, pores size and its distribution among others.

2.4.1 Adsorption Models

One of the ways used to demonstrate equilibrium state of an adsorption system to give data concerning sorbate-sorbent interaction is the adsorption isotherm. It is also useful in determining the pore volume and size distribution, the heat of adsorption, surface area, and the relative absorbability of gas or vapour on a given adsorbent.

The key adsorption isotherms are the Brunauer-Emmett-Teller (BET), the Dubinin, the Langmuir, the Freundlich, and the Temkin equations. The last three isotherm equations play a major role in chemisorption, although the Freundlich and Langmuir isotherms are useful in physisorption.

2.4.1.1 Langmuir Isotherm

Langmuir equation, (1916), is based on a theoretic model and assumes that the maximum adsorption corresponds to a saturated homogeneous monolayer with adsorbate molecules on the adsorbent surface. This is represented by the next equation:

$$q_e = \frac{Q_0\, b\, C_e}{1+bC_e} \quad \ldots\ldots\ldots (11)$$

Where

b = relative constant of adsorption energy (l mg^{-1})

q_e = amount of solute adsorbed at equilibrium, mg/L

C_e = concentration of solute in the solution concentration of adsorbate in the liquid at equilibrium (mol/L)

Q_0 = maximum adsorption capacity ($mg.g^{-1}$)

Considering the Langmuir model, adsorption occurs homogenously on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at this site.

Thus, the Langmuir model is given by the equation (Chegrouche *et al.*, 1997)

$$1/q_e = 1/Q_0 + 1/b\, Q_0 C_e \ldots\ldots\ldots (12)$$

where

b and Q_0, the Langmuir constants, are the sorption equilibrium constant and the saturated monolayer sorption capacity, respectively.

A plot of $1/q_e$ versus $1/Q_e$ would result in a straight line with a slope of $(1/b\,Q_0)$ and intercept of $1/Q_0$ as shown in Figure 2.5 below.

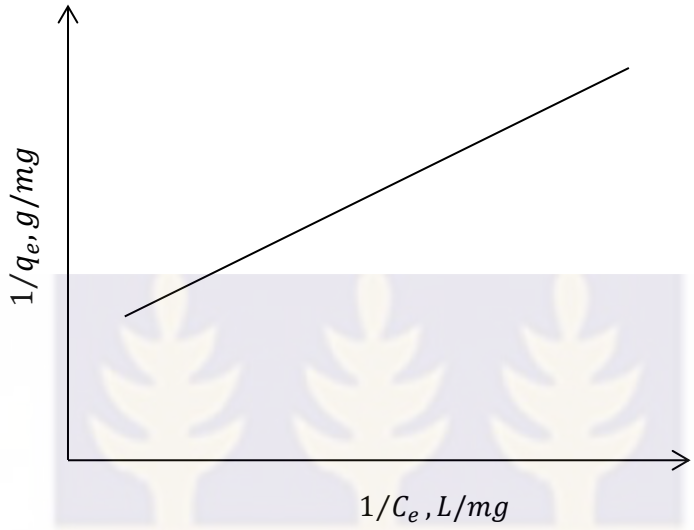


Figure 2.5 Langmuir adsorption isotherm

2.4.1.2 Freundlich Isotherm

The Freundlich equation is a model which takes into account diverse adsorptive energies on the adsorbent surface. The model states that the ratio of solute adsorbed to the solute concentration is a function of the solution. The model was shown to be consistent with the exponential distribution of active centres characteristic of heterogeneous surfaces. The concentration of solute in the solution, C_e, and the amount of solute adsorbed at equilibrium q_e, are related by equation (Mellah *et al.*, 2006):

$$q_e = K_F C_e^{1/n} \text{.....(12)}$$

The linear form of this expression is given as

$$\ln q_e = \ln K_F + 1/n \ln C_e \text{.....(13)}$$

where n and K_F are the Freundlich constants, which denotes sorption intensity and sorption capacity, respectively. A plot of ln q_e versus ln C_e gives a resulting straight line with intercept of log K_F and a slope of (1/n) as shown below in Figure 2.6.

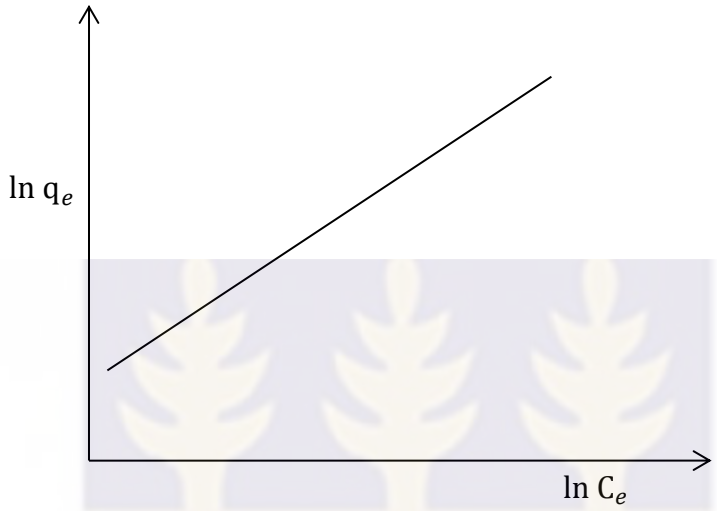


Figure 2.6 Freundlich adsorption isotherm

2.5 Factors Affecting Adsorption

The retention ability of AC is dependent on the sorbent-sorbate properties and also the conditions of the gas and liquid phases.

2.5.1 Properties of Carbon

Provision of sorption sites and the proper channels for the transportation of the adsorbate can be facilitated by the right spread of the different pore sizes in the carbon matrix. Pore volume is another important parameter to ascertain the adsorption capacity of the ACs and is determined by the volume of liquid of adsorbate adsorbed (N_2) at a relative pressure. The ash content in a carbon has adverse effects that can be summarised in:

a) It reduces overall activity of activated carbon

b) It reduces efficiency of reactivation

2.5.2 Properties of the adsorbate

An adsorbate is a substance or a molecule that is to be adsorbed onto a solid surface which is the adsorbent . Nearly all types of organic molecules can be adsorbed. On the other hand, inorganic molecules are not adsorbed by AC although silver salts or iodine are exemptions. Molecular weight of organic compounds plays a role in their retention by AC surface; the greater the molecular weight the greater the adsorption, In addition, adsorption is efficient when the pore size is greater than the molecular size of the adsorbate.

2.5.3 Properties related to the gas or liquid temperature

A reduction in pH, generally aids in the adsorption process in a liquid phase, most especially with the adsorption of organic pollutants (Çeçen and Aktaş, 2012). At elevated temperatures the mobility of adsorbate is increased due to enlarged pore size of the adsorbent (Pathania *et al.*, 2017). Table 2.3 shows some properties of activated carbons used for commercial purposes. The adsorbate at higher temperatures experience less resistance to movement therefore are able to occupy pores easily. Summing up, as the temperature increases so do the adsorption.

Table 2.3 Shows the typical range of values for commercial activated carbons

Parameter	Value
Specific surface area, BET (m^2/g)	600 – 1500
Total pore volume (m^3/g)	0.6 – 1.8
Apparent density (g/cm^3)	0.3 – 0.7
Granularity (mm) a: dust	0.05 – 0.1(a)
b: granular	0.1 – 2 (b)
Ash percentage (%)	2 - 10
Uniformity coefficient (grain)	1.1 – 12

Source: (Aznar, 2011)

2.6 Properties

The categorization of the AC requires data on the physicochemical properties of the materials (Sivakumar *et al.*, 2012). In relation to the physical properties, one must have information on the moisture and ash content, as well as the pore structure and size which would determine how adsorption takes place (International Organization for Standardization [ISO], 2017). The chemical properties to have in consideration are the specific surface area and the surface chemistry.

2.6.1 Physical Properties

2.6.1.1 Moisture Content

In general, activated carbons are stored in arid environment; else, it might adsorb substantial moisture. They may take up to 30% moisture and still look dry (Kidd & Killeen, 1992). Though the moisture content is independent of the adsorption capacity, however, it dissolves the carbon. In this sense, an extra mass of moist carbon is desired to offer the needed dry weight.

2.6.1.2 Ash Content

In the manufacture of AC the raw material source and the activating agent used contributes to the total quantity of inorganic constituents present in the product. Reorganization procedure during recovery, increased hydrophilicity and catalytic effect are caused by high ash content. Generally ash content of AC ranges between 2% and 10% as shown in Table 2.3 above.

2.6.1.3 Pore Structure

A pore is a type of cavity that links the solid surface and permits the connection of fluids in a material. Defined by their diameter, below are the three basic categories of pores that exist by the assertion of IUPAC, (2014) and also as shown below in Figure 2.7:

a) Micropores: D < 2 nm

b) Mesopores: 2 < D < 50 nm

c) Macropores: D > 50 nm

All the three pores in AC function differently (IUPAC, 2014). The most important of the three are the micropores with a high adsorptive capacity due to their high surface area and smaller size (Pelekani and Snoeyink, 2000) . Microporosity of activated carbon makes them efficient in the removal of odour or flavor generating compounds, solvents and volatiles (Yu et al., 2007).

Mesopores retain molecules that are intermediate between micropores and macropres. They serve a dual purpose that is in forming a meniscus during condensation at high pressures, secondly serve as an antecedent to the micropores (Bansal and Goyal, 2005). Macropores amongst the three are the biggest in pore size and their primary role is to communicate the external surface of the AC with the mesopores. Actually, the surface of the macroporous may be regarded as nonporous, though its importance lies in the liquid retention that may occur. For that reason, one of the main functions of the macropores is ensuring the speedy arrival of adsorbate to the smaller size pores located deeper in the AC. Molecules of the size of humic acid produced by the breakdown of organic matter can also be retained by macropores (Nalwa, 2001).

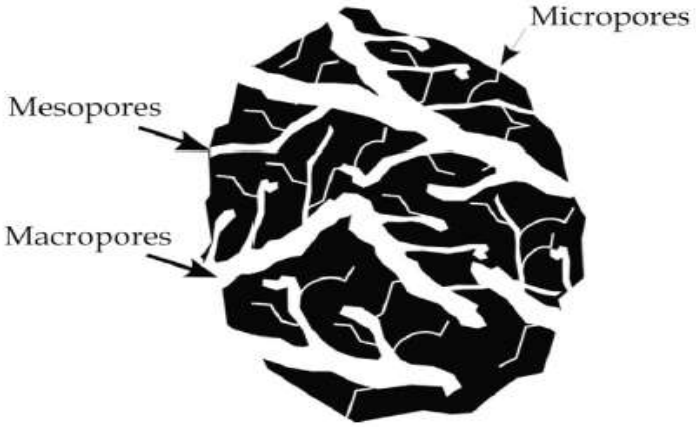


Figure 2.7 Schematic representation of pore structure of activated carbon material (Hassan *et al.*, 2015)

In that sense, activated carbons show different properties controlled by the precursor employed and activation conditions and it would undoubtedly determine the adsorption capacity that is usually attributed, besides to its surface area, for an appropriate inner pore capacity that may be spread in pores reaching 2 nm to 50 nm (Puziy *et al.*, 2002).

The porous structure is characterised by several methods like gas adsorption by nitrogen (N_2), carbon dioxide (CO_2) or vapours as benzene, SEM and TEM (Lawrence and Jiang, 2017).

2.6.1.4 Surface Area

High specific surface area in the range 500 m^2/g to 3000 m^2/g explained by the micropore structure provides information on porosity development of activated carbons (Al-Qodah and Shawabkah, 2009; Dias *et al.*, 2007). One can think that for a higher surface area, the adsorption characteristics as adsorbent is going to be good because there will be more adsorption site for the retention of adsorbate. Conversely**,** if the molecular size of the adsorbate is bigger than the micropore size, surfaces available for adsorption will be limited. Also to be considered before adsorption is the shape of the adsorbate.

2.6.2 Chemical Properties

The physicochemical make-up of the starting material, including the procedures involved in activation, aids in pore size spreading, formation and the adsorptive capacity of ACs (Haimour and Emeish, 2006).

A factor that differentiates carbonaceous substances is the structural content. Lignin rich precursors develop ACs predominated with macroporosity. However, microporous ACs are produced by materials with high cellulose content (Ioannidou and Zabaniotou, 2007).

Furthermore, of the porosity properties, the chemical surface characteristics of the solid develop specific surface complex which is also important in the adsorptive process. Their lack of specificity notwithstanding water, oxygen and nitrogen are among compounds that are not retained by activated carbon but hydrocarbons and dyes (apolar molecules) are retained.

The chemistry of the carbons occurs basically on the ends of the graphitic layer where oxygen groups and other functional groups are resident. Other compounds as hydrogen, nitrogen, phosphorous or sulphide could be mixed with carbon to form a superficial complex but in less quantity. The resulting superficial complex in an AC surface has got to do with the heteroatoms in the carbon matrix (Considine *et al.*, 2001; Figueiredo *et al.*, 1999)

Polar molecules are weakly retained on carbon surfaces, but their affinity can be increased when functional groups like carboxylic acids and lactones are formed on their surfaces. Heteroatoms are responsible for the formation of these functional groups and their presence

on the carbon surface can be attributed to the precursor, a method of activation and treatment conditions (Considine *et al.*, 2001).

The adsorptive capacity and the surface chemistry of carbons accounts for the extent to which a pollutant is removed. Particularly, removal of substances with high polarity and low molecular weight will be very complicated and will take place easily if the carbon is impregnated with specific chemicals or are used properly the catalytic properties of the carbon.

2.7 Parameters to evaluate the properties of the adsorption

Below are some specifications that must met for the assessment of adsorption:

a) Adsorption efficiency which is determined by the pore structure and degree of activation is proportional to surface area.
b) Pore size
c) Smaller particle size gives greater rates of adsorption.
d) Adsorption capacity favored by lower temperatures.
e) Rate of adsorption is proportional to adsorbate concentration.
f) Adsorption efficiency is favoured by acidic media (low pH).
g) Adsorption rate increases with low ash content.

2.8 Regeneration and recovery

Industrial ACs are costly and prized adsorbents therefore must be recovered after use. Spent ACs may be renewed when their capacity to adsorb is reached. The following methods can be used during regeneration:

i. Low pressurize steam passed through a bed of activated carbon can be used to vaporize and remove solvents, volatile compounds, surface recovery and sterilisation.

ii. Elimination of adsorbate with acidic or alkaline solutions.

iii. Thermal regeneration is carried out in ovens with ten percent (10%) loss during each regeneration, which means that in 10 or 12 regenerations it must be replaced.

iv. Oxidising gases treatment

CHAPTER THREE

3.0 METHODOLOGY

3.1 Materials, Chemicals and Instrumentation

This chapter describes the sampling sites and the raw materials used. It also gives detailed description of the experimental procedure and the various instruments used in producing and characterizing the activated carbon.

3.1.1 Raw Materials and sampling sites

The Greater Accra Region is one of the ten regions of Ghana. It is located at the South Eastern corner of Ghana with latitude 9.8°- 11.O° north and longitude 1.6°- 3.0º west. It covers a geographical area of 18,476 square kilometers which represents 12.7% of the total land area of Ghana. Dome and Madina are part of the Ga-East Municipality and La Nkwantanang-Madina Municipality respectively in the Greater Accra Region. The two municipalities according to the 2010 Population and Housing Census have a population of 147,742 and 111,926 respectively (Ghana Statistical Service, 2014a). About 70 percent of the population in both municipalities aged 15 years and older are economically active while about one-third (30.0%) are economically not active. Approximately 5.3 percent of households in these municipalities are engage in agriculture most of which are crop farming (Ghana Statistical Service, 2014b). Coconut shells were sampled around Dome market in the Ga-East Municipality while the Palm kernel shells were acquired around the Madina market in the La Nkwantanang-Madina Municipality. These sites were chosen because they are the collection point of most of the used coconut shells and palm kernel shells in the municipality. Figure 3.1 below shows an area map of the two sampling sites.

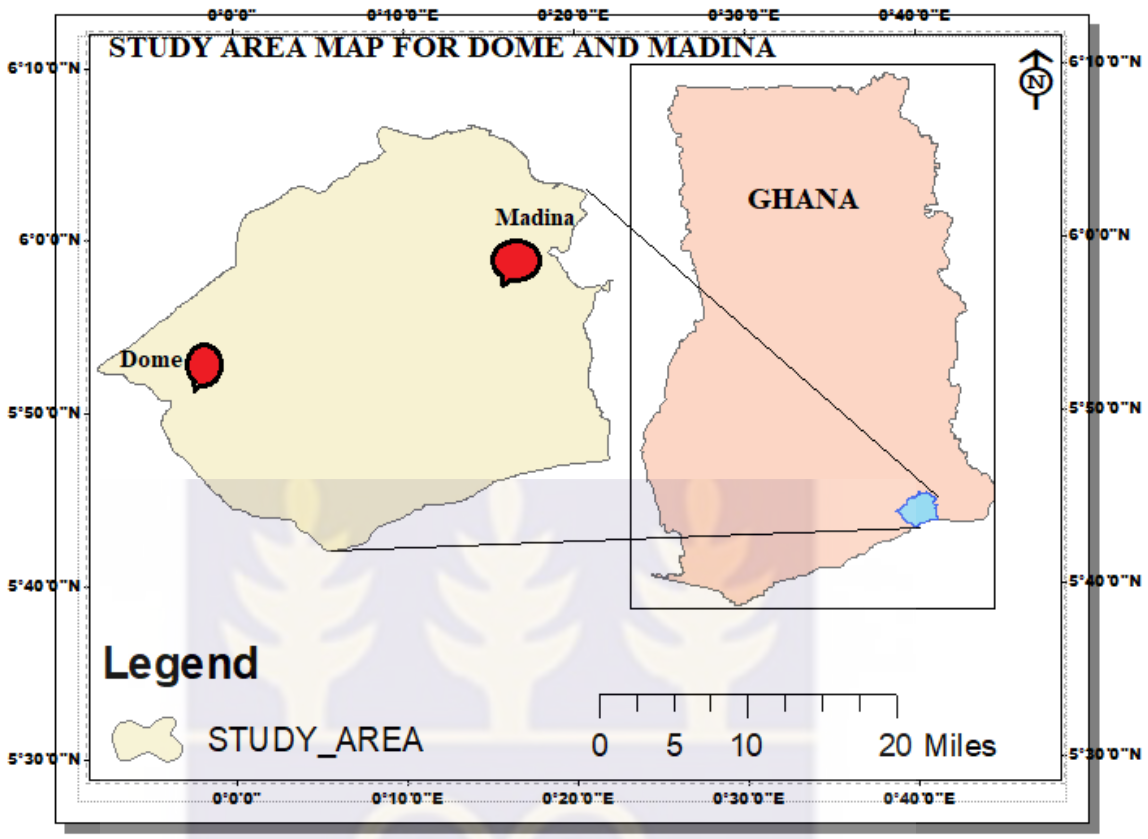


Figure 3.1 Study area map for Dome and Madina

3.1.2 Chemicals

In all experiments in this study, all chemicals used were of analytical reagent grade. All solutions were prepared using distilled water. Phosphoric acid (H_3PO_4) with purity 99 %, sodium hydroxide (NaOH) with purity of 99% and calcium chloride ($CaCl_2$) with purity 99 % that were used for impregnation were from Daejung chemicals and company limited, Korea.

3.1.3 Instrumentation

Retsch Mill Type-SM1 and the US sieve size 350 µm were used to obtain the uniform size of palm kernel shell and coconut shell particles. Griffin-grundy Oven and Thermolyne Muffle Furnace were used for carbonization. The microstructure of the activated carbon was showed by SEM, Make JEOL, JSM-6390LV, Japan. An engine lathe machine was

used in building canisters from stainless steel pipes purchased from Timber market in Accra Central. Sartorius digital lab analytical balance L 2200 P was used in weighing right quantities of samples.

3.2. Sample Identification and Preparation

3.2.1 Sample Identification

In order to differentiate the precursors used prior to the preparation of the activated carbons by chemical activation (CA), the PKS and CS samples were named as shown in Table 3.4 below.

The abbreviation PKS and CS refers to palm kernel shell and coconut shell respectively. The letters A, B and S correspond to the activating agents respectively being phosphoric acid, sodium hydroxide and calcium chloride. The number 1 next to the activating agents refers to the time to be varied and the one after representing the varying impregnating ratios. The last number indicates carbonisation temperature. In the first two instances, PKS_A_1_0.6_400^{o}C and CS_A_1_0.6_400^{o}C imply that the palm kernel shell and coconut shell have been treated with 1M H_3PO_4 solution at an impregnation ratio of 0.6 and carbonisation temperature of 400^{o}C. Also, the samples named PKS_B_1_0.6_500^{o}C and CS_B_1_0.6_500^{o}C refers to palm kernel shell and coconut shell that have been treated with 1M NaOH solution at an impregnation ratio of 0.6 and a carbonisation temperature of 500^{o}C and so on. A total of 72 samples were studied varying temperature, time and impregnating ratio. This was to help obtain optimum operating parameters for the production of activated carbon.

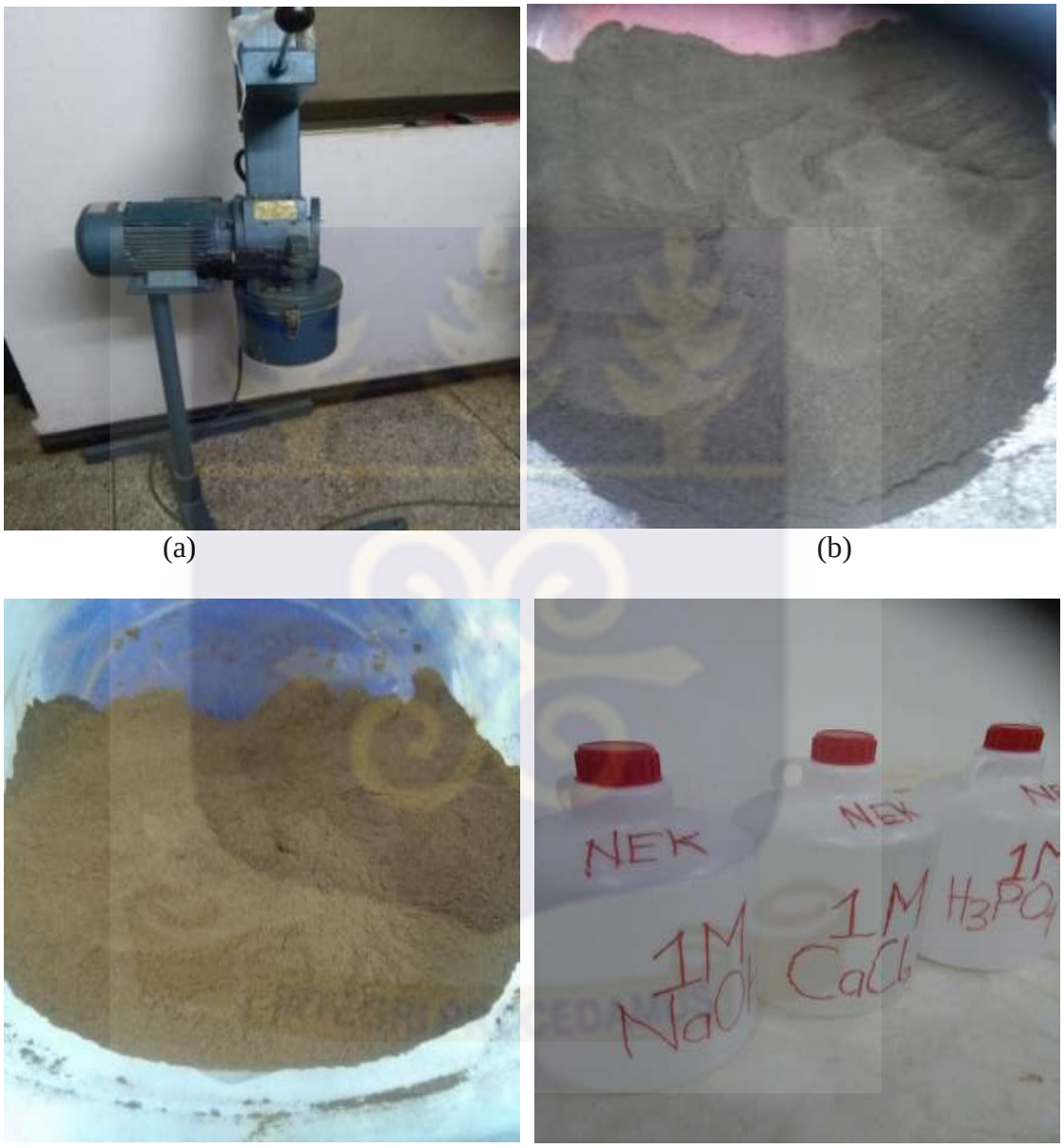
Table 3.1 List of samples

PKS Samples	CS Samples
PKS_A_1_0.6_400°C	CS_A_1_0.6_400°C
PKS_B_1_0.6_400°C	CS_B_1_0.6_400°C
PKS_S_1_0.6_400°C	CS_S_1_0.6_400°C
PKS_A_1_0.6_500°C	CS_A_1_0.6_500°C
PKS_B_1_0.6_500°C	CS_B_1_0.6_500°C
PKS_S_1_0.6_500°C	CS_S_1_0.6_500°C
PKS_A_1_0.6_600°C	CS_A_1_0.6_600°C
PKS_B_1_0.6_600°C	CS_B_1_0.6_600°C
PKS_S_1_0.6_600°C	CS_S_1_0.6_600°C
PKS_A_1_0.6_700°C	CS_A_1_0.6_700°C
PKS_B_1_0.6_700°C	CS_B_1_0.6_700°C
PKS_S_1_0.6_700°C	CS_S_1_0.6_700°C

3.2.2 Sample Preparation

The precursors, CS and PKS were washed with purified water to remove foreign materials. The washed CS and PKS were then sun dried for twenty-one days with reference to work done by Adinata *et al.* (2007). The dried CS and PKS were crushed in a Retsch mill as shown in Figure 3.1 (a) below to reduce their particle sizes. The crushed PKS and CS [Figure 3.1 (b) and (c) respectively] were sieved to the required particle size, using the 350 µm sieve. About 50.0 g each of the precursors were measured (in a beaker) and impregnated by mixing with an appropriate activating agent (1M H_3PO_4, 1M NaOH and

1M $CaCl_2$ solutions respectively) to obtain a homogenous mixture. The impregnating ratios used for each activating agent were 0.6, 0.8, 1.0 and 1.2 (Pandharipande *et al.*, 2012). The impregnated samples were dried at 100 ºC for 12 hours in a Griffin-Grundy oven.



(a) (b)

(c) (d)

Figure 3.2 (a) Retsch Mill (Type-SM1), (b) PKS, (c) CS and (d) Solutions

3.3 Carbonisation and Optimisation Processes

The dried samples shown below in Figure 3.2 (a) were transferred into canisters [Figure 3.2 (b)] and labeled according to sample type, activating agent, time, impregnating ratio and temperature. The labeled canisters were introduced by the use of tongs into the Thermolyne furnace maintaining impregnating ratio (0.6), carbonisation time (1hour) whilst varying temperature of the Thermolyne furnace (400, 500, 600 and 700^{o}C respectively). The temperature (optimum temperature) corresponding to the maximum yield was recorded.

This procedure was repeated by maintaining the optimum temperature (T_{opt}) obtained, impregnating ratio whilst varying the carbonisation time (1, 1.5, 2 and 2.5 hours). The optimum carbonisation time (t_{opt}) was recorded.

T_{opt} and t_{opt} were maintained whilst impregnating ratios (0.6, 0.8, 1.0 and 1.2) were varied to obtain optimum impregnating ratio (IR_{opt}).

Finally, the samples were collected in sealed bags and stored in a desiccator. The following picture in Figure 3.2 shows the experimental system:

(a) (b)

(c)

(d)

Figure 3.3 (a) Dried samples from oven, (b) Canisters, Thermolyne furnace (c) loaded with canisters and (d) Carbonization in progress

3.4 Scanning Electron Microscope (SEM)

Samples for the SEM were obtained from the ground precursors and the prepared activated carbons. Small quantities of the powdered and carbonized samples were collected to fit the specimen stub. Subsequently, they were mounted onto the stub with the help of a stainless steel curved forceps. Finally, the sample surfaces were placed in the chamber of the auto fine coater (JFC-1600, Japan) and an inert atmosphere of argon created. The samples were sputter coated with atomized platinum to make them conductive before being viewed with the SEM. The powdered samples were visualized for their surface morphology using the scanning electron microscope (SEM, Make JEOL, JSM-6390LV, Japan) at a magnification of ×5000. In all eight samples were examined namely - the powdered coconut and palm kernel shell at their raw stage and their activated carbons impregnated by H_3PO_4, NaOH and $CaCl_2$. This procedure followed were modifications of the method used by (Achaw

and Afrane, 2008). The instrumentation of the method described above is shown in Figure 3.4 below.

(a) (b)

Figure 3. 4 Instrumentation (a) Auto fine coater and (b) Scanning Electron Microscope (SEM)

3.5 Characterization of Samples

Various properties of the prepared activated carbon were characterized by following the standard procedures. The pH was measured using a pH meter, moisture content was found by oven-drying test method (ASTM D2867-09, 2009). The percentage of volatile matter of the AC sample was determined by the standard method (ASTM D5832-98, 2004) for the ash content (ASTM D2866-11, 2004) method was followed. The bulk density of activated carbon was determined following the method described by (Ahmedna *et al.*, 2000) using a measuring cylinder and the iodine number was determined using the standard method described by (ASTM D4607- 94, 2006). Electrical conductivity was measured using Ecoscan conductivity meter (Eutech, Singapore), and values were presented in micro Siemens, µS/cm as described by (Ahmedna *et al.*, 2000).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter highlights on the results obtained from the experiment and the plausible scientific explanations were given accordingly.

4.1 Effects of various parameters on activated carbon

4.1.1 Effect of Temperature on Activated Carbon Yield

From Table 4.1 below it is can be seen that PKS at 400 ^{o}C gave maximum activated carbon yield of 25.7 g with H_3PO_4 as activating agent, followed by 25.0 g with $CaCl_2$ as activating agent and the least was 22.3 g with NaOH as activating agent. CS also recorded a maximum activated carbon yield of 22.2 g with H_3PO_4 as activating agent at 400 ^{o}C. This was followed by 20.4 g of activated carbon with $CaCl_2$ as activating agent. The least mass of activated carbon produced was 13.4 g with NaOH as activating agent. A similar work conducted by (Okoroigwe and Saffron, 2012) in which PKS was the precursor and the activating agent used was H_3PO_4 also recorded optimum temperature between 400 ^{o}C and 500 ^{o}C.

Table 4.1 Effect of temperature on activated carbon yield

Temperature (°C)	Activating Agent	Carbon Yields (g)	
		PKS	CS
400	H_3PO_4	25.7	22.2
	NaOH	22.3	13.5
	$CaCl_2$	25.0	20.4
500	H_3PO_4	24.1	20.5
	NaOH	20.7	16.5
	$CaCl_2$	23.4	19.2
600	H_3PO_4	22.6	19.4
	NaOH	19.5	15.5
	$CaCl_2$	22.0	17.9
700	H_3PO_4	22.2	19.2
	NaOH	19.4	14.9
	$CaCl_2$	22.4	17.7

4.1.2 Effect of Carbonisation time on Activated Carbon Yield

Table 4.2 shows that the maximum yield of activated carbon for PKS was 25.7 g (H_3PO_4 as activating agent). This corresponded to carbonisation time of 1 hour. Hence, there was complete decomposition of PKS within 1 hour of carbonisation. Maximum mass of activated carbon produced from CS was 22.3 g (H_3PO_4 as activating agent). This mass of activated carbon produced from CS occurred within 1.5 hours of carbonisation time. Comparing PKS and CS, one can say that economically, production of activated carbon using PKS as precursor may be a better option. However, Jin *et al.*, 2012 reported that at higher carbonistaion time less amount of activated carbon was produced. This was in sharp contrast with this study. This may probably be explained by the fact that different activating agent was used.

Table 4.2 Effect of carbonisation time on activated carbon yield

Time(h)	Activating Agent	Carbon Yield (g)	
		PKS	CS
1	H_3PO_4	25.7	22.2
	NaOH	22.3	13.5
	$CaCl_2$	25.0	20.4
1.5	H_3PO_4	25.6	22.3
	NaOH	21.9	14.9
	$CaCl_2$	24.6	20.2
2	H_3PO_4	25.4	21.9
	NaOH	21.7	17.1
	$CaCl_2$	24.2	19.7
2.5	H_3PO_4	25.4	22.2
	NaOH	21.6	17.4
	$CaCl_2$	24.4	20.3

4.1.3 Effects of Impregnation ratio on Activated Carbon Yield

Generally, Table 4.3 shows that as the impregnation ratio of activating agent to precursor increased, average mass of activated carbon produced also increased. A similar observation was reported by Mozammel *et al.*, (2002). PKS and CS had maximum yield of activated carbon of 27.6 g and 24.2 g respectively (H_3PO_4 as activating agent in each case). These maximum masses (27.6 g and 24.2 g) corresponded to impregnating ratio of 1.2.

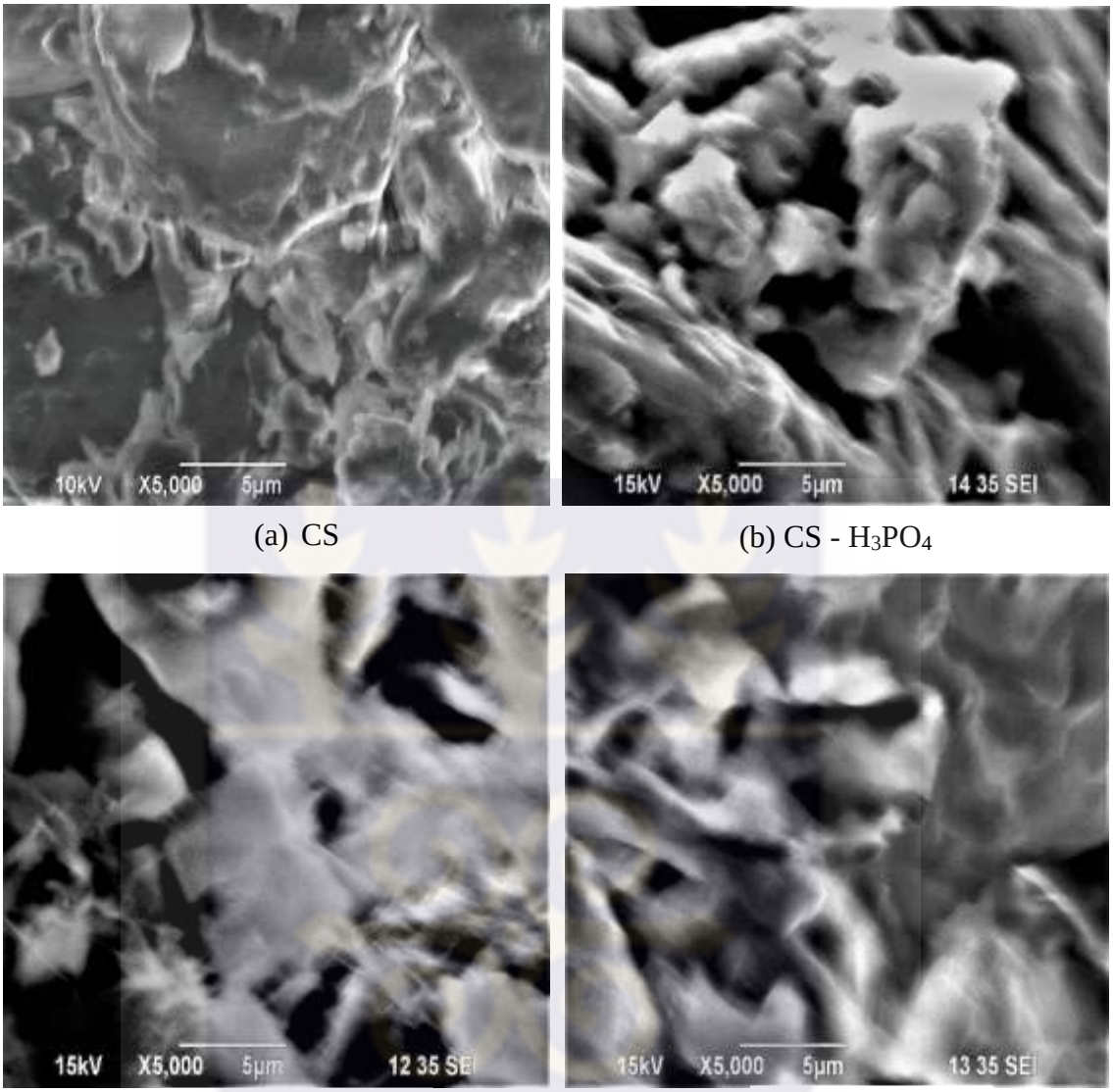
Table 4.3 Effect of impregnating ratio on activated carbon yield

Impregnating ratio	Activating Agent	Carbon Yield (g)	
		PKS	CS
0.6	H_3PO_4	25.4	22.2
	NaOH	21.6	17.2
	$CaCl_2$	24.4	20.3
0.8	H_3PO_4	26.0	22.9
	NaOH	21.7	17.4
	$CaCl_2$	25.3	20.7
1.0	H_3PO_4	26.5	23.2
	NaOH	21.9	17.5
	$CaCl_2$	25.7	21.4
1.2	H_3PO_4	27.6	24.2
	NaOH	22.5	18.0
	$CaCl_2$	26.4	21.6

4.2 Scanning Electron Microscope (SEM)

4.2.1 Micrographs of coconut shell carbons

Figure 4.1 shows micrographs of coconut shell carbons before (a) and after [(b, c, d)] activation. This gives an appreciation of the porosity of the adsorbents and hence a qualitative evaluation of their ability to adsorb pollutants in solution. Prior to chemical activation, the SEM micrographs of the precursor, Figure 4.1 (a) shows a cliff-like mass of flowing lava with no initial pore development on the surface. On the other hand, the external surface of the chemically activated carbons as shown in Figures (b), (c) and (d) are rich with cavities indicating enhanced porosity for improved application in adsorption processes.



(a) CS (b) CS - H_3PO_4

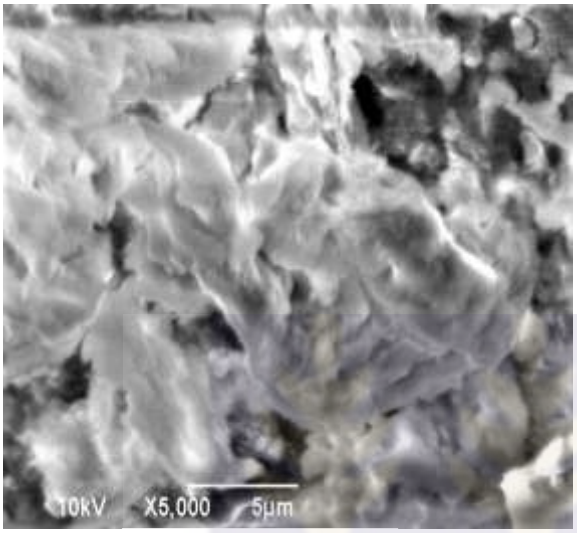
(c) CS - NaOH (d) CS - $CaCl_2$

Figure 4. 1 Micrographs of sections of the outer surface of coconut shells at different stages: (a) raw coconut shell, (b) H_3PO_4-coconut shell activated carbon, (c) NaOH-coconut shell activated carbon, (d) $CaCl_2$- coconut shell activated carbon

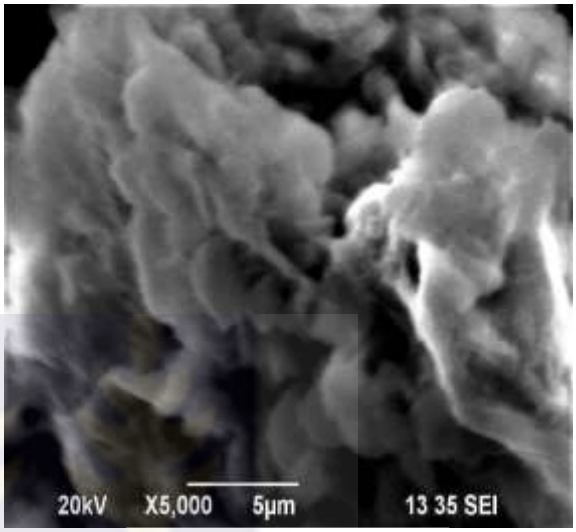
4.2.2 Micrographs of palm kernel shell carbons

Figure 4.2 is a representation of the micrographs of the palm kernel shell carbons before (a) and after [(b, c, d)] activation. The porosity is less in the case of Figure 4.2 (a) as compared to the surface morphologies of Figures 4.2 [(b, c, d)] which indicates the impact

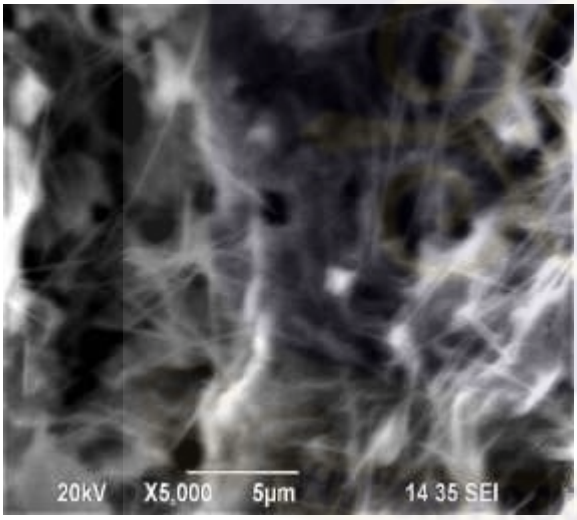
of activating agents on the carbon samples. The porous morphology presented by the chemically activated PKS carbons concludes that the prepared AC make a better adsorbent.



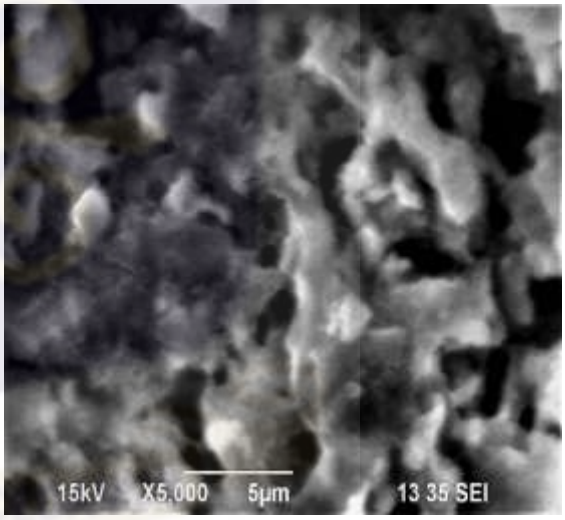
(a) PKS



(b) PKS - H_3PO_4



(c) PKS - NaOH



(d) PKS - $CaCl_2$

Figure 4.2 Micrographs of sections of the outer surface of palm kernel shells at different stages: (a) raw palm kernel shell, (b) H_3PO_4-palm kernel shell activated carbon, (c) NaOH-palm kernel shell activated carbon, (d) $CaCl_2$-palm kernel shell activated carbon

4.3 Characterisation of activated carbon

4.3.1 pH

Table 4.4 below shows the pH values obtained in this study. Activated carbon adsorption is affected by pH. At lower pH activated carbon are more effective than at high pH (Evbuomwan *et al.*, 2013). The base activated PKS carbon recorded the highest pH of 9.4 while the acid activated CS carbon recorded the lowest pH of 2.6. This indicates that the activated carbon may probably be an L-type and may have acidic oxides predominating its surface as has been reported by Matos *et al.*, (2012). However, the pH values obtained in this study falls within the range of most commercial activated carbons used for adsorption purposes (Erhayem *et al.*, 2016).

4.3.2 Moisture Content

An excellent precursor for the production of adsorbent should be low in moisture content (Ekpete *et al.*, 2017). The lowest moisture content recorded in this study was 1.94 % (Table 4.4) for PKS-AC (H_3PO_4) which was lower than works conducted by Ulfah *et al.*, (2016) whose moisture content was about 5.42 %. A high moisture content, 5.41 %, was obtained for CS-AC (H_3PO_4) which was concordant to similar works by Devi *et al.*, (2012). The results obtained suggest that PKS will make a better adsorbent since it has a lower moisture content. Relative to the moisture content obtained by Ulfah *et al.*, (2016) and Devi *et al.*, (2012), it could be concluded that the activated carbon produced from the two precursors (PKS and CS) are of appreciable quality and thus, will be more effective in water treatmnent.

4.3.3 Volatile Matter

A low volatile matter of 30.46 % was obtained for CS-AC ($CaCl_2$) whiles that of CS-AC (H_3PO_4) was 35.64 % (Table 4.4). The values were lower compared to works conducted

by Sanni *et al*., (2017) who obtained 57 % volatile matter using coconut shells. The difference could be attributed to the varying molarities of the phosphoric acid used. The low percentage of volatile matter in this study may also be as a result of the dehydrating effect of the acid and the chloride salt which caused the water in the biomass to vapourize and strengthening the covalent bond in the carbon matrix leaving no room for carbon loss (Sanni *et al.*, 2017 ; Cobb *et al.*, 2012).

4.3.4 Ash Content

Ash content level of carbon derived from PKS-AC ($CaCl_2$) were higher (14.96 %) than the other activated carbons as shown in Table 4.4. The ash content of the samples substantiate that PKS-AC ($CaCl_2$) may have higher inorganic constituents thereby increasing the amount of non-ignitable residue as leftover in the furnace. The ash content (7.17 %) recorded for CS-AC (H_3PO_4) was in agreement with the study conducted by Sanni *et al.*, (2017) whom, in their analysis obtained an ash content of 7.2 % useful inorganic contaminants removal (Sivakumar *et al*., 2012).

4.3.5 Carbon content

Carbon content refers to the percentage char that remains after the mass of the volatiles are eliminated (Ikelle and Ivoms, 2014). Table 4.4 shows a high carbon content of 57.78 % in CS-AC (NaOH) which is desirable than a rather low one of 46.63 % obtained in PKS-AC ($CaCl_2$). The disparity may be due the difference in precursor and activating agents used (Danyuo et al., 2014).The findings also suggest that coconut shell might be a better precursor than the palm kernel shell.

4.3.6 Bulk density

Bulk density is the mass of carbon that can be contained in a filter of a given solid capacity and the amount of treated liquid that can be retained by the filter cake. The higher the density the better the filterability of activated carbons (Verla *et al.*, 2012). Bulk density of carbons obtained from all the samples studied shows that PKS-AC (H_3PO_4) carbon has the higher bulk density of 0.65 g/cm^3 which may be due to its high fibre content and CS-AC (NaOH) had the lower bulk density 0.31g/cm^3 (Table 4.4), which can be attributed to the material hardness. This value of bulk density in this work was in concordance with similar works obtained by (Li Lee *et al*., 2016; Jambulingam *et al*., 2007)

4.3.7 Pore volume

Pore volume recorded in this study for PKS-AC (H_3PO_4) was 0.94 ml/g (Table 4.4). This value agreed closely to works done by Sethupathi *et al.*, 2015. A lower pore volume of 0.50 ml/g was obtained for CS-AC (NaOH). The observation can be linked to the intrinsic features of PKS such as the type of lignocellulosic make-up, textural and botanical family (Daud and Ali, 2004).

4.3.8 Porosity

The porosity of any porous material is defined as the ratio between the total void spaces within the solid porous material and the material bulk volume (Hassan *et al*., 2015). A high porosity of 0.49 (Table 4.4) was obtained for PKS-AC (H_3PO_4) whiles CS-AC (NaOH) and CS-AC ($CaCl_2$) recorded the lowest porosity of about 0.24 in this study. The difference in porosities of the activated carbons produced could be credited to the different raw materials used (Ilomuanya *et al*., 2017). Pore volume supports the concept that porosity is better in chemically activated carbons (Fierro *et al.*, 2007). Adsorptive capacity is

determined by porosity (Verla *et al*., 2012) and it could be stated that PKS-AC (H_3PO_4) produced in this study may perform better as an adsorbent.

4.3.9 Iodine Number/Value

Iodine number is defined as the number of milligrams of iodine absorbed by one gram of activated carbon powder (Gawande and Kaware, 2017). The removal of iodine by the activated carbons is related to their porosity characteristics which determine the degree of accessibility of these molecules. Table 4.4 shows the iodine values obtained in this study. The highest iodine number recorded in this study is 743.02 mg/g for CS-AC (H_3PO_4) activated carbon and 651.66 mg/g was the lowest as recorded for PKS-AC ($CaCl_2$). The higher iodine number of CS-AC (H_3PO_4) is indicative of larger adsorption area than those of lower iodine value (Marton *et al.*, 2006). More so the values obtained are relatively close to the works conducted by Jaguaribe *et al.*, (2005) and in the range of values (minimum of 500 mg/g) recommended by the American Water Works Standards as reported by (Verla *et al.*, 2012).

4.3.10 Electrical conductivity

High electrical conductivity is a desirable characteristic for commercial activated carbons used as electrode material for supercapacitors (Fan et al., 2011). 2130 µS/cm of the conductance recorded for PKS-AC ($CaCl_2$) was reportedly higher than the other carbons produced. The high electrical conductivity of the PKS-AC ($CaCl_2$) is suggestive of its utility in electrochemical devices (Viswanathan *et al.*, 2009). Also, the high electrical conductivity of PKS-AC ($CaCl_2$) indicates that its elemental carbon are in graphitic structure and can be useful in adsorption of gold ions (Soleimani and Kaghazchi, 2008). The electrical conductivities in this study are presented in Table 4.4.

Table 4.4 Physicochemical characteristics of prepared activated carbons

S/No	Parameters	Results							
		CS pdr	**PKS pdr**	**CS-AC H_3PO_4**	**PKS-AC H_3PO_4**	**CS-AC NaOH**	**PKS-AC NaOH**	**CS-AC $CaCl_2$**	**PKS-AC $CaCl_2$**
1	**pH**	5.7	5.7	2.6	2.8	8.7	9.4	7.2	7.0
2	**MC**	9.65	8.00	5.41	1.94	3.40	2.86	3.77	3.50
3	**VM**	42.49	37.38	35.64	31.86	30.82	35.05	30.46	34.91
4	**Ash**	1.95	9.63	7.17	11.88	8.00	12.95	8.01	14.96
5	**CC**	45.91	45.00	51.78	54.32	57.78	49.13	57.75	46.63
6	**BD**	0.47	0.54	0.41	0.65	0.31	0.50	0.32	0.60
7	**PV**	0.48	0.52	0.62	0.94	0.50	0.75	0.65	0.72
8	**Por.**	0.35	0.41	0.31	0.49	0.24	0.37	0.24	0.45
9	**IV**	194.83	173.01	743.02	682.11	682.11	712.57	712.57	651.66
10	**EC**	491	308	2010	778	662	1212	1732	2130

Pdr : Powder, MC : Moisture content (%), VM : Volatile matter (%), Ash : Ash content (%), CC : Carbon content (%), BD : Bulk density (g/cm^3), PV : Pore volume (ml/g), IV : Iodine value (mg/g), EC : Electrical conductivity (µS/cm), Por. : Porosity

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

This chapter of the research concludes the whole study and gives some recommendations to be considered in the future.

5.1 CONCLUSION

This study set out to optimize the production activated carbon from two agricultural by-products, palm kernel shell and coconut shell, through chemical activation using H_3PO_4, NaOH and $CaCl_2$. Chemical activation of the PKS and CS to produce activated carbon was successfully accomplished in a well-controlled laboratory with the application of appropriate instrumentation. PKS activated carbon and CS activated carbon showed a wider, meso- and macro-porosity. Palm kernel shell compared to Coconut shells produced more activated carbons with the same operating parameters and conditions. However, according to the physicochemical results obtained, PKS activated carbons may be a better adsorbent compared to CS activated carbons. PKS-AC (H_3PO_4) compared to CS-AC (H_3PO_4) make a better adsorbent according physicochemical parameters realized. Physicochemical characteristics of PKS-AC (NaOH) was also observed to be better than that of CS-AC (NaOH). PKS-AC ($CaCl_2$) was advantageous in moisture content, bulk density, pore volume, porosity and electrical conductivity. CS-AC ($CaCl_2$) also had advantages in volatile matter, ash content, carbon content and iodine number. However, a higher yield was obtained using phosphoric acid (H_3PO_4) as an activating agent compared to the calcium chloride ($CaCl_2$) and sodium hydroxide (NaOH). Such activated carbons have high carbon content, bulk density, pore volume, porosity and iodine number and are virtually dust-free. Also, the pore structure is very uniform, with the majority of pores

falling in the macropore range, particularly effective for decontamination and industrial pesticide residual removal.

5.2 RECOMMENDATION

In the present study the sampling sites were restricted to the Accra metropolis and the raw materials used were limited to CS and PKS which might have narrowed the spectrum of analysis to the type of biomass material used. To enhance understanding of the effects of operating parameters considered in this study a wider sample size should be considered.

Three dimensional and topographical imaging measured by the scanning electron microscope (SEM) is inadequate to completely describe the ACs developed.

Nevertheless, further studies could be done in future by the transmission electron microscope (TEM) to evaluate the crystal structure, view samples at the molecule level, making it easier to have an in-depth analysis of the texture and structure of the AC.

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APPENDICES

APPENDIX : Sample Identification

PKS_A_1_0.6_400°C	CS_A_1_0.6_400°C	PKS_A_1_0.6_400°C	CS_A_1_0.6_400°C
PKS_B_1_0.6_400°C	CS_B_1_0.6_400°C	PKS_B_1_0.6_400°C	CS_B_1_0.6_400°C
PKS_S_1_0.6_400°C	CS_S_1_0.6_400°C	PKS_S_1_0.6_400°C	CS_S_1_0.6_400°C
PKS_A_1_0.6_500°C	CS_A_1_0.6_500°C	PKS_A_1.5_0.6_400°C	CS_A_1.5_0.6_500°C
PKS_B_1_0.6_500°C	CS_B_1_0.6_500°C	PKS_B_1.5_0.6_400°C	CS_B_1.5_0.6_500°C
PKS_S_1_0.6_500°C	CS_S_1_0.6_500°C	PKS_S_1.5_0.6_400°C	CS_S_1.5_0.6_500°C
PKS_A_1_0.6_600°C	CS_A_1_0.6_600°C	PKS_A_2_0.6_400°C	CS_A_2_0.6_600°C
PKS_B_1_0.6_600°C	CS_B_1_0.6_600°C	PKS_B_2_0.6_400°C	CS_B_2_0.6_600°C
PKS_S_1_0.6_600°C	CS_S_1_0.6_600°C	PKS_S_2_0.6_400°C	CS_S_2_0.6_600°C
PKS_A_1_0.6_700°C	CS_A_1_0.6_700°C	PKS_A_2.5_0.6_400°C	CS_A_2.5_0.6_700°C
PKS_B_1_0.6_700°C	CS_B_1_0.6_700°C	PKS_B_2.5_0.6_400°C	CS_B_2.5_0.6_700°C
PKS_S_1_0.6_700°C	CS_S_1_0.6_700°C	PKS_S_2.5_0.6_400°C	CS_S_2.5_0.6_700°C

PKS_A_2.5_0.6_400°C	PKS_A_2.5_0.8_400°C	PKS_A_2.5_1.0_400°C	PKS_A_2.5_1.2_400°C
PKS_B_2.5_0.6_400°C	PKS_B_2.5_0.8_400°C	PKS_B_2.5_1.0_400°C	PKS_B_2.5_1.2_400°C
PKS_S_2.5_0.6_400°C	PKS_S_2.5_0.8_400°C	PKS_S_2.5_1.0_400°C	PKS_S_2.5_1.2_400°C
CS_A_2.5_0.6_400°C	CS_A_2.5_0.8_400°C	CS_A_2.5_1.0_400°C	CS_A_2.5_1.2_400°C
CS_B_2.5_0.6_400°C	CS_B_2.5_0.8_400°C	CS_B_2.5_1.0_400°C	CS_B_2.5_1.2_400°C
CS_S_2.5_0.6_400°C	CS_S_2.5_0.8_400°C	CS_S_2.5_1.0_400°C	CS_S_2.5_1.2_400°C