

**ASSESSMENT OF SAWDUST ACTIVATED CARBON (SAC) IN THE
TREATMENT OF AQUACULTURE EFFLUENT**

BY

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ABSTRACT

This study is aimed at the assessment of sawdust activated carbon in the treatment of aquaculture effluent with various objectives which includes the determination of the SAC properties, effluent parameters, effect of operating conditions and application of relevant adsorption isotherms. The sawdust was first precarbonized at 500°C , then impregnated with potassium carbonate (activating agent) and activated at 450°C in a furnace. The surface morphology of the sawdust activated carbon (SAC) was determined using scanning electron microscope (SEM) which showed a very porous media. It was further characterized using BET surface area at 77K, and the resulting surface area was $831.83\text{m}^2/\text{g}$. The aquaculture effluent (AE) was found to be very polluted compared to the NESREA discharge standard, in COD, TSS, BOD, NITRATES and lead(II) ion. An optimization studies was done using batch treatment process at varying dosage, time and initial concentrations, and the optimum treatment dosage and time were found to be 2g/l at 60minutes which gave an overall 83.33% reduction of COD, 90.80% reduction of BOD, 73.24% removal of nitrate(NO_3), 93.23% removal of TSS, and 99.35% removal of lead (Pb) ions. According to the R^2 values, the kinetic studies showed that the adsorption process was a pseudo second order reaction with a R^2 value of 0.99. After the assessment, it was found that among other uses of sawdust, it is also a good precursor for the production of activated carbon, which is has been found in this study to be a good treatment media for the treatment of the polluted aquaculture effluent prior to its disposal into the environment.

DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled “**Assessment of sawdust activated carbon in the treatment of aquaculture effluent**” in the fulfillment of the requirements of the award of the degree of **Masters of Science in Water Resources and Environmental Engineering**, submitted to the department of Water Resources and Environmental Engineering, Ahmadu Bello University, was carried out by me under the supervision of of Dr. U.A Abubakar and Prof. C.A Okuofu of the department of Water Resources and Environmental Engineering, Ahmadu Bello University. Literatures consulted have been duly acknowledged by means of references and the work embodied in this dissertation has not been submitted for the award of any other degree.

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CERTIFICATION

This is to certify that this dissertation entitled “**Assessment of sawdust activated carbon in the treatment of aquaculture effluent**” submitted by Adebimpe Moyosore ADERIBIGBE with registration number P15EGWR8019, meets the regulations governing the award of the degree of Masters of Science in Water Resources and Environmental Engineering in Ahmadu Bello University and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

I dedicate this work firstly to the grace our Lord Jesus Christ. Then to my Husband, Dr. Adefila Williams and my guardian, Engr. Ademola Adesiyun. You are the two strong pillars that carried me this far.

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ABBREVIATIONS

SAC....Sawdust activated carbon

AE.....Aquaculture effluent

COD....Chemical oxygen demand

BOD....Biological oxygen demand

TSS.....Total suspended solids

TDS....Total dissolved solids

SEM....Scanning electron microscope

A.C.....Activated carbon

FTIR....Fourier transform infrared spectroscopy

BET.....Brunauer-Emmett-Teller

IUPAC....International union of pure and applied chemistry

DFT.....Density functional theory

CHAPTER ONE

INTRODUCTION

1.1 General Background

Aquaculture can be described as the production of aquatic organisms, both plant and animal under controlled or semi-controlled conditions (Summerfelt, 2003). However, Adewumi(2015), defined aquaculture practice in Nigeria as the rearing of fish in an enclosed and fairly shallow body of water where all its life processes is being controlled.

According to Sanjaya (2013), untreated aquaculture effluent generally contains high levels of organic material, numerous pathogenic micro-organisms, as well as nutrient and its indiscriminate discharge may lead to serious environmental and health hazards if not treated appropriately before final disposal. Therefore, as the population increases and aquaculture practice expands, it is important to provide for an adequate waste management strategy to ensure a favourable environmental condition.

Typical wastewater from an aquaculture facility may include faeces and nutrients from excretion by aquatic animals, as well as uneaten feeds and chemicals such as drugs and cleanser residues (Boyd, 2003). Aquacultural effluents contains dissolved and suspended solids that are basically oxygen demanding materials which makes the effluent to be high in biochemical oxygen demand(BOD) and nutrients like phosphorus (P) and nitrogen (N) which stems from fish excretion, faeces, and uneaten feed (Boyd, 2000). Overtime, significant discharge of this untreated effluent into lakes, rivers, estuaries or any other receiving waters could cause adverse environmental impacts such as eutrophication.

Although , there is a suggestions on the re-use of aquaculture effluent (Yeo *et al.*, 2004), which includes its use in irrigation of crops, but this has been found to be impractical in urban areas where aquaculture is thriving but crop farming is done on a very small scale. Therefore, since discharge of aquaculture effluent is inevitable, several environmental protection agencies and Global Aquaculture Alliance (GAA) which advocates, educates and demonstrates responsible aquaculture practices for the industry, have recommended waste water treatment and also set an effluent discharge limit (Boyd and Gautier, 2000).

In many instances however, secondary wastewater treatment such as trickling filters, oxidation ponds and aerated lagoons has been found inadequate in the treatment of certain waste water, hence the need to apply appropriate tertiary/advanced wastewater treatment methods, among which is adsorption. Common advanced wastewater treatment methods are ion exchange, membrane separation, electrolysis and adsorption. Among these methods, adsorption technology has gained a wider application due to its inherent low cost, versatility and robustness (Dimple, 2014). The other related technology are quite expensive, requiring a high level of technical know-how, steady energy supply, and chemicals along with specific equipments which may not be readily available, especially in developing countries.

Activated carbons are produced from a solid carbonaceous based material, which is non-graphitic, which has an initial isotropic structure (Diaz and Martin, 2006). The raw material is activated by means of medium to high temperature treatments, which removes solid mass, and at the same time, create pores where the removed mass was previously

located (Marshahida *et al*, 2016). The common properties of activated carbons and other kinds of carbon adsorbents is their well-developed pore network (McDougall, 1991).

Since an activated carbon is structurally a non-graphitic carbonaceous material, almost any carbonaceous solid material can be converted into activated carbon. There are therefore plenty of possible raw materials such as wood, lignocellulosic biomass, peat, lignite and coals that can be used to make activated carbon. In practice, wood, coconut shells, fruit stones, coals, lignites and petroleum coke, are all inexpensive materials with high carbon content and low inorganic content, and consequently, these are suitable precursors for use as an activated carbon (Diaz and Martin, 2006).

Saw dust is a waste material from the timber industry, produced when timber is sawn into planks at saw mills. This process is a daily activity causing heaps of saw dust to be generated after each day. The need to convert this waste product into a useful by-product is the focus of the study. The size of sawdust particles depends on the kinds of wood from which the sawdust is obtained and also on the size of the saw teeth (Afuwape, 1983). About 10-13% of the total volume of the wood log is reduced to sawdust in milling operations and this sawdust generally depends largely on the average width of the saw kern and the thickness of the timber sawed (Paulrud *et al.*, 2002). Sawdust has been used for several purposes, including sawdust briquettes, partial replacement of concrete, soil stabilization and also as an adsorbent

1.2 Research Problem

- I. The untreated aquaculture effluents discharged into the environment is increasingly becoming a source of concern, as it causes eutrophication in surface water bodies (Boyd 2003)
- II. There are tonnes of sawdust being produced annually, which is an environmental nuisance when burnt and an hazardous material when left in heaps as it is highly combustible.
- III. The problem of acid wash into the environment, which stems from the use of acid as an activating agent.

1.3 Justification

Boyd (2003), pointed out that aquaculture effluent has become large enough to have significant impacts on the environment, mainly in the form of eutrophication in rivers, as well as heavy metal pollution, which is supported by environmental activists and several scientists (Dierberg and Kiattisimukul, 1996; Goldberg and Triplett, 1997; Naylor *et al.*, 1998, 2000) whose serious concern have been the pollution of limited fresh water (Boyd and Gautier, 2000; Boyd and Tucker, 2000). Since aquaculture effluent is being disposed indiscriminately (Omofunmi *et al.*, 2016a), mainly because farmers see wastewater treatment as being an added expense that does not contribute to fish production. Hence, there is need to develop a viable, cost effective, and environmentally friendly means of treating fish farm effluent before its disposal.

According to Ogunwusi (2014), about $1,000,000m^3$ of sawdust is been produced annually from sawmills in Nigeria, which is an environmental nuisance when burnt and also a hazardous material when left in heaps as it is highly combustible. However, its use as

an adsorbent in the treatment of aquaculture effluent will be an environmentally friendly way of using waste to treat waste and in effect, protect the environment.

1.4 Aim and Objectives

The aim of this research is to evaluate the feasibility of using sawdust activated carbon (SAC) in the treatment of aquaculture effluent.

The specific objectives are:

1. Determination of the physiochemical characteristics of aquaculture effluent
2. Characterization of the produced SAC
3. Assessment of potassium carbonate (K_2CO_3) as an activating agent
4. Evaluation of the efficiency of SAC in the treatment of aquaculture effluent
5. Determination of the effects of operating conditions such as solution contact time and adsorbent dose on the adsorption capacities in batch testing method
6. Adsorption Kinetics study

1.5 Scope and Limitation

For the purpose of this study, fishpond (catfish) effluent will be considered and the effluent will be obtained from a catfish farm within Zaria. This study is focused on the production of activated carbon from sawdust to serve as an adsorbent in the treatment of aquaculture effluent towards safe disposal. The efficiency of the experimental batch treatment will be considered in terms of removal of organic and inorganic matter based on chemical oxygen demand (COD), biological oxygen demand(BOD), removal of total dissolved solids (TDS), total suspended solids (TSS), nitrates, phosphates along with removal of heavy metals.

1.5.1 Limitation

As a result of time and cost constraints, the study will not include regeneration of the used adsorbent. Also, a mechanical shaker will be used for the experiment. The batch treatment method and not the continuous test will be used for the research.

CHAPTER TWO

LITERATURE REVIEW

2.1 Aquaculture Effluent

In Nigeria, aquaculture industry products like fish and shrimps are gradually replacing animal meat as a source of dietary protein and business hub for teeming million youth (Jeje, 1992, as cited in Omofunmi *et al*, 2016a) with the most commonly grown fish being *Clarias Gariepinus* (catfish), (Adewumi and Olaleye, 2011). There are numerous studies on the subject of catfish pond effluents such as Tucker (2000), Boyd (2000), Tucker (2002), and Tucker and Hargreaves (2008), which reported that effluents released during pond harvest contains high concentration of pollutants (Boyd 2003; Schwartz and Boyd 2004).

Wastewater from catfish ponds usually has higher concentrations of nitrogen, phosphorus, organic matter and biochemical oxygen demand than natural surface waters in the vicinity (Boyd and Tucker, 2000). Boyd (2005) and Tucker and Robinson (1990) have reported that Concentrated Aquatic Animal Production (CAAP) facilities such as hatchery and fish ponds are major sources of oxygen demanding waste, which produces objectionable odor in the receiving adjacent streams where most fish farmers consider a convenient site for their effluent disposal.

According to Omofunmi *et al*. (2016b), indiscriminate disposal of untreated wastewater from fish pond on streams results into over- enrichment of water body with nutrients, hereby causing eutrophication, preventing sunlight penetration and decay of algae weeds which add odourous compounds to the aquatic system and eventually destroys the

aesthetic value of the water body. The negative effects of pond effluents on the receiving stream and land has been reported by Boyd (2001a, 2001b, 2003, 2005, as cited in Omofunmi 2016b), as ranging from offensive odour, lowering of dissolved oxygen, and the impairment (negative impact) to water bodies rendering it unfit for domestic, industrial and agricultural purposes.

The impact of catfish effluent on water quality has also been seen to depend on the method employed in draining of the pond and the amounts of water drained during the fish harvest. Usually, about 20 to 30 percent of nitrogen and phosphorus applied in feed is recovered in the effluent at harvest (Boyd and Tucker, 1998). The fish culture system commonly practiced in Nigeria includes stagnant tank, flow through, earthen pond and water recirculation systems. In stagnant and flow-through tank culture systems, all dissolved and suspended solid wastes are released into the environment on continuous basis throughout the production cycle. While on the other hand, wastes from earthen ponds are released periodically, in most cases, at the end of production cycle and consist of a mixture of inorganic and organic particulate materials (Akinrotimi *et al.* 2007a). In the recirculation system, Gabriel *et al.* (2009, as cited in Adewumi 2015) observed that the volume of wastewater that is released is low, compared to tanks and earthen pond culture.

Aquaculture effluent is constituted mainly of faeces, ammonia, uneaten food in the forms of dissolved compounds and suspended solids along with heavy metals which according to a research by Anhwange (2012) been traced to be a product of the fish feeds which constitutes the bulk of aquaculture waste (Jennifer *et al.*, n.d). Uneaten food and fish faeces are usually in the form of suspended solids, which can make natural waters more turbid and eventually form organic deposits on the bottom of water bodies.

The organic deposits in the effluent can reduce the oxygen content of the water through natural oxidation, which includes microbial respiration and aerobic decomposition. The feed and fecal wastes also contribute to biological oxygen demand (BOD) which is used as an index of pollution by dissolved organic substances or suspended particulate matter.

Schwartz and Boyd (2004) measured average concentration of selected water quality variables in surface water on Alabama channel catfish ponds over a 2-year period and the result showed the average concentration of total suspended solids, total nitrogen, total phosphorus, and 5-day biochemical oxygen demand during fish harvest to be 1,027 mg/L, 9.58 mg/L, 1.59 mg/L, and 31.8 mg/L respectively.

Likewise, Omofunmi *et al.* (2016a) also carried out a study to assess the effect of catfish effluents on water quality of stream where five catfish farms are localized in Lagos, Nigeria. Water samples were taken on monthly basis, 20 cm below water surface from the waterbody that receives effluent from these surrounding fish ponds. Water quality indicators like dissolved oxygen, biochemical oxygen demand, nitrate, nitrite, water temperature, ammonia and pH were examined in sampled water in accordance with the APHA standards and the result indicated that improper discharges of catfish effluents into environment results into environmental contamination.

A number of physical, chemical and biological methods used in conventional wastewater treatment have been applied in aquaculture systems. Solids removal is accomplished by sedimentation, sand or mechanical filtration while biological processes such as submerged biofilters, trickling filters, rotating biological contactors, and fluidized bed reactors are employed for the oxidation of organic matter, nitrification, or denitrification (Van-Rijn, 1996). Rotating microscreens are commonly used in land-based intensive fish-farms in Europe, with a screen mesh pore size of 60–200 μm (Cripps and

Bergheim, 2000). These methods do help with phosphorus removal but are costly in terms of capital investment, energy consumption and maintenance requirements. Researchers have demonstrated that wetland systems can also remove significant amounts of suspended solids, organic matter, nitrogen, phosphorus, trace elements and microorganisms contained in wastewater (Lin et al., 2002). However, in urban areas with little or no space for wetlands, there is need for a more compact system like an adsorption batch or column treatment process which is equally effective in the removal of the various pollutants in aquaculture effluents, including heavy metals.

2.2 Adsorption

Dabrowski (2001) defined adsorption as the process of accumulation of any substance giving higher concentration of molecular species on the surface of another substance as compared to that in the bulk. When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface.

Adsorption is a well-established and powerful technique for treating domestic and industrial effluents (Revathi *et al.* 2016) and the most widely used method for water treatment is “adsorption” onto the surface of activated carbon (Ferhan and Ozgur, 2011). The substance that concentrates at the surface is called adsorbate, while adsorbent is the material upon whose surface the adsorption takes place. A good adsorbent must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption (Lawrence *et al.*, 2015).

The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapors.

Depending on the type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types, namely: Physical adsorption and chemical adsorption.

2.2.1 Physical adsorption

When the force of attraction existing between adsorbate and adsorbent are weak Vander Waal forces of attraction, the process is called physical adsorption or physisorption (Bali, 2014). Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption and takes place at low temperatures. As the temperature increases, process of physisorption decreases.

2.2.2 Chemical adsorption

When the force of attraction existing between adsorbates and adsorbents are chemical forces of attraction or chemical bonds, the process is called chemical adsorption or chemisorption. Chemisorptions usually takes place with formation of unilayer/monolayer of adsorbate on adsorbent and it is characterized with high enthalpy of adsorption. This process has been known to take place at all temperatures (Vinay 2012).

2.2.3 Factors influencing adsorption

Bali (2014) expounded that adsorption on a solid is influenced by a number of factors such as, surface area, nature of the adsorbate, hydrogen ion concentration (pH) of the solution, temperature, nature of adsorbent and mixed solutes.

2.2.3.1 *Surface area*

Adsorption is a surface phenomenon and as such the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption. Thus the amount of adsorption accomplished per unit weight of solid adsorbent is greater if the solid is more finely divided and more porous.

2.2.3.2 *Nature of adsorbate*

The solubility of the solute (pollutant) is to a large extent a controlling factor for adsorption equilibrium. The Landelius rule states that an inverse relationship can be anticipated between the extent of adsorption of a solute and its solubility in the solvent from which adsorption occurs, therefore implying that adsorption increases with decrease in the solubility of the solvent. The greater the solubility, the stronger the solute-solvent bond and the smaller the extent of adsorption (Bali, 2014).

2.2.3.3 *Hydrogen ion concentration*

The pH of a solution from which adsorption occurs influences the extent of adsorption. Because, hydrogen and hydroxide ions are adsorbed quite strongly, such that the adsorption of other ions is influenced by the pH of the solution.

2.2.3.4 *Temperature*

Temperature effects on adsorption equilibrium are generally not significant over the range of temperature practically encountered in water and wastewaters, indicating that small variations in temperature do not alter the adsorption process to any significant extent (Bali, 2014)..

2.2.3.5 *Mixed solutes*

In the application of adsorption for purification of waters and wastewater, the material to be adsorbed commonly will be a mixture of many compounds rather than a single compound. The compounds may mutually enhance adsorption or may act relatively independently or may interfere with one another. In mixed solutes, each solute competes in some way with the adsorption of the other. The degree of mutual inhibition could be related to the relative size of the molecules being adsorbed, adsorptive affinities and the concentrations of the solutes (Bali, 2014).

2.2.3.6 *Nature of adsorbent*

The physiochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Adsorption by activated carbon is a surface phenomenon and is affected by the surface functional groups and the structural details. Significant amount of the carbonyl and carboxyl groups are present on activated carbon surfaces. The behaviours of activated carbon as an adsorbent have to be related to the surface functionality of the material and the chemical interaction at the surface between carbonyl and carboxyl groups and organic adsorbates. The adsorption capacity of activated carbon may well be accomplished by increasing the concentration of the appropriate functional groups.

2.2.4 Adsorption processes

At the equilibrium, the net loading on the adsorbent cannot increase further as the rates of adsorption and desorption become equal. The thermodynamics of the system ensures maximum possible interaction between the adsorbent and the adsorbate. Thermodynamic equilibrium between the adsorbate and the adsorbent is usually studied

with one of three ways, namely, batch process, fixed bed process, and moving bed process (Thomas & Crettenden, 1998).

2.2.4.1 *Batch process*

In this process, a batch of adsorbent mixes with a batch of fluid, most commonly a liquid. After a predetermined period of time, the adsorbent and the solution are separated, either by sedimentation, filtration, decantation or centrifugation. If sufficient time is allowed for equilibrium to be reached then the loading of the adsorbent-adsorbate interactions will be related to the final concentration of the adsorbate in the solution by the thermodynamic isotherm which applies at the final temperature in the process. If the equilibrium for the adsorption is highly favourable, a single-stage batch process will reduce the concentration of solute in solution (Ruthven 1984, Ruthven and Ching 1989). When large quantities of adsorbent are to be used, a multiple batch or cross-flow system may be required. Here, the adsorbate is first contacted with a fresh batch of adsorbent, and after separation of the fluid (adsorbate) from the adsorbent, the adsorbate is contacted with another fresh batch of adsorbent. Each subsequent batch of adsorbent removes less and less impurity as the concentration of the impurity in the solution decreases (Crittenden 1991). A more competent way to perform the multiple batch-wise contacting process is to perform the adsorption steps counter-currently (Fox and Kennedy, 1985).

2.2.4.2 *Fixed bed process*

In the fixed bed process, a degree of separation and removal is achieved that would require many steps in a batch process. The column configuration has often been modelled as a multiple-stage batch adsorption process. The uppermost portions of the bed are

constantly being contacted by fresh adsorbate solution and the lower portions of the bed are contacted by solution containing adsorbate not adsorbed by the upper portion. Thus, the bed becomes fully loaded at the top of the column first and then downward. This results in the formation of an adsorption front in the column which moves downward (Ruthven and Ching 1989).

2.2.4.3 *Moving bed process*

Two general possibilities exist for having the adsorbent in motion. In the first, the adsorbent particles move relative to the walls of the containing vessel such that adsorption, regeneration and back-washing can take place simultaneously, though in different locations. In the second, the particles remain in a fixed position relative to the walls of the vessel. Typically, during operation, all contact of adsorbent with fluid takes place for a precise period of time. The continuous counter-current mode is more efficient in regeneration than fixed bed mode. But these processes also have some disadvantages as the capital costs are higher than the fixed bed systems. The operation of the process is complex and requires automatic controls and extensive process instrumentation.

2.2.5 Adsorption kinetic models

Kinetic studies provide the information about the mechanism of adsorption and suitable optimum conditions for batch process. Adsorption kinetics which describes the adsorbate adsorption rate, which is an important characteristic in evaluating the efficiency of adsorption. According to literature (Bhattacharya and Gupta 2006) initial high rate of metal uptake could be due to the bare surface of adsorbent. Later on available adsorption sites decreases as Pb(II) ion adsorption increases. Pseudo first-order and pseudo second-

order adsorption kinetic models have been used to study the experimental data. Pseudo first-order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake with time.

Parameters from the two kinetic models, pseudo first-order [Ho, 2004] and pseudo second-order (Ho, 2006; Azizian, 2004), are normally used to examine the adsorption kinetics of adsorbate uptake by adsorbent. This is on the assumptions that sorption is a pseudo chemical reaction and that the measured adsorbate concentrations are equal to cell surface concentrations (Chojnacka, 2005). Sorption rate could then be determined by the pseudo first- and second-order reaction rate equations. The two sorption kinetic models are based on the Ritchie equation (Equation 2.14), where a number of surface sites, n , are occupied by each adsorbate molecule (Vilar *et.al.*, 2006).

$$r_{ads} = \frac{dq}{dt} = k_n (q_e - q_t)^n \quad (2.1)$$

Where r_{ads} the rate of adsorption and k_n is the associated rate constant;

2.2.5.1 Pseudo-first order model

The pseudo first-order equation (Lagregren's equation) describes adsorption in solid-liquid systems based on the sorption capacity of solids [Ho, 2004]. It is assumed that one metal ion is sorbed onto one sorption site on the adsorbent surface:



Where A represents a non-occupied sorption on the site on the adsorbent and k_1 is the pseudo first order rate constant. The pseudo-first-order kinetic model as given by Lagregen (Sivaraj *et. al.*, 2001) is given below:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (2.3)$$

where q_e (mg/g) is the solid phase concentration of the adsorbate at equilibrium, q_t (mg/g) the average solid phase concentration of adsorbate at contact time t (min) and k_1 (min^{-1}) is the pseudo-first-order rate constant. The simplified linear expression of first-order equation can be given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2.4)$$

2.2.5.2 Pseudo-second order model

The pseudo second-order rate expression, which has been applied for analyzing chemisorptions kinetics from liquid solutions (Ho, 2006, Azizian, 2004), which is represented by (Ho, 2004):

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (2.6)$$

Where k_2 (g/mg) is the pseudo-second-order rate constant

Pseudo-second-order rate model is based on the assumption that chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate is the limiting step (Ho and McKay, 1999). This model assumes that one metal ion is sorbed onto two sorption sites on the adsorbent surface:



The linear form of the Ho pseudo-second-order equation is:

$$\frac{t}{q} = \frac{1}{k_2 q_o^2} + \frac{1}{q_o} t \quad (2.8)$$

Thus, a plot of t/q versus t gives a straight line and the values of the constants k_2 (g/mg) and q_e (mg/g) can be calculated.

2.3 Activated Carbon

Activated carbon is the most widely used adsorbent since most of its chemical (surface groups) and physical properties, like pore size distribution and surface area can be modified according to what is needed (Bansal *et al.*, 1988). Activated carbon is manufactured in such a way as to produce extremely porous carbon particles whose internal surface area is very large. This porous structure attracts and holds organic molecules as well as certain metal and inorganic molecules (Revathi *et al.*, 2016). Adsorption occurs because the contaminant has low solubility in the waste and the contaminant has greater affinity for the carbon than for the waste (Lemly *et al.*, 1995). Adsorption is a surface phenomenon in which soluble particles from a solution are bonded onto a particular substrate. One of the most desirable properties of an adsorbent is a high surface area ranging from 500 to 1000 m²/g, which is regarded as a good adsorbent for effective removal of organic compounds (Javie, 2011).

According to Ho (2004), the most widely used adsorbent for industrial applications is activated carbon and is produced from a solid carbonaceous based material, which is non-graphitic in nature, with an initial isotropic structure. The precursor is transformed or 'activated' by means of medium to high temperature treatments, which remove solid mass, and at the same time, create pores where the removed mass was previously located (Menendez-Diaz and Martin-Gullon, 2006). It is a well-known adsorbent due to its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. The structure consists of a distorted three dimensional array of aromatic sheets and strips of primary hexagonal graphic crystallites and this structure creates angular pores between the sheets of molecular dimensions which give rise to many of the useful adsorption properties of activated carbon (Stoeckli, 1990). The porous structure is the main

physical property that characterizes activated carbons as this is formed by pores of different sizes which according to IUPAC recommendations (Sing et al., 1985) can be classified into three major groups, namely, Micropores, Mesopores and Macropores. The pore diameter, pore volume, surface area, density, and porosity are all interwoven together to characterize an activated carbon as being macroporous, mesoporous or microporous. The typical classification according to Ruthven, 1984, is shown in Table 2.1

Table 2.1: Characteristics of Typical Activated Carbons (Ruthven, 1984)

Characteristics of carbons	Micro pores	Meso pores	Macro pores
Diameter (nm)	< 2	2 – 50	> 50
Pore volume (cm ³ /g)	0.15 – 0.5	0.02 – 0.1	0.2 – 0.5
Surface area (m ² /g)	100 – 1000	10 – 100	0.5 – 2
Particle density	(0.6 – 0.9 g/cm ³)	<0.6	<0.6
Porosity	(0.4 – 0.6)		

Pore size ranges from 1 nm to 1000 nm, and the extensive porosity (Yusufu *et al.*, 2012) is said to be responsible for the high surface area of the material usually in the range of 500 - 1500 m² /g (Cooney, 1980). Any carbon material can be used to make activated carbon; however, commercial activated carbon is manufactured from only a few carbon sources, such as wood, peat, coal, oil products, nut shells and pits. Sun *et al.*, (1997) explained that wood products and low-grade coal have some original porosity and are

easier to activate than dense materials such as anthracite (Sun *et al.*, 1997). Figure 2.1 shows a schematic representation of the pore network of a typical activated carbon.

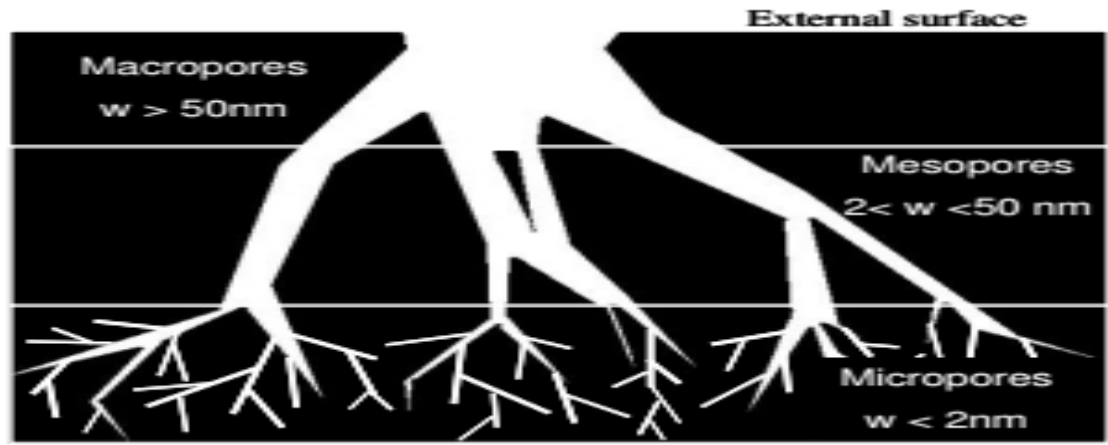


Figure 2.1: Schematic representation of the pore network of a carbon adsorbent (Daiz and Martin, 2006).

The first reported application of activated carbons as a gas phase adsorbent did not take place until as late as 1793 AD, when Dr. D.M. Kehl applied wood char in order to mitigate the odours emanating from gangrene. The above gentleman also recommended filtering water with wood char (Dabrowski, 2001). The first application of activated carbon in the industrial sector took place in England in 1794, when it was used as a decolorizing agent in the sugar production industry, this event marking the beginning of research with activated carbons in liquid phase.

Activated carbon material, as it is known nowadays, was discovered by Ostrejko R., who is considered the father and/or inventor of activated carbon (Rodriguez, 1997). In 1901, he patented two different methods of producing activated carbons which are the carbonization of lignocellulosic materials with metal chlorides (the basis of chemical

activation) and the mild gasification of chars with steam or carbon dioxide at red temperatures (thermal or physical activation).

2.4 Activation Processes

Basically, there are two different processes for the preparation of activated carbon, the physical or thermal and chemical activation. Usually, the first step is the carbonization of the raw material which is performed in an oxygen free environment in order to reduce oxidation (mostly done in a nitrogen or argon atmosphere) at temperature of about 700°C (Dileck and Oznuh, 2008). Carbonization simply means producing charcoal from the raw material, but the obtained charcoal still has a low surface area, so it's not yet an active carbon material, hence, there is need for it to be activated. This means that the pores has to be opened to enhance its porosity and surface area. According to Sang et al. (1997), activation can be physical/thermal with the use of air, carbon dioxide or water vapour at high temperature or a chemical process employing activating agents such as potassium hydroxide (KOH), potassium carbonate (K_2CO_3), phosphoric acid (H_3PO_4) or zinc chloride ($ZnCl_2$).

Chemical activation is a single step process, as both carbonization and activation occur simultaneously at temperatures ranging between 400°C and 700°C, which is lower than that of physical activation (Katesa et al., 2013). However, in some cases, additional carbonization or a pre-carbonization step is performed to produce char prior to chemical impregnation and activation (Abechi et al., 2013a). This means that activation can be achieved through either direct chemical activation or char-impregnated chemical activation, however, char-impregnated chemical activation is more favourable in the manufacture of activated carbon as compared to direct chemical activation. Pre-carbonization, executed in

some studies (Muniandy et al., 2014; Yu et al., 2014), produced some advantages in the textural properties of the activated carbon, although activating agents like Potassium hydroxide (KOH) is a strong base which supports single step activation. According to Zaini and Kamaruddin (2013), the need for precarbonization is determined by the chemical nature of the raw material and the activators used. A starting material which undergoes precarbonization (in air or N) could offer larger specific surface area and some initial pore development.

At an activation temperature above 800°C and an activation time of more than 30 min, an activated carbon with a specific surface area greater than 900 m²/g was obtained by researchers like Wang et al., (2014) and Adibfar et al. (2014). However, some studies have revealed a lower product yield of 17% to 31% when a temperature above 800°C was used (Okman *et al.*, 2014; Rugayah *et al.*, 2014). In other words, higher activation temperature and longer retention time could promote the further development of pores, which consequently leads to a greater surface area of up to 2696 m²/g, and at the same time suffers a lower carbon yield.

During the process of carbonization, volatile components are removed and the residual carbonaceous material is then activated in air/steam at temperatures higher than 800°C (Physical activation) or in the presence of an activating agent at lower temperatures (Chemical activation). As reported by several authors, activation temperature significantly affects the production yield of activated carbon and also the surface area of activated carbon (Yusufu *et al.*, 2012; Abechi *et al.*, 2013b), so the optimum and best activating temperature for the raw material of interest has to be evaluated. Sang et al. (1997) reported that at temperatures above 1000°C, the reaction in the pores become prohibited and limits

the reactions to the outer layer of the carbon particle. In chemical activation, the raw material or carbonized sample is impregnated with an activating agent and heated in an inert atmosphere, and during the activation process, the spaces between the elementary crystallites become cleared of less organized, loosely bound carbonaceous material (Obiora-Okafor, et al., 2014). According to Rodriguez and Solano (1989), the resulting channels through the graphitic regions, the spaces between the elementary crystallites, together with fissures within and parallel to the graphitic planes all constitutes the porous structure of the activated carbon.

Guo and Lua (2001) mentioned that the characteristics of activated carbon depend on the physical and chemical properties of the raw materials as well as the activation method used. The physical properties of carbon are important in determining which form is best suited for specific applications (Yusufu et al., 2012). For instance, abrasion resistance or hardness of activated carbon will be important if the carbon is to be used in applications where frequent back-washing is required. Density varies with the raw materials, so the density characteristics can also be a major consideration for specific applications because a little quantity of carbon with a lower density will fit into a given container as compared to a carbon with high density. This is significant because, while a container may require less carbon weight of low density to make a fill, its contaminant removal performance may be severely reduced as compared to a high-density carbon.

The iodine value and the ash content is also an important characteristic of activated carbon, as the iodine value gives a measure of the micro pore volume of carbon and it approximates the total internal surface of the carbon while the ash level reflects the purity of the carbon. The ash content is quite important in water filtration applications, because

activated carbon with high phosphate ash can bring about cloudy water during use because the ash could combine with metal ions to form magnesium or calcium precipitates (Ecologix systems, 2008).

Couto et al. (2012), prepared activated carbon (AC) from eucalyptus sawdust using both physical activation with CO_2 and chemical activation with potassium carbonate (K_2CO_3). The activated carbon obtained from the eucalyptus sawdust was tested for the adsorption of pollutants commonly found in industrial effluents such as phenol and dye. The two ACs prepared were microporous and with a specific surface area around $535\text{ m}^2/\text{g}$ under the preparation conditions. Although the AC_{CO_2} and $AC_{K_2CO_3}$ had several similarities, they had different adsorption capacities with respect to the tested contaminants (methylene blue and phenol) and the $AC_{K_2CO_3}$ was most effective in the adsorption of methylene blue (81 mg/g) and phenol (330mg/g), concluding that chemical activation yielded a better result.

Micro-porous activated carbon (pore width $<2\text{nm}$) is usually employed in traditional applications. However, the development of highly meso-porous activated carbon ($2\text{ nm} < \text{pore width} <50\text{ nm}$) has been gaining considerable attention due to its wide range of applications. In air and wastewater treatment, mesoporous carbon material is more suitable for macro-pollutants removal. For example, methylene blue (cationic dye) molecules are more susceptible to lodge on an adsorbent with a pore diameter larger than 2 nm (Altenor *et al.*, 2009) while on the other hand, microporous activated carbon is most widely used, and limited only for the adsorption of micro-pollutants and heavy metal ions, because of its small pore diameter ($<2\text{nm}$), which obstructs the adsorption of larger size molecules (macro-pollutants).

The mesoporous texture commonly aids in the mass transfer of dye molecules into the bulk of the carbon matrix (Vix-Guterl et al., 2004). Hu and Srinivasan (2001) considered the nature of the porosity and adsorption capacity of different molecular size adsorbates and they reported a higher methylene blue (larger molecular size adsorbate) adsorption of 448 mg/g by mesoporous coconut shell activated carbon ($V_{mes}/V = 71\%$; specific surface area = $2191 \text{ m}^2/\text{g}$).

Similarly, Sun et al. (2010) reported that activated carbon with a mesoporous ratio of 61% and a specific surface area of $1608 \text{ m}^2/\text{g}$ attained a high methylene blue uptake of 1012 mg/g. Therefore, it is sufficient to conclude that mesoporous activated carbon is more efficient for the removal of larger adsorbates.

2.4.1 Activating agents

In chemical activation process, carbonization of organic precursor is done in the presence of a chemical agents (activating agent). In this method, a solid activating agent like alkali and alkaline earth metals or acids is employed. The activating agent employed functions as dehydrating agents that influence pyrolytic decomposition which inhibits the formation of tar and thereby enhancing the yield of carbon (Viswanathan et al., 2009). In spite of the above mentioned virtuous aspects, the chemical method has its own inherent drawbacks like the need for washing of the product to remove the residual activating agent (inorganic material) which could cause serious pollution problem and this has prompted the need to critically evaluate the activating agent in consideration (Hui and Zaini, 2014).

Even though, the use of alkali metal hydroxides like KOH and NaOH as activating agents offers the advantage of producing high specific surface area carbon materials, they (alkali metal hydroxides) are corrosive, hazardous and environmentally unfriendly and the

use of alkali metal carbonates such as K_2CO_3 has been seen as a substitute to the use of alkali metal hydroxides. Among the chemical activation agents, potassium carbonate (K_2CO_3) has great advantages in comparison to other activation agents, especially in consumption of water in recovery process, production of low environmental pollutants and relatively low activation temperature (Mohammad and Zaker, 2010).

Salts of Potassium (K) were found to act as better activating agents than others owing to the formation of atomic K during the activation process as reported by Viswanantha *et al.* (2009), and this subsequently intercalates into the inter layers of adjacent hexagonal network plane of C atoms.

According to Viswanantha *et al.* (2009), the adjacent graphene planes were separated because of the K intercalation. Even after removal of K, either by washing with water (H_2O) or acid, the rearranged or disordered graphene sheets of the carbon crystallite doesn't go back to their original position thus leaving pores and voids. This results in an activated carbon material with high porosity and specific surface area value.

Activated carbon was prepared by Jin *et al.* (2010) through the chemical activation of lignin from a straw pulping precursor, using K_2CO_3 and KOH as activating agents. To optimize the preparation method, the effect of the main process parameters (such as impregnation ratio, activation temperature, and activation time) was investigated, and the actions of the activating agents were compared. The activated carbon prepared by K_2CO_3 , under optimum conditions, had a BET surface area of $1104\text{ m}^2/\text{g}$, including an external non- microporous surface of $417\text{ m}^2/\text{g}$, an average adsorption pore width of 2.0nm, the amount of methyl blue, iodine number and the yield of activated carbon being 10.6ml/0.1g, 1310 mg/g and 19.8%, respectively. As to the carbon activated by KOH under optimum

conditions, its BET surface area was $917\text{m}^2/\text{g}$, including the external or non-microporous surface of $213\text{m}^2/\text{g}$, the average adsorption pore width of 2.5nm , while the amounts of methylene blue, iodine number and yield of activated carbon were of $9.6\text{ ml}/0.1\text{g}$, 1180 mg/g , 18.7% , respectively (Jin et al., 2010).

2.4.2 Characterization of activated carbon

According to Ogunbile *et al.* (2014), qualitative and quantitative characterizations of activated carbon is highly essential in order to adequately assess its feasibility for normal removal of contaminant and hence design the most effective manner in which it can be used (Itodo *et al.*, 2010). These characteristics include, pore volume, bulk density, surface area, moisture content, methylene blue number, iodine number, fixed carbon, ash content and carbon yield. Different grades of granulated activated carbon adsorbent used to harvest priority pollutants from waste water were reported by Shaski and Tenkie (2002) and among other parameters, carbon yield, surface area, pore size and volume, iodine number, methylene blue adsorption, apparent density, hardness (abrasion) number, ash content, particle size and adsorption rate are important properties whose studies were found to be essential and relevant for the exploitation of activated carbon for commercial and industrial purposes (Haro *et al.*, 2012).

2.5 Sawdust Activated Carbon

The first commercial chemically activated carbon (Carboraffin) was produced in Aussig, The Czech Republic, in 1914, using sawdust as raw material and ZnCl as activating agent (Diaz and Martin, 2006) and since this time, so many researchers have employed sawdust as a precursor for activated carbon. Wood sawdust is a solid residue, generated in the timber industry, which can cause serious environmental problems if disposed

inadequately. Economical disposal of sawdust and wood shavings is a problem of growing concern to the wood industries as a result of the enormous quantities of sawdust which are produced annually by sawmills. According to John (1961), the sawdust produced in cutting a thousand board feet ($2.36m^3$) hardwood lumber with a saw cutting a $0.635cm^3$ width is at least $0.59m^3$ of solid wood. At a typical green weight of $832.96\text{ kg}/m^3$ for solid hardwood, this amount of sawdust would weigh 492.15 kg. The same air-dry wood (12 % moisture content) would weigh $576.67\text{ kg}/m^3$, hence the sawdust would weigh 340.19 kg when dried to 12% moisture content. Planning and machining of lumber and other manufacturing activities from wood also produces more residues. A planning mill produces about 272.16kg of dry residue per thousand board feet ($2.36m^3$) (John, 1961).

Couto *et al.* (2012) aimed in their study to use eucalyptus sawdust in the preparation of activated carbons (AC) and test them as adsorbents for methylene blue (MB) and phenol, a representative pollutant from aqueous effluents of various industries. The eucalyptus sawdust was characterized by instrumental analysis such as elementary analysis (CHN-O), thermo-gravimetric analysis (TGA), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The activated carbons were prepared by physical activation with carbon dioxide AC_ CO_2 , ($10^\circ\text{C}/\text{min}$, 850°C , 1h) and by chemical activation with potassium carbonate AC_ K_2CO_3 ($10^\circ\text{C}/\text{min}$, 850°C , 3h). The AC_ CO_2 and AC_ K_2CO_3 were characterized by CHN-O, TGA, FTIR, N adsorption/desorption (BET) to evaluate the specific surface area and SEM. The activated carbons produced showed specific surface area of about $535\text{ m}^2/\text{g}$. The AC_ K_2CO_3 was more effective in the adsorption of MB (81 mg/g) and phenol (330 mg/g) than AC_ CO_2 (32 mg/g and 172 mg/g, respectively, for MB and phenol).

Man and Ridzuan (2008) produced activated carbon from sawdust using steam activation in a high temperature muffle furnace (800°C). Prior to the activation process, fast pyrolysis process was carried out in a fluidized bed furnace to produce char. Experiments were conducted to investigate the influence of various process parameters such as particle size, pyrolysis temperature and activation time on the quality of the activated carbon. In addition, batch adsorption studies were done using methylene blue and the experimental data were analyzed by the Langmuir and Freundlich adsorption isotherms. The Langmuir isotherms showed a satisfactory fit based on the correlation coefficient (R^2) value. The rate of adsorption showed that the pseudo-second-order rate fitted the adsorption kinetics better than the pseudo-first-order rate equation and a good activated carbon was obtained with particle size of 0.5mm at pyrolysis temperature of 500°C and activated with steam at 800°C for 2 hours. The maximum adsorption capacity of carbon produced from sawdust was found to be 370.37 mg/g for the methylene blue dye. In addition, the maximum Brunauer–Emmett–Teller (BET) surface area obtained was $1091.5\text{m}^2/\text{g}$. After comparing the properties of prepared activated carbon with a commercial activated carbon, Man and Ridzuan (2008) concluded that sawdust activated carbon (SAC) could be employed as a low cost alternative to commercial activated carbon.

Prompted by the continuous release of heavy metals into the environment which is now a worldwide major concern, Al-Riyami et al., (2014) carried out a research on the treatment of Battery Waste Water Using Meranti Wood Sawdust as an adsorbent. In this research work, adsorption of Pb (II) ions on Meranti tree sawdust was studied using batch techniques. The equilibrium adsorption level was determined to be a function of the solution of pH, contact time, amount of adsorbent, shaking speed and initial concentration.

Results showed that a pH of 7 was the most suitable, while the maximum adsorbent capacity was at a dosage of 2.5 g/L, recording a sorption of 41% of lead. The percentage metal removal approached equilibrium within 90 min for the lead ions. The meranti Sawdust was then shown to be an efficient and practical biomass for the removal of heavy metal ions from aqueous solutions.

Adeyi et al., (2014), in an investigation, studied the removal of direct blue dyestuff (an organic pollutant) from wastewater effluents of textile industry by adsorption. Activated charcoal was produced from sawdust using aqueous zinc chloride, $ZnCl_2$ as the activating agent and carbonized at $500^{\circ}C$ for 45 minutes. The effectiveness of the AC was measured in terms of absorbance using colorimeter and the result showed a very sharp reduction from 600 mg/dm^3 to 40 mg/dm^3 . The ability of activated sawdust to bind phenol was likewise investigated by Larous and Meniai (2012) and the result showed that carbonized sawdust (CAS) has good adsorption capacity to remove phenol from wastewaters.

Ansari and seyghali (2013), applied sawdust prepared from Narra wood (SD) modified with cationic surfactant of cetyltrimethyl-ammonium bromide (SD/CTAB) for the removal of two typical acid dyes, commercially named as Acid Green 25 (AG25) and Acid Red 14 (AR14) from aqueous solutions. The effects of experimental variables, such as pH, initial dye concentration, adsorbent dose, contact time and temperature was investigated in order to find out the optimized conditions for removal of selected test dyes. The Langmuir and Freundlich Isotherms were used to analyze the experimental adsorption data while the Pseudo- first and second order models were used for the kinetic study. The monolayer maximum adsorption capacity of SD/CTAB toward AG25 and AR14 dyes was calculated using Langmuir isotherm model and was given as 17.5 mg/g and 18.9 mg/g at 298 K.

Based on kinetics and thermodynamic studies, it was found that adsorption process using SD/CTAB follows pseudo second-order rate equation and the adsorption investigated system is spontaneous and endothermic in nature. At the end of the study, it was discovered that exhausted adsorbent can also be regenerated for reuse with high performance and that through simple treatment of agricultural wastes such as wood sawdust with cationic surfactants; it is possible to improve the adsorption capacity of sawdust for removal of anionic dyes from aqueous wastes considerably.

As a low cost activated carbon, Markovic *et al.* (2011) used Sawdust and cardboard for the removal of heavy metals from the wastewater from mining activities. The sawdust was obtained from the oak and fir-wood and it showed efficiency in the removal of the iron. Good results were obtained for the removal of zinc and nickel also, and the best result for copper adsorption degree was achieved using the sawdust from fir-wood, with 98.31% efficiency.

Literatures have shown that sawdust activated carbon is a good adsorbent in the treatment of many industrial and agricultural waste water including pharmaceutical effluent and according to Bajpai *et al.* (2011), who studied the adsorptive removal of ciprofloxacin hydrochloride from simulated wastewater using sawdust. It was reported that there was a dynamic uptake of the antibiotic drug ciprofloxacin hydrochloride (CH). The sawdust was characterized by FTIR and SEM analysis and the sorbent particles were confirmed to be highly porous with average pore diameter of nearly 10 μm . The optimum pH and solid/liquid ratio for adsorption of CH were found to be 5.8 and 2.0, respectively. The experimental equilibrium uptake values (q) were in close agreement with those evaluated

from the pseudo second order equation for initial sorbate concentrations of 10 and 20 mg/L at 33°C.

2.6 Common AC Adsorbents

Activated carbon for adsorption process can be produced from any high carbon content and low inorganic containing raw material (Herawan *et al.*, 2013). Nigeria is blessed with different types of waste materials from which activated carbon, can be produced. There are abundance of nut shells (coconut shells, almond shells), sawdust and other agricultural wastes (corn cob, stalks) (Baily *et al.*, 1999; Sud *et al.*, 2008). The disposal of these agricultural by product currently constitutes a major economic and environmental issue, and the conversion of these agro products into adsorbents, such as activated carbon represents a possible outlet for waste management. Research works carried out on some of these locally available materials have indicated their usefulness in the production of low cost adsorbents (Ogunsile *et al.* 2014).

The conversion of these materials into adsorbents for wastewater treatment would help to reduce the cost of waste disposal and provide an alternative to commercial activated carbon (Kurniawan *et al.*, 2006). The adsorption of toxic waste from industrial wastewater using agricultural waste and industrial by-products has been massively investigated by various researchers like Basu *et al.*, (2006), Wan and Hanafiah, (2007), and Srivastava *et al.*, (2006).

Several reviews can be referred to that discussed low-cost adsorbents application for industrial wastewater treatment such as Kurniawan *et al.*, (2006), Babel and Kurniawan, (2003), Crini, (2005), and Pollard *et al.*, (1992). Karnitz *et al.*, (2007) reported the use of chemically modified sugarcane bagasse to adsorb heavy metal ions and Mukherjee *et al.*,

(2007) also studied the adsorption of phenol using an adsorbent derived from sugarcane bagasse as well. This shows that agricultural wastes are versatile and they can be used for sorption of both inorganic and organic wastes.

Awoyale *et al.* (2013) experimented on the efficiency of activated carbon from local waste bamboo gotten from construction sites of the rain forest belt of the Niger Delta region of Nigeria for a typical adsorption and treatment of wastewater from a typical refinery. The bamboo was carbonized at temperatures between 300°C - 400°C and activated using ZnCl₂ at 800°C to produce granulated activated charcoal. Adsorption of heavy metals from the refinery waste stream on the activated carbon produced was examined at ambient temperature and the influence of different operating conditions, such as contact time, carbon dosages, pH, and metal ion concentration before and after adsorption were used in determining the amount absorbed (q_t , mg/g) and the percentage removal efficiency of the metal ions. The experiment showed that the adsorbents can be effectively used for the treatment and removal of Pb and Cu from a typical refinery wastewater stream for re-use. The optimum operating conditions for carbon dosage and pH also gave a 100% removal of both metal ions. Thus it was concluded that, using activated carbon produced from local bamboo for the adsorption process was quite efficient and could be employed for other adsorption purposes.

Okoroigwe *et al.* (2013) produced activated carbon (AC) from palm kernel shells (PKS) by acid activation method at temperature of 600°C. The effects of carbonization and acid impregnation time on the adsorption potential of the ACs on purification of contaminated rain and flowing river water bodies were examined and the results were compared with results of similar analysis based on commercial AC purchased from a

nearby chemical shop. The results showed that the AC produced from PKS upon 2 days acid impregnation followed by 3 h carbonization periods, purified both water bodies better than the others on reduction of microbial and micro impurity contents of the water bodies. The implications of the results shows that production of AC from PKS is value addition to oil palm processing, boost to the national economy and positive environmental impact to the people that produce and use PKS. Hence, a multiple-product derivation, such as bioenergy and bio-char production for adsorption purposes from palm kernel shells was encouraged.

The adsorption and treatment of organic contaminants using activated carbon from Nigerian bamboo was investigated by Ademiluyi *et al.* (2009). The bamboo was carbonized at 400°C-500°C and activated with acid at 800°C to produce granular activated carbon (GAC). Adsorption of organics from the refinery waste on the activated carbon produced was examined at 28°C. The experimental batch equilibrium data was correlated by Freundlich and Langmuir isotherms and the adsorption data fitted well into the Freundlich isotherm. Breakthrough time of about 1.5 hours was observed for the fixed bed adsorption process. The organic concentration expressed as chemical oxygen demand (COD) was reduced from an initial value of 378 mg/l to 142 mg/l for the first hour, 143mg/l for the second hour, 152 mg/l for the third and fourth hours, and 156 mg/l for the final hour., which also compare favorably with the refinery effluent specification of 150 mg/l. Results from the study therefore shows that waste Nigerian bamboo can be converted into high capacity adsorbent and used for the remediation of polluted industrial waste waters.

More studies have been carried out on the feasibility of using industrial adsorbents such as sawdust (Ismadji *et al.*, 2005), and other agriculture wastes like peanut shells

(Wafwayo *et al.*, 1999), poultry litter (Kelleher *et al.*, 2002), coffee husk (Kumar, 2006), rice husk (Kumar and Bandyopadhyay, 2006), cow dung (Das *et al.*, 2000), soybean hull and almond hull (Marshall *et al.*, 2000), among others for adsorption process.

Argun *et al.* (2007) investigated the effects of the shaking speed, contact time, dose and pH by varying one parameter at a time, maintaining others constant during the adsorption of Cu, Ni and Cr from aqueous solution using sawdust while Bulut and Tez (2007) also investigated the effects of contact time, initial concentration and temperature on the removal of Pb (II), Cd (II) and Ni (II) from aqueous solution using sawdust from walnut tree.

McSweeney *et al.* (2006) showed that reacting citric acid with corn fiber, ground corn cobs, starch, and cellulose fiber can greatly increase the sorption of Cu^{2+} ion by these materials and this finding is supported by the findings of Marshall *et al.* (2000) who studied the use of soybean hulls, peanut shells, almond hulls and cotton seeds, which were similarly modified by 0.6 M citric acid for enhanced heavy metal sorption at pH 4.8 and adsorption capacities greater than 1.0 mg/g were obtained for all the metal ions studied.

2.7 Carbon Regeneration System and Disposal

To make activated carbon economically feasible for wastewater treatment in most applications, the exhaust carbon must be regenerated and reused. When the effluent quality reaches the minimum effluent quality standards or when a predetermined carbon dosage is achieved, spent carbon is removed from the column and it is regenerated once its adsorption capacity is reached. The regeneration methods are as follows:

- I. Passing vapour through the bed at low pressure to evaporate and remove the solvents. It can be used to remove volatile compounds and it is useful for the surface recovery and its sterilization.
- II. Removal of the adsorbate with a chemical (acid or alkali).
- III. Thermal regeneration is the most used technique. There are a lot of kinds of ovens but the loss of activated carbon is about 10% for each regeneration, which means that in 10 or 12 regenerations it must be replaced. Thermal regeneration generally involves drying at around 105°C, pyrolysis under an inert atmosphere, which is a complicated process consisting of thermal decomposition and cracking, desorption of decomposition products, followed by polymerization of the residuals and finally the gasification of residual organics by oxidizing gas, such as steam or carbon dioxide, resulting in the elimination of the charred residue formed in the pyrolysis and the exposure of the original carbon-pore structure. After maximum use of the activated carbon, the residue could be disposed using a land fill system, in order to avoid further environmental pollution.

2.8 Summary

Akinrotimi *et al.* (2005) reported that in some parts of the country, especially in the rural areas, there is a combination of fish production with planting of arable crops such as vegetables. The West and Central African Council for Agricultural Research and Development (WECARD) and University of Ibadan (UI) are also recently promoting the integration of fish, poultry/pig and rice farming, as this is supposed to translate to viable and sustainable aquaculture (Adewumi 2015). However, the amount of aquaculture effluent being produced subsequently from fish farms in urban communities where there is little or

no space for crop farming demands treatment before its disposal into storm drains and nearby streams. This has therefore necessitated the development and implementation of innovative methods and technologies for the treatment of fish farm effluent. This is done in order to ameliorate the pollution of fresh water sources and preserve the environment, considering downstream users of various streams also, who are the recipient of untreated aquaculture effluent. Among these innovations is the adsorption process using activated carbon.

From the review of several literatures, facts have been gleaned concerning the pollution caused by aquaculture effluent, yet the available conventional treatment method may not be feasible here in Nigeria, based on cost, expertise and power among other constraints. Though several studies have been done on the chemical activation of sawdust carbon, focus has been on the use of acid, with little report on activation with basic salts like potassium carbonate, therefore there is need to explore the effectiveness of potassium carbonate activated sawdust and further use it as an adsorption medium to remove pollutants from aquaculture effluent before its disposal.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

In this research, three main categories of materials were adopted, these are the raw materials mainly in the form of the aquaculture effluents and sawdust; reagents and glassware; and the laboratory equipment.

3.1.1 General materials

- Saw dust(800g)[*Oro* tree]
- Distilled water
- Effluent (10litres Catfish pond effluent)

3.1.2 Equipment

- Furnace (Gemco furnaces, Holland)
- Hot air oven (Gallenkamp, England)
- Shaker (Griffin shaker)
- Drying crucibles (Halden wanger, Berlin)
- Desiccator (Monax, Scotland)
- UV visible spectrophotometer (Tery 300: Agilent technology, Germany)
- *FTIR* Spectrophotometer *Model* (Model 1615; Perkin Elmer 1600 Series)
- Reflux condenser (Gallenkamp)
- Water bath (Gallenkamp)
- pH meter (metrohm 744, USA)

- Atomic absorption spectrophotometer (AAS) (Shimadzu Jenway Spectrophotometer 6400)
- Autosorb-1, Quantachrome equipment
- SEM Balzers 050 evaporator

3.1.3 Chemical reagents

- Sodium thiosulphate ($N_2S_2O_3$) [BDH chemicals, England]
- Hydrochloric acid (HCl) [M&B, England]
- Potassium carbonate (K_2CO_3) [BDH chemicals, England]
- Methylene blue [BDH chemicals, England]
- Tetraoxosulphate (VI) acid (H_2SO_4) [M&B, England]
- Mercury (II) tetraoxosulphate (VI) ($HgSO_4$) [BDH chemicals, England]
- Silver (I) tetraoxosulphate (VI) solution ($AgSO_4$) [Kem light laboratories]
- Potassium heptaoxochromate (VI) ($K_2Cr_2O_7$) [M&B, England]
- Nitric Acid (HNO_3) [BDH chemicals, England]
- Lead (II) nitrate ($Pb(NO_3)_2$) [JDH chemicals, England]
- Ferroin indicator
- Iron ((II) ammonium tetraoxosulphate (VI) ($FeSO_4(NH_4) 2SO_4 \cdot 6H_2O$)

3.1.4 Glassware

- Beakers [Kimax, USA]
- Volumetric flasks [Technico, England]
- Refluxing flasks [Kimax, USA]
- Sintered glass crucible [Halden wanger, Berlin]

- Measuring cylinders [Kimax, USA]

3.2 Methods

The methodology for this research involved the processes listed below:

- I. Activation of sawdust
- II. Characterization of aquaculture effluent
- III. Characterization of SAC
- IV. Batch adsorption test
- V. Data analysis

3.2.1 Preparation of activated carbon

The preparation of the sawdust activated carbon started with the collection of the sawdust from a local sawmill at Sabon-Gari, Zaria and it was then sieved, dried, carbonized, washed, dried, impregnated, activated and then finally washed with a weak acid to adjust the pH accordingly.

- Sawdust (SD) sample of 2kg weight was collected from a local sawmill at Sabon-gari, Zaria, Nigeria.
- According to the process described by Suleiman *et al.* (2010), the sawdust was oven dried at 100°C overnight for 17hours.
- The sample was sieved with a 2 mm mesh size sieve and the less than 2 mm samples were stored in an airtight container to avoid absorption of moisture
- Adopting the process used by Atef (2016), the two-step activation involving precarbonization and activation was adopted. The raw sample was weighed into

clean and pre-weighed crucibles and they were introduced into a muffle furnace at 500°C for 10 minutes for pre-carbonization.

- Also, in accordance to Atef, (2016), the SD char was then poured from the crucible into a bath of cold water and then the excess water was drained off.
- The carbonized sample was washed, using 0.1 M HCl to remove surface ash which was followed by hot water wash and further washing with distilled water to remove residual acid (Suleiman *et al.*, 2012; Atef, 2016)
- The sample was then further dried in the oven overnight at 100°C.
- Following the procedure of Adinata *et al.* (2007), Mohammad and Zaker (2010), and Couto *et al.*(2012), the process of char impregnation was carried out overnight and an activating agent to carbon precursor ratio (wt. /wt. %) of 1.0 was adopted.
- According to the procedure of Jin *et al.* (2012) and Ogunbile *et al.* (2014), potassium carbonate (K_2CO_3) was dissolved in distilled water to prepare a solution (40g K_2CO_3 : 100ml: 40g of sawdust).
- As described by Atef (2016), Zang *et al.* (2010), Birbas (2011), and Chandrasekar and Mohamad, (2004), the impregnated SD was introduced into the furnace and heated at 450°C for 5 minutes.
- The activated sample was washed with ice-cold water, and excess water was drained off.
- Washing was continued until the pH of sample solution was in the range of 6 -8,
- The washed sawdust activated carbon was then dried in the oven at a temperature of 105°C and stored in an airtight container to prevent moisture uptake.

3.2.2 Characterization of the sawdust activated carbon

The produced activated carbon was further characterized based on the carbon yield, pH, solubility in water, moisture content, ash content, methylene blue number, bulk density, surface morphology and surface area, in order to fully understand the effectiveness of the activation process and also for comparison with previous researches on activated carbon.

3.2.2.1 Carbon yield

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

$$Y_{CH} = \frac{W_s}{W_o} \times 100 \quad (3.1)$$

Where, Y_{CH} is carbon yield (%), W_s is dried weight of AC prepared and W_o is pre-treated sample used in the carbonization and activation processes

3.2.2.2 pH

The standard test method for determination of activated carbon pH ASTM D3838-80 was used. 1.0 g of SAC was weighed and transferred into a beaker. One Hundred milliliters (100ml) of distilled water was measured and added and stirred for 1 hr. The samples were allowed to stabilize before the pH was measured. The pH was determined using a pH meter (metrohm 744, USA).

3.2.2.3 Solubility in Water

For water solubility (S), 0.5 g SAC samples were added to 100 ml of distilled water in 250 ml flask and shaken at 200 rpm in a shaker for 2 hrs at ambient temperature. The mixtures were filtered through pre-weighed filter papers. The filter papers containing the residual carbons were dried in the oven for 12 hrs at 105°C. After cooling to ambient temperature, in a desiccator, the filter papers together with residual carbons were weighed. The percentage solubility in water was calculated as the weight ratio of unrecovered carbon to the original sample.

$$S (\%) = \frac{\text{Loss in weight on dissolution}}{\text{Weight of original carbon}} \times 100 \quad (3.2)$$

3.2.2.4 Moisture Content

Thermal drying method was used in the determination of moisture content of the SAC according to Atef (2016). 1g of the powdered SAC was taken in a previously weighed crucible. The crucible was placed in an electric hot air oven maintained at about 110°C. After one hour the crucible was taken out, cooled in a desiccator and weighed again. The loss in weight of the powder reported on percentage basis gives moisture content in the sample as:

$$\text{Moisture content (100\%)} = \frac{\text{Loss in weight on drying}}{\text{Initial sample weight}} \times 100 \quad (3.3)$$

3.2.2.5 Ash Content

The ash content of the SAC was determined using the standards ASTM procedure D2866-94. This method involves heating the sample at 650°C for several hours until

constant weight has been achieved (Kalderis, 2008). The ash is then weighed and the ash content of the SAC is calculated as:

$$\text{Total ash (\%)} = \frac{D-B}{C-B} \times 100 \quad (3.4)$$

Where, B is the weight of the crucible (g), C is the weight of crucible plus original carbon sample (g) and D is weight of crucible plus ash containing sample (g).

3.2.2.5 Bulk Density

In accordance to standard ASTM methods, an empty dry graduated cylinder was weighed. A sample of dry activated carbon SAC was packed into the cylinder and reweighed as:

$$\text{Density (g cm}^{-3}\text{)} = \frac{\text{Weight of dry activated carbon}}{\text{Volume of dry material}} \quad (3.5)$$

3.2.2.7 Determination of Methylene Blue Number

The methylene blue number of the SAC was determined in accordance with the method described by Atef (2016). 2.0 g of SAC powder was dissolved in 200 ml of deionized water and 100 mg L⁻¹ methylene blue solution was added to the adsorbent suspension and agitated in a shaker for 2h. Thereafter, it was kept for 24 h to reach equilibrium, after which 10 mL aliquot was then analyzed in a UV/visible spectrophotometer at maximum wavelength of 660 nm to determine the amount of methylene blue absorbed. Also 200, 300, 400, 600 and 700 mg L⁻¹ solutions of methylene blue were then added sequentially and the previous steps repeated. A graph of

concentration of MB added versus the absorbed MB was used to identify the point of complete cation replacement.

3.2.2.8 *Determination of Surface Area and Surface Morphology*

The surface area and pore size distribution of the materials was determined by means of N_2 adsorption/desorption isotherms at 77K in an Autosorb-1, Quantachrome. The surface area was calculated by the BET method and the pore size distribution was calculated by DFT method. The surface morphology of the produced activated carbons was investigated using scanning electron microscopy (SEM). The samples were prepared in stub holders with double face carbon tape, placed on an aluminum sheet and covered with gold, using a Balzers SCD 050 evaporator.

3.2.2.9 *Infra Red Spectroscopy analysis*

This was done using Perkin Elmer 1600 Series *FTIR* Spectrophotometer *Model* 1615. The samples prior to this analysis were prepared by crushing the sample with an oily-milling agent, (usually nujoll) using a mortar and pestle. A beam of infra red light was then passed through the sample and absorption will occur when the frequency of the infrared is the same with the vibrational frequency of a bond. The transmitted light was then examined to reveal the quantity of energy absorbed at each frequency (or wavelength). This was done by making measurement over the whole wavelength range using a Fourier Transform instrument and then a transmittance or absorption spectrum was generated.

3.2.3 Adsorbate preparation and characterization

A 10 litre effluent sample was collected from a local fish farm in Zaria, Kaduna State, Nigeria. A 10 litre sample container (jerry can) was filled to the brim with the effluent in order to expel entrapped air. The can was corked and remained sealed until the commencement of the analysis in accordance with Obiora-Okafo and Onukwuli (2013). Physicochemical analyses including COD, BOD, nitrates, phosphates, pH and metal ion concentration of the effluent sample were determined following the standard method of water and wastewater purification.

3.2.3.1 Physical tests

The temperature and pH of the samples were obtained using the thermometer and multi-parameter photometer respectively. The total suspended solids (TSS) was determined using membrane filters of 0.45 μm that were dried at 103°C for one hour after which they were weighed and placed in a desiccator until they were ready for use. Sample was collected in sterile container and mixed thoroughly by inverting the bottles several times to obtain a uniform mix. 100 mL of sample was poured into the membrane filter assembly holding the previously weighed membrane filter and attached to a suction pump and then filtered. The filter paper was then dried at 103°C and re-weighed. Total suspended solids (TSS) in mg/L was then determined by subtracting the initial weight of the filter paper from its final weight.

3.2.3.2 *Physicochemical tests*

Physicochemical analyses of the effluent sample including nitrates, phosphates, were all determined using Standard Methods for the Examination of Water and Wastewater 18th edition (APHA, 2012).

3.2.3.3 *Determination of COD*

The chemical oxygen demand test was carried out by placing 50ml of the effluent sample in a 500 ml refluxing flask and glass boiling beads was added to serve as anti-bumping aid followed by the addition of 1g of mercury (II) tetraoxosulphate (VI) ($HgSO_4$) crystal. 5 ml of concentrated tetraoxosulphate (VI) acid (H_2SO_4)/silver (I) tetraoxosulphate (VI) solution ($AgSO_4$) was added, and mix until the $HgSO_4$ was dissolved in the solution.

Accurately measured 25 ml of 0.25N potassium heptaoxochromate (VI) ($K_2Cr_2O_7$) was added and mixed; while mixing, an additional 70 ml of concentrated H_2SO_4 - $AgSO_4$ solution was added. After thorough mixing, the flask was attached to the reflux condenser; the mixture was gently heated in a water bath, and reflux for 2 h. The apparatus was then cooled to room temperature ($28^{\circ}C$) after the refluxing period. Washing down of the interior of the condenser and flask twice, with approximately 25 ml portions of distilled water was carried out. The flask was removed from the condenser and diluted to a final volume of approximately 350 ml with distilled water and, further cooling was done with running tap water. 2 to 3 drops of ferroin indicator was added and stirred with a magnetic stirring bar. The resulting mixture was rapidly titrated with 0.1 N iron ((II) ammonium tetraoxosulphate (VI), $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, to the first red-brown endpoint. The same procedure was repeated for other samples. Also, the blank run was done; it was prepared

using 50 ml of distilled water, by treating it with the same reagents as the samples to determine the blank value. The concentration of COD of respective samples was calculated using the following formula:

$$\text{COD} = \frac{1000(a-b)N}{\text{volume of sample used (ml)}} \text{ mg/L} \quad (3.6)$$

Here, a and b are the respective volumes of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ used for blank and sample (ml), VIS the volume of sample used (ml) and N normality of $Fe(NH_4)_2SO_4$.

3.2.3.4 Determination of metal ion content

The atomic absorption spectrophotometer (AAS) (Shimadzu Jenway Spectrophotometer 6400) was used to determine the quantities of some metals present in the effluent samples. Using distilled water, standard stock solutions was prepared using soluble salts, after which calibration standards was prepared for the determination of the various cations.

3.2.4 Batch adsorption test

According to the procedure of Obiora-Okafor *et al.* (2014), the batch experiment was done at room temperature to determine the equilibrium adsorption isotherms. Each batch study was done by adding different adsorbent mass (0.2, 0.4, 0.6, 0.8, & 1.0g) of SAC into 0.1L of the effluent and was shaken with a mechanical shaker at varying contact time (20, 40, 60, & 80 minutes).

3.2.4.1 Preparation of lead ion adsorbate

For the kinetics study, stock solution of lead ions was prepared according to the procedure specified in the standard method for the examination of water and waste water (APHA, 1998). Specifically a known mass (1.599g) of Lead nitrate ($Pb(NO_3)_2$) was dissolved in

200mL of distilled water, 10ml of concentrated HNO₃ was then added and the resulting solution was diluted to 1000mL mark using deionized water. Working solution of 100mg/l was then prepared from the stock solution by diluting with deionized water. The adsorption was carried out using 1g of SAC per litre of the solution over varying time until equilibrium was achieved. The amount of adsorbate adsorbed by SAC at equilibrium was calculated using Equations 3.6.

$$q_e = \frac{(C_o - C_e) V}{M} \quad \text{Equation 3.7}$$

Where; C_o = Initial liquid phase concentrations of TDS

C_e = liquid phase concentrations of TDS at equilibrium,

M = Mass of the dry adsorbent (g)

V = Volume of the solution (litres)

3.3 Data Analysis

The kinetics of adsorption was analysed using two kinetic models, namely; pseudo first order and pseudo second order kinetic models. Other data were fully analysed using different mathematical tools which include; graphs, charts and tables to illustrate the treatment process.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Aquaculture Pond Effluent Characteristics

The result of the physicochemical analyses of the effluent sample is presented in Table 4.1. Concentrations of the parameters including pH, phosphate, and some of the heavy metals (cadmium, zinc, iron, copper) were below the National Environmental Standards and Regulations Enforcement Agency (NESREA) effluent discharge limits; While others, like chemical oxygen demand(COD), total suspended solids(TSS), lead (Pb), nitrate (NO_3) and biological oxygen demand (BOD_5) values were far beyond the limits with very wide margins.

Table 4.1: Physicochemical Characteristics of Aquaculture Effluent

PHYSICOCHEMICAL PARAMETERS	EFFLUENT CONCENTRATION	NESREA LIMIT
pH	6.3	6-9
COD(mg/l)	600	60
Nitrates(mg/l)	19.88	10
Phosphates(mg/l)	3.48	3.5
TSS(mg/l)	787.5	35
<i>BOD</i> ₅ (mg/l)	120	20
Lead (mg/l)	1.54	0.05
Zinc (mg/l)	0.0021	2.0
Cadmium (mg/l)	0.0012	0.01
Copper (mg/l)	0.001	0.5
Iron (mg/l)	0.0239	0.5

Comparing the results with the findings of Boyd(2000) and Omofunmi et al. (2016b) on the pollution of aquaculture effluent, it is confirmed that the effluent ought to be treated before final disposal into the environment. Boyd (2001) reported the average

concentration of total suspended solids, total nitrogen, total phosphorus, and 5-day biochemical oxygen demand during fish harvest to be 1,027 mg/L, 9.58 mg/L, 1.59 mg/L, and 31.8 mg/L, respectively, which results are similar to the results in this study, in which 787.5mg/l, 19.8mg/l, 3.48mg/l and 120mg/l were obtained for TSS, Nitrates, Phosphates and BOD respectively.

4.2 Activated Carbon Characteristics

The characteristics of the sawdust activated carbon (SAC) are presented in Table 4.2.

Table 4.2: Result of Characterization of Sawdust Activated Carbon (SAC)

Parameters	Values
Carbon yield (%)	31.25
Ash content (%)	4.92
Solubility in H_2O (%)	12.0
Moisture content (%)	3.54
pH	8.07
Bulk density (g/cm^3)	0.27
Methylene blue number	61.10
Surface area (m^2/g)	831.83
Pore volume (cm^3/g)	0.34
Surface morphology	Plates I

4.2.1 Carbon yield

The yield of activated carbons was calculated from sample weight after activation relative to its initial weight according to equation 18. Table 4.2 shows the percentage yield of SAC to be 31.1%, prepared at temperature of 450°C , at time 10 min, and impregnation ratio of 1:1 with potassium carbonate.

A similar result of 29% carbon yield from sawdust precursor was reported by Ogunsile et al. (2014) after preparing the activated carbon under similar conditions, with, 500°C activation temperature and 1:1 impregnation ratio with potassium carbonate. In another research, Nwabenne and Igbokwe, (2011) obtained the highest carbon yield of 34% at the lowest temperature of 500°C , activation time of 1h and impregnation ratio of 1:1 in chemical activation of Nipa Palm Nut.

4.2.2 Ash content

The inorganic constituents in the sawdust activated carbon were found to be 4.9% when the carbon was washed; this is lower when compared to the 6.5% and 6.6% ash content obtained by Obiora-Okafor et al. (2014) and Atef (2016) respectively, from acid activated sawdust carbon. Ash content can lead to increased hydrophilicity and can have catalytic effects, causing restructuring during regeneration of used activated carbon. According to Yang (2003), the inorganic material contained in activated carbon measured as ash content should generally be in the range of 2 and 10%. High ash content raw materials contain high levels of impurities that lead to blockage of pores during activation process, thereby reducing the surface area of the activated carbon, it also affect the

efficiency of reactivation of spent carbon (Atef, 2016). Therefore, the lower the ash content, the better the activated carbon can be used as an adsorbent.

4.2.3 Solubility in water

The water solubility of the sawdust activated carbon was found to be 12%. Any degree of solubility in either water or acid is an indication of presence of impurities. Pure carbon does not dissolve in either water or acid, since carbon is very unreactive due to lack of electron donating or accepting species in its structure such as lone pair of electrons (Minkova et al., 2001). A lower solubility of 8.4% was reported by Atef (2016) from phosphoric acid activated sawdust. The high value of water soluble matter expressed in this carbonate activated sawdust suggests that a large amount of carbonate salts could have been incorporated into the carbon structure which was also reported by Karthikeyan et al. (2008).

4.2.4 Moisture content

The moisture content obtained for the activated carbon in this study is 3.54% which is better than the 5.6% moisture content reported by Obiora-Okafor et al. (2014) from the study of NH_4Cl -activated sawdust. Srihari and Das, (2009) reported a much higher percent moisture of 10.35 and 12.57 %, for prepared activated carbon and that of commercial activated carbon respectively, while on the other hand, lower percentage moisture of 4.8 % was observed by Nwabanne and Igbokwe (2011). Also, a range of 4.91-6.17 % has been reported by Sivakumar et.al.(2012).

According to Helleur et al. (2001), the recommended AC storage moisture content is <3%. So the produced sawdust activated carbon in this study has its moisture content

within the recommended limit. If the moisture content of AC is high, fungi and other micro-organisms degrade the carbon, utilizing it in their metabolic processes. The micro-organisms can also multiply within the AC, blocking the pore structure, thereby reducing the adsorptive capacity of the carbon (Atef, 2016).

4.2.5 pH

The pH result obtained is shown in Table 4.2. A pH of 9.03 was reported which is quite basic and not suitable for most adsorption as it has been reported that for water treatment, carbon pH 6-8 is acceptable (Ahmedna, *et. al.*, 2007, Okieimen *et. al.*, 2007). Thus the activated carbon to be applied in the adsorption process was further neutralised with 0.1 M HCL and washed to a pH of 8.07, which is more within the acceptable range, which can be reduced with further washing . A similar result was reported by Verla *et. al.*, (2012), who obtained a pH range of 6.3, 6.8, 7.6 and 7.6 - 8.7, for physically activated carbon and chemically activated carbon respectively. The initial high pH is as a result of the basicity of the activating agent.

4.2.6 Bulk density

The value of bulk density of prepared sawdust activated carbon as shown in Table 4.1 is $0.27\text{g}/\text{cm}^3$ and according to Suleiman et al. (2012), bulk density for a good adsorbent should not be less than $0.25\text{g}/\text{cm}^3$. Activated carbon was prepared from palm kernel shell (PKS), Coconut shell (CS) and sawdust (SD) by Ogunsile et al. (2014) and the result of the study indicated that the activated carbon from sawdust (SD) had the lowest bulk density of $0.142\text{g}/\text{cm}^3$ and the highest was from the palm kernel shell (PKS) at $0.722\text{g}/\text{cm}^3$.

4.2.7 Methylene blue (MB) number

The analytical grade cationic dye; methylene blue, was chosen in this study to measure adsorptive properties of the produced activated carbons. MB is adsorbed on the acidic sites of the activated carbon (Hirata *et. al.*, 2002) and accessible to pores with diameters larger than 1.5 nm (Deng *et. al.*, 2010a). The methylene blue value represent the adsorptive capacity of activated carbon for molecules with dimensions similar to that of methylene blue; and a surface area which results from the presence of pore sizes greater than 1.5 nm (Abdulhalim *et.al.*, 2001). As shown in table 4.1, a methylene blue no of 61.1mg/g was recorded. This shows that the sawdust activated carbon is highly microporous with little mesoporous pores which is supported by the report of mehtylene blue adsorption capacity of 81mg/g by Couto et al. (2012) resulting from a potassium carbonate- activated sawdust carbon. A similar result was obtained by Abdulhalim *et.al.* (2001), who also recorded a methylene blue number of 51 mg/g at 30 % w/w $ZnCl_2$ using activated carbon from Gelam wood bark. The difference in the values of methylene blue number may be due to differences in the composition of the precursor, activating agents and generally differences in preparation conditions of activated carbon.

4.2.8 Surface area and pore volume

A high surface area of $831.8m^2/g$ and pore volume of $0.34m^3/g$ was gotten obtained the sawdust activated carbon using BET analysis, which signifies a microporous carbon and an enormous improvement to the pure washed sawdust with BET surface area of $1.21m^2/g$ according to Sunil et al. (2012). Attia et al. (2015) also produced sawdust carbon activated with phosphoric acid and reported a BET surface area of $831m^2/g$ and pore volume of $0.39 cm^3/g$. Garba *et al.* (2016) likewise reported a BET surface area and

pore volume of potassium hydroxide treated (PHAC) and potassium carbonate treated (PCAC) carbons as $305 \text{ m}^2/\text{g}$ and $0.16 \text{ cm}^3/\text{g}$ and $708 \text{ m}^2/\text{g}$ and $0.31 \text{ cm}^3/\text{g}$ respectively. This shows clearly that basic activating agents are as effective as the acidic activating agents and even more effective sometimes as the result in this study shows.

Generally, the larger the specific surface area of the adsorbent, the better its adsorption performance will be (Guo and Lua, 2003). The most widely used commercial active carbons have a specific surface area of the order of $600\text{-}1200 \text{ m}^2/\text{g}$ (Ng et.al, 2002).

4.2.9 Surface morphology

The SEM image of the sawdust activated carbon is as shown in Plate I. The figure shows that the activation process produced extensive external surface areas with oval shaped pores which was accomplished through the evaporation of the chemical reagent during activation process, hereby leaving empty pores (Deng *et.al.*, 2010b). The pores are of different shapes and are irregular in their distribution. Raw sawdust is usually characterized by a highly oriented structure in the form of filaments filled with materials, conferring an anisotropic character to the sawdust (Attia et al., 2015); which was eliminated by treatment with potassium carbonate. Firstly, it clears the filament, thereby eliminating sawdust anisotropy and leaving empty channels. Then it further reacts with the sawdust component leaving a honey comb structure as seen in the Plate (Singh et al., 2011).

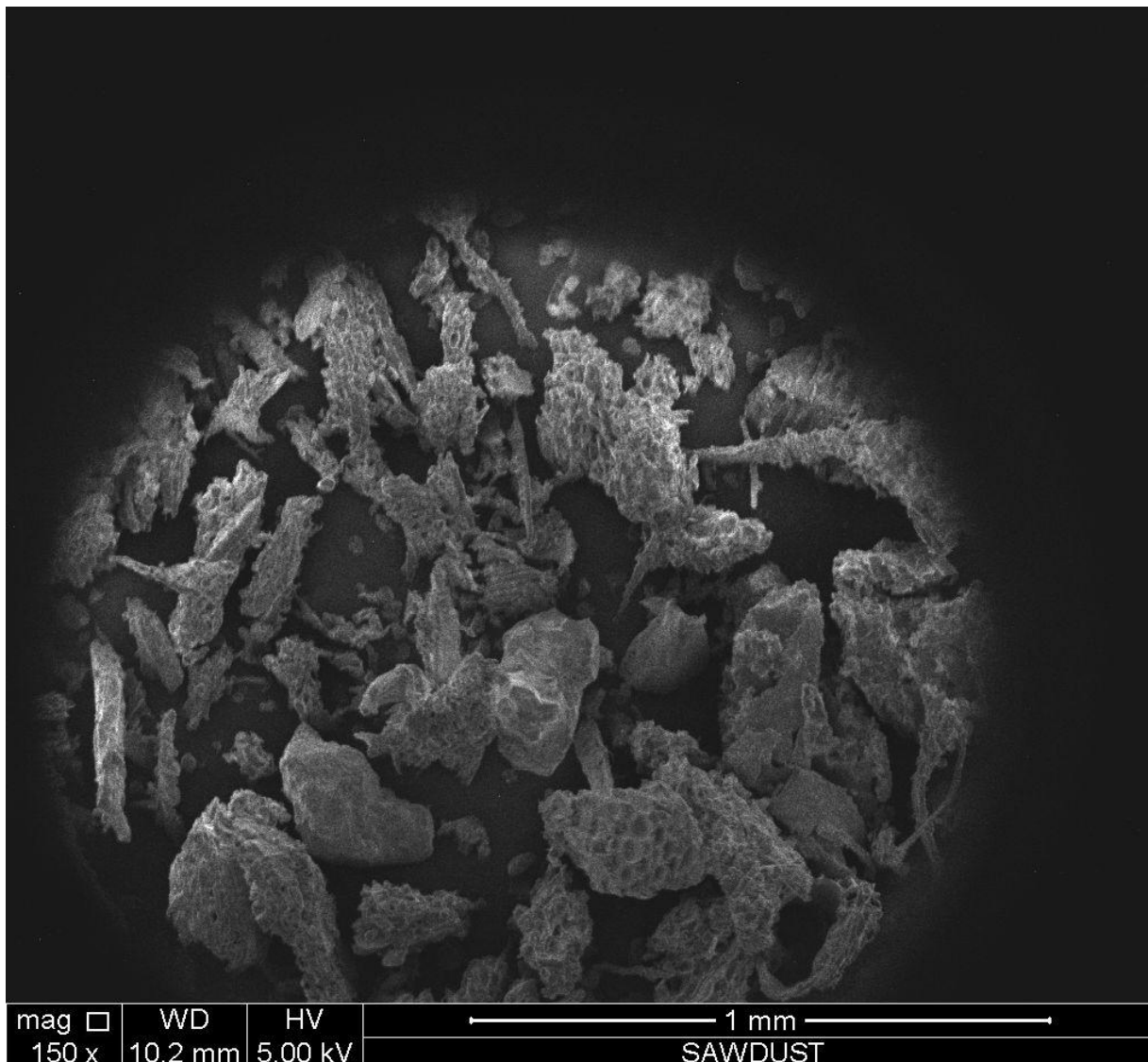


Plate. I: SEM image of sawdust activated carbon at 150x magnification

4.2.10 FTIR analysis

The FT-IR has been employed for the investigation of activated carbon surface chemistry as a result of difference in the temperature of carbonisation. The FT-IR of the activated carbons revealed complex surface by presence of several peaks. Table 4.3 presents the peaks wavelength and possible assigned functional groups. The intensity of the

peaks generally increased with increasing temperature as can be observed from Figure 4.0 below.

Table 4.3: Functional Groups Present on the Activated Carbon

SAC (cm^{-1})	Functional group assignment
3630.4	O-H stretching
3328.5	O-H stretching
2113.4	Alkyne stretching
990.4	=C-H bending
1561.8	C=C
1375.4	N-O stretching
1287.5	C-N stretching
745.5	=C-H bending
875.9	=C-H bending

A characteristic peak of the sawdust activated carbon are the peaks at 2113.4cm^{-1} (Alkyne triple stretch bond) and the peak at 990.4 cm^{-1} (=C-H bending). Other prominent ones are 745.5 cm^{-1} and 875.9 cm^{-1} (=C-H bending).

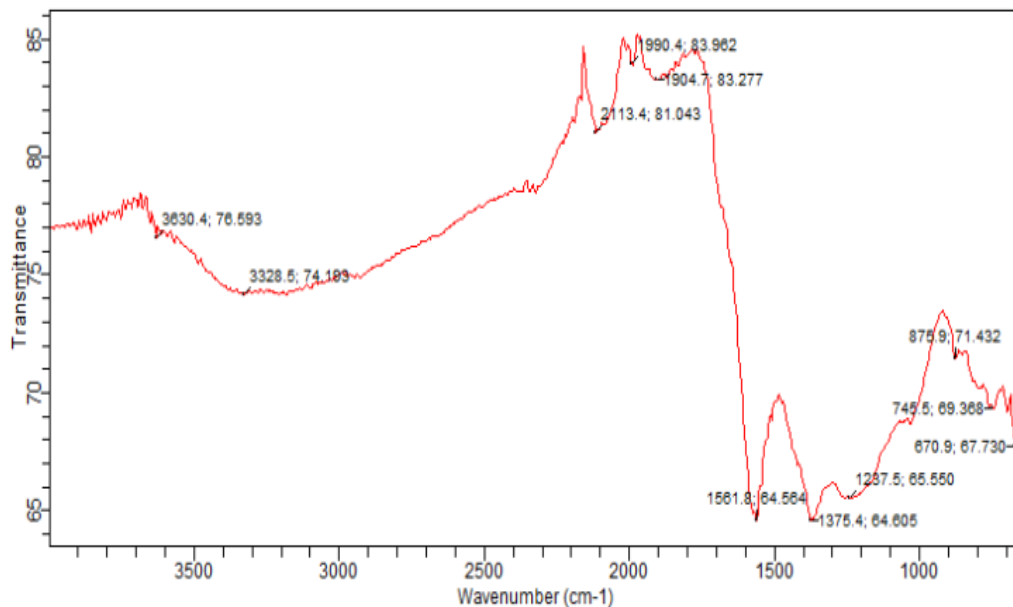


Figure 4.1: FTIR spectra of SAC

4.3 Batch Adsorption

The batch adsorption was carried out with varying adsorbent dosage and contact time at ambient room temperature. The effect of adsorbent dosage was studied at 2g/l, 4g/l, 6g/l, 8g/l and 10g/l, while the effect of contact time was observed at 20min, 40min, 60min and 80min. The overall treatment process showed a maximum removal efficiency of 99.17% (5mg/l), 96.61% (26.67mg/l), 99.35% (0.01mg/l) and 87.53% (2.48mg/l) for COD, TSS, lead and nitrate respectively as shown in Figure 4.1.

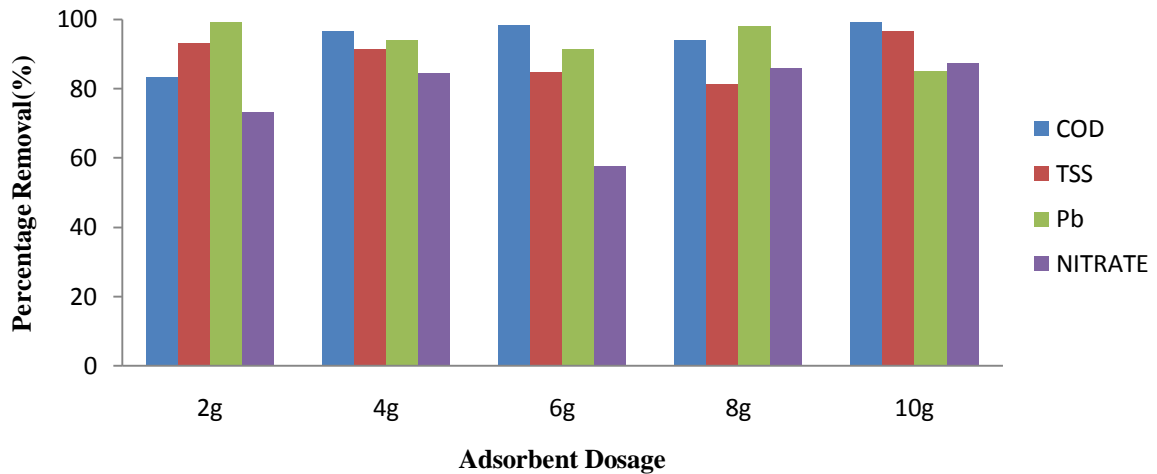


Figure 4.2: Optimum Percentage Removal at Varying Dosages

4.3.1 Effect of adsorbent dosage and contact time on adsorption

The effect of the adsorbent dosage and contacted time is presented by means of graphs as shown in Figures 4.3, 4.4, 4.5 and 4.6. At 2g of adsorbent dose per litre of effluent, removal efficiencies were 83.33% (100mg/l), 93.23% (53.33mg/l), 99.35% (0.01mg/l) and 73.24% (5.32mg/l) for COD, TSS, lead and nitrate respectively; at a contact time of 60min.

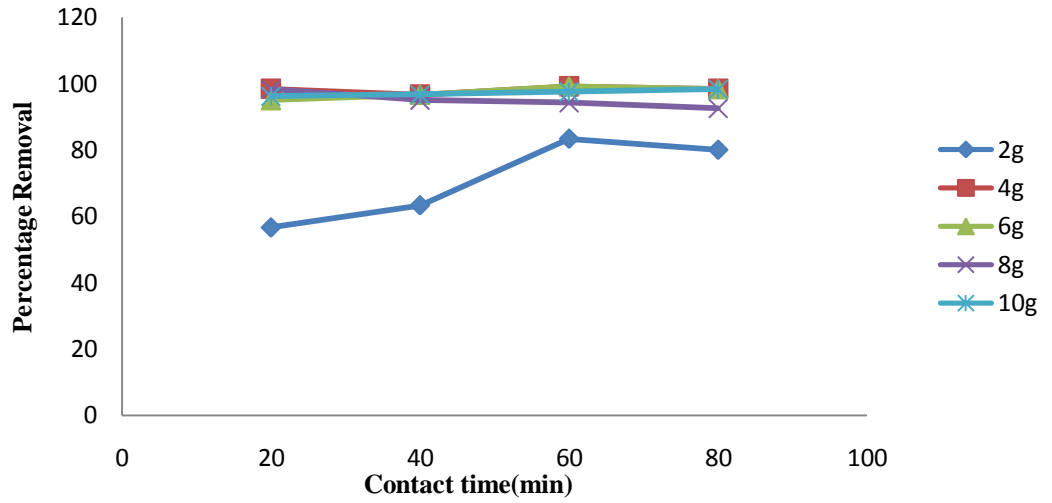


Figure 4.3; Effect of Contact Time and Dosage on Removal of Organic Content(COD)

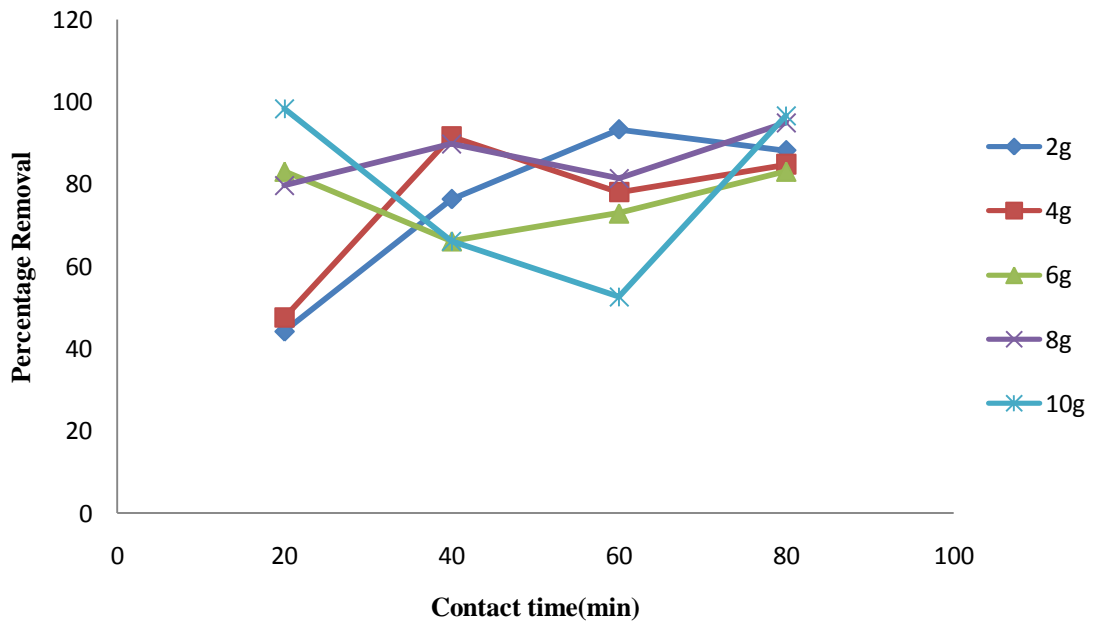


Figure 4.4; Effect of Contact Time and Dosage on Removal of TSS

Also, at an adsorbent dose of 4g/l of effluent, removal efficiencies were 96.67% (20mg/l), 91.53% (66.67mg/l), 94.15% (0.09mg/l) and 84.51% (3.08mg/l) for COD, TSS, lead and nitrate, respectively, with a contact time of 40min. Furthermore, when contact time was 80minutes, removal efficiencies were 98.33% (10mg/l), 84.76% (120mg/l), 91.56% (0.13mg/l) and 57.74% (8.4mg/l)for COD, TSS, lead and nitrate, respectively, at an adsorbent dose of 6g/l. Likewise, at a dose of 8g/l, and 60min contact time, removal efficiencies were 94.17% (35mg/l), 81.38% (146.67mg/l), 98.05% (0.03mg/l) and 86.02% (2.78mg/l) for COD, TSS, lead and nitrate, respectively. Lastly, batch adsorption studies were carried out with 10g of adsorbent per litre of effluent and contact time for best removal efficiency was recorded to be 80min. The removal efficiencies were 98.33% (10mg/l), 96.61% (26.67mg/l), 85.06% (0.23mg/l) and 87.53% (2.48mg/l) for COD, TSS, lead and nitrate respectively.

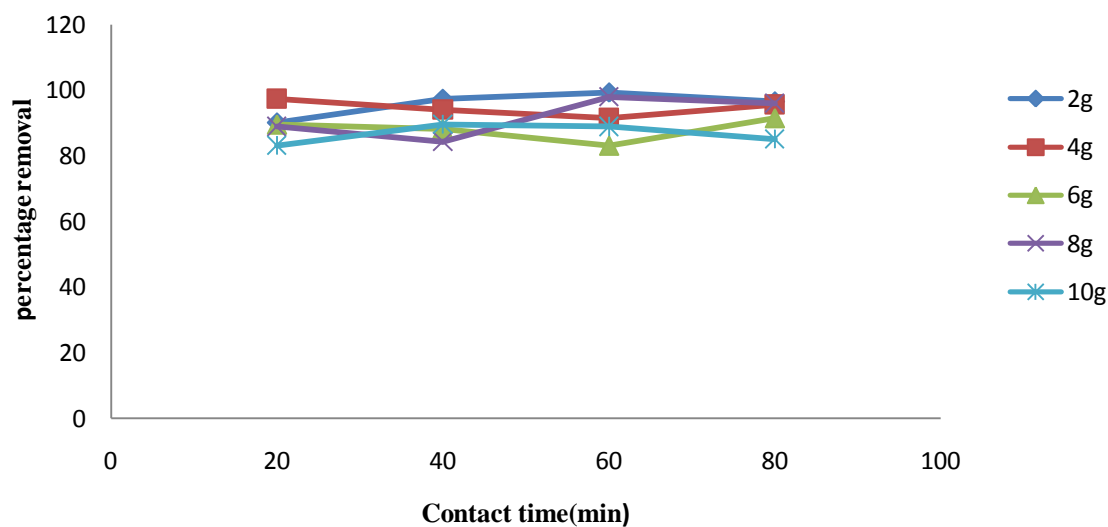


Figure 4.5; Effect of Time and Dosage on Removal of pb

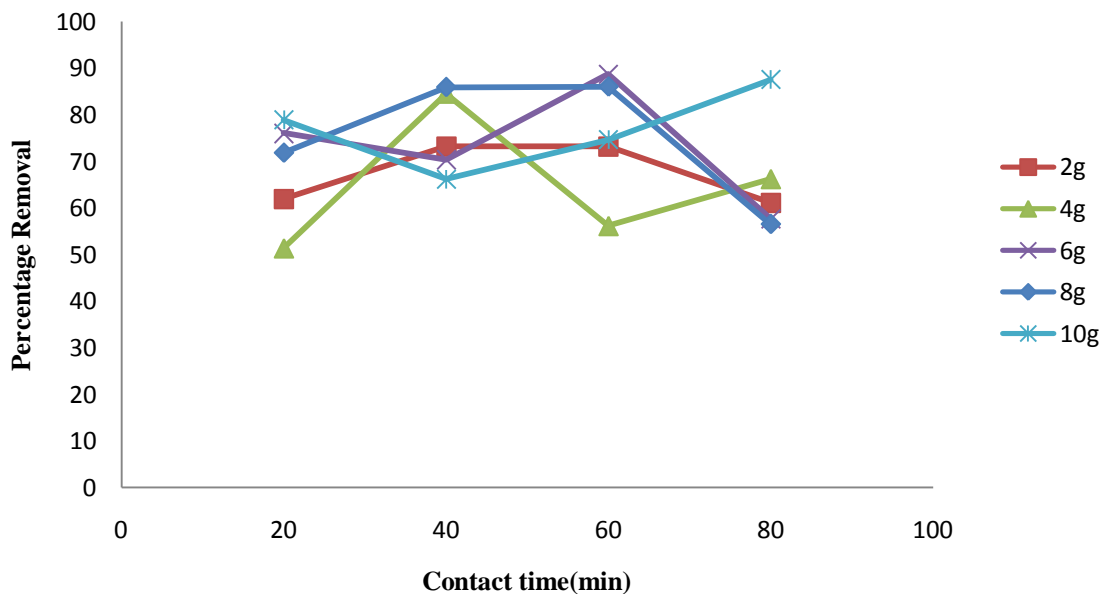


Figure 4.6; Effect of Time and Dosage on Removal of Nitrate

The effect of contact time and dose of adsorbents is important in adsorption processes because it exercises a great deal of influence on the adsorption capacity of adsorbents. Generally, the rate at which adsorption occurred was rapid initially between 20 to 40 min, and became slower between 60 mins and 80 mins. This phenomenon may be due to the fact that a large number of empty surface sites were available for adsorption during the initial stage, and that after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive force between solute molecules on the solid and bulk phases (Ahmed et al., 2007)

The adsorption capacity of the 2g adsorbent dosage per litre of effluent for the different adsorbate is shown in figure 4.7- 4.10, calculated using equation 3.6. The result showed a steady increase in the adsorption capacity with increase in contact time until it reached equilibrium at 60 min.

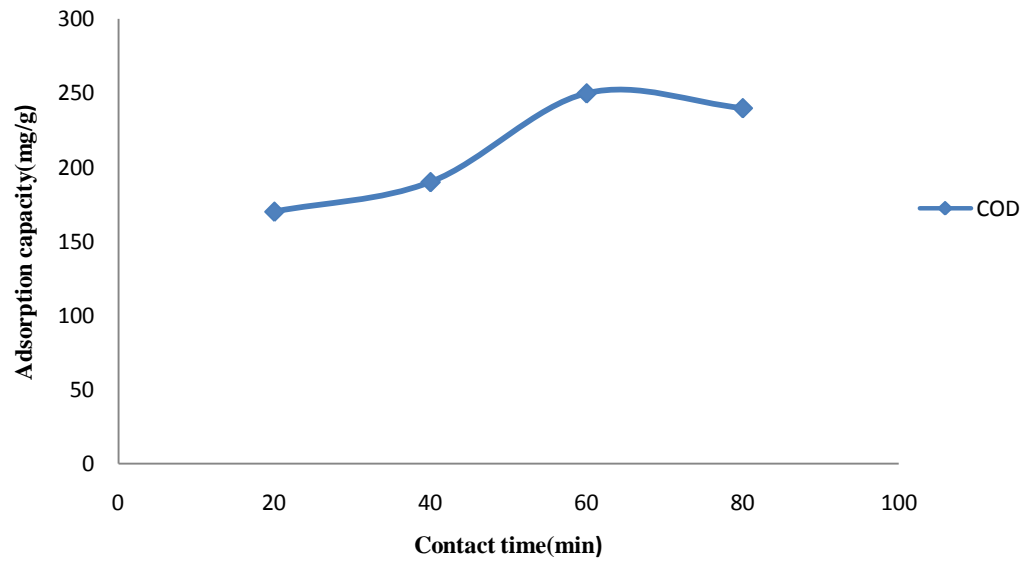


Figure 4.7; Equilibrium Plot for Removal of Organic Content (COD)

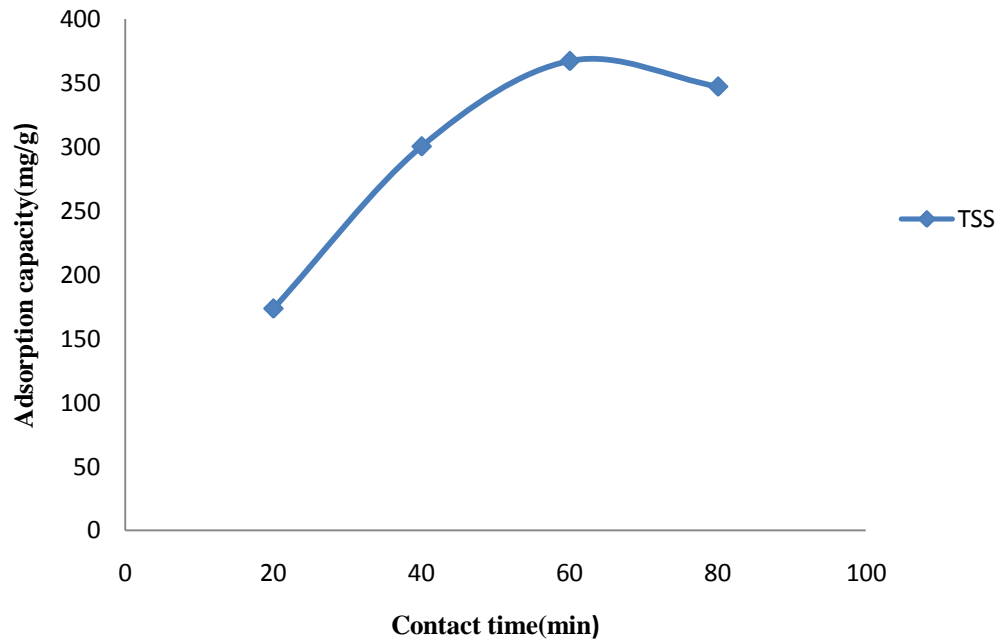


Figure 4.8; Equilibrium Plot for Removal of TSS

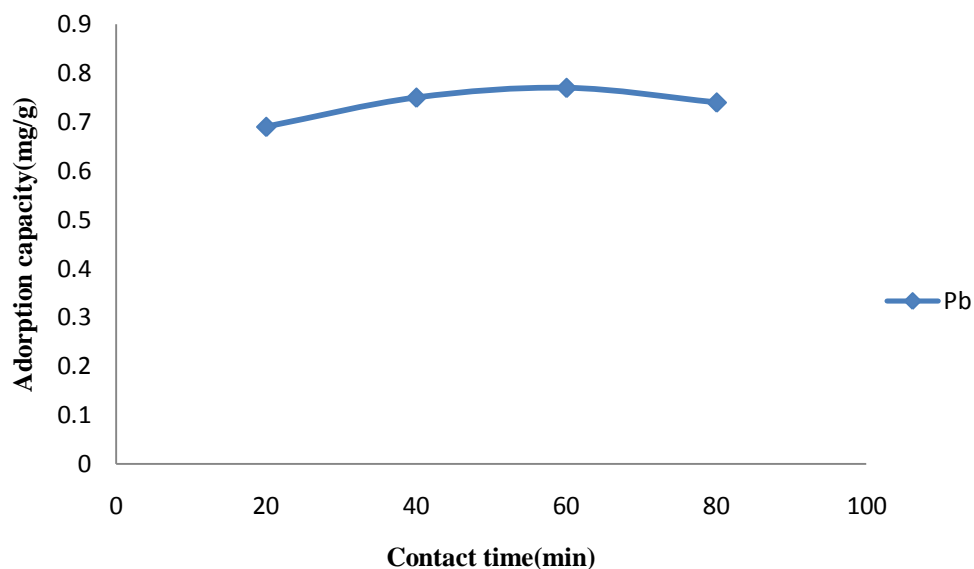


Figure 4.9; Equilibrium Plot for Removal of pb

This result is in correlation with the findings of Obiora-Okafor et al. (2014), who obtained equilibrium time at 60 minutes at an adsorbent dose of 50g/l for 80.5% removal efficiency of total suspended solids (TSS). Olafadehan et al. (2012) studied the removal of COD from brewery effluent, then achieved 98% COD removal with an initial COD of 2856.72mg/l, and a carbon dosage of 15g/0.1L of brewery wastewater using granular activated carbon from coconut shell. Al-Riyami et al. (2014) reported a 41% sorption of lead ion using meranti sawdust as an adsorbent, equilibrium time of 90 min and adsorbent dose of 2.5g/l.

Adeolu et al. (2016) observed that increasing adsorbent dosage decreased the amount of chromium adsorbed onto activated carbon from plantain wastes. The report showed percentage removal of the metal ion to follow a reverse trend. The maximum percentage removal was reported to be 68.91% at adsorbent dose of 2.0g, while adsorption capacity decreased at corresponding increase in adsorbent dose. Similar trends have also

been observed by various researchers in heavy metals adsorption, including Ho et al. (2015), Adebowale et al. (2009) in the adsorption of lead(pb) and cadmium(Cd) and Okareh and Adeolu (2015) in the adsorption of lead(pb) from effluent using activated carbon from plantain waste. It should be noted that after a certain dose of adsorbent, the maximum adsorption set in and hence the amount of metal ion bounds to the adsorbent and the amount of free ions remain constant (i.e Equilibrium) even with further increase of the dose of adsorbate.

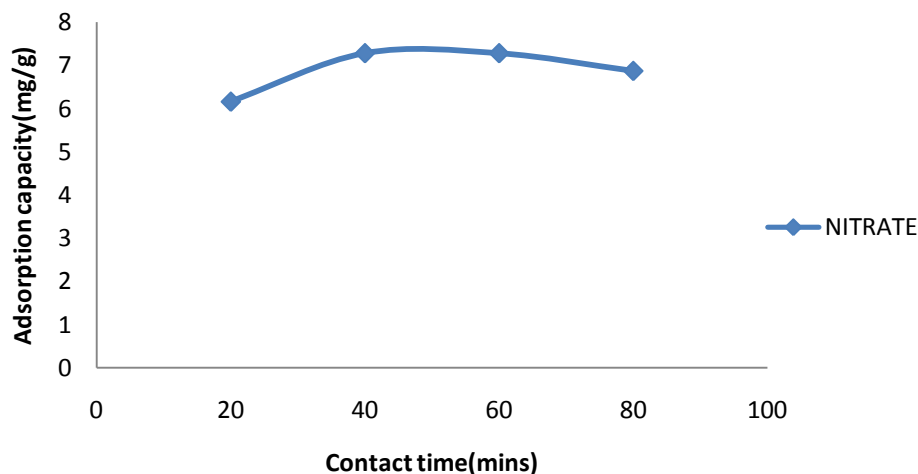


Figure 4.10; Equilibrium Plot for Removal of Nitrate

After the batch treatment process, all the parameters of the aquaculture effluent (AE) that were beyond the range of the effluent discharge limit set by NESREA were reduced to meet the disposal standard except COD and TSS as shown in Table 4.4.

Table 4.4: Removal of organic and inorganic matter from Aquaculture Effluent (AE)

Parameters	Raw effluent	Treated effluent	NESREA limit	% Removed
COD (mg/l)	600	100	60	83.3
Nitrate (mg/l)	19.88	5.33	10	73.2
Phosphate (mg/l)	3.48	1.39	3.5	60
BOD ₅ (mg/l)	120	9.2	20	92.33
Lead (Pb) (mg/l)	1.54	0.01	0.05	99.3
TSS (mg/l)	787.5	53.33	35	93.2

4.4 Adsorption Kinetics Studies

The linearized pseudo-first order equation is stated by Equation 2.16. In most cases, this model does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 min of adsorption process (Varank *et.al.*, 2012). The plot of linearized form of the equation is shown in Figure 4.15, which is a plot of $\log (q_o - q_t)$ against time (minutes). The pseudo first-order rate constant k_1 , amount of lead ion adsorbed at equilibrium q_e , and correlation coefficients are shown in Table 4.6 as 0.009027, 23.94mg/g and 0.376. The results showed that, the correlation coefficients, R^2 obtained for pseudo first order kinetics model was 0.376 which is very low compared to the pseudo second order kinetics model constants. The pseudo-second order plot showed a R^2 value of 0.997, experimental q_e value of 500mg/g and the pseudo-second order rate constant k_2 value of 0.0044 as shown in Figure 4.16, which is a plot of t/q against t . Therefore,

pseudo second-order kinetic model describes the adsorption process, judging from the correlation coefficient.

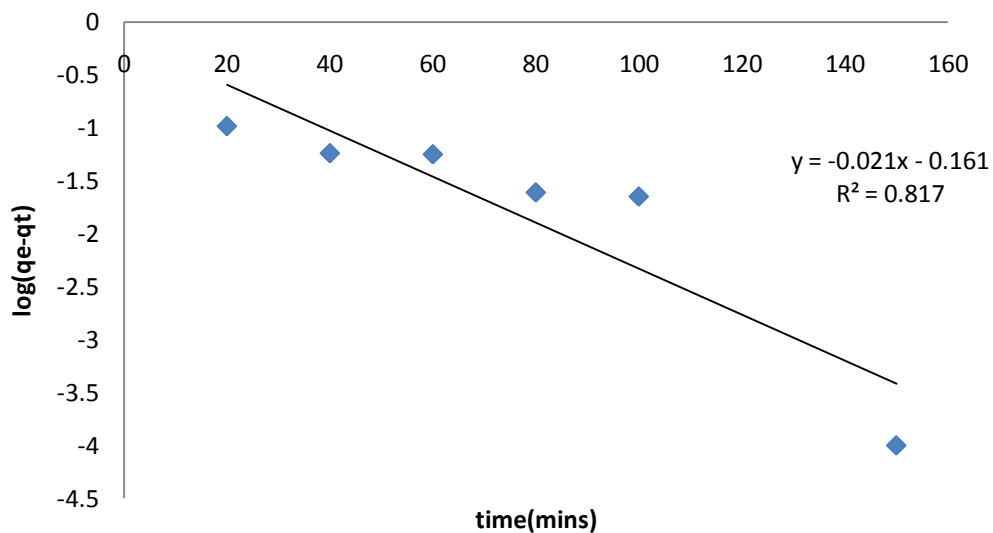


Figure 4.11; Pseudo-first Order Plot

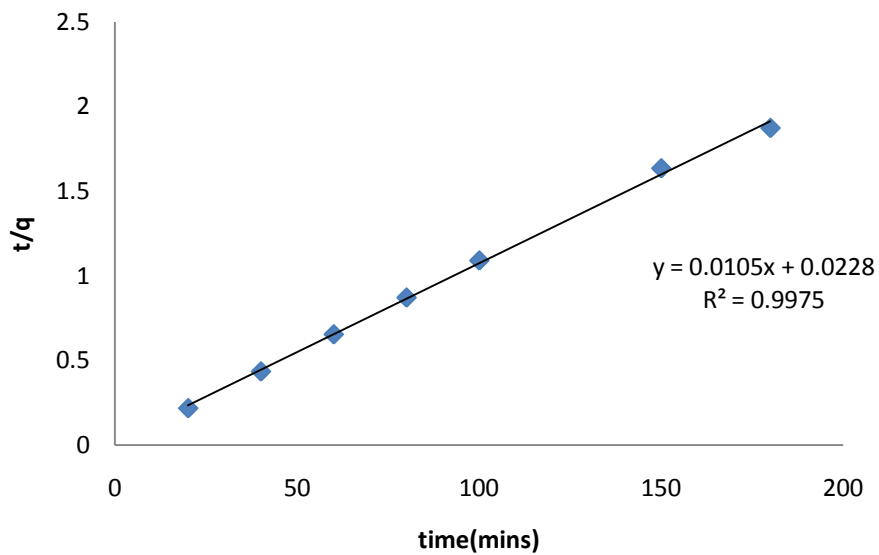


Figure 4.12: Pseudo-second order Plot

Table 4.6: Adsorption Kinetic Parameters

Kinetic Model	PARAMETERS	SAC
Pseudo 1 st	k_1 (min^{-1})	0.05
	q_e (mg/g)	1.45
	R^2	0.376
Pseudo 2 nd	k_2 ($\text{gmg}^{-1}\text{min}^{-1}$)	0.004
	q_e (mg/g)	95.23
	R^2	0.997

Suresh *et. al.* (2013) reported an inconsistency in the agreement of the experimental q_e for the adsorption of PNP with granular activated carbon. Experimental q_e value of 27.41 mg/g was reported and values of 95.70 mg/g and 99.74 mg/g were reported for pseudo-first and pseudo-second kinetic models respectively. Also, Srihari *et. al.* (2009) reported pseudo-first order rates of 0.0104 min^{-1} and pseudo-second order rate of $0.0003 \text{ gmg}^{-1}\text{min}^{-1}$ which is similar to what has been observed in this study.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Summary of Key Findings

Activated carbon was prepared from sawdust by chemical activation with potassium carbonate in the 1:1 w/w ratio, at an activation temperature of 450°C. Different parameters like pH, moisture content, bulk density, methylene blue adsorption, iodine number, surface morphology and BET surface area were determined and the results obtained indicated that the prepared sawdust activated carbons has good adsorptive properties with as much as 831m²/g for the surface area. After the optimization study, an equilibrium time of 60min was recorded and an adsorbent dosage of 2g per litre of the effluent.

The physicochemical tests on the raw effluent showed that the raw aquaculture effluent is polluted and should be treated before disposal according to NESREA standard. At the end of experimental batch treatment process, the physicochemical parameters of the fishpond effluent had been reduced to meet the NESREA standards for effluent disposal. So, it can be concluded that “potassium carbonate sawdust activated carbon” is a good adsorbent for the treatment of aquaculture effluent.

Pseudo-second-order kinetic model fits very well with the experimental data showing a R^2 value of 0.997, clearly indicating that one metal ion is sorbed onto two sorption sites on the adsorbent surface.

5.2 Conclusions

After the various assessment of the use of sawdust activated carbon in the treatment of aquaculture effluent, it can be concluded that;

- Aquaculture effluent contains pollutants that are beyond the NESREA discharge limit, hence, should be treated prior to disposal.
- The use of sawdust activated carbon in the treatment of aquaculture effluent, it can be concluded that, while potassium carbonate is a good activating agent, producing a large surface area ($831.8 \text{ m}^2/\text{g}$), SAC is also a good adsorbent for the treatment of aquaculture effluent with a success of 66.67%.
- The bulk density (0.27 g/cm^3), moisture content (3.54%), pore volume ($0.34 \text{ cm}^3/\text{g}$), surface morphology and BET Surface area (831 g/cm^3) properties of the SAC showed it to be a good adsorbent.
- SAC is an effective medium in the treatment of aquaculture effluent prior to disposal with a COD, BOD, Nitrate, Suspended solids, Pb ion and phosphate percentage removal of 83.3, 92.3, 73.2, 93.2, 99.3 and 60% respectively.
- Optimum operating conditions are concluded to be a contact time of 60 minutes at an adsorbent dosage of 2g at ambient room temperature.
- The kinetic data fitted well with the pseudo-second order model
- Finally, while potassium carbonate is a good activating agent, producing a large surface area, SAC is also a good adsorbent for the treatment of aquaculture effluent, meeting 66.67% of the discharge standard.

5.3 Recommendations

It is recommended that further research on the prepared activated carbons should be carried out, such as reduction of the precursor to activating agent ratio, in order to minimize cost of production, the use of a continuous test, and also the regeneration of the spent carbon.

However, the research work would have been easier and faster, if the facilities available to the researcher in the institution were greatly increased. The researcher risks life as well as spends unnecessarily for analysis, I hereby recommend that more research facilities should be provided to enhance quality research.

Also, there is need for financial supports to aids researches, to increase quality, and as well as encourage researchers.

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APPENDIX

Concentration-time data for adsorption of pb on SAC at temperature 28^oc for kinetics study plot

time(mins)	C_t (mg/l)	q_t (mg/l)	$(q_e - q_t)$	$\log(q_e - q_t)$	t/q_t
20	8.4028	91.5972	0.014	-0.9829	0.2183
40	8.3565	91.6475	0.0577	-1.2388	0.4364
60	8.3552	91.6448	0.0564	-1.2487	0.6547
80	8.3234	91.6766	0.0246	-1.609	0.8726
100	8.3213	91.6787	0.0225	-1.6478	1.0907
150	8.2989	91.7011	0.0001	-4	1.6357
180	8.2988	91.7012			
200	8.2988	91.7012			

$q_e=91.7012$