

# CHAPTER ONE

## INTRODUCTION

### 1.1 Background of the study

Energy is the prime mover for all developed and developing nations. Crude oil is the major global source of energy. However, its exploration has resulted in serious environmental pollution ranging from air, water and soil pollutions. One of the main sources of water pollution is crude oil spill. The result of crude oil activities leaves most of our surface water heavily contaminated with several pollutants including dissolved and dispersed oils. These pollutants pose threats to aquatic animals and make our soil infertile. Oil spill over the oceans and seas requires prompt attention due to their environmental and economic impacts (Annunciado *et al.*, 2005).

Whenever oil is produced, stored, transported, and used, there is a risk of spillage with the potential to cause adverse environmental impact (Hussein *et al.*, 2008). The spilt oil eventually contaminates the food chain and affects our health. Therefore, spilled oil causes enormous environmental problems unless it is removed as quickly as possible (Sayed and Zayed, 2006).

Oil pollution, particularly of sea and navigable water has elicited more public concern than other waste or spilt material. Oil pollution of the sea has steadily increased with the increased oil production. The total annual influx of petroleum hydrocarbon is about 10million metric tonnes. The bulk of this influx is due to transportation related activities, spillage from tanker unloading operation, pipeline rupture which may be due to industrial waste as leakage from engines, incorrect operation of valves and

discharge of oily waste (Hussein *et al.*, 2009). Oil pollution of the shorelines in addition to the reduction of amenity, also affects marine, shore life and vegetation.

Crude oil consists of different hydrocarbons that range from a light gas to heavy solid. When oil spills on water, the physical and chemical properties of oil change progressively i.e. these physico-chemical changes enhance oil dissolution in sea water (Sheet *et al.*, 2010). This process is referred to as weathering which includes evaporation, dissolution, adsorption onto suspended materials, agglomeration e.t.c (Alade *et al.*, 2011). The adverse impact of oil spill on the ecosystem and the long term effect of environmental pollution calls for an urgent need to develop a wide range of materials for cleaning up oil from oil impacted areas especially as the effectiveness of oil treatment varies with time, the type of oil and spill, the location and weather conditions (Adebajo *et al.*, 2003).

Large amount of agricultural waste (corn cob, corn husk, plantain peel, plantain pseudostem, bread fruit seed husk, borassus coir e.t.c) are produced in many countries of the world. However, many of these waste materials are not reused. One of the features of these organic materials is that it can absorb by capillary forces an amount of oil and/or water greater than it's own weight (Bodirlau and Teaca, 2009).

Furthermore, these natural materials can be completely degraded in nature by biological, physical, chemical and photochemical processes. (Tronc *et al.*, 2006).

In small scale spills, oil can be removed with a sorbent. The sorbent in use today can be classified as either polymers, natural materials, or treated cellulosic materials. (Deschamps *et al.*, 2003). Adebajo *et al.*, (2003) recently reviewed the porous materials used for spill cleanup, and several studies of different natural, synthetic and mineral sorbents have also been conducted (e.g Choi and Cloud, 1992;

Deschamps *et al.*, 2003; Tease *et al.*, 2001). Most recently used commercial sorbents are synthetic sorbents made of polypropylene or polyurethane (Tease *et al.*, 2001). They have good hydrophobic and oleophilic properties, but their non-biodegradability is a major disadvantage (Choi and Cloud, 1992, Deschamps *et al.*, 2003).

Since most oil products are biodegradable, oil could be disposed of for example by composting. A biodegradable material with excellent absorption properties would be advantageous in this respect. A number of natural sorbents have been studied for use in oil-spill clean-up e.g cotton (Choi and Cloud, 1992; Choi *et al.*, 1993; Choi, 1996), wool (Choi and Moreau, 1993; Choi, 1996; Radetic *et al.*, 2003), bark (Haussard *et al.*, 2003, Saito *et al.*, 2003), milkweed (Choi and Cloud, 1992, Choi, 1996) kapok,(Choi, 1996, Hori *et al.*, 2000) kenaf (Choi and Cloud, 1992, Choi; 1996) barley straw (Ibrahim *et al.*, 2009) olive waste (El-hamouz *et al.*, 2007), rice straw(Sun *et al.*, 2002). (Srinivasen and Viaraghvan, 2008),Most of them have better absorption capacities than synthetic ones, but they often sorb water well which is a disadvantage when used in marine environments (Wei *et al.*, 2005).

Nwadiogbu *et al.* (2015) studied the equilibrium and kinetic studies of the removal of crude oil from aqueous medium by sorption on hydrophobic corncobs. They observed that the sorption process occurred via a surface reaction and intra-particle diffusion mechanism. They further reported that the maximum monolayer sorption capacities were 0.0768mg/g and 0.0043mg/g for the acetylated and raw corn cobs respectively.

Sun *et al.* (2004) esterified sugar bagasse with acetic anhydride using N-bromosuccinimide as a catalyst under mild condition. The acetylation increased

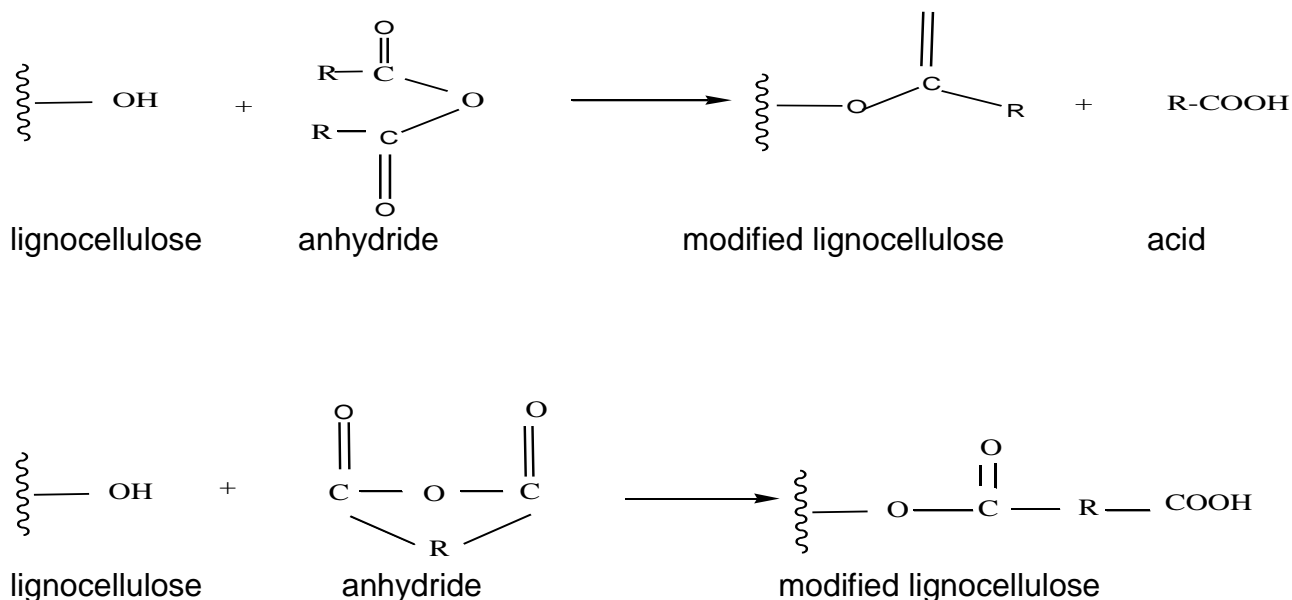
hydrophobic properties of the bagasse obtained at 80°C for 6 hours and was found to be 1.9 times better than the commercial synthetic sorbent.

Once plant derived sorbent are applied to saturated environments, preferential water sorption is naturally favored over the sorption of oil because the sorbents are typically hydrophilic in nature. Agricultural by-products have well documented problems with water sorption and lack of dimensional stability due to their associated hydroxyl functionality. These groups are abundantly available in all the major chemical components of plant-base materials are responsible for the hydrophilicity (Bordilau and Teaca, 2009).

The use of sorbents to clean-up oil spill presents many advantages due to simplicity of approach and the inexpensive nature of the materials (Chung and Vennosa, 2008). In addition, plant derived organic sorbents are biodegradable thus leaves no permanent residue. Agricultural by products can be considered polymeric composites made up primarily of cellulose, hemicelluloses and lignin (Kumar, 1994., Homan *et al.*, 2000). These polymers make up the cell wall and are responsible for most of the physical and chemical properties exhibited by these materials (Bordilau and Teaca, 2009).

Hydrophobicity (oleophilicity) is one of the major determinants of sorbent properties influencing the effectiveness of oil sorption in the presence of water. The effectiveness of the sorbents in natural environments would be enhanced if the density of the hydroxyl functionality is decreased (Bordilau and Teace, 2009). The hydroxyl functionality of these fibers can be reduced by chemical modification, such as acetylation, methylation, cyanoethylation, benzylation, acrylation and acylation. (Hofle *et al.*, 1978; Breitenbeck *et al.*, 1997; Sun *et al.*, 2004).

Acetylation reaction is one of the most common techniques employed for hydrophobic treatment of lignocellulosic materials (like wood) which involves a substitution reaction of a hydroxyl group (hydrophilic) into an acetyl group (hydrophobic) as shown in figure 1.1.



**Fig 1.1:** Scheme of Reaction of acetic anhydride with lignocellulose (Bodirlau and Teaca, 2009).

The reaction is usually carried out by heating lignocellulosic material in the presence of anhydride with or without catalyst (Rowel *et al.*, 1999). Various catalysts have been used for enhancing the efficiency of acetylation reaction. Pyridine and 4-dimethyl amino pyridine(DMAP) have been commonly applied for acetylation for many years (Hofle *et al.*, 1978). However, they are too toxic and/or expensive for commercial use. Sun *et al.*,(2004) reported that acetylation of sugarcane bagasse with N-bromosuccinimide (NBS) as catalyst in a solvent-free system was a convenient and effective method for enhancing the oil sorption capacity of the sorbent material. In addition, they claimed modified bagasse applied in oil-water

system presented an enhanced oil sorption capacity exceeding that of commercial synthetic sorbents.

## **1.2 STATEMENT OF PROBLEM**

When oil is spilt into the environment, it causes different kinds of pollution that have serious adverse effects on man, animals and plants. These adverse impacts to the ecosystems and the long term environmental pollution calls for urgent need to develop a wide range of material for clean-up of oil from impacted areas. Some of the problems that necessitated this study include

- 1 Loss of aquatic lives and arable land for farming to oil spills.
- 2 Crude oil pollution affects tourism, leisure activities and economy (due to loss in domestic use and export quantity).
- 3 High cost of oil clean-up processes due to high cost of imported synthetic sorbent materials.
- 4 Non-biodegradability of imported sorbent materials which further adds to the environmental problems.
- 5 Lack of adequate natural, inexpensive and biodegradable substitutes of synthetic sorbents
- 6 . Agricultural by-products have well documented problems with water sorption and lack of dimensional stability due to their associated hydroxyl functionality.

### **1.3 AIM AND OBJECTIVES OF STUDY**

The aim of this research is to acetylate selected agro-wastes (borassus coir, corn husk, African bread fruit seed husk, plantain peel and plantain pseudostem) and study their kinetics and application in crude oil spill clean-up.

Specifically, the objectives of this study are to:

1. Acetylate the five different agricultural waste materials.
2. Trial oil spill cleanup using the acetylated sorbent materials.
3. Determine the effect of acetylation on oil absorption capacity and structure of modified materials using Fourier transform infra-red (FT-IR) spectroscopy and scanning electron microscopy (SEM) respectively.
4. Determine the kinetics of acetylation and crude oil sorption with their mechanisms.
5. Statistical determination of significant variables involved in oil sorption which includes time and catalyst concentration.

### **1.4 SCOPE OF STUDY**

The study covered the chemical modification by acetylation of borassus coir, corn husk, African bread fruit seed husk, plantain peel and plantain pseudostem. It's subsequent trial in oil spill cleanup application. Techniques used in the study are Fourier transfer-infrared spectrometry, X-ray fluorescence, Scanning Electron Microscopy and gravimetry.

These techniques helped in determination of structural changes, extent of acetylation, elemental and physical composition of the materials, the spatial variation in chemical composition of the materials and oil sorption capacity, the external morphology and orientation of materials making up the sample. Variables (time and concentration) used enabled the investigation of the mechanism and kinetics of reaction. Statistical tools used enabled the determination of the statistical differences.

## **1.5 SIGNIFICANCE OF THE STUDY**

In riverine areas of Nigeria, especially where petroleum exploitation activities are taking place, most of the water bodies are polluted with oil resulting from either pipeline vandalization, or accidental discharge of oil during extraction, distribution, storage or usage. These areas are adversely impacted by oil spillage which has a great influence on the ecosystem by putting the marine and human lives at high risk.

The treatment/clean-up process employed by the oil companies are not very effective or sometimes dangerous to the aquatic life and affect the food chain (Mario, 2000). Therefore, there is an urgent need to develop a wide range of materials for cleaning up oil from oil impacted areas.

Absorbent materials are attractive for some applications because of the possibility of collection and removal of the oil from the oil spill site. The possibilities of cleaning oil pollution by sorbent on the basis of fibers, polymers and wood products, however, have not yet been sufficiently investigated, (Nwadiogbu, 2014)



No known or recorded work has been done on the acetylation of corn husk, plantain peel, African breadfruit seed husk, plantain pseudostem, and borassus coir and their application in oil spill cleanup.

The potential contribution of this research to existing knowledge includes:

1. Conversion of undervalued and neglected agricultural waste residues such as corn husk, African bread fruit seed husk, plantain peel, plantain pseudostem and borassus coir to valuable sorbents for oil spill clean-up which has the potential of providing economic incentives.
2. Treatment of oil-spill polluted water resources, thereby conserving the natural mangroves, water supply and reduce the incidence of forest wild fires which results from accumulated crude oil residues
3. Application of the chemistry of the modification (acetylation) procedure and the kinetics of oil sorption in the development and improvement of the agro-based residues for several other applications.
4. To substitute the expensive synthetic sorbent materials used in removal of oil from oil-spill polluted water with relatively cheaper agro-wastes as natural organic sorbent materials.
5. Converting waste to wealth through the use of agro-waste which before now were allowed to waste away in the treatment of oil polluted water and for employment generation.
6. Reduction of over dependence on imported synthetic sorbent materials which will increase our local content in the downstream sector.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1. OIL SPILLAGE

Oil spills are leakages or spillage of petroleum and their byproducts into the environment particularly onto the surface of large water bodies such as oceans, lakes and rivers as a result of human activities. For this reason, oil spill is regarded as a form of pollution as the term is mostly applied to define spillage of oil in marine systems. Oil spill may occur on land as well, but the most documented incidences are those that happen in marine areas. It is a global issue that has been occurring since the discovery of crude oil, which was part of the industrial revolution. Oil spills constitute a menace in any place where it occur and have been a source of serious concern for people and governments (Oyinloye *et al.*, 2013).

Pollution by crude oil affects the sea, economy, tourism and leisure activities because of the coating properties of these materials. Oil spill harm the beauty of polluted sites; the repulsive odour can be felt miles away (Annunciado *et al.*, 2005).

The extent of risk of oil spill is dependent on the type and volume of the oil in addition to other abiotic factors such as the sensitivity limit of the marine habitat (Jamalin *et al.*, 2013). Furthermore, the nature and magnitude of oil spills on water habitat depends on the rate of water flow and the habitat's specific characteristics. Where there is proximity of high density human population, when these spills occur, human health and environmental quality are put at high risk (Frost *et al.*, 2007). Oil pollution of the shore, in addition to the reduction of amenity, also affects marine, shore life and vegetation (Wardley, 1983).

## **2.2 Nature of Crude Oil**

Crude oil is a dark yellow to black oily liquid that is usually found in natural underground reservoirs. It is a mixture of variety of constituents and a complex combination of hydrocarbons, which are chemicals composed of hydrogen and carbon. It consists predominantly of aliphatic, alicyclic and aromatic hydrocarbons. Crude oil contains hundreds of substances that include benzene, chromium, iron, mercury, nickel, nitrogen, oxygen, sulphur, toluene, xylene and polynuclear aromatic hydrocarbons (Smith, 1983).

Crude oil is a known teratogen and can cause birth defects and changes in fetal development. The target organs for crude oil are the hematopoietic (blood forming) system, lymphatic system, nervous system and the reproductive system. The benzene component is a known carcinogen (Kano *et al.*, 1990).

Crude oil is not readily biodegradable and the effects of exposure to these toxins will be felt not only acutely, but from generation to generation. Children and pregnant mothers are at significant risk. There are a number of toxic compounds which are of

great concern since they are present in significant quantities within the crude oil (Mobbs, 1996). Some of them are discussed below.

- a. Benzene:** It is highly volatile, colourless, flammable liquid with a sweet odour. Benzene is recognized as a human leukamogen and is found in air, water and soil. It comes from both industrial and natural sources. The major sources of benzene in water are atmospheric deposition, spills from petroleum and other petroleum products, chemical plant effluents, industrial discharge. Benzene enters the body through inhalation of the vapour, absorption through the skin or ingestion. The adverse health effect of benzene depends on the route, duration and dose of exposure. Human and animal studies indicate that benzene is harmful to the immune system, increasing the chance for infections and perhaps lowering the body's defense against tumor (Mobbs, 1996 ). When benzene is inhaled, it irritates the lining of the airways. Chronic exposure can cause a serious bone marrow disorder called pancytopenia (Vendrel, 1993). This causes chronic anaemia and increase risk for serious infections.
- b. Toluene:** It is a major component of crude oil. It can enter surface and underground water from spills of solvents and petroleum products and from leaking underground storage tanks. The central nervous system (CNS) is the primary target organ for toluene toxicity in both humans and animal for acute (short term) and chronic (long term) exposures (USEPA, 2004). Teratological and epidemiological evidence relating toluene exposures to reproductive issues have been reported (Louise, 1997; Bukowski, 2001). Effects on fertility such as abortion were reported in rabbits by inhalation. Several studies have

shown toluene to be a developmental toxicant in rodents (Vee Gee Scientific, 2004).

### **c. Polynuclear Aromatic Hydrocarbons (PAHs)**

PAHs are a group of chemicals that occur naturally in coal, crude oil and gasoline and are also present in products made from fossil fuels. PAHs are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms (Tedesco 1985). They are ubiquitous pollutants formed from the combustion of fossil fuels and are always found as a mixture of individual compounds (WHO, 1998).

The PAHs that are present in the marine environment in relevant concentrations are divided into two groups depending on their origin, namely pyrogenic and petrogenic. (Mascarelli, 2010).

PAHs represent the group of compounds in oil that has received the greatest attention due to their carcinogenic and mutagenic properties (White, 1986).

PAHs can persist in the environment for many years. In some cases, continuing to harm the organisms long after the spill. They are absorbed through ingestion, inhalation and dermal contact according to animal study.

Once absorbed, it enters the lymph, circulates in the blood, and are metabolized primarily in the liver and the kidney (Aguilera *et al.*, 2010)).

Health effects from chronic or long term exposure to PAHs may include decreased immune function, cataract, kidney and liver damage, breathing problems and lung function abnormalities. (Collins *et al.*, 1998).

### **Cresols**

Cresols are organic compounds which are methyl phenols. It occurs as a natural component of crude oil, coal tar and even in plants. In humans, cresol

ingestion results in burning of the mouth and throat, abdominal pain and vomiting. The target organs of ingested cresols in human are the blood and kidneys, and effects in heart and CNS have been reported.(Goldfrank, 2011).

### **2.3 Causes of Oil Spill**

Oil spills may originate in many ways especially through natural or anthropogenic causes.

**Natural causes** - such as oil that seeps from the bottom of oceans which enters the marine environment. Crude oil is formed during long periods of time through natural processes involving organic matter from dead organisms. Thus, oil exists in many environments and may be naturally spilled due to various factors (including climatic conditions, disturbance, etc.). Such natural oil spills may occur in oceans, due to eroding of sedimentary rocks from the bottom of the ocean (Marine spill response Corp, 1994).

**Anthropogenic causes** - including accidental oil spills as well as leaks and spills due to a large variety of human activities related to oil refining, handling and transport, storage and use of crude oil and any of its distilled products(Yender, 2002). The most commonly encountered anthropogenic sources are the following:

**Accidental Spills;**Accidental spills may occur in various circumstances, most often during the following activities:

- i. *Storage* - oil and oil products may be stored in a variety of ways including underground and aboveground storage tanks. Such containers may develop leaks over time.

- ii. *Handling* - during transfer operations and various uses.
- iii. *Transportation* - these could be large oil spills (up to million and hundreds of million gallons) on water or land through accidental rupture of big transporting vessels (e.g., tanker ships or tanker trucks).
- iv. *Offshore drilling* –there has been massive oil spill in the Gulf of Mexico, with its terrible consequences on the environment, marine life and humans.
- v. *Routine maintenance activities* - such as cleaning of ships may release oil into navigable waters. This may seem insignificant; however, due to the large number of ships even a few gallons spilled per ship maintenance could build up to a substantial number when all ships are considered.
- vi. *Road runoff* - oily road runoff adds up especially on crowded roads. With many precipitation events, the original small amounts of oil from regular traffic would get moved around and may build up in our environment(Ross, 2002).

### **Intentional Oil Discharges**

Intentional oil discharges are not necessarily malevolent. Most of them occur in the following circumstances:

- i. Through drains or in the sewer system. This include any regular activities such as changing car oil if the replaced oil is simply discharged into a drain or sewer system
- ii. Indirectly through the burning of fuels, including vehicle emissions; they release various individual components of oils and oil products, such as a variety of hydrocarbons (out of which benzene and PAHs could pose health risks).

## 2.4 Effects of Oil Spill

The effects of oil spills reach far beyond the location of the original spill. Within a short period of time even a small spill can impact miles of habitat. The effects reach much farther than the ocean, and it is more than just the animals that are affected. From the economy to the ecosystem, oil spills disrupt lives. Some of the adverse effects are highlighted below.

**a. Environmental Effects:** The animal that lives in the water or near the shore are the ones most affected by the spill. In most cases, the oil simply chokes the animals to death (Mario, 2000). Others that live face a number of other problems. The oil works its way into the fur and plumage of the animals. As a result, both birds and mammals find it harder to float in the water or regulate their body temperatures.

Many baby animals and birds starve to death, since their parents cannot detect their natural body scent. Birds that preen themselves to get rid of the oil accidentally swallow the oil and die due to the toxic effects. (Kingston, 2002).

**b. Effect on Economy:** The second major effect of the oil spill is seen on the economy. When crude oil or refined petroleum is lost, it affects the amount of petroleum and gas available for use and for export. Then comes the process of cleaning the oil spill, which requires a lot of financing.

**c. Effect on Tourism Industry:** The local tourism industry suffers a huge setback as most of the tourists stay away from such places. Dead birds, sticky oil and huge tarballs become common sight. Due to this, various activities such as sailing, swimming, rafting, fishing, parachute gliding cannot be performed.



**d. Effect of Spills on Wildlife:** Probably one of the areas of greatest concern is the effect of the oil spill on wildlife. From the smallest plankton to the largest whale, all marine life is impacted by an oil spill. Plankton is not only a habitat for fish eggs and larvae, but is also the main diet of many ocean creatures. Without this basic organism, the entire ecosystem can be thrown off. (Valera *et al.*, 2006). Many seabirds dive for their food. Often, they must dive through a layer of oil to get to the fish they eat. This leaves the oil residue on their feathers, which can cause numerous problems. When the birds attempt to preen, or clean themselves, they ingest the oil, which is toxic. (O'Brian and Dixon 1976).

## **2.5 Oil Spill Clean Up Procedures**

Oil spill can be extremely hazardous and environmentally threatening, and therefore needs to be contained and cleaned up as soon as possible. These serious environmental consequences have long been recognized and considerable research and technological development has been carried out to develop appropriate remediation techniques (Ventikos *et al.*, 2004., Sun *et al.*, 2004). Many variables can directly and indirectly affect the cleanup response which include water temperature, size of spill, duration of time of clean up, wind speed, resources and habitats at risk, economics at risk, public interest, responsible party, and availability of funds to carry out a successful operation.

Understanding the risk of potential spills will help to create a universal plan for management and operational tasks for events in sensitive areas. The volume of oil

spilled and the type of petroleum involved have a direct correlation with the risk involved.

Decision regarding cleanup methods must balance two factors; which are the potential environmental impact with the no-action alternative and the potential environmental impact associated with a response method or group of methods. Some of the major methods for cleaning oil spills are highlighted below:

### **2.5.1 Mechanical Spill Response**

Mechanical oil spill response uses physical barriers and mechanical devices to redirect and remove oil from the surface of the water. It is the transfer of oil from water surface to some transportable form of temporary storage by the help of booms to contain or divert oil, skimmers or sorbents to recover or remove it from the water surface, hoses and pumps. Performance of any of these equipment however can be severely limited by oceanic conditions and weather, including current, waves, winds and by the nature of the oil slick (National Research Council, 1985). The major limitations of some of these techniques are their high cost and inefficient trace level adsorption (Wei *et al.*, 2005). A principal factor in removing oil expeditiously and effectively by mechanical means is the thickness of the oil spill. The rate of oil recovery by any mechanical device decreases with decreasing oil thickness. Thus rapid response with co-ordinated use of oil containment booms, skimmers, transfer pumps, temporary storage and auxiliary craft all deployed and operated by a skilled team of men is what is required for the recovery to be successful (Eba *et al.*, 2010).

Use of sorbents is another effective method used to recover oil through the mechanisms of absorption, adsorption or both. Absorbents allow oil to penetrate into

pore spaces in the material they are made of, while adsorbents attract oil to their surfaces but do not allow it to penetrate into the material. To be useful in combating oil spills sorbents need to be both oleophilic and hydrophilic. Although they may be used as the sole clean up method in small spills. Once sorbents have been used to recover oil, they must be removed from the water and properly disposed on land or cleaned up for reuse (Lessard *et al.*, 2000).

Sorbents can be divided into three basic categories; natural organic, natural inorganic and synthetic. Natural organic sorbents include peat moss, straw, hay, sawdust, ground corn cobs, feathers and other carbon based products. They are relatively inexpensive and usually readily available. Natural inorganic sorbents include clay, perlite, glass, wool, sand and volcanic ash. Synthetic sorbents include man-made materials that are similar to plastics such as polyurethane, polyethylene and nylon fibers. Some factors that must be considered before choosing sorbents for cleaning up spills are rate of absorption, oil retention, ease of application (Kemsley, 2012).

### **2.5.2 Chemical Methods**

Chemical methods have been used extensively in many parts of the world, and they have been successfully employed in response to several oil spills. This method is generally approved for spills at least 5KMs from shore and in water at least 10M deep, where dispersed oil's impact on marine life is likely to be low (Ventikov *et al.*, 2004). Chemical method involves the use of dispersants, sinking agents, demulsifier, gelling agents and neutralizing agents.

Dispersants act by reducing the surface tension that stops oil and water from mixing. Small droplets of oil are then formed, which helps promote rapid dilution of the oil by water movements. The formation of droplets also increases the oil surface area, thus increasing the exposure to natural evaporation and bacteria action (Cormack *et al.*, 1987).

Sinking agent is a material that is spread over the surface of an oil slick to adsorb oil and cause it to sink. Common sinking agents include treated sand, fly ash, china clay, coal dust, brick dust and cement (Fingas, 2000). These materials are rarely used, because they provide a purely cosmetic approach to oil spill cleanup and may cause considerable damage to bottom-dwelling organisms. Also emulsion breakers and neutralizing agents are also used. Other methods include in-situ burning, phytoremediation, bioremediation and others (Hoff, 1993). Bioremediation is the acceleration of the process of biodegradation through the addition of exogenous microbial population, through manipulation of the contaminated media using techniques such as aeration or temperature control (Atlas, 1995., Swanellet *al.*, 1996). Phytoremediation can also be used which is the use of plants and their associated microorganisms for remediation. (Fingas and Charles, 2001).

## **2.6 Sorbents for Oil Spill Clean Up**

Sorbents are substances that have the property of collecting molecules of another substance by sorption. They have a significant capacity for oil recovery from the surface of the sea with minimum harmful effects on ecosystems, and a low price. Sorbents recover the spilled oil by either adsorption or absorption mechanism. Adsorption is the distribution of the adsorbate over the surface of the adsorbent, while absorption is the distribution of the absorbate throughout the body of the

absorbent (Jin *et al.*, 2016). Hydrophobicity and oleophilicity are the most important properties of a sorbent to be considered in oil spill cleanup. (Abdullah *et al.*, 2010).

At small scale oil spill, sorbents are good agents to remove the oil from water. The use of different types of sorbents for the recovery of the oil from water surface depends on its ability to change form from oil liquid phase into semi-solid or solid phase (Doerffer, 1992., Adebajo *et al.*, 2003). When widely used in spill response, sorbents should be employed with caution to minimize inappropriate and excessive use that can present major logistical difficulties associated with secondary contamination, retrieval, storage and disposal. (Smith, 1983).

## **2.7 Sorbent Types**

A wide variety of materials can be used as sorbents. Sorbents can be either natural organic, natural inorganic, synthetic sorbent or even a mixture of two or all (Bayat *et al.*, 2005; Frost *et al.*, 2007).

### **2.7.1 Natural Organic Sorbents**

They are natural sorbents that contain carbon. This include peat moss, sawdust, feathers, paper pulp, bark, bagasse ( the waste product from processing sugar cane), cork, straw, wool, human hair, wood fibres, kenaf, corncob and other readily available carbon based products (Likon *et al.*, 2013 ). Organic sorbents can adsorb between 3 to 15 times their weight in oil. Some organic sorbents tend to adsorb water as well as oil, causing the sorbents to sink. Many of them are loose particles and are difficult to collect after they are spread on the water. These problems can be counterbalanced by adding floatation devices. They are relatively inexpensive and

generally readily available. Also plant derived organic sorbents are biodegradable thus leaves no permanent residue(Choi and Cloud,1992).

### **2.7.2 Natural Inorganic Sorbents**

Many natural organic sorbents exist as loose material. They consist of clay, perlite, vermiculite, glasswool, sand and volcanic ash. They can adsorb from 4 to 20 times their weight in oil. They are inexpensive and readily available in large quantities. These types of sorbents are not used on the water surface. These materials do not show adequate buoyancy retention, and their oil sorption capacity is generally low.

### **2.7.3 Synthetic Organic Sorbents**

This includes man made materials that are similar to plastics such as polyurethane, polyethylene, polypropylene and nylon fibres. They are designed to adsorb liquid onto their surfaces. Other synthetic sorbents include cross-linked polymers and rubber materials, which absorb liquids into their solid structure, causing the sorbent material to swell (Teaseet *al.*, 2001). Most synthetic sorbents can absorb up to 70 times their own weight in oil (Adebajo and Frost,2004 ).

Typically, the low density (less than  $1.0\text{g/cm}^3$ ) of the synthetic sorbent allows it to float on water. They are the most commonly used commercial sorbent in oil clean-up because of their oleophilic and hydrophobic characteristics. Some types can be cleaned and reused several times. However, their non-biodegradability is a major disadvantage (Schrader 1993).

## **2.8 Modification of Natural Sorbents for Oil Spillage Treatments**

Use of agricultural wastes both raw and modified as an abundant and low cost adsorbent for oil products spill cleanup has been developed to control these spills. They are inexpensive, locally and readily available. Their relatively high sorption capacity and biodegradability and the fact that they are more economical makes these natural sorbents particularly attractive as possible alternatives to synthetic fibers (Radetic *et al.*, 2008).

All these materials function in different degrees in oil sorption by virtue of their having oleophilic surfaces because of their waxy nature and they trap oil in the mat of crisscross strands of fibres rather than by actual capillarity (Zhang *et al.*, 2001). However, most of these materials absorb water slowly so that if fibres are left lying in water, they will gradually float over and may finally sink altogether. They also have poor buoyancy characteristics, relatively low sorption capacity and low hydrophobicity. Fortunately, this defect can be changed by chemical modification. Numerous researchers have made significant modifications of natural sorbents to improve their sorption capacity (Artemiev and Pinkin, 2008).

Chemical modification of plant or wood materials to improve their dimensional stability has been the subject of research for many years. A wide variety of chemicals have been studied including anhydrides, acid chlorides, carboxylic acids, isocyanates, acetals, esters, acetyl chloride, B-propiolactone, acrylonitrile and epoxides. Cellulosic sorbents have been chemically treated (Sun *et al.*, 2005) and research into the use of their modified products as absorbents for the removal of crude oil from aqueous solutions have been on increase (Okoro *et al.*, 2007b). Adebajo and Frost (2004b) studied the acetylation of cotton in order to develop hydrophobic, biodegradable cellulosic material for subsequent application for oil spill

cleanup. Okoro and Ejike (2007) discussed and investigated the chemical modification of cellulose and its sorption model as crude oil sorbents, using treated wood pulp. The procedure was carried out using toluene di-isocyanate and benzoyl chloride in the presence of 10% ethanolic sodium hydroxide as catalyst, to show increased sorption capacity of the modified cellulose. Nwadiogbu *et al.*, (2015) investigated the chemical modification of corncobs using acetic anhydride in the presence of N-bromosuccinimide as a catalyst. They observed that the oil sorption capacity of the corncob was substantially enhanced.

Several natural organic sorbents have been studied for the removal of oil spill e.g. raw sugarcane bagasse (Hussein *et al.*, 2008; Said *et al.*, 2009; Brandao *et al.*, 2010), raw and fatty-acid grafted sawdust for oil (Banerjee *et al.*, 2006) and other pollutants (Shukla *et al.*, 2002), black and white rice husk ash (Vlaev *et al.*, 2011), barley straw (Hussein *et al.*, 2009), banana trunk fibers. (Sathasjvam and Haris, 2010), acetylated sugarcane bagasse (Chung *et al.*, 2001; Sun *et al.*, 2003), Carbonized peat bagasse (Hussein *et al.*, 2008), Peat-based Sorbents (Cojocaru *et al.*, 2011), hydrophobic aerogels for emulsified oil (Wang *et al.*, 2010), acetylated corncob and mango kernel (Nwadiogbu *et al.*, 2014 ). The most studied of all the chemical modification chemistry is acetylation. Even though several studies have been performed in this area, more research is still required. In the current study, the performance of five natural organic sorbents, namely African breadfruit seed husk, borassus coir, plantain peel, plantain pseudostem and corn husk in oil sorption were investigated.

## **2.9 Acetylation of Natural Sorbents**



Acetylation is a chemical reaction that is called ethanoylation in the IUPAC nomenclature. It describes a reaction that introduces an acetyl functional group into a chemical compound. The process of introducing an acetyl group results in an acetoxy group. It involves the substitution of an acetyl group for an active hydrogen atom. A reaction involving the replacement of the hydrogen atom of a hydroxyl group with an acetyl group (CH<sub>3</sub>CO) would then yield a specific ester, the acetate. Acetic anhydride is commonly used as the acetylating agent reacting with the free hydroxyl groups. In the acetylation of natural fibres, the product obtained contains acetyl groups bonded to the hydroxyl(OH) sites in wood cell wall. It has been shown that the rate of reaction is diffusion dependent with rapid reaction of the anhydride molecule with the cell wall polymer OH site (Hill *et al.*, 1998). Reaction can be increased by raising the temperature and using catalysts. The extent of acetylation of acetic anhydride with wood is invariably reported as acetyl weight percent gain (WPG) (Hill, 2006).

The weight percent gain (WPG) was determined by gravimetric method as described by Thompson, Emmanuel, Adagadzu, and Yusuf (2010); Azeh, Olatunji, Mohammed, and Mamza (2013). It was calculated on the basis of oven-dried unreacted sorbent (DRPs) fibers. The dried sorbent obtained were reweighed to determine the weight gain on the basis of initial oven dry measurements. Weight percent gain (WPG) of the sorbent due to acetylation was calculated using the expression

$$\text{WPG (\%)} = \frac{\text{Weight gain}}{\text{Original weight}} \times 100 \quad 2.1$$

Although the reaction can take place using ketene, acetic acid or acetic chloride, the most useful process is acetylation due to reaction with acetic anhydride.



In this reaction acetic acid is produced as a by-product and it is important to remove this as well as unreacted anhydride at the end of the reaction. CELL-OH represents the hydroxyl site of the cellulosic natural sorbents (Tapio *et.al.*, 1994).

### 2.9.1 Wood Swelling due to Acetylation

Wood is swollen by acetylation because the chemically bonded acetyl groups occupy space within the cell wall. Invariably, the swelling is determined by measuring the external dimensions of oven dry wood samples before and after modification. The swellability of wood is calculated thus:

$$S(\%) = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100 \quad 2.3$$

Where S is the swellability,  $W_{\text{wet}}$  is the wet weight of the sample after soaking in water;  $W_{\text{dry}}$  is the oven dry weight after soaking.

### 2.9.2 Dimensional Stability

When wood is acetylated, it is far less susceptible to shrinking and swelling in the presence of varying atmospheric conditions. The reason for this is simply because the cell wall is now filled with chemically bonded acetyl groups in swollen conditions, the extent of which depend upon the level of modification. There is very little residual swelling when wood is soaked in water. A very common method is the method of Rowell and Ellis, (1978), which is to soak the wood for five days in water and determine the swellability. Although this is a useful determination of the dimensional stability, a much better indicator is the anti shrinking efficiency (ASE) determined as shown in equation 2.4.

$$\text{ASE} = [(S_0 - S/S_0) \times 100]$$

2.4

$S_0$  = Volumetric swelling of untreated samples and  $S$  = Volumetric swelling of treated samples

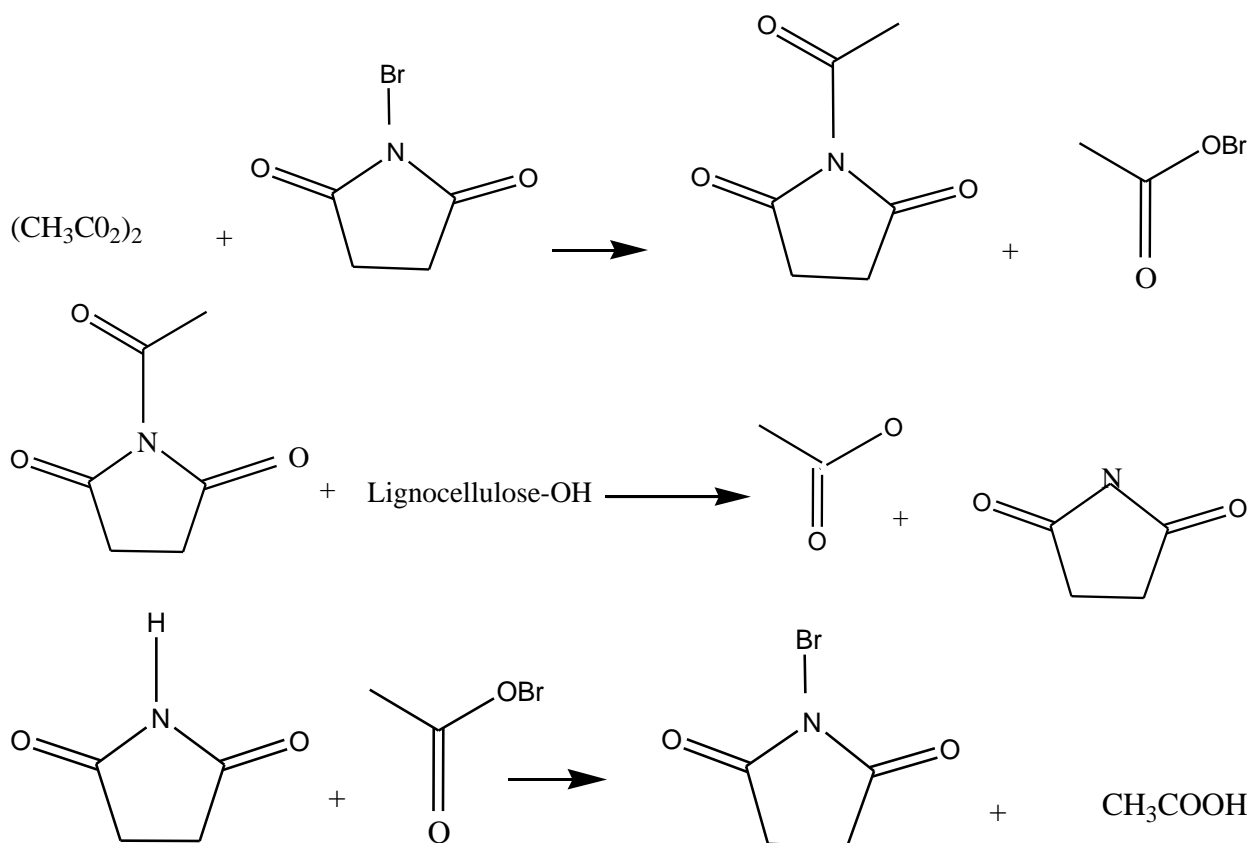
### 2.9.3 Catalysts for Acetylation

The inability of acetic anhydride to acetylate natural fibres has received much attention from different research workers. It can be assumed that the energy of interaction between acetic anhydride and cellulose in the absence of a catalyst is insufficient to weaken the intermolecular action in cellulose. A large number of substances have been proposed as catalyst for acetylation, of these, sulphuric acid and perchloric acid in cellulose acetylation was studied by measuring the conductivity of acetylation mixtures, with or without catalysts. The early work was done using acetic anhydride to catalyze with either zinc chloride (Ridgway and Wallington, 1946) or pyridine. Through the years, many other catalyst have been tried both with liquid and vapour systems. Some of the catalysts used include urea-ammonium sulphate, dimethyl formamide, sodium acetate, magnesium persulfate, trifluoroacetic acid, boron trifluoride and  $\gamma$ -rays. For many years, 4-dimethylamino pyridine (DMAP) has been used as an acetylation catalyst in chemical synthesis.

Sun *et al*, (2004), also demonstrated that acetylation of free hydroxyl groups in rice straw with acetic anhydride without solvent provided a suitable and effective method for the preparation of rice straw acetate that have a more hydrophobic characteristics and high sorption capacity. The reaction was performed at different reaction times and temperatures in the presence of different catalysts. Among the different catalyst used, 4-dimethyl amino pyridine was found to be the most effective. Compared to

pyridine, DMAP in chemical synthesis was found to be approximately over ten times more active when used as acylation catalyst (Hofle *et al.*, 1978). DMAP is too expensive and is not a commercially available reagent, which limits its industrial use. However from the standpoint of green and sustainable chemistry, another approach to create cleaner and more selective catalytic systems for the organic transformations has become increasingly important in recent years (Karimi and Zareyee, 2008). More recently, based on the study of acetylation of alcohol under mild reaction condition, Karimi and Seradi (2001) reported that N-bromosuccinimide (NBS) is an inexpensive and commercially available reagent and is a novel and highly effective catalyst for the acetylation of free alcohols under mild conditions. Karimi and Zareyee (2008) introduced N-bromosuccinimide (NBS) as a mild and nearly neutral electrophilic catalyst for a variety of functional group transformations such as acetalization and acylation of carbonyl compounds, acetylation of alcohols, de-oxygenation of sulfoxides and deprotection of 1, 3-oxatioacetals. Sun *et al* (2004) successfully carried out the acetylation of sugarcane bagasse using NBS as new catalyst in the presence of acetic anhydride under solvent free system. The modification with acetic anhydride substituted the hydroxyl groups modifying the properties of these polymers so that they become hydrophobic. Fourier Transform Infrared (FTIR) and solid state carbon 13 nuclear magnetic resonance (NMR) spectroscopy were used to investigate the acetylation reaction. The acetylated products using NBS were able to absorb almost 20 times their weight.

#### **2.9.4 Chemistry of Acetylation**



**Fig 2.1: Reaction Mechanism for Acetylation using N-Bromosuccinimide as Catalyst**

The mechanism is one of free radical reactions. The first step involves the reaction of NBS with acetic anhydride to produce a strong acetylating agent. The homolytic cleavage of the N-Br bond generates a Br radical, which abstracts a radical group from the acetic anhydride (fig 2.1).

The acyl carbon centre of the acetyl group forms an acetyl succinimide, which is a very reactive and unstable acetylating agent, with the nitrogen radical of the succinimide. The second stage involves a nucleophilic attack on the acyl carbon centre of the acetylating agent by a lone pair of the hydroxyl group followed by the subsequent reduction of the acetylating agent to succinimide and thus generating the lignocellulosic acetates. In the third stage, the succinimide produced reacts with the brominated acetate group produced in step-1, resulting in the loss of acetic acid and the regeneration of the NBS. The acetates are washed with excess acetone and

ethanol to remove the by-products acetic acid, NBS and the unreacted acetic anhydride.

### 2.10.1 Kinetic Considerations

The Kinetics was studied by fitting obtained data in rate curves of first order, second order (Hill *et al.*, 1998), pseudo second order (Ho, 1995), intra-particle diffusion and liquid diffusion models.

Pseudo- first order equation used can be derived thus;

$$\text{Rate of acetylation (R}_1\text{)} = \frac{d\theta}{dt} = -k_1\theta \quad (3.13)$$

Rearranging equation 3.13 gives 3.14

$$-\frac{d\theta}{\theta} = k_1 dt \quad (3.14)$$

Solution can be obtained by integrating equation 3.14 as follows

$$\int_{\theta_0}^{\theta_t} -d\theta/\theta = k_1 \int_0^t dt \quad (3.15)$$

Solution to equation 3.15 is

$$-[\ln\theta] = k_1 t \quad (3.16)$$

Rearranging equation 3.16, gives the required pseudo-first order equation used

$$\ln\theta_t = \ln\theta_0 - k_1 t \quad (3.17)$$

Oils are transported from the aqueous phase to the surface of the adsorbent and subsequently they can diffuse into the interior of the particles if they are porous. When the transport of the adsorbate from the liquid phase up to the solid phase

plays a significant role in the sorption, liquid film diffusion may be applied. Equation representing liquid film diffusion kinetics is Taffarel and Rubio (2009);

$$\ln (1-F) = -K_{fd} \cdot T \quad (3.18)$$

Where F is the fractional attainment of equilibrium ( $F = qt/q_e$ ) and  $K_{fd}$  is the rate constant.

**Table 2.1 Linear forms of Kinetic Models used**

Type	Linear form	Plot	Parameters
First-order Kinetics	$\ln \theta_t = \ln \theta_0 - k_1 t$	$\ln \theta_t$ vs $t$	$K_1 = \text{Slope}$ , $\theta_0 = \ln^{-1} \text{Intercept}$

Hill second order Kinetics	$i/\Theta_t = i/\Theta_0 - k_2 t$	$i/\Theta_t$ vs $t$	$\Theta_0 = 1/\text{Intercept}$ $K_2 = \text{slope}$
Pseudo Second order Kinetics	$t/\Theta_t = 1/k^2 + \Theta_0^2 + 1/\Theta_0 t$	$t/\Theta_t$ vs $t$	$\Theta_0 = 1/\text{slope}$ $K^2 = \text{slope}$
Intra-particle Diffusion	$\Theta = K_d t^{1/2} + C$	$\Theta$ vs $t^{1/2}$	$K_d = \text{Slope}$ $C = \text{Intercept}$
Liquid Film Diffusion	$\ln(1-F) = -k_{fd} \cdot t$	$\ln(1-F)$ vs $t$	$K_{fd} = \text{slope}$

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## 2.10.2 Sorption Isotherm

The Langmuir and Freundlich isotherms were used to describe the adsorption phenomena. The Langmuir isotherm is based on the assumption that adsorption occurs uniformly on the active sites of the sorbent. (Miretzky et al., 2010). In addition, once an adsorbate occupies a site, no further sorption can occur at that site (Nwadiogbu et al., 2015). The linear form of the Langmuir model can be expressed as:

$$C_e/q_e = 1/q_0 b + C_e/q_0 \quad (3.19)$$

Where  $q_0$  is the equilibrium monolayer adsorption capacity of the adsorbent (mg/g),  $b$  is the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate



and  $q_0$  is the maximum monolayer adsorption capacity of the adsorbent (mg/g). The  $q_0$  and  $b$  constants can be determined from a linear plot of  $C_e/q_e$  as a function of  $C_e$ . The essential feature of Langmuir isotherm can be expressed in terms of a dimensionless constant (i.e. the separation factor  $R_L$ ), which is defined by the following relationship (Langmuir, 1918).

$$R_L = \frac{1}{1 + bC_0} \quad (3.20)$$

Where  $C_0$  is the initial concentration of crude oil in mg/L. The separation factor provides information regarding the nature of the adsorption process. The adsorption can be considered irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), and unfavourable ( $R_L \Rightarrow 1$ )

The second model applied is the Freundlich isotherm model. This has been applied to non-ideal sorption on heterogeneous surfaces, and the linear form of this equation can be expressed as (Dawodu and Akpomie, 2014):

$$\ln q_e = \ln k_f + (1/n) \ln C_e \quad (3.21)$$

where  $k_f$  (mg/g)  $(\text{mg/L})^{1/n}$  and  $1/n$  are the Freundlich adsorption capacity and the intensity of the adsorbents respectively. The constants were determined from the intercept and slope of the linear plot of  $\ln q_e$  as a function of  $\ln C_e$ .

### 2.11.1 Availability of Corn Husk as Agro Based Sorbent

Corn (Maize) is a major food crop in many parts of the world. In Nigeria, corn is processed to a variety of diets used for weaning. It is a major component of animal feeds and is consumed by many Nigerians as snack, either boiled or roasted (Bolanle and Alhassan, 2012). According to Food and Agriculture (FAO) data, 589

million tonnes of maize was produced worldwide in the year 2000 (FAO, 2005). The United States was the largest maize producer having about 43% of the world's production. Africa produced about 7% of the world's maize (IITA, 2002). The maize plant comprises of the stalks, husks, shanks, silks, leaf blades, leaf sheaths, tassels and cobs (Bolanle and Alhassan, 2012).

Husk (or hull) is the outer shell or coating of a seed and refers to the leafy outer covering of an ear of maize (corn) as it grows on the plant. Corn Husks are the outside green leaves on a cob of corn that we usually peel off and discard after harvesting (Nwamma 2009). Corn husk forms about 30% of maize agro wastes of which application in biofuels industry are the focus of many researchers aimed at achieving an effective waste management scheme (Bolanle and Alhassan, 2012). This cornhusk is always readily available especially around August to November, when corn is being harvested. It contains varying percentages of cellulose, hemicelluloses and lignin.

### **2.11.2 Availability of African Breadfruit Seed Hull as an Agro Waste**

*Treculia africana*, the African breadfruit, is a tree species of the genus *Treculia* used as a food plant. The fruits are hard and fibrous and can be the size of a volleyball with weight up to 8.5 kg. Many names are given to this species, but the native/Ibo name is "ukwa", while it is called *afon* in Yoruba, *izea* in Ijaw, *ize* in Benin and *ediang* in Efik.

African breadfruit seed husk is a typical waste biomass or plant residue. They have relatively large surface areas that can provide intrinsic adsorptive sites to many substrates and can inherently adsorb waste chemicals such as dyes and cations in water due to coulombic interaction and physical adsorption. These agricultural wastes are renewable and abundantly available at little or no cost. Considerable quantities of breadfruit husk are generated and discarded after processing of breadfruit. Carbohydrates are the major component of breadfruit seed husk and contain hydroxyl groups which makes it hydrophilic therefore limits its application as an oil sorbent in an aqueous environment. However, this defect can be considerably reduced by chemically modifying its constituents thereby improving its hydrophobic properties.

### **2.11.3 Availability of Borassus Coir as an Agro Waste**

*Borassus aethiopum* is a specie of borassus palm from Africa. It is variously referred to as African fan palm, African palmyra palm, black rhun palm and ronier palm. It is widespread across much of tropical Africa from Senegal to Ethiopia and south to northern South Africa. It grows in Nigeria and it is planted massively within the Nnamdi Azikiwe University Awka, Anambra State Nigeria.

The trunk has been used in constructing bridges, and telegraphic poles due to its tough and termite resistant nature (Kumar *et al.*,2016 ).Borassus coir is what makes up the fibrous husks of the inner shell of the borassus nut and is used for all sorts of products. It is the thickest and most resistant of all commercial natural fibres. The nut is edible and once harvested the coir is left to rot away. These coir can be put to good use by using them as oil spill sorbents after proper chemical modification.

### **2.11.4 Availability of Plantain Peel as Agro Waste**

Plantain (*Musa paradisiaca*) is a member of musaceae family and is one of the earliest cultivated crops, originating from the South East Asia. Over 2.11 million metric tons of plantain are produced in Nigeria annually which contributes substantially to the nutrition of subtropical local population (FAO, 2005). Plantain which are grown mostly with banana ( *Musa sapientum* ) are found mostly in the Southern states; Edo, Oyo, Ondo, Cross River, Akwa Ibom, Abia, Imo, Rivers, Bayelsa, Enugu and Delta states.

Plantain peels are the major by-product of plantain fruits, constituting about 40% of the bulk of the fruit but are presently underutilized. However, they can also be modified chemically and subsequently used in oil spill mop up.

#### **2.11.5 Availability of Plantain Pseudostem as Agro Waste**

Pseudo stem is a false stem formed on the swollen leaf bases found in plantain and banana. The plantain plant grows for about six to seven months to reach maturity for fruiting, after which the pseudostem (aerial stem) is felled, the fruit cut off and the stem is allowed to rot away. This is because the plant is propagated by the sucker, an underground stem which produces new shoots. (Nurul *et al.*,2011 ).

These pseudostems are largely available in all the plantain plantations wasting away because it has not been put into good use and are not replanted. It can be used as a natural sorbent and has high potential in absorbing spilled oil (Klemm *et al.*, 2005).

#### **2.12 Survey of Previous works on Oil Sorption**

The potential of many low cost adsorbents for removal of oil spill have been investigated by many researchers. These wastes are locally available, inexpensive and biodegradable which has made researchers to study them as alternatives to the

imported synthetic sorbent materials which are expensive and non-biodegradable. These low cost adsorbents include agricultural by-products and waste materials, fly ash, seaweeds and alginate, peat moss, biomass materials and many others. Some of the studies are discussed below:

The acetylation of corn silk and its application for oil sorption was reported by Asadpour *et al.*, (2015). The acetylation was done with acetic anhydride using N-Bromosuccinimide catalyst. The effect of contact time, concentration of catalyst and temperature were studied. The result showed that the highest oil sorption was 11.45% weight percent gain (WPG) and was achieved at 3% catalyst concentration in acetic anhydride and temperature of 120°C for 6 hours. They observed that the sorption capacity of Tapis and Arabian crude oil using corn silk was 8.6 and 9.4 g/g respectively. It was found that the best condition for acetylation was 3% catalyst for 6 hour reflux at 120°C, which showed maximum WPG and oil sorption capacity of 14.02 and 16.68 g/g, and optimum contact time of 30 and 40 minutes for Tapis and Arabian crude oil respectively. The characteristics of raw and acetylated corn silk were examined using FTIR and SEM and the treated corn silk was found to have higher sorption capacity than that of the raw sample.

Ola *et al.*, (2017) investigated the efficiency of raw and modified palm fibers as adsorbent for different oils. Their result revealed that the adsorption capacity of the fibers was found to increase with time, thickness of oil film, temperature and particle size while it decreases with mass of adsorbent. They described the adsorption process as monolayer coverage and the maximum adsorption capacity of palm fibers was found to be 35.71, 22.73 and 21.74g oil/g adsorbent for diesel, crude and vegetable oil respectively.

El-Din *et al.* (2017) analyzed the oil sorption capacity of banana peel from local fruit wastes. The research showed that surface properties, oil type, oil film thickness, sorption time, temperature and salinity all affect sorption capacity. It was observed that the best condition for sorption was at an average particle size of 0.3625mm at 25<sup>0</sup>c, 15 minutes sorption time, 3.5% artificial seawater and 5mm oil thickness. They noted that the sorbent can be reused more than 10 times to reach 50% of the first sorption value. It was concluded that sorption capacity of banana peel gave a good result as a new and low cost agriculture waste for oil spill cleanup.

The use of a by-product of peat excavation and cotton grass fibre as a sorbent for oil spills was investigated by Suni *et al.* (2004). They observed that cotton grass fibre has absorbed oil approximately two to three times as much, and two to three times as fast as the synthetic one. In removing diesel oil from the surface of water, the efficiency was over 99% up to an absorbing factor of 20 times its own weight. The biodegradable cotton grass fibre proved to be effective oil sorbent with low raw-material cost.

Reza *et al.* (2013) studied the application of phragmites australis, sugarcane leaves straw and sugarcane bagasse for crude oil sorption in dry (only oil) systems. The results indicated that sugarcane bagasse had a higher oil sorption capacity compared to the others due to its higher porosity and lower density. The effect of sorbent contact time and its particle size on oil adsorption capacity were evaluated for the systems of dry and crude oil layer on water. The results showed that the maximum adsorption capacity of raw sugarcane bagasse for dry system and crude oil layer system was about 8 and 6.6g/g respectively. It was also observed that most

oil was adsorbed at the early stage of the process (within a few minutes) and, afterwards, a small amount of oil will be adsorbed.

Nurul *et al.* (2011) studied the sorption equilibrium and kinetics of oil sorption using banana pseudostem fibers (BP) in Malaysia. It was observed to be an efficient sorbent for the removal of oil in water and it may be an alternative to more costly adsorbents such as activated carbon. The batch studies clearly suggest that BP exhibit almost 100% adsorption at lower concentration of oil. Equilibrium data fitted well with Freundlich model, which suggests a heterogeneous coverage of oil molecules on the surface of BP. The kinetic data were best fitted to pseudo second-order kinetic model.

The effect of kapok fiber treated with various solvents on oil absorbency was investigated by Jintao *et al.* (2012). The fiber was treated with various solvents like water, HCl, NaOH, NaClO<sub>2</sub> and chloroform to improve the efficiency for oil absorbency. The structure of untreated and treated kapok fiber was investigated and compared using FTIR, SEM and XRD. The effects of treatment concentration, temperature and time on oil absorbency were assessed with toluene, chloroform, n-hexane and xylene as the model oils. The results indicated that except for chloroform, kapok fibers treated with other solvents show enhanced oil absorbency, with increase in percentage found to be 19.8%, 30.0%, 21.55 and 24.1% for toluene, chloroform, n-hexane and xylene respectively. In addition, the solvent-treated kapok fiber exhibits better re-useability, suggesting its great potential for oil recovery.

Onwuka *et al.* (2016) determined the kinetics of surface modification of lignocellulosic delonix regia pods (DRPs) as sorbent for crude oil spill in water. FTIR

and SEM were used to investigate the influence of acetylation and crude oil sorption on the extent of acetylation. Intra particle diffusion was the rate controlling mechanism for acetylating DRPs while the contributing mechanisms depend on the temperature of acetylation. The crude oil sorption capacity of modified DRPs was significantly higher than that of unmodified DRPs. It was observed that the physical and chemical reactions were faster in the crude oil sorption by modified DRPs than the unmodified while diffusion into the pores of the modified DRPs was slower than in the unmodified. Hydrophobic functional groups were enhanced by acetylation and crude oil molecules were adsorbed at these functional groups. FTIR and SEM showed clear evidence of successful acetylation and crude oil sorption. It was observed that DRPs was effectively acetylated at room temperature (303K). FTIR studies indicated that acetyl functional groups were successfully attached to the sorbent and crude oil was adsorbed at hydrophobic functional groups.

Rotar *et al.* (2014) reviewed the efficiency of using natural sorbent materials for cleanup of water surface from oil spills. The oil capacity, buoyancy, solubility of hydrocarbons in water and water absorption were the indicators used to compare sorption efficiency. They determined that the peat moss carbonized at the temperature of 200- 250<sup>0</sup>C and modified by acetic acid has high sorption capacity. Also the sorbents increased the efficiency of water surface cleaning up until the water is almost clean and the residual oil content in water was less than 0.03g/L. As the calcification degree of the sorbent increased, its technical application characteristics improve. It was observed that the sorbents were porous with rather developed cell structure allowing them to absorb oil products well and retain them for a long time.



Acetylation of raw cotton for Oil Spill Cleanup Application was investigated by Adebajo and Frost (2004). FTIR and  $^{13}\text{C}$  MAS NMR spectroscopy was used to investigate the acetylation of raw cotton samples with acetic anhydride without solvents in the presence of different amounts of 4-dimethylaminopyridine (DMAP) catalyst. The FTIR data provided a clear evidence for successful acetylation. The NMR results further confirmed the successful acetylation. The extent of acetylation was quantitatively determined using the weight percent gain (WPG) due to acetylation and by calculating the ratio R between the intensity of the acetyl C=O stretching band at 1740-1745  $\text{cm}^{-1}$  and the intensity of CO stretching vibration of the cellulose backbone at about 1020-1040  $\text{cm}^{-1}$ . The FTIR technique was found to be highly sensitive and reliable for the determination of the extent of acetylation.

Similarly, Ola (2014) assessed raw luffa as a natural hollow oleophilic fibrous sorbent for oil spill clean-up. He observed that the luffa fibres exhibited high selectivity for various oils and excellent repellency for water in its native form. The batch study revealed that the adsorption was a function of shaking time and dose of adsorbent. The adsorption capacity was reduced when the dose of adsorbent increased while it was increased with temperature and reached maximum at  $40^{\circ}\text{C}$  after which it decreased again. He described desorption intensity applying the first order reaction and pore diffusion model. First order reaction was found to be dominant mechanism over pore diffusion. It was also noted that large capillaries in fibres contributed to excellent oil absorbency and retention capacity. Therefore luffa was considered as a better alternative to the widely used synthetic sorbent material.

Nnaji *et al.* (2016) investigated the acetylation and reuse of *dacryodes edulis* leaf (DEL) and its crude oil sorption studies. The acetylation was very successful with best acetylation conditions at increased time of acetylation, low acetylation

temperature and low amount of catalyst. This was found to be in agreement with some thermodynamic parameters. They found the acetylation to be very effective and took place under mild or non-severe temperature and atmospheric pressure conditions. The crude oil sorption kinetic data were best fitted by liquid film diffusion and pseudo-first order kinetic models for the raw DEL. Pseudo-second order kinetic model best fits crude oil sorption data for acetylated DEL. The Langmuir and Freundlich isotherms gave the best fit to the equilibrium crude oil sorption data for the acetylated and raw DEL respectively. The crude oil and water sorption properties of raw DEL were reduced and enhanced respectively. In contrast, acetylated DEL had its sorption properties enhanced and reduced respectively for crude oil and water sorption processes.

Nwadiogbu *et al.* (2015) reported the equilibrium and kinetics of removal of crude oil from aqueous medium by sorption on hydrophobic corncobs. The corn cob was treated with acetic anhydride to increase their hydrophobic properties and improve their sorption effectiveness in aqueous environment. The kinetic model employed suggested that the sorption process occurs via a surface reaction and intra particle diffusion mechanism. Equilibrium isotherm data were analyzed using the Langmuir and Freundlich isotherms. Based on the regression co-efficient, the Langmuir isotherm provided the best fit to the experimental data. The maximum monolayer sorption was determined to be 0.0768mg/g and 0.0043mg/g for the acetylated and raw corn cob respectively.

Acetylated rice husks (ARH) was studied as sorbents for crude oil spill cleanup operations in the aqueous environment by Nwankwere *et al.* (2010). Sorption kinetics and isotherm studies were carried out under various experimental conditions. The experimental data were particularly tested with the pseudo-second-order kinetic

model, the Langmuir isotherm model and the Freundlich isotherm model. The crude oil absorptive behavior of the acetylated rice husks and the experimental methods adopted for the determination and estimation of the sorption coefficients were analyzed. The correlation values for the isotherms models studied showed that the data better fitted the Langmuir model than the Freundlich model. Adsorption was therefore monolayer and the optimum theoretical monolayer sorption capacity was 10.31g/g rice husks. These values indicated that the acetylated rice husks are suitable sorbents with potential for further development for oil spill treatment.

Hussein *et al.* (2012) examined the absorption capacity of raw barley straw for different petroleum products and water pick up. The oil sorption capacity was found to be dependent on the sorption time and the system condition such as oil temperature and film thickness. The results showed the maximum values of sorption capacity at 11.23 for 1 day weathered oil (1 DWO), 12.2 for 7DWO and 7.8 for gas oil at 250µm particle size, 15 minutes sorption time, 5 minutes dripping time, film thickness of 5mm at temperature of 25<sup>0</sup>C. Furthermore, the amount of water pick up was small due to wax layer covering the barley straw tissue. It was also determined that the sorbed oil was removed from sorbent by simple mechanical press suggesting the reuse of the sorbent for several times.

Idris *et al.* (2014) carried out a preliminary study of biodegradable waste as sorbent material for oil-spill cleanup. The work focused on the preliminary study of empty palm fruit bunch fibre as a promising sorbent material. The morphology of the unmodified empty palm fruit bunch, EPFB fibre, was examined using an optical microcopy, scanning electron microcopy coupled with EDX and X-ray diffraction. The effects of oil volume, fibre weight, and time on oil absorption of EPFB fibre were evaluated with new engine oil from the model oil. The results show that EPFB fibre

consists of numerous micro pores, hydrophobic, and partially crystalline and amorphous with approximately 13.5% carbon. The oil absorbency of the fibre increased with the increase in oil volume, immersion time, and fibre weight. However, sorption capacity decreased beyond 3 g in 100 mL. Additionally unmodified EPFB fibre showed optimum oil sorption efficiency of approximately 2.8 g/g within three days of immersion time.

A study on the equilibrium and kinetics of oil spill cleanup using acetylated corn cobs (ACC) was done by Nwabueze *et al.* 2014. The study investigated the potential of acetylated corn cobs as an adsorbent for oil spills cleanup. The equilibrium, isotherm and kinetics of the acetylated corn cobs were all carried out at room temperature, different reaction times as well as oil concentration. The sorption model and crude oil absorptive behavior of the ACC were studied using the Langmuir and Freundlich isotherm models. The results showed the maximum values of oil sorption capacity of the acetylated corn cobs was gotten as 68.8g/g ACC at a temperature of 20<sup>0</sup>C, sorption time of 10mins, sorbent weight of 1.5g and 1.4mm particle size. A high WPG of 17.6% is also an evidence of successful acetylation. Equilibrium data fitted well with Freundlich model, which suggests a heterogeneous coverage of oil molecules on the surface of ACC. The kinetic data were best fitted to pseudo second-order kinetic model.

Nduka *et al.* (2008) compared the mopping ability of chemically modified and unmodified biological wastes on crude oil and its lower fractions. Activated and unactivated powders of protein wastes (feather, goat hair) and cellulosic wastes (coco-nut husk (coir), corn-cob) were used in the study. It was observed that all the sorbents mopped up appreciable quantities of all the sorbates within an average of 90mins contact time. Large volumes of the hydrocarbon liquids were equally

recovered by mere pressing, high percentage retention was also observed. The mechanism involves adsorption of sorbates on the surface of the sorbent and absorption into the pores and capillaries of the sorbents, sorbates on the surface were easily desorbed while most in the pores were retained. After mopping and recovery, each sorbent can be re-used several number of time. Each sorbent has a distinct feature that enhances its mopping ability. The sorbates were mopped in the order: crude oil > diesel > kerosene > petrol. It was further observed that proteinous sorbents (feather and goat hair) with oleophilic and aquaphobic properties absorbed more of all the hydrocarbon liquids than cellulosic sorbent(coco-nut husk and corn cob) at any particle size and contact time, although both showed high sorption capacity for the sorbates. Each sorbent whether carbonized or uncarbonized has a feature that makes it a good oil mop. If the sorbates are ranked, the order is generally: Crude oil > diesel > kerosene > petrol.

Nduka (2012) studied combination of sorbents and modification of its constituents to enhance the mopping ability of chemically modified and unmodified biological wastes on crude oil and its lower fractions. Carbonized and uncarbonized protein wastes (feathers, goat hair) and cellulosic wastes (corn cob, coconut husks) were used for the study. About 1.5g were each used to mop up spilled crude oil, diesel, kerosene and petrol (separately before combining) by encasing them in a sac like boom of 2cm x 2cm x 1cm dimension so as to determine the efficacy of waste sorbents in cleaning hydrocarbon spills. The result showed that the sorbents mopped, desorbed and retained an average of more than 500%, 350% and 300% of their weight of the hydrocarbon sorbates within average of 90 minutes contact time, the volume of sorbates mopped up increased significantly when equal weight of activated and unactivated sorbents were combined, the results of equal combination of activated

and unactivated sorbents at each particle size and contact time were compared with that of calculated values, high percentage retention observed were a function of mechanism of absorption/adsorption. Each sorbent have a distinct feature that enhances its mopping ability. Large volumes of the hydrocarbon liquids were recovered by mere pressing, the sorbates were mopped up in the order; crude oil > diesel > kerosene > petrol. Protein sorbents with oleophilic and aqua phobic properties absorbed more of all the hydrocarbon liquids than cellulosic sorbents at any particle size and contact, the later tend to be more abundant and therefore cost effective. It was observed that both carbonized and un-carbonized sorbents are good hydrocarbon mops and therefore good alternative to synthetic polyurethane foam already in use.

The capacity of human hair to adsorb crude oil, vegetable oil and diesel fuel was analysed by Ukotije-Ikwut *et al.* (2016) with the aim of establishing its potential for oil spill clean-up. The result obtained indicates that there was rapid increase in the sorption of the various oils in the first 5 minutes after which it proceeded at a slower rate until equilibrium at 60 minutes. The relationship between sorption capacity and temperature was also examined and the result indicates that an increase in temperature reduces the sorption capacity of human hair, except for crude which shows a slight increase. Similarly, investigation on Type X,Y and Z human hair indicates that Type X performed impressively well with an adsorption capacity of 7470mg/g and 6176mg/g, 5246mg/g for Type Y and Z respectively. The kinetics of adsorption was found to fit pseudo second order than first order model. The adsorption isotherm experiment established a relationship between an increase in the dosage of human hair with the uptake efficiency as well as the concentration of oil adsorbed. All the experimental data fit well with Freundlich isotherm model

indicating elements of chemisorption and oil retention occurring on heterogeneous sites with a non-uniform distribution of energy. The efficiency of human hair when subjected to the process of recovery and reuse was also examined and found to be effective after four consecutive times with little variation from the first to the fourth in its sorption capacity. Hence, this is an indication that human hair can be modified into boom and used as low-cost, environmentally friendly adsorbent for cleaning up oil spill, especially considering its potential for reusability without significantly altering the sorption features.

Oil Spill Cleanup using stearic-acid-modified natural cotton was examined by Nguyen *et al.* (2015). It was observed that natural cotton sponges after modification by stearic acid in the presence of 4-(dimethyl-amino) pyridine and *N, N'*-dicyclohexyl carbodiimide were hydrophobic, with water contact angles in the range of 141–144°. The modified cotton samples could be applied as oil/organic solvent sorbents with absorption capacities in the range of 21–32 times their weights, depending on the types of oils and organic solvents. The absorption capacity of the modified cotton was mostly unchanged after using them up to ten times. Their results implied that cotton modified by stearic acid could be a good candidate for crude oil sorbent material.

Modification oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal was studied by Sidik *et al.* (2012). The removal of crude oil from water by lauric acid (LA) modified oil palm leaves (OPL<sub>LA</sub>) was investigated by batch adsorption after varying pH (2–11), contact time (10–60 min), adsorbent dosage (0–52 g L<sup>-1</sup>), initial oil concentration (0–6400 mg L<sup>-1</sup>) and temperature (303–323 K). The modification significantly increased the hydrophobicity of the adsorbent, thus creating OPL<sub>LA</sub> with much better adsorption capacity for crude oil removal. The results gave

the maximum adsorption capacity of  $1176 \pm 12.92 \text{ mg g}^{-1}$  at 303 K. The significant uptake of crude oil from water was proven by FT-IR and FE-SEM analyses. The isotherms studies revealed that the experimental data agrees with the Freundlich isotherm model. The pseudo-second-order kinetics model fitted well the experimental results. Boyd's and Reichenberg's equation on adsorption dynamic revealed that the adsorption was controlled by internal transport mechanism and film-diffusion was the major mode of adsorption. The prepared adsorbent showed the potential to use as a low-cost adsorbent in oil-spill clean-up.

The ability of corncob (an agro waste material) as a natural adsorbent to remove crude oil from effluent water was investigated by Olufemi *et al.* (2014). The results demonstrated that crude oil removal by adsorption onto biodegradable corncobs with good availability at almost no cost, being a waste material is feasible. The adsorption and percentage removal of crude oil from effluent water was found to be dependent on adsorbent dose, adsorbate dose, contact time, temperature and particle size and also speed of agitation. The adsorbed oil-water ratio of the corncob adsorbent was more than unity in all cases investigated, which indicates higher adsorption selectivity for crude oil over water by the adsorbent. The test adsorbents were evaluated for their initial and final capacities, with respect to oil pickup and potential as observed. Meshed corncobs (CC), especially  $80 \mu\text{m}$ , exhibit high affinity for oil adsorption, with time. The adsorption is due to larger surface areas. The considered adsorption temperature range lies between  $15 - 60^{\circ}\text{C}$ , with the maximum adsorption observed at  $15^{\circ}\text{C}$ . The correlation coefficient indicated that the sorption process was dominated by the adsorption process. Based on the high affinity for oil with low water pick up, meshed corncobs used as an adsorbent could be expressly regarded as an oleophilic or hydrophobic substance. The equilibrium adsorption isotherm analysis



using Langmuir and Freundlich, was carried out as presented. Langmuir and Freundlich isotherm models fitted the equilibrium data reasonably well. However, the results from the Freundlich isotherm model seems to be most significant than that of Langmuir.

This result is similar to the findings of Sidik *et al.* (2012), when modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal was studied. The authors observed that the isotherms studied revealed that the experimental data agreed more with the Freundlich isotherm model.

Sidiras *et al.* (2013) chemically modified a widely found lignocellulosic agricultural residue (wheat straw) to obtain low cost adsorbents for diminishing an oil-products spill in seawater. The lignocellulosic adsorbent was modified by auto-hydrolysis, i.e. pure water as a chemical, in a PARR autoclave at 160-240°C for 0-50 minutes. The oil adsorbency tests were performed, using diesel and crude oil spills (of predetermined quality specifications) in seawater. Diesel and crude oil adsorbency-values were found to increase up to a maximum by intensifying the auto hydrolysis conditions (time and reaction-ending temperature). Optimal modification conditions were found at 200°C for auto hydrolysis time 10 minutes giving diesel adsorbency-value up to 6.65 g/g and crude oil adsorbency-value up to 6.91 g/g. The relative diesel adsorbency-value (RDA) was 71% and the relative crude oil adsorbency-value (RCOA) was 72% at these conditions.

Acetylation of sugarcane bagasse using NBS as a catalyst under mild reaction conditions for the production of oil sorption-active materials was reported by Sun *et al.* (2004). The sugarcane bagasse was esterified with acetic anhydride using N-bromosuccinimide as a catalyst under mild conditions in a solvent free system. The extent of acetylation was measured by weight percent gain, which varied from 2.1%

to 24.7% by changing the reaction temperature (25-130 degrees C) and duration (0.5-6.0 h). N-Bromosuccinimide was found to be a novel and highly effective catalyst for acetylation of hydroxyl groups in bagasse. At a concentration of 1% of the catalyst in acetic anhydride, a weight percent gain of 24.7% was achieved at 120 degrees C for 1 h, compared with 5.1% for the un-catalyzed reaction under the same reaction condition. FT-IR and CP-MAS <sup>13</sup>C-NMR studies produced evidence for acetylation. The thermal stability of the products decreased slightly upon chemical modification, but no significant decrease in thermal stability was observed for WPG > or = 24.7%. More importantly, the acetylation significantly increased hydrophobic properties of the bagasse. The oil sorption capacity of the acetylated bagasse obtained at 80 degrees C for 6 h, was 1.9 times higher than the commercial synthetic oil sorbents such as polypropylene fibres. Therefore, these oil sorption-active materials can be used to substitute non-biodegradable materials in oil spill cleanup.

Onwuka *et al.*, 2018 treated crude oil contaminated water with chemically modified natural fiber. They investigated crude oil sorption from water using acetylated and un-acetylated oil palm empty fruit bunch (OPEFB) and cocoa pod (CP) under mild conditions. Sorption of oil from water was found to be time and concentration dependent. Equilibrium studies showed that CP has higher sorption capacity than OPEFB and acetylation enhanced the crude sorption capacities of the sorbents. They found that the sorption was a monolayer process that might have progressed from multilayer processes. Kinetic studies showed that sorption of crude oil by the sorbents was diffusion controlled with the aid of physio-sorption and chemisorption mechanisms. FTIR and SEM analyses showed clear evidence of successful acetylation and oil sorption.

### **2.13 Literature Gap**

It can be seen that several low cost agricultural materials have been utilized for oil spill clean-up by different local and international researchers. However, the use of borassus coir, corn husk, breadfruit seed husk, plantain peel and plantain pseudostem for oil spill clean-up is still unknown and needs to be investigated.

From the numerous literature reviewed, it was clearly observed that no studies on acetylation of the five selected agricultural wastes have been carried out. Also no kinetics and equilibrium studies on the five samples have been investigated hence the need for this study to fill the literature gap.

## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1 Sample Collection

Corn husk, African breadfruit seed husk and plantain peel were collected from Kenyatta Main Market in Enugu metropolis. Plantain pseudostem was collected from a plantain plantation in Idaw river Enugu while Borassus Coir was collected from Nnamdi Azikiwe University Awka, Anambra State, Nigeria. All the samples were identified by a renowned plant taxonomist Prof J. C. Okafor. The crude oil samples were collected from Nigerian National Petroleum Corporation (NNPC) Port-Harcourt, Nigeria.

#### 3.2 Sample preparation

The five samples were thoroughly washed separately to remove dust, fungus, foreign material and water soluble components. The washed samples were sun-dried for twenty hours (five hours for four days) and then left to dry at 65°C in the oven for 24 hours. They were size reduced and sieved through 20 and 25 British Standard Sieve (BSS Sieves) and stored in an air tight container for use.

##### 3.3.1 Materials and equipment

Borassus coir, Bread fruit seed husk, Corn husk, Plantain peel, Plantain pseudostem, Distilled water, Conical flask, Steam bath, Heating mantle, Beakers (100mL, 250mL, 1000L), Test tubes, Glass funnel, Washing Bottle, Bunsen burner, Measuring Cylinders (100mL, 1L), Volumetric flask (100mL, 1L), Glass rod,

Spatula, Density Bottle, Top Loading Balance, Analytical balance, Petri dishes, Sample bottles, Round bottomed flask, Whatmann filter paper, Oven, Muffle Furnace, Stop watch, Viscometer (NDJ-85 Digital rotary), Condenser, Porcelain crucible, Crude oil, Fourier Transform Infrared Spectrometer (FTIR) Shimadzu 8400s, Energy Dispersive X-Ray Fluorescence (XRF) Spectrometer (Oxford), Scanning Electron Microscopy (SEM) Spectrometer (Phenom World).

### 3.3.2 Reagents

All reagents used in this research were analytical grade chemicals from British Drug House (BDH) and include; Acetic anhydride, N-Bromosuccinimide (NBS), Acetone, Ethanol, N-hexane.

### 3.4 Characterization of the Samples

Proximate analysis and physical characteristics of the materials were determined as follows;

**Bulk and tapped Density:** A portion (25g) of the samples was accurately measured into a 100ml graduated cylinder. The cylinder was stoppered and the bulk volume  $V_0$  was recorded. For the tapped density, the cylinder was tapped on a hard surface to a constant volume (until no more settling of the material occurred). The final constant volume ( $V_1$ ) was noted to be the tapped volume.

The bulk and tapped densities  $D_{\text{bulk}}$  and  $D_{\text{tap}}$  were determined as follows;

$$D_{\text{bulk}} = \frac{W}{V_0} \quad (3.1)$$

$$D_{\text{tap}} = \frac{W}{V_1} \quad (3.2)$$

**True density:** A portion (25g) of the samples was accurately weighed and poured into a 100ml graduated cylinder, and distilled water was carefully measured into the cylinder to the level of the material. The true density was calculated as follows;

$$\text{True density} = \frac{W}{V} \quad (3.3)$$

Where  $W$  is the weight of the sample and water and  $V$  is the volume of the sample.

**Moisture Content:** A portion (2g) each of the sorbents was measured into a wash glass. The samples were placed in the oven for 24 hours at 105°C. After 24 hours, the oven dried samples was reweighed and the moisture content was determined using the formula

$$Mc = [(W_0 - W_1) / W_0] \times 100 \quad (3.4)$$

where  $Mc$  is the moisture content;  $W_1$  is the new weight after drying;  $W_0$  is the initial weight of the dry samples (ASTM, 1994).

**Ash content:** Ash content was determined using the methods employed by Dara, (1991), Aloko and Adebayo (1997). Dry samples (2g) were placed in a pre-weighed porcelain crucible and transferred into a pre-heated muffle furnace set at a temperature of 600°C for 1 hour after which the crucible and its content were transferred to a desiccator and allowed to cool. The crucible and its content were reweighed and the new weight noted. The percentage ash content was calculated with the formula

$$Ac (\%) = (W_a / W_0) \times 100 \quad (3.5)$$

where  $Ac$  is the ash content in percentage;  $W_a$  is the weight of ash after cooling and  $W_0$  is the original weight of dry sorbent.

**Porosity:** The porosity of the materials was calculated using the formula for porosity.

$$\text{Porosity} = 1 - (\text{BD}/\text{TD}) \quad (3.6)$$

where BD is the bulk density and TD = true density

**Lignin Content:** 2g sample was placed in a flask and 15 ml of 72% sulphuric acid was added. The mixture was stirred frequently for two and half hours at 25°C and 200 ml of distilled water was added to the mixture. Then the mixture was boiled for next two hours and cooled. After 24 hours, the lignin was transferred to the crucible and washed with hot water repeatedly until it became acid free. The collected lignin was dried at 105°C and cooled down in desiccator and weighed. The drying and weighing were repeated until constant weight was gotten.

**Cellulose content:** Holocellulose (2.0g) were placed in a beaker and 10 ml of sodium hydroxide solution (17.5%) was added. The fibres were stirred vigorously with glass rod so that they could be soaked with sodium hydroxide solution vigorously. Then sodium hydroxide solution was added to the mixture periodically (once every five minutes) for half an hour and the mixture temperature was kept at 20°C. About 33 mL of distilled water was added in the beaker and kept for an hour. The holocellulose residue was filtered and transferred to the crucible and washed with 100 ml of sodium hydroxide (8.3%), 200 ml of distilled water, 15 mL of acetic acid (10%) and again water successively. The crucible with celluloses was dried and weighed.

### **Hausner Ratio**

It is used in a wide variety of industries as an indication of the flowability of a powder. If the value is greater than 1.25, it is considered to be an indication of poor

flowability. The Hausner ratio (H) is related to the Carr index (C), another indication of flowability.

The Hausner ratio is calculated by the formula:

$$H = \frac{\rho_T}{\rho_B} \quad (3.6b)$$

where  $\rho_B$  is the freely settled bulk density of the powder, and  $\rho_T$  is the tapped bulk density of the powder.

### 3.5 Characterization of crude oil

**Viscosity:** The viscosity of the oil samples was obtained using an NDJ-85 Digital rotary viscometer at 27°C. The samples were pre-warmed and placed in the sample chamber of the apparatus. The samples were brought to room temperature within 30 minutes and the motor started. The viscosity was automatically measured at 1 minute interval. The mean of the viscosity was calculated and recorded.

**Density:** The density of the oil samples was obtained using the methods of Hassanet *al.*, (2006) with a specific gravity bottle. The bottle was filled with the oil and weighed at 30°C in a thermostated water bath. The density of the oil was calculated using the formula

$$\rho = (M_s - M_b) / V_b \quad (3.7)$$

where  $M_s - M_b$  is the mass of the oil used and  $V_b$  is the volume of water used.

**Specific gravity:** The specific gravity of the oil samples was calculated using the results obtained for density. The specific gravity being a more standard



measurement was obtained by multiplying the density obtained with the density of water 0.998g/dm<sup>3</sup>.

**The American Petroleum Institute (API)- Gravity:** This was obtained using the formula API gravity given in (Nwankwere, 2010) and expressed thus:

$$\text{API}_o = (141.5/\text{S.g})-131.5 \quad (3.8)$$

Where s.g is the specific gravity of the oil used.

### **3.6 Soxhlet Extraction**

To reduce the influence of the fibre extractives (oil, wax and fat) on acetylation, the sieved materials (10g) was extracted with a mixture of acetone and n-hexane (4:1 v/v) for 5hours. The extracted samples were dried in a laboratory oven for 16hours.

### **3.7 Acetylation of samples**

The acetylation of the five samples under mild conditions, in the presence of N-Bromosuccinimide catalyst, using acetic anhydride was carried out using the method of Sun *et al.* (2004). The amount of substrate and reactant were combined in a ratio of 1:20 (g dried sorbent/mL acetic anhydride). The reaction temperature was 30°C, time was differently varied from 30 minutes to 2hrs at 30 minutes interval and the catalyst concentration varied from 0.2g to 1.6g at 0.2g interval. The mixture of raw sorbents, acetic anhydride and catalyst was placed in a round bottom flask fitted to a condenser. The flask was placed in an oil bath on top of a thermostatic heating device, thereafter, the flask was removed from the bath and the hot reagent was decanted off. The sorbents were thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid as by-products. The new products were dried in an oven at 60°C for 16hours prior to analysis. The degree of

acetylation was estimated from the infrared spectra by calculating the ratio (R) between the intensity of the acetyl C=O stretching band around 1740-1745 cm<sup>-1</sup> and the intensity of the C-O stretching vibrations of cellulose backbone at about 1020-1040 cm<sup>-1</sup> as shown below (Adebajo and Frost, 2004):

$$R = \frac{I_{1740}}{I_{1020}} \quad (3.9)$$

### 3.8 Treatment protocol

#### 3.8.1 Oil sorption capacity

The sorption of oil from water was carried out using the methods of Bannerjee *et al.*,(2006). To simulate the situation of oil spill and minimize experimental variation, the crude oil sample was held in beakers for one day in open air to release volatile hydrocarbon contents. The raw and acetylated samples were then subjected to crude oil sorption test. To 100 mL of distilled water in a 250 mL beaker, 5 g of crude oil was added. A portion (1 g) of the sorbent was added into the mixture in the beaker. The mixture was allowed to stand for about 3 minutes with little agitation. The sorbents were removed from the beakers using sieve net and left to drain by hanging the net over the beaker in an oven for 30 minutes at 60°C and reweighed. The same procedure was repeated for the other four samples. The oil sorption capacity was calculated by taking into account the weight of sorbent, weight of sorbent and oil and weight of sieve net.

$$\text{Oil sorption capacity (g/g)} = \frac{(S_{st} - S_o)}{S_o} \quad (3.10)$$

where  $S_o$  is the initial mass of the dry sorbent,  $S_{st}$  is the mass of the sorbent with oil at the end of the sorption test and the  $(S_{st} - S_o)$  quantity is the net oil sorbed (all of the masses were measured in grams). The amount of crude oil adsorbed ( $q_e$ ) in milligrams per gram was determined using the following mass balance equation;

$$q_e = \frac{(C_o - C_e) V}{m} \quad (3.11)$$

where  $C_o$  is the initial oil concentration in mg/L,  $C_e$  is the equilibrium oil concentration in mg/L,  $V$  is the volume of the solution in litres, and  $m$  is the mass of the adsorbent in g.

### 3.8.2 Water Absorption Capacity.

1 g each of the five samples were allowed to absorb water for specific soaking time of 20, 50, 80, 100 and 120 minutes. Afterwards, the water loaded samples were allowed to drain on the filter paper for thirty minutes and the samples reweighed. The water absorption capacity (g/g) was calculated using the equation below.

$$\text{Water absorption capacity (WAC)} = \frac{AW - AD}{AD} \quad (3.12)$$

Where  $AW$  is the mass of the wet sorbent after water absorption and  $AD$  is the mass of the dry sorbent.

### 3.9.1 Fourier Transform Infrared Spectroscopic Analysis

The properties of raw and acetylated samples were characterized using FT-IR Shimadzu 8400s spectrophotometer in the range of 4000-400  $\text{cm}^{-1}$ . Samples were run using the KBr pellet method at the National Research Institute for Chemical Technology (NARICT) Zaria, Kaduna-Nigeria.

### **3.9.2 X-ray Fluorescence (XRF)**

The elemental composition of the raw corn husk (RCH), raw African breadfruit seed husk (RBF), raw Borassus coir (RBC), raw plantain pseudostem (RPS) and raw plantain peel (RPP) were characterized using Oxford Energy dispersive X-ray fluorescence. The scanning region were between 0 – 30(KeV) energy region. Samples were run at Multipurpose Research Laboratory, Ahmadu Bello University Zaria, Nigeria.

### **3.9.3 Scanning Electron Microscopy (SEM)**

The topographical and morphological information about the five samples were provided by SEM through the high-resolution, three dimensional and high depth-of-field images of the sample surface and near-surface. It revealed spatial variations in chemical compositions of the samples and their porous natures.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 Result of Sample Characterization

##### 4.1.1 Result of Physical and Mineral Characterization of Samples.

The results of the physical properties of the raw sorbents are presented in Table 4.1.

**Table 4.1 Physical Properties of the Sorbents**

Property	Borassus Coir	Plantain Pseudostem	Plantain Peel	African Breadfruit Seed Husk	Corn Husk
Moisture Content (%)	4.995 $\pm 0.003$	4.304 $\pm 0.184$	4.342 $\pm 0.002$	4.199 $\pm 0.001$	4.978 $\pm 0.015$
Ash Content (%)	2.295 $\pm 0.001$	11.366 $\pm 0.002$	14.556 $\pm 0.003$	2.399 $\pm 0.012$	2.140 $\pm 0.002$
Bulk Density g/cm <sup>3</sup>	0.125 $\pm 0.021$	0.182 $\pm 0.005$	0.322 $\pm 0.003$	0.349 $\pm 0.001$	0.272 $\pm 0.018$
Tapped Density(g/cm <sup>3</sup> )	0.209 $\pm 0.001$	0.229 $\pm 0.002$	0.402 $\pm 0.013$	0.545 $\pm 0.003$	0.303 $\pm 0.011$
Porosity %	40.20 $\pm 0.30$	20.50 $\pm 0.30$	19.90 $\pm 0.01$	36.00 $\pm 0.18$	10.20 $\pm 0.10$
Lignin (%)	26.25 $\pm 0.02$	28.50 $\pm 0.10$	17.50 $\pm 0.10$	28.00 $\pm 0.08$	14.25 $\pm 0.30$
Cellulose (%)	37.30	44.60	14.80	4.70	21.27

	$\pm 0.01$	$\pm 0.30$	$\pm 0.20$	$\pm 0.04$	$\pm 0.01$
Hemicellulose (%)	24.00	28.20	17.13	4.13	43.36
	$\pm 0.10$	$\pm 0.08$	$\pm 0.01$	$\pm 0.02$	$\pm 0.20$
Hausner ratio	1.672	1.250	1.249	1.562	1.114
	$\pm 0.001$	$\pm 0.002$	$\pm 0.013$	$\pm 0.003$	$\pm 0.011$

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Results are average of 3 determinations

The moisture content reported in this study is within the acceptable limit of 5%. Moisture content (less than 5%) is needed for the best acetylation reaction. Values above this level will cause hydrolysis of anhydrides to carboxylic acid. This accounts for a 5.7% loss of anhydride for each 1% of water in the wood (Bordilau and Teaca, 2009). The bulk and tapped densities measures the flowability of a material. A higher density indicates a better potential for a material to flow and re-arrange itself under compression. The results derived from this study are moderate and are consistent with findings elsewhere (Azubike and Okhamafe, 2012). Hausner indices were estimated as the ratio of the difference between tapped and bulk densities. A Hausner index estimates cohesion between particles (Wells, 1988). A value less than 1.25 indicates good flowability, whereas a value of 1.50 or higher suggests that the material will have poor flow properties (Azubike and Okhamafe, 2012). In our findings, the Hausner ratio for plantain pseudostem, plantain peel and corn husk fell within 1.25. This suggests good flowability of the materials. However, it was observed that borassus coir and African breadfruit seed husk has a Hausner ratio above 1.50 which implies that they have poor flow properties.

The ash content reports the percentage of inorganic constituents in the agro wastes. Plantain peel had the highest ash content of 14.56% while corn husk had the least

value of 2.14%. Plantain pseudostem had relatively high ash content of 11.37% while borassus coir and breadfruit seed husk had low values of 2.30% and 2.40% ash respectively.

Cellulose is an important structural component of the primary cell wall of green plants, many form of algae and the oocytes. It is the main constituent of agricultural residues. In plants, cellulose is the compound that gives rigidity to the cells. The bonds between each cellulose molecule are very strong, which makes cellulose very hard to break down. Approximately 35–45% of the dry substance in most straw and grass species is cellulose, located predominantly in the secondary cell wall. Plantain pseudostem had the highest cellulosic content of 44.60% followed by borassus coir at 37.30%. Breadfruit seed husk had the least value at 4.70%.

Lignin is a class of complex organic polymers that form key structural materials in the support tissues of vascular plants. Lignin is generally the most complex and smallest fraction, representing about 10–25% of the biomass by weight. It acts like a glue by filling the gap between and around the cellulose and hemicellulose complex with the polymers. All the samples gave moderately high lignin value below 30 with plantain pseudostem giving the highest value of 28.50%.

The results of the Mineral analysis of the raw samples are presented in Table 4.2 .

**Table 4.2: Mineral Composition of Borassus Coir, Breadfruit seed husk, Corn Husk, Plantain Peel, Plantain Stem and Corn Husk.**

Mineral	Borassus Coir	Breadfruit Seed Husk	Corn Husk	Plantain Peel	Plantain Pseudostem
K <sub>2</sub> O	60.100	22.000	34.200	79.800	23.600
CaO	27.300	30.800	6.830	-	59.900
CuO	1.300	1.100	0.860	0.240	0.250
Cl	-	-	26.700	7.110	11.100
Eu <sub>2</sub> O <sub>3</sub>	8.700	-	1.800	0.400	0.410
TiO <sub>2</sub>	-	-	0.450	0.470	0.390
SO <sub>3</sub>	-	-	20.000	0.530	-
MnO	-	0.500	-	0.030	0.460
ZnO	-	0.330	0.100	0.083	0.110
Rb <sub>2</sub> O	-	-	-	0.370	0.060
RuO <sub>2</sub>	-	10.000	-	-	-
Sb <sub>2</sub> O <sub>3</sub>	-	-	-	8.310	-
Re <sub>2</sub> O <sub>7</sub>	-	-	0.500	0.240	-
PbO	-	-	0.880	-	-
SrO	-	-	-	-	0.100
Fe <sub>2</sub> O <sub>3</sub>	-	9.120	6.880	2.400	2.360
Yb <sub>2</sub> O <sub>3</sub>	2.600	-	0.300	-	-
In <sub>2</sub> O <sub>3</sub>	-	23.000	-	-	-



I	-	2.000	-	-	-
Bi <sub>2</sub> O <sub>3</sub>	-	1.100	-	-	-
NiO	-	-	0.009	-	-
As <sub>2</sub> O <sub>3</sub>	-	-	0.200	-	-

The mineral analysis was done by X-ray fluorescence (XRF) and it showed that corn husk, borassus coir, plantain pseudostem, African breadfruit seed husk and corn husk contained essential minerals like potassium and calcium in high proportion. Calcium plays a significant role in photosynthesis, carbohydrate metabolism, nucleic acids and binding agents of cell wall. It also assists in teeth development (Brody, 1994). Copper is a trace mineral and was found present in all the samples in trace amounts. It helps the body make red blood cells and keeps nerve cells and your immune system healthy. It also helps form collagen, a key part of bones and connective tissue. It may also act as an antioxidant, reducing free radicals that can damage cells and DNA (Fowomolo, 2010). In plants, copper activates some enzymes which are involved in lignin synthesis and it is essential in several enzyme systems. It is also required in the process of photosynthesis, is essential in plant respiration and assists in plant metabolism of carbohydrates and proteins (Barker *et al.*, 2007).

Iron was found present in all the samples except borassus coir in little quantity as a micro nutrient and it is involved in the manufacturing process of chlorophyll, and it is required for certain enzyme functions. Manganese was found in very minute amounts in all except corn husk and borassus coir and is a major contributor to various biological systems including photosynthesis, respiration, and nitrogen assimilation in plants. (Epstein *et al.*, 2005). The presence of the minerals in the samples

contributed to the hydrophilic nature of the materials under investigation (Ribeiro and Rubio, 2000).

#### **4.1.2 Results of Crude Oil Characterization**

The characterizing properties of crude oil carried out were specific gravity, viscosity, density and API gravity. The properties are shown in Table 4.3

**Table 4.3 Result of Characterization of Crude Oil**

<b>Property</b>	<b>Crude Oil</b>
Specific gravity at 25 <sup>0</sup> C	0.8825
Viscosity at 25 <sup>0</sup> C (MPa.S)	67.5000
Density (g/cm <sup>3</sup> )	0.8956
API gravity (o)	28.8400

The specific gravity of the crude oil at 0.8825 shows that the crude oil is less dense than water and therefore can float on it. Viscosity is a measure of an oil's resistance to flow. Crude oil gave a high viscosity value of 67.5 which shows that it is thick with a moderately high internal resistance to flow.

## **4.2 Acetylation of agricultural wastes**

### **4.2.1 Structural Characteristics of Borassus Coir**

FTIR spectroscopy has the ability to predict structural differences not seen by other physicochemical analysis. Structural units that undergo various changes are functional groups located on the glucose monomer of the cellulose, observable in the FTIR spectra (Bordilau and Teaca, 2009). The FTIR spectrum of the raw and acetylated borassus coir are in Appendices 16 and 29 respectively.

Table 4.4 presents the assignment of IR spectra bands of functional groups in raw and acetylated borassus coir.

**Table 4.4: Assignment of the IR spectra bands of functional groups in raw and acetylated borassus coir.**

Raw Sample IR freq (cm <sup>-1</sup> )	Modified Sample IR freq (cm <sup>-1</sup> )	Band Assignment
3855, 3741, 3404	3994, 3909, 3749, 3407	OH- stretching of hydroxyl group.
2931	2933	CH stretch
2366	2367	CH <sub>3</sub> -O group cellulose
-	2255	CH <sub>3</sub> group, stretching vibrations in aliphatic group
1649	1643	C=O esters
1519	1507	C=O stretch lignin
1140	1142	C=O stretching vibrations in acetyl group ( lignin)
1043	-	-C-O stretching vibration in cellulose, hemicelluloses and primary alcohol.

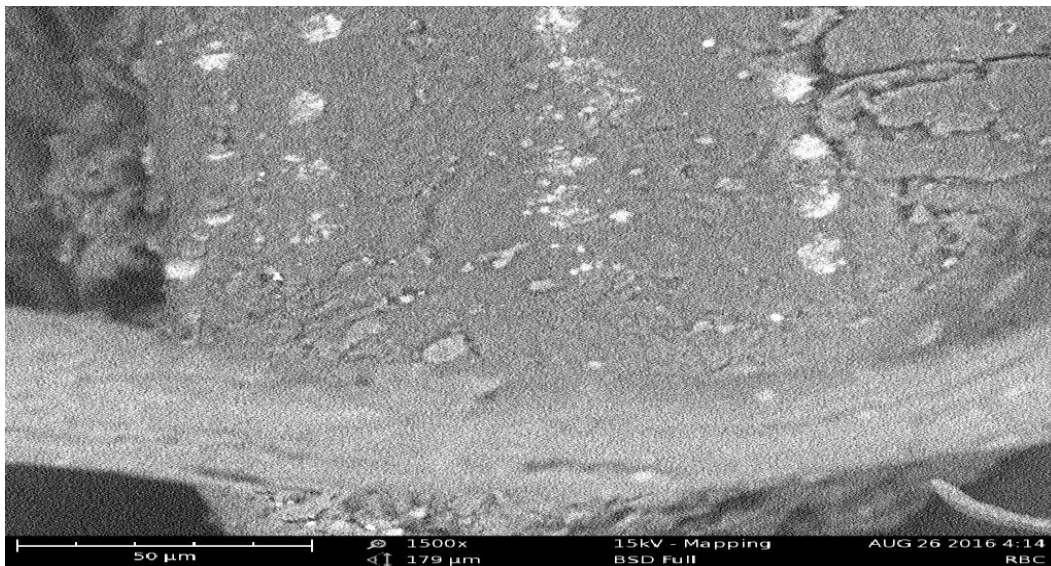
865	861	Tri-substituted C-H bend, alkanes
630	626	Cis out of plane C-H bond
468	487	Si-O-Si bend, Silica

The following peak intensities 3994, 3909, 3749 and 3407  $\text{cm}^{-1}$  as reflected on the IR spectra of acetic anhydride treated samples are characteristic absorption of bonded –OH group stretching vibrations in cellulose and hemicelluloses. The intensities increased which is a good evidence of acetylation, (Mohebbly, 2008; Bordilau and Teaca, 2009; Yakubu *et al.*, 2012). However, at some points a slight increase in the intensity of OH stretching band indicating a gradual lowering of the extent of acetylation as the reaction time and quantity of catalyst increased. The presence of the band at 1643-1649 $\text{cm}^{-1}$  is characteristic absorption of carbonyl (C=O ester) stretching vibration of acetate group in cellulose and uronic ester in hemicelluloses. This band showed evidence of acetylation (Indrayam *et al.*, 2000; Adebajo and Frost, 2004b; Mohebbly, 2008). The increase in band absorption at 1140-1142  $\text{cm}^{-1}$  is assigned to C=O stretching vibrations in acetyl group (lignin) (Bordilau and Teaca, 2009; Yakubu *et.al.*,2012).

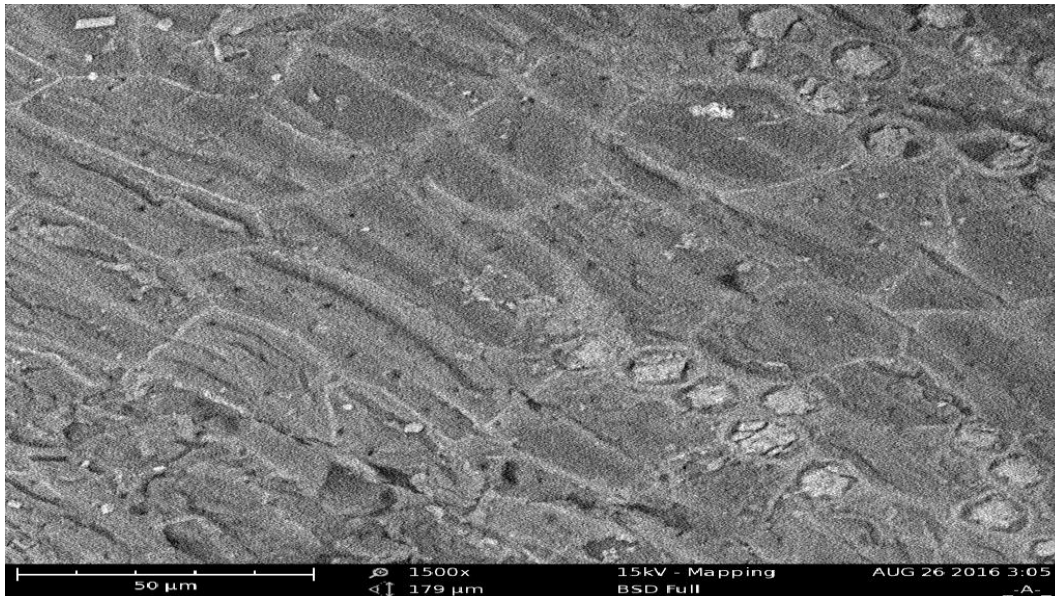
The absence of the band at 1840-1760  $\text{cm}^{-1}$  in all the treated samples showed that the acetylated samples were free of unreacted acetic anhydride (Sun *et. al.*, 2002; Adebajo and Frost, 2004b). The absence of the peak at 1700  $\text{cm}^{-1}$  in all the treated samples also indicated that the acetylated products are free of acetic acid by-product. This indicated that FTIR is quite sensitive and good technique for identifying contamination. Hence it is always necessary to wash the treated samples with ethanol and acetone to prevent contamination (Adebajo and Frost, 2004b).

#### 4.2.2 Morphological Characteristics of Borassus coir

The SEM micrograph of the raw and acetylated borassus coir are presented in Plates 4.1a and b respectively. The SEM analysis showed the surface morphologies and cross section of raw and treated borassus coir. The amount and rate at which oil is adsorbed into the sorbent is closely related to the physical configuration of the sorbent such as surface roughness, hollow lumen, porosity and twist. Oleophilicity and surface energy of the sorbent are mainly dependent on the chemical property and the surface wax, which are significant properties in the absorption mechanisms.



**Plate 4.1a: SEM micrograph for raw Borassus coir**



**Plate 4.1b: SEM micrograph for acetylated Borassus coir**

As can be seen from plate 4.1 (a), the surface of the untreated sample is smoother with tiny ripples. Plate 4.1 (b) presents the surface and cross section of treated borassus coir showing a tubular structure with holes and voids. The acetylation process changed the physical configuration of the raw borassus coir, and thus the finesse property of the surface was transformed and became rough and porous. It also showed that the surface of the modified sorbent was more ruptured along with different degrees of wrinkles and grooves which increased the surface area. There is also noticeable increase in the number of pores in the sorbent after acetylation. These pores can make oil entrance into the internal parts of the material easier and helpful in the sorption process. It is believed that high percentage of oil can be trapped into the porous interior of the sample by capillary mechanism. The macro porous interior fiber enhances the capillary action and the diffusion of oil through the fiber and improves the sorption properties of borassus coir.

### 4.2.3 Structural Characteristics of African Breadfruit Seed Husk.

The FTIR spectra for the acetylated and raw African breadfruit seed husk are in appendix 37 and 48 respectively.

Table 4.5 presents the summary of assignment of functional groups to the IR spectra bands in both the raw and acetylated samples of African breadfruit seed husk.

**Table 4.5: Assignment of the IR spectra bands of functional groups in raw and acetylated African breadfruit seed husk,**

Raw Sample IR freq (cm <sup>-1</sup> )	Modified Sample IR freq (cm <sup>-1</sup> )	Band/Functional Group Assignment
3857, 3742, 3403	3861, 3743, 3402	-OH stretching, hydroxyl group
2929	2939	-CH stretch, CH <sub>3</sub> -O group cellulose
2415	2385	CH <sub>3</sub> group, stretching vibrations of aliphatic CH <sub>3</sub> group
2277	2301	CH <sub>3</sub> group, stretching vibrations in aliphatic groups

1647	1645	C=C alkanes and C=O ester
1524	1524	C=O stretch lignin
1244	1432	C=O stretch, acetyl group (lignin)
1126, 1028	1242, 1027	C=O stretching vibrations in acetyl group (lignin)
843	868	Tri-substituted C-H bend, alkanes
598	590	-OH out-of-plane bending
394	396	Si-O-Si bend, silica

All the spectra of the treated sample showed evidence of acetylation. The following enhanced peaks and bands at 3861, 3743, 3402  $\text{cm}^{-1}$  as seen on the IR spectra of modified African breadfruit seed husk are characteristic absorption of bonded -OH stretching vibrations in cellulose and hemicelluloses (Yakubu *et al.*, 2012). The OH absorption bands of the raw sample were detected predominantly at 3857, 3742  $\text{cm}^{-1}$  and were enhanced after acetylation suggesting that poly-hydroxyl functional groups of African breadfruit seed husk were involved in the acetylation process. The band at 1647 broadened after acetylation as a result of carbonyl absorption.

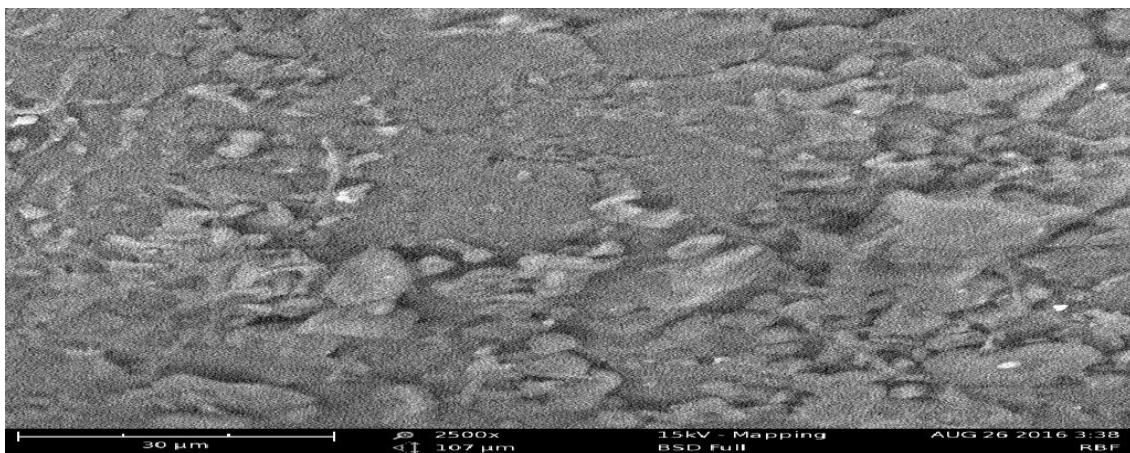
The band absorption at 1028-1000  $\text{cm}^{-1}$  is assigned to C-O stretching vibration in cellulose, hemicelluloses and primary alcohol. (Yakubu *et al.*, 2012; Bordilau and Teaca, 2009.). Stretching signal of C=O attached to lignin are observed around 1432  $\text{cm}^{-1}$  in the spectrum of the treated sample which is an evidence of acetylation. The absence of the band at 1840-1760  $\text{cm}^{-1}$  in all the treated samples showed that the



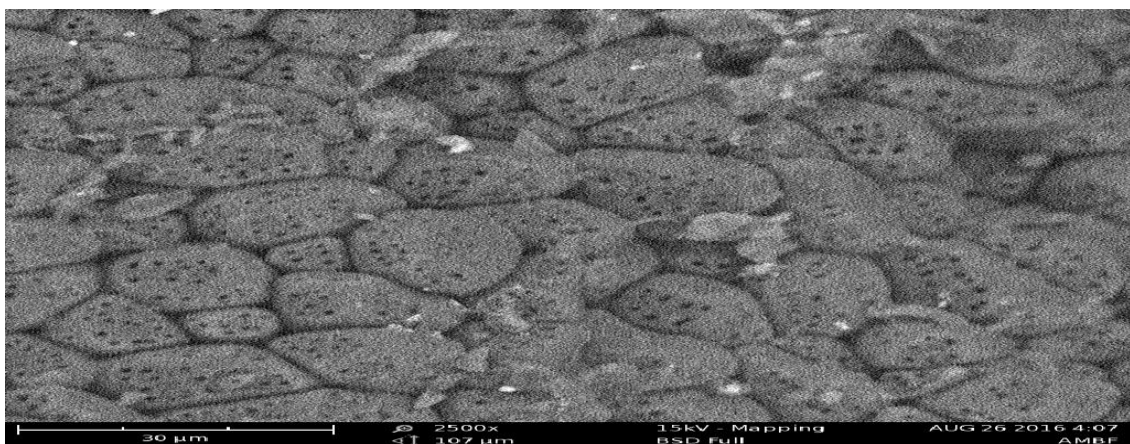
acetylated samples were free of unreacted acetic anhydride (Sun *et al.*, 2002; Adebajo and Frost, 2004b). The absorption band at 1524-1525  $\text{cm}^{-1}$  is assigned to the C=O stretch of the lignin. The band at 1242-1244  $\text{cm}^{-1}$  is assigned to the stretching of C-O and the deformation in the acetate bond formed during acetylation in xylan and lignin(Mohebby, 2008).

#### 4.2.4 Morphological Characteristics of African breadfruit seed husk

The morphological structure of the untreated and treated African breadfruit seed husk are presented in Plates 4.2a and b respectively. The SEM analysis showed the surface morphologies and cross section of raw and treated samples.



**Plate 4.2a: SEM micrograph for raw African breadfruit seed husk**



**Plate 4.2b: SEM micrograph for acetylated African breadfruit seed husk**

As can be seen, the surface of the untreated sample is very smooth with tiny ripple and became rough with high degree of wrinkles and grooves. Plate 4.2(b) presents the surface and cross section of treated breadfruit seed husk showing a tubular structure with holes and voids. The acetylation process changed the physical configuration of the raw breadfruit seed husk, and thus the smoothness of the surface was transformed and became rough and porous. It also showed that the surface of the modified sorbent was more ruptured along with different degrees of wrinkles and grooves which increased the surface area. There is also noticeable increase in the number of pores in the sorbent after acetylation. These pores can make oil entrance into the internal parts of the material easier and helpful in the sorption process. It is believed that high percentage of oil can be trapped into the porous interior of the sample by capillary mechanism.

#### 4.2.5 Structural Characteristics of corn Husk

Table 4.6 presents the assignment of IR spectra bands of functional groups in raw and acetylated corn husk. The FTIR spectra of the raw and acetylated samples are in Appendix 16 and Appendix 3 respectively.

**Table 4.6 Assignment of the IR spectra bands of functional groups in raw and acetylated Corn Husk**

Raw Sample IR freq (cm <sup>-1</sup> )	Modified Sample IR freq (cm <sup>-1</sup> )	Band Assignment
3858, 3741, 3403	3921, 3750, 3405	OH stretch of hydroxyl group
2932	2926	CH stretch, CH <sub>3</sub> -O group cellulose
2355	2363	CH <sub>3</sub> group, stretching vibrations of aliphatic CH <sub>3</sub> group
1914	-	

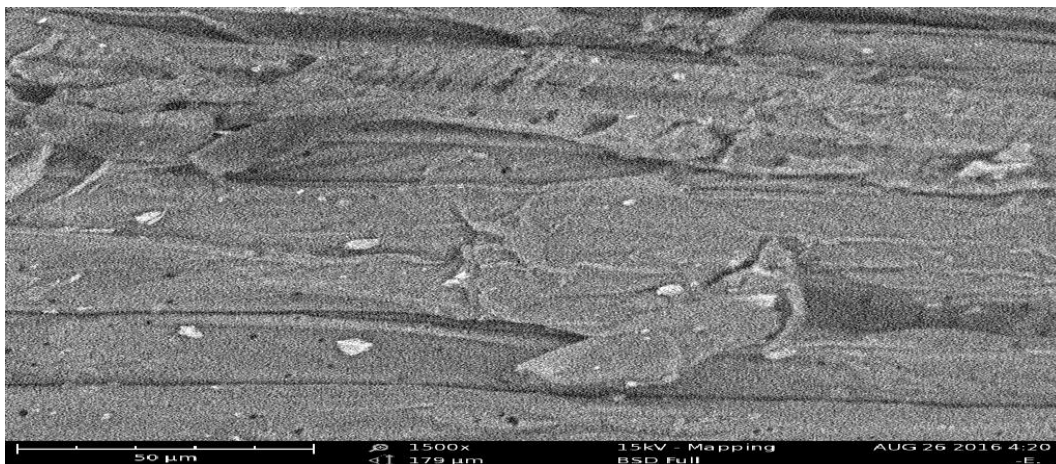
1648	1644	C=C alkene and carbonyl absorption
1525	1504	C=O stretch, lignin
1416	1413	CH deformation in $-O(O=O)-CH_3$ group
1250	1245	C=O stretch, acetyl group (lignin)
1133	-	C-O-C anti-symmetric bridge stretching in cellulose and hemicelluloses
-	1052	C-O stretching vibration of cellulose, hemicelluloses and primary alcohol
861	-	Tri-substituted C-H bend alkanes

The following peak intensities 3921, 3750 and 3405  $\text{cm}^{-1}$  as reflected on the IR spectra of acetic anhydride treated samples are characteristic absorption of bonded  $-OH$  group stretching vibrations in cellulose and hemicelluloses. The bands at 2926 – 2931  $\text{cm}^{-1}$  is attributed to CH stretch,  $CH_3-O$  group of cellulose while the peak around 2355 – 2363  $\text{cm}^{-1}$  is assigned to stretching vibrations of aliphatic  $CH_3$  group. The absorption band at 1504-1525  $\text{cm}^{-1}$  is assigned to the C=O stretch of the lignin. The band at 1648 broadened after acetylation as a result of carbonyl absorption. Stretching signal of C=O attached to lignin was seen around 1413-1416 $\text{cm}^{-1}$  (Nwadiogbu *et al.*, 2014) The band around 1245-1250  $\text{cm}^{-1}$  corresponds to C=O stretching of lignin and the band at 1052  $\text{cm}^{-1}$  represents the C-OR stretching. The band absorption at 1133  $\text{cm}^{-1}$  is assigned to C-O anti-symmetric bridge stretching vibration in cellulose, hemicelluloses and primary alcohol. (Yakubu *et al.*, 2012; Bordilau and Teaca, 2009; Nasar *et al.*, 2010). The absence of the band at 1840-1760  $\text{cm}^{-1}$  in all the treated samples showed that the acetylated samples were free of

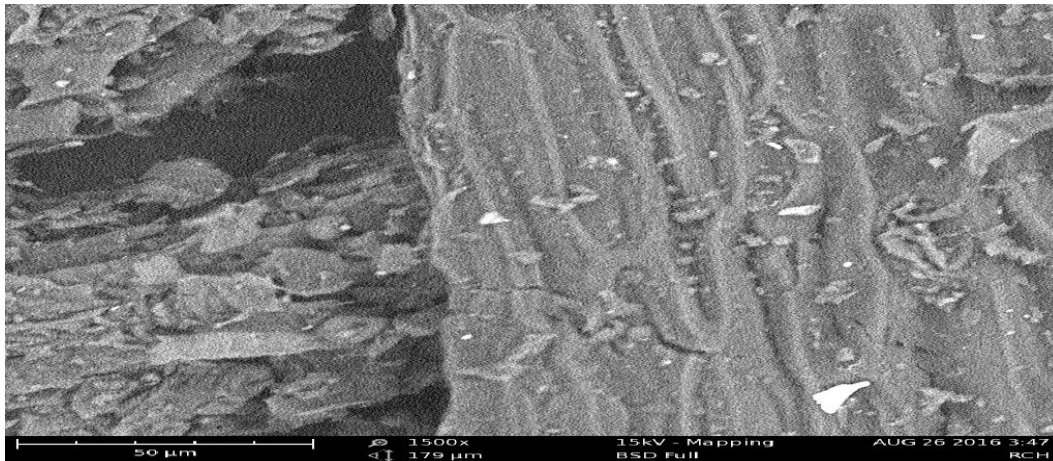
unreacted acetic anhydride (Sun *et al.*, 2002; Adebajo and Frost, 2004b). The absence of the peak at  $1700\text{ cm}^{-1}$  in all the treated samples also indicated that the acetylated products are free of acetic acid by-product.

#### 4.2.6 Morphological Characteristics of Corn husk

The SEM micrograph of the raw and acetylated corn husk are presented in Plates 4.3a and b respectively. The SEM analysis showed the surface morphologies and cross section of treated and raw corn husk.



**Plate 4.3a: SEM Micrograph of raw Corn Husk**



**Plate 4.3b SEM Micrograph for treated Corn Husk**

Plate 4.3 (a) presents the surface and cross section of raw corn husk which exhibits a smooth surface without any ripple due to the coverage of plant wax, while the surface of treated samples (Plate 4.3b) is rough along with different degree of wrinkles and grooves which increased the surface area for oil absorption. In general, the coarse surface can increase the specific surface area of corn husk enables the oil to adhere to the outer surface and enter easily into the inner surface of lumen of the material, ensuring thus high oil absorbency for the acetylated sample (Wang *et al.*, 2012).

There is also noticeable increase in the number of pores in the sorbent after acetylation. These pores can make oil entrance into the internal parts of the material easier and helpful in the sorption process. It is believed that high percentage of oil can be trapped into the porous interior of the sample by capillary mechanism (Yuh-Shan and Malarvizhi 2009). The macro porous interior fiber enhances the capillary action and the diffusion of oil through the fiber and improves the sorption properties of corn husk. However in fig 4.9b, the surface of the untreated sample is smoother with tiny ripple which became rough with high degree of wrinkles and grooves on acetylation.

## 2.7 Structural Characteristics of Plantain Peel

The FTIR spectra for the acetylated and raw plantain peel are in appendix 49 and 63 respectively.

Table 4.7 presents the summary of assignment of functional groups to the IR spectra bands in both the raw and acetylated samples of plantain peel.

**Table 4.7: Assignment of the IR spectra bands of functional groups in acetylated and raw Plantain Peel.**

Raw Sample IR freq (cm <sup>-1</sup> )	Modified Sample IR freq (cm <sup>-1</sup> )	Band Assignment
3768, 3400	3987,3765, 3403	OH- stretching, hydroxyl group
2930	2932	CH stretch, CH <sub>3</sub> -O group cellulose
2383	2374	CH <sub>3</sub> group, stretching vibration of

		aliphatic CH <sub>3</sub> group
1632	1639	C=C alkanes and H-O-H bending of adsorbed water
	1728	C=O, esters (ascribed to hemicelluloses)
1409	1416	CH deformation in -O-C=O-CH <sub>3</sub> group
-	1505	C=O stretch lignin
1258	1132	C=O stretch, acetyl group (lignin)
1032	1039	-C-O stretching vibration in cellulose, hemicelluloses and primary alcohol.
854	856	
609	602	Cis out of plane C-H band, alkanes
489	422	Si-O-Si bend, silica

The following peak intensities and bands at 3987, 3765, 3403 cm<sup>-1</sup> as seen on the IR spectra of modified plantain peel are characteristic absorption of bonded -OH stretching vibrations in cellulose and hemicelluloses (Yakubu *et al.*, 2012). The OH absorption bands of the raw sample which were detected predominantly at 3768 cm<sup>-1</sup> and 3400cm<sup>-1</sup> were enhanced after acetylation suggesting that poly-hydroxyl functional groups of plantain peel were involved in the acetylation process. This is consistent with the FTIR spectra of acetylated cellulosic materials reported by other researchers (Adebajo and Frost 2004; Nwadiogbu *et al.*, 2014). The absorption peaks around 2930 - 2932 cm<sup>-1</sup> suggests the CH stretch and CH<sub>3</sub>-O group of cellulose while the band at 2383cm<sup>-1</sup> is assigned to the CH<sub>3</sub> group and stretching vibration of aliphatic CH<sub>3</sub> group. The spectra of the acetylated sorbent showed the enhancement

of sharp peaks from  $1409\text{ cm}^{-1}$  to  $1416\text{ cm}^{-1}$  and is assigned to the  $\text{-C=O}$  stretching vibrations of aromatic rings caused by lignin. The band at  $1632 - 1639\text{ cm}^{-1}$  represents absorbed water and the band at  $1258 - 1241\text{ cm}^{-1}$  represents the  $\text{C=O}$  stretch of acetyl group (lignin). The absorption band was increased slightly from  $1028-1032\text{ cm}^{-1}$  and suggests the  $\text{-C-O}$  stretching vibration in cellulose, hemicelluloses and primary alcohol (Bordilau and Teaca, 2009; Nwadiogbu *et al.*, 2014).

#### 4.2.8 Morphological Characteristics of Plantain peel

The SEM micrograph of the acetylated and raw borassus coir are presented in Plates 4.4a and b respectively which showed the surface morphologies and cross section of raw and treated plantain peel.

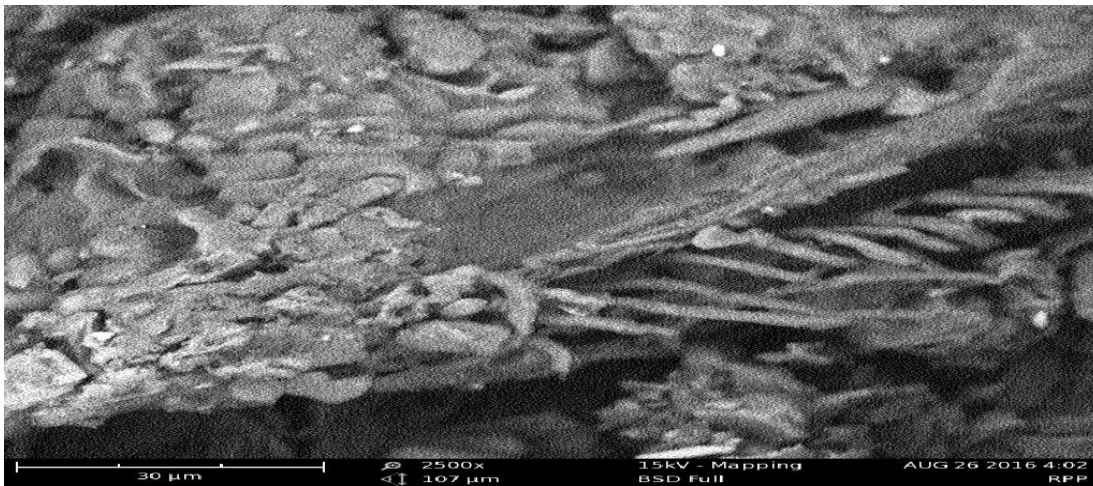
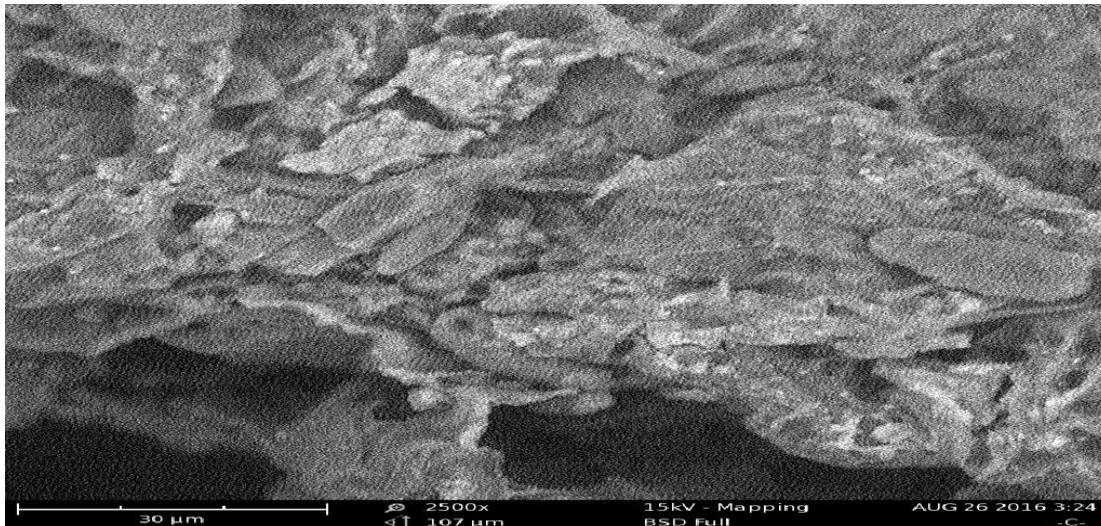


Plate 4.4a: SEM Micrograph for Raw Plantain Peel





**Plate 4.4b: SEM Micrograph for Acetylated Plantain Peel**

As can be seen in plate 4.4a, the surface of the untreated sample appeared a bit smooth with tiny ripples and became rough with high degree of wrinkles and grooves on acetylation. Plate 4.4 (b) presents the surface and cross section of treated plantain peel showing a tubular structure with holes and voids. The acetylation process changed the physical configuration of the raw plantain peel, and thus the smoothness of the surface was transformed and became rough and porous. These pores can make oil entrance into the internal parts of the material easier and helpful in the sorption process. It is believed that high percentage of oil can be trapped into the porous interior of the sample by capillary mechanism. The macro porous interior fiber enhances the capillary action and the diffusion of oil through the fiber and improves the sorption properties of plantain peel.

#### **4.2.9 Structural Characteristics of Plantain Pseudostem**

The FTIR spectra for the acetylated and raw plantain pseudostem are in appendix 72 and 78 respectively. Table 4.8 presents the summary of assignment of functional groups to the IR spectra bands in both the raw and acetylated samples of plantain pseudostem.

**Table 4.8: Assignment of the IR spectra bands of functional groups in acetylated Plantain Pseudostem.**

Raw Sample IR freq (cm <sup>-1</sup> )	Modified Sample IR freq (cm <sup>-1</sup> )	Band Assignment
3856, 3405	3743, 3875, 3751, 3404	OH – stretching, hydroxyl group
2930	2930	-CH stretch, CH <sub>3</sub> -O group cellulose
2375	2353	CH <sub>3</sub> group, stretching vibrations of aliphatic CH <sub>3</sub> group
1646	1641	C=O esters
1525	1500	C=O stretch lignin
-	1426, 1240	CH deformation in –O-C=O-CH <sub>3</sub> group
1133	1128	C=O stretching vibration in acetyl group (lignin)
1036	1037	C-O stretching vibrations in cellulose, hemicelluloses and primary alcohol.
857	862	Tri-substituted C-H bend, alkanes
617	605	Cis out of plane C-H bond

Table 4.8 presents the assignment of the IR spectra bands of functional groups in raw and acetylated plantain pseudostem. The following primary absorption peaks were observed. The broad and strong peaks at 3875, 3751, 3404 cm<sup>-1</sup> as seen on the IR spectra of modified plantain pseudostem are characteristic absorption of bonded –OH stretching vibrations in cellulose and hemicelluloses (Yakubuet *al.*, 2012; Nwadiogbuet *al.*, 2014). The strong peak around 2930cm<sup>-1</sup> was assigned to

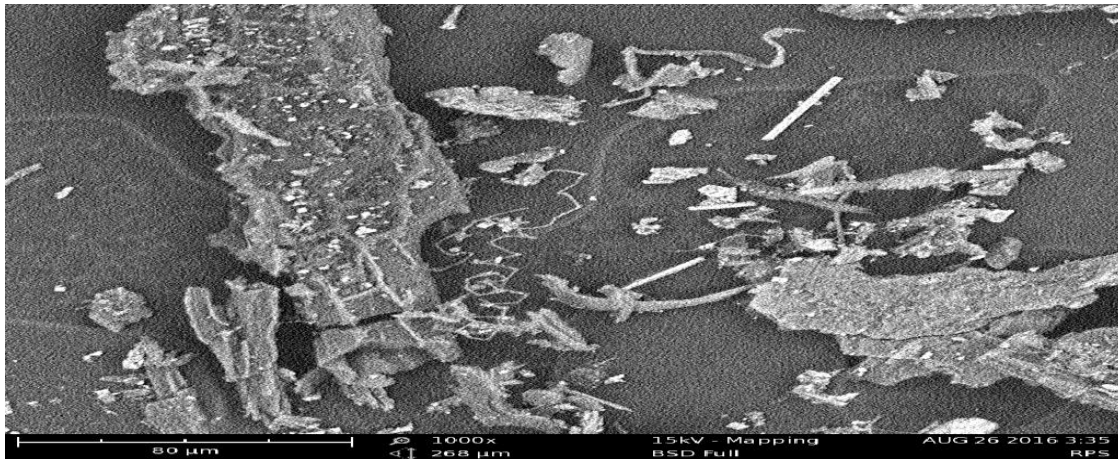
asymmetric and symmetric CH stretching vibration of CH<sub>2</sub> and CH<sub>3</sub> groups ( Lim and Huang,2007b).

By comparing the spectra of the treated and untreated plantain pseudostem sorbent, it was observed that the increase of absorption bands above 3856 cm<sup>-1</sup> was observed for the treated sample. This implies the removal of plant wax from the sample surface and the increment of cellulose hydroxyl groups in the sorbent walls due to the breaking of the hydrogen bond (Lim and Huang, 2007b, Jintaoet *al.*, 2012). The band at 1641 cm<sup>-1</sup> was assigned to the carbonyl (C=O ester) stretching vibration of acetate group in cellulose. This band showed evidence of acetylation (Mohebbby, 2008; Nasaret *al.*,2010, Nwadiogbuet *al.*, 2014). The band at 1508-1526cm<sup>-1</sup> was assigned to the C=O stretch of the lignin while the bands at 1133-1240cm<sup>-1</sup> suggests the C=O stretching vibration in acetyl group (lignin).

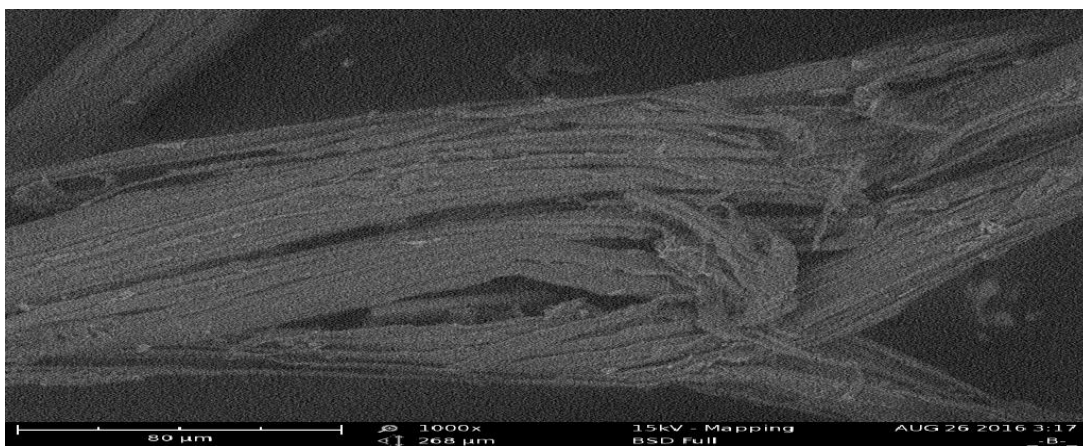
The absence of the band at 1840-1760cm<sup>-1</sup> in all the treated samples showed that the acetylated samples were free of unreacted acetic anhydride (Sunet *al.*,2002; Adebajoand Frost, 2004b). The absence of the peak at 1700 cm<sup>-1</sup> in all the treated samples also indicated that the acetylated products are free of acetic acid by-product. .The band at 605 - 617 cm<sup>-1</sup> was assigned to cis out of plane C-H bond while the band at 494 - 424 cm<sup>-1</sup> was assigned to Si-O-Si bend of silica.

#### **4.2.10 Morphological Characteristics of Plantain pseudostem**

The SEM micrograph of the raw and acetylated plantain pseudostem are presented in Plates 4.5a and b respectively which showed their surface morphologies and cross section.



**Plate 4.5a: SEM Micrograph of raw plantain pseudostem**



**Plate 4.5b: SEM micrograph for Acetylated Plantain Pseudostem**

Plate 4.5b presents the surface and cross section of treated plantain pseudostem showing a tubular structure with holes and voids. The acetylation process changed the morphological structure of the raw plantain pseudostem, and thus the smoothness of the surface was transformed and became rough and porous. These pores can make oil entrance into the internal parts of the material easier and helpful in the sorption process. It is believed that high percentage of oil can be trapped into the porous interior of the sample by capillary mechanism (Wang *et al.*, 2012).

### **4.3 Effect of Changes in Time and Catalyst**

### 4.3.1 Effect of Time and Catalyst on Extent of Acetylation of Borassus coir

Table 4.9 showed how the parameters which include time and catalyst used for acetylating the borassus coir were varied. It also presented the result of degree of acetylation which was estimated from the infrared spectra as shown in Table 4.9.

The varying acetylation conditions and the calculated degree of acetylation is presented in Table 4.9.

**Table 4.9: Acetylation conditions for borassus coir and extent of its acetylation**

Sample-ID	Solid-Liquid ratio (g/ml)	Time (min)	Catalyst (% , g/mL)	Extent of Acetylation
ABC1	1:20	30	0.2	0.80

ABC2	1:20	60	0.2	0.83
ABC3	1:20	90	0.2	0.90
ABC4	1:20	120	0.2	0.81
ABC5	1:20	150	0.2	0.86
ABC6	1:20	180	0.2	0.85
ABC7	1:20	210	0.2	0.93
ABC8	1:20	240	0.2	0.87
ABC9	1:20	60	0.4	0.89
ABC10	1:20	60	0.6	0.85
ABC11	1:20	60	0.8	0.86
ABC12	1:20	60	1.0	0.85
ABC13	1:20	60	1.2	0.94
ABC14	1:20	60	1.4	0.89
ABC15	1:20	60	1.6	0.78

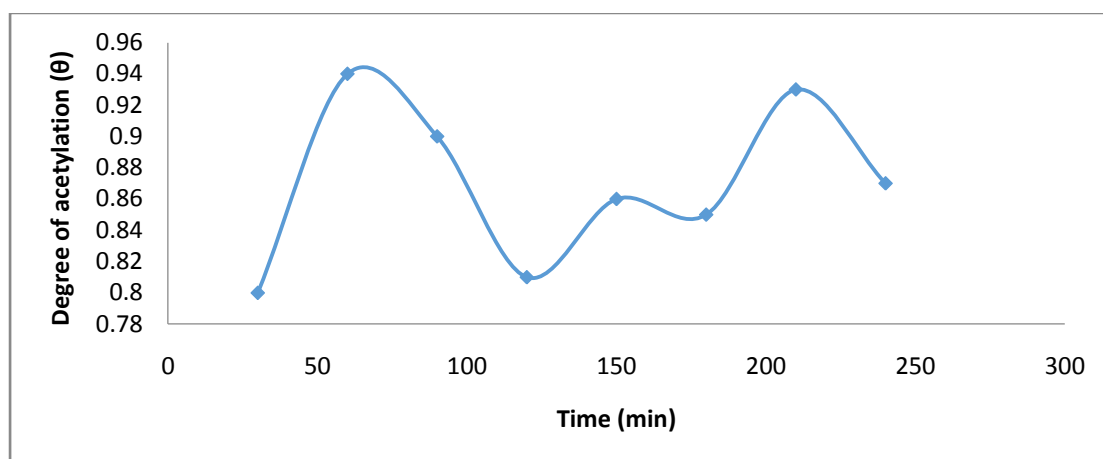
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ABC = Acetylated Borassus coir

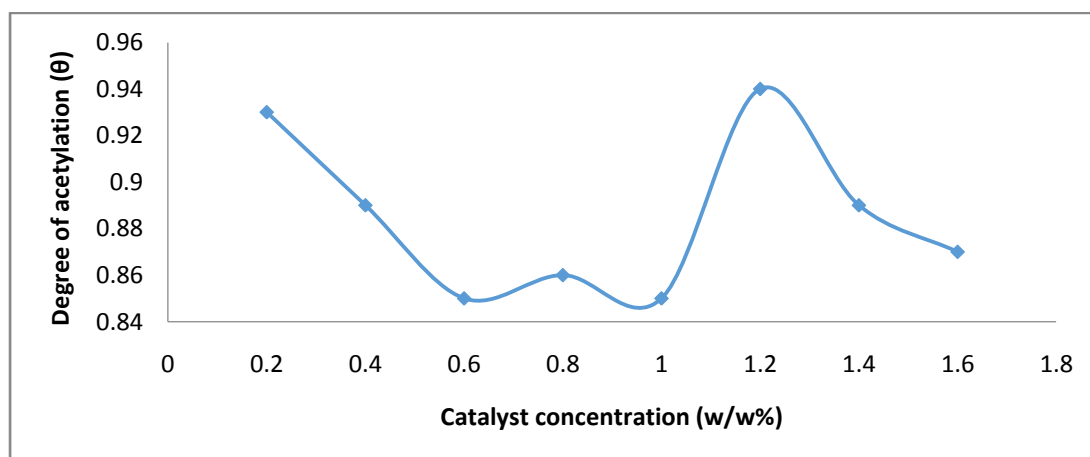
From Table 4.9, it could be seen that time and catalyst concentration were varied for eight times each parameter. The time was varied from 30 to 240 minutes at 30 minutes interval. The concentration of catalyst used for the acetylation was 0.2g/mL and later varied from 0.2 to 1.6g/mL at 0.2 interval. The extent of acetylation as

calculated was presented and it could be observed that the highest value of 0.94 for sample called ABC13 was at 60 minutes at catalyst concentration of 1.2g/mL.

The effect of time and catalyst on extent of acetylation of borassus coir are graphically shown in figures 4.1 and 4.2.



**Fig 4.1: Effect of time on degree of acetylation of borassus coir**



**Fig 4.2: Effect of catalyst on degree of acetylation of borassus coir**

The trends observed are not steady (neither decreasing nor increasing) in the variations of the extent of acetylation with reaction time and catalyst. No linear relationship was observed between degree of acetylation and time/catalyst concentration. However a haphazard movement with optimal degree of acetylation of

0.94 observed at 60 minutes and catalyst concentration of 1.2g/ mL was observed. This may be due to the complex nature of borassus coir. From the study, we observed that the lignin content was 26.25%, cellulose 37.3% while hemicellulose was found to be 24%. Evidence as reported by Reddy *et al.*, (2012) showed that cellulose is the major component of borassus coir (about 53.4%) from his study. Other constituents include hemicelluloses 29.6% and lignin 17%.

Different types of hydroxyl group will react differently with acetic anhydride. For instance, in the study of acetyl distribution in acetylated (whole wood and reactivity of isolated wood cell wall components to acetic anhydride by Rowell *et al.*, (1994), they observed the order of reactivity to be lignin > hemicelluloses >> holocellulose. Holocellulose is the remaining product after removal of lignin from wood). It was also observed that cellulose did not react with acetic anhydride in the absence of a catalyst. Therefore, the unsteady pattern of the extent of acetylation could be attributed to the complex nature of the sample as explained above.

The effect of time on degree of acetylation of the five samples was tested for statistical difference. Analysis of variance (ANOVA) results are presented in Table 4.10.

**Table 4.10: ANOVA result on the effect of Time on the Extent of Acetylation of Corn Husk, *Borassus aethopum* coir, African breadfruit seed husk, Plantain peel and Plantain pseudostem.**



	<b>Sum of</b>				
	<b>Squares</b>	<b>df</b>	<b>Mean Square</b>	<b>F</b>	<b>p-value</b>
Between					
Groups	.079	7	.011	2.426	.041
Within Groups	.149	32	.005		
Total	.228	39			

Table 4.10 presents the analysis of variance of the effect of time on the extent of acetylation using corn husk, borassus coir, African breadfruit seed husk, plantain peel, and plantain pseudostem as replications.

The null hypothesis ( $H_0$ ), is that time did not affect the acetylation of the five samples. Rejection of the hypothesis  $H_0$  implies the acceptance of the alternative hypothesis ( $H_1$ ), that time affected the acetylation of the five samples. This statistical analysis was performed at 5% significant level. In this case, we reject  $H_0$  if p-value is less than 0.05 and conclude that there is significant difference in the performance of the different variables. The table revealed that time has a significant effect on the extent of acetylation with an F-statistic of 2.426 and a p-value of 0.041 which is less than the level of significance  $\alpha=0.05$ . This therefore implied that time have significant effects on the extent of acetylation of the five samples studied.

Table 4.11 presents the analysis of variance of the effect of catalyst on the extent of acetylation using corn husk, borassus coir, African breadfruit seed husk, plantain peel, and plantain pseudostem

**Table 4.11: ANOVA result on the effect of Catalyst on the Extent of Acetylation of Corn Husk, Borassus coir, African breadfruit seed husk, Plantain peel and Plantain pseudostem.**

	Sum of Squares	df	Mean Square	F	p-value
Between Groups	.132	7	.019	6.973	.001
Within Groups	.087	32	.003		
Total	.219	39			

The null hypothesis ( $H_0$ ), is that catalyst did not affect the acetylation of the five samples. Rejection of the hypothesis  $H_0$  implies the acceptance of the alternative hypothesis ( $H_1$ ), that catalyst affected the acetylation of the five samples. This statistical analysis was performed at 5% significant level. In this case, we reject  $H_0$  if p-value is less than 0.05 and we conclude that there is significant difference in the performance of the different variables. Therefore catalyst concentration affected the acetylation of the five samples.

Table 4.11 revealed that catalyst has a significant effect on the extent of acetylation with an F-statistic of 6.973 and a p-value of 0.001 which is less than the level of significance  $\alpha=0.05$ .

#### **4.3.2: Effect of Time and Catalyst on Extent of Acetylation on corn husk**

Table 4.12 showed how the parameters, time and catalyst were varied in the acetylation process. It also presented the result of degree of acetylation which was estimated from the infrared spectra.

**Table 4.12: Acetylation conditions for Corn Husk and the extent of its acetylation.**

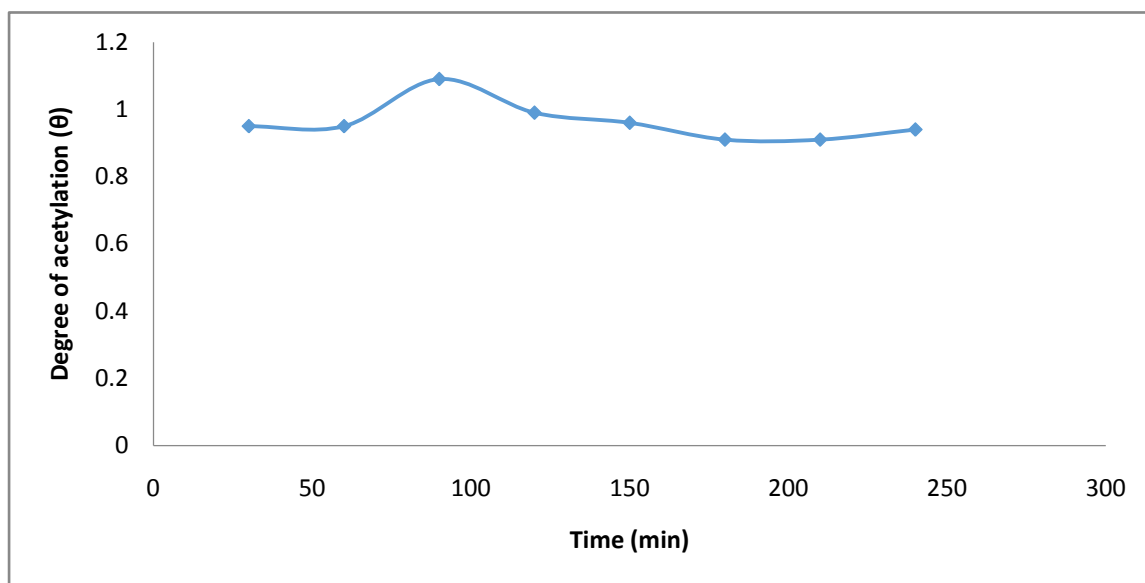
Sample-ID	Solid-Liquid ratio (g/mL)	Time (min)	Catalyst (% g/mL)	Extent of Acetylation
ACH1	1:20	30	0.2	0.95
ACH2	1:20	60	0.2	0.95
ACH3	1:20	90	0.2	1.09
ACH4	1:20	120	0.2	0.99
ACH5	1:20	150	0.2	0.96
ACH6	1:20	180	0.2	0.91
ACH7	1:20	210	0.2	0.91
ACH8	1:20	240	0.2	0.94
ACH9	1:20	60	0.4	0.88
ACH10	1:20	60	0.6	0.85
ACH11	1:20	60	0.8	0.91
ACH12	1:20	60	1.0	0.93
ACH13	1:20	60	1.2	0.91
ACH14	1:20	60	1.4	0.83
ACH15	1:20	60	1.6	0.90

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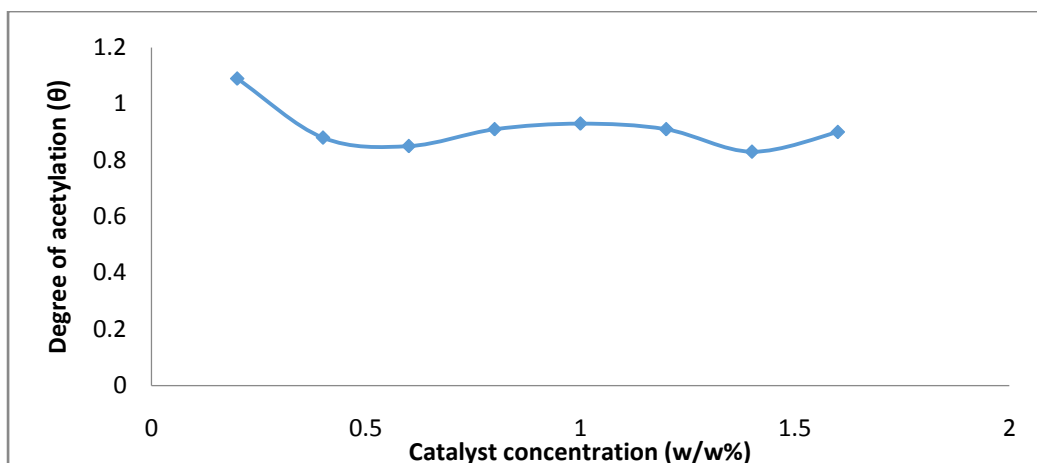
ACH = Acetylated corn husk

From Table 4.12, it can be seen that time and catalyst concentration were varied for eight times for each variable. The time was varied from 30 to 240 minutes at 30 minutes interval while the concentration of catalyst used for the acetylation was 0.2g/mL and later varied from 0.2 to 1.6g/mL at 0.2 interval. The extent of acetylation as calculated was presented and it could be observed that the highest value of 1.09 was observed at 90 minutes at catalyst concentration of 0.2g/mL for the corn husk sample with Id ACH3.

The effect of time and catalyst on the extent of acetylation is graphically presented in figures 4.3 and 4.4 below.



**Fig 4.3: Effect of time on degree of acetylation of Corn Husk**



**Fig 4.4: Effect of catalyst on degree of acetylation of corn husk.**

It was observed from the plot of effect of time on degree of acetylation that there was an increase on the degree of acetylation when time was varied from 30 to 90 minutes. The optimal degree of acetylation was observed at 90 minutes after which there was a downward trend with a very slight increase at 240 minutes. The same trend was observed for the effect of catalyst on the degree of acetylation. The optimal degree of acetylation was achieved with 0.2g of catalyst after which the degree of acetylation gradually reduced as the catalyst concentration was increased.

The effect of time and catalyst on degree of acetylation of corn husk was tested for statistical difference. Analysis of variance (ANOVA) results are shown in Table 4.10 and 4.11 earlier presented. Table 4.10 revealed that time has a significant effect on the extent of acetylation with F-statistic of 2.426 and a p-value of 0.041 which is less than the level of significance  $\alpha=0.05$ . This therefore implied that time have significant effects on the extent of acetylation of corn husk. Table 4.11 revealed that catalyst has a significant effect on the extent of acetylation with an F-statistic of 6.973 and a p-value of 0.000 which is less than the level of significance  $\alpha=0.05$ .

### 4.3.3 Effect of Time and Catalyst on extent of acetylation of African breadfruit seed husk

Table 4.13 presents how time and catalyst were varied in the acetylation process. It also showed the degree of acetylation which was estimated from the infrared spectra.

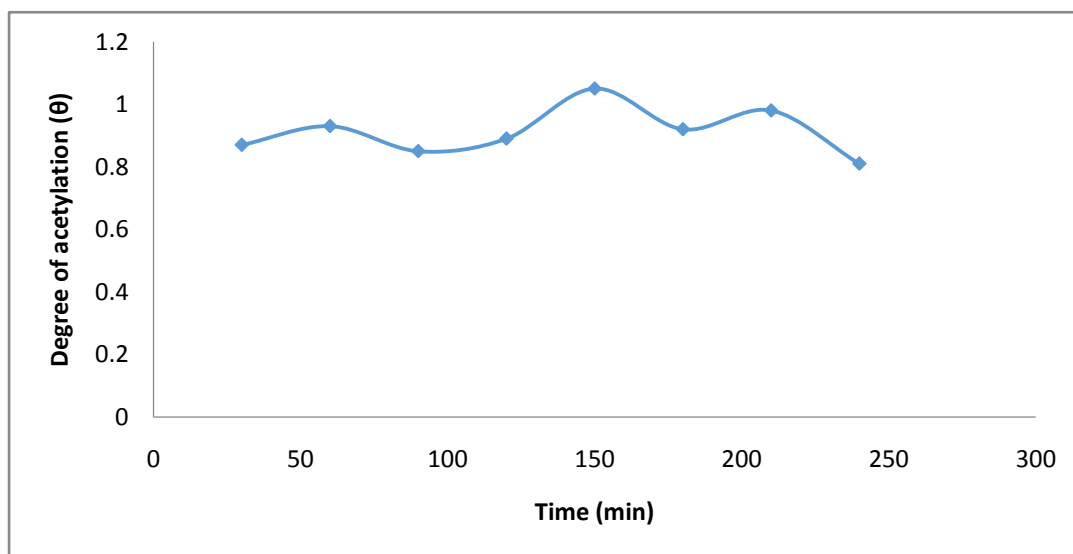
**Table 4.13 Acetylation conditions for African breadfruit seed husk and the extent of its acetylation.**

Sample-ID	Solid-Liquid ratio (g/ml)	Time (min)	Catalyst (% g/mL)	Extent of Acetylation
ABF1	1:20	30	0.2	0.87
ABF2	1:20	60	0.2	0.93
ABF3	1:20	90	0.2	0.85
ABF4	1:20	120	0.2	0.89
ABF5	1:20	150	0.2	1.05
ABF6	1:20	180	0.2	0.92
ABF7	1:20	210	0.2	0.98
ABF8	1:20	240	0.2	0.81
ABF9	1:20	60	0.4	0.89
ABF10	1:20	60	0.6	0.98
ABF11	1:20	60	0.8	0.80
ABF12	1:20	60	1.0	0.86
ABF13	1:20	60	1.2	0.88
ABF14	1:20	60	1.4	0.91
ABF15	1:20	60	1.6	0.95

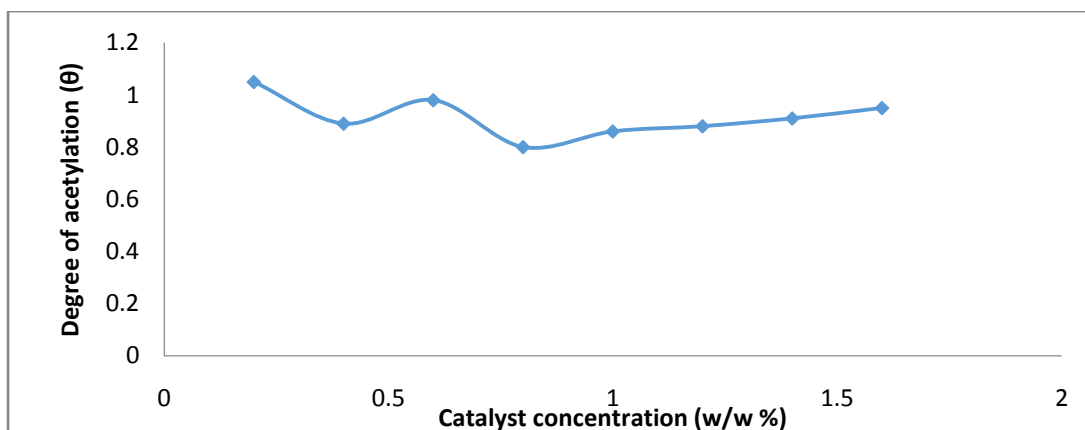
ABF = African breadfruit seed husk

It could be seen from Table 4.13 that time and catalyst concentration were equally varied for eight times. The time was varied from 30 to 240 minutes at 30 minutes interval while the concentration of catalyst used for the acetylation was 0.2g/mL and later varied from 0.2 to 1.6g/mL at 0.2 interval. The extent of acetylation as calculated was presented and it could be observed that at 150 minutes at catalyst concentration of 0.2g/mL, the degree of acetylation was found to be 1.05 which is the highest value. African breadfruit seed husk with sample ID ABF5 gave the optimal extent of acetylation.

The effect of time and catalyst on extent of acetylation is shown graphically in figures 4.5 and 4.6 respectively.



**Fig 4.5: Effect of time on degree of acetylation of African breadfruit seed husk**



**Fig 4.6: Effect of catalyst on degree of acetylation of African breadfruitseed husk**

The trend observed is also not steady (neither decreasing nor increasing) in the variations of the extent of acetylation with reaction time with optimal degree of acetylation at 150 minutes. For effect of catalyst on degree of acetylation, there were fluctuations with optimal degree of acetylation achieved at catalyst concentration of 0.2g. From concentration of 0.8g, a gradual increase was noticed till concentration of 1.6g. However the increase was not up to the optimal degree of acetylation of 1.05.

From this study we observed that lignin is the major component of African breadfruit seed husk with 28%. Other constituents are cellulose 4.70% and hemicellulose with 4.13%. Different types of hydroxyl group will react differently with acetic anhydride. For instance, in the study of acetyl distribution in acetylated (whole wood and reactivity of isolated wood cell wall components to acetic anhydride by Rowellet *al.*, (1994), they observed the order of reactivity to be lignin > hemicelluloses >> holocellulose. It was also observed that cellulose did not react with acetic anhydride in the absence of a catalyst. Therefore, the unsteady pattern of the extent of acetylation could be attributed to the complex nature of the sample as explained above.



The effect of time and catalyst on degree of acetylation of African breadfruit seed husk was tested for statistical difference. Analysis of variance (ANOVA) results are shown in Table 4.10 and 4.11 earlier presented. Table 4.10 revealed that time has a significant effect on the extent of acetylation with F-statistic of 2.426 and a p-value of 0.041 which is less than the level of significance  $\alpha=0.05$ . This therefore implied that time had significant effects on the extent of acetylation of African breadfruit seed husk. Table 4.11 revealed that catalyst has a significant effect on the extent of acetylation with an F-statistic of 6.973 and a p-value of 0.001 which is less than the level of significance  $\alpha=0.05$ .

#### **4.3.4 Effect of Time and catalyst on extent of acetylation of plantain peel**

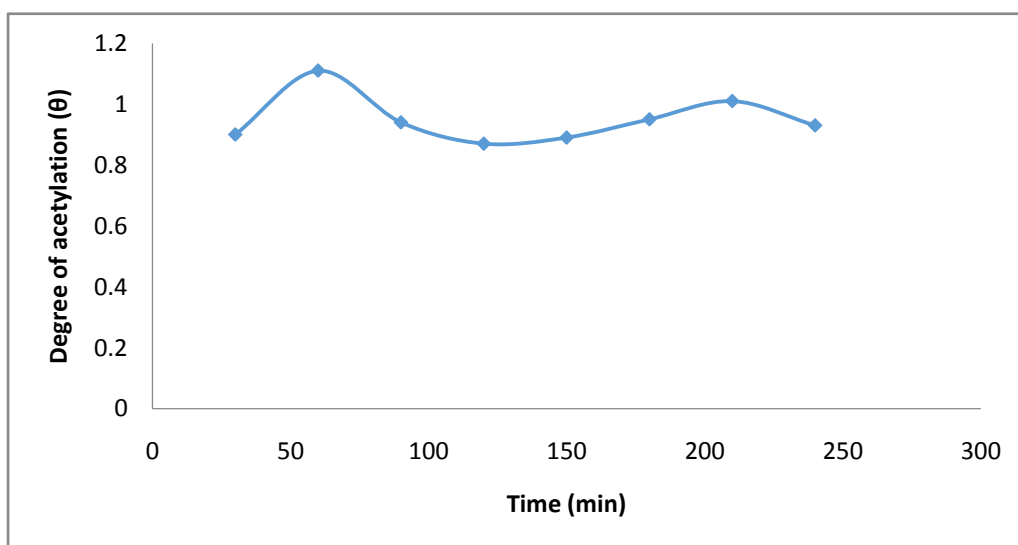
Table 4.14 presents how time and catalyst were varied in the acetylation process. It also showed the degree of acetylation which was estimated from the infrared spectra.

**Table 4.14: Acetylation conditions for Plantain Peel and the results obtained**

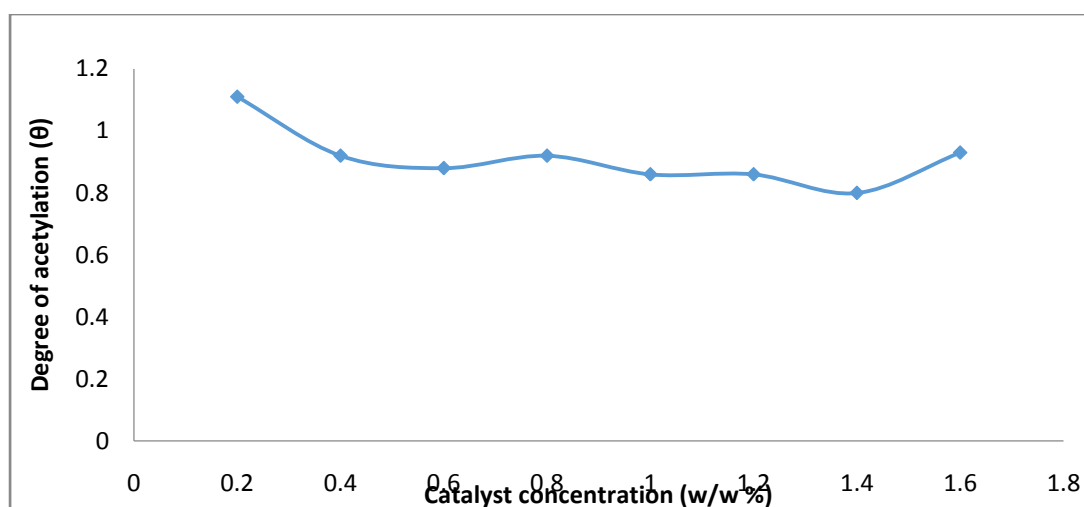
Sample-ID	Solid-Liquid ratio (g/mL)	Time (min)	Catalyst (% , g/mL)	Extent of Acetylation
APP1	1:20	30	0.2	0.90
APP2	1:20	60	0.2	1.11
APP3	1:20	90	0.2	0.94
APP4	1:20	120	0.2	0.87
APP5	1:20	150	0.2	0.89
APP6	1:20	180	0.2	0.95
APP7	1:20	210	0.2	1.01
APP8	1:20	240	0.2	0.93
APP9	1:20	60	0.4	0.92
APP10	1:20	660	0.6	0.88
APP11	1:20	60	0.8	0.92
APP12	1:20	60	1.0	0.86
APP13	1:20	60	1.2	0.82
APP14	1:20	60	1.4	0.86
APP15	1:20	60	1.6	0.80

APP = Acetylated plantain peel

From Table 4.14, it can be seen that time and catalyst concentration was varied for eight times at 30 minutes interval and at 0.2g/mL respectively. The extent of acetylation as calculated was presented and it could be observed that the optimal degree of acetylation of 1.1 was achieved at 60 minutes with catalyst concentration of 0.2g/mL. The effect of time and catalyst on degree of acetylation are shown in figures 4.7 and 4.8 respectively.



**Fig 4.7:** Effect of time on degree of acetylation of plantain peel



**Fig 4.8:** Effect of catalyst on degree of acetylation of plantain peel

The trends observed are not steady (neither decreasing nor increasing) in the variations of the extent of acetylation with reaction time and catalyst. The optimal degree of acetylation of 1.1 was observed at 60 minutes and catalyst concentration of 0.2g.

The effect of time and catalyst on degree of acetylation of plantain peel was tested for statistical difference. Analysis of variance (ANOVA) results are shown in Table 4.10 and 4.11 earlier presented. Table 4.10 revealed that time has a significant effect on the extent of acetylation with F-statistic of 2.426 and a p-value of 0.041 which is less than the level of significance  $\alpha=0.05$ . This therefore implied that time have significant effects on the extent of acetylation of plantain peel. Table 4.11 revealed that catalyst has a significant effect on the extent of acetylation with an F-statistic of 6.973 and a p-value of 0.001 which is less than the level of significance  $\alpha=0.05$ .

#### **4.3.5 Effect of Time and Catalyst on extent of acetylation of Plantain Pseudostem**

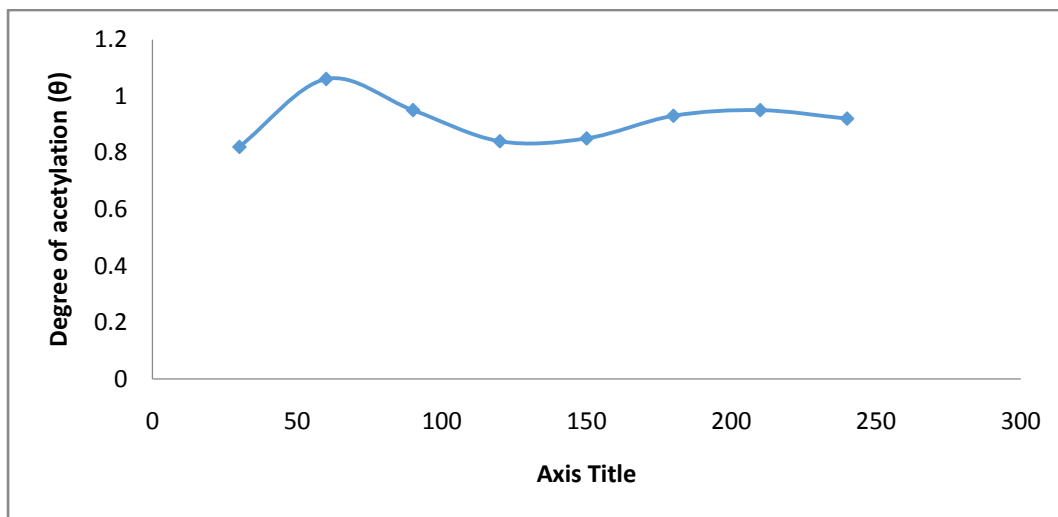
Table 4.15 presents the variation of time and catalyst in the acetylation process and the extent of acetylation as determined from the FTIR spectra. The varying acetylation conditions and the calculated degree of acetylation is also presented in Table 4.15.

**Table 4.15: Acetylation conditions for Plantain Pseudostem and the results obtained.**

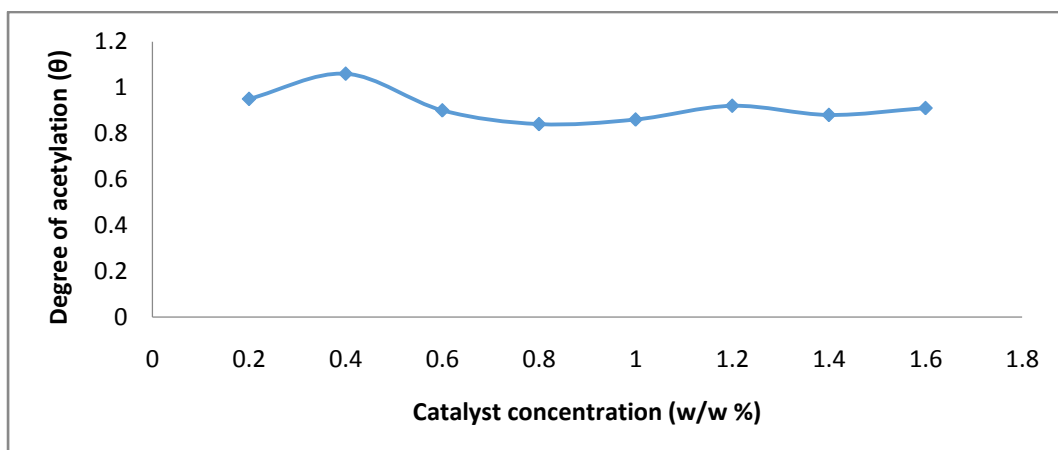
Sample-ID	Solid-Liquid ratio (g/mL)	Time (min)	Catalyst (% , g/mL)	Extent of Acetylation
APS1	1:20	30	0.2	0.82
APS2	1:20	60	0.2	0.86
APS3	1:20	90	0.2	0.95
APS4	1:20	120	0.2	0.84
APS5	1:20	150	0.2	0.85
APS6	1:20	180	0.2	0.93
APS7	1:20	210	0.2	0.95
APS8	1:20	240	0.2	0.92
APS9	1:20	60	0.4	1.06
APS10	1:20	60	0.6	0.90
APS11	1:20	60	0.8	0.84
APS12	1:20	60	1.0	0.86
APS13	1:20	60	1.2	0.82
APS14	1:20	60	1.4	0.88
APS15	1:20	60	1.6	0.91

APS = Acetylated plantain stem

From Table 4.15, it can be seen that time and catalyst concentration was varied for eight times each. The time was varied from 30 to 240 minutes at 30 minutes interval. The concentration of catalyst used for the acetylation was 0.2g/mL and later varied from 0.2 to 1.6g/mL at 0.2 intervals. The extent of acetylation as calculated was presented and it could be observed that optimal acetylation of 1.06 was achieved at 60 minutes at catalyst concentration of 0.4g/mL. The sample that gave the optimal acetylation was APS9. The effect of time and catalyst on the extent of acetylation is shown in figures 4.9 and 4.10 respectively.



**Fig 4.9:** Effect of time on degree of acetylation of plantain pseudostem.



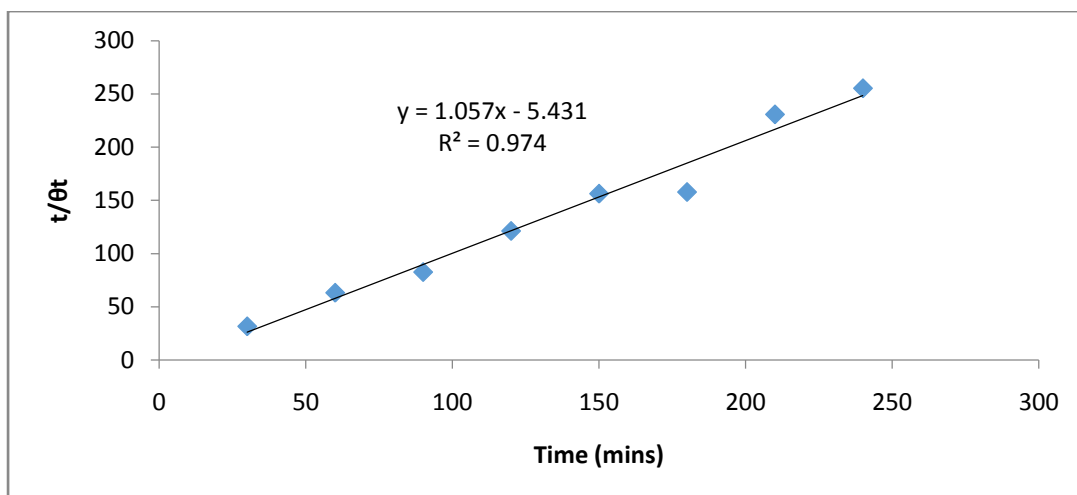
#### **Fig 4.10: Effect of catalyst on degree of acetylation of plantain pseudostem**

It was observed from the plot of effect of time on degree of acetylation that there was an increase on the degree from 30 to 90 minutes. The optimal degree of acetylation was seen at 60 minutes after which there was a downward trend that fluctuated to 240 minutes. The same trend was observed for the effect of catalyst on the degree of acetylation. The optimal degree of acetylation was achieved with 0.4g of catalyst after which the degree of acetylation gradually reduced as the catalyst concentration was increased. The effect of time and catalyst on degree of acetylation of corn husk was tested for statistical difference. Analysis of variance (ANOVA) results are shown in Table 4.10 and 4.11 earlier presented and discussed.

### **4.4 Kinetics of Acetylation**

#### **4.4.1 Kinetics of Corn Husk acetylation**

The kinetics for the acetylation of corn husk was studied by fitting obtained data in rate curves presented earlier in (Table 3.1). The predicted kinetics from the linear plots of first order, second order, pseudo-second-order, intra-particle diffusion and liquid film diffusion models were all considered. However, the plot of only the pseudo-second order kinetics which gave the best fit was presented in fig 4.11.



**Fig 4.11: Pseudo-Second-Order Kinetics of Corn Husk Acetylation**

The summary of the calculated kinetics derived from the constants are shown in Table 4.16.

**Table 4.16: Summary of Kinetics from the Plots of Corn Husk Acetylation**

<b>Kinetic Model</b>	<b>Values</b>
$\Theta_{0exp}(mg/g)$	1.09
<b>First Order</b>	
$\Theta_{0theo}(mg/g)$	1.02
$R^2$	0.286
$K^1$	$-5 \times 10^{-4}$
<b>Second-Order</b>	
$\Theta_{0theo}(mg/g)$	1.02
$R^2$	0.3175
$K^2$	$6 \times 10^{-4}$
<b>Pseudo- Second-Order</b>	
$\Theta_{0theo}(mg/g)$	0.96
$R^2$	0.9747
$K^2$	1.058
<b>Intra-Particle Diffusion</b>	



$K_d$ ( meq g <sup>-1</sup> s <sup>1/2</sup> )	$-7.9 \times 10^{-3}$
$R^2$	0.1918
C	1.0475
<b>Liquid Film Diffusion</b>	
$K_{fd}$ ( meq g <sup>-1</sup> s <sup>1/2</sup> )	0.0012
$R^2$	0.19411

Table 4.16 presents the summary of the calculated kinetics derived from the constants. From the table, the very low values for the regression ( $R^2$ ) for first and second order expression 0.286 and 0.3175 respectively suggests that it is inappropriate to use this kinetics to represent the acetylation of corn husk. Coefficient of regression ( $R^2$ ) within  $0.43 \leq R^2 \leq 0.83$  are considered high and moderate (Dowine and Heath, 1974). It was also observed that the first and second order produced theoretical values of 1.02 and 1.023 respectively while the experimental value was 1.09.

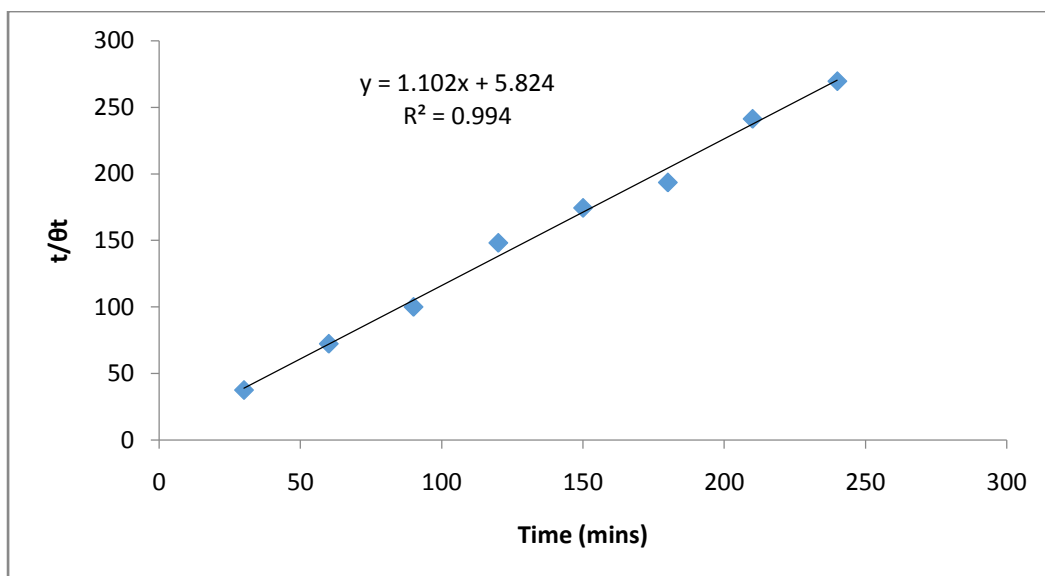
The pseudo second order gave a high  $R^2$  value of 0.9747 and also a theoretical value of 0.946 which is equally close to the experimental value of 1.09. The very high  $R^2$  therefore suggests that it is the optimum expression to represent the acetylation of corn husk. High and moderate values of  $R^2$  obtained at room temperature for first, second and pseudo second order kinetic plots also suggests that acetylation of corn husk is energy efficient since physical and chemical reaction between the modifier (acetic anhydride and NBS catalyst) and corn husk could take place at room temperature.

A low value of  $R^2$  value of 0.1918 was obtained for intra- particle diffusion model and the plot did not pass through the origin. This indicates that the rate determining step

may not be intra particle diffusion and could be other mechanism. A plot of  $\ln(1-F)$  as a function of  $t$  with a zero intercept would suggest that the kinetics of acetylation are controlled by diffusion through the liquid film surface surrounding the solid sorbent. The linearity of the plot for the liquid film diffusion model indicated the high applicability of this model (Nwadiogbu *et al.*, 2016), though it this did not pass through the origin. Furthermore, the liquid film mechanism produced a poor but slightly higher  $R^2$  (0.194) while the intra-particle diffusion model gave  $R^2$  value of (0.1918) for the acetylated corn husk. Therefore, from the results we can conclude that liquid film diffusion model is more applicable to acetylation of corn husk.

#### **4.4.2 Kinetics of Borassus Coir acetylation**

The kinetics for the acetylation of borassus coir was studied by fitting obtained data in rate curves (Table 3.1) earlier presented. The predicted kinetics from the linear plots of first order, second order, pseudo-second-order, intra-particle and liquid film diffusion models were all considered. However, the plot of only the pseudo-second order kinetics which gave the best fit was presented in fig 4.12.



**Fig 4.12: Pseudo Second-Order kinetics for Acetylation of Borassus coir**

The summary of the calculated kinetics derived from the constants are shown in Table 4.17.

**Table 4.17: Summary of Kinetics from the Plots of Borassus coir Acetylation**

<b>Kinetic models</b>	<b>Values</b>
$\Theta_{0exp}$	0.94
<i>First Order</i>	
$\Theta_{0theo}$	1.24

R <sup>2</sup>	0.398
K <sub>1</sub>	4 x 10 <sup>-4</sup>
<i>Second Order</i>	
Θ <sub>0theo</sub>	0.807
R <sup>2</sup>	0.4137
K <sub>1</sub>	-5 x 10 <sup>-4</sup>
<i>Pseudo- Second-Order</i>	
Θ <sub>0theo</sub>	0.907
R <sup>2</sup>	0.994
K <sub>1</sub>	1.1
<i>Intra-Particle Diffusion</i>	
K <sub>d</sub>	8.5 x 10 <sup>-3</sup>
R <sup>2</sup>	0.4178
C	0.7658
<i>Liquid Film Diffusion</i>	
K <sub>fd</sub> ( meq g <sup>-1</sup> s <sup>1/2</sup> )	-0.0057
R <sup>2</sup>	0.2098

From the table, very low values were obtained for regression (R<sup>2</sup>) for first and second order kinetic plots with values of 0.398 and 0.4137 respectively which is considered low. This suggests that it is inappropriate to use this kinetics to represent the acetylation of *Borassus coir*. It was also observed that the first and second order produced theoretical values of 1.24 and 0.807 respectively while the experimental value was 0.94.

The pseudo second order gave a very high R<sup>2</sup>value of 0.994 which was close to 1 indicating that the pseudo second order kinetic model produced a better fit to the data and also a theoretical value of 0.907 which is closer to the experimental value

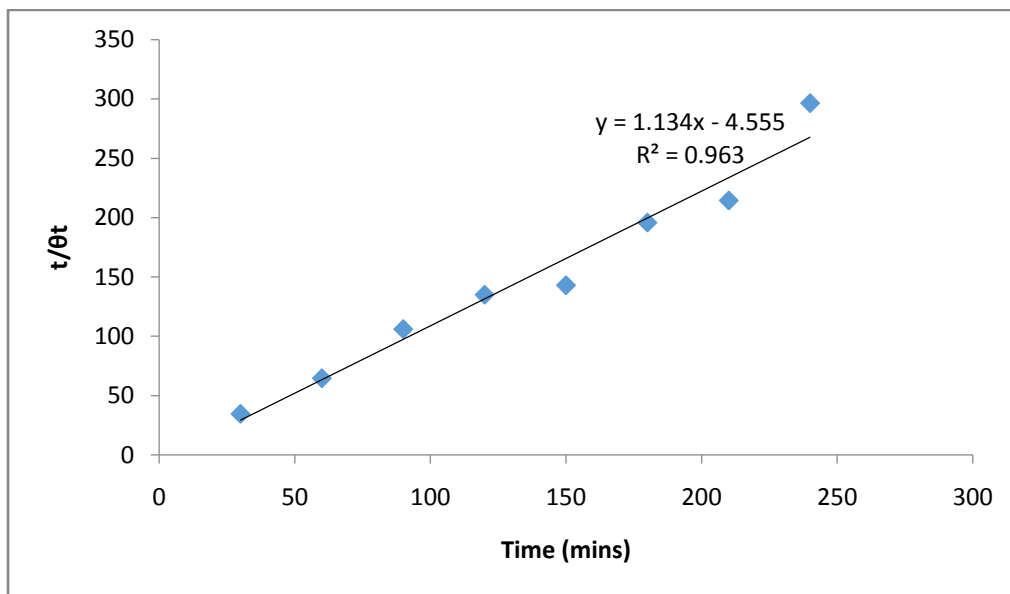
of 0.94 suggesting that it is the best kinetic model to represent the acetylation of borassus coir. High value of  $R^2$  obtained at room temperature for pseudo second order kinetic plots also suggests that acetylation of borassus coir is energy efficient since physical and chemical reaction between the modifier (acetic anhydride and NBS catalyst) and borassus coir can take place at room temperature.

Intra-particle diffusion model was also used to further study the mechanism of acetylation. The  $R^2$  obtained was low 0.4178 which is considered to be moderate. It was expected that the plot of  $q_t$  versus  $t^{1/2}$  would give a linear relationship when intra-particle diffusion is involved in the acetylation process and that it would be the controlling mechanism if the line passed through the origin (Hill *et al.*, 1998; Igwe and Abia, 2006; Krishnaiah *et al.*, 2008). The plot is linear but did not pass through the origin and this may be because intra-particle diffusion was not the only mechanism involved in the acetylation process due to some degree of boundary layer control (Bulut *et al.*, 2008; Nwadiogbu *et al.*, 2014).  $C$  is a constant that gives an idea about the thickness of the boundary layer. The larger the value of  $C$  the greater the boundary layer effect. From this study the value of  $C$  was small at a value of 0.766 implying that the boundary layer effect is very minimal.

The liquid film mechanism produced a poor  $R^2$  (0.2098) while the intra-particle diffusion model gave a better  $R^2$  value (0.4178) for the acetylated borassus coir. The results of the kinetic studies revealed that, acetylation of borassus coir is by surface reaction on borassus coir. This is in agreement with results elsewhere (Hill *et al.*, 1998).

#### **4.4.3 Kinetics of African Breadfruit Seed Husk acetylation**

The kinetics for the acetylation of African breadfruit seed husk was studied by fitting obtained data in different rate curves listed below. The predicted kinetics from the linear plots of first order, second order, pseudo-second-order, intra-particle diffusion and liquid film diffusion models were all considered. However, the plot of only the pseudo-second order kinetics which gave the best fit was presented in fig 4.13.



**Fig 4.23: Pseudo Second-Order kinetics for Acetylation of African Breadfruit Seed Husk**

The summary of the calculated kinetics derived from the constants is presented in Table 4.18.

**Table 4.18: Summary of Kinetics from the Plots of African Breadfruit Seed Husk Acetylation**

Kinetic model	Values
$\Theta_{0exp}$	1.05
<i>First Order</i>	
$\Theta_{0theo}$	1.11

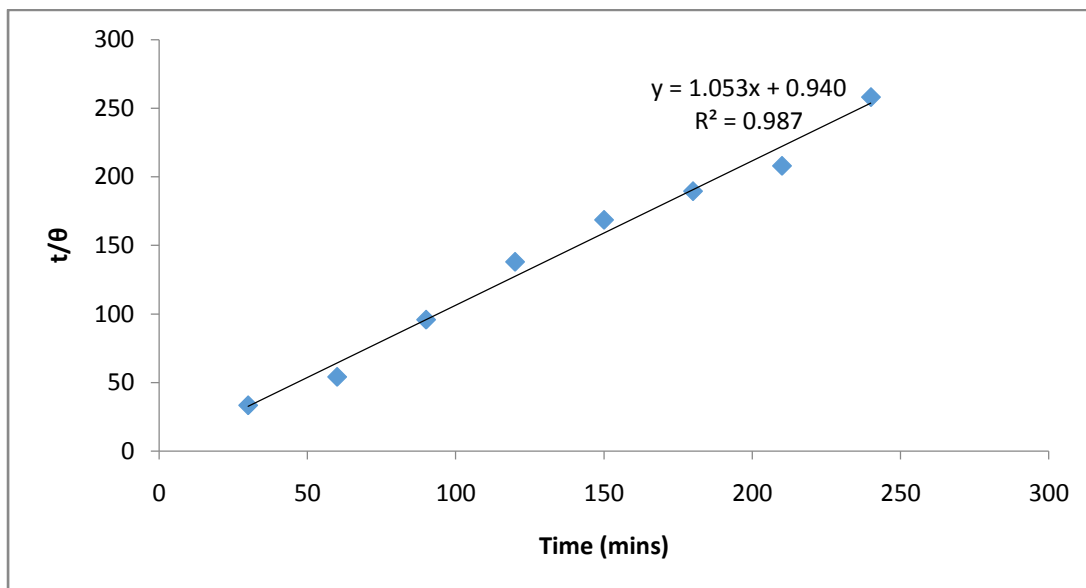
$R^2$		0.0036
$K_1$		$5 \times 10^{-8}$
<i>Second Order</i>		
$\Theta_{\text{theo}}$		0.90
$R^2$	0.0012	
$K_1$		$5 \times 10^{-4}$
<i>Pseudo- Second-Order</i>		
$\Theta_{\text{theo}}$		0.882
$R^2$	0.9637	
$K_1$		1.1345
<i>Intra-Particle Diffusion</i>		
$K_d$		$2.9 \times 10^{-3}$
$R^2$		0.0169
C		0.8803
<i>Liquid Film Diffusion</i>		
$K_{fd} \text{ ( meq g}^{-1} \text{ s}^{1/2})$		0.0002
$R^2$		0.0015

From Table 4.18, very low values were obtained for the regression ( $R^2$ ) for first and second order expression at 0.0036 and 0.0012 respectively which could be said to be very low. This suggests that it is inappropriate to use this kinetics to represent the acetylation of African breadfruit seed husk. The pseudo second order gave a very high  $R^2$  value of 0.9637 which was close to 1 indicating that the pseudo second order kinetic model produced a better fit to the data. It also suggests that it is the best kinetic model to represent the acetylation of African breadfruit seed husk.

Intra-particle and liquid film diffusion models were also used to further study the mechanism of acetylation. The  $R^2$  obtained were very low (0.0169) for intra particle

and 0.0015 for liquid film diffusion. Therefore we cannot say for sure that either surface reaction or diffusion mechanism was involved. It was expected that the plot of  $q_t$  versus  $t^{1/2}$  would give a linear relationship when intra-particle diffusion is involved in the acetylation process and that it would be the controlling mechanism if the line passed through the origin (Hill *et al.*, 1998; Igwe and Abia, 2006; Krishnaiah *et al.*, 2008). **4.4.4: Kinetics of Plantain Peel Acetylation**

The kinetics for the acetylation of plantain peel was studied by fitting obtained data in rate curves listed earlier. The predicted kinetics from the linear plots of first order, second order, pseudo-second-order, intra-particle and liquid diffusion models were all considered. However, the plot of only the pseudo-second order kinetics which gave the best fit was presented in fig 4.14.



**Fig 4.14: Pseudo Second-Order Kinetics for Plantain Peel Acetylation**



The summary of the calculated kinetics derived from the constants is presented in Table 4.19.

**Table 4.19: Summary of Kinetics from the Plots of Plantain Peel Acetylation.**

Kinetic model	Values
$\Theta_{0exp}$	1.11
<i>Pseudo First Order</i>	
$\Theta_{0theo}$	1.05
$R^2$	0.002
$K_1$	$-5 \times 10^{-6}$
<i>Second Order</i>	

---

$\Theta_{\text{theo}}$	0.96
$R^2$	0.0334
$K_2$	$2 \times 10^{-4}$
<i>Pseudo- Second-Order</i>	
$\Theta_{\text{theo}}$	0.949
$R^2$	0.9875
$K^2$	1.05
<i>Intra-Particle Diffusion</i>	
$K_d$	$-2.2 \times 10^{-3}$
$R^2$	0.0093
C	0.9743
<i>Liquid Film Diffusion</i>	
$K_{fd} \text{ ( meq g}^{-1} \text{ s}^{1/2})$	-0.002
$R^2$	0.2497

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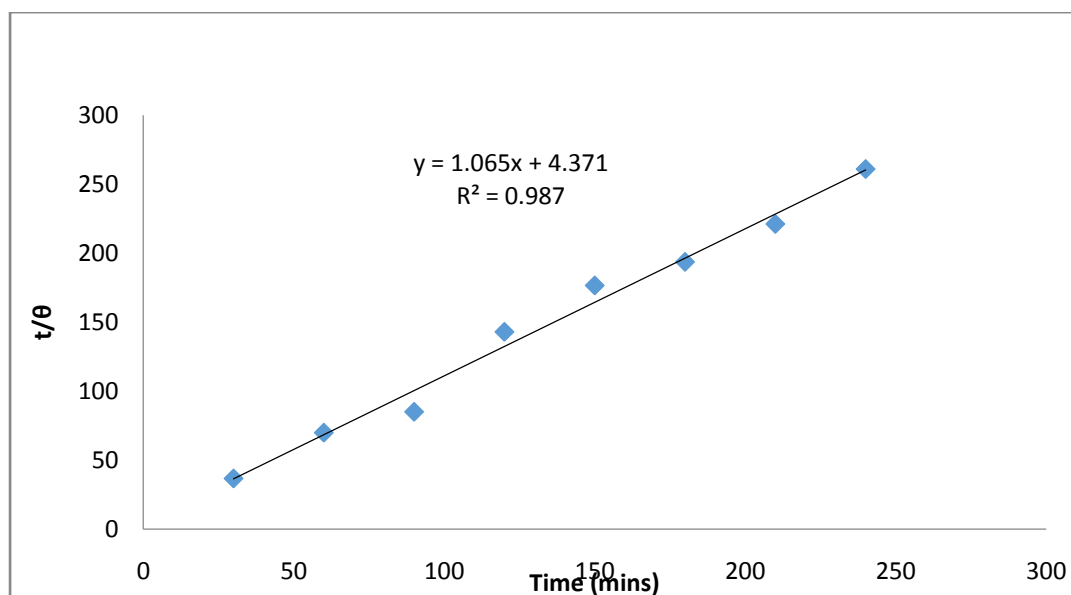
It can be seen from table 4.19 that the value of regression ( $R^2$ ) for first and second order kinetic models were very low at 0.002 and 0.0334 respectively and is considered very low. This suggests that it is inappropriate to use this kinetics to represent the acetylation of plantain peel. It was also observed that the first and second order produced theoretical values of 1.05 and 0.960 respectively while the experimental value was 1.11. The pseudo second order gave a very high  $R^2$  value of 0.9875 which was close to unity indicating that the pseudo second order kinetic model produced a better fit to the data. It also suggests that it is the best kinetic model to represent the acetylation of plantain peel.

High value of  $R^2$  obtained at room temperature for pseudo second order kinetic plots also suggests that acetylation of plantain peel is energy efficient since physical and chemical reaction between the modifier (acetic anhydride and NBS catalyst) and

plantain peel can take place at room temperature. Intra-particle and liquid film diffusion models were also used to further study the mechanism of acetylation. The  $R^2$  obtained for intra-particle and liquid film were very low at 0.0093 and 0.2497 respectively. Therefore we cannot conclude that diffusion mechanism or surface reaction was involved. It was expected that the plot of  $q_t$  versus  $t^{1/2}$  would give a linear relationship when intra-particle diffusion is involved in the acetylation process and that it would be the controlling mechanism if the line passed through the origin (Hill *et al.*, 1998; Igwe and Abia, 2006; Krishnaiah *et al.*, 2008).

#### 4.4.5 Kinetics of Plantain Pseudostem Acetylation

The kinetics for the acetylation of plantain pseudostem was studied by fitting obtained data in rate curves. The predicted kinetics from the linear plots of first order, second order, pseudo-second order, intra-particle diffusion and liquid film diffusion models were all considered. However, the plot of only the pseudo-second order kinetics which gave the best fit was presented in fig 4.15.



**Fig 4.15: Pseudo Second-Order Kinetics for Plantain Pseudostem Acetylation**

The summary of the calculated kinetics derived from the constants is presented in Table 4.20.

**Table 4.20: Summary of Kinetics from the Plots of Plantain Pseudostem Acetylation**

<b>Kinetic models</b>	<b>Values</b>
$\Theta_{0\text{exp}}$	1.06
<i>Pseudo first order</i>	
$\Theta_{0\text{theo}}$	1.17
$R^2$	0.109
$K_1$	$4 \times 10^{-4}$

---

<i>Second order</i>	
$\Theta_{\text{theo}}$	0.85
$R^2$	0.1101
$K_2$	$-4 \times 10^{-4}$
<i>Pseudo- second-order</i>	
$\Theta_{\text{theo}}$	0.938
$R^2$	0.9871
$K^2$	1.067
<i>Intra-particle diffusion</i>	
$K_d$	$7.7 \times 10^{-3}$
$R^2$	0.101
$C$	0.8226
<i>Liquid film diffusion</i>	
$K_{fd} \text{ ( meq g}^{-1} \text{ s}^{1/2})$	-0.0016
$R^2$	0.1235

---

It can be seen from Table 4.20 that the value of regression ( $R^2$ ) for first and second order expression were very low at 0.109 and 0.1101 respectively. Coefficient of regression ( $R^2$ ) within  $0.43 \leq R^2 \leq 0.83$  are considered high and moderate (Dowine and Heath, 1974) therefore the  $R^2$  value for first and second order could be said to be extremely low. Therefore it is inappropriate to use this kinetics to represent the acetylation of plantain pseudostem. It was also observed that the first and second order produced theoretical values of 1.17 and 0.85 respectively while the experimental value was 1.06.

The pseudo second order gave a very high  $R^2$  value of 0.9871 which was close to unity indicating that the pseudo second order kinetic model produced a better fit for

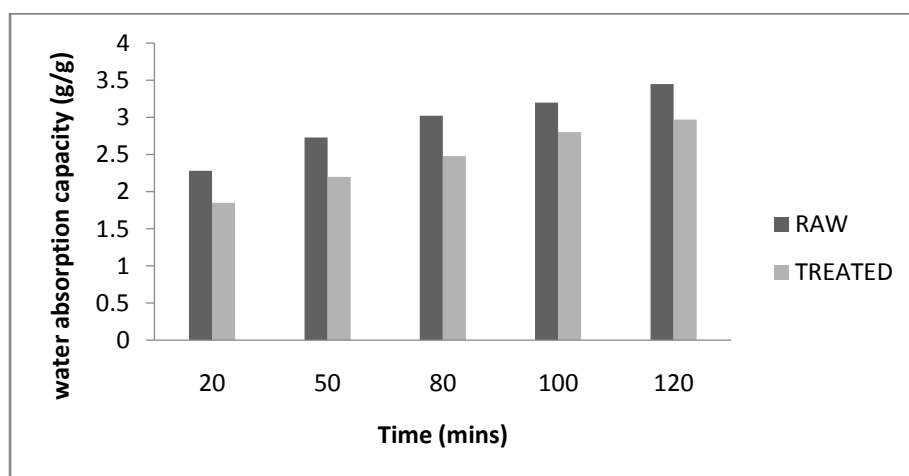
the data. It further suggests that it is the best kinetic model to represent the acetylation of plantain pseudostem.

High value of  $R^2$  obtained at room temperature for pseudo second order kinetic plots also suggests that acetylation of plantain pseudostem is energy efficient since physical and chemical reaction between the modifier (acetic anhydride and NBS catalyst) and plantain peel can take place at room temperature. Intra-particle and liquid diffusion models were also used to further study the mechanism of acetylation and the  $R^2$  obtained were very low at 0.101 and 0.1235, therefore we cannot conclude completely which mechanism was involved.

#### 4.5 Water Absorption Capacity

##### 4.5.1 Water absorption Capacity of Corn Husk

The main essence for studying corn husk acetylation is to determine whether the modification of corn husk (by acetylation) can alter its water absorption capacity, thereby increase the hydrophobic properties. Figure 4.16 presents the results of effect of time on water absorption capacity for raw and modified corn husk with effect to time variation.



**Fig 4.6: Effect of time on water absorption capacity of modified and raw corn husk**

The above figure revealed that the water absorption capacity of raw corn husk (RCH) of 3.45g/g at 120minutes is higher than the value for the acetylated corn husk (ACH) of 2.97g/g at 120minutes. The figure also shows that the water absorption capacity of RCH was higher at all times than for ACH. The figure also revealed that both raw and acetylated corn husk had maximum water absorption at 120 minutes. Replacements of the poly-hydroxyl groups of RCH with acetyl groups are most likely the cause for the observed reductions in water absorption capacity values of ACH. Similar trends have been reported by Nwadiogbu *et al.*, (2014). Comparing water absorption capacities of some microcrystalline celluloses with those of ACH and RCH, the microcrystalline celluloses have lower water sorption capacities (Kudaybergenov *et al.*, 2012). The reduction in water absorption capacity value was tested for significance.

Table 4.21` shows the result for the significant effects of time on corn husk, borassus coir, plantain peel, plantain pseudostem and African breadfruit seed husk water absorption capacity.

**Table 4.21: ANOVA Results on the effect of time on water absorption capacity of Rawcorn husk, borassus coir, plantain peel, plantain pseudostem and African breadfruit seed husk.**

	<b>Sum of Squares</b>	<b>df</b>	<b>Mean Square</b>	<b>F</b>	<b>p-value</b>
Between Groups	3.066	4	0.767	7.384	0.001
Within Groups	2.076	20	0.104		
Total	5.143	24			

The null hypothesis (Ho) is that time has no effect on the water absorption capacity of the five raw samples. Rejection of the hypothesis Ho means that the alternative hypothesis (H<sub>1</sub>) is accepted and that acetylation have reduced the water absorption capacity. This statistics was done at 5% significant level.

In this case we reject Ho if p-value is less than 0.05 and conclude that there is significant difference in the performance of the two variables. The results are presented in Table 4.21. A statistically significant difference was found among the various levels of time on the water absorption capacity of the various raw test media with  $F_{(4,20)}=7.384$  and p-value of 0.001 which is less than the level of significance  $\alpha=0.05$ . This therefore implied that time and acetylation has significant effects on water absorption capacity of the raw samples.

The result of the analysis of variance on the effect of time on water absorption capacity of the treated samples is presented in Table 4.22.

**Table 4.22: ANOVA Results on the effect of time on water absorption capacity of treated corn husk, borassus coir, plantain peel, plantain pseudostem and African breadfruit seed husk.**

	<b>Sum of Squares</b>	<b>Df</b>	<b>Mean Square</b>	<b>F</b>	<b>Sig.</b>
Between Groups	2.944	4	.736	8.909	.000
Within Groups	1.652	20	.083		

A statistically significant difference was found among the various levels of time on the water absorption capacity of the various treated test media with  $F_{(4,20)}=8.909$  and p-value of 0.000 which is less than the level of significance  $\alpha=0.05$



An independent samples t test was carried out to check the effect of treatment on the water absorption capacity of the test media. The result is presented in Table 4.23

**Table 4.23: Independent Samples T –TEST on the effect of treatment on the water absorption capacity test media.**

t-test for Equality of Means							
	T	df	P- value	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
						Lower	Upper
WATER ABSORPTION CAPACITY	2.66 9	48	0.010	0.34000	0.12741	0.0838	0.5962

Group Statistics					
	TYPE	N	Mean	Std. Deviation	Std. Error Mean
WATER ABSORPTION CAPACITY	RAW	25	2.3932	.46291	.09258
	TREATED	25	2.0532	.43763	.08753

An independent samples t test was carried out to check the effect of treatment on the water absorption capacity of the test media. With a  $T_{(48)} = 2.669$  and a p-value of 0.010 which is less than the level of significance  $\alpha = 0.05$ . We conclude that treatment has an effect on the water absorption capacity. A further look at the confidence interval reveals that difference between the raw and treated mean is a positive one and this led us to a regression analysis to determine the extent of this difference.

**Table 4.24: Regression analysis for the effect of time and acetylation on the water absorption capacity of the five test medium.**

Model Summary				
Model	R	R Square	Adjusted R Square	Std. Error of the Estimate

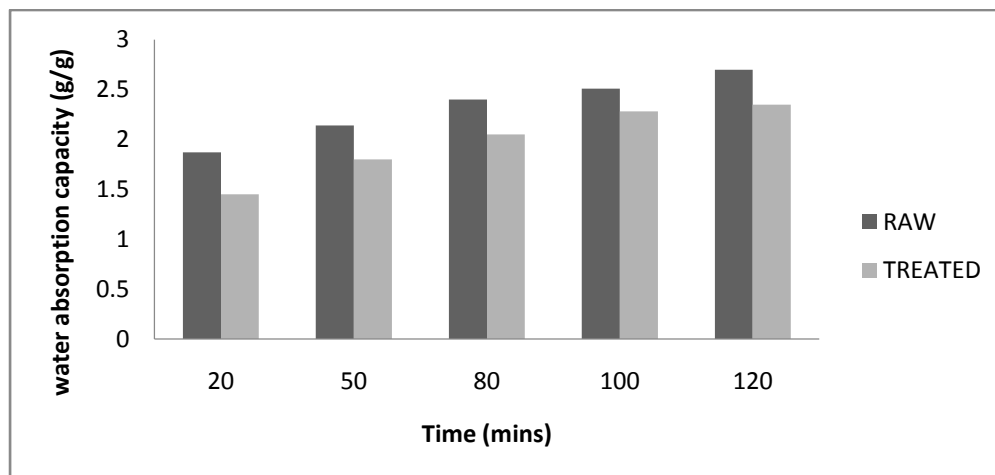
1	0.815 <sup>a</sup>	0.664	0.649	0.28290	
<b>ANOVA<sup>a</sup></b>					
<b>Model</b>	<b>Sum of Squares</b>	<b>df</b>	<b>Mean Square</b>	<b>F</b>	<b>p-value</b>
Regression	7.423	2	3.712	46.376	0.000
Residual	3.761	47	0.080		
Total	11.184	49			
<b>Coefficients<sup>a</sup></b>					
	<b>Unstandardized</b>		<b>Standardize</b>		
	<b>Coefficients</b>		<b>d</b>		
<b>Model</b>	<b>B</b>	<b>Std. Error</b>	<b>Beta</b>	<b>t</b>	<b>p-value</b>
(Constant)	2.000	0.152		13.126	0.000
TYPE	-0.340	0.080	-0.359	-4.249	0.000
TIME(Mins)	0.245	0.028	0.731	8.643	0.000

The model summary presented in Table 4.24 shows that the multiple correlation coefficient (R) using all the predictors simultaneously is 0.82 and the adjusted R<sup>2</sup> is 0.649 which implies that 65% of the variation in the level of water absorption is accounted for by treatment and time. The ANOVA table shows that F<sub>(2,47)</sub>=46.376 is significant and show that the combination of treatment and time significantly combine to predict water absorption capacity. The coefficients and their significance are evaluated in the table of coefficients and it shows that the coefficients are all significant and worthy to note is the negative contribution of type of test media to the water absorption capacity which implies that treatment reduces water absorption capacity. The fitted regression equation is given as:

$$\text{Water Absorption Capacity} = 2 + (-0.34) \cdot \text{TYPE} + 0.245 \cdot \text{TIME}. \quad (4.1)$$

#### .4.5.2 Water absorption Capacity of Borassus coir

Figure 4.17 presents the results of effect of time variation on water absorption capacity for raw and modified borassus coir.



**Fig 4.17: Effect of time on water absorption capacity of modified and raw borassus coir**

From the above figure, it can be seen that the water absorption capacity of raw borassus coir (RBC) was 2.7g/g which is higher than the value for the acetylated corn husk (ABC) which was 2.35g/g at 120mins. The figure also shows that the water absorption capacity of RBC was higher at all times than for ABC.

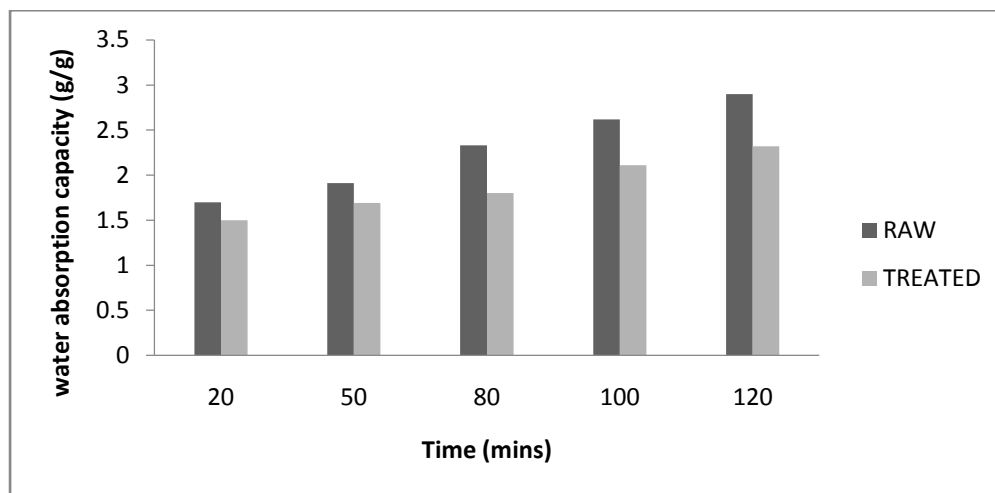
Raw borassus coir can hold significant amount of water due to hydrogen bonding between hydroxyl group and water molecule. It has been established that when the accessible hydrogen of the hydroxyl group in the cell wall polymer have been substituted by acetyl group, reduction in water and moisture sorption are observed. (Yakubu *et al.*, 2012).

The result in Table 4.22 earlier presented shows the result of ANOVA for effects of time and acetylation on borassus coir water absorption capacity. Table 4.23 ad 4.24 presents the Independent sample T- test and regression analysis to ascertain the

effect of time and treatment on the water absorption capacity of the various test media as earlier presented and discussed.

#### 4.5.3 Water absorption Capacity of Plantain peel

Figure 4.18 presents the results of effect of time on water absorption capacity for raw and modified plantain peel.



**Fig 4.18: Effect of time on water absorption capacity of modified and raw plantain peel.**

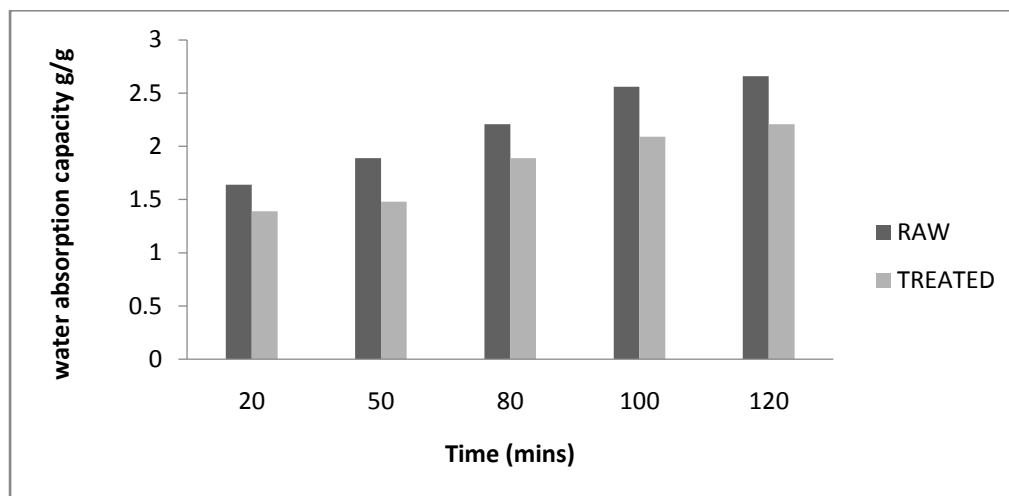
Figure 4.18 showed that at all times, the water absorption capacity of plantain peel was higher at 2.90g/g for the raw sample and lower for the modified sample at 2.32g/g. Also, it was observed that the modified sample reached saturation point faster than the raw sample which is attributed to enhanced hydrophobicity. The figure also revealed that both raw and acetylated plantain peel had maximum water absorption at 120 minutes.

The result in Table 4.22 earlier presented shows the result of ANOVA for effects of time and acetylation on plantain peel water absorption capacity. Table 4.23 and 4.24 presents the Independent sample T- test and regression analysis to ascertain the

effect of time and treatment on the water absorption capacity of the various test media as earlier presented and discussed in 4.5.1.

#### 4.5.4 Water absorption Capacity of African breadfruit seed husk.

Figure 4.19 present the results of effect of time on water absorption capacity for raw and modified African breadfruit seed husk.



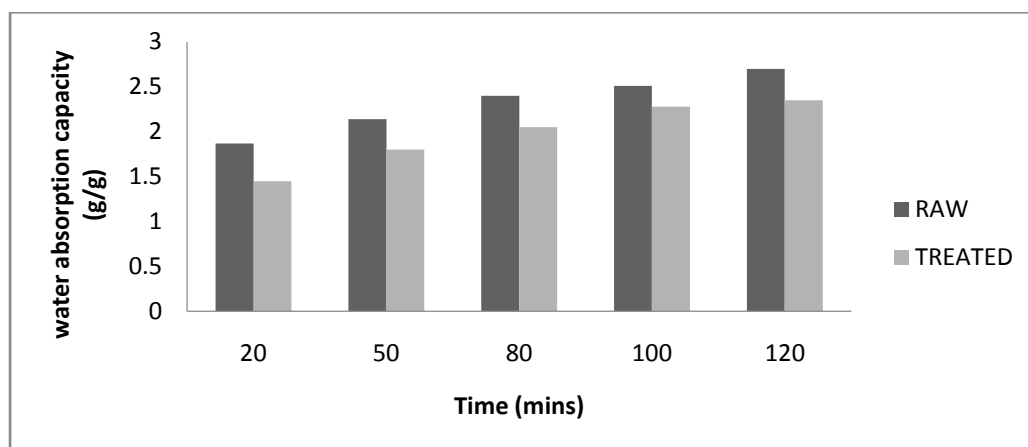
**Fig 4.19: Effect of time on water absorption capacity of modified and raw African breadfruit seed husk**

The pores of African breadfruit seed husk can hold significant quantity of water due to hydrogen bonding between hydroxyl groups and water molecule. It can be seen from the figure above that the water absorption capacity of raw African breadfruit seed husk (RBF) of 2.66g/g at 120mins is higher than the value for the acetylated African breadfruit seed husk (ABF) of 2.21g/g at 120mins. The reduction in water absorption capacity value was tested for significance. The result in Table 4.22 earlier presented shows the result of ANOVA for effects of time and acetylation on African breadfruit seed husk water absorption capacity. Table 4.23 and 4.24 presents the Independent sample T- test and regression analysis to ascertain the effect of time

and treatment on the water absorption capacity of the various test media as earlier presented and discussed in 4.5.1.

#### 4.5.5 Water absorption Capacity of Plantain Pseudostem

Figure 4.20 presents the results of effect of time on the water absorption capacity of raw and modified plantain pseudostem.



**Fig 4.20: Effect of time on water absorption capacity of modified and raw plantain pseudostem.**

From figure 4.20, it can be seen that the water absorption capacity of raw plantain pseudostem (RPS) was 2.97g/g and is higher than the value for the acetylated plantain pseudostem (APS) 2.58g/g at 120mins. The figure also shows that the water absorption capacity of RPS was higher at all times than for APS. The figure equally revealed that both raw and acetylated plantain pseudostem had maximum water absorption at 120 minutes. Replacements of the poly-hydroxyl groups of RPS with acetyl groups are most likely the cause for the observed reductions in water absorption capacity values of APS. Comparing water absorption capacities of some microcrystalline cellulose with those of APS and RPS, the microcrystalline celluloses have lower water sorption capacities (Roja *et al.*, 2011).

Raw plantain pseudostem can hold significant amount of water at 120minutes due to hydrogen bonding between hydroxyl group and water molecule. It has been established that when the accessible hydrogen of the hydroxyl group in the cell wall polymer have been substituted by acetyl group, reduction in water and moisture sorption are observed. (Yakubu *et al.*, 2012). Furthermore, it was observed that the modified sample reached saturation point faster than the raw sample which is attributed to enhanced hydrophobicity.

The reduction in water absorption capacity value was tested for significance. The result in Table 4.22 earlier presented shows the result of ANOVA for effects of time and acetylation on plantain pseudostem water absorption capacity. A statistically significant difference was found among the various levels of time on the water absorption capacity of the various treated test media with  $F_{(4,20)}=8.909$  and p-value of 0.000 which is less than the level of significance  $\alpha=0.05$

An independent samples t test was carried out to check the effect of treatment on the water absorption capacity of the test media. The result is presented in Table 4.23. With a  $T_{(48)}=2.669$  and a p-value of 0.010 which is less than the level of significance  $\alpha=0.05$ . We conclude that treatment has an effect on the water absorption capacity. A further look at the confidence interval reveals that difference between the raw and treated means is a positive one and this led us to a regression analysis to determine the extent of this difference.

The model summary presented in Table 4.24 shows that the multiple correlation coefficient (R) using all the predictors simultaneously is 0.82 and the adjusted  $R^2$  is 0.664 which implies that 66% of the variation in the level of water absorption is accounted for by treatment and time. The ANOVA table shows that  $F_{(2,47)}=46.376$  is

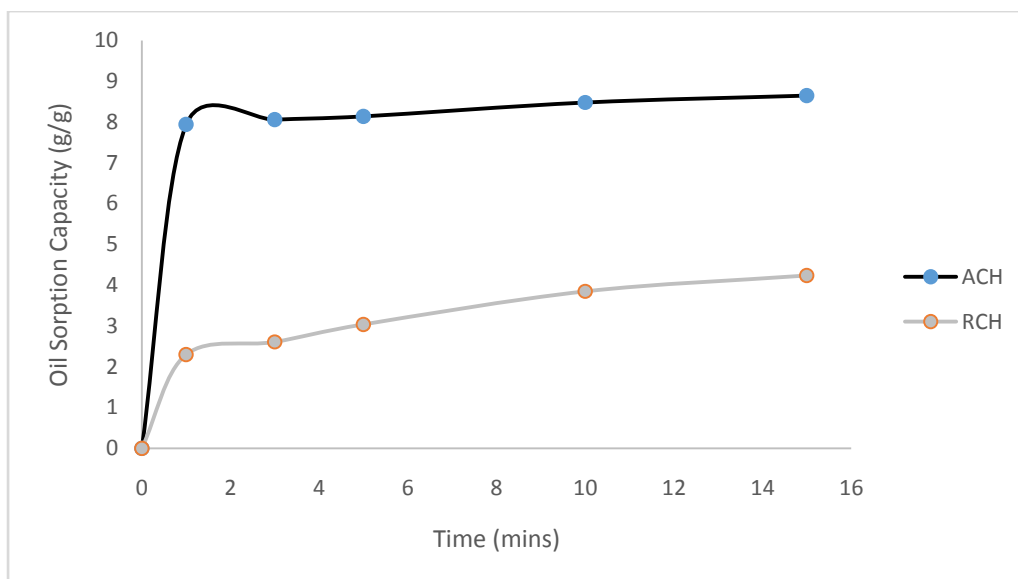
significant and show that the combination of treatment and time significantly combine to predict water absorption capacity. The coefficients and their significance are evaluated in the table of coefficients and it shows that the coefficients are all significant and worthy to note is the negative contribution of type of test media to the water absorption capacity which implies that treatment reduces water absorption capacity.

## **4.6 Sorption Studies of Crude Oil**

### **4.6.1 Effect of time on crude oil sorption onto Corn Husk**

The uptake of crude oil by the corn husk was studied in batch experiments and the results are illustrated in Fig 4.21.





**Fig 4.21: Effect of time on Oil Sorption Capacity of Acetylated and Raw Corn husk.**

From Fig 4.21, the results of oil sorption capacity as expected increased with increase in sorption time from 1 to 15 minutes. Maximum oil sorption capacity of 8.65g/g for ACH and 4.24g/g for RCC was observed at 15 minutes. Also, crude oil sorption capacity values for the acetylated sample was always higher than those of the raw samples. This might be due to initial adsorption unto the surface of the material and subsequent penetration into the inner microscopic voids of the acetylated samples (Amer *et al.*, 2007). The results further showed the fast and stable nature of the process as only a slight difference was observed between the initial and final contact time. This result is consistent with findings by other researchers (Hussein *et al.*, 2008; Nwankwere *et al.*, 2010; Nwadiogbu *et al.*, 2016). Considering that oleophilicity is a measure of enhanced non-aqueous sorption property, Fig 4.56 demonstrates that ACH is more oleophilic than RCH. Explanation for this is due to the decrease in hydroxyl functionality of RCH by acetylation as

ascertained elsewhere (Bordilau and Teaca, 2009). The effect of variation of time (modified and raw) was tested with ANOVA for statistical difference.

Table 4.25 presents result of ANOVA for the significant effects of time and acetylation on oil sorption capacity of all the samples under study which includes corn husk, borassus coir, African breadfruit seed husk, plantain peel and plantain pseudostem.

**Table 4.25: Summary of ANOVA results on the effect of time on the oil sorption capacity of raw corn husk, borassus coir, African breadfruit seed husk, plantain peel and plantain pseudostem.**

	Sum.of Squares	Df	Mean Square	F	p-value
Between Groups	19.514	4	4.878	28.784	0.001
Within Groups	3.390	20	0.169		
Total	22.904	24			

A statistically significant difference was found among the various levels of time on the oil sorption capacity of the various raw test media with  $F_{(4,20)}=28.784$  and p-value of 0.001 which is less than the level of significance  $\alpha=0.05$

The null hypothesis ( $H_0$ ) is that acetylation has not affected oil sorption capacity of corn husk. If null hypothesis ( $H_0$ ) is rejected, then the alternative hypothesis ( $H_1$ ) will be accepted. This statistic was performed at 5% significant level.

In this study, we reject  $H_0$  if p-value is less than 0.05 and conclude that there is significant difference in the performance of the two variables. This implies that the

alternative hypothesis (H1) is accepted indicating that acetylation have increased the oil sorption capacity. The results as shown in Table 4.25 indicated that the P-value 0.01 is less than 0.05. This therefore implied that time and acetylation had significant effects on oil sorption capacity of the five raw samples under study.

**Table 4.26: Summary of ANOVA results on the effect of time on the oil sorption capacity of acetylated corn husk, borassus coir, African breadfruit seed husk, plantain peel and plantain pseudostem.**

	<b>Sum of Squares</b>	<b>Df</b>	<b>Mean Square</b>	<b>F</b>	<b>p-value</b>
Between Groups	64.805	4	16.201	5.381	0.004
Within Groups	60.220	20	3.011		
Total	125.025	24			

A statistically significant difference was found among the various levels of time on the oil sorption capacity of the various acetylated test media with  $F_{(4,20)}=5.381$  and p-value of 0.004 which is less than the level of significance  $\alpha=0.05$

The null hypothesis (Ho) is that acetylation has not affected oil sorption capacity of corn husk. If null hypothesis (Ho) is rejected, then the alternative hypothesis (H1) will be accepted. This statistic was performed at 5% significant level.

In this study, we reject Ho if p-value is less than 0.05 and conclude that there is significant difference in the performance of the two variables and the alternative hypothesis (H1) will be accepted. The results as shown in Table 4.26 indicated that the P-value 0.004 is less than 0.05 therefore the alternative hypothesis is accepted while the null hypothesis is rejected. This implied that acetylation have increased the

oil sorption capacity therefore indicated that time and acetylation had significant effect on oil sorption capacity of the five acetylated samples under study.

For better understanding of the direction of these effects, regression analysis was performed and the results are presented in the Table 4.27.

**Table 4.27: Summary of Regression analysis on the effect of time and acetylation on the oil sorption capacity of the five test media.**

<b>Model Summary</b>				
<b>Model</b>	<b>R</b>	<b>R Square</b>	<b>Adjusted R Square</b>	<b>Std. Error of the Estimate</b>
1	.901 <sup>a</sup>	.812	.804	1.24333

<b>ANOVA<sup>a</sup></b>					
<b>Model</b>	<b>Sum.of Squares</b>	<b>df</b>	<b>Mean Square</b>	<b>F</b>	<b>p-value</b>
Regression	314.378	2	157.189	101.683	0.000
Residual	72.656	47	1.546		
Total	387.033	49			

The model summary table shows that the multiple correlation coefficient (R) using all the predictors simultaneously is 0.901 and the adjusted  $R^2$  is 0.804 which implies that 80% of the variation in the level of oil sorption capacity is accounted for by treatment and time. The ANOVA table shows that  $F_{(2,47)}$  is 101.683 is significant and showed that the combination of treatment and time significantly combine significantly to predict oil sorption capacity. The coefficients and their significance are evaluated in the table of coefficients as presented in Table 4.28.

**Table 4.28: Summary of coefficients and their significance on the effect of time and acetylation on the oil sorption capacity of the five test medium.**

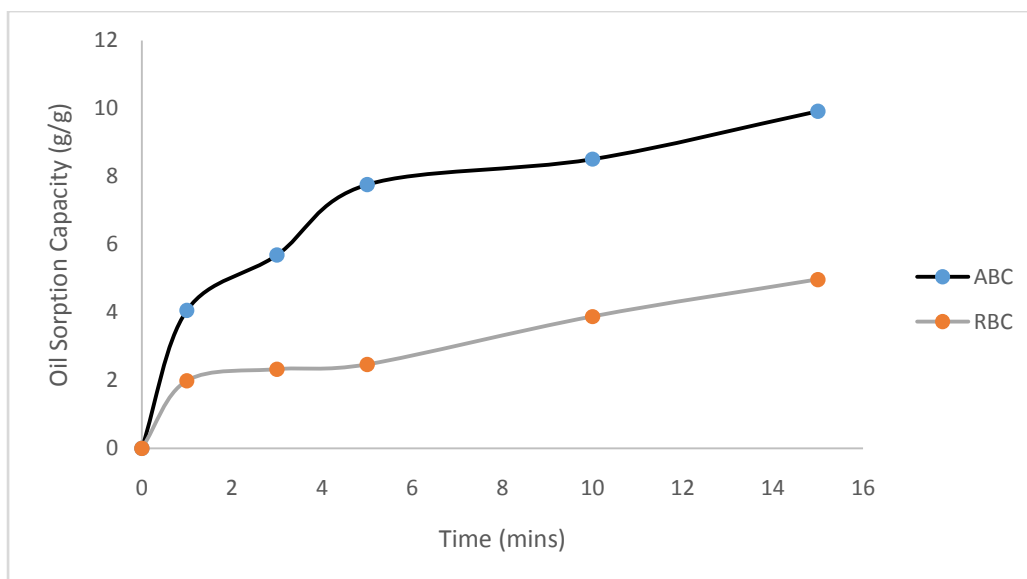
<b>Co-efficients<sup>a</sup></b>					
<b>Model</b>	<b>Unstandardized</b>		<b>Standardized</b>		
	<b>Coefficients</b>		<b>Coefficients</b>	<b>t</b>	<b>p-value</b>
	<b>B</b>	<b>Std. Error</b>	<b>Beta</b>		
(Constant)	-3.985	.670		-5.952	.000
TIME (Mins)	.868	.124	.441	6.978	.000
TYPE	4.374	.352	.786	12.437	.000

The coefficients and their significance are evaluated in the table of coefficients and it shows that the coefficients are all significant and worthy to note is the positive contribution of time and treatment of test media to the oil sorption capacity which implied that time and treatment increases oil sorption capacity. The fitted regression equation is given as:

$$\text{Oil Sorption Capacity} = -3.985 + 4.374 * \text{TYPE} + 0.868 * \text{TIME}. \quad (4.2)$$

#### **4.6.2 Effect of time on crude oil sorption onto borassus coir**

The uptake of crude oil by borassus coir was studied in batch experiments and the results are illustrated in Fig 4.42.



**Fig 4.42: Effect of time on Oil Sorption Capacity of Acetylated and Raw Borassus coir.**

From figure 4.42, the results of oil sorption capacity as expected increased with increase in sorption time from 1 to 15 minutes. The maximum oil sorption capacity of 9.92g/g for ABC and 4.97g/g for RBC was observed at 15minutes. The crude oil sorption capacity values for the acetylated sample were always higher than those of the raw samples. This might be due to initial adsorption unto the surface of the material and subsequent penetration into the inner microscopic voids (Amer *et al.*, 2007). The results as seen from Fig 4.42 showed that acetylated borassus coir absorbed higher amount of oil when compared to the raw borassus coir. Considering that oleophilicity is a measure of enhanced non-aqueous sorption property, figure 4.57 demonstrates that ABC is more oleophilic than RBC. Explanation for this is due to the decrease in hydroxyl functionality of RBC by acetylation as ascertained elsewhere (Bordilau and Teaca, 2009).

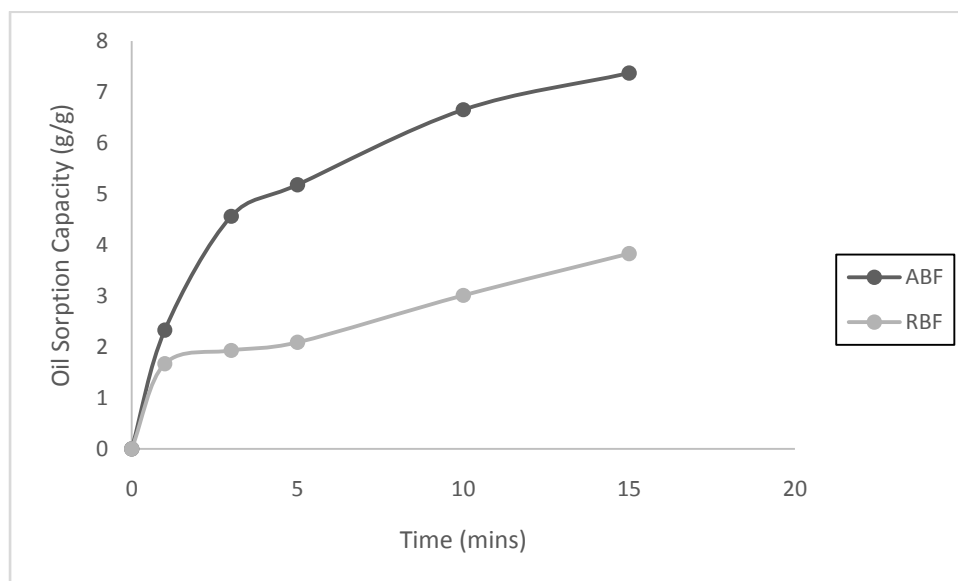
The effect of time and variation of material (modified and raw) was tested with ANOVA for statistical difference. The result for the significant effects of time and

acetylation on oil sorption capacity of all the samples was earlier presented in Table 4.27. The summary of regression analysis and the coefficients and their significance on the effect of time and acetylation on the oil sorption capacity of the sample was presented in Table 4.27 and 4.28 earlier presented and discussed.

From the coefficient, there is a positive contribution of time and treatment of borassus coir on the oil sorption capacity which implied that time and treatment increases the oil sorption capacity of borassus coir.

#### 4.6.3 Effect of time on crude oil sorption onto African breadfruit seed husk

The uptake of crude oil by the African breadfruit seed husk was studied in batch experiments and the results are illustrated in Fig 4.43.



**Fig 4.43: Effect of time on Oil Sorption Capacity of Acetylated and Raw African Breadfruit seed husk.**

From figure 4.43, the results of oil sorption capacity as expected increased with increase in sorption time from 1 to 15 minutes. At 15 minutes, maximum oil sorption capacity of 7.37g/g for ABF and 3.83g/g for RBF were observed. Also, crude oil sorption capacity for the acetylated sample was always higher than those of the raw

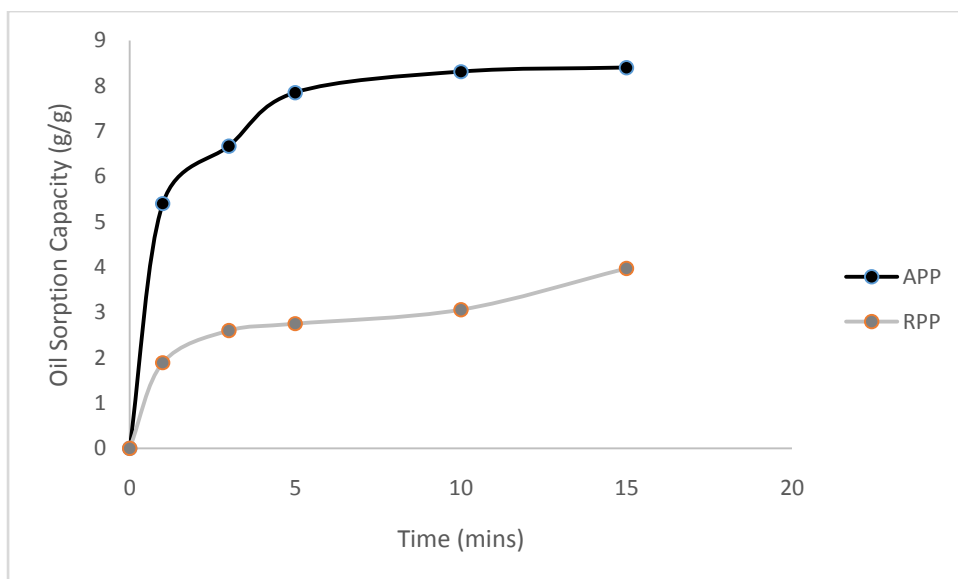
samples. This might be due to initial adsorption onto the surface of the material and subsequent penetration into the inner microscopic voids (Amer *et al.*, 2007). The results as seen from Figure 4.43 showed that ABF absorbed higher amount of oil when compared to the RBF.

The effect of time and variation of material (modified and raw) was tested with ANOVA for statistical difference. The result for the significant effects of time and acetylation on oil sorption capacity of all the samples was earlier presented in Table 4.27. The summary of regression analysis and the coefficients and their significance on the effect of time and acetylation on the oil sorption capacity of the sample was presented in Table 4.27 and 4.28. The tables showed that the multiple correlation coefficient (R) using all the predictors simultaneously is 0.901 and the adjusted  $R^2$  is 0.804 which implied that 80% of the variation in the level of oil sorption capacity is accounted for by treatment and time. Also it showed that the coefficients are all significant and worthy to note is the positive contribution of time and treatment of test media to the oil sorption capacity which implied that time and treatment increases oil sorption capacity.

#### **4.6.4 Effect of time on crude oil sorption capacity of plantain peel**

The effect of time on the crude oil sorption capacity of plantain peel was illustrated in Figure 4.44.





**Fig 4.44: Effect of time on Oil Sorption Capacity of Acetylated and Raw Plantain Peel.**

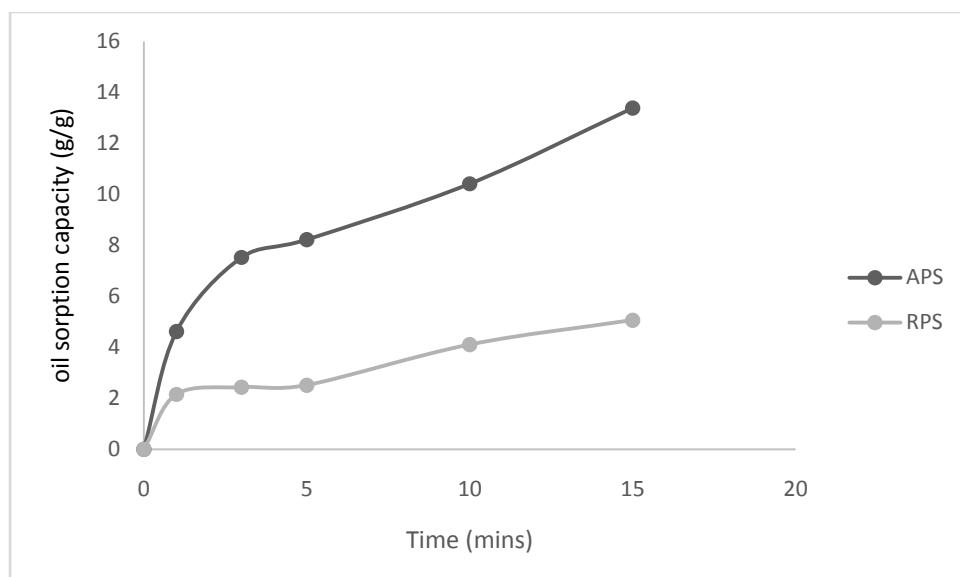
From figure 4.44, the results of oil sorption capacity as expected increased with increase in sorption time from 1 to 15 minutes. Maximum oil sorption capacity of 8.4g/g for acetylated sample (APP) and 3.97g/g for raw sample(RPP) were observed. Crude oil sorption capacity for the acetylated sample was always higher than those of the raw samples. This could be attributed to the hydrophobic nature of the sorbent surface after modification, as earlier shown by the FTIR studies. It further showed that there was an increase in oil sorption capacity of the sorbents (raw and acetylated), with increase in contact time up to 15 minutes when the sorption process reached equilibrium. This may be due to adsorption of crude oil on the surface of the sorbents first, before the crude oil starts to penetrate the inner microscopic voids (Amer *et. al.*, 2007, Onwuka *et al.*, 2016.) The results as seen from Fig 4.44 showed that APP absorbed higher amount of oil when compared to the RPP. Since oleophilicity is a measure of enhanced non-aqueous sorption property, figure 4.44 demonstrates that APP is more oleophilic than RPP. Explanation for this

is due to the decrease in hydroxyl functionality of RPP by acetylation as ascertained elsewhere (Bordilau and Teaca, 2009).

The effect of time and variation of material (modified and raw) was tested with ANOVA for statistical difference. The result for the significant effects of time and acetylation on oil sorption capacity of all the samples was earlier presented in Table 4.27. The summary of regression analysis and the coefficients and their significance on the effect of time and acetylation on the oil sorption capacity of the sample was presented in Table 4.27 and 4.28 and showed that the multiple correlation coefficient (R) using all the predictors simultaneously is 0.901 and the adjusted  $R^2$  is 0.804 which implied that 80% of the variation in the level of oil sorption capacity is accounted for by treatment and time.

#### 4.6.5 Effect of time on crude oil sorption capacity of plantain pseudostem

The uptake of crude oil by the plantain pseudostem are illustrated in Fig 4.45.



**Fig 4.45: Effect of time on Oil Sorption Capacity of Acetylated and Raw Plantain Pseudostem.**

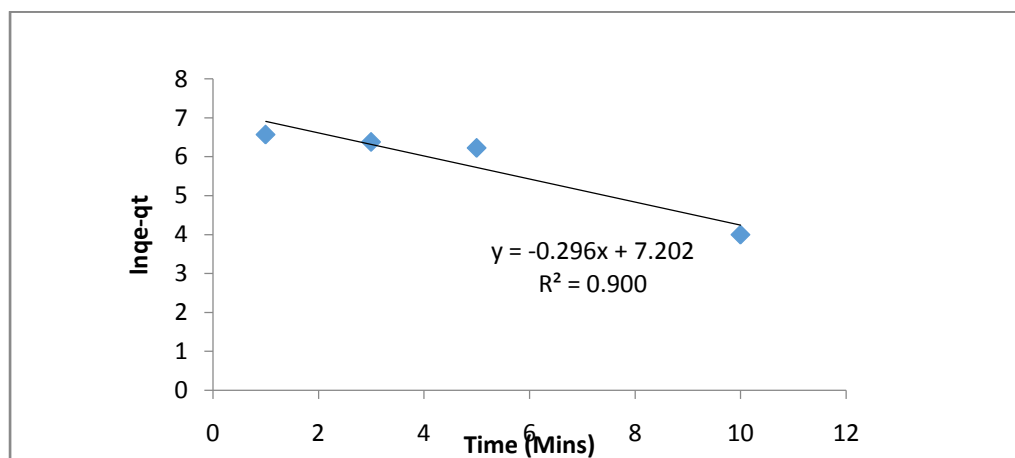
From figure 4.45, the results of oil sorption capacity as expected increased with increase in sorption time from 1 to 15 minutes. Maximum oil sorption capacity of 13.39g/g for the acetylated sample(APS) and 5.07g/g for the raw sample(RPS) was observed at 15 minutes. This could be attributed to the hydrophobic nature of the sorbent surface after modification, as earlier shown by the FTIR studies. The results as seen from Fig 4.45 showed that APS absorbed higher amount of oil when compared to the RPS at all times. Since oleophilicity is a measure of enhanced non-aqueous sorption property, figure 4.45 confirmed that APS is more oleophilic than RPS

The effect of time and variation of material (modified and raw) was tested with ANOVA for statistical difference. The result for the significant effects of time and acetylation on oil sorption capacity of all the samples was earlier presented in Table 4.27. The summary of regression analysis and the coefficients and their significance on the effect of time and acetylation on the oil sorption capacity of the sample was presented in Table 4.27 and 4.28 earlier presented. Table 4.27 showed that the multiple correlation coefficient (R) using all the predictors simultaneously is 0.901 and the adjusted  $R^2$  is 0.804 which implied that 80% of the variation in the level of oil sorption capacity is accounted for by treatment and time. The ANOVA table shows that  $F_{(2,47)}$  is 101.683 and is significant. This showed that the combination of treatment and time combined significantly to predict oil sorption capacity. Table 4.28 suggests that the coefficients are all significant. It is worthy to note is the positive contribution of time and treatment of test media to the oil sorption capacity which implies that time and treatment increases oil sorption capacity.

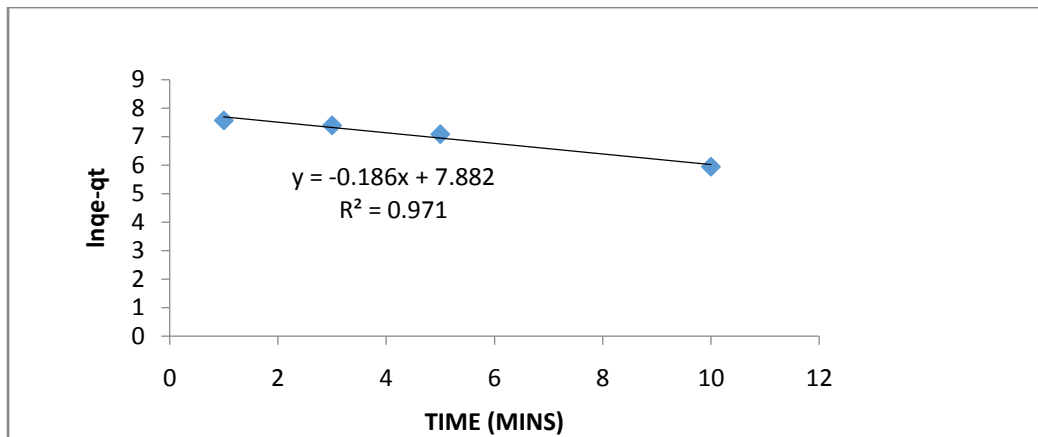
## 4.7 Kinetics of Crude Oil Sorption

### 4.7.1 Kinetics of crude oil sorption onto corn husk.

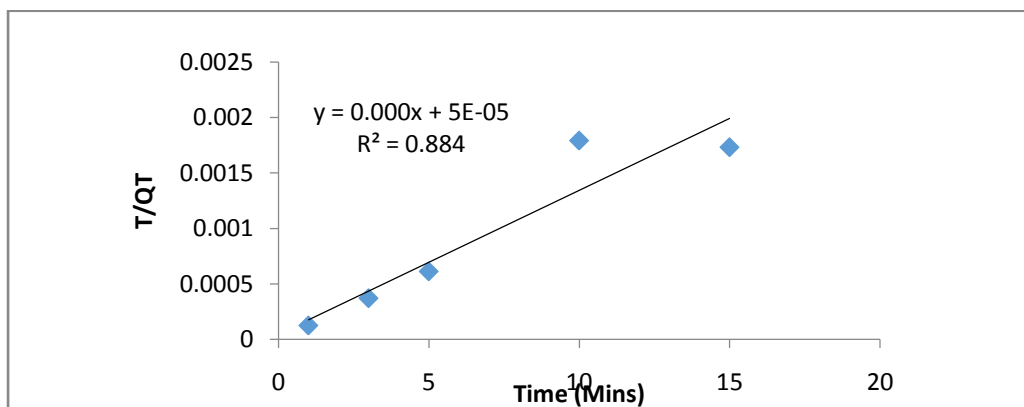
The sorption kinetic models were applied to the experimental data to analyze the rate and mechanism of crude oil sorption of corn husk. The kinetic models applied to this study are the pseudo first-order, pseudo second-order and intra-particle diffusion models. The predicted kinetics from the linear plots of the models for raw and acetylated samples are presented in Figures 4.46 - 4.48( a& b) respectively. The linear plots of this kinetics and how to obtain the rate constants were presented earlier in Table 3.1 in chapter 3. The calculated kinetics derived from the constants are shown in Table 4.29.



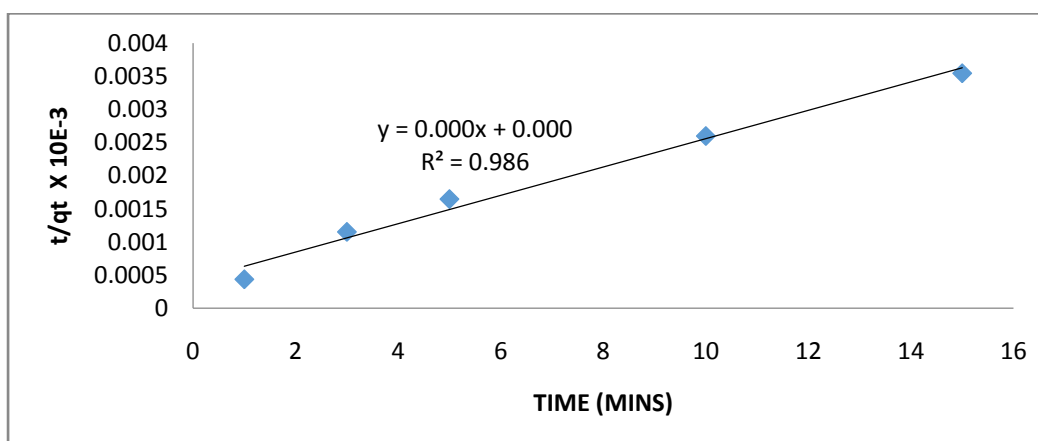
**Fig 4.46(a): Pseudo-first order Kinetic model for sorption of oil onto raw Corn Husk.**



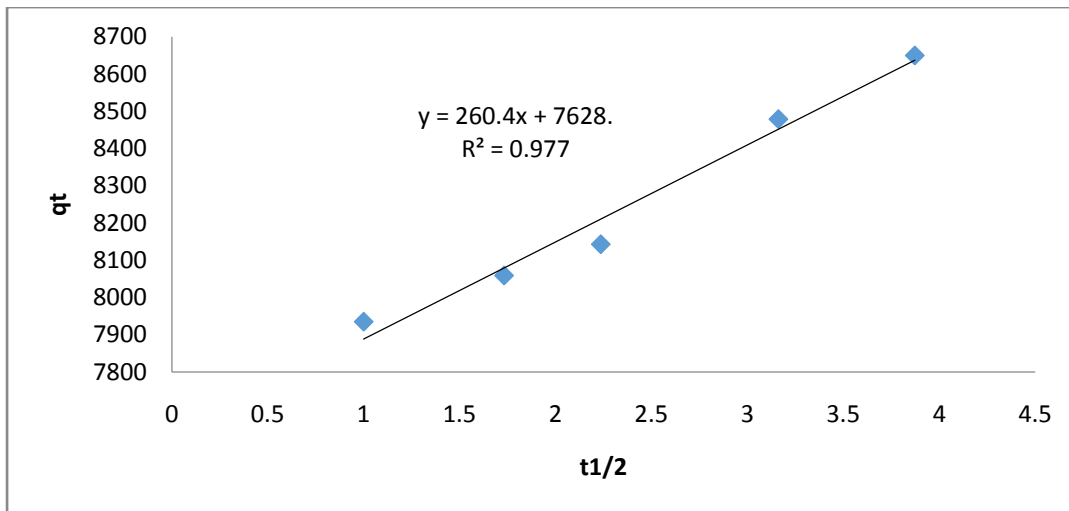
**Fig 4.46(b): Pseudo-first order Kinetic model for sorption of oil onto acetylated Corn Husk.**



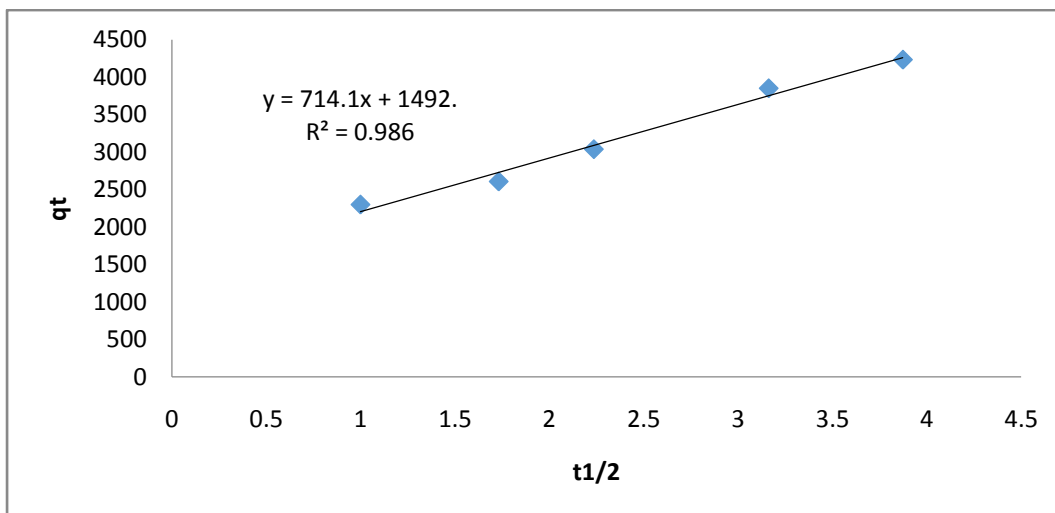
**Fig 4.47(a): Pseudo-second order Kinetics for the sorption of oil onto raw Corn Husk**



**Fig 4.47(b): Pseudo-second order Kinetics for the sorption of oil onto acetylated Corn Husk.**



**Fig 4.48(a): Intra-particle diffusion Kinetics for the sorption of oil onto raw Corn Husk**



**Fig 4.48(b): Intra-particle diffusion Kinetics for the sorption of oil onto acetylated Corn Husk**

Table 4.29 shows a comparison of the kinetic parameter for crude oil sorption on ACH and RCH.

**Table 4.29: Summary of kinetics of crude oil sorption onto Corn Husk.**

Type		Acetylated (ACH)	Corn Husk	Raw corn husk (RCH)
$Q_{e \text{ expected}}$	mg/g	4234		8650
Pseudo first Order				
$q_{e \text{ calc}}$		2650		945.7
$R^2$		0.9716		0.9537
$K_1$		0.1862		0.1623
Pseudo Second Order				
$q_{e \text{ calc}}$	mg/L	5000		10,000
$R^2$		0.9865		0.8847
$K_2$		0.0001		0.0008
Intra Particle Diffusion				
$K_d$		714.14		260.41
C		1492.2		7628.1
$R^2$		0.9862		0.9776

Understanding the kinetics of crude oil sorption onto RCH and ACH is vital for practical applications. Particularly, the industrial applications can be feasible if some kinetic parameters are obtained and used in process designs and scale up procedures (Faith, 2013).

From table 4.29, it could be seen that the coefficient of regression ( $R^2$ ) for crude oil sorption onto ACH was 0.9716 for the pseudo-first order and 0.9865 for the pseudo-

second order. Pseudo-second order gave the best fit for crude oil sorption of ACH because it gave the highest  $R^2$  value (0.9865). Also the predicted adsorption capacity value obtained for pseudo second order was 5000mg/g and is closer to experimental adsorption capacity value of 4234mg/g than 2650 for pseudo first order. Therefore it implies very likely that the kinetics of crude oil sorption unto corn husk follows the pseudo first order kinetic model. For RCH,  $R^2$  values are lower for both the pseudo-first and pseudo-second orders at 0.9537 and 0.8847 respectively when compared with that of ACH. This can be attributed to the hydrophobic nature of the modified sorbent (Onwuka *et al.*, 2016).

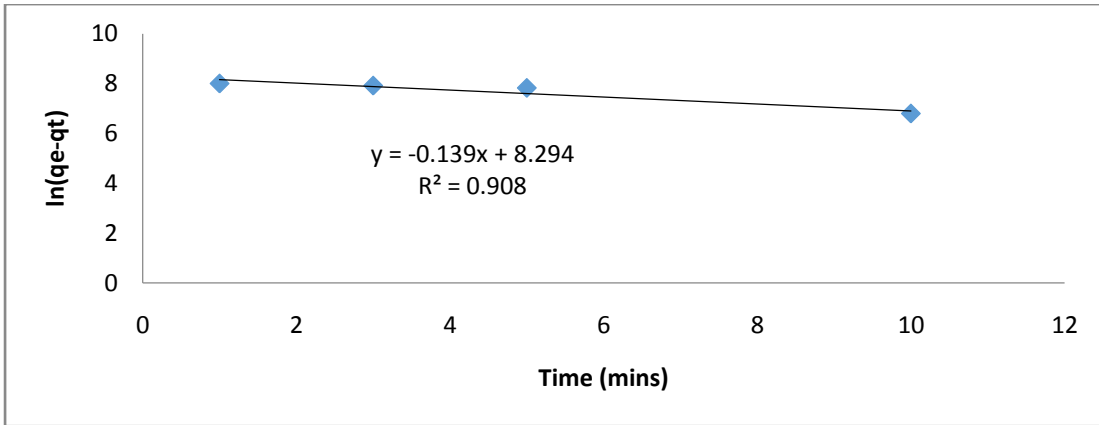
Intra-particle diffusion becomes the sole rate-determining step if the plot is linear, and passed through the origin. As seen from Table 4.29, the  $R^2$  values for the intra-particle diffusion were high for both ACH (0.9862) and RCH (0.9776). Also there was presence of intercept (C) though the plot did not pass through the origin but was close to it. The deviation from origin may be due to the difference in mass transfer in the initial and final stages of the sorption process (Das and Mondal, 2011). The good regression indicated the existence of an intra-particle diffusion mechanism for the sorption of crude oil on ACH and RCH.

It was also observed that intra-particle diffusion was the rate controlling mechanism for the sorption process but it was not the sole mechanism since the line did not pass through the origin.

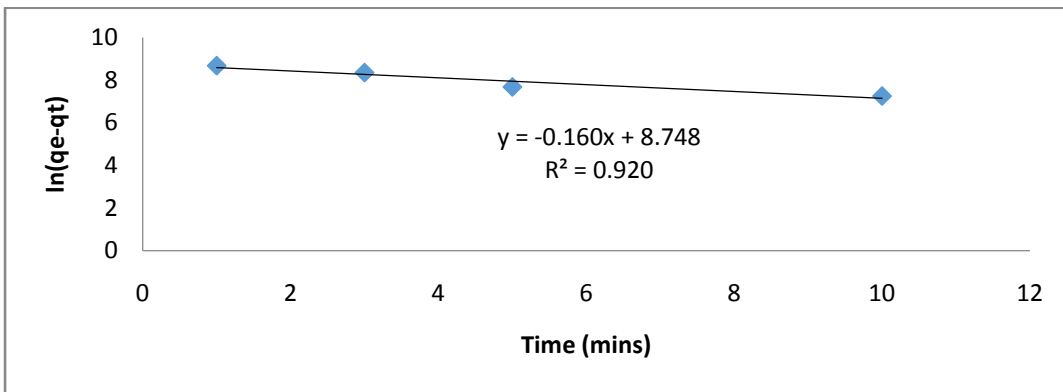
#### **4.7.2 Kinetics of Crude Oil sorption unto Borassus coir**

The kinetic models applied to this study are the pseudo first-order, pseudo second-order and intra-particle diffusion models. The predicted kinetics from the linear plots of the models are presented in Figures 4.49 – 4.51 (a & b) respectively.

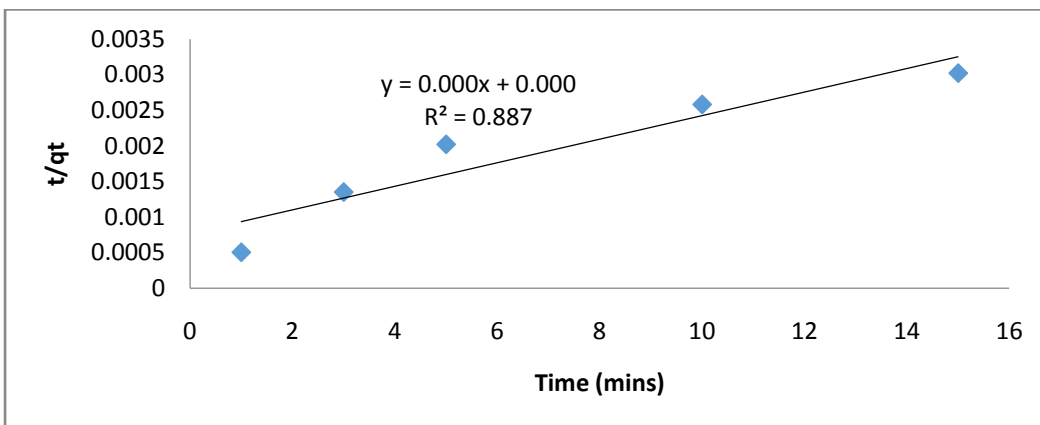




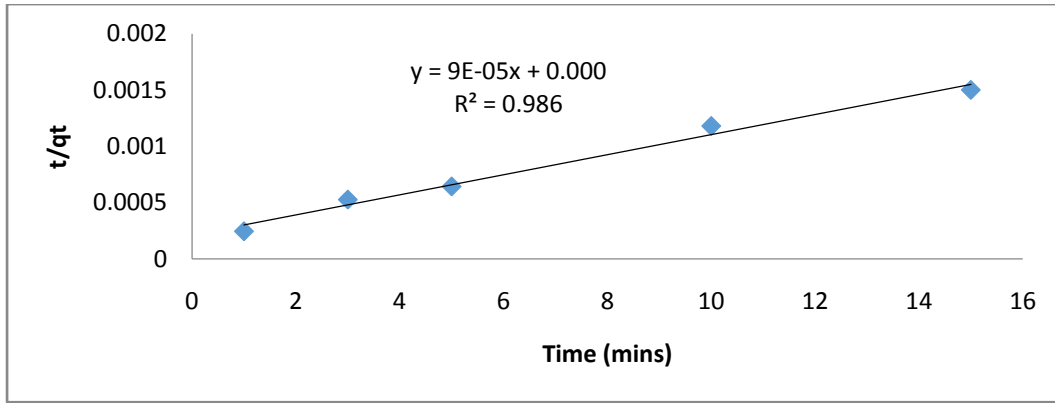
**Fig 4.49(a): Pseudo-first order kinetic model for sorption of oil onto raw Borassus coir.**



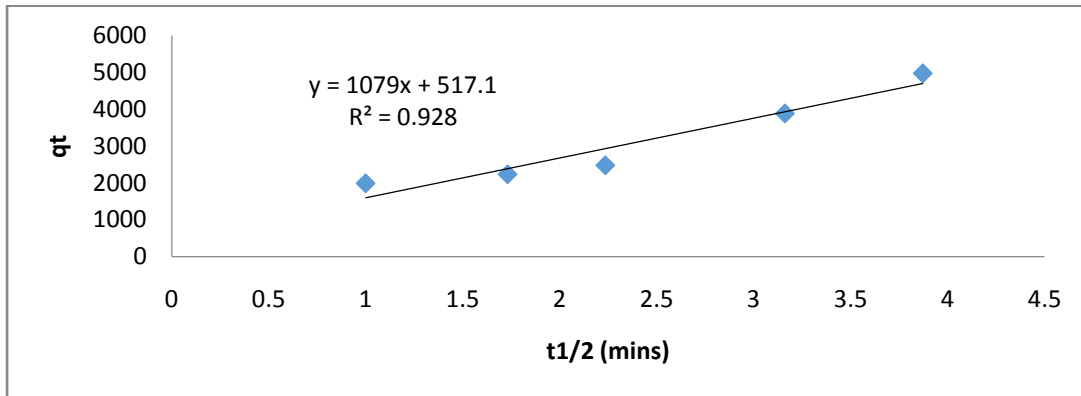
**Fig 4.49(b): Pseudo-first order Kinetic model for sorption of oil onto acetylated Borassus coir**



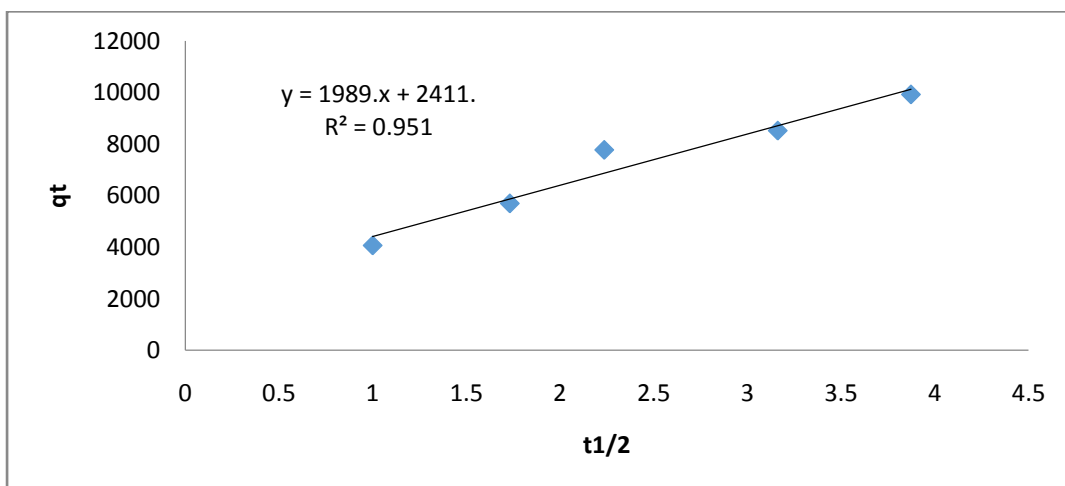
**Fig 4.50(a): Pseudo-Second order Kinetic model for sorption of oil onto Raw Borassus coir.**



**Fig 4.50(b): Pseudo-second order Kinetic model for sorption of oil onto Acetylated Borassus coir.**



**Fig 4.51(a): Intra-particle diffusion Kinetics for the sorption of oil onto Raw Borassus Coir**



**Fig 4.51(b): Intra-particle diffusion Kinetics for the sorption of oil onto Acetylated Borassus Coir.**

The summary of the derived kinetics from the plots for crude oil sorption onto borassus coir is presented in Table 4.30.

**Table 4.30: Summary of Kinetics of Crude Oil Sorption onto Borassus Coir**

Type	Acetylated Borassus coir	Raw Borassus coir
$Q_e$ expected	9915	4970
Pseudo first Order		
$Q_e$ calc	6299	4003
$R^2$	0.9207	0.9085
$K_1$	0.1605	0.1392
Pseudo Second Order		
$Q_e$ calc	11,111	5000
$R^2$	0.9867	0.8871
$K_1$	0.00009	0.0002
Intra Particle Diffusion		
$K_d$	1989.6	1079
C	2411.8	517.11
$R^2$	0.9517	0.9289

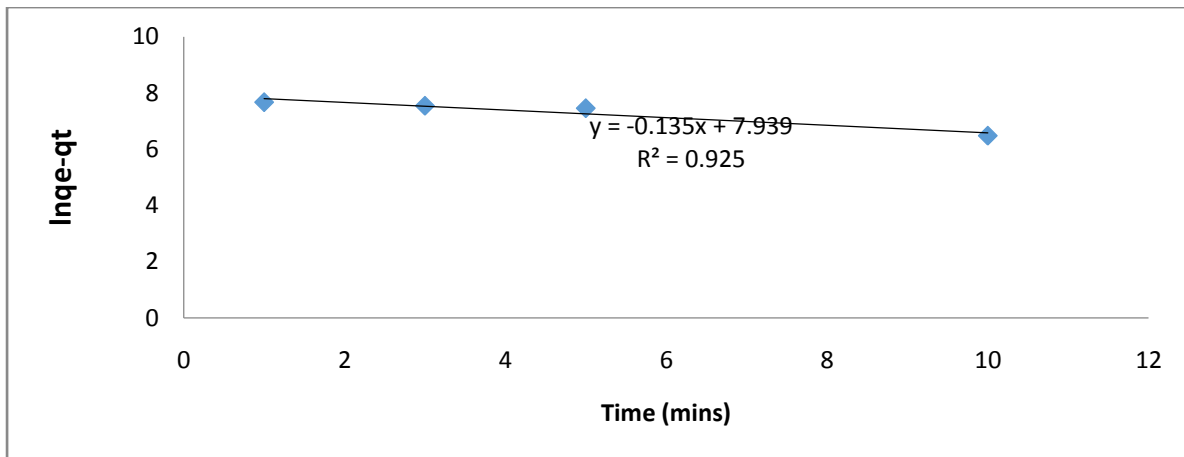
From Table 4.30, it could be seen that the coefficient of regression ( $R^2$ ) for crude oil sorption onto ABC was 0.9207 for the pseudo-first order and 0.9867 for the pseudo-second order. Pseudo-second order gave the best fit for crude oil sorption of ABC because it gave the highest  $R^2$  value (0.9867). Also the predicted adsorption capacity value obtained for pseudo second order was 11,111mg/g and is wide when compared to experimental adsorption capacity value of 9915mg/g, though it was closer than that of pseudo-first order at 6299mg/g.. For RBC,  $R^2$  values are lower for

both the pseudo-first and pseudo-second orders at 0.9085 and 0.8871 respectively when compared with that of ABC. This can be attributed to the hydrophobic nature of the modified sorbent which gave it a higher  $R^2$  (Onwuka et al., 2016).

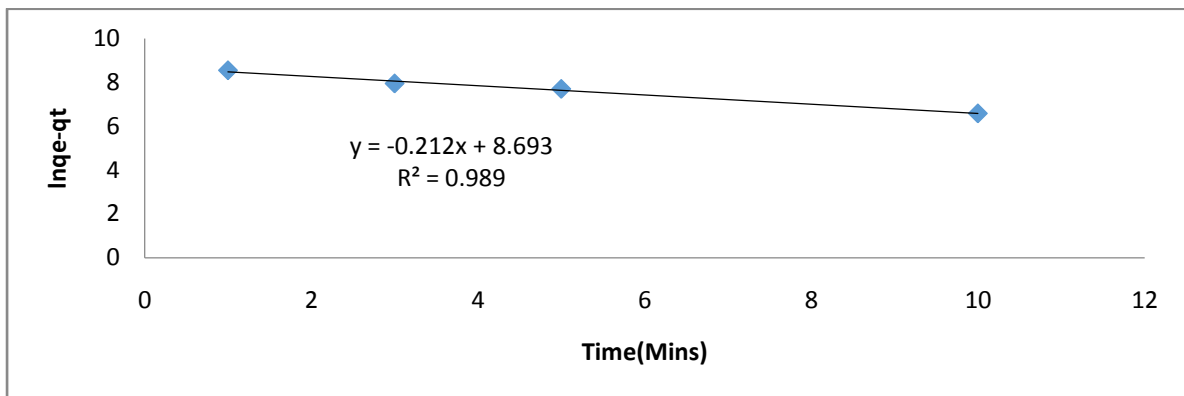
Intra-particle diffusion becomes the sole rate-determining step if the plot is linear, and passes through the origin. As seen from Table 4.30, the  $R^2$  values for the intra-particle diffusion was higher for both ABC (0.9517) than RBC (0.9289). Also there was presence of intercept (C) though the plot did not pass through the origin but was close to it. The deviation from origin may be due to the difference in mass transfer in the initial and final stages of the sorption process (Das and Mondal, 2011). The good regression indicated the existence of an intra-particle diffusion mechanism for the sorption of crude oil on ABC and RBC. It can be inferred that intra-particle diffusion was the rate controlling mechanism for the sorption process though may not be the sole mechanism since the line did not pass through the origin.

#### **4.7.3 Kinetics of Crude Oil sorption unto African Breadfruit Seed Husk**

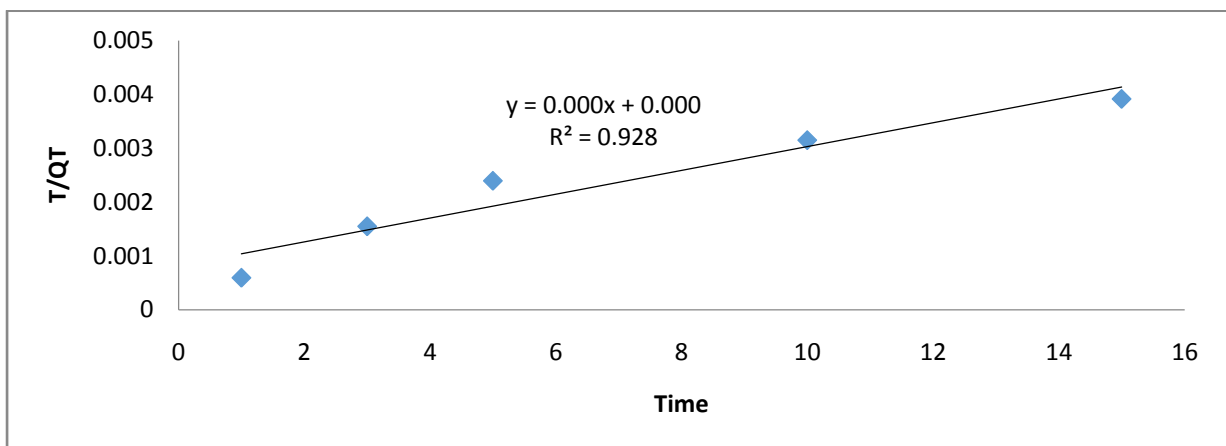
The rate and mechanism of crude oil sorption of African breadfruit seed husk was analyzed by applying the sorption kinetic models to the experimental data. The kinetic models applied to this study are the pseudo first-order, pseudo second-order and intra-particle diffusion models. The predicted kinetics from the linear plots of the models are presented in Figures 4.52 – 4.54( a& b) respectively.



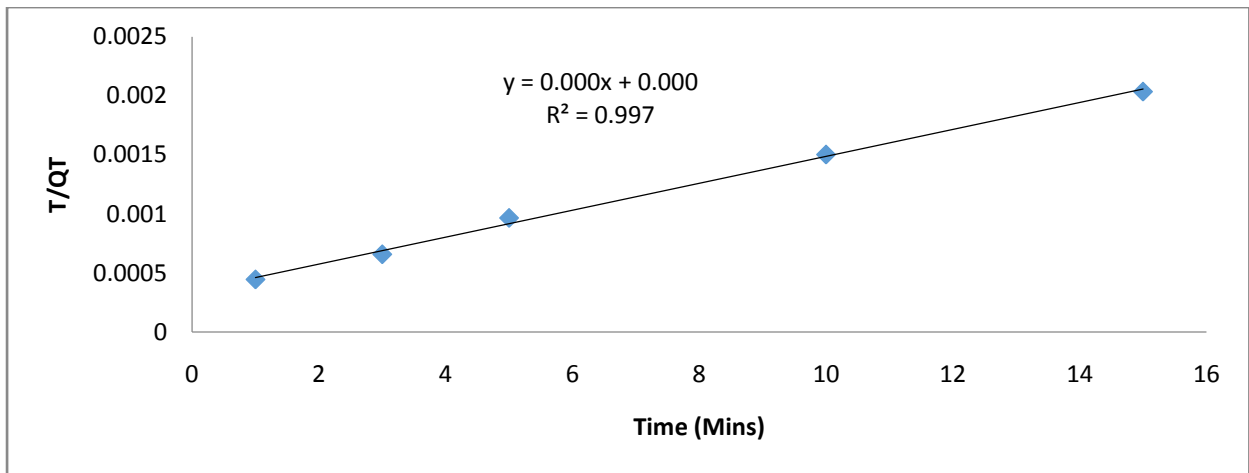
**Fig 4.52(a): Pseudo-first-order Kinetics for the sorption of oil onto raw African breadfruit seed husk.**



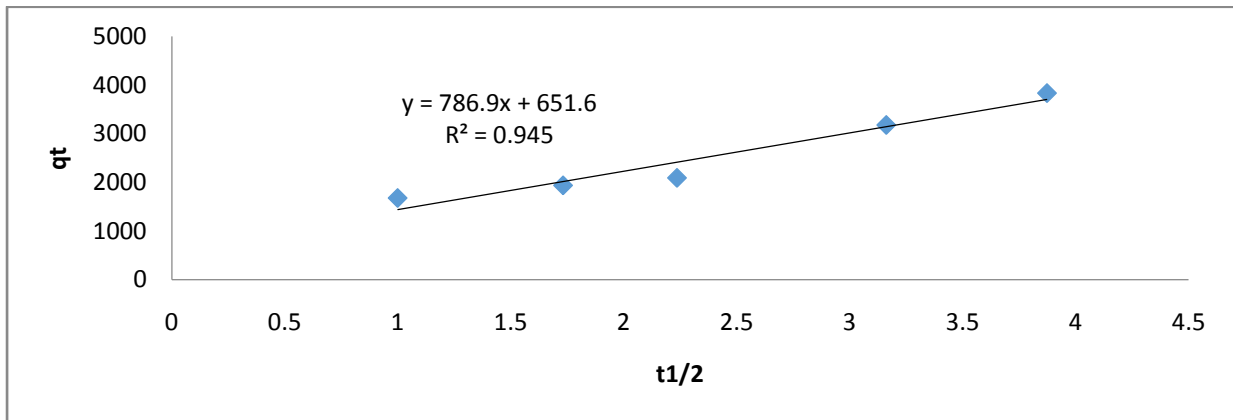
**Fig 4.52(b): Pseudo-first-order Kinetics for the sorption of oil onto acetylated African breadfruit seed husk.**



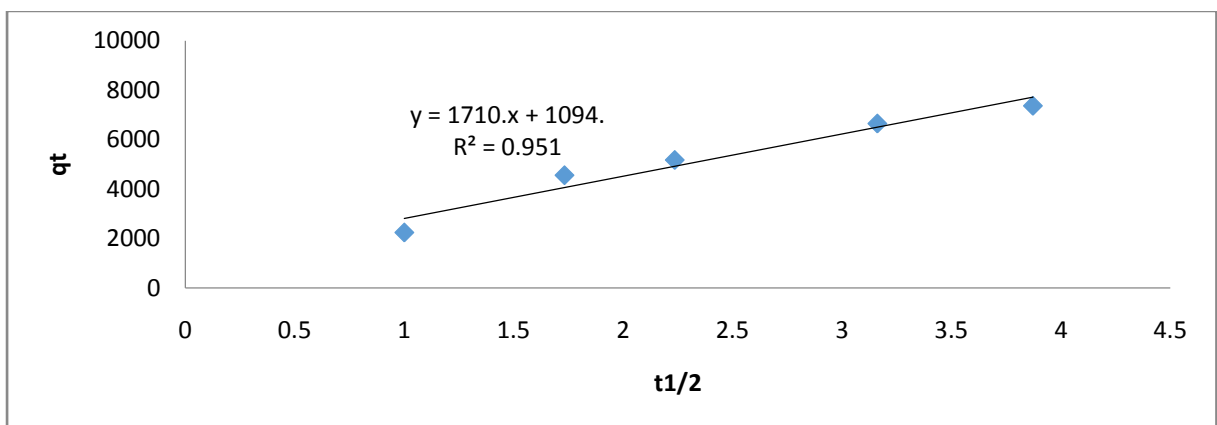
**Fig 4.53(a): Pseudo-second-order Kinetics for the sorption of oil onto raw African breadfruit seed husk.**



**Fig 4.53(b): Pseudo-second-order Kinetics for the sorption of oil onto acetylated African breadfruit seed husk.**



**Fig 4.54(a): Intra-particle diffusion Kinetics for the sorption of oil onto raw African breadfruit seed husk.**



**Fig 4.54(b): Intra-particle diffusion kinetics for the sorption of oil onto acetylated African breadfruit seed husk.**

The summary of derived kinetics from the plots of crude oil sorption onto African breadfruit seed husk are shown in Table 4.31.

**Table 4.31: Summary of Kinetics of Crude Oil Sorption onto African Breadfruit Seed Husk.**

Type	Acetylated African breadfruit seed husk (ABF)	Raw African Breadfruit seed husk (RBF)
$Q_e$ expected	7368	3832
Pseudo first Order		
$q_{e \text{ calc}}$	5965.8	2805.7
$R^2$	0.9898	0.9256
$K_1$	0.212	0.1359
Pseudo Second Order		
$q_{e \text{ calc}}$	2500	5,000
$R^2$	0.9778	0.9285
$K_1$	0.0004	0.0005
Intra Particle Diffusion		
$K_d$	1710.7	786.94
C	1094	651.68
$R^2$	0.9511	0.9454

Table 4.31 shows a comparison of the kinetic parameters for crude oil sorption on ABF and RBF. The coefficient of regression  $R^2$  for ABF and RBF were 0.9898 and 0.9256 respectively for pseudo-first order. The pseudo-second order gave 0.9778

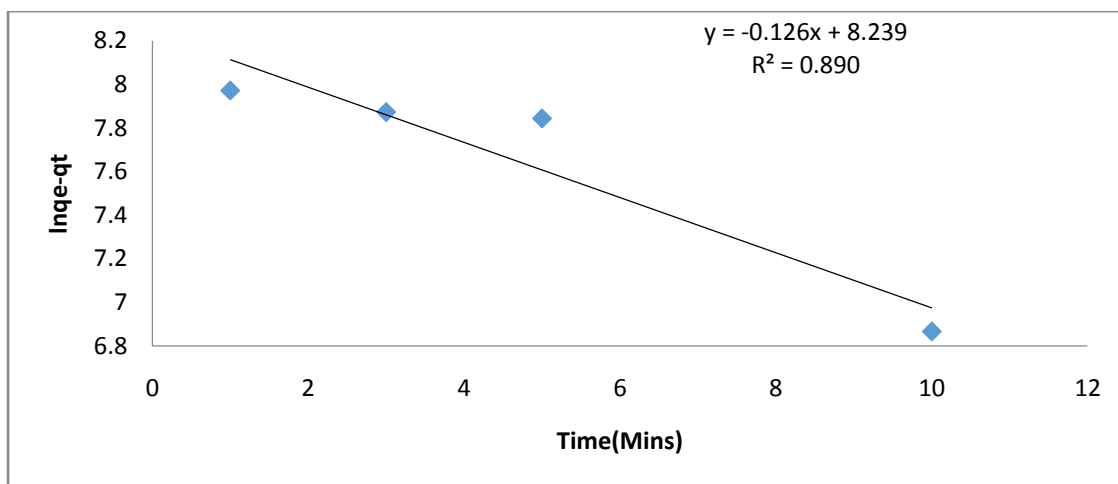
and 0.9285  $R^2$  values for ABF and RBF respectively. It could be seen that the  $R^2$  values for the pseudo- first order for ABF was higher than that of the pseudo-second order. This result indicates that the pseudo-first order model produced a better fit for the data. Also the predicted adsorption capacity value obtained for pseudo-first order was 5985.8mg/g and is wide when compared to experimental adsorption capacity value of 7368mg/g, though it was closer than that of pseudo-second order at 2500mg/g. Therefore it implies very likely that chemisorption was not the only mechanism involved or was not majorly involved during crude oil sorption onto ABF.

Intra-particle diffusion becomes the sole rate-determining step if the plot is linear, and passes through the origin. From Table 4.31, it was observed that  $R^2$  values for the intra-particle diffusion were high for both ABF (0.9511) and RBF (0.9454). Also there was presence of intercept (C) though the plot did not pass through the origin but was close to it. The good regression indicated the existence of an intra-particle diffusion mechanism for the sorption of crude oil on ABF and RBF. It was also observed that intra-particle diffusion was the rate controlling mechanism for the sorption process but it was not the sole mechanism since the line did not pass through the origin.

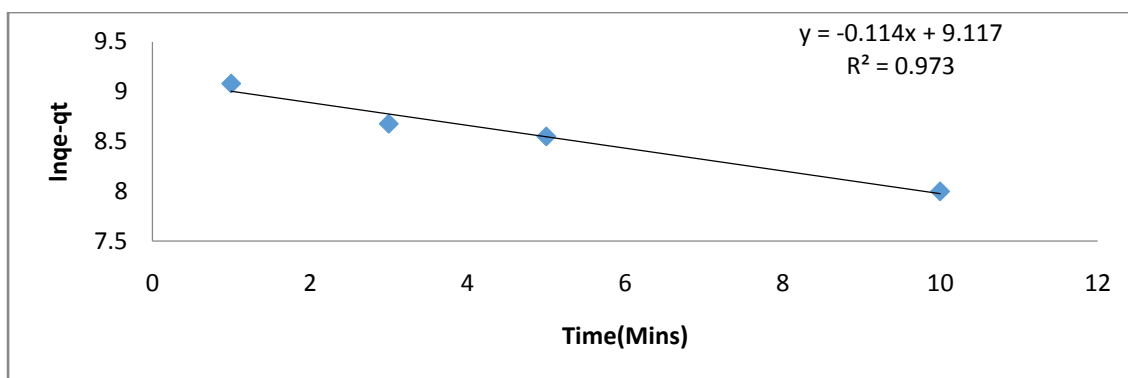
#### **4.7.4 Kinetics of Crude Oil Sorption onto Plantain Pseudostem**

The kinetic models applied to this study are the pseudo first-order, pseudo second-order and intra-particle diffusion models. The predicted kinetics from the linear plots of the models are presented in Figures 4.55 – 4.57( a& b) respectively.

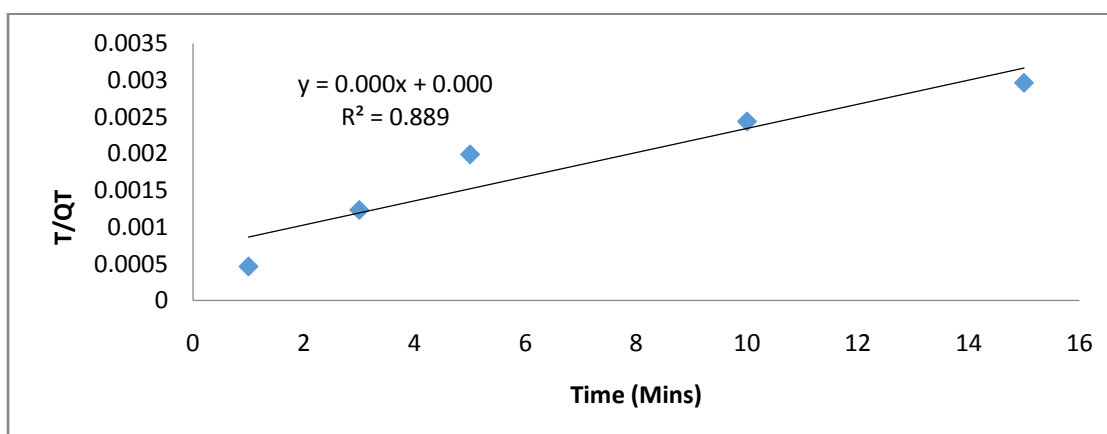




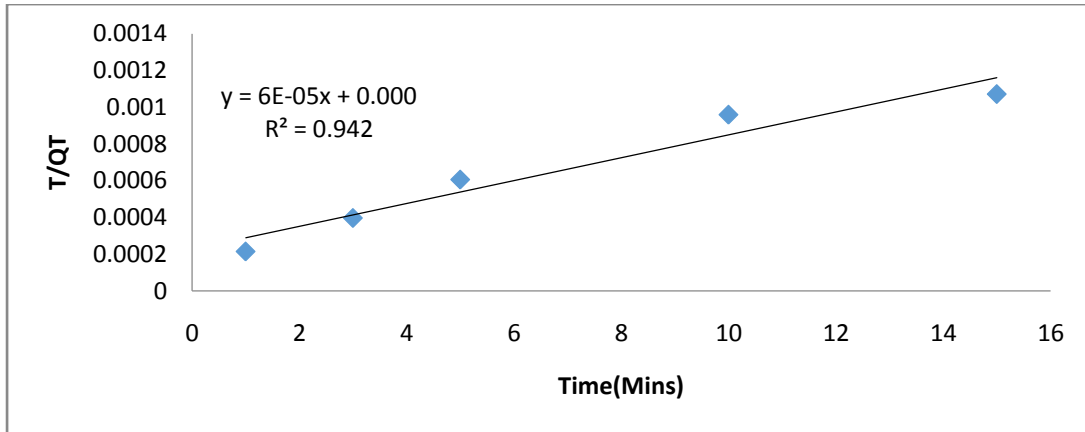
**Fig 4.55(a): Pseudo-first order Kinetic model for sorption of oil onto raw Plantain Pseudostem.**



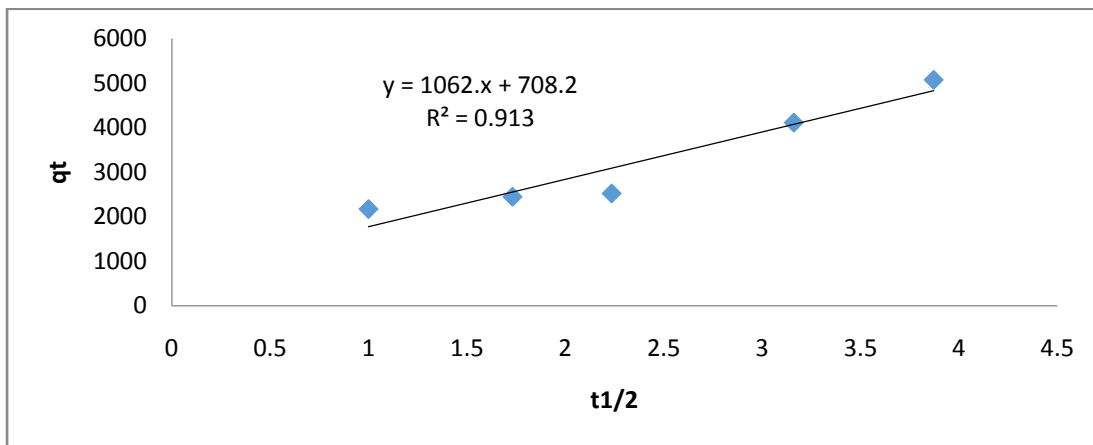
**Fig 4.55(b): Pseudo-first order Kinetic model for sorption of oil onto acetylated Plantain Pseudostem.**



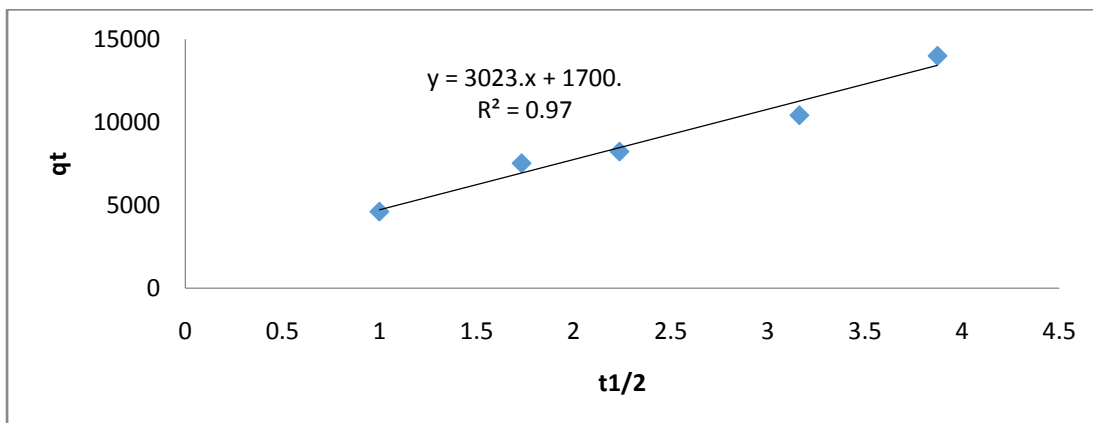
**Fig 4.56(a): Pseudo-second order Kinetics for the sorption of oil onto raw plantain pseudostem**



**Fig 4.56(b): Pseudo-second order Kinetics for the sorption of oil onto acetylated plantain pseudostem.**



**Fig 4.57(a): Intra-particle diffusion Kinetics for the sorption of oil onto raw plantain pseudostem**



**Fig 4.57(b): Intra-particle diffusion Kinetics for the sorption of oil onto acetylated plantain pseudostem**

The summary of the derived kinetics from the plots of crude oil sorption onto plantain pseudostem are shown in Table 4.32.

**Table 4.32: Summary of Kinetics of Crude Oil Sorption on Plantain Pseudostem.**

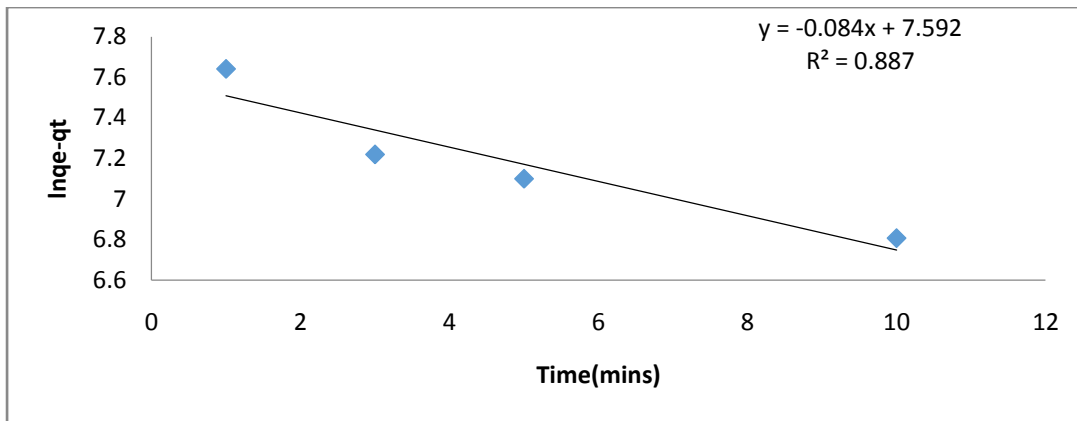
Type		Acetylated Pseudostem (APS)	Plantain Raw Plantain Pseudostem (APS)
$Q_e$ expected	mg/L	13,393	5,065
Pseudo first Order			
$q_{e \text{ calc}}$	mg/L	9,109.7	3789
$R^2$		0.9732	0.8908
$K_1$		0.114	0.1265
Pseudo Second Order			
$q_{e \text{ calc}}$	mg/L	16,666.67	5,000
$R^2$		0.9424	0.8897
$K_1$		0.000018	0.000057
Intra Particle Diffusion			
$K_d$		3023.5	1062.1
C		1700.5	708.22
$R^2$		0.97	0.9139

An in-depth understanding of the kinetics of crude oil sorption onto RPS and APS is vital for practical applications. The industrial applications can be feasible if some kinetic parameters obtained are used in process designs and scale up procedures (Faith. 2013). From Table 4.32, it could be seen that the coefficient of regression ( $R^2$ ) for crude oil sorption onto APS was 0.9732 for the pseudo-first order and 0.9424 for the pseudo-second order. Pseudo-first order gave the best fit for crude oil sorption of APS because it gave the highest  $R^2$  value (0.9732). For RPS,  $R^2$  values are lower for both the pseudo-first and pseudo-second orders at 0.9256 and 0.9285 respectively when compared with that of APS. This can be attributed to the hydrophobic nature of the modified sorbent which gave them higher  $R^2$  values (Onwuka *et al.*, 2016).

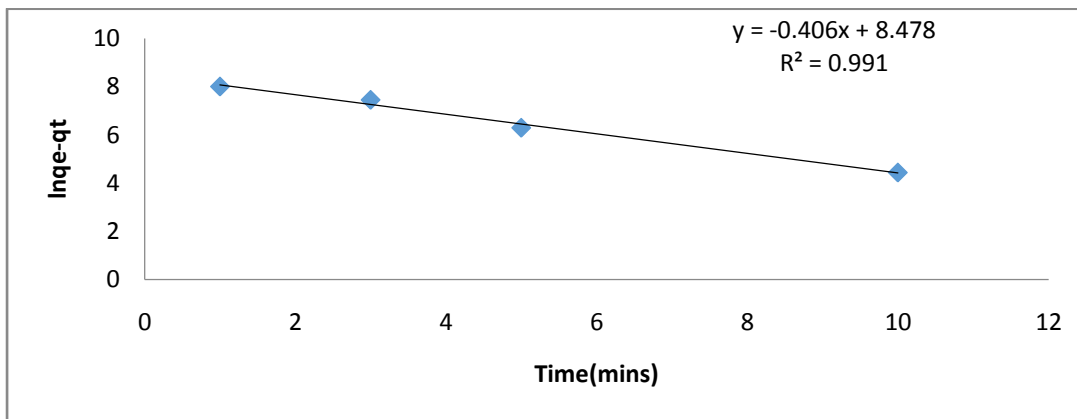
Intra-particle diffusion becomes the sole rate-determining step if the plot is linear, and passes through the origin. As seen from Table 4.32, the  $R^2$  values for the intra-particle diffusion were high for both APS (0.9511) and RPS (0.9454). The good regression indicated the existence of an intra-particle diffusion mechanism for the sorption of crude oil. It was also observed that intra-particle diffusion was the rate controlling mechanism for the sorption process but it is not the sole mechanism since the line did not pass through the origin.

#### **4.7.5 Kinetics of Crude Oil sorption unto Plantain Peel**

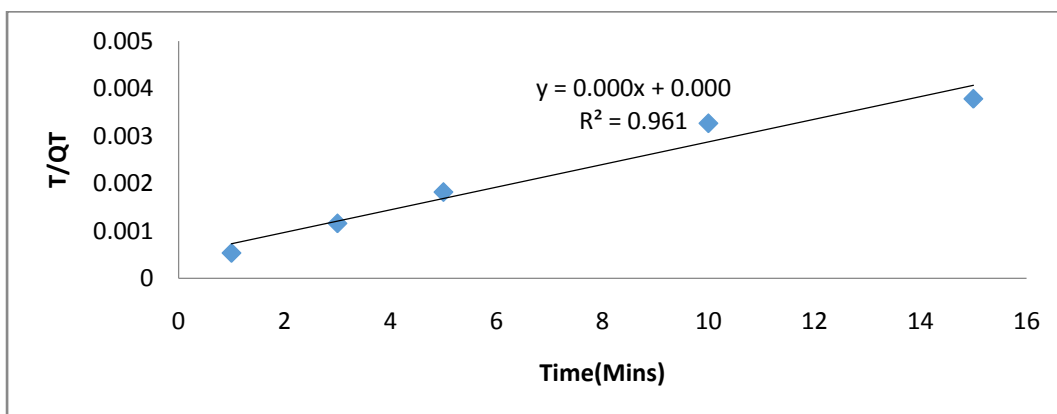
The predicted kinetics from the linear plots of the models are shown in Figures 4.58–4.60 (a & b) for the raw and acetylated samples respectively.



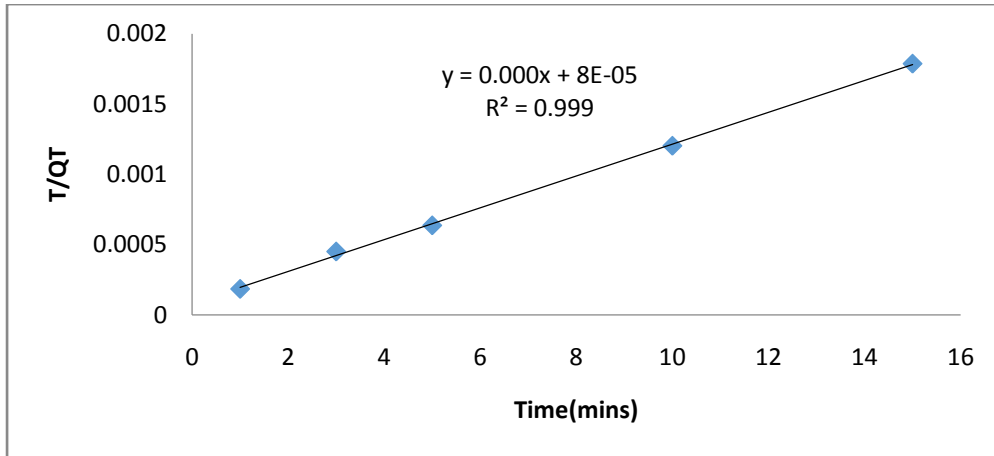
**Fig 4.58 (a): Pseudo-first order Kinetic model for sorption of oil onto raw Plantain Peel**



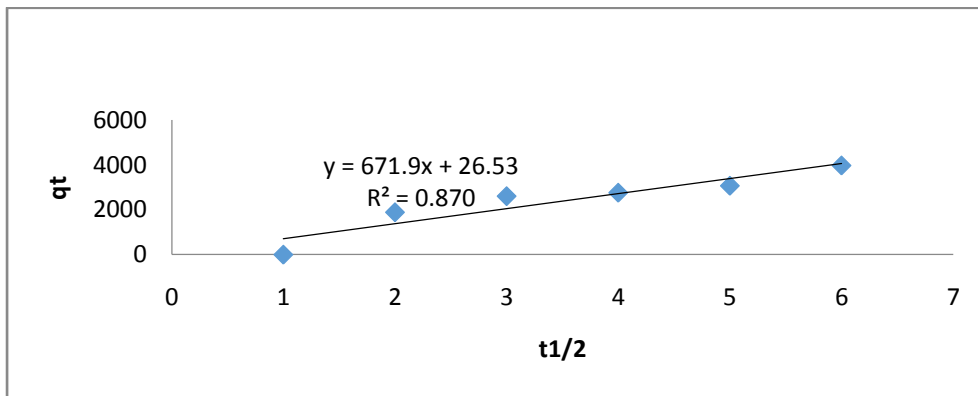
**Fig 4.58(b): Pseudo-first order Kinetic model for sorption of oil onto acetylated Plantain Peel**



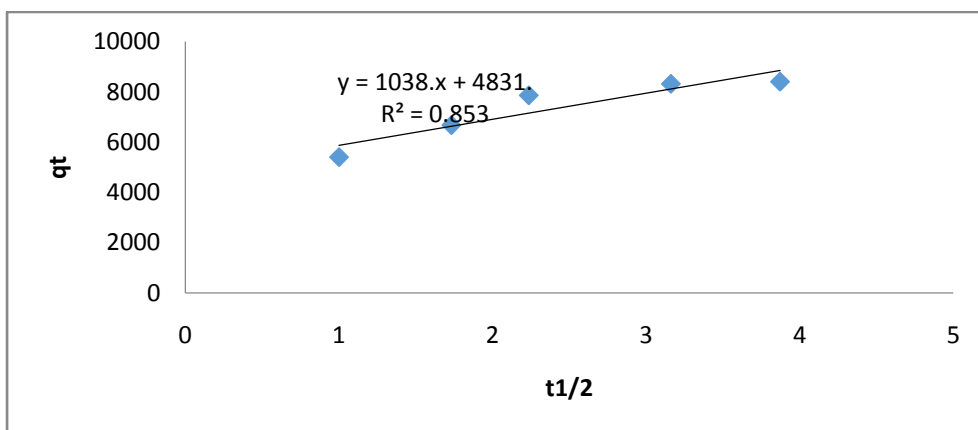
**Fig 4.59(a): Pseudo-second order Kinetic model for sorption of oil onto raw Plantain Peel.**



**Fig 4.59(b): Pseudo-second order Kinetic model for sorption of oil onto acetylated Plantain Peel.**



**Fig 4.60(a): Intra-particle diffusion Kinetics for the sorption of oil onto raw plantain peel.**



**Fig 4.60(b): Intra-particle diffusion Kinetics for the sorption of oil onto acetylated plantain peel**

The summary of the derived kinetics from the plots of plantain peel is presented in Table 4.33.

**Table 4.33: Summary of Kinetics of Crude Oil Sorption onto Plantain Peel.**

Type	Acetylated Plantain Peel (APP)	Raw Plantain Peel (RPP)
$Q_e$ expected	8395	3966
Pseudo first Order		
$Q_e$ calc	2650	1983.5
$R^2$	0.9912	0.8873
$K_1$	0.406	0.845
Pseudo Second Order		
$Q_e$ calc	10,000	5000
$R^2$	0.9992	0.9616
$K_1$	0.000125	0.00008
Intra Particle Diffusion		
$K_d$	1038.3	671.9
C	4831.4	26.533
$R^2$	0.853	0.8701

Table 4.33 showed that the coefficient of regression ( $R^2$ ) for crude oil sorption onto APP was 0.9912 for the pseudo-first order, 0.9992 for the pseudo-second order and 0.853 for intra-particle diffusion. Pseudo-second order gave the best fit for crude oil sorption of APP because it gave the highest  $R^2$  value (0.9992). Also the predicted adsorption capacity value obtained for pseudo-second order was 10000mg/g which is the closest to experimental adsorption capacity value of 8395mg/g. For RPP,  $R^2$  values are lower for both the pseudo-first and pseudo-second orders at 0.8873 and 0.9616 respectively when compared with that of APP. This can be attributed to the hydrophobic nature of the modified sorbent which gave them higher  $R^2$  values (Onwuka *et al.*, 2016).

In the reaction kinetics (i.e. pseudo-first and pseudo-second order), the pseudo-second order rate constants for the sorbents were found to be lower than the pseudo-first order rate constants. This means that surface sorption being the slowest step in the reaction kinetics is not the only rate controlling step in the sorption process.

Intra-particle diffusion becomes the sole rate-determining step if the plot is linear, and passes through the origin. As seen from Table 4.33, the  $R^2$  values for the intra-particle diffusion were moderately high for both APP (0.853) and RPP (0.8701). Also there was presence of intercept (C) and the plot did not pass through the origin but was close to it. The deviation from origin may be due to the difference in mass transfer in the initial and final stages of the sorption process (Das and Mondal, 2011). The good regression indicated the existence of an intra-particle diffusion mechanism for the sorption of crude oil on APP and RPP. It was also observed that intra-particle diffusion was the rate controlling mechanism for the sorption process



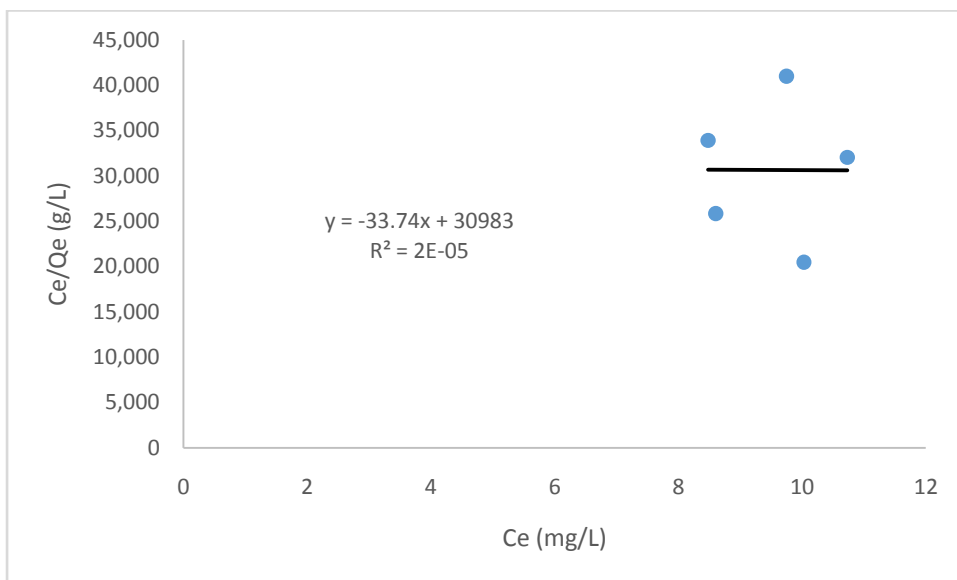
but it is not the sole mechanism since the line did not pass through the origin(Nwadiogbu *et al.*, 2014).

#### 4.8 Sorption Isotherm

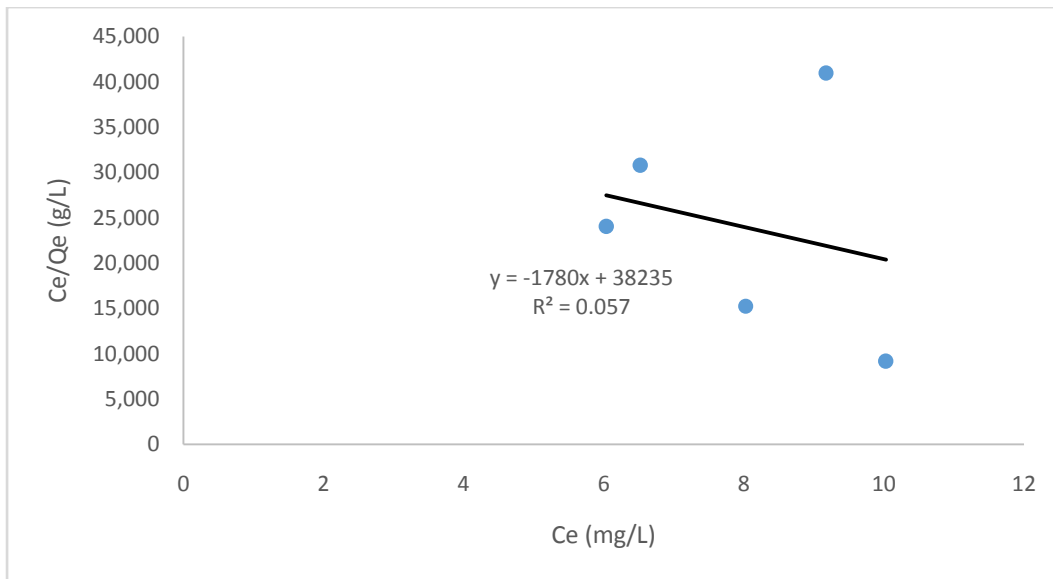
In this study, Langmuir and Freundlich isotherms earlier described in chapter three were used to analyze the equilibrium data.

##### 4.8.1 Sorption Isotherm for Corn Husk

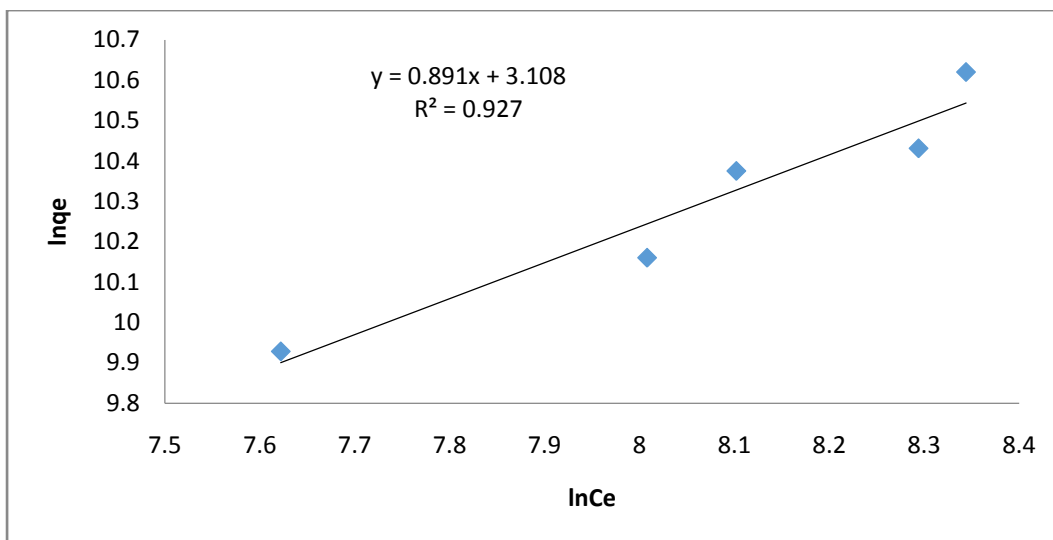
Langmuir and Freundlich isotherms were tested to analyze the equilibrium data for corn husk and the plots are presented in Figures 4.61 – 4.62( a& b) respectively.



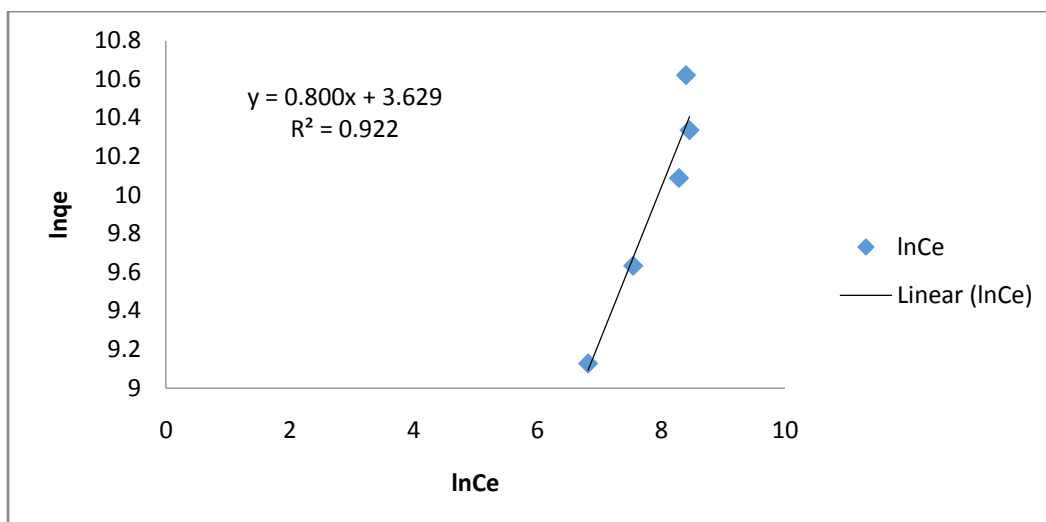
**Fig 4.61(a): Plot of Langmuir model of adsorption of acetylated corn husk**



**Fig 4.61(b): Plot of Langmuir model of adsorption for raw corn husk**



**Fig 4.62(a): Freundlich Model of adsorption Plot of acetylated corn husk**



**Fig 4.62(b): Freundlich Model of adsorption Plot of raw corn husk**

The result of the comparison of the Langmuir and Freundlich isotherm constants for crude oil sorption onto corn husk is presented in Table 4.34.

**Table 4.34: Comparison of Isotherm Constants for crude oil Sorption onto Corn husk.**

Isotherm Model	ACH	RCH
Langmuir		
$q_0$ (g/g)	$2 \times 10^6$	33,333
B (L/g)	$5.24 \times 10^{-8}$	$3.43 \times 10^{-6}$
$R_L$	0.997	0.172
$R^2$	0.00002	0.579
Freundlich		
$k_f$ (g/g)	22.39	37.71
n (g/L)	1.122	1.249
$R^2$	0.9275	0.9222

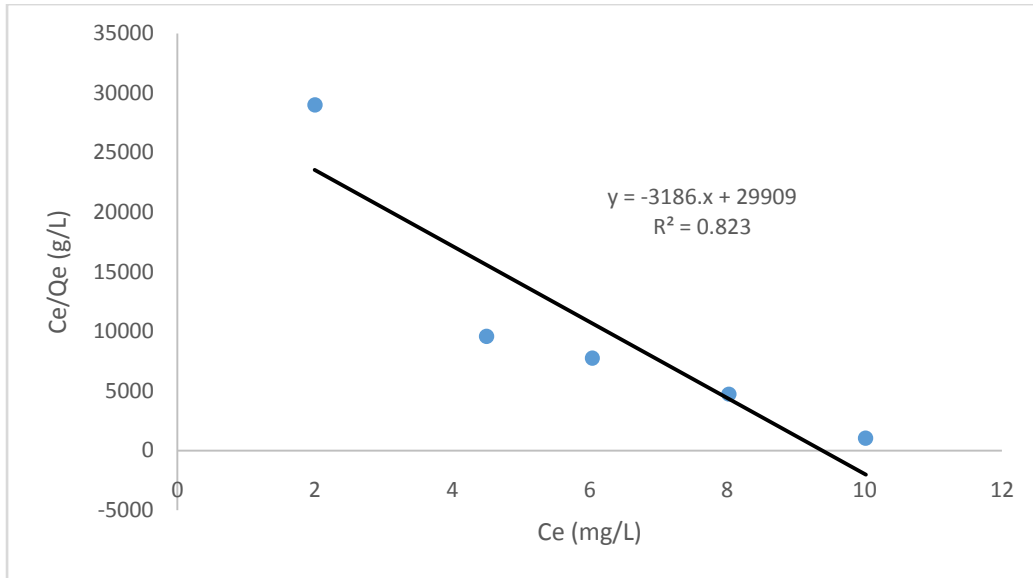
As shown in Table 4.34 the co-efficient of regression ( $R^2$ ) for Langmuir isotherm was 0.00002 which is very poor. This indicates that the monolayer adsorption isotherm did not provide a good fit for the sorption of crude oil onto acetylated corn husk. The separation factor  $R_L$  provides information regarding the nature of the adsorption process. The adsorption can be considered irreversible if ( $R_L = 0$ ), favourable if ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ). The  $R_L$  obtained for this study was 0.997, indicating favourable sorption of crude oil on acetylated corn husk.

The Freundlich isotherm model has been applied to non-ideal sorption on heterogeneous surfaces. As shown in Table 4.34, the value of the coefficient of regression  $R^2$  was 0.9275 which is higher than that obtained for Langmuir model (0.00002). This result indicates that Freundlich model is suitable for describing the sorption equilibrium of crude oil on acetylated corn husk. This is in agreement with results elsewhere (Ahmad *et al.*, 2005, Nurul *et al.*, 2011).

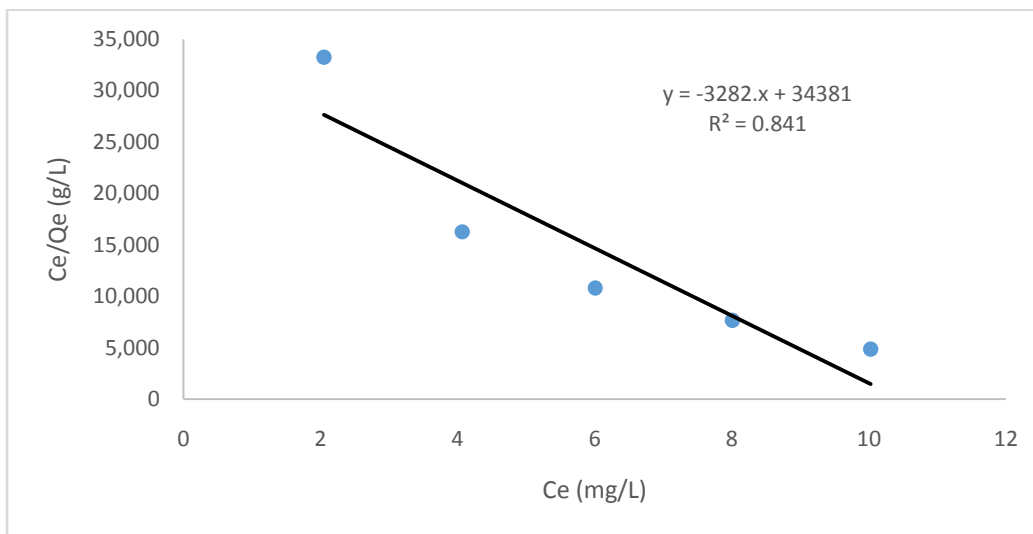
Also the value of the exponent,  $1/n$ , gives an indication of the favorability of adsorption. Values of  $n > 1$  represents favourable adsorption condition (Ho and Mckay, 1998). The value of  $1/n$  was determined from the plot and the value of  $n$  calculated was 1.122 which is greater than unity. This further indicates the favorability of adsorption on acetylated corn husk. Thus it is reasonable to conclude that the adsorption of oil on the corn husk consist of heterogeneous adsorption sites that are similar to each other in respect to adsorption phenomenon. This favourability of adsorption can also be attributed to the increased pores and surface area of the surface material as shown by SEM analysis on the acetylated sample.

#### **4.8.2 Sorption Isotherm for borassus coir**

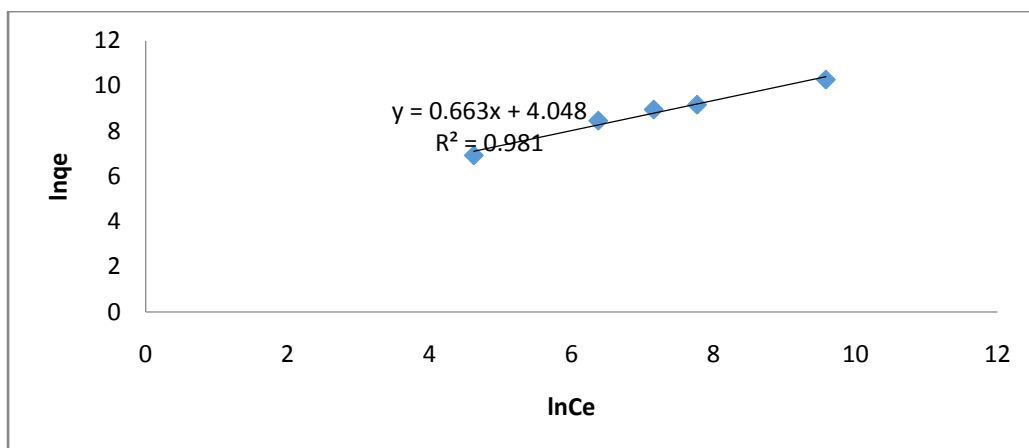
In this study, Langmuir and Freundlich isotherms were used to analyze the equilibrium data for borassus coir and the plots are presented in Figures 4.63 – 4.64 (a & b) respectively.



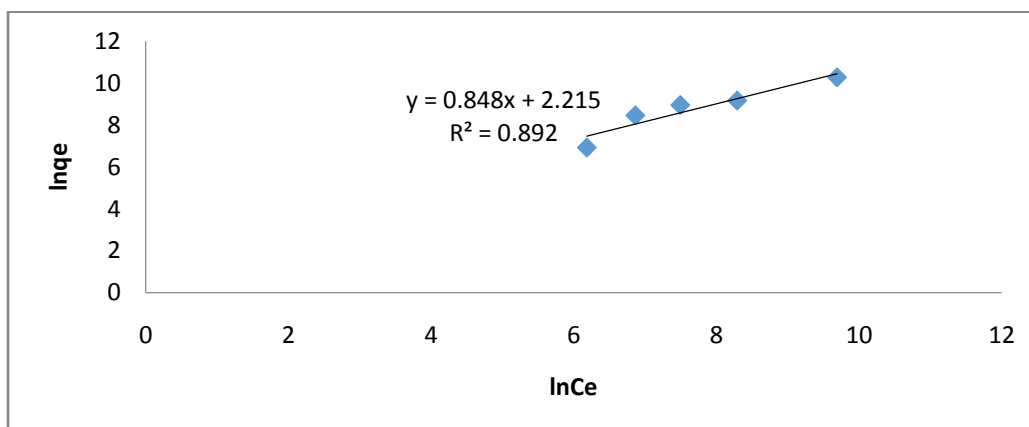
**Fig 4.63(a): Plot of Langmuir Model of Adsorption for acetylated borassus coir**



**Fig 4.63(b) Plot of Langmuir Model of Adsorption for raw borassus coir**



**Fig 4.64(a): Plot of Freundlich Model of Adsorption for acetylated borassus coir**



**Fig 4.64(b): Plot of Freundlich Model of Adsorption for raw borassus coir**

The result of the comparison of the Langmuir and Freundlich isotherm constants for crude oil sorption onto borassus coir is presented in Table 4.35.

**Table 4.35: Comparison of Langmuir and Freundlich Isotherm Constants for Borassus Coir.**

Isotherm Model	ABC	RBC
Langmuir		
$q_0$	3333.33	3333.33
B	0.0000341	0.0000370
$R_L$	0.370	0.395
$R^2$	0.8233	0.8415
Freundlich		
$k_f$	57.32	9.165
$1/n$	0.663	0.8488
$R^2$	0.9813	0.8921

As shown in Table 4.35 the co-efficient of regression ( $R^2$ ) for Langmuir isotherm was 0.8233 and 0.8415 for ABC and RBC respectively. The separation factor  $R_L$  provides information regarding the nature of the adsorption process. The adsorption can be considered irreversible if ( $R_L = 0$ ), favourable if ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ). The  $R_L$  obtained for this study was 0.370 and 0.395 for ABC and RBC respectively, indicating favourable sorption of crude oil on borassus coir.

As shown in Table 4.35, the value of the coefficient of regression  $R^2$  was 0.9813 and 0.8921 for ABC and RBC respectively which is higher than that obtained for



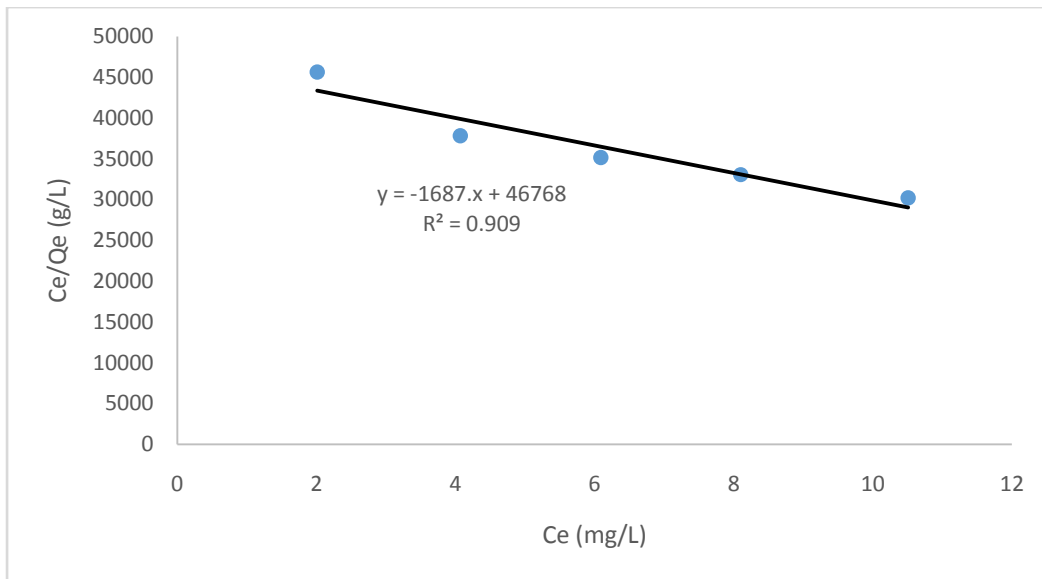
Langmuir model (0.8233 and 0.8415). This result indicates that Freundlich model is more suitable for describing the sorption equilibrium of crude oil on acetylated borassus coir. This equally implies a non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. This is in agreement with results obtained elsewhere (Ahmad *et al.*, 2005, Nurul *et al.*, 2011).

Applying the Freundlich model, the values of  $K_f$  are 57.32 and 9.165 for ABC and RBC respectively. The higher values indicating more sorption, so the results showed that ABC offered a maximum sorption capacity compared with the raw sample RBC. This could be attributed to effect of acetylation which increased the sorption ability of the ABC.

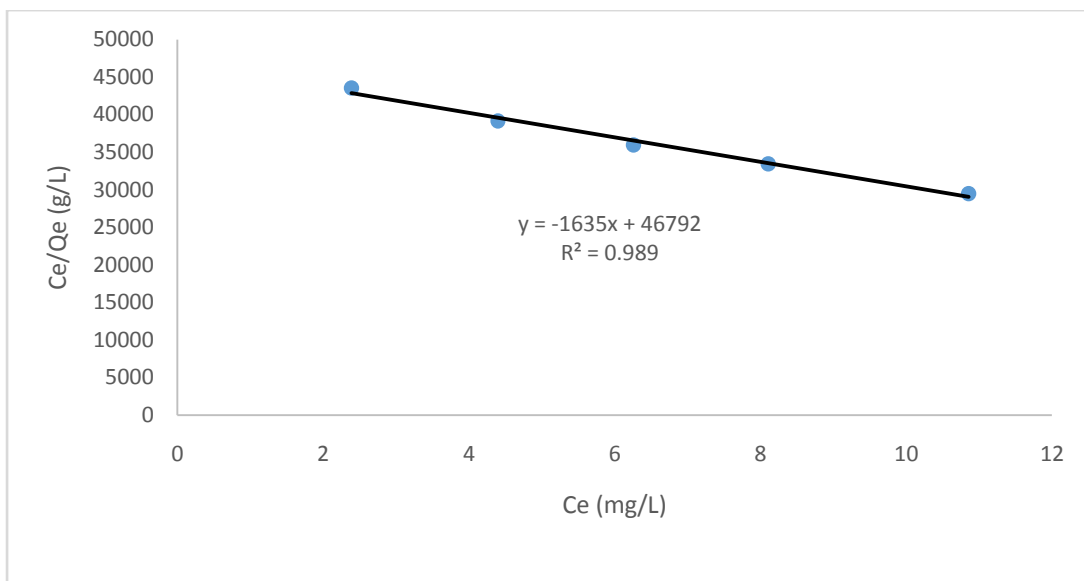
The value of  $1/n$  for ABC and RBC were 0.663 and 0.8488 respectively. The smaller the values of  $1/n$  values, the higher the affinity between adsorbate and adsorbent and the result indicates the ABC has a lower value thereby having more affinity between the acetylated sorbent material and the crude oil. Similar trend was also observed by Deepa *et al.*, (2005). Thus it is reasonable to conclude that the adsorption of oil on the borassus coir consist of heterogeneous adsorption sites that are similar to each other in respect to adsorption phenomenon.

#### **4.8.3 Sorption Isotherm for African breadfruit seed husk**

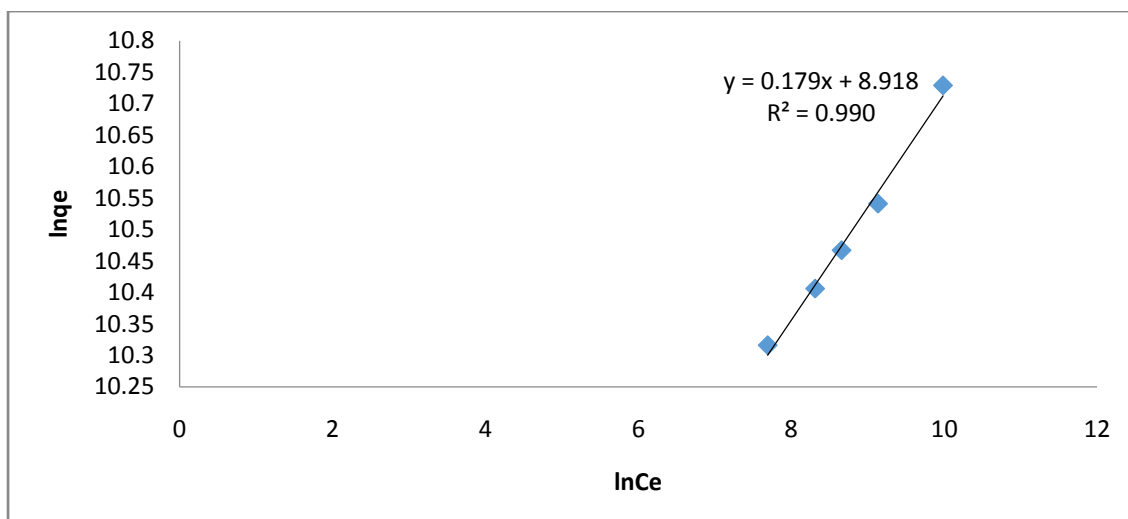
In this study, Langmuir and Freundlich isotherms were tested to analyze the equilibrium data for African breadfruit seed husk and the plots are presented in Figures 4.65 – 4.66 ( a & b) respectively.



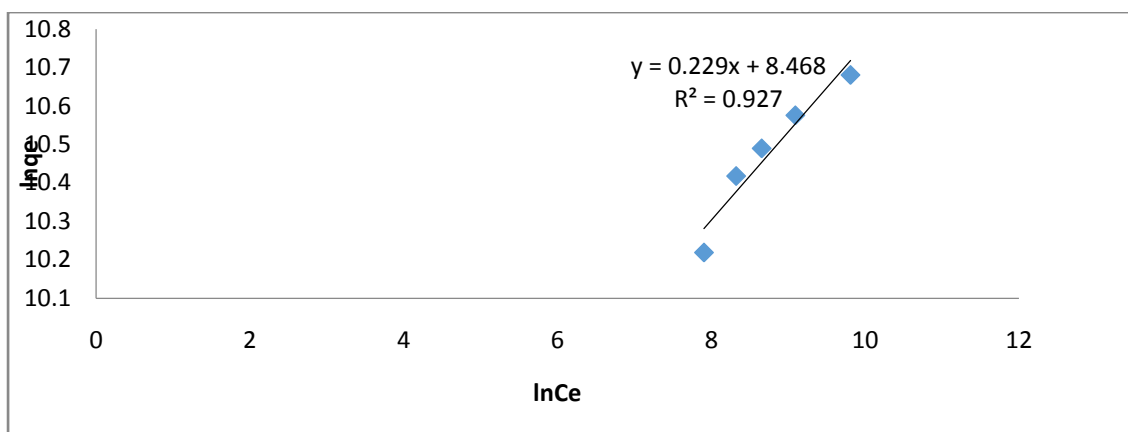
**Fig 4.65(a): Plot of Langmuir Model of Adsorption for acetylated African breadfruit seed husk.**



**Fig 4.65(b): Plot of Langmuir Model of Adsorption for raw African breadfruit seed husk**



**Fig 4.66(a): Plot of Freundlich Model of Adsorption for acetylated African breadfruit seed husk**



**Fig 4.66(b): Plot of Freundlich Model of Adsorption for raw African breadfruit seed husk.**

The result of the comparison of the Langmuir and Freundlich isotherm constants for crude oil sorption onto African breadfruit seed husk is presented in Table 4.36.

**Table 4.36: Comparison of Langmuir and Freundlich Isotherm Constants for African Breadfruit Seed Husk.**

Isotherm Model	ABF	RBF
Langmuir		
$q_0$	2000	1666.67
B	0.0000194	0.000021
$R_L$	0.507	0.486
$R^2$	0.909	0.9898
Freundlich		
$k_f$	7471.1	4762.4
$1/n$	0.1796	0.229
$R^2$	0.9902	0.9279

As shown in Table 4.36 the co-efficient of regression ( $R^2$ ) for Langmuir isotherm was 0.909 and 0.9898 for ABF and RBF respectively. The  $R_L$  obtained for this study was 0.507 and 0.486 for ABF and RBF respectively, indicating favourable sorption of crude oil on African breadfruit seed husk.

The Freundlich isotherm model has been applied to non-ideal sorption on heterogeneous surfaces. As shown in Table 4.36, the value of the coefficient of regression  $R^2$  was 0.9902 and 0.9279 for ABF and RBF respectively. The value for

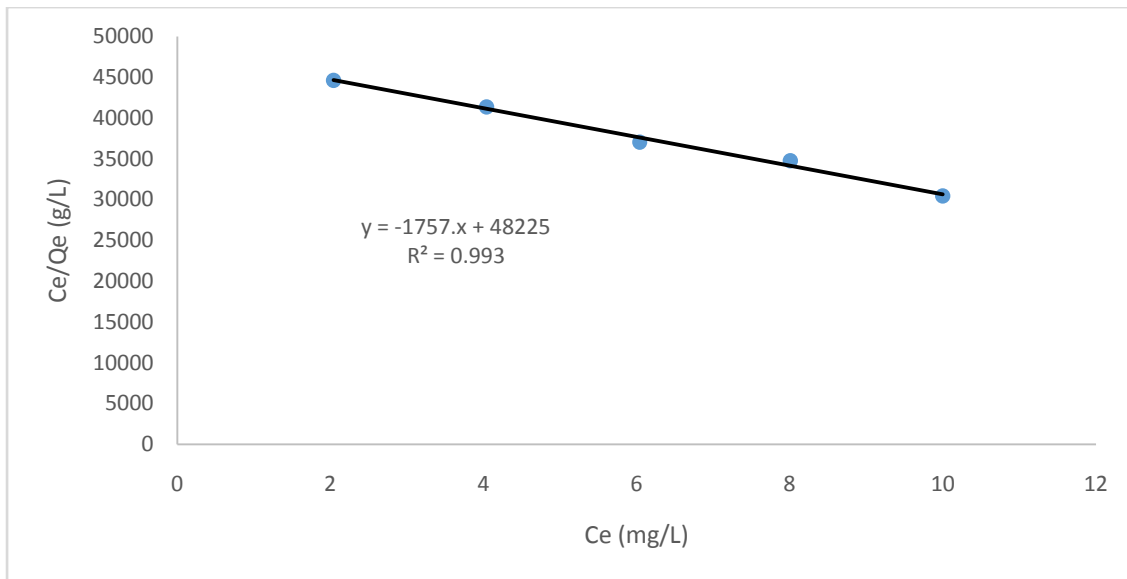
the acetylated sample ABF is higher than that obtained for Langmuir model at 0.909. This result indicates that Freundlich model is more suitable for describing the sorption equilibrium of crude oil on acetylated African breadfruit seed husk. This equally implies that mechanism of sorption is a non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. This is in agreement with results obtained elsewhere (Ahmad *et al.*, 2005, Nurul *et al.*, 2011).

Applying the Freundlich model further, the values of  $K_f$  (Freundlich adsorption capacity) are 7474.1 and 4762.2 for ABF and RBF respectively. The higher values indicating more sorption, so the results showed that ABF with a higher value of 7474.1 offered a maximum sorption capacity compared with the raw sample RBF.

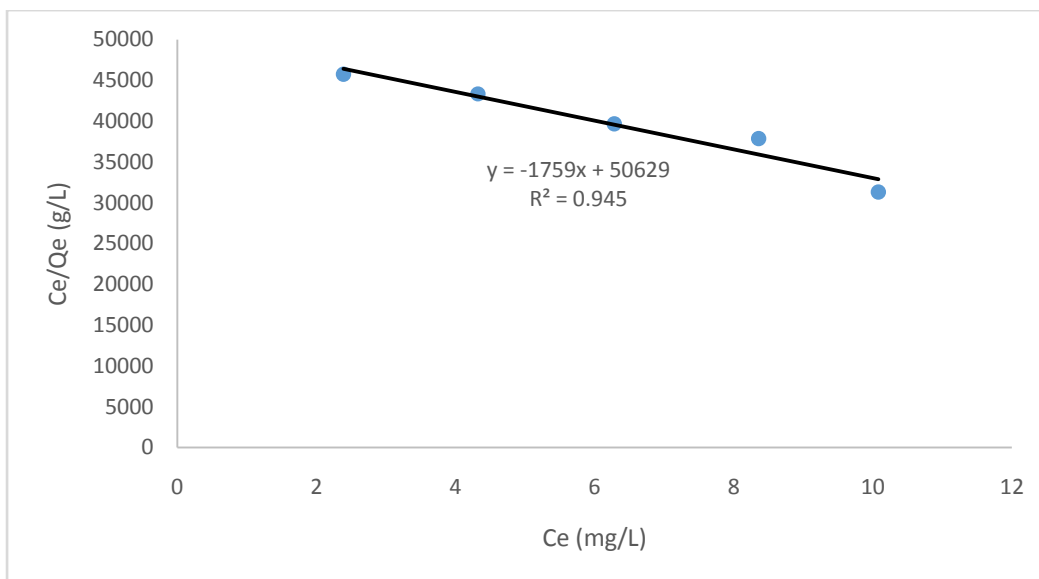
The value of  $1/n$  (intensity of the adsorbent) for ABF and RBF were 0.1796 and 0.2290 respectively. The smaller the values of  $1/n$  values, the higher the affinity between adsorbate and adsorbent and the result indicates that ABF had a lower value thereby having more affinity between the acetylated sorbent material and the crude oil. Similar trend was also observed by Deepa *et al.*, (2005) and Shashwat *et al.*, (2006). Thus it is concluded that the adsorption of oil on the African breadfruit seed husk consist of heterogeneous adsorption sites that are similar to each other in respect to adsorption phenomenon.

#### **4.8.4 Sorption Isotherm for Plantain Peel**

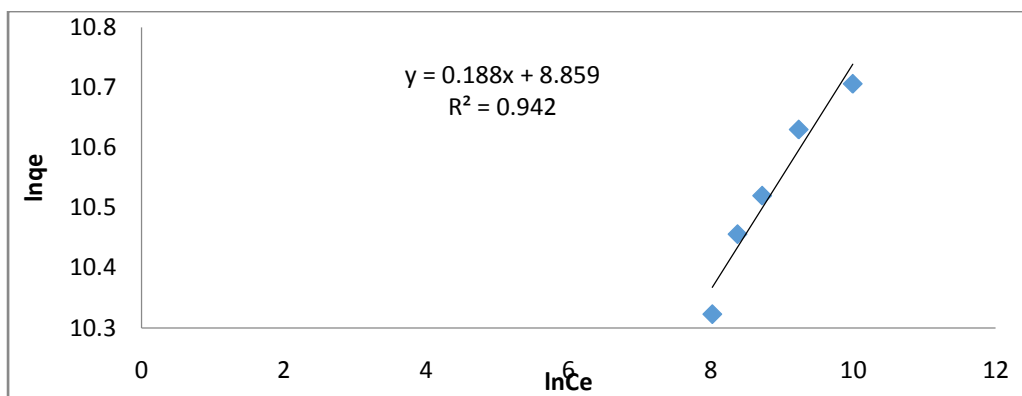
Langmuir and Freundlich isotherms were used to analyze the equilibrium data and the plots are presented in Figures 4.67 – 4.68 (a & b) respectively.



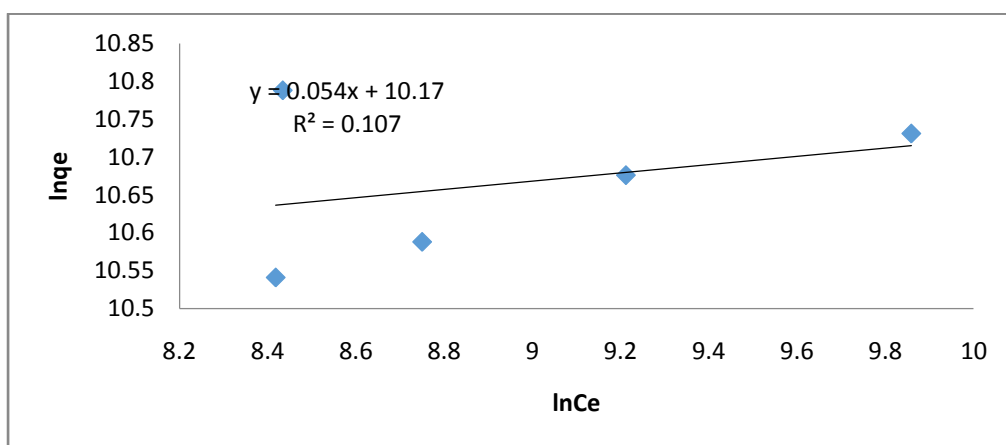
**Fig 4.67(a): Plot of Langmuir Model of Adsorption for acetylated plantain peel**



**Fig 4.67(b): Plot of Langmuir Model of Adsorption for raw plantain peel**



**Fig 4.68(a): Plot of Freundlich Model of Adsorption for acetylated plantain peel**



**Fig 4.68(b): Plot of Freundlich Model of Adsorption for raw plantain peel**

The result of the comparison of the Langmuir and Freundlich isotherm constants for crude oil sorption onto plantain peel is presented in Table 4.37.

**Table 4.37: Comparison of Langmuir and Freundlich Isotherm Constants for Plantain Peel.**

Isotherm Model	APP	RPP
Langmuir		
$q_0$	1666.67	2000
B	0.000022	0.000018
$R_L$	0.4764	0.524
$R^2$	0.9935	0.9451
Freundlich		
$k_f$	7038.2	1.1948
$1/n$	0.0545	0.188
$R^2$	0.9426	0.1075

From Table 4.37 it can be seen that the co-efficient of regression ( $R^2$ ) for Langmuir isotherm was 0.9935 and 0.9451 for APP and RPP respectively. The  $R^2$  value for Freundlich isotherm was found to be lower at 0.9426 and 0.1075 for APP and RPP respectively. This result indicates that the Langmuir model is more suitable for describing the sorption equilibrium of crude oil on acetylated plantain peel which is in agreement with results obtained by Nwankwere et al., (2010). The separation factor  $R_L$  obtained for this study was 0.4764 and 0.524 for APP and RPP respectively, indicating favourable sorption of crude oil on plantain peel.

Applying the Freundlich model further, the values of  $K_f$  (Freundlich adsorption capacity) are 7038.2 and 1.1948 for APP and RPP respectively. The higher values indicating more sorption, so the results showed that APP with a higher value of 7038.2 has a higher sorption capacity compared with the raw sample RPP.

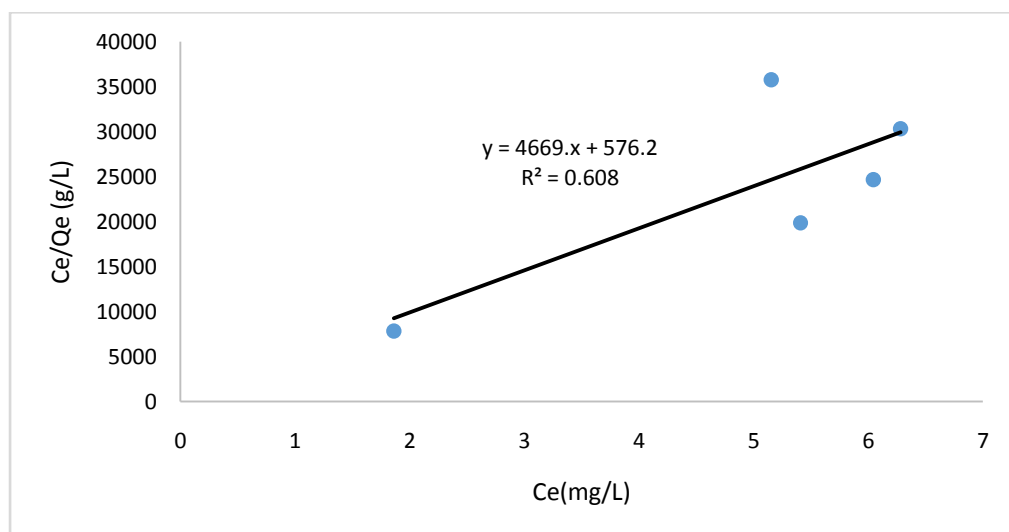


The value of  $1/n$  (intensity of the adsorbent) for APP and RPP were 0.0545 and 0.188 respectively. The smaller the values of  $1/n$  values, the higher the affinity between adsorbate and adsorbent and the result indicates the ABF has a lower value thereby having more affinity between the acetylated sorbent material and the crude oil. Similar trend was also observed by Deepa et al.,(2005).

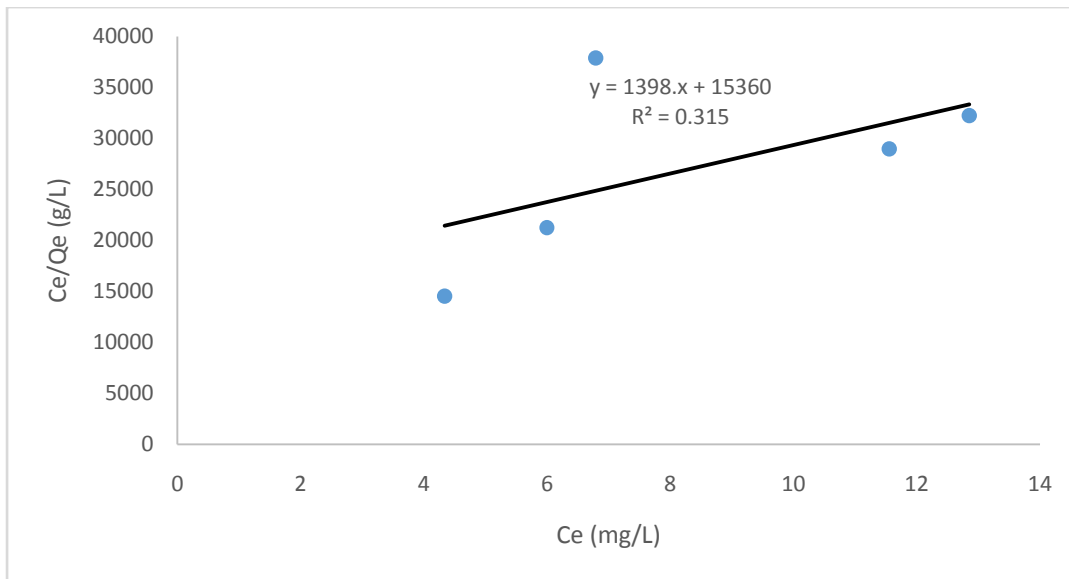
Therefore, we conclude that the adsorption occurred uniformly on the active sites of the plantain peel and the sorption process could be said to be homogeneous i.e. monolayer sorption.

#### 4.8.5 Sorption Isotherm for Plantain Pseudostem

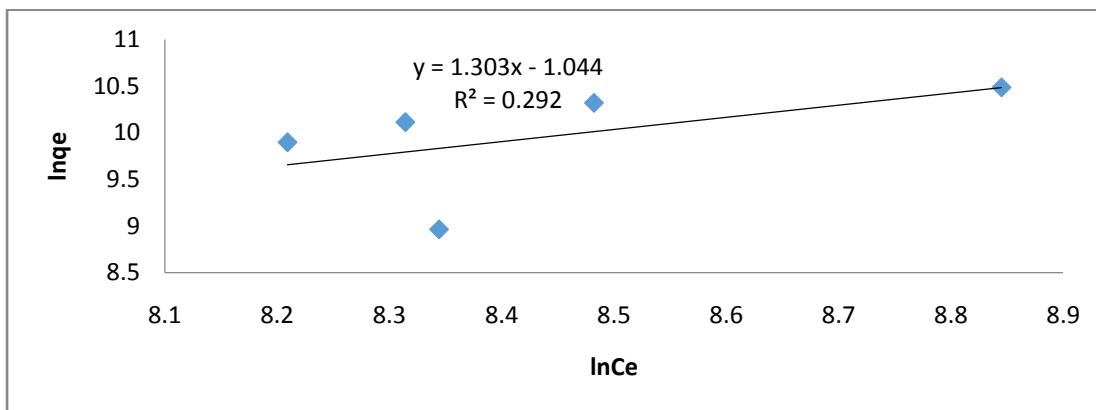
In this study, Langmuir and Freundlich isotherms were tested to analyze the equilibrium data and the plots are presented in Figures 4.69 – 4.70( a& b) respectively.



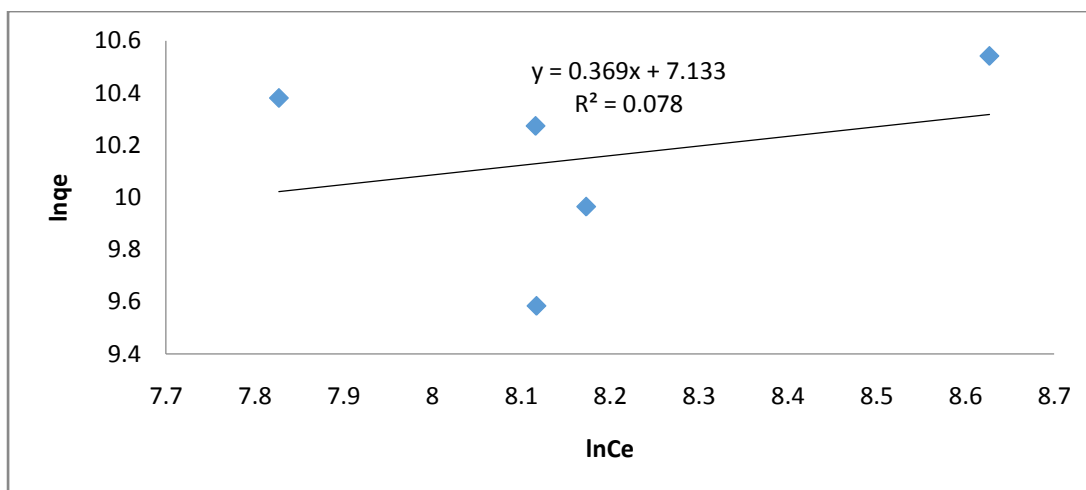
**Fig 4.69(a): Plot of Langmuir Model of Adsorption for acetylated plantain pseudostem.**



**Fig 4.69(b): Plot of Langmuir Model of Adsorption for raw plantain pseudostem**



**Fig 4.70(a): Plot of Freundlich Model of Adsorption for acetylated plantain pseudostem**



**Fig 4.70(b): Plot of Freundlich Model of Adsorption for raw plantain pseudostem**

The result of the comparison of the Langmuir and Freundlich isotherm constants for crude oil sorption onto plantain pseudostem is presented in Table 4.38.

**Table 4.38: Comparison of Langmuir and Freundlich Isotherm Constants for Plantain Pseudostem.**

Isotherm Model	APS	RPS
Langmuir		
$q_0$	10,000	5000
B	0.0000537	0.00009
$R_L$	0.271	0.181
$R^2$	0.6087	0.3159
Freundlich		
$k_f$	2.84	1253
$1/n$	1.3036	0.3691
$R^2$	0.2923	0.0786

From Table 4.38, the co-efficient of regression ( $R^2$ ) for Langmuir isotherm was 0.6087 and 0.3159 for APS and RPS respectively. The separation factor  $R_L$  obtained for this study was 0.271 and 0.181 for APS and RPP respectively, indicating favourable sorption of crude oil on plantain pseudostem because the values are less than unity.

The Freundlich isotherm as shown in Table 4.38 gave  $R^2$  value of 0.2923 and 0.0786 for APS and RPS respectively which are considered very poor. This result indicates that Langmuir model is more suitable for describing the sorption equilibrium of crude oil on acetylated plantain pseudostem due to the moderate value of  $R^2$  which was 0.6087. Thus it is concluded that the adsorption of crude oil on plantain pseudostem occurred uniformly on the active sites of the sorbents(monolayer adsorption).

## CHAPTER FIVE

### SUMMARY, CONCLUSION AND RECOMMENDATIONS

#### 5.1 Summary

Five selected agricultural wastes including corn husk, borassus coir, African breadfruit seed husk, plantain peel and plantain pseudostem which are commercially available and biodegradable were acetylated under mild conditions using NBS catalyst. The acetylated and raw sorbent materials were subsequently used in oil spill mop up.

The mineral analysis for the five samples was done by X-ray fluorescence (XRF) and it showed that all the five samples contain essential minerals like potassium and calcium in high proportion. The presence of the minerals in the samples contributed to the hydrophilic nature of the materials under investigation. FTIR data provided a clear evidence of acetylation. The SEM micrographs further confirmed the successful acetylation morphologically. The extent of acetylation was quantitatively determined by calculating the ratio R between the intensity of the acetyl group C=O stretching band at 1740-1745  $\text{cm}^{-1}$  and the intensity of C-O stretching vibration of the cellulose backbone at about 1030 –1040  $\text{cm}^{-1}$ . The oil sorption capacity of the sorbents were greatly enhanced by acetylation.

The equilibrium, isotherm and kinetics of the raw and acetylated samples were all done at room temperature, different reaction times as well as catalyst concentrations. The kinetics of acetylation were studied by fitting the obtained data in rate curves of first order, second order, pseudo second order, intra particle and liquid

film diffusion models for all the five samples. The kinetics of crude oil sorption unto the samples were equally investigated by fitting the obtained data into the rate curves of pseudo-first order, second order and intra-particle diffusion models. Langmuir and Freundlich adsorption models were applied to describe the experimental isotherm and isotherm constants.

The results presented and discussed in this study indicates that all the acetylated samples are suitable sorbents for oil spill clean-up with the potential for further development and commercialization.

## **5.2 Conclusion**

This work showed that the extent of acetylation of the five sorbent materials has been affected by time and catalyst concentration. The acetylation was successful at room temperature therefore very energy efficient and cost effective.

The mineral analysis was done by X-ray fluorescence (XRF) and it showed that all the five samples contained essential minerals like potassium and calcium in high proportion which contributed to the hydrophilic nature of the materials under investigation. The result of FTIR analysis suggested alterations in the chemical structure and subsequent increase in hydrophobicity of all the acetylated samples.

The micrographs from SEM analysis clearly showed that the surface morphology of the acetylated sorbents were more ruptured along with different levels of wrinkles and grooves which increased the surface area..

The oil sorption capacity of the acetylated samples at various contact times and catalyst concentrations were greatly enhanced when compared with that of the raw samples. The water absorption capacity (WAC) of the acetylated sorbents was

greatly reduced indicating that acetylation made them less hydrophilic and more oleophilic. The water absorption capacity and oil sorption capacity values were tested for statistical difference using ANOVA and the result showed that time and acetylation had significant effects in predicting the water and oil sorption capacities of the five samples investigated.

The kinetics of acetylation of corn husk, borassus coir, African breadfruit seed husk, plantain peel and plantain pseudostem were optimally fitted by the pseudo-second order model. The kinetic studies of crude oil sorption by all the five samples were analyzed by fitting the experimental data into the pseudo-first, pseudo-second kinetic models and intra-particle-diffusion model. The data for acetylated corn husk and borassus coir both fitted into the pseudo-second order kinetic model with high values of  $R^2$ . Crude oil sorption kinetic data were best fitted by intra-particle diffusion and pseudo-first order kinetics model for acetylated breadfruit seed husk, plantain peel and plantain pseudostem with  $R^2$  values close to unity.

Langmuir and Freundlich isotherm models were used to analyze the equilibrium data for the five samples. Equilibrium crude oil sorption data for corn husk, borassus coir and African breadfruit seed husk were best fitted into Freundlich isotherms with a high  $R^2$  values implying multilayer sorption process. Langmuir isotherm model fitted adequately the experimental data of plantain peel and plantain pseudostem with high  $R^2$  values therefore implying that the sorption was mono-layered. The  $R_L$  values which are less than unity for all samples indicates that sorption of crude oil onto the five samples were favourable.

Considering that the five sorbent samples are agricultural waste materials, abundantly and readily available, cheap, biodegradable, economical to modify

through acetylation, they are therefore recommended for non-aqueous sorption processes.

### **5.3 Recommendation**

i) There is need for further research and development on the reuse and recycling of used acetylated sorbent materials as it will be more economically beneficial in oil spill clean-up operations.

ii). Furthermore, research on more efficient methods to enhance the oil sorption capacity of the modified materials should be explored and encouraged.

iii). Since oil spill clean-up is a very important aspect of environmental protection and preservation, it is very imperative that more work be done on scaling up the processes industrially for effective mass production of acetylated sorbent materials for subsequent application.

### **5.4 Contribution to Knowledge**

Chemical modification of biosorbents derived from some agricultural residues ( borassus coir, corn husk, Africa breadfruit seed husk, plantain peel and plantain pseudostem) for enhanced surface hydrophobicity and functionality was achieved via acetylation. All adsorbents showed high removal efficiencies (13.39 – 7.37 %) for crude oil in water as supported by equilibrium and kinetic oil sorption parameters.

The use of borassus coir, corn husk, African breadfruit seed husk, plantain peel and plantain pseudostem for oil spill clean-up was hitherto unknown and was therefore



investigated. This study will increase the existing knowledge and database on the use of locally sourced raw materials as sorbent in oil spill cleanup.

Importantly, the agricultural wastes that are explored will help in ameliorating the problem of waste management and enhance the phenomenon of converting waste to wealth.

The study has x-rayed and confirmed the use of five agro residues (Borassus aethopum coir, corn husk, African breadfruit seed husk, plantain peel and plantain pseudostem) as effective sorbents for oil spill mop up.

This work is also an indispensable reference and an essential reading for everyone concerned with oil spill cleanup in mangroves and wetlands, providing strategies for the conversion of agricultural wastes to effective oil spill sorbents.

Furthermore, understanding the kinetics of crude oil sorption is very vital for practical applications particularly in process designs and scale up procedures. These kinetic data for the five agro-wastes has been established.

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