

THE USE OF MANGO (*MANGIFERA INDICA*) SEEDS AND DATES (*PHOENIX DACTYLIFERA*) SEEDS AS COAGULANTS IN WASTEWATER TREATMENT

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A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER OF SCIENCE IN WATER RESOURCES AND ENVIRONMENTAL ENGINEERING

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ZARIA, NIGERIA

DECEMBER, 2019

DECLARATION

I declare that the work in this dissertation titled "THE USE OF MANGO (*MANGIFERA INDICA*) SEEDS AND DATES (*PHOENIX DACTYLIFERA*) SEEDS AS COAGULANTS IN WASTEWATER TREATMENT" has been carried out by me in the department of Water Resources and Environmental Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Edward Agwam KUHIYOP	•••••	•••••
P15EGWR8027	SIGNATURE	DATE

CERTIFICATION

This dissertation titled "THE USE OF MANGO (*MANGIFERA INDICA*) SEEDS AND DATES (*PHOENIX DACTYLIFERA*) SEEDS AS COAGULANTS IN WASTEWATER TREATMENT" by KUHIYOP Edward Agwam meets the regulations governing the award of Master of Science degree in Water Resources and Environmental Engineering, of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research is dedicated to all the millions of people in the world and especially in this country who lack access to clean water and to governments around the globe who are trying hard to ensure the teeming populace are provided with clean water.

ACKNOWLEDGEMENT

I am most grateful to the Almighty God who has enabled me by His mercies to have life and to have the privilege to undertake this course of study. For this and many more, I will remain forever grateful.

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ABSTRACT

The use of chemicals in water treatment comes with some challenges including cost and environmental concerns. This has necessitated the need for alternative means of treatment that is relatively cheap and environmentally friendly. This research was aimed at studying the possibility of combining Mangifera indica and Phoenix dactylifera seeds powder as coagulants in wastewater treatment. The seeds were characterized for their composition, active compounds and proximate constituents using Atomic Adsorption Spectroscopy (AAS), Scanning Electron Microscopy (SEM) analysis, and X-ray Diffraction (XRD) analysis. Jar test was carried out using the seeds extracts separately and in combination at varying dosages and the Electrical Conductivity EC, Total Dissolved Solids TDS, Chemical Oxygen Demand COD, Biochemical Oxygen Demand BOD, Turbidity, temperature, pH, and total coliform were measured with every varying dosage. Isothermal studies using Langmuir and Freundlich isotherm models were carried out, and kinetic behavior for the removal of BOD using the seed powders over certain concentration ranges was studied using the Pseudo-first and second order kinetic models. The sludge from the Jar test experiment was analyzed for its total nitrogen, organic carbon, organic matter, total volatile solids, and carbon nitrogen ratio. The Mangifera indica removed 89 % turbidity, 96 % BOD, 84 % COD and 99 % total coliform of the wastewater, while Phoenix dactylifera removed 75 % turbidity, 85 % BOD, 78 % COD and 88 % total coliform of the wastewater. Their combination removed 96 % turbidity, 96 % BOD, 87 % COD and 98 % total coliform of the wastewater. The experiment was observed to fit the Freundlich isotherm model based on the Freundlich constants and the coefficient of determination, R^2 . The experiment was observed to have followed the pseudo-second order kinetic model as indicated by the K_2 , R^2 , and Error analyses carried out on the experimental data. The study has shown that Mangifera indica

seed and *Phoenix dactylifera* seed powders can be used as viable coagulants for water and wastewater treatment using adsorption and charge neutralization.

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Abbreviations, Definitions, Glossary and Symbols

Abbreviations	Description	Units	
TDS	Total Dissolved Solids		
AAS	Atomic adsorption Spectro-photometer		
COMB	Combination of mango and Dates seeds		
EDX	Energy Dispersive X-ray		
MI	Mangifera indica (Mango)		
PD	Phoenix dactylifera (Dates)		
SEM	Scanning Electron Microscope		
BOD	Biochemical Oxygen Demand	mg/L	
COD	Chemical Oxygen Demand	mg/L	
n	Hecterogenic factor	dimensionless	
Ce	Equilibrium concentration	g/L	
Qm	Maximum uptake of adsorbate	g/g	
KL	Langmuir constant	L/g	
R _L	Separation factor	dimensionless	
Co	Initial concentration of adsorbate in the mixture	g/L	
K _F	Freundlich constant	L/g	
qe	Equilibrium amount of adsorbate exchanged by adsorbent	mg/g	
qt	Amount of adsorbate adsorbed at any time t	mg/g	
K ₁	1 St order rate constant	min ⁻¹	
K ₂	2 nd order rate constant	min ⁻¹	

CHAPTER ONE

INTRODUCTION

1.1 General Background of the Study

Two third of the Earth's surface is covered by water and yet water demand constantly exceeds supply in most parts of the world, and many more areas are expected to experience this imbalance in the near future. This is partly due to the fact that only 2.5% of the global water is fresh water, and over two thirds of this fresh water is frozen in glaciers and polar ice caps. Closely following this, is the ever-increasing world population which depletes many major aquifers alongside the impact of climate change on these aquifers (IAEA, 2011; Turral *et al.*, 2011)

The world population is growing at an alarming rate with water resources increasingly becoming scarce. The need for water conservation and management has never been more urgent. This is because our very existence as humans depends on the continued availability of this resource in good quantity and quality (UN Water, 2015). At the heart of this, is the ability to utilize water and wastewater effectively. To achieve this goal, wastewater must be treated in an economic manner (Raman and Krishnamoorthy, 2014). In places where fresh water is in abundance, people have to put on with the problem of heavy pollution. This makes it very expensive to treat water to meet the minimum standard required for domestic uses such as drinking and cooking and industrial uses.

Polluted water when not treated can be harmful to humans, animals and the environment. According to WHO (2019), 829,000 people die from water related diseases every year. Similarly, 785 million people lack access to safe drinking water and 297,000

children under the age of five die annually, mostly in low-income countries (WHO, 2019).

Treatment of water involves any process that makes water more acceptable for a specific enduse. The end use can include domestic, industrial, irrigation, river flow maintenance, water recreation or many other uses, including being safely returned to the environment. Wastewater treatment process includes physical, chemical, and biological processes aimed at removing contaminants in order to get the water to an acceptable standard for specific use. Conventional methods used in treating water include coagulation, sedimentation, filtration and disinfection (Tchobanoglous and Burton, 1991).

Dissolved and suspended particles form a major part of the impurities in most natural waters. These suspended materials mostly arise from erosion of the top soil, the dissolution of minerals, the decay of vegetation and from several domestic and industrial waste discharges. Large solids can be removed by allowing them to settle (sedimentation) and then filtered (Filtration). Suspended particles and dissolved solids settle too slowly and may also pass through filters. Coagulation and flocculation processes are used to separate the dissolved and suspended particles from the water.

In coagulation, a chemical, such as alum, is added which produces positive charges to neutralize the negative charges on the particles (Pizzi, 2010; Auer, 2003), and then the particles can stick together, forming larger particles which easily sediment and thenn removed. Examples of chemicals used in coagulation include Aluminum sulphate, ferric chloride, ferric sulphate and polyaluminum chloride (Braul and Leader, 2001), however, the use of chemicals in this process does not come without its challenges. All coagulants produce sludge which contain the metal hydroxide together with the colored and colloidal matter that has been removed from the raw water (Gebbie, 2006). Inorganic coagulants

decrease the alkalinity of water as well as increase the concentration of the total dissolved solids concentration of the treated water. The organic coagulants do not decrease the alkalinity and tend to produce low concentrations of total dissolved solids but are very expensive (Gebbie, 2006). At high concentrations there are evidences linking aluminum sulphate to effects on the nervous system, with possible connections to several diseases, such as Parkinson's, Alzheimer's, and Lou Gehrig's disease (Peterson, 2017).

The demand for water treatment chemicals has increased substantially in emerging economies such as Brazil, China, and India (TechSci, 2017). The conventional methods of assuring potable water in developing economies are unsustainable at the moment and may remain so for a long time. This necessitates the need to consider the application of sustainable technologies using locally available materials in water treatment. A prospective area is the Plant kingdom and the use of seeds in particular. Some seeds have the potentials of serving as alternative sources of coagulants owing to their advantages over the conventional organic and inorganic coagulants such as polyamines and aluminum sulphate.

This is more so considering the following advantages of using plant based coagulants;

They are biodegradable and effective either as coagulants or flocculants, they are non-Toxic, they potent no-physical hazard, they are metal-free, their use reduces the operating cost of water treatment facility, they are environmentally friendly, and produce low sludge from treatment.

Bio-coagulants which have been used as effective coagulants include dried *Moringa Oleifera* seed powder, Chitosan Powder, *Nephelium lappaceum*, *Jatropha curcas, Plantago ovato*, Guar gum and others, (Nandini and Sheba, 2016; Yongabi, 2010). Some are currently being researched including *Mangifera indica* (Mango) and *Phoenix dactylifera* (Dates) seeds.

Mangoes are juicy stone fruit (drupe) from numerous species of tropical trees belonging to the flowering plant genus *Mangifera*, cultivated mostly for their edible fruit. The majority of these species are found in nature as wild mangoes. The genus belongs to the cashew family Anacardiaceae. Mangoes are native to South Asia, from where the "common mango" or "Indian mango", *Mangifera indica*, has been distributed worldwide to become one of the most widely cultivated fruits in the tropics (Arakelyan *et al*, 2019). Other *Mangifera* species (e.g. horse mango, *Mangifera foetida*) are also grown on a more localized basis.

The date palm (*Phoenix dactylifera*) is a member of the palm family, Arecaceae (sometimes known by the alternative name Palmae). Arecaceae is a family of monocotyledon flowering plants. There are over 200 genera in the palm family with around 2,600 species, most of which are native to tropical or subtropical climates (Preedy *et. al.* 2011) It is characterized by pinnate, "feather-like" gray-green leaves and an edible fruit in the form of a drupe with a thin, papery skin, and a single, long, narrow, hard seed. The nutritious and flavorful date is a traditional staple food of the Middle East and also the source of syrup, alcohol, and vinegar. Other date palm components—seeds, wood, and leaves—are used for a wide diversity of applications. This work will attempt the use of *Mangifera indica* and *Phoenix dactylifera* seeds as coagulants in wastewater treatment.

1.2 Statement of Research Problem

The use of chemicals in the coagulation process of water treatment comes with several challenges including cost of chemicals, increase in volume of sludge, depression of the pH of the effluent and potential health implications such as Parkinson and Alzheimer. This often

makes it very expensive to treat water to meet the minimum standard required for domestic uses for the teeming populace, especially those in rural areas. Therefore, there is the urgent need for an alternative means of treatment which is simple, relatively cheap, less hazardous to health and environmentally friendly.

1.3 Justification of Research

Bio coagulants have been known to have some advantages over the conventional chemicals such as non-toxicity, bio degradability, low sludge formation, and overall cost reduction in water treatment facilities. Added to this is the factor of the extracted plant being indigenous to the locals and the relatively simple technology involved in the coagulant extraction. For these reasons, combining *Mangifera indica* and *Phoenix dactylifera* seeds may be possible substitutes for the conventional organic and inorganic coagulants in water treatment.

1.4 Aim and Objectives

The aim of this research is to investigate the efficiency of combining *Mangifera indica* (Mango) and *Phoenix dactylifera* (Dates) seeds extract as coagulants in wastewater treatment. The specific objectives are to:

- characterized the seed powders of *Mangifera indica* and *Phoenix dactylifera*, and the wastewater. The mineral composition, proximate analyses, and active compounds will be determined.
- perform treatability studies to determine the effect of graduated combined dosage of *Mangifera indica* and *Phoenix dactylifera* seed powder on the physicochemical and bacteriological water quality parameters
- perform isothermal and kinetic studies of the combined dosage of Mangifera indica and

Phoenix dactylifera seed powder.

• develop a mathematical model of the combination of *Mangifera indica* and *Phoenix dactylifera* seed powder introduction in the removal of wastewater quality parameters.

1.5 Scope of the Study

This research is limited in scope to the combined use of *Mangifera indica* and *Phoenix dactylifera* seeds extract- sourced locally- as coagulants in wastewater treatment. Wastewater will be sampled from the influent of the Wastewater stabilization pond of the Ahmadu Bello University, Zaria and a conventional Jar test will be carried out to coagulate the turbid water sample. Laboratory analyses, including BOD, COD, and Total Coliform, to determine the physicochemical and bacteriological water quality parameters of the raw and untreated water sample will be carried out.

CHAPTER TWO

LITERATURE REVIEW

2.1 Wastewater

Wastewater may be defined as a combination of the liquid- or water-carried wastes removed from residences, institutions, and industrial establishments, together with such groundwater, surface water, and storm-water as may be present (Tchobanoglous and Burton, 1991). It is also known as "sewage" and originates from household wastes, human and animal wastes, industrial wastewater, storm runoff, and ground water infiltration and can be said to be the flow of used water from a community. It is 99.94% water and the remaining 0.06% is material dissolved or suspended in the water (Lin, 2007). Wastewater can be classified based on their sources, into the following

2.1.1 Domestic wastewater (Sewage)- these are waters produced by the mere act of living such as laundry, washing, bathing. It also includes all wastewater generated by public restrooms, hotels, restaurants, motels, resorts, schools, places of worship, sports stadiums, hospitals and other health centers. They all produce high volumes of wastewater.

2.1.2 Non-sewage- these include water from floods (storm water), runoff (rain water running through cracks in the ground and into gutters), water from swimming pools, water from car garages and cleaning centers. They also include used water from Laundromats, beauty salons, commercial kitchens, energy generation plants and so on. Wastewater is also generated from agricultural facilities such as water used for cleaning animal farms, washing harvested produce and cleaning farm equipment.

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2.1.3 Industrial wastewater- there are many types of industrial wastewater based on different industries and contaminants; each sector produces its own particular combination of pollutants. Like the various characteristics of industrial wastewater, the treatment of industrial wastewater must be designed specifically for the particular type of effluent produced (Shi, 2009). Some of the harmful chemicals from industries are arsenic, cadmium, chromium, lead, mercury, nitrogen, iron, zinc, and metallic sulphates, chlorides, nitrites, fluorides, phosphates, and sulphides (Rao, 2004)

Wastewater, according to Singh et al. (2018), is broadly classified into three main types:

- 1 Blackwater- This is wastewater that originates from toilet fixtures, dishwashers and food preparation sinks. It is made up of all the things that you can imagine going down the toilets, bath and sink drains. They include poop, urine, toilet paper and wipes; body cleaning liquids. They are known to be highly contaminated with dissolved chemicals, particulate matter and are very pathogenic.
- 2 Graywater- This is wastewater that originates from non-toilet and food fixtures such as bathroom sinks, laundry machines, spas, bathtubs and so on. Technically it is sewage that does not contain poop or urine. Graywater is treated very differently from Blackwater and is usually suitable for re-use.
- 3 Yellowwater- This is basically urine collected with specific channels and not contaminated with either blackwater or graywater.

2.2 Water Quality Parameters

Waterquality refers to the physical, chemical, biological, and radiological characteristics of water. It is a measure of the condition of water relative to the requirements

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of one or more biotic species and or to any human need or purpose. It refers to a set of parameters used as a yardstick to assess the suitability or otherwise of water to be used for certain defined purposes. These parameters need constant monitoring because water quality issues influence human and environmental health, so the more water is monitored the better the ability to recognize and prevent contamination problems.

2.9.1 Physical water quality parameters

•

- Temperature- The temperature of water is an important quality to be monitored as it gives an indication of the general health of the water. It affects the dissolved oxygen in water and degradation rate of the biodegradable pollutants in the water. Temperature is also important because of its influence on water chemistry. The rate of chemical reactions generally increases at higher temperature, which in turn affects biological activity. Thermal pollution (a temporal increase in temperature) can occur as a result of discharge of municipal or industrial effluents, also in urban areas, runoff that flows over hot asphalt and concrete pavement before entering a lake will be artificially heated and could cause lake warming albeit very minimal. Higher temperatures also decrease the maximum amount of oxygen that can be dissolved in water, leading to oxygen stress if the water is receiving high loads of organic matter (Michaud, 1991).
- Turbidity- This is a measure of the relative clarity in water. It is an optical characteristic of water and is an expression of the amount of light that is scattered by material in the water when light is shined through the water sample (Michaud, 1991). The greater the amount of total suspended solids (TSS) in the water, the murkier it appears and the higher the measured turbidity. Very high turbidity, or cloudiness, in

- drinking water is aesthetically unappealing, and may also be indicative of pollution that may be of health concern. Turbidity can provide food and shelter for pathogens. If not removed, turbidity can promote regrowth of pathogens in the distribution system, leading to waterborne disease outbreaks (Jadhav and Mahajan, 2011). It also adds to the costs of the treatment of surface water supplies used for drinking since the turbidity must be virtually eliminated for effective disinfection to occur.
 - Odor and Taste- The major organic cause of taste and odor problems in water are algae and bacteria. However, other anthropogenic sources such as wastewater discharges and chemical spills also act as sources of chemicals that cause tastes and odors. An unwanted odor coming from a water body is often the sign of bigger issues plaguing the water. Often this smell does not signify the presence of a harmful contaminant, but it could indicate that the water is not the cleanest and should be inspected to be restored to its purest state (Vanwyngarden, 2016).
 - Suspended solids- Solids can be scattered in water in both suspended and dissolved forms. These solids may be inorganic or organic particles or of immiscible liquids. Inorganic solids such as clay, silt, and other soil constituents are common in surface water (Howard *et al.*, 1987). Organic material such as plant fibers and biological solids (algal cells, bacteria, etc.) are also common constituents of surface water. These materials are often natural contaminants resulting from the erosive action of water flowing over surfaces. Other suspended material may result from human use of the water (Spellman and Drinan, 2002). Suspended particles are unwanted in water because they make the water aesthetically displeasing and may provide adsorption sites for chemical and biological agents which may include disease causing organisms and toxic strains of algae.

Color- One of the characteristics of pure water is that it is colorless. Color in water is usually caused by foreign substances. If the color is due to suspended solids it is said to be apparent color but if it is due to dissolved solids that remain after the removal of suspended solids, it is termed true color. Colored water is aesthetically unacceptable to the public. While true color is not usually considered unsanitary or unsafe, the organic compounds causing true color may exert a chlorine demand and thereby seriously reduce the effectiveness of chlorine as a disinfectant (Howard *et al.*, 1987).

2.9.2 .2 Chemical water quality parameters

- pH- The pH of a sample of water is a measure of the concentration of hydrogen ions in the water. A pH of 7 is considered to be neutral. Substances with pH of less than 7 are acidic; substances with pH greater than 7 are basic. The pH of water determines the solubility and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (lead, copper, cadmium). When pollution results in higher algal and plant growth (e.g., from increased temperature or excess nutrients), pH levels may increase, as allowed by the buffering capacity of a water body (Michaud, 1991).
- Dissolved Oxygen- Dissolved oxygen analysis measures the amount of gaseous oxygen (O₂) dissolved in an aqueous solution. It is one of the most important water quality parameters as oxygen is an important element to all forms of life. Sufficient dissolved oxygen is necessary for good water quality. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a waste product of photosynthesis.

- Electrical conductivity- Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water which come from dissolved salts and inorganic materials in the water. Due to the fact that dissolved salts and other inorganic chemicals conduct electrical current, conductivity increases as salinity increases. Aquatic animals and plants are adapted for a certain range of salinity. Outside of this range, they will be negatively affected and may die (Environmental Monitor, 2010).
- Alkalinity- Alkalinity is a measure of the water's ability to neutralize acidity. Total alkalinity is a measurement of all alkaline substances dissolved in the water. These substances are primarily hydroxides, carbonates and bicarbonates, along with a few others. These compounds result from the dissolution of mineral substances in the soil and atmosphere. They can also originate from carbon dioxide, a constituent of the atmosphere and a byproduct of microbial decomposition of organic matter. These alkaline substances buffer pH in the water. In other words, total alkalinity is a measurement of the water's ability to resist change in pH (Fondriest Environmental inch, 2016). Total alkalinity is measured in parts-permillion (ppm)
- Hardness- Water hardness is the amount of dissolved calcium and magnesium in the water. Hard water is high in dissolved minerals, both calcium and magnesium. Hardness is caused by compounds of calcium and magnesium, and by a variety of other metals. Hardness is classified as carbonate hardness and noncarbonate hardness, depending upon the anion with which it associates. The hardness that is equivalent to the alkalinity is termed carbonate hardness, with the remaining hardness being called noncarbonate harness (Howard *et al.*, 1987).

- BOD- Biological Oxygen Demand is one of the most common measures of organic pollutants in water. It is a measure of the quantity of oxygen used by microorganisms (e.g., aerobic bacteria) in the oxidation of organic matter. The BOD value is most commonly expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20 °C. BOD indicates the amount of putrescible organic matter present in water. Therefore, a low BOD is an indicator of good quality water, while a high BOD indicates polluted water (Carayannis, 2012). It can be used as an indication of the effectiveness of the performance of a wastewater treatment plant. When abnormally high levels of aerobic bacterial activity take place, the level of dissolved oxygen can drop dramatically. Generally, this occurs when there is some sort of abnormal pollution introduced into the system. This can occur in the form of organic pollution from sources such as domestic sewage, septic tank leakage, and fertilizer runoff, or could be in the form of inorganics from domestic or industrial sources (APEC Water, 2017). Natural sources of organic compounds can also come into aquatic systems through floods, landslides, and erosion.
- COD- Chemical Oxygen demand is a measure of water and wastewater quality. The COD is the amount of oxygen consumed to chemically oxidize organic contaminants to inorganic end products. The COD test is often used to monitor water treatment plant efficiency. This test is based on the fact that a strong oxidizing agent, under acidic conditions, can fully oxidize almost any organic compound to carbon dioxide (Jena, 2017).

2.9.3 **Biological water quality parameters**

Pathogens and Pathogen Indicators- For human consumption and use angle, the most important biological organisms in water are pathogens, those organisms capable of infecting and transmitting diseases to humans. Water-borne pathogen contamination in water resources and related diseases are a major water quality concern throughout the world (Pandey *et al.*, 2014). Test for all the known pathogens would be laborious and expensive. The purity of water can be checked using an indicator organism. An indicator organism is one whose presence presumes that contamination has occurred and suggests the nature and extent of the contaminant. Certain bacteria can be used as indicator organisms in particular situations. The presence of bacteria commonly found in human feces, termed coliform bacteria (e.g. E. coli), and in surface water is a common indicator of fecal contamination. Indicator organisms need not be pathogenic.

2.9.4 .4 Heavy metals in water

All metals are soluble to some extent in water. While excessive amounts of any metal may present health hazards, only those metals that are harmful in relatively small amounts are commonly labeled toxic (Howard *et al.*, 1987).

Toxic metals are harmful to humans and other organisms in small quantities. Toxic metals that may be dissolved in water include arsenic, barium, cadmium, chromium, lead, and mercury. Cumulative toxins such as arsenic, cadmium, lead, and mercury are particularly hazardous. These metals are concentrated by the food chain, thereby posing the greatest danger to organisms near the top of the chain (Howard *et al.*, 1987). Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply through industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater (Lenntech, 2017).

Table 2.1 gives some standards for water to be used for drinking purposes, extracted from the Nigerian Standard for Drinking Water Quality, 2007. This identifies contaminants to regulate in drinking water to protect public health. This standard sets parameters and maximum allowable limits in drinking water in Nigeria. The Nigerian Standard for Drinking Water Quality contains mandatory limits concerning constituents and contaminants of water that are known to be hazardous to health and/or give rise to complaints from consumers.

Parameters	Units	Max Limit	Reference
pH		6.5 - 8.5	
TDS	mg/L	500	
Color			
Odor and Taste			
Alkalinity			
Temperature	⁰ Celsius	ambient	
Turbidity	NTU	5	
Conductivity	µS/cm	1000	
Total Coliform	CFU/100ml	10	
BOD	mg/L	5	WHO 2016
COD	mg/L	5	WHO 2016
Zinc	mg/L	3	
Sodium	mg/L	200	
Magnesium	mg/L	0.2	
Manganese	mg/L	0.2	
Lead	mg/L	0.01	
Hardness (as CaCO ₃)	mg/l	150	

 Table 2.1 Nigerian Standard for Drinking Water Quality

Source: Extracted from the Nigerian Industrial Standard NIS 554: 2007

The National Environment (Standards for Discharge of Effluent into Water or on Land) Regulations, 1999, stipulates the following as maximum permissible limits; BOD, 50 mg/L; COD, 100 mg/L; Lead, 0.1 mg/L; Calcium, 100 mg/L Magnesium, 100 mg/L, Manganese, 1.0 mg/L; Iron, 10 mg/L; Zinc, 5 mg/L; Turbidity, 300 NTU.

3.3 Wastewater Treatment Processes

Wastewater treatment involves the process of removing contaminants from sewage. It includes physical, chemical, and biological processes to remove these contaminants and produce environmentally safer treated wastewater. The main aim of wastewater treatment is to remove as much of the contaminants as possible before the remaining water, called effluent, is discharged back to the environment. Wastewater collected from domestic and other sources must ultimately be returned to receiving water or land. Hence there is the need to always determine which contaminants is to be removed and to what extent should they be removed on a case by case basis. Wastewater treatment generally involves three stages, called primary, secondary and tertiary treatment. Methods used for treating municipal wastewaters are often referred to as either unit operations or unit processes. Generally, unit operations involve contaminant removal by physical forces, while unit processes involve biological and/or chemical reactions (Howard *et al.*, 1987)

3.3.1 Pre-treatment

Pre-treatment removes all materials that can be easily collected from the raw sewage before they damage or clog the pumps and sewage lines of primary treatment clarifiers. Objects commonly removed during pretreatment include trash, tree limbs, leaves, branches, and other large objects. The influent in sewage water passes through a bar screen to remove all large objects like cans, rags, sticks and plastic packets, carried in the sewage stream. Pre- treatment may include a sand or grit channel or chamber, where the velocity of the incoming sewage is adjusted to allow the settlement of sand, grit, stones, and broken glass (Rainiero, 2012).

3.3.2 **Primary treatment**

When wastewater arrives at the treatment facility, it goes through the primary treatment process. Primary treatment consists of temporarily holding the sewage in a quiescent basin where heavy solids can settle to the bottom while oil, grease and lighter solids float to the surface. The settled and floating materials are removed and the remaining liquid may be discharged or subjected to secondary treatment. The treatment unit used to settle raw wastewater is referred to as primary sedimentation tank (basin). Sedimentation is the oldest and most widely used process in the effective treatment of wastewater (Lin, 2007). The effluent from primary treatment will ordinarily contain considerable organic matter and relatively high BOD (Tchobanoglous and Burton, 1991); hence primary treatment is rarely used solely as the only method but serves as a precursor to secondary treatment.

3.3.3 3 Secondary treatment

Secondary treatment is directed principally toward the removal of biodegradable organics and suspended solids. Conventional secondary treatment is defined as the combination of processes customarily used for the removal of these
constituents and includes biological treatment by activated sludge, fixed-film reactors, or lagoon systems and sedimentation (Tchobanoglous and Burton, 1991). Secondary treatment is typically performed by indigenous, water-borne micro-organisms in a managed habitat and may require a separation process to remove the micro-organisms from the treated water prior to discharge or tertiary treatment. Secondary sludge is usually combined with primary sludge for further treatment by anaerobic biological processes.

3.3.4 **Tertiary treatment**

Tertiary treatment is the final cleaning process that improves wastewater quality before it is reused, recycled or discharged to the environment. It is sometimes defined as anything more than primary and secondary treatment (Lin, 2007) in order to allow ejection into a highly sensitive or fragile ecosystem. The treatment removes remaining inorganic compounds, and substances, such as nitrogen and phosphorus. Wastewater effluent becomes even cleaner in this treatment process through the use of stronger and more advanced treatment systems. It includes sedimentation, coagulations, membrane processes, filtration, ion exchange, activated carbon adsorption, electrodialysis, nitrification and denitrification, etc. Tertiary treatment is costly as compared to primary and secondary treatment methods.

3.3.5 Sludge treatment/disposal

Treatment and disposal of sewage sludge are major factors in the design and operation of all wastewater treatment plants. Two basic goals of treating sludge before final disposal are to reduce its volume and to stabilize the organic materials. Treatment of sewage sludge may include a combination of thickening, digestion, and dewatering processes. The final disposal of sewage sludge may be by landfilling, agricultural fields as soil conditioner/fertilizer or other recycling outlets (EEA, 1997).

4.4 Coagulation and Flocculation

Coagulation-flocculation processes are typically applied prior to sedimentation and filtration (Fu and Wang, 2011), to enhance the ability of a treatment process to remove particles. The process involves the addition of a chemical (e.g. alum) and then a rapid mixing to dissolve the chemical and distribute it evenly throughout the water neutralizing the negatively charged colloids forming bridges between particles and causing them to bond together forming larger particles and thus settling by gravity thereby enhancing filtration (Noyes, 1994). According to Mackenzie (2010), coagulation and flocculation are essential components of conventional water treatment process designed to

- Remove infectious agents
- Remove toxic compounds that have adsorbed to the surface of particles
- Remove precursors to the formation of disinfection by-products and
- Make the water palatable

In water treatment, coagulation and flocculation are practically always applied subsequently before a physical separation (Mazille and Spuhler, 2018). The Coagulation- Flocculation process consists of the following steps:

- 1 The use of chemical reagents to destabilize and increase the size of the particles; mixing; increasing of floc size,
- 2 A physical separation of the solids from the liquid phase. This separation is usually

achieved by sedimentation (decantation), flotation or filtration.

Surface water systems contain organic and inorganic particles such as algae, bacteria, cysts and erosion produced clay, silt and mineral oxides. Groundwater treated to remove hardness, or iron or manganese, by precipitation contains finely divided particles. The object of coagulation (and subsequently flocculation) is to turn the small particles into larger particles called flocs (Mackenzie, 2010)

• Coagulation theory

Inorganic coagulants used for treatment of potable water should have the following characteristics

- They should be non-toxic at the working dosage
- They must have high charge density
- They should be insoluble in the neutral pH

There are four mechanisms employed to destabilize natural water suspensions

- 1 Compression of the electric double layer- If the double layer is compressed, the repulsive force is reduced and particles will come together as a result of Brownian motion and remain attached due to van der Waals forces of attraction. Both the ionic strength and the charge of counter-ions are important in the compression of the double layer (Mackenzie, 2010).
- 2 Adsorption and charge neutralization- Some chemical species are capable of being adsorbed at the surface of colloidal particles. If the adsorbed species carry a charge opposite to that of the colloids, such adsorption causes a reduction of surface potential and a resulting destabilization of the colloidal particle. Reduction of surface

charge by adsorption is a much different mechanism than reduction by double layer compression (Mackenzie, 2010)

- 3 Adsorption and inter-particle bridging- Many different natural compounds such as starch, cellulose, polysaccharide gums, and proteineous materials, as well as a wide variety of synthetic polymeric compounds are known to be effective coagulating agents. Polymer chains such as poly-DADMAC and epi-DMA adsorb on particle surfaces at one or more sites along the polymer chain. Other sites on the polymer chain extend into solution and adsorb on surfaces of other particles, thus creating a "bridge" between the particles. This bridge results in a larger particle that settles more quickly and forms a denser sludge (Mackenzie, 2010)
- 4 Enmeshment in a precipitate- If certain metal salts are added to water or wastewater in sufficient amounts, rapid formation of precipitates will occur. Colloids may serve as condensation nuclei for these precipitates or may become enmeshed as the precipitates settle. Removal of colloids in this manner is frequently referred to as sweep-floc coagulation (Mackenzie, 2010)

Inorganic coagulants are cost effective and applicable for a broad variety of water and wastewater. They are also effective in raw water with low turbidity. The inorganic coagulants mostly used fall into two broad categories

- 1 Those based on aluminum- Examples include
 - 1.1 Aluminum Sulphate Al₂(SO₄)₃

1.2 Aluminum Chloride – AlCl₃

1.3 Sodium aluminum – NaAl(OH)4

2 Those based on Iron- Examples include

2.1 Ferric Sulphate - Fe₂(SO₄)₃

- 2.2 Ferrous Sulphate FeSO₄XH₂O
- 2.3 Ferric Chloride FeCl₃
- 2.4 Ferric Chloride sulphate FeClSO₄

Organic coagulants are generally used for solids and liquids and may be

- I. Polyamines- Works by charge neutralization and are effective at treating higher turbidity raw water and wastewater
- II. Melamine Formaldehydes and Tannins- absorb organic materials such as oil and grease and are suited for operations that generate hazardous materials.

Two important factors in coagulation are pH and dose. The optimum dose and pH must be determined from laboratory test for coagulants to be effective.

Flocculation theory

According to Howe *et al.* (2012), flocculation theories have evolved due to the following observations:

- Small particles undergo random Brownian motion due to collision with fluid molecules which then results in particle to particle collisions.
- Stirring water containing particles creates velocity gradients that bring about particles collisions

This is the basis for the mechanisms of flocculation as described below

- I. Microscale Flocculation- This aggregation is also called perikinetic flocculation. It involves flocculation of small particles (less than 0.1µm) caused by diffusion. The rate of flocculation is relative to the rate of diffusion of the particles. Thus, the primary mechanism of agglomeration is through Brownian motion (Mackenzie, 2010)
- II. Macroscale Flocculation- Mixing is the major flocculation mechanism for particles greater than 1 μ m in diameter. This mechanism is known as macroscale flocculation or orthokinetic flocculation. Mechanical mixing is employed to achieve orthokinetic flocculation.
- III. Differential Settling- Another form of flocculation occurs due to differential settling in which large particles settling in a quiescent basin overtake small particles to form larger particles (Howe *et al.*, 2012). Because the floc particles are of different size, they settle at different rates. Differences in the settling velocities cause the particles to collide and flocculate.

Mixing theory

The crux of efficient coagulation (and subsequently, flocculation), is the efficiency of mixing the coagulants with the raw water. Efficient flocculation requires mixing to bring the particles into contact with one another. Following coagulation, flocculation, a gentle mixing stage, increases the particle size from submicroscopic microfloc to visible suspended particles. Important aspects of mixing are as follows:

• Velocity gradient- Different velocity gradients are appropriate for different processes. Mackenzie (2010) asserted that coagulation requires very high velocity gradient

- while flocculation requires a velocity gradient high enough to cause particle contact and keep the flocs from settling but low enough to prevent the flocs from tearing apart.
 - Mixing time- Coagulation reactions are very fast (Lin, 2007). Thus, nearly instantaneous and rapid mixing of coagulants is of critical importance. This is especially true when the metal salts are used to adsorb and destabilize the particles. The time requirements for flocculation are more dependent on the requirements of downstream processes (Mackenzie, 2010)

The jar test is used to identify the most adapted mix of chemical compounds and concentrations for coagulation-flocculation. It is a batch test consisting of using several identical jars containing the same volume and concentration of feed, which are charged simultaneously with six different doses of a potentially effective coagulant.

2.5 Use of Plants as Coagulants

Since the evolution of mankind, plants have been used for water treatment. In their review on the use of indigenous plants in water treatment, Megersa *et al.* (2014), reported that Africa has as much as 300, 000 medicinal plants and that historical accounts of traditionally used medicinal plants depict that different medicinal plants were in use as early as 5000 to 4000 BC in China, and 1600 BC by Syrians, Babylonians, Hebrews and Egyptians. They further stated that beyond their human health and livestock treatments, plants have been used historically for water treatment. There is evidence to suggest that communities in the developing world have used plant based materials as one strategy for purifying drinking water.

2.5.2 Plant species used as coagulants and disinfectants

Natural plant extracts have been used for water purification for many centuries and Egyptian inscriptions afforded the earliest recorded knowledge of plant materials used for water treatment, dating back perhaps to 2000BC, in addition to boiling and filtration (Edogbanyan *et al.*, 2013; Megersa *et al.*, 2014). This has been largely due to the high cost of the conventional treatment techniques involving the use of chemicals.

Megersa *et al.* (2014) reported that forty plant species, belonging to 38 genera and 22 families, are reported to be used as coagulant and disinfectant. The following are some of the many plant species that have been used in water and wastewater treatment; *Moringa oleifera Lam* (drumstick tree), *Phaseolus vulgaris L.* (green bean); *Opuntia ficus indica* (cactus pear); *Dolichos Lablab L.* (hyacinth bean); *Castanea sativa Mill* (sweet chestnut); *Jatropha curcas L.* (physic nut); *Citrus aurantifolia* (sour lime); *Adansonia digitata* (baobab), etc.

2.5.3 Effect of natural coagulants on turbidity

Jar Test has been used to study the efficiency of plants in the removal of turbidity. Various studies have been carried out to determine the efficiencies of different plants in the removal of turbidity. Nandini and Sheba (2016) reported the following plants with their turbidity removal efficiencies: *Nephelium lappaceum* (rambutan) seed, 99 %; *Cassia alata* (ringworm shrub) leaves, 93.33 %; *Coccinia indica* (Ivy gourd) fruit, 94 %; *Parkinsonia aculeate* (Jerusalem

thorn) seeds, 99.7 %; *Opuntia spp* (cactus pear) plant, 98 %; *Phaseolus vulgaris L.* (green bean) seeds, 87.4 %. Hendrawati *et al.* (2016) carried out a research to observe the effect of *Moringa oleifera* seed as natural coagulant to replace synthetic coagulant and found out that *Moringa oleifera* reduced 98.6 % turbidity of wastewater, 10.8 % of its conductivity, 11.7 % of its BOD and reduced its metal contents (Cd, Cr, Mn). When applied to ground water, *Moringa oleifera* was observed to have removed the turbidity of ground water as much as 97.5 %, while reducing the conductivity and BOD of ground water 53.4 % and 18%, respectively. The use of *Moringa oleifera* also reduced the total number of coliforms.

Patale and Pandya (2012), studied the use of mucilage isolated from *coccinia indica* (Ivy gourd) as flocullent for the treatment of turbid water containing synthetic turbidity of kaolin and observed that *coccinia indica* mucilage had higher efficiency in removing high turbidity in comparison with low turbidity. Highest turbidity removal of 94 % was obtained with a high (1000NTU) initial turbidity.

Abidin *et al.* (2011) investigated the capability of *Jatropha curcas* seed and presscake (the residue left after oil extraction) to reduce the turbidity of wastewater through coagulation and came out with the findings that the *Jatropha* seed was found to be an effective coagulant with more than 96 % of turbidity removal at pH 1-3 and pH 11-12. The turbidity removal was high (>98 %) at all turbidities (100 NTU to 8000 NTU), suggesting its suitability for a wide range of industrial wastewater.

D'Aquino and Teves (1994), carried out an experiment on the natural biocidal activity of lemon juice in order to explore its possible use as a disinfectant and inhibitor of Vibrio cholera in drinking water for areas lacking water treatment plants and the results show that lemon juice can actively prevent survival of Vibrio cholera but that such activity is reduced in markedly alkaline water.

Birima *et al.*, (2013) investigated the potential of peanut seeds extract as an environmental friendly and natural coagulant for the treatment of high turbid water using synthetic water with 200 NTU. They reported that peanut extracted with NaCl (PC-NaCl) could effectively remove 92 % of the 200 NTU turbidity using only 20 mg/l, while peanut seeds extracted with distilled water (PC-DW) could remove only 31.5 % of the same turbidity with the same dosage. They also observed that the coagulant dosage was not affected by the concentration of the salt solution, however, residual turbidity decreased with increasing concentration of the salt.

Muhammad *et al.*, (2015), studied the use of water melon seed as a potential coagulant for water treatment. Laboratory scale studies using jar test experiments were performed on medium turbid water to determine the effect of dosage, pH, stirring time and speed on coagulation. Results obtained showed that watermelon seed can be used as a natural coagulant for water treatment.

Thakur and Choubey (2014), used tannings extracted from bark of acacia catechu to use as primary coagulant for natural turbid water and observed from their experiment that acacia catechu powder can remove turbidity up to 91 % at the optimal dosage of 3.0 mL/L. On the other hand, the powder of acacia catechu can remove total dissolve solids by 57.3 %.

Nnaji (2017) studied the coagulation and antimicrobial efficiency of Garcinia

kola at different concentrations on turbid surface water samples. Microbial reduction after treatment with *Garcinia kola* seed extract at different concentrations ranged from 41.67 - 75.00 % for Total coliform, 34.81 - 73.92 % for E. coli, 12.87-70.96 % for Faecal streptococcus, 36.18 - 68.09 % for Staphylococcus aureus and 45.30 - 65.81 % for total heterotrophic bacteria. He also reported that *Garcina kola* seed is non-toxic and did not significantly affect the pH and conductivity of the treated water. These few studies point to the fact that the use of plants in water and wastewater treatment holds certain promises.

2.5.4 Advantages and disadvantages of bio coagulants

The natural based coagulants have a great number of advantages over traditional alternatives (inorganic and synthetic coagulants):

- > The handling of these coagulants is safer for people because they are natural.
- They improve subsequent biological treatment and biodegradability of the sludge produced.
- These natural coagulants generate smaller volumes of sludge which are less toxic reducing the costs associated with sludge handling
- They are non-toxic and non-corrosive eco-products, thus contributing to a longer useful life of equipment and to the security of operators
- They are applicable over a wide range of pH without altering the pH of the effluent thereby reducing and or eliminating the need for acidic or basic agents reducing the overall cost of treatment.

They are cost effective especially when the plant is indigenous to the community and also involves relatively simple technology to extract the coagulant.

Some of the disadvantages include

- > High organic load and residual (storage). Therefore, purification of natural coagulants is vital in order to reduce organic load
- > the crude extract is not generally suitable for large water supply systems where the hydraulic residence time is very high (Gebremichael *et al.*, 2005)
- Another disadvantage of natural coagulants for example *Moringa oliefera* is its efficacy only for highly turbid water (Megersa, 2014)

2.6 Mangifera Indica

Mangifera indica commonly known as mango, is a specie of flowering plant in the sumac and poison ivy family Anacardiaceae. Mango is among the most economically and culturally important tropical fruits (Shapiro, 2012). It was originally found in the foothills of the Himalayas in northeastern India, Burma, and Bangladesh and domesticated thousands of years ago. It is now grown in most tropical countries and some subtropical ones. It is a large evergreen tree with a dark green, umbrella-shaped crown. The Mango tree grows to be 30 to 45 feet tall and almost 50 feet wide with an irregularly egg-shaped and slightly compressed fleshy drupe, 8-12 cm long, attached at the broadest end on a pendulous stalk. The skin smooth, greenish-yellow, sometimes tinged with red. The underlying yellow-orange flesh varies in quality from soft, sweet, juicy and fibre-free in high-quality selected (clonal) varieties to turpentine flavoured and fibrous in wild seedlings (Orwa *et al.*, 2009). Some people are allergic to the pollen, the sap and even the fruit (Gilman and Watson, 1994). Parves (2016), writing on the Pharmacological

activities of mango, stated the following as some of the uses of the various parts of mango;

1. Roots and Bark- Used as astringent, acrid, refrigerant, styptic, anti-syphilitic, vulnerary, anti-emetic, anti-inflammatory and anti-constipating. They are useful in vitiated conditions of pitta, metrorrhagia, calonorrhagia, pneumorrhagia, lecorrhoea, syphilis, uteritis, wounds, ulcers and vomiting. The juice of fresh bark has a marked action on mucous membranes, in menorrhoea, leucorrhoca, bleeding piles and diarrhea

2. Leaves- used as astringent, refrigerant and styptic. They are also useful in vitiated conditions of cough, hiccup, hyperdipsia, burning sensation, hemorrhages, haemoptysis, haemorrhoids, wounds, ulcers, diarrhoea, dysentery, pharyngopathy, scorpion string and stomachopathy. The ash of burnt leaves is useful in burns and scalds. The smoke from burning leaves is inhaled for relief of throat diseases.

3. Flowers- used as astringent, refrigerant, styptic, vulnerary, constipating and haematinic. The dried flowers are useful in vitiated conditions of pitta, haemorrhages, haemoptysis, wounds, ulcers, anorexia, dyspepsia, uroedema gleet, catarrh of bladder, diarrhoea, chronic dysentery and anemia

4. Fruits- the unripe fruits are acidic, acrid, antiscorbutic, refrigerant, digestive and carminative. They are useful in dysentery ophthalmia, eruptions, urethrorrhoea and vaginopathy. The ripe fruits are refrigerant, sweet, emollient, laxative, cardiotonic, haemostatic, aphrodisiac, and tonic. They are also used in vitiated conditions vata and pitta, anorexia, dyspepsia, cardiopathy, haemoptysis, haemorrhages from uterus, lungs and intestine, emaciation, and anemia.

5. Seeds- The seed kernel is rich source of protein (8.5%) and gallic acid. It is sweet, acrid,

astringent, refrigerant, anthelmintic, constipating, haemostatic, vulnerary and uterine tonic. It is useful in vitiated conditions of pitta and cough, helminthiasis, chronic diarrhea, dysentery, haemorrhages, haemoptysis, haemorrhoids, ulcers, bruises, leucorrhoea, menorrhagia, diabetes, heat burn and vomiting.

Shah *et al.* (2010) in their studies indicated that mango possesses antidiabetic, anti- oxidant, anti-viral, cardio tonic, hypotensive, anti-inflammatory properties. Various effects like antibacterial, anti-fungal, anthelmintic, anti-parasitic, anti-tumor, anti HIV, anti-bone resorption, antispasmodic, antipyretic, antidiarrheal, anti-allergic, immunomodulation, hypolipidemic, anti-microbial, hepatoprotective, gastroprotective have also been studied.

Mutua *et al.* (2016) evaluated some of the biochemical characteristics and antimicrobial potential of mango seed kernel extracts on medically important human bacterial and fungal pathogens. They reported that mangoes contain on average, 6.74–9.20 % protein content; fat content of between 9.84 to 13.04 %; the ash, fiber, and carbohydrate contents ranged from 1.78 to 2.87 %, 2.64 to 3.71 % and 72.86 to 75.92 %, respectively.

Dange and Lad (2015) carried out a study on upgrading conventional sewage treatment process by using *Mangifera Indica*. The study concentrated on the use of natural coagulant for sewage treatment and also quality and uses of sludge generated by using natural coagulants during treatment of sewage. The results they came up with showed that Mango (*Mangifera indica*) seeds, as natural coagulant removed around 32 % BOD and 30 % TSS in primary treatment when used alone but when combined with Alum at different ratios, higher percentages of BOD and

TSS removal were observed.

Saha and Saha (2013), researched the use of mango leaves in the removal of hexavalent chromium from contaminated water by adsorption and they concluded that the sorption was feasible, spontaneous, and endothermic in nature which means that mango leaves can be used as an effective and environmentally friendly biosorbent for the treatment of hexavalent chromium (chromium 6) containing aqueous solutions.

In their study of mango biomass (*Mangifera indica*) as a cationic biosorbent, Ashraf *et al.* (2010) tested the efficacy of the biosorbent for the removal of lead, copper, zinc and Pizziel metal ions using batch experiments in single and binary metal solution under controlled experimental conditions. At highest experimental solution concentration used (150 mg/L), the removal of metal ions was found to be 82.76 % for lead, 76.60 % for copper,

63.35 % for zinc and 59.35 % for Pizziel while at lowest experimental solution concentration (25 mg/L), the removal of metal ions were 92.00% for lead, 86.84 % for copper, 83.96 % for zinc and 82.29 % for Pizziel, indicating its effectiveness and presented comparable biosorption capacity for lead, copper, zinc and Pizziel metal ions with other types of biosorbent materials.

2.7 Phoenix Dactylifera

It is a monocot plant in the Arecaceae family, cultivated in dry tropical regions of the Arabian Peninsula, North Africa, and the Middle East (Chao and Krueger, 2007). Date palms produce many products that are useful to humans.

The primary product is the date fruit which is high in sugars and potassium. It can be eaten fresh, dried, or in various processed forms in prepared foods and desserts. In addition to the edible fruits, seeds can be ground into edible flour, traditionally used to make bread in times of scarcity. The flowers are also edible, used in salads or dried and ground as a condiment. Date fruit also can be made into juice, vinegar, wine, beer, sugar, syrup, honey, chutney, pickle, paste, dip, and food flavoring (Chihcheng *et al.*, 2007). Dates are added to animal feed or fed directly to animals in the certain regions.

The palm tree is one of the most important trees as it is abundant, locally available and is a principal fruit grown in many regions of the world. It is an effective material that could be used as an adsorbent for the removal of different pollutants from aqueous solution. Harrasi *et al.* (2014) in their nutritional assessment and antioxidant analysis of 22 date palm varieties, reported the following ranges from results of the proximate analyses of the seeds: (15 %-21 %), dry matter (78 %-86 %), ash content (1.0 %-2.0 %), fiber (1.0%-2.5 %), fat (0.1 %-0.7 %), protein (1.8 %-3.8 %), nitrogen (0.25 %-0.55 %), and carbohydrates (74.5 %-82.4 %).

In their review, Ahmad *et al.* (2011), reviewed the application of date palm as adsorbent to include the following,

- Removal of heavy metals such as the removal of copper and lead ions by activated date pits carbon as well as raw date pits
- Removal of dyes such as adsorption kinetics and isotherms of methylene blue on raw and physically activated date pits

- Removal of phenolic pollutants including Adsorption of phenolic compounds onto activated carbon prepared from date fruit pits
- Removal of pesticides such as paraquat dichloride from aqueous solution by calcium oxide-activated date stone carbon

 Removal of miscellaneous pollutants such as sulfur from diesel fuel Asgari *et al.* (2013) studied the removal of a cationic dye from wastewater during purification by *Phoenix dactylifera*. The activated carbon prepared from *Phoenix dactylifera* fruit stones was tested for the removal of methylene blue (MB) dye from aqueous solutions. The results showed that the adsorption of MB was favorable at neutral pH and also demonstrated that the Langmuir isotherm model best represented the equilibrium data with a maximum MB adsorption capacity of 478.32 mg/g.

Ahmed (2016), in his study reviewed the preparation of activated carbons from date (*Phoenix dactylifera*) palm stones and application for wastewater treatment, and reported that according to collected data, the surface areas of date stone-carbons were in the range from 490 to $1282 \text{ m}^2/\text{g}$ and yields from 17 to 47 % with highest values obtained by chemical activation. He also reviewed the application of date stones-carbon for adsorption of organic and inorganic pollutants and also reported that low-cost carbons derived from date pits biomass demonstrated maximum capacities of 612.1, 359.1, 238.1, and 1594.0 mg/g for dyes, phenols, pesticide, and heavy metals respectively.

In their experiment to remove Boron from seawater using date palm (*Phoenix dactylifera*) seed ash, Al Haddabi *et al.* (2016), studied the feasibility of using date seed ash for the removal of boron from aqueous solution using SEM

and EDX analyses, and found out that the maximum removal efficiency of boron was around 47 % at neutral pH which indicated that the application of date seed ash is a promising adsorbent for boron removal where it can be used as pretreatment before reverse osmosis desalination process.

2.8. Isothermal Studies

Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir and Freundlich (Desta, 2013). Langmuir, Freundlich, Temkin and Redlich-Peterson Isotherms are some Isotherms used commonly in engineering for isothermal studies. The important thing is to develop an equation which will accurately represent the experimental result and which can be used for design purposes (Volesky, 2001; Aksu, 2002). The Langmuir model is based on three assumptions; adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one adsorbed atom; and the ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites; at equilibrium there is no net change in surface coverage (Adie *et al*, 2012). The isotherm is represented by

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_l} + \frac{C_e}{Q_m}$$

(2.1)

where Q_e is the equilibrium amount of adsobate exchanged by the adsorbent (g/g), C_e is the equilibrium concentration of adsorbate in the solution (g/L), Q_m (g/g) is the maximum uptake of adsorbate exchanged and K_L is the Langmuir constant (L/g).

The Langmuir constants Qm and K_L can be evaluated from the linear regression

analysis of the plot C_e vs C_e/Q_e . R_L is the dimensionless separator which provides the essential features of Langmuir isotherm (Omer *et al*, 2017), and expressed by Eq. (2.2)

$$\boldsymbol{R}_{\boldsymbol{L}} = \frac{1}{1 + \kappa_{l} c_{0}} \tag{2.2}$$

where Co is the initial concentration of the adsorbate in the mixture.

The Freundlich isotherm describes the heterogenic nature of adsorption process. It is an empirical relationship which often gives a more satisfactory model of experimental data (Oke, 2008). The linear form of it is given by Eq. (2.3)

$$\operatorname{Ln}Q_{e} = \operatorname{Ln}K_{F} + \frac{1}{n}\operatorname{Ln}C_{e}$$
(2.3)

Where K_F is Freundlich constant (L/g) and 1/n is the heterogeneity factor. The constants n and K_F can be evaluated from the linear regression analysis of the plot ln C_e vs ln Q_e.

The regression coefficients (\mathbb{R}^2) derived from the linear regression plots of the adsorption studies enables the assessment of the best model that fits the experiment (Omer *et al*, 2017).

In the research carried out by Adeogun and Balakrishnan, (2015), electrocoagulation was used for the removal of basic dye rhodamine B from aqueous solution, and the process was carried out in a batch electrochemical cell with steel electrodes in monopolar connection. The effects of some important parameters such as current density, pH, temperature and initial dye concentration, on the process, were investigated. Experimental data were analyzed using six model equations: Langmuir, Freudlinch, Redlich–Peterson, Temkin, Dubinin– Radushkevich and Sips isotherms and it was found that the data fitted well

with Sips isotherm model. The study showed that the process depends on current density, temperature, pH and initial dye concentration. The calculated thermodynamics parameters (Δ G- change in useful energy, Δ H- change in Enthalpy, and Δ S- change in Enthropy) indicated that the process is spontaneous and endothermic in nature.

Mahiya *et al.*, (2016), investigated the adsorptive behavior, isothermal studies, and kinetic modeling involved in removal of divalent lead from aqueous solutions, using *Carissa carandas* (bengal currant) and *Syzygium aromaticum* (Clove). The study focused on the biosorption of lead(II) oxide (PbO) ion onto surface of *Carissa carandas* and *Syzygium aromaticum* biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time, initial metal ion concentration, and temperature were observed to have considerably affected the biosorption efficiency of Pb(II) oxide. Biosorbent *Carissa carandas* leaf powder showed higher sorption efficiency than that of biosorbent *Syzygium aromaticum* powder under identical experimental conditions. It was also observed that the lead(II) removal percentage was found highest of 95.11 % for *C. carandas* and 91.04 % for *S. aromaticum* at contact period of 180 min.

Bhatia and Khan (2014) studied the kinetic and isothermal removal of Zn (II) Ions from aqueous solutions by using *Lawsonia inermis* (henna) as a novel biosorbent. They studied different operational parameters such as the effect of pH, biomass dose, equilibrium time, temperature and initial metal ion concentrations. They reported that maximum adsorption of Zn (II) took place at optimum conditions of pH 5.0 and biomass dose of 0.2 g/L. They also observed that the interactions between zinc ions and *Lawsonia inermis* were complicated, and the pH of solution was a key governing factor of such interactions. Biosorption equilibrium was achieved in 60 minutes. The adsorption kinetics followed Pseudo second order kinetic model and the value of rate constant was found to be 1.23×10^{-2} g mg⁻¹min. Fourier transform infrared (FTIR) spectroscopy was used to characterize the surface functional groups of the biosorbent. FTIR analysis was used to reveal the involvement of hydroxyl and carboxyl groups in the removal of Zn (II) from aqueous streams. Linear Langmuir and Freundlich models were synchronic. The Langmuir adsorption capacity (qm) was found to be 76.92 mg g⁻¹. Desorption experiments indicated that 0.5 M HCl was efficient desorbent for the recovery of Zn (II) from biomass. They stated that the experimental facts reveal the efficiency of *Lawsonia inermis* based Zn (II) removal technology.

In their research, Omer *et al.* (2017) treated leather tannery effluent with Clinoptilolite at different parameters of varying concentrations, pH and time interval. BOD and COD were adsorbed up to 75 % and 65 % respectively. Their Studies on Langmuir and Freundlich isotherms reveal that the experimental data fits best in the Langmuir isotherm

2.9 Kinetic Studies

Kinetics is the study of rates in chemical process to understand the factors that influence the rates. The study of chemical kinetics includes careful monitoring of the experimental conditions which influence the speed of a chemical reaction and hence, help attain equilibrium in a reasonable length of time (Neto et al, 2013).

The most popular kinetic models are the Lagergren pseudo-first order and pseudo- second order kinetics. A reaction which is not first-order reaction naturally but made first order by increasing or decreasing the concentration of one or the other reactant is known as Pseudo first order reaction. The pseudo second order is based on the assumption that the adsorption follows a second order chemisorption (Aly *et al*, 2014). The linear form of Lagergren's first order rate equation is as shown by Eq. (2.4)

$$\ln (q_e - q_t) = \ln q_e - K_1 t.$$
(2.4)

where q_e is the amount of adsorbate adsorbed onto the adsorbent at equilibrium (mg/g), q_t is the amount of dye adsorbed onto the adsorbent at any time t (mg/g), and K₁ (min-1) is the rate constant of the pseudo-first-order adsorption. K₁ and q_e can be evaluated from the graph of ln (q_e-q_t) versus t, if a straight line, and hence the adsorption follows a pseudo first order kinetics model. The linearized form of the pseudo-second-order model is given by Eq. (2.5).

$$\frac{t}{q_t} = \frac{1}{K_2 2 q_e^2} + \frac{1}{q_e} t$$
(2.5)

where K_2 (gm g⁻¹min⁻¹) is the rate constant of the pseudo-second-order adsorption, qe is the mount of adsorbate adsorbed on the adsorbent at equilibrium (mg/g), and qt is the amount of adsorbate adsorbed on the adsorbent at any time, t (mg/g). K_2 (gm g⁻¹min^{-1j}) can be calculated from the slope and intercept of the plot of t/qt against t (Vijyakumar *et al*, 2012).

Neto *et al.*, (2013) investigated the parameters that influence the performance of metal ion adsorption, such as, effect of initial metal ion concentration, pH, flowrate, bed height, and adsorption isotherm in order to select the most suitable treatment of wastewater. Modeling of adsorption isotherm (Langmuir, Freudlich, Temkin, and Halsey equations), adsorption kinetics (pseudo-first, pseudo-second and intraparticle equations) and breakthrough curves (Thomas equation) were also applied to the experimental data to find a better application and performance of the bio-adsorbent on the metal ion removal.

Vijayakumar *et al.*, (2011) carried out the studies on adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite. Batch adsorption experiments were carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature. They reported that dye adsorption equilibrium was rapidly attained after 50 minutes of the contact time, and it was described by the Langmuir and Freundlich adsorption isotherms over the entire concentration ranges from 20-100 mg/L⁻¹. Adsorption data were used for modelling, from the first and second order kinetic equation and intraparticle diffusion models. Thermodynamic parameters such as Δ H-change in Enthalpy, Δ Schange in Enthropy, and Δ G-change in useful energy, were calculated, which indicated that the adsorption was spontaneous and exothermic in nature, which was evident by decreasing the randomness of the dye at the solid and liquid interface.

In their equilibrium and kinetic studies on biosorption potential of charophyte biomass to remove heavy metals from synthetic metal solution and municipal wastewater, Sooksawat *et al.*, (2016) studied the efficiency of metal removal under varied conditions in different sorbent dosages, pH, and contact times.

Biosorption isotherm and kinetics were used to clarify heavy metal preference and biosorption mechanism. They reported that *C. aculeolate* (beautyberry) and *N. opaca* (american holly) performed well in the biosorption of all three metal ions, with preference towards Pb, followed by Cd and Zn, in the single-metal solutions. Also, Pb adsorption onto algal biomass followed first-order rate kinetics (*N. opaca*) and intraparticle diffusion (*C. aculeolata* and *N. opaca*) indicating physical adsorption whereas Cd and Zn biosorption kinetics fitted the second-order rate model, indicating chemical adsorption between metal ions and both algae. They observed that *C. aculeolata* exhibited slightly higher maximum uptake of Pb, Cd, and Zn (105.3 mgPb/g, 23.0 mgCd/g, 15.2 mgZn/g) than did *N. opaca* (104.2 mgPb/g, 20.5 mgCd/g, 13.4 mgZn/g)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Table 3.1 gives a list of Equipment used for this research work and their specifications including manufacturers, while Table 3.2 shows the chemicals used for laboratory analysis.

Table 3.1 Apparatus and equipment used in research

S/N	EQUIPMENT/APPARATUS	MODEL	SPECIFICATION	MANUFACTURER
1	Jar Test Machine	BENT	6 Beakers Semi-	Peterson Candy
			Auto	
2	Soxhlet Extractor		500ml	Biological
				Enterprises
3	Magnetic Stirrer & Magnet	MS 500	2 litres, $0 - 1250$	Intllab Magnetic
			rpm	
4	Water Bath	SWBS	6ltrs $100^{\circ}C \pm 0.2$	Stuart
			°С,	Manufacturing Inc
5	Muffle Furnance	D874	$121^{\circ}C \pm 5 \%$	Pyradia Inc
6	Stop watch	Adanac	± 0.1 second	Marathon Watch
		4000	accuracy	Company
7	Weighing Balance		500 g ±0.1 g	Gallenkamp
				Engineering
8	Elemental Analyzer	DANI	100 ppm- 100	DANI
		89.00	%, 30 samples	Instruments
			carousel.	
9	Muslin Cloth			
10	Fume Cupboard		6 inches	Fisher America
11	Funnel			
12	Turbidity Meter	HM-DGT	0 – 9000 ppm	Hack Chemical
				Limited
13	EC/TDS Meter	TDS-EZ	0 - 9990 ppm, ± 3	Hanna Instrument
			%	USA
14	pH Meter			Hanna Instrument
				USA

3.11 Equipment used in the research

a. Jar Test machine- The jar test machine used was manufactured by Peterson candy, USA. It is a 6 beaker semi-automatic machine with a rpm of 5 - 150 and an accuracy of \pm 0.1 rpm. The stirring paddles are 6 in numbers and are made of stainless steel. The unit is fitted with fluorescent white light as source of illumination with a 100-hr timer.

b. Soxhlet extractorh- This equipment was manufactured by Biological Enterprises, India. It has a flask volume of 500 ml with an extractor volume of 300 ml. The setup of the apparatuses allows vapors to travel up the arm where a thimble blocks solid material from escaping. It is designed to have cooling vapor enter the solid contained chamber, pot and then circulate the heated solvent in liquid form to dissolve the desired oil.

c. Elemental analyzer- The DANI 89.00 elemental analyzer was manufactured by DANI Instruments, Italy. It has a detection range of 100 ppm to 100% with capacity for automation of 30 samples. It uses Helium or Oxygen of 99% purity as carrier gas and has an analyses time of less than 5 minutes with an analytical sensitivity of less than 1 microgram.

S/N	CHEMICALS/MATERIALS	MANUFACTURER/SOURCE
1	Mangifera Indica	Sourced locally
2	Phoenix Dactilifera	Sourced locally
3	Boric Acids solution	Meyer And Baker
4	Sodium Hydroxide solution	Meyer And Baker
5	Sodium Sulphate powder	Meyer And Baker
6	Copper Sulphate powder	Meyer And Baker
7	Methyl Red Indicator	Meyer And Baker
8	Hydrochloric acid	Meyer And Baker
9	Ethanol	Meyer And Baker
10	Hydrogen Sulphate solution	Meyer And Baker
11	Phenolphthalein Indicator	Meyer And Baker
12	Eriochrome Black	Meyer And Baker
13	Aluminum Sulphate powder	Meyer And Baker

Table 3.2: Chemicals used in laboratory analysis

3.2 Methods

3.2.1 Wastewater sample collection

Wastewater was sampled from the influent of the wastewater stabilization pond of ABU Zaria. This was done by using two 20 litres rubber Jerri cans at a point where the velocity of the water was low enough to allow for obtaining a representative sample. The samples collected were grab samples.

3.2.2 Mangifera indica and Phoenix dactylifera seeds powder and oil preparation

The seeds (Mango and Dates) were sourced locally. They were washed, cleaned and dried under the sun for fourteen days until they were completely dried, and any foreign material noticed was removed from the seeds. The dry clean seeds were then crushed after the removal of the husk or seed coating and separation of the seeds from chaff to reduce their particle sizes to between $2mm - 70\mu m$. Solvent extraction was used to separate oil from the seeds. 200g of the pre-processed seeds was treated in a multistage counter current process with hexane (500ml) as the solvent in soxhlet extractor until the oil content was reduced to the lowest possible level. The mixture of oil and solvent were then separated by distillation with the cake washed with distilled water, dried in an oven to constant weight. It was then sieved and used as the coagulants.

3.2.3 .3 Determination of mineral composition of the seeds powder

The mineral contents of the samples (*Mangifera indica* seeds powder and *Phoenix dactylifera* seeds powder) were analyzed using the Atomic Absorption Spectro-photometer (AAS instrument). The minerals analyzed using AAS were Ca, Fe, Mn, Mg and Pb. Flame Photometer was used to analyze for K and Na. Samples of *Mangifera indica* and *Phoenix dactylifera* seeds to be digested were prepared in concentrated HNO₃. Working standards and blank samples were prepared for each of the mineral elements. Readings were then taken and the concentration of each of the elements were computed in mg/L according to Orijajogun, et al., (2014)

3.2.4 Proximate analysis of the seeds (Mangifera i. and Phoenix d.) powder

The analyses included in this group, also known as Weende proximate analyses, are applied firstly to materials to be used in formulating a diet as a protein or energy source and to finished feedstuffs, as a control to check that they meet the specifications or requirements established during formulation. These analyses showed the moisture, crude protein (total nitrogen), crude fibre, crude lipids, ash and nitrogen-free extract content of the sample (FAO Corporate Document Repository, 1994).

3.2.5 .5 Crude protein determination: using the kjeldahl method

The following steps were followed:

1 g of sample to was weighed and transferred to a Kjeldahl flask; 10g potassium sulphate, 0.6-0.7 g mercuric oxide, 25 ml sulphuric acid and a few grains of pumice stone were then added. The flask was moderately heated at first, shaking occasionally until the material was carbonized and the bubbles disappeared, then the temperature was raised and brought to a gentle boil. The flask walls were not allowed to overheat so that organic particles do not adhere to them. When the solution looked clear and colorless, boiling was extended for 2 hours longer, then cooled. The analysis was repeated using more sulphuric acid when crystals were formed in the solution after digestion and cooling. 250-350 ml of distilled water was carefully added to the flask, stirring the contents at the same time; then allowed to cool and added a few zinc pellets. 25 ml of sulphuric acid solution 0.5N was transferred to the collecting flask of the distilling apparatus according to the anticipated nitrogen value of the sample, and a few drops of methyl red indicator was added. Taken care not to lose ammonia, 100 ml sodium hydroxide solution and then 25 ml sodium thiosulphate solution were carefully added to the sample, mixed thoroughly and connected immediately to the distilling apparatus. Then the flask was heated so as to distil about 150 ml of the liquid in 30 minutes and the pH of the distillate was measured with litmus paper, and when it was found to be alkaline, distillation was continued. During this process, the contents of the flask were stirred occasionally. In the collecting flask, the excess sulphuric acid was titrated with sodium hydroxide 0.25N, according to the normality of the acid used, to the final point of the methyl red or methyl red-methylene blue indicator. A reagent blank was ran using 1 g of sucrose instead of the sample which was to be used in calculating results

Calculations

The H₂So₄ consumed was determined thus, 1 ml acid \equiv 1.4 mg nitrogen.

The percentage of nitrogen in the sample was calculated and converted to percentage of protein by multiplying the result by 6.25. The presence of ammonia nitrogen or nitrates was suspected in the sample and was evaluated by subtracting from total nitrogen. The protein and non-protein nitrogen content were evaluated and also subtracted from the total nitrogen. The percentage nitrogen was calculated using Eq. (3.1)

$$\% N = \frac{x \operatorname{moles}}{1000 \operatorname{cm}^3} \times \frac{(v_s - v_b) \operatorname{cm}^3}{m \operatorname{g}} \times \frac{14 \operatorname{g}}{\operatorname{moles}} \times 100$$
(3.1)

Where:

 $V_s = titration$ volume for sample

 V_b = titration volume for blank

3.2.6 .6 Determination of ash

The following steps were followed:

4 g of dry sample was placed in a crucible previously calcined and brought to constant weight. The crucible was then placed in a furnace and heated at 550°C for 12 hours; leaving to cool and transferred to a dryer. Then the crucible was carefully weighed again with the ash.

Calculations

The ash content was calculated using Eq. (3.2)

Ash content (%) =
$$100 \frac{A-B}{C}$$
 (3.2)

Where:

A = weight of crucible with sample (g)

B = weight of crucible with ash

(g)

C = weight of sample (g)

The ash was determined on the basis of wet and dry. The equation for the wet and ash basin calculations are presented as Eq. (3.3) and (3.4)

% Ash (dry basis) =
$$\frac{M_{ASH}}{M_{DRY}} \times 100$$
 (3.3)

% Ash (wet basis) =
$$\frac{M_{ASH}}{M_{WET}} \times 100$$
 (3.4)

Where

 $M_{Ash}=Mass$ of ash

M_{Dry}= Mass of dry sample

sample

4.2.1 .7 Determination of crude fiber

This method gave the crude fiber content of the sample after it had been digested in sulphuric acid and sodium hydroxide solutions and the residue calcined. The difference in weight after calcination indicated the quantity of fiber present. The following steps were followed:

3 g of defatted, dry sample was weighed and placed in a flask and then 200 ml boiling sulphuric acid solution was added. The condenser was then attached and brought to boiling point in one minute; adding antifoam. The content was then boiled for 30 minutes, maintaining the volume of distilled water constant and swirling the flask periodically to remove particles adhering to the sides. Buchner funnel with the filter paper was then lined up and pre-heated with boiling water at the same time. At the end of the boiling period, the flask was removed and the content allowed to rest for one minute and then filtered carefully, using suction. Filtration was carried out in less than 10 minutes, and the filter paper was washed with boiling water. The residue was then transferred to the flask using a retort containing 200 ml of boiling NaOH solution and boiled for 30 minutes. The filtration crucible was then preheated with boiling water and the hydrolyzed mixture carefully filtered after letting it rest for 1 min. The residue was then washed with boiling water, then with the HCI solution and then again with boiling water, finishing with three washes with petroleum ether and then placed the crucible in a kiln set at 105°C for 12

hours and thereafter cooled in dryer. The crucible was quickly weighed with the residue inside and then placed in the crucible furnace at 550° C for 3 hours, leaving it to cool in a dryer and then weighed again.

(3.5)

Calculations

The crude fiber content is expressed by Eq. (3.5) Crude fibre content (%) = $100 \frac{A - B}{C}$

Where:

A = weight of crucible with dry residue (g) B =

weight of crucible with ash (g)

C = weight of sample (g)

4.2.2 Determination of ether extract

The following steps were followed for the extraction of the ether extract.

Sample drying:

2 g of ground sample was weighed into a thimble recording the weight to nearest 0.1 mg (W1). A second sub-sample was weighed for dry matter determination. The sample was then dried for 5hrs at 100°C. The beakers were then dried for 1 hr at 100°C for fat determination and then cooled the beakers in a desiccator, then weighed and recorded the weight to the nearest 0.1 mg (W2). After drying of the beakers was over, the samples were removed from the oven to a desiccator.

Extraction:

The fat beakers were lined up in front of the extractor and then matched the thimbles with their corresponding fat beakers. The thimble was then slipped into a thimble holder and clipped into position on the extractor. 40 ml of diethyl ether was added to each fat beaker, and the beakers slipped into the ring clamp and tightly clamped onto the extractor. The heater was raised into position and 1/4-inch gap was left between the beaker and the heating element. The heater was then switched on. Extraction was then carried out for 4hr on a High setting (condensation rate of 5 to 6 drops per second). After the extraction, the heater was shut, and the ether was allowed to drain out of the thimbles for another 30 min.

Ether Distillation and Weighing of Fat Residue:

The thimble was removed from the holder, and rinsed with a small portion of diethyl ether from the wash bottle. Then an ether reclaiming tube was clipped in place and the fat beaker reattached. The heater was repositioned and then electricity and water turned on. Then proceeded to distill the ether using a high setting and watching closely. The Distillation was done until a thin layer of ether remained in the bottom of the beaker, and then the heater was switched off. The exterior of the beaker was wiped with a clean Kim wipe as it was being removed from the extractor. Then the reclaiming tubes were emptied into the "used" diethyl ether container with beakers placed in an operating hood to finish evaporating the ether. A steam-bath was used to speed up the evaporation with the beakers remaining in the hood until all traces of ether was gone. Then each beaker was carefully sniffed to determine if any ether remained, and then the beakers were placed in a 102°C gravity convection oven and dried for 1/2 hr. After the drying of the beakers, they were then cooled in a desiccator, weighed and recorded weight to the nearest 0.1 mg (W2). The fat beakers were then cleaned by warming on a hot plate on a low setting while adding some used ether to dissolve the fat. Then the beakers were soaked in Alconox detergent, washed using hot water. The thimbles were cleaned by blowing with air.

Calculations: Percent Crude Faulther (DM basis) = $\frac{W1x(\frac{LabDM}{100})}{W1x(\frac{LabDM}{100})}$ (3.6)

- W1 = initial sample weight in grams
- W2 = tare weight of beaker in grams
- W3 = weight of beaker and fat residue in grams

4.2.3 .9 Determination of moisture content

The following steps were followed:

10 g of previously ground sample was weighed and placed in an oven to dry at 105°C for 12

hrs. Then the sample was allowed to cool in dryer and the weight taken again, taken care not to expose the sample to the atmosphere.

Calculation

The moisture content calculation is as shown by Eq. (3.7)

Moisture content (%) =
$$100 \frac{(B - A) - (C - A)}{(B - A)}$$
 (3.7)

Where:

A = weight of clean, dry scale pan(g)

B = weight of scale pan + wet sample (g)

C = weight of scale pan + dry

sample (g)

4.2.4 10 Determination of crude lipids

The following steps were followed:

Extraction flask was cooled in a dryer and weighed, then 5 g of dry sample was weighed in an extraction thimble, handling it with tongs and placed it in the extraction unit. The flask containing petroleum ether was connected to the extractor at 2/3 of total volume. The content was boiled and the heat adjusted to obtain 10 refluxes per hour. When heating was finished, the ether was evaporated by distillation and then the flasks was cooled in a dryer and weighed. The defatted sample was then used in determining crude fibre.

Calculations

The crude lipid content is expressed by Eq. (3.8) Crude lipid content (%) = $100 \frac{B-A}{C}$ (3.8) Where:

A = weight of clean dry flask (g) B =

weight of flask with fat (g) C =

weight of sample (g)

4.2.5 Determination of nitrogen free extract (NFE)

This included all the nutrients not assessed by the prior methods of proximate analysis. They are composed mainly of digestible carbohydrates, vitamins and other nonnitrogen soluble organic compounds. The result was obtained by subtracting the percentages calculated for each nutrient from 100.
Calculations

The nitrogen free extract is expressed by Eq. (3.9)

Nitrogen-free extract (%) = 100 - (A + B + C + D + E) (3.9)

Where:

A = humidity content (%)

B = crude protein content (%) C =

crude lipid content (%)

D = crude fibre content (%) E =

ash content (%)

4.2.6 Determination of the active compounds

The active ingredients in *Mangifera indica* and *Phoenix dactylifera* seeds were determined using the scanning electron microscope (SEM) combined with X-ray diffraction. Specimens of the samples were prepared and a beam of electrons was focused on the sample surface which then gave information on the composition and surface topography of the samples. The samples were analyzed before they were used as coagulants.

4.2.7 Water quality test

a) Total Dissolved Solids

The following steps were followed:

Washed the filter paper and then dried it in evaporating dish and the weight was taken. The sample was stirred and 50 ml pipetted while stirring. The content was then filtered and washed three times and the filtrate transferred to evaporating dish & dried. It was then cooled and weighed.

The total dissolved solid is expressed by Eq. (3.10)

mg Dissolved Solids/L =
$$\frac{(A-B) \times 100}{mL Sample}$$
 (3.10)

where:

A = weight of dried residue + dish, mg B =

weight of dish, mg.

b) pH

A digital pH meter was used to obtain the reading of the pH level. The meter was inserted directly into the wastewater sample and several readings were taken for accuracy and precision. The meter was also used to take the treated wastewater sample pH readings after the coagulation process was completed for each of the coagulants at their different dosages. c) Temperature

A hand held digital thermometer was used to obtain the temperature of the samples. This was inserted into the sample and allowed to adjust to the temperature of the wastewater after a period of 120 seconds. Then the readings were taken.

d) Turbidity

A hand-held Turbidity meter was used and the results recorded. Once inserted into the wastewater sample in a clean and dry beaker, it gave the turbidity readings. This was repeated severally to test for consistency. Readings were also taken after the application of the different coagulants and their various dosages.

e) Electrical Conductivity

A digital conductivity meter was used to measure the conductivity of the different samples. Several readings were taken and averaged to give the conductivity of the samples. Readings were taken for both fresh and treated wastewater samples.

f) BOD Determination

The following steps were followed

The raw water sample was collected and the BOD bottle was carefully filled with sample water without making air bubbles. 2 ml of manganese sulfate was then added to the BOD bottle carefully by inserting the pipette just below the surface of water to avoid formation of bubbles. Another 2 ml of iodide azide reagent was added in the same manner and the bottle was closed and inverted several times to form a brownish cloud indicating the presence of oxygen. The brown precipitate was then allowed to settle out at the bottom and 2 ml of

concentrated H₂SO4 was carefully added without forming air bubbles. The bottle was then closed and the solution mixed thoroughly to dissolve the precipitate. The bottle was then kept in the BOD incubator for 5 days of incubation. After incubation, 50 ml of the sample was titrated with 0.025N Sodium thiosulphate to a pale-yellow color. Then 2 ml of starch solution was added which turned the sample into blue color initially. The titration was continued until the sample turned clear and the readings were noted. The concentration of dissolved oxygen used up was taken to be equivalent to the number of milliliters of titrant used.

g) COD determination

The following steps were followed to determine the COD

20 ml of sample was pipetted in 250 ml of refluxing flask and 400 mg (a pinch) of mercuric sulphate was then added. 10 ml of potassium dichromate was added to the mixture. 30 ml of the concentrated sulphuric acid reagent was then added to the mixing of the sample. The reflux flask was then connected to the condenser and reflux for a period of 2hrs at 150°C. 80 ml of distilled water was added through the condenser to cool the mixture to room temp and titrated with standard sulphate using 4 drops of ferroin indicator. This was done until a sharp colour change from blue-green to brick red was observed. The titrate value was marked 'B' in ml. A blank was also prepared with distilled following the procedure above. The titrate value was marked 'A' in ml.

The COD (mg/L) was calculated as shown by Eq. (3.11)

$$\frac{\mathrm{mg}}{\mathrm{L}}COD = \frac{\lfloor (A-B)\mathrm{C} \ge 8000 \rfloor - 50\mathrm{D}}{ml \ of \ sample} x1.2$$

(3.11)

where:

A = mL Fe(NH4)2(SO4)2 for blank;

B = mL Fe(NH4)2(SO4)2 for sample; C = normality of Fe(NH4)2(SO4)2; D =

chloride correction from curve

1.2 = compensation factor to account for the extent of chloride oxidation which is dissimilar in systems containing organic and non-organic material.

i) Jar Test

The following steps were followed:

5 gallons of sample of water to be tested were collected. Then 1,000 ml beakers were filled with 1,000 ml of samples and placed on the gang stirrer. The stirrer was started and set to run at 100 rpm. The coagulant solution was then added accordingly to each of the sample beakers, and mixed for 60 seconds. The mixture was then stirred rapidly for 60 seconds and slowly for 60 minutes. The rate of floc formation and size of floc were observed and

recorded. The stirrer was then stopped and the samples allowed to settle for 5 minutes. The

following were observed:

- ➢ Settling rate
- Floc separation (floating separate clumps)
- Supernatant clarity

Supernatant turbidityh) Bacteriological Examination

Presumptive Test and MPN.

The following steps were followed:

50 ml of water to be tested was collected and the water sample to be tested was vigorously shook by moving it 25 times through a 12- inch arch and then transferred 10 ml of the sample into each of the three, triple strength lactose tubes. 1 ml of the sample was then transferred into each of three regular strength lactose tubes. Using the same pipet, 0.1 ml of the sample was then transferred to each of the three remaining regular strength lactose tubes and incubated all tubes at 37°C for 24hrs.

Confirmed Test

The tubes from the presumptive test were examined to determine if any had produced an acid/gas reaction. This was a positive presumptive test. the number of tubes positive for acid/gas in each of the three volume categories were determined. Then the MPN of the water sample was determined by comparing these numbers to the MPN Determination chart. From one of the tubes showing 10 % gas production and more, one loopful of the broth was streaked onto an EMB plate and incubated the plate at 37°C for 24hrs

4.2.8 Treatability studies

Mangifera indica (MI) and *Phoenix dactylifera* (PD) were used separately and in combination in different proportions to carry out the Jar test. Table 3.3 shows the different proportions of the mixture. Jar test was then carried out with rapid mixing at 100 rpm for 1 minute and slow mixing at 30 rpm for 30 minutes. Residual turbidity for different combinations of coagulant dosages were then measured in the interval of 60, 120 and 720 minutes (Dange and Lad, 2015)

Particulars	Proportions (%) by volume
[MI: PD]	100: 0
[MI: PD]	80: 20
[MI: PD]	60: 40
[MI: PD]	50: 50
[MI: PD]	40: 60
[MI: PD]	20: 80
[MI: PD]	0: 100

Table 3.3: Treatment ratios of MI and PD

4.2.9 Data analysis

Regression analysis was used to ascertain the proportion of the variance in the dependent variable (turbidity) that is predictable from the independent variable (dosage) and to determine statistical significance of the overall model using ANOVA. Microsoft excel 2010 was used to carry out the regression analysis and the analysis of variance.

Correlation analysis was also carried out to ascertain the relationships between the variables and to also study the nature of that relationship. Microsoft excel 2010 was used to carry out the correlation analysis.

A mathematical model of the second order was developed using XLSTART Microsoft software to show the optimal set of experimental parameters producing the optimum response value and interactive effects of the response parameters were represented through a 3-dimensional surface plot (Raissi, 2009).

4.2.10 Isothermal studies

The experimental data for the reduction in BOD by dosage with *Mangifera Indica, Phoenix dactylifera*, and their combination over the studied concentration range of 5-25 mg/L were processed using the Langmuir and Freundlich adsorption Isotherm models. The adsorption data were represented by these adsorption isotherms. Linear plots were employed to determine the values of Langmuir and Freundlich constants and a deduction was made based on these constants whether the experimental data followed these adsorption isotherm models or not. The Langmuir isotherm is represented by Eq. (3.12)

$$\frac{c_e}{Q_e} = \frac{1}{Q_m K_l} + \frac{c_e}{Q_m}$$
(3.12)

where Q_e is the equilibrium amount of adsorbate exchanged by the adsorbent (g/g), C_e is the equilibrium concentration of adsorbate in the solution (g/L), Qm (g/g) is the maximum uptake of adsorbate exchanged and K_L is the Langmuir constant (L/g). R_L is given by Eq. (3.13)

$$\boldsymbol{R}_{\boldsymbol{L}} = \frac{1}{1 + \kappa_{\boldsymbol{L}} \boldsymbol{c}_{\boldsymbol{o}}} \tag{3.13}$$

Where C_o is the initial concentration of the adsorbate in the mixture. The Langmuir constants Q_m and K_L were evaluated from the linear regression analysis of the plot C_e vs C_e/Q_e ($Q_m = 1/slop$, $K_L = 1/[Q_mx Intercept]$).

The linear form of the Freundlich isotherm model is given by Eq. (3.14)

$$\operatorname{Ln}Q_{e} = \operatorname{Ln}K_{F} + \frac{1}{n}\operatorname{Ln}C_{e}$$

$$(3.14)$$

Where K_f is Freundlich constant (L/g) and 1/n is the heterogeneity factor. The constants n and K_f were evaluated from the linear regression analysis of the plot of lnC_e vs. lnQ_e ($K_f = Log$ Intercept, n = 1/slop)

4.2.11 Kinetic studies

The Pseudo-first-order and second-order kinetic models were tested at different concentrations (amount of BOD removed) in this study to determine which model is in good agreement with experiment qe (adsorption capacity) value, thus suggesting which model the sorption system follows. The Pseudo-first-order-model can be expressed as shown in Eq. (3.15)

$$Ln(q_e - q_t) = Ln(q_e) - \frac{K_1 t}{2.303}$$
(3.15)

Where q_e , q_t (mg/g) are the mass of BOD adsorbed at equilibrium (adsorptive capacity), and mass adsorbed at any time't', K₁, (min-¹) is the equilibrium constant of the Pseudo-first- order adsorption. The values of K₁ and qe were determined respectively from the slope and intercept of the plot of LN (q_e-q_t) versus t (q_e = e (intercept), K₁= 2.303×slop). The pseudo second order is given by Eq. (3.16)

$$\frac{t}{q_t} = \frac{1}{K_2 2 q_e^2} + \frac{1}{q_e} t$$
(3.16)

Where, K_2 (gmg-¹min-¹), t, and qe, are the Pseudo-second-order rate constant, time, and adsorption capacity at equilibrium respectively. The value of the qe is determined from the plot of t/qt versus t (qe = 1/slop, intercept =1/K₂q²)

4.2.12 Statistical evaluation for adsorption kinetics for bod removal

The Total Error and Root Mean Square Error statistical expressions were used to evaluate the performance of the kinetic model. Model estimate values were compared with observed experimental values and deductions were made as to the best fit.

a. Total Error (Err^2) . Total error (in terms of adsorption experiment) is the sum of the

squares of the error between the calculated adsorption capacity and the expected adsorption capacity of a kinetic model. This is a measure of variation in value not explained by the values obtained. The lower the value of total error obtained, the higher the accuracy, validity and good fitness of the method (model). Mathematically, Total error is given by Eq. (3.17)

$$\mathbf{Err}^{2} = \sum_{i=1}^{n} (Y_{o} - Y_{e})^{2}$$
(3.17)

Where n, Y_o, Y_e, are the number of data points, obtained experimental adsorption capacity values, and computed adsorption capacity value respectively (for the kinetic models).

b. *Root Mean Square Error (RMSE)*. It is an absolute measure of fit can be interpreted as the standard deviation of the unexplained variance. It has the useful property of being in the same units as the response variable. Lower values of RMSE indicate better fit. It is represented by Eq. (3.18)

$$RMSE = \frac{1}{\pi} \sqrt{\sum_{i=1}^{n} (Y_o - Y_e)^2}$$
(3.18)

Where n, Yo, Ye, are the number of data points, obtained experimental adsorption capacity values, and computed adsorption capacity value respectively (for the kinetic models)

4.2.13 Determination of sludge characteristics

a. *Total Nitrogen Determination:* DANI 89.00 CHN elemental analyzer was used to determine the nitrogen content of the sludge. This instrument automatically determines C-H-N by combustion of the sample, separation of the combustion products by means of a programmed temperature desorption system, and measurement by thermal conductivity.

b. Organic Carbon: DANI 89.00 CHN elemental analyzer was used to determine the total

organic carbon of the waste content. Determination was carried out by running replicates at 500° and 1100°C with the Analyzer

c. *Organic Matter*: The organic matter in the sludge was determined by oxidation using potassium permanganate by gravimetric method of chemical analyses.

d. *Total Volatile Solids*: Total volatile solids were determined using gravimetric method as outlined by the USEPA Method 1684 for the determination of total solids and the fixed and volatile fractions in such solid and semisolid samples as soils, sediments, biosolids (municipal sewage sludge), sludge separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other sludge dewatering processes.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Chemical Composition and Active Compounds.

Table 4.1 and 4.2 shows the results of the analyses of chemical composition and active compounds in Mangifera indica and Phoenix dactylifera seeds powders respectively carried out in the Department of Water Resources Engineering and Multiuser laboratories of ABU Zaria. Both seeds were found to contain potassium and sodium as macro elements while calcium, iron, manganese, magnesium, lead and zinc are micro elements. All the elements except Lead and Magnesium, fall within the acceptable limits for drinking water as contained in the Nigeria Drinking Water Standards (Table 2.1). All the elements were found to be below the maximum allowable limits for effluent discharge by the National Environment Standards for Discharge of Effluent into Water or on Land Regulations, 1999. Table 4.2 gives the result of the SEM and XRD analyses carried out at the department of Physics, Umaru Musa Yar'adua University, Kastina. The result showed that Mangifera indica contains mango starch, p-Carboxybenzaldehyde, which is a polyphenolic compound and o-Phthalic acid, while *Phoenix dactylifera* contains Potassium Aluminum Silicate and Potassium Copper Chloride Hydrate as the active compounds. P-Carboxybenzaldehyde is used as Intermediate for Pharmaceuticals and as a metabolite in ampicillin (PubChem, 2004). O-Phthalic acid is used in the production of chemicals such as dyes, perfume and saccharin. Potassium Aluminum Silicate is mostly used as an anti-caking agent (Frank, 2015).

	Potassium %	Sodium %	Calcium ppm	lron ppm	Manganese ppm	Magnesium ppm	Lead ppm	Zinc ppm
Mangifera I	1.14	0.4	8.14	4.63	0.18	12.15	0.13	0.08
Phoenix D	0.36	0.28	6.95	2.39	0.00	6.82	0.22	0.12

Table 4.1 Chemical Compositions of Mangifera indica and Phoenix dactilyfera seeds

Table 4.2 Active compounds in *Mangifera indica* and *Phoenix dactylifera* seeds

SAMPLE	ACTIVE COMPOUNDS
	Carbon hydrogen
	Mango starch (C₀H10O₅)n
	p-Carboxybenzaldehyde (CଃH₅O₃)
Mangifera Indica	o-Phthalic acid (C₈H₆O4)
	Potassium Aluminum Silicate (KAISi₃O₅)
Phoenix Dactylifera	Potassium Copper Chloride Hydrate (K2CuCl4·2H2O)

4.2 Proximate Analysis of Mangifera indica and Phoenix dactylifera seeds

Table 4.3 shows that Mangifera indica and Phoenix dactylifera have protein values of

6.81 % and 4.94 % respectively, ash content of 2.44 % and 1.61 %, crude fiber of 8.01 % and 19.33 %, oil of 3.63 % and 5.36 % respectively. This is within the range of the results of the similar studies on mangoes and dates reported by Mutua *et al.* (2016) and Harrasi *et al.* (2014) respectively. However, the results of the proximate analysis differ slightly from those of other seeds like *moringa* which has been reported by Mikore and Mulugeta (2017) to have a crude protein value of between 24 to 28 %, ash content of between 14 to 16 %, crude fiber of between 5 to 7 % and oil of between 3 to 7 %.

	Moisture	Dry	Crude	Crude	Oil	Ash	Nitrogen
	Content %	Matter %	Protein %	Fiber %	%	%	FE %
Mangifera							
1	9.33	90.67	6.81	8.01	3.63	2.44	69.78
Phoenix D	16.18	83.82	4.94	19.33	5.36	1.61	52.58

 Table 4.3 Proximate Analysis of Mangifera indica and Phoenix Dactylifera seeds

4.3 3 Treatability Studies

Table 4.4 shows the parameters of the raw water before application of the treatment with the natural coagulants, while Tables 4.5, 4.6 and 4.7 show the results of the parameters after the application of graduated dosages of *Mangifera indica*, *Phoenix dactylifera*, and the combination of the two seeds on the raw water respectively. Finally, Table 4.8 shows the results of the parameters with the application of Alum as the coagulant.

The result as given in Table 4.5 shows that 90 % of the Turbidity was removed at a dosage of 25 mg/L. 96 % of BOD and 99 % of Coliforms were removed with a dosage of 25 mg/L at a pH of 6.9. Similarly, the electrical conductivity was reduced by 32 %, COD by 84

%, and TDS by 19 % using *Mangifera indica* at a dosage of 25 mg/L. This result was observed to be consistent with results from similar experiments with other plants as coagulants. Birima *et al.* (2015) reported 92 % turbidity removal efficiency with peanut seeds, while Thakur and Choubey (2013) reported 91 %. The 99 % total Coliform removal efficiency is higher than the 75 % reported by Nnaji (2017) using Garcinia kola. Kalibbala (2007) reported an increase in conductivity with the use of moringa as coagulant and as coagulant aid.

Jar test results are presented in Table 4.6 with Phoenix dactylifera as the

coagulant. It had 99 % and 96 % efficiency in removing total coliforms and BOD at a dosage of 25 mg/L and 20 mg/L respectively but had only 75 % efficiency in the removal of Turbidity of the wastewater at a dosage of 5 mg/L. 81 % of the COD was removed at a dosage of 25 mg/L, EC was reduced by 28 % and TDS by 16 % all at a dosage of 25 mg/L. The BOD level was lowered to 5 mg/L and the Coliform to 3 CFU/100 ml all at a dosage of 25 mg/L. These values are within the range set by the Drinking Water Quality standards of Nigeria (Table 2.1).

Table 4.7 shows the result of the Jar test with Mangifera indica and Phoenix dactylifera combined in varying dosages as coagulants. Turbidity removal efficiency of 91 % was observed at a combined dosage of 20 mg/L and 5 mg/L of Mangifera indica and Phoenix dactylifera respectively. 86 % BOD removal and 88 % total coliforms removal was observed while COD was reduced by 78 %, all at a combined dosage of 5 mg/L Mangifera indica and 20 mg/L Phoenix dactylifera. EC was reduced by 30 %, and TDS by 19 % at a combined dosage of 5 mg/L and 20 mg/L, 12.5 mg/L each of Mangifera indica and Phoenix dactylifera respectively. The reduction in efficiency of the combined seeds is consistent with the observation by Neeraj (2013) when he combined chitosan and moringa as coagulants to treat wastewater. The reduced efficiency of the combined seeds may be attributed to coagulant extract deterioration. This occurred possibly due the seeds extract being stored for more than 24 hours at room temperature before it was used (Saulawa et al. 2008). Freshly prepared seed extracts have been shown to lose their potency when stored at room temperature for more than 24 hours (Dishna 2000; Saulawa 2008,). Another possible explanation for the reduction in their combined efficiency

is due to inter particle interaction of the two seeds. When extract of crushed seeds are added to raw water, the proteins produce positive charges acting like magnets and attracting the predominantly negatively charged particles such as clay, silk, bacteria, and other toxic particles in water (Dishna, 2000; Muruganandam *et al.*, 2017), but in this case, instead of attracting the negatively charged particles from the raw water, the acid–base equilibria was dominated by preferential solvation of the ions by water molecules in the mixtures, forming new compounds (Cox, 2015.) and furthering the loss of the potency of the extracts.

Table 4.8 shows the result of the Jar test with Alum as the coagulant. The removal efficiency was similar to that of the bio coagulants used in the experiment. It reduced the BOD of the wastewater by 96 %, COD by 87 %, turbidity by 97 %, total coliforms by 99% at a dosage of 25 mg/L. TDS was reduced by 11 % and EC by 24 % at a dosage of 12.5 mg/L.

 Table 4.4 Natural Turbid Wastewater Parameters

SAMPLE	EC µS/cm	BOD mg/L	COD mg/L	TURB NTU	TDS mg/L	рН	Temp °C	Coliforms CFU/100ml
RAW	4000	140	1000	796	1728	6.9	26.6	>350x10 ⁴

Table 4.5 Jar Test results with Mangifera indica

SAMPLE	DOSAGE mg/L	EC μS/c	BOD mg/L	COD mg/L	TURB NTU	TDS mg/L	рН	Temp °C	Coliforms CFU/100ml
		m							(X 10 ⁴)
MI	5	2736	55	380	185	1449	7.8	28.4	75
MI	10	2803	35	200	185	1503	7.1	28.2	28
MI	12.5	2994	15	190	155	1510	7.1	27.5	21
MI	15	2846	10	180	118	1469	7.5	27.5	7
MI	20	2996	5	170	99.3	1773	7.0	28.1	2
MI	25	2955	5	160	79.9	1396	6.9	27.7	9

SAMPLE	DOSAGE mg/L	EC μS/cm	BOD mg/L	COD mg/L	TURB NTU	TDS mg/L	рН	Temp °C	Coliforms CFU/100ml
PD	5	3187	90	330	198	1584	69	26.9	75
PD	10	3069	80	320	226	1532	6.8	28.1	68
PD	12.5	2861	25	310	238	1504	6.9	28.2	65
PD	15	2986	20	270	225	1480	7.6	28.6	36
PD	20	2940	5	220	237	1466	6.8	27.0	3
PD	25	2912	5	190	241	1452	6.8	28.3	7

Table 4.6 Jar Test results with PD

Table 4.7 Jar Test result with combination of MI and PD

SAMPLE	DOSAGE	EC	BOD	COD	TURB	TDS	рΗ	Temp	Coliforms
	mg/L	μS/cm	mg/L	mg/L	NTU	mg/L		°C	CFU/100
									ml
MI: PD	20:5	2811	50	350	74.9	1418	7.1	25.4	235
MI: PD	15:10	2849	40	280	107	1437	7.3	24.9	250
MI: PD	12.5:12.5	2860	35	270	125	1405	6.9	24.7	60
MI: PD	10:15	2852	35	220	132	1426	7.1	25.0	46
MI: PD	5:20	2800	20	220	151	1416	6.8	25.4	42

Table 4.8 Jar test results with Alum

SAMPLE	DOSAG E mg/L	EC µS/cm	BOD mg/L	COD mg/L	TURB NTU	TDS mg/L	рН	Temp °C	Coliforms CFU/100ml
	0,	1 /	0,	0,		0,			,
Al	5	3100	45	340	54.8	1555	6.9	26.1	125
Al	10	3127	30	240	53.3	1572	6.7	25.9	85
Al	12.5	3026	25	210	44.2	1527	7.5	26.2	29
Al	15	3186	15	200	27.0	1578	7.2	24.5	250
Al	20	3046	10	180	21.6	1560	6.8	27.7	87
Al	25	3153	5	130	24.8	1575	6.5	26.8	5

4.4 4 Regression Analyses

Tables 4.9 to 4.11 show the regression analysis for the *Mangifera indica* dosage with turbidity and pH as well as the analysis of variance. Table 4.9 shows the regression analysis of the Jar test results with *Mangifera indica* as the coagulant. From the analysis, 98.3 % change in dependent variable (Turbidity) of the wastewater can be predicted by the independent variables (Dosage and pH). The regression model has a strong correlation of 99.14 %. Table 4.10 shows the ANOVA result of the Jar test results with *Mangifera indica* as the coagulant. With F statistics of 86.76 and P-value of 0.0022, it shows that the model is statistically significant (McLeod, 2019). Table 4.11 gives the individual P-values and standard errors of the independent variables.

Tables 4.12 to 4.14 show the regression analysis for the *Phoenix dactylifera* dosage with turbidity and pH as well as the analysis of variance. Table 4.12 shows the regression analysis of the Jar test results with *Phoenix dactylifera* as the coagulant. From the analysis, 95.6 % change in dependent variable (Turbidity) of the wastewater can be predicted by the independent variables (Dosage and pH). The regression model has a strong correlation of 97.77 % (Weaver, 2003). Table 4.13 shows the ANOVA result of the Jar test with *Phoenix dactylifera* as the coagulant. With F statistics of 14.5 and P-value of 0.06, it shows that the model is statistically significant. Table 4.14 gives the coefficients of the regression model.

Regression Analysis with MI							
Multiple P (Correlation)	0.001465857						
R Square	0.983004545						
Adjusted R Square	0.971674242						
Standard Error	7.517190294						
Observations	6						

Table 4.9 Regression Analysis of Mangifera indica dosage

Table 4.10 Analysis of variance of *Mangifera indica* dosage

Analysis of Variance										
	df	SS	MS	F	Significance F					
Regression	2	9805.168884	4902.584	86.75889	0.00221564					
Residual	3	169.5244498	56.50815							
Total 5 9974.693333										

Table 4.11 Regression Coefficients

	Coefficients	Standard Error	t Stat	P-value
Intercept	623.3719474	113.7205999	5.48161	0.01194
DOSAGE mg/L	-7.821799073	0.705323566	-11.0897	0.001571
pН	-51.46599691	14.62805034	-3.51831	0.038965

Analysis model of dosage with Phoenix dactylifera Regression Statistics

Regression	Juisues
Multiple R	0.977773526
R Square	0.956041069
Adjusted R Square	0.890102672
Standard Error	5.265652456
Observations	6

ANOVA with Phoenix dactylifera							
	df	SS	MS	F	Significance F		
Regression	3	1206.045808	402.0152695	14.49900388	0.065208353		
Residual	2	55.45419157	27.72709578				
Total	5	1261.5					

Table 4.13 Analysis of variance for dosage with *Phoenix dactylifera*

Table 4.14 Regression coefficients with Phoenix dactylifera

	Coefficients	Standard Error	t Stat	P-value
Intercept	1552.758575	364.6003305	4.258796401	0.050957298
DOSAGE mg/L	-2.978520574	1.344913477	-2.214655906	0.157181951
TDS mg/L	-0.723537873	0.198158586	-3.651307208	0.067501072
pН	-27.89632455	9.807916593	-2.844266087	0.104577759

4.5 5 Correlation Analyses

Tables 4.15 to 4.17 show the correlation analysis between dosage with turbidity and total coliforms. Table 4.15 shows a strong negative correlation (95.5%) between dosage and Turbidity, meaning that an increase in the dosage gives a corresponding decrease in turbidity, while table 4.16 shows a strong negative correlation (77.98%) between dosage and total coliforms, meaning that increasing the dosage decreases the total coliforms correspondingly.

Table 4.17 shows the correlation analysis for the Jar test of *Phoenix dactylifera* dosage with turbidity. It shows a strong positive correlation (80.8 %) between dosage and turbidity.

Tables 4.18 to 4.19 show the correlation analyses of the Jar test results with combined dosage of *Mangifera indica* and *Phoenix dactylifera* in different proportions. The analyses show a strong positive correlation between the combined dosage and the turbidity, but a weak negative correlation between the combined dosage and coliforms. This suggests that only 30 % reduction in total coliform can be attributed to the combination of the seeds extract. The reason for this may be due to inter particle interaction between *Mangifera indica* and *Phoenix dactylifera* seeds (Cox, 2015; Dishna, 2000).

	DOSAGE mg/L	TURB NTU
DOSAGE mg/L	1	
TURB NTU	-0.955446748	1

Table 4.15 Correlation analysis between dosage with MI andTurbidity

Table 4.16 Correlation between dosage with MI and coliforms

	DOSAGE mg/L	Coliforms CFU/100ml (X 104)
DOSAGE mg/L	1	
Coliforms CFU/100ml (X 104)	-0.779844004	1

Table 4.17 Correlation between dosage with PD and turbidity

	DOSAGE mg/L	TURB NTU
DOSAGE mg/L	1	
TURB NTU	0.808509308	1

	DOSAGE mg/L	TURB NTU
DOSAGE mg/L	1	
TURB NTU	0.908772	1

Table 4.18 Correlation analysis for the combination of MI and PD with turbidity

 Table 4.19 Correlation analysis for the combination of MI and PD with coliforms

	DOSAGE mg/L	Coliforms CFU/100ml
DOSAGE mg/L	1	
Coliforms CFU/100ml	-0.30902	1

4.6 Mathematical Model of Turbidity Removal

Tables 4.20 to 4.24 show the different parameters for the mathematical model. Table

4.20 shows the equation of the model, Table 4.21 the analysis of variance for the model,

Table 4.22 goodness of fit statistics for the model, Table 4.23 model parameters and

Table

4.24 standardized coefficients of the model.

The mathematical model was developed with the help of XLSTAT statistical software with the objective of optimizing the response (Turbidity removal) which is influenced by some independent variables (dosage, pH). A P-value of 0.005 from the analysis of variance (Table 4.21) shows that the model is very significant in describing the outcome of the experiment (McLeod, 2019). The percentage variation of the dependent variable (Turbidity) that can be accounted for by the independent variables (Dosage and pH) is given by R^2 which is shown from the goodness of fit table to be 0.875 (Table 4.22). Thus, the proportion of the variability in the response (Turbidity) that is fitted by the model is 87.5 % (Weaver, 2003).

Figure 4.2 shows the 3-D plot for the model. The optimum dosage is given by the blue shaded area on the plot.

Table 4.20 Equation of model Equation of the model:

Turbidity

2.5821*Dosage+4.875*pH+145.0625*Dosage^2+25.5625*pH^2-

10.25*Dosage*pH

=

Table 4.21 Model ANOVA

Analysis of variance for the Model							
Source	DF	Sum of squares	Mean squares	F	Pr > F		
Model	5	147362.838	29472.568	9.772	0.005		
Error	7	21111.162	3015.880				
Pure error	4	0.000	0.000				
Corrected Total	12	168474.000					

Table 4.22 Goodness of fit

Goodness of fit statistics for the model	
Observations	13
Sum of weights	13
DF	7
R ²	0.875
Adjusted R ²	0.785
MSE	24067.714
RMSE	155.138
Q ²	0.109

Table 4.23 Model parameters

Model parameters:							
Source	Value	Standard error	t	$\Pr > t $	Lower bound (95%)	Upper bound (95%)	
Intercept	0.000	24.560	0.000	1.000	-58.074	58.074	
Dosage	2.582	19.416	0.133	0.898	-43.330	48.494	
рН	4.875	19.416	0.251	0.809	-41.037	50.787	
Dosage^2	145.063	20.821	6.967	0.000	95.828	194.297	
pH^2	25.562	20.821	1.228	0.259	-23.672	74.797	
Dosage*pH	-10.250	27.459	-0.373	0.720	-75.179	54.679	

 Table 4.24 Standardized coefficients

Standardized coefficients:						
Source	Value	Standard error	t	$\Pr > t $	L bound (95%)	U bound (95%)
Dosage	0.018	0.134	0.133	0.898	-0.299	0.334
pН	0.034	0.134	0.251	0.809	-0.283	0.350
Dosage^2	0.940	0.135	6.967	0.000	0.621	1.259
pH^2	0.166	0.135	1.228	0.259	-0.153	0.485
Dosage*pH	-0.050	0.134	-0.373	0.720	-0.366	0.266



Fig 4.1 Contour plot for the model



Fig 4.2 3D model plot of the experiment

4.7 Isothermal studies

The experimental data over the concentrations ranges of 5-25mg/l was processed using the Langmuir isotherm model at a temperature of 28 O C. Linear plots of C_e/q_e vs.C_e (Figures 4.3-4.5) were employed to determine the values of Langmuir constants Qm (mg/g) and K_L (L/mg) from the slope and intercept of the plots respectively. Table 4.25 shows the Langmuir isotherm parameters for dosages with *Mangifera indica*, *Phoenix dactylifera* and a combination of the two in varying proportions. The R_L values were calculated from Equation (3.13). Table 4.26 shows the separation factor (R_L) for the dosages. The constants K_L and Q_M relate to the energy of adsorption and maximum adsorption capacity (Desta, 2013).

From Table 4.25, it was observed that the combination of the seeds extract gave a higher value of maximum adsorption capacity Q_M , than either of the individual seeds. The coefficient of determination R^2 , for MI was the highest which shows the degree to which the model fits the experiment.

The separation factor R_L , which is indicative of the isotherm shape that predicts whether an adsorption system is 'favourable' or 'unfavourable' (Saswati and Gosh, 2005), obtained for different initial concentrations for MI and PD and the combined dosage were between the values $0 < R_L < 3$. According to Mamdouth *et.al.* (2004) Saswati and Gosh, (2005), R_L values between 0 and 1 indicate favourable adsorption, however, the negative sign on the separation factor for both seeds and their combination, for the different initial concentration indicates that the model is not linear and does not fit into the Langmuir isotherm model (Maarof *et al.*, 2005; Igwe *et al.*, 2007 Kiurski *et al.*, 2012;).

 Table 4.25 Langmuir Isotherm Parameters and R²

Parameters	MI	PD	Combination (MI &PD)
Qm	3.62	3.55	19.08
K _L	-0.13	-0.12	-0.98
\mathbb{R}^2	0.92	0.86	0.87

Initial Concentration	R _L Values			
	MI	PD	Combination (MI & PD)	
5	2.86	2.50	-0.26	
10	-3.33	-5.00	-0.11	
12.5	-1.60	-2.00	-0.09	
15	-1.05	-1.25	-0.07	
20	-0.63	-0.71	-0.05	
25	-0.44	-0.50	-0.04	

Table 4.26: Separation Factor (R_L) of MI, PD, and Combination (MI &PD at Different Initial Concentrations



Figure 4.3 Langmuir Isotherm for Dosage with MI



Figure 4.4 Langmuir Isotherm for Dosage with PD



Figure 4.5 Langmuir Isotherm for Combined Dosage (MI & PD)

The Freundlich isotherm is introduced as an empirical model, where q_e represents the amount adsorbed per amount of adsorbent at the equilibrium (mg/g), Ce represents the equilibrium concentration (mg/L), K_f and n are parameters that depend on the adsorbate and adsorbent (Desta, 2013). Freundlich equilibrium

constants were determined from the plot of Log q_e vs. Log C_e (Fig 4.3-4.5), with the intercept = Log K_f, and the gradient = 1/n. The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is a chemical process; if n>1, then adsorption is a physical process (Desta, 2013). Values of n (which reflects the intensity of adsorption) ranging between 1 and 10; represents favorable adsorption (Adie *et al.*, 2012). The values obtained (Table 4.27) were in the range of 0<n<1 for both MI and PD, suggesting that each of the process follows the Freundlich Isotherm model and is a chemical process (Al.Jlil *et al.*, 2013; Desta, 2013; Kilic *et al.*, 2014). The combination (MI & PD) gave a value of n>1 which indicates that the experiment was more of a physical rather than a chemical process. The coefficient of determination R², were above 0.7 (70%) for all the dosages suggesting the high degree to which the experimental data fits the model.

Parameters	MI	PD	Comb	
$K_f(mg/g)$	0.48	0.56	0.23	
n (g/mg)	0.59	0.49	2.18	
\mathbb{R}^2	0.92	0.84	0.74	

 Table 4.27 Freundlich Isotherm Parameters and R²



Figure 4.6 Freundlich Isotherm for Dosage with MI



Figure 4. 7 Freundlich Isotherms for Dosage with PD



Figure 4.8 Freundlich Isotherm for Combined Dosage (20 mg/L MI & 5 mg/L PD)

4.8 Kinetic Studies

Kinetics is of great significance to evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms. The study provides information about the possible mechanism of adsorption and the different transition states on the way to the formation of the final adsorbate-adsorbent complex and helps develop appropriate models to describe the interactions (Vijayakumar *et al.*, 2011, Adie *et al.*, 2012). The Pseudo-first and second order kinetic models were studied from the plots of time versus amount (mg/l) of BOD removed using MI, PD and the combination of the two.

a. *Pseudo-first-order kinetic model*: The Pseudo-first order model is as expressed in Equation (3.15). The values of K_1 and qe were determined respectively from the slope and intercept of the plot of Log (qe-qt) versus t, as shown in Figures 4.9 - 4.11 and the values of K_1 , qe and coefficients of determination (\mathbb{R}^2) are tabulated in Table 4. 28
b. *Pseudo-second order Kinetic Model*: The Pseudo-second order model equation is as expressed in Equation (3.16). The values of K_2 (g/mg/min), and qe (mg/g), were determined respectively from the intercept and slope of the plot of t/qt versus t as shown in Figs 4.12 – 4.14.

From Table 4.28 it was observed that the calculated value of the adsorption capacity from the Pseudo-second-order models (plots) q_e calc. (mg/g), are closer to the observed experimental values of the adsorption capacity of both adsorbent from experiment q_e exp. (mg/g) for the BOD removal. The coefficients of determination, R² are closest to unity for the pseudo-second-order kinetics than the pseudo-first-order kinetic. This suggests that the adsorption system can be better represented by the pseudo-second-order model (Adie *et al.*, 2012). The high correlation coefficient, R² for the pseudo-first-order may indicate that the present system may be followed by pseudo-first-order (Vijayakumar *et al.*, 2011, Neto *et al.*, 2013)

REACTION OR	DER	MI	PD	COMB
Pseudo-first	q e exp . (mg/g)	55	80	50
order	$K_1(min^{-1})$	0.058	0.064	0.054
Parameters	q e calc. (mg/g)	43.68	86.23	30.12
	R ²	0.95	0.93	0.97
Pseudo-second	q _e exp. (mg/g)	55	80	50
order	$K_2(min^{-1})$	0.00104	0.00167	0.00138
Parameters	qe calc. (mg/g)	60.61	83.33	54.35
	\mathbb{R}^2	0.99	0.99	0.99

 Table 4.28 Kinetic Parameters for BOD removal with MI, PD, and their combination



Figure 4.9 Pseudo first order model for BOD removal with MI



Figure 4.10 Pseudo first order model for BOD removal with PD



Figure 4.11 Pseudo first order model for BOD removal with combined dosage



Figure 4.12 Pseudo second order for BOD removal with MI



Figure 4.13 Pseudo second order for BOD removal with PD



Figure 4.14 Pseudo second order for BOD removal with combined dosage

4.9 Statistical Evaluation of Adsorption Kinetics for BOD Removal.

Statistical evaluation of the BOD removal with *Mangifera indica*, *Phoenix dactylifera* and their combination was carried out using the Total Error and the Root Mean Square Error (RMSE) as given by equations (3.17) and (3.18). Table 4.29 shows the error parameters for the pseudo-first and second order. From Table 4.29, it was observed that the pseudo-second-order kinetic model was statistically significant for the BOD removal using *Mangifera indica* and *Phoenix dactylifera* based on the higher correlation coefficients, lower total error and

root mean square error values. Generally, the lower the values of Total error and RMSE, the higher the accuracy, validity and good fitness of the model (Hooper *et al.*, 2008, Adie *et al.*, 2012, Samarghandi *et al.*, 2009). This result also agrees with similar studies carried out on the evaluation of performance for BOD removal using statistical tools such as the RMSE, Regression analysis and Total error (Abyaneh, 2014; Pompeu, 2017; Wei, 2013).

Reaction Order		MI	PD	COMB
Pseudo-first order	Total Error (Err ²)	128.14	38.81	395.21
Parameters	Root Mean Square	11.32	6.23	19.88
	Error (RMSE)			
	\mathbb{R}^2	0.9509	0.9333	0.9733
Pseudo-second order	Total Error (Err ²)	31.47	11.09	18.92
Parameters	Root Mean Square	5.61	3.33	4.35
	Error (RMSE)			
	\mathbb{R}^2	0.9954	0.9993	0.9987

Table 4.29 Statistical Evaluation for Adsorption Kinetics for BOD Removal with MI, PD and their combination

4.10 Sludge Characterization

To treat and dispose of the solids produced from wastewater treatment plants in the most effective manner, it is important to know the characteristics of the solids that will be processed. Some of the characteristics of the wastewater sludge from this research are given in Table 4.30.

Parameters	Results (mg/L)	
Total Nitrogen (N)	8070	
Organic Carbon (O.G)	10400	
Organic Matter (O.M)	17900	
Total Volatile Solids (TVS)	570	
Carbon-Nitrogen Ratio	29:1	

Table 4.30 Sludge Parameters

Nitrogen and phosphorus are the most abundant major plant nutrients in sludge (Tchobanoglous and Burton, 1991; Mtshadi *et al.*, 2014). Sludge that is treated typically contains 1 - 6 percent nitrogen by dry weight (Dean and Smith, 1973). Hence sludge can be a reliable source of nitrogen and phosphorus which are major nutrients required by plants for proper growth. The nitrogen content of this sludge was observed to be less than 1 % (0.8 %) which is typical of treated waste (Mtshadi *et al.*, 2014 Nourmohammadi *et al.*, 2013). The result of the sludge sample shows low content of organic carbon and organic matter (1.04 % organic carbon, 1.7 % organic matter). The knowledge of carbon content in sludge samples is an important element in sludge treatment and disposal. Using TOC measurements, several compounds with carbon content can be determined. Organic matter present in sludge can pose a challenge for efficient treatment (Yang *et al.*, 2014; Indra and Sivaji, 2004). Typical content of organic carbon and organic matter in sludge treated with conventional chemicals have been reported to be in the range 10 % - 50 % (Mtshadi *et al.*, 2014; Tchobanoglous and Burton, 1991).

Total volatile solid (TVS) is a water quality measurement obtained from the loss on ignition of total suspended solids. It has great importance in water and wastewater treatment. The greater the concentration of organic or volatile solids, the stronger the wastewater. A test of TVS in sludge is very useful in the design and operation of sludge digest, vacuum filter and incineration plants (Spellman, 2004). The TVS value obtained for the sludge was found to be lower compared to sludge that has been treated (Wilkie *et al.*, 2004). This implies that this sludge will be suitable for land applications, as higher degradable organic material in sludge can lead to odor problems and attract vectors such as rodents (Tchobanoglous and Burton, 1991).

The amount of nitrogen mineralized is inversely proportional to the carbon to nitrogen (C/N ratio). Soils with large C/N ratio result in low quantities of mineralized nitrogen (Mtshadi *et al.*, 2014). A high C/N ratio of sludge ensures that there is limited mobilization of nitrogen by incorporation into cell mass. This in turn makes this nitrogen available at a later period when nitrogen is needed most for plants during the growing period (Mtshadi *et al.*, 2014; Sengupta, 2015). The C/N ratio falls within the range reported in the studies by Mtshadi *et al.*, (2014). The high C/N ratio is optimum for composting as a C/N weight ratio of 25 to 35 has been found to provide optimal conditions for compost process (Alidadi *et al.*, 2007).

4.11 Summary of Key Findings

A summary of the key findings of this research work are listed below

a) Both seeds (*Mangifera indica* and *Phoenix dactylifera*) contain Potassium (1.14%, 0.36% respectively) and Sodium (0.4%, 0.28% respectively) as macro elements while Calcium (8.14ppm, 6.95ppm respectively), Iron (4.63ppm, 2.39oom respectively), Manganese (0.18ppm, 0.00ppm respectively), Magnesium (12.15ppm, 6.82ppm respectively), Lead (0.13ppm, 0.22ppm respectively), and Zinc (0.08ppm, 0.12ppm respectively) are in the micro range.

b) Active compounds and proximate analyses of both seeds where carried out and results obtained are as follows: *Mangifera indica* contains mango starch, p-Carboxybenzaldehyde, and o-Phthalic acid. *Phoenix dactylifera* contains Potassium Aluminum Silicate and Potassium Copper Chloride Hydrate as the active compounds. *Mangifera indica* and *Phoenix dactylifera* have protein values of 6.81% and 4.94% respectively, ash content of 2.44% and 1.61%, crude fiber of 8.01% and 19.33%, oil of 3.63% and 5.36%.

c) *Mangifera indica* as coagulant removed 96% BOD, 84% COD, 89% Turbidity, and 99% Total coliform of the wastewater while *Phoenix dactylifera* removed 89% BOD, 81% COD, 75% Turbidity, and 99% Total coliform.

d) The adsorbate-adsorbent experiment was observed to be a chemical process which fits the Freundlich Isotherm model and follows the pseudo-second-order kinetic model.

e) An analysis of some parameters was carried out on the sludge constituents and results obtained are: 8070mg/L Total Nitrogen, 10400mg/L Organic Carbon, 17900mg/L Organic Matter, 570 mg/L Total Volatile Solids, and Carbon-Nitrogen Ratio is 1:29

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

The research set out to study the efficacy of combining *Mangifera indica* and *Phoenix dactylifera* seed powders as coagulants in wastewater treatment. Based on the research analyses carried out, the following conclusions have been drawn;

Both seeds (*Mangifera indica* and *Phoenix dactylifera*) contain Potassium and Sodium as macro elements while Calcium, Iron, Manganese, Magnesium, Lead, and Zinc are in the micro range.

Active compounds in both seeds were found to be as follows: *Mangifera indica* contains mango starch, p-Carboxybenzaldehyde, and o-Phthalic acid. *Phoenix dactylifera* contains Potassium Aluminum Silicate and Potassium Copper Chloride Hydrate as the active compounds.

The effective combined ratio for turbidity and total coliforms removal was observed to be 20mg/L of *Mangifera indica* combined with 5mg/L *Phoenix dactylifera* at pH of 7.1. *Mangifera indica* as coagulant, removed 96 % BOD, 84 % COD, 89 % Turbidity, and 99 % total coliform of the wastewater at an optimal dosage of 25 mg/L while *Phoenix dactylifera* removed 89% BOD, 81 % COD, 75 % Turbidity, and 99 % Total coliform at an optimal dosage of 25 mg/L.

The result of the Isothermal studies suggested that the experiment is a chemical process and fits the freundlich Isotherm model.

The experiment was observed to have followed the pseudo-second order kinetic model as indicated by the K_2 , R^2 , and Error analyses carried out on the experimental data.

The analyses results obtained from the various dosages suggested that *Mangifera indica* and *Phoenix dactylifera* seeds powders can be used as effective coagulants.

5.2 Recommendation

1. Further studies should be carried out on *Mangifera indica* and *Phoenix dactylifera* seeds especially on how to extract their active components and extend the extract's shelve life, since research has shown their potentials as bio coagulants

2. Research should be encouraged in the area of combining two or more plant extracts as coagulants, to ascertain the chemistry behind such mixtures and the exact mechanism guiding the interactions between the bio-coagulants.

3. Stake holders whose responsibilities include provision of potable water and protecting the environment should carryout sensitization of the communities where *Mangifera indica* and *Phoenix dactylifera* are grown and consumed, on their potentials for pre-treatment of wastewater that can be used for other domestic purposes other than drinking.

4. Government should set appropriate frame work so that the private sector can drive the development of simple technologies that can enhance the harvesting and preserving of seeds of *Mangifera indica* and *Phoenix dactylifera* for the purpose of using them in water treatment especially in rural areas where these fruits are grown.

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APPENDIX I

AAS Data for Compositional Analyses of Mango and Dates



 Analyst
 MUSRL/ABU Zaria

 Date Started
 8:24 AM 12/5/2017 GMT: 4:24 PM 12/5/2017

 Worksheet
 Calcium 86

 Comment
 Kuyihop Edward Agwam

 Methods
 Ca

 Computer name
 AAS-HP

 Serial Number:
 MY 14470001

Method: Ca water (Flame)



 Analyst
 MUSRL/ABU Zaria

 Date Started
 8:33 AM 12/5/2017 GMT: 4:33 PM 12/5/2017

 Worksheet
 Iron 011 11

 Comment
 Kuyihop Edward Agwam

 Methods
 Fe

 Computer name
 AAS-HP

 Serial Number:
 MY14470001

Method: Fe Water (Flame)



9:08 AM 12/5/2017

Page 1 of 1

 Analyst
 MUSRL/ABU Zaria

 Date Started
 9:00 AM 12/5/2017 GMT: 5:00 PM 12/5/2017

 Worksheet
 Manganase 74

 Comment
 Kuyihop Edw ard Agw am

 Methods
 Mn

 Computer name
 AAS-HP

 Serial Number:
 MY 14470001

Method: Mn water (Flame)



 Analyst
 MUSRL/ABU Zaria

 Date Started
 9:10 AM 12/5/2017 GMT: 5:10 PM 12/5/2017

 Worksheet
 Magnesium 001 85

 Comment
 Kuyihop Edward Agwam

 Methods
 Mg

 Computer name
 AAS-HP

 Serial Number:
 MY 14470001

Method: Mg WATER (Flame)



9:32 AM 12/5/2017

Page 1 of 1

 Analyst
 MUSRL/ABU Zaria

 Date Started
 9:24 AM 12/5/2017 GMT: 5:24 PM 12/5/2017

 Worksheet
 Lead 001 011 011 20

 Comment
 Kuyihop Edw ard Agw am

 Methods
 Pb

 Computer name
 AAS-HP

 Serial Number:
 MY 14470001

Method: Pb water (Flame)



10:17 AM 12/5/2017

Analyst	MUSRL/ABU Zaria
Date Started	9:33 AM 12/5/2017 GMT: 5:33 PM 12/5/2017
Worksheet	Zinc 001 38
Comment	Kuyihop Edward Agwam
Methods	Zn
Computer name	AAS-HP
Serial Number:	MY 14470001

Method: Zn Water (Flame)

SEM/XRD SLEVE ANALYSES REPORT FOR DATES SEED

Apr 4, 2018 4:21 PM (ARLservice)

Date seed.xml

Sleve Report

Experiment

 Search Line:
 5.49037A
 D1 Range:
 5.440A - 5.541A

 Search Line:
 5.57276A
 D1 Range:
 5.520A - 5.625A

 Search Line:
 4.40318A
 D1 Range:
 4.371A - 4.436A

 Search Line:
 4.44908A
 D1 Range:
 4.416A - 4.482A

 Search Line:
 5.67931A
 D1 Range:
 5.625A - 5.734A

 Search Line:
 5.67931A
 D1 Range:
 5.625A - 5.734A

 Search Line:
 3.74794A
 D1 Range:
 3.725A - 3.771A

 Search Line:
 2.67276A
 D1 Range:
 2.661A - 2.684A

 Search Line:
 2.65201A
 D1 Range:
 2.641A - 2.663A

 Rotation:
 All 8 Rotations
 X
 X

Preferences

Search Window:	0.15°	Match Window:	0.15°	Search Method:	Hanawalt	Lowest Allowable GOM:	2000
Wavelength:	Cu K1 1.54	056A					

Phases (2)

#	Accepted	PDF #	Compound Name	Int. Ratio	Int. %	I/Ic	Time
12	ชามด ชามอ	01-080-2109 01-076-0098	Potassium Aluminum Silicate Potassium Copper Chloride Hydrate	0.668 0.713	48 52	0.76	30.1s 15.2s

Lines (70 of 127)

Ex d(Å)	Ex I	P1 d(A)	P11	P2 d(Å)	P21	Ex d(A)	Ex I	P1 d(Å)	P11	P2 d(A)	P21
7.64198 7.50622 7.33863 7.19585	644 5					6.66156 6.54384 6.38965 6.24071	4854	6.550860 6.508500	10		

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Page 1/3

APPENDIX III

SEM/XRD SLEVE ANALYSES REPORT FOR MANGO SEEDS

May 1, 2018 9:59 AM (ARLservice)

MANGO SEED.xml

Sleve Report

Experiment

 Search Line:
 3.80488A
 D1 Range:
 3.781A - 3.829A

 Search Line:
 5.90526A
 D1 Range:
 5.847A - 5.964A

 Search Line:
 4.86237A
 D1 Range:
 4.823A - 4.902A

 Search Line:
 5.35198A
 D1 Range:
 5.304A - 5.400A

 Search Line:
 3.90381A
 D1 Range:
 5.304A - 5.400A

 Search Line:
 3.90381A
 D1 Range:
 3.878A - 3.929A

 Search Line:
 4.08461A
 D1 Range:
 4.057A - 4.112A

 Search Line:
 5.27601A
 D1 Range:
 5.229A - 5.323A

 Search Line:
 4.28332A
 D1 Range:
 4.253A - 4.314A

 Rotation:
 All 8 Rotations
 Search Line:
 4.253A - 4.314A

Preferences

Search Window: 0.15° Match Window: 0.15° Search Method: Hanawalt Lowest Allowable GOM: 2000 Wavelength: Cu K1 1.54056A

Phases (4)

#	Accepted	PDF #	Compound Name	Int. Ratio	Int. %	I/Ic	Time
1234	true true true	00-018-1727 00-052-2247 00-047-2046 00-013-0823	Carbon hydrogen Potato starch p-Carboxybenzaldehyde o-Phthalic acid	1.027 1.15 1.454 1.617	20 22 28 31	0.3	4.3s 2.6s 2.2s 2.3s

Lines (60 of 141)

Ex d(Å) Ex I P1 d(Å) P1 I P2 d(Å) P2 I P3 d(Å) P3 I P4 d(Å) P4 I 15.04365 19 12.

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APPENDIX IV

PSEUDO 1ST AND 2ND ORDER REACTION EXPERIMENTAL DATA AND CALCULATIONS FOR PD/MI

Table 4.31 Equilibrium concentratior	I for BOD adsorption	with Phoenix dact	ylifera
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Time (Hrs)	BOD (qt)	qe - qt	
20	65±0.3	15	
40	69 ± 0.4	11	
60	74±0.3	6	
80	76±0.5	4	
100	77±0.2	3	
120	78±0.1	2	
140	80±0.1	0	

Equilibrium conc (PD)= 80mg/g
Time (Hrs)	BOD (qt)	qe - qt				
20	39 ±0.4	16				
40	42 +0.4	12				
40	42 ±0.4	15				
60	46 ±0.2	9				
80	49 ±0.1	6				
100	53 ±0.1	2				
120	54 ±0.3	1				
140	55 ±0.2	0				
	Equilibrium Conc (MI) = 55mg/g					

 Table 4.32 Equilibrium concentration for BOD adsorption with Mangifera indica

Table 4.33 Equilibrium concentration for BOD adsorption with
combination of Mangifera indica and Phoenix dactylifera seeds
extract

Time (Hrs)	BOD (qt)	qe - qt
20	35 ±0.3	15
40	39 ±0.3	11
60	45 ±0.1	5
80	46 ±0.4	4
100	48 ±0.4	2
120	49 ±0.1	1
140	50 ±0.3	0

Equilibrium Conc (COMB) = 50mg/g

Pseudo 1st Order Calculations

 $Q_e = e^{intercept}; K_1 = 2.303 *$ Slop. For MI, from figure 4.9, Y= -0.0254x +3.7768

For COMB, from figure 4.11,

Y = -0.0234x + 3.4053

 $Q_{e \text{ Calculated}} = e^{3.4053} = 30.12 \text{ mg/g}$ $K_1 = 2.303 * 0.0234 = 0.054 \text{ min}^{-1}$

Pseudo 2nd Order Calculations

* intercept) Q_e= 1/slop; K₂= 1/ (q²

For MI, from figure 4.12,

Y = 0.0165x +

0.2624,

 $Q_{e \ Calculated} = 1/0.0165 = 60.61 mg/g$

 $K_2 = 1/(60.61*0.2624) = 0.00104 \text{ gmg}^{-1}\text{min}^{-1}$

For PD, from figure 4.13,

Y = 0.012x +

0.0865,

 $Q_{e\,Calculated}=1/0.012{=}\,83.33mg/g$

 $K_2 = 1/(83.33*0.0865) = 0.00167 \text{ gmg}^{-1}\text{min}^{-1}$

For COMB, from figure 4.14,

Y = 0.0184x + 0.2456,

 $Q_{e \ Calculated} = 1/0.0184 = 54.35 mg/g$

 $K_{2}{=}\;1/\;(54.35{*}0.2456)=0.00138\;gmg^{-1}min^{-1}$

APPENDIX V

LANGMUIR AND FREUNDLICH ISOTHERMS CALCULATIONS

		Langmuir (MI)	Freundlich (MI)	
Ce	q _e	Ce/qe	log C _e	Log q _e
5	55	0.090909	0.69897	1.740363
10	35	0.285714	1	1.544068
12.5	15	0.833333	1.09691	1.176091
15	10	1.5	1.176091	1
20	5	4	1.30103	0.69897
25	5	5	1.39794	0.69897

 Table 4.34 Langmuir and Freundlich isotherm calculations for Mangifera indica

Table 4.35 Langmuii	and Freundlich isotherm calculations for <i>Phoenix</i>
dactylifera	

		Langmuir (PD)	Freundl	ich (PD)
Ce	q e	C_e/q_e	Log C _e	Log q _e
5	90	0.055556	0.69897	1.954243
10	80	0.125	1	1.90309
12.5	25	0.5	1.09691	1.39794
15	20	0.75	1.176091	1.30103
20	5	4	1.30103	0.69897
25	5	5	1.39794	0.69897

Langmuir Calculations

From eqn 3.12

 $Q_m = 1/slop$; $K_L = 1/(Q_m * Intercept)$; $R_L = 1/(1+K_LC_o)$ For

MI, from figure 4.3

Y = 0.2761x - 2.0745

$$Q_m = 1/0.2761 = 3.61g/g; K_L = 1/(3.62 * -2.0745) = -0.13L/g;$$
 For
C₀=5, R_L= 1/(1+(-0.13*5))= 2.86g/L.

Similarly,

For $C_0=10$, $R_L=1/(1+(-0.13*10))=-3.33g/L$

For $C_0=12.5$, $R_L= 1/(1+(-0.13*12.5))=-1.60g/L$, etc

For PD, from figure 4.4 Y=

0.2818x - 2.371

 $Q_m = 1/0.2818 = 3.55g/g; K_L = 1/(3.55 * -2.371) = -0.12L/g$ For

 $C_0=5$, $R_L= 1/(1+(-0.12*5)) = 2.50g/L$.

Similarly,

For $C_0=10$, $R_L=1/(1+(-0.12*10)) = -5.00g/L$

For $C_0=12.5$, $R_L= 1/(1+(-0.12*12.5)) = -2.00g/L$, etc

For COMB, from figure 4.5 Y=

0.0524x - 0.0533

 $Q_m = 1/0.0524 = 19.08g/g$; $K_L = 1/(19.08 * -2.0745) = -0.98L/g$ For

$$C_0=5, R_L=1/(1+(-0.98*5))=-0.26g/L.$$

Similarly,

For $C_0=10$, $R_L=1/(1+(-0.98*10)) = -0.11g/L$

For $C_0=12.5$, $R_L= 1/(1+(-0.98*12.5)) = -0.09g/L$, etc

Freundlich Calculations

From Eqn. 3.14

$$K_f = Log(intercept)$$
; $n = 1/slop$ For

MI, from figure 4.6,

 $Y = -1.6796x + 3.0105 K_{F} =$

Log 3.0105 = 0.48 L/g

$$n = 1/1.6796 = 0.59$$

For PD, from figure 4.7, Y = -

 $2.0482x + 3.6029 \ K_{F}\!\!=$

Log3.6029 = 0.56L/g

$$n=1/2.0482=0.49$$

For COMB, from figure 4.8, Y = -

0.4591x + 1.7289

 $K_{F}\!\!=Log1.7289=0.24L/g~n\!\!=$

1/0.4591 = 2.18

APPENDIX VI

STANDARD DEVIATION OF JAR TEST EXPERIMENTAL DATA

SAMPLE	DOSAGE mg/L	EC µS/cm	BOD mg/L	COD mg/L	TURB NTU	TDS mg/L	Coliforms CFU/100ml (X 10 ⁴)
MI	5	2736 ±10	55±0.5	380 ±2	185±1	1449±8	75 ±3
MI	10	2803 ±6	35 ± 0.8	200 ±1	185 ±3	1503±5	28 ±2
MI	12.5	2994 ±6	15 ± 0.3	190 ±3	155±4	1510 ±6	21 ±2
MI	15	2846 ±8	10 ±0.3	180 ±4	118 ±2	1469±7	7±2
MI	20	2996 ±4	5±0.7	170 ±2	99.3 ±1	1773±5	2 ±3
MI	25	2955 ±9	5±0.2	160±3	79.9 ±1	1396 ±4	9±1

Table 4.36 Standard deviation for Jar test with MI seed extract as the coagulant

Table 4.37 Standard deviation for Jar test with PD seed extract as the coagulant

SAMPLE	DOSAGE mg/L	EC μS/cm	BOD mg/L	COD mg/L	TURB NTU	TDS mg/L	Coliforms CFU/100ml
PD	5	3187 ±11	90 ±1	330±2	198±3	1584±8	75±2
PD	10	3069 ±9	80 ±0.6	320 ±2	226 ±3	1532±5	68 ±2
PD	12.5	2861 ±12	25±0.4	310 ±5	238 ±5	1504 ±6	65 ±1
PD	15	2986 ±10	20 ±0.4	270 ±4	225 ±2	1480 ± 8	36 ±4
PD	20	2940 ±10	5±0.2	220 ±3	237 ±4	1466 ±4	3±5
PD	25	2912 ±9	5±0.6	190 ±3	241 ±3	1452 ±4	7±3

Table 4.37 Standard deviation for Jar test with combination of MI and PD seeds

extract as coagulant

SAMPLE	DOSAGE mg/L	EC μS/cm	BOD mg/L	COD mg/L	TURB NTU	TDS mg/L	Coliforms CFU/100ml
MI: PD	20:5	2811 ±9	50±0.5	350 ±6	74.9 ±1	1418 ±9	235 ±4
MI: PD	15:10	2849 ±6	40 ±3	280 ±4	107±4	1437±8	250 ±3
MI: PD	12.5:12.5	2860 ±11	35 ±2	270 ±5	125±5	1405±8	60 ±6
MI: PD	10:15	2852±9	35 ±2	220 ±3	132±3	1426 ±6	46 ±6
MI: PD	5:20	2800 ±8	20 ±3	220 ±3	151±4	1416±7	42 ±3

APPENDIX VII

SAMPLE CALCULATIONS FOR TREATABILITY STUDIES EFFICIENCY.

The following formula was use:

Efficiency (%) = $\frac{initial - final}{initial} \times 100\%$

The initial parameters for the calculations were taken from Table 4.4 while the final parameters were taken from Tables 4.5, 4.6 and 4.7 (lowest value for the particular parameter) for *Mangifera indica* seed extract as coagulant, *Phoenix dactylifera* seed extract as coagulant and their seeds extract combination.

a. Mangifera indica as coagulant

For BOD removal efficiency: Efficiency (%) = (initial-final)/initial x 100 %

$$=(140-5)/140 \times 100 = 96.4 \%$$

For COD removal efficiency: Efficiency (%) = (initial-final)/initial x 100 %

$$= (1000 - 160)/1000 \text{ x } 100 = 84 \%$$

For Turbidity removal efficiency: Efficiency (%) = (initial-final)/initial x 100 %

For Coliform removal efficiency: Efficiency (%) = (initial-final)/initial x 100 %

 $=(350-2)/350 \times 100 = 99.4 \%$

b. Phoenix dactylifera as coagulant

For BOD removal efficiency: Efficiency (%) = (initial-final)/initial x 100 % = $(140 - 5)/140 \times 100 = 96.4 \%$

For COD removal efficiency: Efficiency (%) = (initial-final)/initial x 100 %

= (1000 - 160)/1000 x 100 = 81 %

For turbidity removal efficiency: Efficiency (%) = (initial-final)/initial x 100 %

$$=(796-198)/796 \times 100 = 75 \%$$

For coliform removal efficiency: Efficiency (%) = (initial-final)/initial x 100 %

$$=(350-3)/350 \times 100 = 99.1 \%$$

c. Mangifera indica and Phoenix dactylifera seeds extract as coagulant:

Similar calculations to the ones carried out for Mangifera indica and Phoenix dactylifera

seeds extract, was done to get the efficiency of the combined seeds extract as coagulants.