DEVELOPMENT OF WATERMELON RIND ACTIVATED CARBON FOR REMOVAL OF BENZENE AND TOLUENE FROM OIL WASTEWATER

BY

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ABSTRACT

This study focused on developed activated carbon from watermelon rind for the removal of benzene and toluene from oil-spilled wastewater in real-time environments. The activated carbon was developed from biochar, which was developed from watermelon rind. The activated carbon was developed via chemical activation using two different reagents (sulphuric acid and zinc chloride). The influence of process parameters like time, temperature, and impregnation ratio (IR) was investigated during the preparation of activated carbon. The adsorbent was characterized with Fourier Transform Infra-Red Spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET) analysis and Scanning Electron Microscopy (SEM). The activated carbon was used in batch adsorption on oil wastewater. The effect of contact time, adsorbent dosage, and temperature on the adsorption process was studied and optimized using response surface methodology. Studies on adsorption isotherms, kinetics, and thermodynamics were carried out. It was discovered that at higher temperature and time, fixed carbon was lowered. The results showed that optimum temperature, time and IR for activated carbon was at 500^{o}C, 2.165 hrs and 2/1 respectively, with fixed carbon of 60%. The activated carbon produced with sulphuric acid showed a better result than zinc chloride, with the BET results showing a surface area of 900.361 m^2/g. FT-IR showed the presence of hydroxyl and carboxyl groups, which have affinity for benzene and toluene and SEM showed that the morphology of the watermelon rind had changed. The effect of temperature, time, and adsorbent dosage on showed an increase in removal efficiency up until equilibrium and thereafter a downward spiral with the optimum temperature, time and adsorption dosage at 32.5^{o}C, 120 mins and 0.7g. Langmuir best fits the benzene adsorption process. The pseudo-second-order kinetics had a better fit during the kinetic studies. The thermodynamic studies showed that the process was exothermic, spontaneous, feasible, and favorable.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Water is a vital resource for life but is increasingly being polluted by anthropogenic activities such as oil spillage, urbanization, population growth, poor land use, and agricultural activities and as such responsible for the deterioration of surface, ground water and drinking water quality.Oil spillage is a serious global environmental concern especially in oil producing regions of the world. The government and various multi-national private oil companies frequently contend with hazards of crude oil spillage, which affected both aquatic and terrestrial ecosystems. Oil spillage occursdue to underground water well blowouts, tanker accidents, storage tank failures, production platform blowouts, intensified petroleum exploration on the continental shelf, transfer operations between ships and shores, economic sabotage and youth restiveness like the Niger Delta militias in South-South, Nigeria.

The spilling of oil into the aquatic environment constitutes serious health risks and most often than not causes the death of sea birds and other aquatic animals. Petrochemical hydrocarbons,including Benzene, Toluene, Ethylbenzene and isomers of Xylene (BTEX) compounds, are known as indicators for exposure to volatile organic compounds as well as petroleum compounds. Contact with BTEX compounds can occur through eating (using water contaminated with BTEX), inhalation of contaminated air, or adsorption through the skin (Sairat *et al*., 2015). Crude-oil-soluble derivatives and refined products include various types of toxic compounds for a wide range of plants and marine organisms. Since the petroleum products are made up of different chemicals, their presence inthe environment

can cause many problems, including the occurrence of disease in cleaning workers, the threat to marine organisms, the risks to pregnant women, neurological disorders, and pulmonary disease. In addition, the effects of oil pollution appear in the long-term or short-term Water contaminated by oil can be lethal depending upon the nature of the petroleum fraction, the exposure rate and time. Water and oil are usually considered to be non-miscible. However, crude oil contains a very small soluble portion referred to as the water-soluble fraction.

In addition to potential contamination due to oil, the extraction of petroleum and gas is usually accompanied by the generation of large quantities of wastewater (produced water), which is the principal waste material involved in the extraction process. This is exacerbated by the fact that many oil deposits lie near groundwater aquifers. During the lifetime of the oilfield, the volume of produced water generated can be 7–10 fold the volume of oil produced (Costa *et al*., 2012). The chemical composition of this wastewater is influencedby the nature of the geological formation. Produced water can contain various toxic compounds of natural origin, such as volatile aromatic fractions of the oil (including BTEX), polycyclic aromatic hydrocarbons (PAHs), organic acids, phenols and alkylated phenols, metals and radionuclides, as well as a very high salt concentration (Dorea *et al.*, 2007). Aromatic compounds, including monoaromatic hydrocarbons such as BTEX, are amongst the significantenvironmental contaminants of produced water.

Human exposure to these compounds can lead to health problems ranging from irritation of the eyes, mucous membranes and skin, to weakened nervous systems, reduced bone marrow function and cancers. The United States Environmental Protection Agency has established a maximum permissible levels of these contaminants in water destined for public supply of 0.005 mg L^{-1} (benzene), 1.0 mg L^{-1} (toluene), 0.7 mg L^{-1} (ethylbenzene) and 10 mg L^{-1}

(total xylenes) (Costa *et al.*, 2012).

The presence of these harmful organic pollutants could lead to several environmental and human health problems. To avert these dangers, there is urgent need to reduce the concentrations of potentially harmful organic contaminants in the soluble petroleum fraction to a tolerable level as approved by national and international guidelines before their final discharge into the environment in order to maintain ecosystem equilibrium.

Spilled oil can be primarily removed by controlled burning, dredging, dispersants, oil booms, skimmers, and vacuum techniques (Ghannam and Chaalal, 2003). However, Sorption on spill clean-up sorbents is considered as the best option. Considerable attention has been devoted to the development of unconventional materials such as agricultural waste materials for remediating oil spillage. This is because they are readily available, affordable; eco- friendly and can have high uptake capacity due to the presence of functional groups (Qiu *et al.*, 2008). It is important to take advantage of the increasing environmental awareness surrounding oil spillage by producing cost–effective, advanced, and sustainable alternative technologies for removal of soluble petroleum fractions from water contaminated by oil.

1.2 Statement of the Research Problem

Benzene and toluene are detrimental to water bodies where they are found. In concentrations lower than fatal, petroleum compounds cause physiological and behavioural disorders, and in advanced stages, it may lead to the development of abnormalities among fish, other animals and man and could lead to their premature death (Sairat *et al*., 2015).

In Nigeria, due to oil spills in the Niger Delta, it is possible to find these hydrocarbon components in rivers ordinarily meant for drinking and fishing. If this problem is not tackled, it could not only affect the livelihood of the inhabitants, but could also pose health problems to the people living in these areas.

It is important to constantly focus on new ways to remediate pollution from oil-spilled wastewater as the damages it can cause can be catastrophic. Adsorption using agricultural products is one way to tackle this problem. This is because it is cost effective, does not need high skill for utilization and can provide high removal efficiency (Qiu *et al.*, 2008).

Watermelon rind is an agricultural waste product that is abundant in Nigeria. It can be used to create activated carbon and act as an adsorbent for the treatment of benzene and toluene from oil-spilled wastewater.

1.3 Aim and Objectives of the Study

The aim of this research is to develop activated carbon from agricultural wastes (watermelon peels/rinds) for the removal of soluble petroleum fractions from water affected by oil spillage. This aim will be achieved through the following objectives;

I. Preparation of activated carbon from watermelon rind and the investigation of the influence of process parameters.

II. Characterization of the new adsorbents with emphasis on proximate analysis, surface electron microscopy (SEM), Fourier Transform Infra-Red Spectroscopy (FT-IR) and Brunauer-Emmett-Teller (BET) analysis.

III. Utilization of batch adsorption process for the removal of benzene and toluene from oil-spilled wastewater.

IV. Investigation of adsorption isotherms, kinetics and thermodynamics on the removal of benzene and toluene.

1.3 Justification of the Research

The relevance of the proposed study is to explore locally made materials prepared from available agricultural wastes to treat oil-spilled water containing monoaromatic hydrocarbons such as benzene and toluene. This study will be useful in the development of technology for detoxification of priority organic pollutants in oil spill water thereby assist in reducing environmental pollution and hence improve water quality. Conversion of these low value agricultural wastes and clay material into adsorbent that can remove toxic soluble petroleum fractions from oil spill affected water would constitute a significant contribution in the search for cheaper adsorbent material with the added elegance of using one environmental problem tohelp solve another. The adsorbent will not only be useful to the industries, but living organisms and the surrounding environment will also benefit from the decrease or elimination of toxicity due to the harmful organic pollutant in the soluble petroleum fraction. Undoubtedly, low-cost adsorbents shall offer many promising benefits for commercial purpose in the future for treatment of oil spill contaminated water especially in developing countries such as Nigeria where agricultural wastes and local clay abound.

1.4 Scope of the Study

This project is limited to developing activated carbon from watermelon rind (WR) and analysing how the performance of WR in the treatment of petroleum compounds in contaminated wastewater.This project consists of characterization of raw WR and activated carbon (WRAC) as well as the analysis of how some process parameters affect adsorption

via adsorption studies. Adsorption studies also include kinetics and adsorption isotherms.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Historical Background

Water pollution is the introduction of pollutants into the natural water environment. Water pollution is an extremely sensitive subject as its effects on sea life is often disastrous, posing instant risk to the ecosystem. In the case of oil spills, many fractions in the water body might be affected. This however, is dependent on the amount of oil spilled and its placement. Oil spills can cause loss of sea life, as a minimum and ultimately make sea animals lose their habitat. Negative health effects caused from oil spills to sea life, are respiratory challenges, feeding and thermo-regulation problems. Additionally, it is possible for the ecosystem to temporarily change due to chemical components of the oil spilled.

It is true that the benefits and usefulness of oil and gas in the economy cannot be overstated in Nigeria. Nigeria makes most of its revenue from crude oil exploration and exportation. Nigeria recorded a significant increase in oil export revenue as the country earned an estimated $26bn in the first seven months of 2018 (Adu, 2018). However, when comparing spills the detriments are often disastrous. In the Niger Delta, shell has recorded nine operational spills of more than 100kg in volume from Shell Companies in Nigeria facilities as at 2017. Spills are also caused due to crude oil theft and sabotage of facilities, as well as illegal refining. The Niger Delta is an example of oil spillage of high magnitude.

In a 15-year period from 1976 to 1991 there were reportedly 2,976 oil spills of about 2.1 million barrels of oil in Ogoniland, accounting for about 40% of the total oil spills of the Royal Dutch/Shell Company worldwide in one region alone. UNEP has forecasted that it

might take about 30 years to restore Ogoniland and that the first five years of rehabilitation would require funding of about US$1 billion (Shell, 2019).

Spills contaminate the surface water, ground water, ambient air, and crops with hydrocarbons, including known carcinogens like polycyclic aromatic hydrocarbon, naturally occurring radioactive materials and trace metals. These spills could be accumulated in food crops, posing problems such as cancer and infertility for animals around areas of oil spill. As such, it is imperative that oil spills be treated with the utmost urgency (Ordinioha and Brisibe, 2013). There are various methods used to clean oil spills; filtration (ultra and micro), reverse osmosis, gravity separation, activated sludge treatment, various flotation methods, membrane bioreactors, biological treatment, chemical coagulation, electro-coagulation and mechanical treatment like boomers and skimmers (Santander *et al*., 2011).

These methods above are available and effective, but adsorption is still the most preferred option because of its low cost, it needs no skill to be used, is flexible and highly effective. Additionally, adsorption can also remove soluble and insoluble organic pollutants without the generation of hazardous by-products (YanJun *et al*., 2015).

2.2 Removal of Organic Pollutants BTEX from Oil Spills

The hazards surrounding oil spill is a major reason that oil spills need to be treated with urgency. Oil spills on water bodies are not static; they spread. Some of the clean-up methods, propagate the spread of the oil while reducing oil spillage; adsorbents do not cause an increase in mobility of oils spills. Due to its density, oils usually accumulate on top of water, but there are organic (soluble) pollutants that dissolve into the water bodies. These dissolved components become part of sea life and increase potential for toxicity. BTEX is a highly

volatile contaminant, usually found in gasoline, with high solubility and toxicity, thus, it represents a high risk for public health (Stefanakis *et al.*, 2014). BTEX (benzene; toluene; ethylbenzene; and *o*-, *m*-, and *p*-xylenes) are classified as priority pollutants regulated by many environmental organizations around the world. This is because these aromatics are soluble in water and more volatile than their aliphatic counterparts. They further state that BTEX is required to be treated as a group for oil spills due to their high toxicity and their threat to the health of humans and sea life (Wang *et al.*, 2013). The effects on BTEX to can express itself as toxic, growth retarding, mutagenic, carcinogenic, teratogenic and metabolic. Exposure to BTEX is associated with male and female reproduction disorders, asthma, allergies, respiratory challenges, and cardiovascular diseases (Sirotkin, 2018).

2.3 Adsorption as a Removal Technique for BTEX Compounds

Adsorption is the removal of an adsorbate using an adsorbent. The adsorbate is usually a fluid that adheres to the surface area of the adsorbent. Adsorbents are used to treat and remove contaminants from wastewater from different industries; from electroplating companies to textile companies, adsorbents have been put to use and perform effectively. (Bailey *et al.*, 1999) states that low costs adsorbents do not need a lot of processing before it is used, can be found easily in nature, a by-product, or waste material from another industry. It is noteworthy to add that additional processing is fine, if it can make up for increased adsorption capacity. There are different types of adsorbents: natural sorbents, organic polymers (synthetic) and mineral materials (inorganic). The area of implementing bio adsorbents as treatment options is currently being heavily researched. It has been discovered that bio adsorbents are lightweight, have good adsorption selectivity, considerable adsorption efficacy, outstanding adsorption recyclability, and can be easily operated, plus it has an

inexpensive preparation technique. As such, it is necessary to explore all the probable agro and horticultural based adsorbents in order to determine their viability for removing heavy metals. A lot of research has gone into the production of adsorbents and its use to remove BTEX or crude oil compounds. Researchers like (Sidik *et al.*, 2012) worked on removing crude oil using Modified oil palm leaves adsorbent with enhanced hydrophobicity. The researcher discovered that removal percentage rate of crude oil was 91.00 ± 1.31%.

(Bina *et al.*, 2014) focused on removing of benzene, toluene, ethylbenzene, and xylene (BTEX) from aqueous solution by multi and single-walled carbon nanotubes (MWCNTs and SWCNTs), hybrid carbon nanotubes (HCNTs) and nanoFe. The researchers discovered that adsorption capacity for SWCNTs (B: 9.98, T: 9.96, E: 9.97, and X: 9.97 mg/g) was higher than for MWCNTs, HCNTs and nanoFe. The adsorption capacity for SWCNTs was 39.89 mg/g. (Arshadi *et al.,* 2016) worked on developing ostrich bone wastes (OBW) covalently modified with citric acid as a bio adsorbent for the uptake of various volatile organic compounds such as benzene, toluene, ethylbenzene, and *p*-xylene. It was discovered that altering these parameters had an influence on the adsorption capacity of the batch process: contact time, the amount of adsorbent, initial pH, temperature, chemical modification process, and initial pollutant concentration.

2.4 Methods for Removing BTEX Compounds

There are many traditional methods, available for the removal of BTEX hydrocarbons from wastewater such as chemical oxidation, membrane separation, aeration, biological treatment and adsorption amongst others (Li *et al.,* 2020).

Chemical Oxidation: This process works to reduce the level of toxicity on organic pollutants as well as inorganic pollutants, hence making these BTEX compounds or cyanide less harmful via oxidation (Zhao *et al.,* 2011). Chemical oxidation can either be total or partial oxidation. A complete oxidation means that the pollutants are completely oxidized to produce CO_2 and H_2O at best. Chemical oxidation can also be combined with other techniques such as biological purification; this is called partial oxidation (Peng and Pan, 2018). A partial chemical oxidation means that the oxidation stage acts a pre-treatment for pollutants, where these pollutants, which are usually tough to degrade, pass through this stage in order to make them more malleable for biological degradation. In chemical oxidation, oxidants like ozone (O_3), chlorine gas (Cl_2), natriumhypochlorite or bleaching liquor (NaOCl), chlorine dioxide (ClO_2), peroxy acetic acid ($C_2H_4O_3$) hydrogen peroxide (H_2O_2), and pure oxygen (O_2). It is also possible to combine oxidants. The most active oxidant is hydroxyl radical (OH°). This can be formed from ozone or hydrogen peroxide after activation with a catalyst (e.g. Fe^{2+} in a Fenton reaction) or via UV light (Ghernaout *et al.,* 2020). Chemical oxidation also occurs at an advanced level, where oxidation happens with hydroxyl radicals (Dhivakar and Rajan, 2018). Advanced oxidation happens when strong oxidants like hydroxyl radicals are formed and when these oxidants react with organic pollutants in wastewater. Advanced oxidation combines chemical oxidants like ozone with water and/or a U.V. light. This method is efficient for environmental organic compounds and is beneficial in the sense that they lower chemical oxygen demand (COD) levels. The oxidants are also easily biodegradable (Dhivakar and Rajan, 2018). There are also disadvantages to this method, for instance, using excess dosage of the oxidant can negatively affect biological treatment as in the case of partial oxidation. Partial oxidations could also produce even more toxic by-products than the original organic pollutants. For advanced oxidation, pH sensitivity is a huge demerit

(Bayrakdar *et al.,* 2013). Fenton reaction experiments are also disadvantageous in that they are expensive; ozone for instance must be produced on site, and while water is not as expensive, combine all three considerably raises investment costs. Chemical oxidation can be increased by increasing oxidant dosage; however, it is important to be careful with cost price as oxidants are not cost effective. It is possible to leverage on certain experimental constraints like radiation intensity to ensure that costs are reduced (Collivignarelli *et al.,* 2017).

Memebrane Separation: Membrane technology has shown tremendous growth over the years as a result of its advantages in wastewater treatment; its low capital cost, energy requirement and equipment lets it be a good choice for treatment experiments (Quist-Jensen *et al.,* 2015). Membranes are barriers separating and controlling the movement of two components (Obotey *et al.,* 2020). Membranes are very advantageous for separating organic chemicals from water, due to their high perm selectivity and permeability as well as its high diffusivity. There are many methods to embark on membrane separation, the most common being reverse osmosis and pervaporation. Pervaporation is useful in reducing wastewater wastewater by two to three orders of magnitude; however, this process is very expensive and is difficult to commercialize and utilize on a very wide scale. It is possible to combine two or more membrane processes or other technologies like adsorption when considering treating wastewater (Yahaya *et al.,* 2008). Apart from cost, this process could experience low performance because of high-pressure drop, short residence time and by-pass challenges. The pressure build-up can be alleviated by using large fiber diameters, especially when using hollow fibers for pervaporation as its small channel has been determined as the reason for pressure build-up, but once the fiber diameter is increase, the high membrane area packing density will be sacrificed. If the hollow fiber membrane is coated, to tackle pressure build-

up, it has to be coated no less than six times and even this significantly raises the cost of the treatment process.

Biological Treatment: These orthodox physical treatments are able to remove pollutants from the environment without damaging them. Biological treatment is known as bioremediation and is expected to tackle environmental pollutants via clean technology. When compared to other treatment methods, they are not as costly and do not require a very high skill to utilize (Mathur and Balomajumder, 2013). It is possible for microorganisms in the soil to be utilized in BTEX removal, especially for petroleum groundwater. The microorganisms are expected to decompose the pollutants and products left after bioremediation should consist of water, carbonic gas and biomass The disadvantages on using microorganisms for bioremediation, is that it can turn non-toxic or low-toxic compounds into potential toxic ones and, in many cases, the products derived from bioremediation are recognizably carcinogenic.

Among them, the promising process for the removal of BTEX from wastewater is adsorption, because the used adsorbent can be regenerated by suitable desorption process and it is highly effective and economical. The most widely used adsorbents for BTEX removal are activated carbon and zeolite. Adsorption is one of the best treatment alternatives for the removal of these pollutants from wastewater because it is possible to recover both the adsorbent and adsorbate. Furthermore, the adsorption process of these pollutants has proven to be highly efficient, even for low concentrations.

There has been numerous research on technologies that can attain the uppermost elimination of organic pollutants from industrial wastewater, and it has been proven that many adsorption processes used to remove organic pollutants showed high effectiveness at high concentrations.

Table 2.2: Biomass as adsorbent for the removal of organic pollutants (benzene and toluene) (Yakout, 2013; Costa *et al.*, 2012)

Biomass	Pollutant	Initial concentration (mg/l)	Removal Percentage (%)
Peat	Benzene	50	32
Peat	Toluene	50	50
Saw dust	Benzene	50	20.2
Saw dust	Toluene	50	36.4
Rice husk	Benzene	10	22
Rice Husk	Toluene	10	33

2.5 The Nature of Adsorbents

According to Richardson *et al.* (2010), a good adsorbent should:

I. Have a large enough internal surface area. A surface area of between 800 to 1500 m^2/g is encouraged.
II. Regeneration is a highly desired trait for a good adsorbent.
III. It should be able to withstand a couple of recycling stages while retaining its adsorptioncapacity.
IV. It should have pores large enough to adsorb the target contaminant but small enough toprevent undesirables from getting into its surface.
V. It should be able to go through bulk handling without crumbling.

2.6 Activated Carbon as an Adsorbent

There are many adsorbents used to treat inorganic and organic pollutants in polluted water and plant or lignocellulose wastes, activated carbons, biopolymers and clays are very well known adsorbents. Activated carbon has the higher popularity out of all the adsorbents that researchers use for water treatment. However, the higher the quality, the more expensive it is. Small-scale industries are looking for cheaper ways to prepare activated carbon; hence, the movements towards agricultural waste produce. In order to consider biomass as activated, it has to show a large internal surface area and porous structure. Activated carbon has high levels of carbon mixed with other elements. The internal surface area for activated carbon is usually at 800 to 1500 m^2/g but can go up to 3,000 m^2/g. Its pore volume could range from 0.20 to 0.60 cm^3/g and the pore diameter is less than 2 nm (Wexler *et al.*, 2010). Activated carbon is formed firstly through pyrolysis or carbonization of the precursor to get biochar and secondly activation via an activating agent. Pyrolysis involves converting biomass into gas, oils, or biochar using temperature or pressure as determining constraints in an inert environment. To create this inert environment, nitrogen gas or argon gas is used. Other factors that are useful in determining interaction between biomass and the pyrolysis environment are the gas flow rate, and retention time (Oghenejoboh, 2018).

2.6.1 Types of activation

There are two types of activation:

I. For chemical activation, a catalyst is used to speed up the process; as such, less temperature is used. Common activators used for this process are H_3PO_4, $ZnCl_2$, KOH, K_2S, H_2SO4, and KCNS (Yang *et al*., 2017). This process minimizes tar formation and volatilization.

II. Physical activation requires a higher temperature and more time and ultimately might produce tar and increase volatilization; chemical activation offers better results and gets recommendations. Chemical activation is also advantageous as the activation targets the carboxyl and hydroxyl groups that are important for adsorption to oil spills. A lot of research on how activated carbon is prepared from biomass and how effective this type of adsorbent is on treating effluents form organic and inorganic sources is ongoing.

2.7 Watermelon Rinds as Activated Carbon for Wastewater Treatment.

Watermelon (*Citrullus lanatus*), being the largest and heaviest fruit, is one of the most abundant and cheapest fruit available in Nigeria. Watermelon consists of a red sweet tasting flesh on the inside, andan outer shell that does not do much, aside from protect the flesh. The outer rind is usually disposed as waste with no commercial value (Quek *et al.*, 2007). Watermelon rind (WR) comprises ofcellulose, phenols, proteins citrulline, and carotenoids the polymers found in watermelon are abundant in functional groups like hydroxyl (cellulose) and carboxylic (pectin) and can easily bind metal and treat oil pollution (Quek *et al.*, 2007). For a precursor to have good adsorption results, the adsorbent should have a high content of carbon or oxygen. Some of the needed physical characteristics for a good precursor are small pores, which ultimately leads to more surface area for adsorption, thermal stability, and high abrasion resistance (Sabir, 2015). In other to develop these physical characteristics, it is important to focus on how certain experimental parameters (temperature and time) affect elements like pore volume, surface area and pore diameter during the production of activated carbon (Gin *et al.*, 2014). The temperature and heating time parameters ranged from 200 to 350^0C for 15, 30, 45 and 60 min. Optimum conditions

were discovered at 300^0C and 60 mins. The impregnation was done using different reagents at different molar concentrations. H_2SO_4, HCl, and $Zncl_2$ (from 0.5 to 1.5 M) was used for the impregnation. The best results were gotten from 1.0M sulphuric acid. Oghenejoboh (2018) researched on adsorbing nickel (ii) ion from synthetic wastewater on watermelon rind activated carbon using response surface methodology (rsm) optimization approach. The temperature and time implemented from carbonization was 380^0C for 120 mins. Impregnation was done using 1.0M zinc chloride. Uner *et al*, (2019) developed activated carbons from waste watermelon rind by using the chemical activation method with zinc chloride. The temperature and time parameters ranged from 400, 500, 600, 700 and 800^0C for 30, 60, 90 and 120 min. $Zncl_2$ were used with impregnation ratios ranging from 0.5/1, 1/1, 2/1, 3/1 and 4/1. Optimal results were obtained at impregnation ratio of 2/1 at the carbonization temperature of 700^0C with the residence time of 60 min, was 1156 m^2/g. Abd and Ramzilah (2017) researched on activated carbon from watermelon rinds using sodium carbonate to activate the precursor. Two activation temperatures were implemented 500^0C and 700^0C and additionally two times 5 and 10 mins. The activating agent sodium carbonate anhydrous was implemented at varying concentrations of, 0.01M, 0.025M, 0.05M, 0.075M, 0.10M, 0.50M, and 1.00M. The best concentration was discovered at 0.05M, with a 99.27% removal of methylene blue. Lin *et al* (2019) produced activated carbon at optimal conditions of 700°C with a heating rate of 5°C/min for 1 h under nitrogen flow. The carbon was activated with a watermelon/potassium hydroxide mass ratio of 1:2 and exhibited a large specific surface area of 1303.3 m^2/g. Ahmad *et al* (2017) carried out research on production of activated carbon from watermelon rind for the removal of synthetic dye. The optimal temperature and time for the production of char was

700 °C and held for 1 h. KOH was used as an activating agent. BET surface area of 776.65 m^2/g. Salem *et al.* (2015) carried out research geared towards removing copper from water bodies using activated carbon as bio adsorbent. The researchers alternated production parameters like activating agents, using calcium hydroxide and citric acid, and operating parameters like adsorbent, contact time, temperature, adsorbent dose pH, initial concentration, and ultrasonic power. The results showed the extent of adsorption of Cu (II) on adsorbents was found to increase with an increase in the operating pH until an optimum value of five. The extent of adsorption also increased with a decrease in the initial concentration and particle size as well as with an increase in ultrasonic power until an optimum. Maximum adsorption capacity was found to be 31.25 mg/g for watermelon treated with calcium hydroxide and 27.027 mg/g for watermelon treated with citric acid. While there is a plethora of material on the adsorption of soluble pollutants (metals) using watermelon as a bio adsorbent, there is little literature that shows any work has been done on watermelon as a method for recovering benzene and toluene.

2.8 Activated Carbon from Different Biomass

Selvaraju and Bakar (2017), worked on producing activated carbon from artocarpus integer (breadfruit) fruit processing waste. The researchers favored steam activation with peak temperature of 750°C and time of 60 min. BET analysis on this AC showed that the surface area was at 1411 mg/g. Other analysis like Fourier Transform Infrared, Scanning Electron Microscope (SEM), Spectroscope (FTIR), and X-ray powder Diffraction (XRD) showed that the AC had the functional groups needed for adsorption purposes and a high micro-porous and amorphous structure. Sugumaran *et al.* (2012) used *Delonix regia* fruit pod and banana empty fruit bunch as precursors when activating carbon via chemical activation. A TGA

analysis showed maximum loss at 500°C, as such the samples went through pyrolysis at 400°C and 450°C respectively. IR was used as an activation factor and BET was implemented immediately after for analysis. The fruit pod treated with H_3PO_4 had a higher surface area than its untreated counterpart did but a lower pore volume than its untreated counterpart.

Rai *et al.* (2016), used mango seed as a precursor of activated carbon to remove Cr (VI) from aqueous solutions. This was a one-step chemical activation process with H3PO4 and a temperature of 600°C for 1 hour. The sample was characterized BET surface area analyzer, FTIR spectroscopy, using elemental analyzer, and SEM analysis. Benadjemia *et al*. (2011) produced activated carbons via the pyrolysis of artichoke leaves to remove of methyl blue dye from wastewater. The activating agent used was phosphoric acid at a temperature of 500 °C and IR was varied at 100, 200, and 300 wt.%.

Saygili and Guzel (2016) produced activated carbon from tomato processing solid with chemical activation. The production variables for this process were carbonization temperature, impregnation ratio, and carbonization time. The peak conditions determined for the production of activated carbon for this process were; 600°C carbonization temperature 6:1 impregnation ratio, and 1 h carbonization time. Characterization using proximate analysis showed that the sample had a carbon content percentage of 53.92% and a yield of 38.20%. BET was another analysis implemented to show surface area recorded at 1093 m^2/g.

Syed (2011) developed activated carbon from kapok hull to remove malachite green from wastewater. The sample was treated with sulphuric acid using an impregnation ratio 1:1 for 24hr. The sample was washed using distilled water and kept in an air oven 383K for 12 hours. Temperature and time was varied to study the changes in yield. The optimal temperature and

time was recorded at 823K for an hour. Particle size was also utilized to study changes in yield using particle sizes of 250,150 and 100 BSS mesh numbers. XRD and SEM were the characterization used to determine the structural and morphological changes.

Tang *et al.* (2012) produced activated carbon, using *Ramulus mori* as a precursor and ammonium hydrogen phosphate as a chemical activation agent. Investigation on operational parameters was carried out. The optimal temperature for carbonization was 400°C, time was 90 min, impregnation ratio of hydrogen phosphate to carbonized sample was 1:2, 800°C for activating temperature, and 120 min for time. The sample was characterized the yield of activated carbon was recorded as 26.56%. It was discovered that hydroxyl and carbonyl group exists on the surface of the activated carbon. Ceyhan *et al.* (2013) used EAS biomass to produce activated carbon using a pyrolysis temperature of range of 150 to 350°C and heating rate of 5^{o}C/min. The sample was treated with zinc chloride with impregnation ratios of 1:1, 1:2, 1:3, and 1:4 and a pre-treatment temperature rate of 30, 50, and 80^{o}C for 3hrs. The time for activation was 3h.

Angin *et al.* (2013) used safflower seed press cake biochar to produce activated carbon. The influence on activation temperature and IR was determined. This was a two-step chemical activation process using zinc chloride and the activated carbon developed was used to treat methylene blue dye. The activated carbon was characterized and carbon content of 76.29% was recorded. The BET surface area was as 801.5 m^2/g and total pore volume 0.393 cm^3/g. Ioannidou *et al.,* (2010) prepared activated carbon using agricultural residues for the treatment of pesticides. The precursors used were olive kernels, corncobs, soya stalks and rapeseed stalks. The influences of operational parameters were investigated. The optimal parameters for the pyrolysis stage at 800°C for temperature and 60 min for time with a flow

rate of 15 mL/min and heating rate of 27 ^{o}C/min for nitrogen. The biochar was activated using physical activation at the same temperature for pyrolysis with a time range of 30 min under steam flow 40 g/min at 0.5 bar. Qian *et al.* (2007) used cattle-manure compost to produce activated carbon via chemical activation using zinc chloride as an activating agent. Operational parameters such as IR, Temperature and time were investigated to determine their influence on production. The activated carbon was characterized using BET to determine the surface area and pore volume which were 2170 m^2/g and 1.70 cm^3/g. The sample was also characterized using Thermogravimetric analysis (TGA). The activated carbon was used to treat phenol. Pallares *et al.* (2018) worked on the production of activated carbon using barley straw as a precursor. The activation method used was physical activation method and the activating agents were steam and carbon dioxide. The operational parameters were investigated to determine influence. It was discovered that temperature and heating rate for the carbonization process were important factors. Additionally, activation temperature and time were necessary operational parameters for the process. The peak conditions discovered for activated carbon using barely straw was 800°C for temperature and time was 1 h for carbon dioxide and 700°C and a hold time of 1 h for steam activation. The BET surface area was 789 m^2/g and micropore volume was 0.3268 cm^3/g for carbon dioxide activation and 552 m^2/g and 0.2304 cm^3/g for steam activation.

Zhong *et al.* (2012) used peanut hull to produce activated carbon via chemical activation using phosphoric acid for Remazol Brilliant Blue R adsorption purposes. The particle size was set at 2.0 mm. The sample was characterized via proximate analysis and the results for cellulose 16.91%, moisture 10.85%, lignin 27.43%, hemicellulose 10.11%, and ash 2.62%. The operational time for the impregnation was set at 24 h. Theydan and Ahmed (2012) developed activated carbon from pits using $FeCl_3$ as a chemical activating agent. The IR for

the process was 100ml of the activating agent to 1.5 g/g. this was run for 24h at 30ºC. The sample was carbonized at a temperature 700 ◦C for an activation time of 1 h. Bello *et al.* (2008) produced activated carbon from periwinkle shells for the adsorption of methylene blue via physicochemical activation. The activation agents used were carbon dioxide (CO2) and potassium hydroxide (KOH). The operational parameters for the activation was determined at 850°C for 2 h.

Demirbas *et al.* (2008) developed activated carbon from apricot stone to use for removal of basic dye. The operational parameters investigated for influence were particle size, at 0.5 to 2.0 mm. The sample was activated with concentrated H_2SO_4 at 250 C for 24 h. The activated carbon sample was characterized for surface area and this was determined at 560 m^2/g. Baccar *et al*. (2013) produced activated carbon from olive-waste cakes to use in the adsorption of tannery dye. The operational parameters utilized to investigate production influence were particle size ranging between 100 and 160 μm. BET (Brunauer–Emmett and Teller) was used to calculate the surface area, pore volume and pore diameter as 793m/g, 0.49cm^3/g and 4.2nm, respectively. Saka (2012) produced activated carbons from acorn shell using zinc chloride (ZnCl2) as an activating agent. The precursor was carbonized at 600°C in nitrogen gas atmosphere and the samples were characterized. The parameters investigated for influence were duration time, activation temperature, IR and impregnation time. The BET surface area was recorded as 1289 m^2/g. The sample was also characterized by FT-IR spectroscopic method to determine surface chemical characteristics.

Kong *et al.* (2013) used leather waste to produce activated carbon via physical and chemical activation means. The conditions investigated for activation optimization were carbonization time, carbonization temperature, and impregnation ratio.

The researchers characterized using thermal gravimetric analysis of LW-$H_4P_2O_7$ showed that using $H_4P_2O_7$ as the activating agent encourages the development of carbonaceous material. Other types of characterization on the activated carbon were scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). Ahiduzzaman and Islam (2016) developed biochar and activated carbon using rice husk. The temperature was varied from 600 to 900°C and heating time from 30 to 120 mins at an interval of 30min. Activation of biochar to activated carbon happened with the reagent zinc chloride at 650^0C for 2hrs. Rostamian *et al.* (2018) prepared biochar and activated carbon from rice husk using pyrolysis by varying temperature from 400 to 800°C. Two activation methods were used; physical activation with steam and chemical activation with potassium hydroxide (KOH). BET characterization was used to determine the surface area, and it was discovered that the chemical activation process provided a higher surface area (2201 m^2/g) and total pore volume (0.96 cm^3/g) than the physical adsorption process.

Sobhanardakani *et al.* (2013) developed activated carbon from rice husk which was used for heavy metal removal. Liu *et al.* (2010) used bamboo to produce activated carbon via chemical activation. The researchers used microwave-induced activation and phosphoric acid and considered how parameters like IR, radiation time and microwave power would activated activation of the sample; they discovered optimum conditions at 1:1, 20 min and 350 W respectively. The activated had a carbon yield of 48% and BET surface area of 1432 m^2/g.

Banat *et al.* (2013) used date pits to produce activated carbon and compared adsorption capacity of the raw and activated date pits when treating dye effluent waters. The researchers considered the effect of parameters like activation temperature; solution pH, solution salinity adsorbent particle size, and solution temperature on the removal of methylene blue removal.

Solution PH was an important parameter for dye removal. Characterization using BET, FT-IR analysis, SEM-EDX and particle size distribution shows how elements like surface area, pore volume; pore diameters have been modified to affect activated carbon adsorption capacity. Hadoun *et al.* (2013) used H_3PO_4 as an activating agent to produce activated carbon from date stems. The parameters varied for this process was temperature, which was varied at 450, 550, and 650°C. Impregnation ratio of 2/1 of the activating agent was used to produce the activated carbon. The Researchers characterized the activated carbon to determine it met with standards of other activated carbon being used for adsorption. One of the characterization was BET which was used to find the surface area and pore volume; surface area for the AC with these three varying temperatures 450, 550 and 650°C respectively was recorded at 682, 1455, 1319 m^2/g and the pore volumes were recorded at 0.343, 1.045 and 0.735 cm^3/g.

2.9 Adsorption Studies

Adsorption studies are used to determine what type of adsorption (chemisorption and physisorption) has been carried out as well as how the contaminants have been adsorbed by the adsorbents. Adsorption studies include both adsorption isotherms and kinetic studies.

2.9.1 Adsorption isotherms

Adsorption isotherms are used to establish the most appropriate correlation from the results at equilibrium and to understand how the contaminants are adsorbed by the adsorbents, as well as to estimate the maximum adsorption capacity. There are a variety of different adsorption isotherm models available, however the most commonly used are the Freundlich and Langmuirisotherms (Febrianto *et al*., 2009; Wang and Chen, 2009). The

Langmuir isotherm assumes thepresence of an adsorbate monolayer on a homogeneous adsorbent surface possessing identical sites and uniform adsorption energies and can be represented in the equation:

$$\frac{1}{q_e} = \left(\frac{1}{bQ_m}\right)\frac{1}{C_e} + \left(\frac{1}{Q_m}\right) \quad (2.1)$$

$$Rt = \frac{1}{1+KtCo} \quad (2.2)$$

According to the value of R_l, isotherm type may be interpreted where R_l > 1.0 is unfavorable,

R_l = 1.0 is linear, 1> R_l> 0 is favorable and $-R_l$ = 0 is irreversible

The temkin isotherm model assumes that the adsorption heat of all molecules decreases linearlywith the increase in coverage of the adsorbent surface, and that adsorption is characterized by auniform distribution of binding energies, up to a maximum binding energy and can be seen in equation 2.3:

$$q_e = \frac{RT}{b} lnA + \frac{RT}{b} lnC_e \quad (2.3)$$

To obtain the liner plot of Temkin isotherm, the equation 2.3 can modified as

$$q_e = B\ lnA + B\ lnC_e \quad (2.4)$$

Where, A and B are constants of Temkin isotherm model and T is temperature.

2.9.2 Kinetics studies

Adsorption kinetics is the study of the adsorption process rate. One reason for the importance of adsorption kinetics is that it provides evidence for the mechanisms of chemical processes. Adsorption kinetics is very important scientifically because the knowledge of reaction mechanisms is of practical use in deciding what is the most effective

way of causing a reaction to occur. In batch adsorption process, kinetic studies provide information about optimum conditions, mechanism of sorption, and possible rate controlling step. For this purpose, pseudo-first- and pseudo-second-order kinetics is applied on adsorption data (Pooresmaeil *et al.*, 2021).

There are two common models used for kinetic studies

I. Pseudo-first-order kinetics: Pseudo-first-order reactions are bimolecular or second-order reactions that are made to behave like first order reactions. A first-order reaction depends on the concentration of only one reactant. As such, a first-order reaction is sometimes referred to as a unimolecular reaction. While other reactants can be present, each will be zero-order, since the concentrations of these reactants do not affect the rate. Adsorption in this model depends only on the nature of the adsorbents. The equation for this is:

$$\ln (q_e - q_t) = \ln q_e - \frac{K_1 t}{2.303} \quad (2.5)$$

This type of kinetics shows that the difference between the amount of adsorbed adsorbate molecules on adsorbents at equilibrium adsorption time and a defined time is determined by the adsorption process rate (Pooresmaeil *et al.*, 2021).

II. Pseudo second order kinetics: The pseudo–second-order kinetic model is based on the assumption that the rate-limiting step is chemical sorption or chemisorption and predicts the behavior over the whole range of adsorption. In this condition, the adsorption rate is dependent on adsorption capacity not on concentration of adsorbate

and can be representedin equation 2.6:

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{1}{qe}t \quad (2.6)$$

Where K_2 is the rate constant of pseudo second order adsorption the slope and intercept is used to determine the second order rate constant K_2 (Pooresmaeil *et al.*, 2021).

2.10 Factors Affecting Adsorption

Adsorption works by attracting pollutants of a gas or liquid phase on an adsorbent. Adsorbate are materials used to adsorb pollutants, while adsorbate is the pollutant. Adsorbents are separated into synthetic, semi-synthetic and natural adsorbent; out of the three, synthetic shows high levels of removal efficiency during treatment, but the cost of production is high. Natural adsorbent while low in cost production is also low in performance. Semi-synthetic adsorbent, which is the processed natural adsorbent by combining with carbon, shows high adsorption capacity and low cost.

Adsorption process is used to remove highly toxic or low concentrated compound that cannot be immediately treated by biological processes and can be separated into batch, column and continuous processes. Batch adsorption process happens in a close system where there is a given amount of adsorbent and a given volume of the adsorbate. This closed system is agitated with a rotating equipment to allow for uniform reaction between the adsorbent and the adsorbate. Batch adsorption is an effective process, in that it is possible to retain good quality recyclable effluent once the process is complete. In addition, this process is cost effective once there is a possibility for regeneration or if the adsorbents are developed from

low cost materials. The batch adsorption process is useful in small-scale pollution removal. It is possible to scale up or scale down the batch adsorption depending on the removal requirements. Batch adsorption is very important for industrial use as it provides data for column adsorption. Column adsorption has more advantages than batch adsorption due to its operating ease, quicker adsorption and the ease for scale up, but batch adsorption is more preferred by researchers for laboratory scale research (Sazali *et al.*, 2020). This is because the amount of material used is smaller than large scale application.

During batch adsorption, there are certain factors to consider, which can improve or degrade the removal efficiency of the pollutants (Aktar, 2021). Some of these factors are PH, temperature, adsorbent dosage, adsorbate concentration, and time and so on:

pHpzc: This factor is a very important component in the batch adsorption process and provides insight on the sorption mechanism. It is assumed that the surface charge of the adsorbent is zero, which lends credence to the possibility that the material surface is positive and can adsorb negatively charged pollutants. PHpzc of the adsorbent can be determined using techniques like immersion and mass techniques (Aktar, 2021).

Adsorbent dose: Once the adsorbent dose is increased, there are more active adsorption sites and it is assumed that removal efficiency is higher. As the adsorbent dose increases, it gets to a certain point that equilibrium is achieved (Aktar, 2021). This means that the active sites are full and as such removal efficiency of the adsorbate on the adsorbent begins to drop.

Temperature: It is possible for alterations in temperature to affect how the adsorbents react, the adosrbate stability and adsorbate-adsorbent interaction. Increase in temperature reduces viscosity and this makes it easier for pollutants to be moved from the bulk solution to the surface of the material. Thermodynamic properties are needed in cases where temperature is used as a factor to determine its effect on adsorbent and removal efficiency. These properties

provide insight into the characteristic of the batch adsorption process to determine whether it is exothermic or endothermic, spontaneous or random nature. This also shows how favourable temperature is in the batch adsorption process (Aktar, 2021).

Pressure: Once pressure is increased during the adsorption process, adsorption and removal efficiency is high, until the adsorbent is saturated with adsorbate. Once the equilibrium is reached, there can be no more adsorption even if the pressure keeps increasing. This means that it is not possible for adsorption of pollutants to take place (Aktar, 2021).

Surface Area: Adsorption happens on the surface of the adsorbent, which means that it is proportional to specific surface area. The specific surface area is the available area for adsorption in a total surface area. The larger the particles the smaller their surface area, which means that these large particles will have less access to particle pores. The pore size is directly proportional to pore accessibility (Aktar, 2021). In order to achieve smaller pore sizes, it is necessary to break larger particles to smaller sizes through technology like, to open scales and increase surface area for better adsorption.

Coexisting Ions: If coexisting ions occur in the pollutant, it can affect the removal efficiency of the adsorbent, as these ions will compete for active sites on the surface of the adsorbent. If the wastewater used for the batch adsorption experiment is not simulated, it means there will be a number of coexisting ions in occurrence. However, different compounds in the wastewater can improve adsorption process. The removal of mixed solution pollutants are dependent on molecular size of adsorbents, solute concentration and relative affinity (Aktar, 2021).

2.11 Optimization

This involves designing or modelling a process that focuses on the interactions between two or more constraints for determining the optimal interaction. Optimization in recent times is possible with different software one of which is design expert.

2.11.1 Response surface methodology

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques useful for analysing problems where several independent variables influence a dependent variable or response, and the goal is to optimize this response. A popular optimization design is the CCD (central composite design). The CCD is advantageous in the sense that it provides precise results and doesn't need a three-level factorialexperiment to design a second-order quadratic model. For experiments with two or more constraints, CCD can be used for response surface modelling and optimization.

If the response is well modelled by a linear function of the independent variable, then the approximating function is the first-order model.

$$\eta = \beta 0x0 + \beta 1x1 + \beta 2x2 + \ldots . \beta kx \qquad (2.7)$$

For second-order models, they can be used when nonlinearity is discovered. For the second-order model, the factor level must be at three before it can be fitted into the model in equation 2.8:

$$Y = \beta o + \beta 1X1 + \beta 2X2 + \beta 12X1X2 + \beta 11X12 + \beta 22X22 + \epsilon \qquad (2.8)$$

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 List of chemical reagent and equipment

The chemical precursor for the production of activated carbon from WR was zinc chloride $ZnCl_2$ and sulphuric acid H_2SO_4 respectively. They were all analytical grades (AR) as supplied and utilized without any additional purification. Benzene (C6H6 MW: 78.11 gmol-1) and Toluene (C7H8 MW: 92.14 gmol-1) were the pollutants used to test the effectiveness of the WR activated carbon.

Table 3.1: List of Chemicals used

S/N	Chemicals	Purity	Manufacturer	Source
1	Sulphuric acid	97%	BHD	Chemistry lab FCFMT
2	Zinc Chloride	96%	Avondale	Chemistry lab FCFMT
3	Sodium Hydroxide	99%	Avondale	Chemistry lab FCFMT
3	Distilled Water			Chemistry lab FCFMT
4	Oil spill wastewater			Zorbukeh river, Barabedom Kegbara Dere, Delta State.

*****FCFMT: Federal College of Fisheries and Marine Technology.

Table 3.2: List of Analytical Equipment

S/N	Equipment	Model	Location
1	SEM/EDX	Seron microscope, model AIS2100	All school labs, Lagos.
2	XRD	GB36SR	All school labs, Lagos.
4	BET	NOVA 2400e	STEP-B, FUTMINNA.
5	UV-Spec	Shimadzu UV- 180.	STEP-B, FUTMINNA.
6	FT-IR	FT-IR Spectra machine	University of Ilorin.

*FUTMINNA: Federal University of Technology, Minna.

3.1 Methods

3.1.1 Watermelon rind sample collection and pre-treatment

Watermelon rinds were collected from a fruit market in Federal university of technology, Minna,Niger Sate, Nigeria. The WR were washed with distilled water to remove impurities. WR was cut into smaller pieces and dried in an electric oven at 105^0C for 24 hrs to reduce moisture content and the dried WR was reduced in size with a mortar and pistol. The precursor was stored in an airtight container, awaiting further use.

3.2 Production of Biochar

Fifty gram (50g) of the precursor was weighed and put in a pyrolysis equipment. Nitrogen gas was purged intothe reactor to create inert condition. Experimental conditions like time (2 -4hrs) and temperature (400 - 600^0C) were varied. The influence of the parameters temperatureand time were studied by using the response surface methodology (CCD design) The flow rate of nitrogen gas and the heating rate was held at 150 cm^3/min and 10 °C/min,

respectively. The dry char was be kept in an airtight container awaiting further use after the carbonization process.

3.2.1 Experimental Design

To determine the optimal temperature a two variable central composite design (CCD) was used for response surface methodology to model the interactions between temperature and time. The working minimum (350^0C and 2 hrs) and maximum (650^0C and 4 hrs) time and temperature for this design were extracted from literature review (Gin *et al.*, 2014, Oghenejoboh, 2018).

Table 3.3: Preliminary Calculation for CCD for a Response Surface

Parameters	-α	Lower (-1)	Midpoint (0)	Upper limit +α (+1)	
Temperature (^{0}C)	416.5	450	500	550	583.5
Time (hr)	2.165	2.5	3	3.5	3.835

Table 3.4: Selection of Values for a Response Surface

No of Exp	Coded Experiments		Actual Experiments	
	X_1	X_2	X_1 (^{0}C)	X_2 (hrs)
1	-1	-1	450	2.5
2	+1	-1	550	2.5
3	-1	+1	450	3.5
4	+1	+1	550	3.5
5	+α	0	583.5	3
6	- α	0	416.5	3
7	0	- α	500	2.165
8	0	+ α	500	3.835
9	0	0	500	3
10	0	0	500	3
11	0	0	500	3
12	0	0	500	3

3.3 Preparation of Activated Carbon

The biochar is activated via chemical activation method using zinc chloride and sulphuric acid zinc chloride was poured into beakers containing the activated carbon and stirred until a paste is formed. The same was done for sulphuric acid. The impregnation ratio (IR) used for this 0.5/1, 1/1, 2/1, 3/1 and 4/1 and can be calculated by the equation:

$$IR = \frac{W1}{W2} \quad (3.1)$$

Where, W_1 is the dry weight (g) of the activating agent (zinc chloride and sulphuric acid) and W_2 is the dry weight (g) of the char.

Once zinc chloride and the biochar was mixed, the paste was transferred into a dry crucible, oven dried for 1 hr at 105°C, and finally introduced into the reactor and heated at 800°C for 2 hrs. It was cooled at room temperature, washed with distilled water until the filtrate reaches a pH of about 7. The washed activated carbon was dried for about 2 hrs in an oven at 105 °C.

The char was also mixed with sulphuric acid, placed in an oven and activated at 700^0 C for about 15 mins. The samples was allowed to cool to room temperature, washed with distilled water and soaked in 1% NaoH solution to remove any remaining acid. The sample was dried in an air oven at 105 ^{0}C for 2 hrs (Oghenejoboh, 2018; Kobya *et al.*, 2005; Madhumitha *et al.*, 2016).

The char yield after the carbon has been activated will be determined using equation 3.2:

$$\%yield - \frac{W1}{W2} * 100 \quad (3.2)$$

Where, W_1 is the weight of the sample after pyrolysis and W_2 is the weight of the sample before pyrolysis.

3.4 Treatment of the Wastewater

3.4.1 Batch adsorption experiments

Batch adsorption experiments were implemented by placing activated carbon of varying dosages 0.3 - 1 g in 100 mL conical flasks with 10 mL of oil spill wastewater. The flasks were

tightly covered to avoid possible losses of the aromatic compounds due to volatilization during the course of the experiments. The glass flasks containing the solution and carbons were tightly covered and then placed in thermostatic shake water bath which was shaken at an agitation rate of 200 rpm for different agitation times ranging from 95 -135 mins.

The effect of varying parameters such as temperature, contact time and adsorption dosage were implemented via response surface methodology, to determine optimal conditions for the removal of benzene and toluene.

The BTEX concentration in solution before and after the adsorption was determined using UV spectroscopy using the following wavelengths: benzene, 252 nm and toluene, 260 nm. The calibration curves for BTEX were constructed by diluting the solution to various known concentrations and recording their absorbance.

Table 3.5: Selection of Values for a Response Surface for Adsorption

Run	Temp C	Time min	Adsorbent dosage G
1	25	135	0.5
2	40	105	0.9
3	32.5	120	0.7
4	40	135	0.9
5	45.1134	120	0.7
6	32.5	145.227	0.7
7	32.5	120	0.7
8	32.5	94.7731	0.7
9	40	135	0.5
10	19.8866	120	0.7
11	32.5	120	0.7
12	32.5	120	0.363641
13	25	105	0.9
14	32.5	120	0.7
15	32.5	120	0.7
16	32.5	120	1.03636
17	25	135	0.9
18	40	105	0.5
19	32.5	120	0.7
20	25	105	0.5

The amount of BTEX adsorbed, (qe) in milligrams per gram was determined using the equation 3.3:

$$qe = \frac{(Co-Ce)\times V}{m} \quad (3.3)$$

Where Co = the initial BTEX concentration in mg/L, Ce = the equilibrium BTEX concentration in mg/L, V = the volume of the solution in litres and m = the mass of the adsorbent in g.

The removal efficiency will be calculated as follows:

$$Removal\ efficiency\ (\%)\ =\ \frac{Co-Ce\times 100}{Co} \quad (3.4)$$

Where Co and Ce are the initial and equilibrium metal concentrations (mg/L) respectively.

3.6 Characterization of Biochar, Activated Carbon and Treated Wastewater

3.6.1 Proximate analysis

The physical and chemical properties of WR, bio char and activated carbon was determined via proximate analysis. The proximate analysis was determined using the standards as set by the Association of Analytical Chemistry (AOAC), (2016).

3.6.1.1 Moisture content

Three grams (3 g) of the carbonized sample was placed in a clean, dry petri-dish and dried in an oven at 105^0C for 90 mins. The sample was then cooled in a desiccator for 30 mins and the weight of the sample before and after heating will be determined. The percentage moisture content was calculated using equation 3.5:

$$Moisture\ content\ =\ \frac{(W1-W2)\times 100}{W1} \quad (3.5)$$

Where, W1 = Weight of sample before drying, g and W2 = Weight of sample after drying.

3.6.1.2 Ash content

Three grams (3 g) of watermelon peel was weighed in a crucible and oven dried at a temperature of 400^0C for 1 hr. The sample was allowed to cool in a desiccator and after

cooling it was weighed. The ash content was calculated with equation 3.6:

$$\frac{W1}{W2} \tag{3.6}$$

Where W1 = Weight of ash and W2 = Weight of dry sample

3.6.1.3 Volatile content

Four grams (4 g) of activated carbon was put in a crucible and oven dried at a temperature of 450^0C for 10 mins. The sample was weighed before and after drying to determine the amount of volatile matter as shown in equation 3.7:

$$Percentage\ volatile\ content\ = \frac{(W1-W2)}{W1} \times\ 100 \tag{3.7}$$

Where, W1 = Weight of sample before drying (g), and W2 = Weight of sample after drying (g).

3.6.1.4 Fixed carbon content

This was gotten using equation 3.8:

$$100 - (Ash\ content + volitile\ matter\ content + moisture\ content)\% \tag{3.8}$$

3.6.2 Characterization of prepared activated carbon

3.6.2.1 Surface electron microscopy (SEM) analysis

About 0.05 g of WR and activated carbon samples was sprinkled on a carbon tape that was fixed onto an aluminum stub. The zinc oxide and phyto-enhanced zinc oxide synthesized were coated with gold-palladium (Au:Pd; 60:40) using Quorum T15OT for five (5) min

preceding the analysis. The essence of this is to prevent charging which interfere with images during analysis. To examine the morphology and elemental makeup of the samples, the Zeiss Auriga SEM was used.

3.6.2.2 Brunauer-emmett-teller (BET) analysis

The analysis for the surface area, pore volume and pore size distribution of the samples was determined by Brunauer - Emmett- Teller (N_2 BET) technique using a NOVA 4200e surface area and pore analyzer instrument. 100 mg each of the zinc oxide and phyto-enhanced zinc oxide synthesized photocatalyst powder was weighed and degassed by flowing N_2 at 90 °C for 1 hr, and then held at 350 °C for 2 hrs. As the temperature is increased, water vapor was adsorbed from the surface and pores of the sample. The sample was left to cool down and weighed again. The instrument uses physical adsorption and capillary condensation of N2 principles to obtain information about the surface area and porosity of Activated carbon.

3.6.2.3 Fourier transform infra-red spectroscopy (FT-IR) analysis

The FT-IR spectra was recorded using the Nicolet 6700 spectrophotometer instrument and the result was obtained by feeding the dry samples of WRAC into an impact 360 FT-IR spectrometer under dry air at room temperature using KBr pellets. This was initiated by transferring some KBr out into a mortar, adding about 10 mg of the WRAC sample to the mortar, mixing, and grinding the mixture to a fine powder. The concentration of the sample in KBr should be in the range of 0.2% to 1%. The sample was ground finely to reduce scattering losses and absorption band distortions (Chao *et al.*, 2014). It is important to grind the samples to about 5 mm in diameter. Otherwise, large particles scatter the infrared beam and cause a slope baseline of spectrum. All absorbance spectra were obtained in the 4000–

400 cm^{-1} range by 100 scans at 1.0 cm^{-1} resolution.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter presents the results of the characterization of the WR, activated carbon and their application for adsorption studies. Also, presented are the experiment results of effect of selected process parameters on the adsorption of benzene and toluene.

4.1 Preliminary Proximate Analysis Studies on Raw WR, BC and Activated Carbon

Table 4.1 shows the properties of raw watermelon rind, biochar (BC) and activated carbon. It was discovered that the moisture content for BC and activated carbon were lower than the moisture content for WR. Ash content has a big responsibility in affecting the quality of activated carbon. Excess ash can usually block the pores in the activated carbon, reducing the surface area of the activated carbon and ultimately affecting the adsorption efficiency of the activated carbon. The proximate analysis shows that the ash content for BC at 31.9% was higher than WR at 2% but the ash content for activated carbon at 13.05% was lower than BC at 31.9%. The higher content in BC than AC and WR could be as a result of mineral salt formation during the pyrolysis process (Ultrasonik, 2017). High ash content is undesired in AC processing because it represents amount of inorganic material from the precursor activation and a numerous treatment needed to be take place. This is consistent with (Ultrasonik, 2017).

The results show that volatile matter was reduced from 60.07% for WR, to 27.3% for BC to 20.70% for AR. Volatile matter for WR got lower during pyrolysis due to the decomposition of biomass and reduced even lower for activated carbon because the

addition of activators causes changes in the structure and properties of activated carbon absorption. H_2SO_4 activators cause degradation of organic material that weakens the surface structure of activated carbon. In addition,this activator also releases volatile substances and develops an active carbon micro-pore structure.The activator is able to cleanse and enlarge the pore surface by releasing non-carbon elements, especially hydrogen, oxygen, and nitrogen in liquid form known as tar and gases. These results arein accordance to Maulina and Iriansyah (2018).

Table 4.1: Proximate analysis of WR, BC and AC

S/N	Property	WR (%wt)	Biochar (%wt)	AC (%wt)
1	Moisture Content	15.38	1.4	5.8
2	Volatile Matter	60.07	27.3	20.70
3	Ash Content	4.00	31.9	13.05
4	Fixed Carbon	20.55	39.4	60

Fixed carbon is the solid combustible residue that remains after a coal particle is heated and the volatile matter is expelled. Fixed carbon content is affected by cellulose and lignin content that can be converted to carbon atoms. Temperature and time affects fixed carbon levels during pyrolysis while activator concentration and temperature have an effect on fixed carbon for Activated carbon. The fixed carbon saw a tremendous increase from 20.55% for WR to 39.4% for BC and 60% for activated carbon. The increase in activated carbon is due to the lower volatilecontent and ash content. These results correspond to Junna *et al.* (2016).

4.2 Influence of Process Parameters on the Production of Biochar

Temperature and time were the parameters used to produce biochar from activated carbon. The temperature and time were determined from response surface methodology in conjunction with central composite design. This section focuses on how these process parameters affect certain elements like carbon yield. The carbon yield is optimized and ANOVA for the model is discussed.

4.2.1 Influence of temperature and time on psychochemical properties of carbon yield

The biochar yield reduced as temperature and time increased. For example, at 450^0C and 2.5 hrs,the carbon yield was at 37.46% but dropped to 31.56% at 550^0C and 2.5 hrs. It was discovered that temperature affected the carbon yield more than time, as there was a massive drop in carbon yield 30.22% at the highest temperature 583.5^0C and time of 3 hrs. It was observed, that while the biochar yield was dropping, the volatile matter was affected in a directly proportional matter, while the fixed carbon was affected in an inversely proportional manner; this is due to the decomposition of biomass during the pyrolysis process and the release of volatile matter. These results correspond to Junna *et al.* (2016). Response surface methodology analysis for CCD gave the equation:

$$\text{Yield} = +36.03-215A-0.3677B+0.6675AB-1.70A^2+0.2426B^2 \quad (4.1)$$

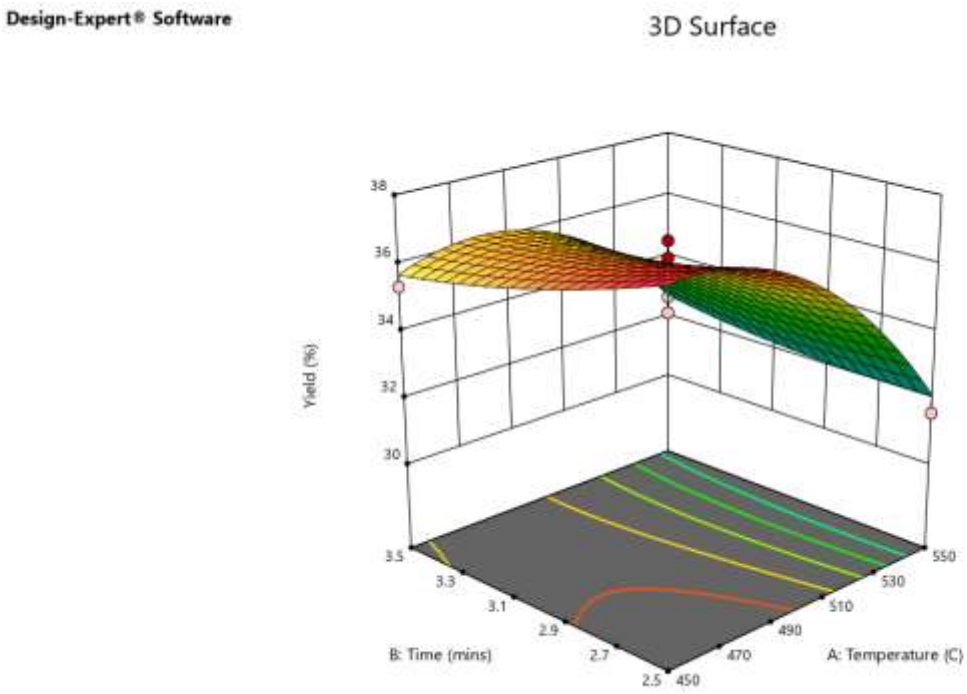

Figure 4.1: A plot of temperature and time vs. yield for WRBC

4.2.2 ANOVA for Quadratic model

The Model F-value of 30.88 from figure 4.1 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 2.36 implies the Lack of Fit is not significant relative to the pure error. There is a 21.24% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

Table 4.2 ANOVA for Quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
A-Temperature	37.12	1	37.12	93.13	< 0.0001	
B-Time	1.08	1	1.08	2.71	0.1435	
AB	1.78	1	1.78	4.47	0.0723	
A^2	20.04	1	20.04	50.28	0.0002	
B^2	0.4095	1	0.4095	1.03	0.3445	
Residual	2.79	7	0.3986			
Lack of Fit	1.78	3	0.5946	2.36	0.2124	not significant
Pure Error	1.013	4	0.2517			
Cor Total	64.34	12				

4.3 Influence of Process Parameters on the Production of Activated Carbon

The activated charcoal from this method was used to make activated carbon using Zinc chloride and sulphuric acid. The impregnation ratio used for this was 0.5, 1, 2, 3 and 4. The influence of impregnation ratio on surface area, pore diameter and pore volume on the activated carbon was studied. It was discovered that the method that produced activated carbon with the largest surface areas and pore volumes for the reagents zinc chloride and sulphuric acid respectively was sulphuric acid at IR of 2.

4.3.1 Influence of impregnation ratio on the surface area of activated carbon

As impregnation ratio increases from 0.5 to 2, the surface area of WAC increases, but increasing impregnation ratio from 2 to 4 leads to decrease the surface area of WRAC. The surface area is a maximum value 900 m^2/g at the temperature of 700^oC with sulphuric acid activation and 800^oCat 492.172 m^2/g at in which impregnation ratio is 2/1 but the surface areas 447 m^2/g for sulphuric acid and 456 m^2/g for zinc chloride drastically reduced as the impregnation ratio increased.

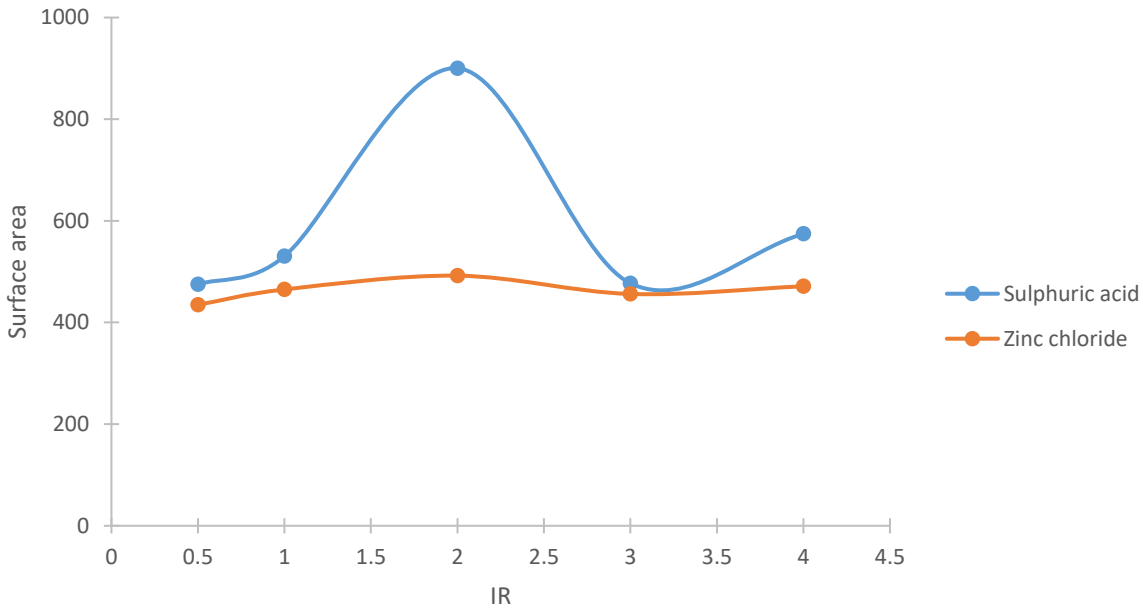

Figure 4.2: Effect of IR on surface area

From the results as seen in figure 4.2, the method that produced activated carbon with the largest surface areas for the reagents zinc chloride and sulphuric acid respectively is the IR 2/1 with the surface areas for these activated carbon at 492.172 m^2/g and 900.361 m^2/g respectively. This increase in surface area can be due only to the degradation of the matrix

of the lignocellulosic precursor, which gives rise to more surface area (Naima *et al.*, 2009).

4.3.2 Influence of impregnation ratio on pore volume of activated carbon

The influences of impregnation ratio on pore volume for prepared activated carbon at 800 ^{o}C and 700 ^{o}C for zinc chloride and sulphuric acid respectively is seen in Figure 4.3.

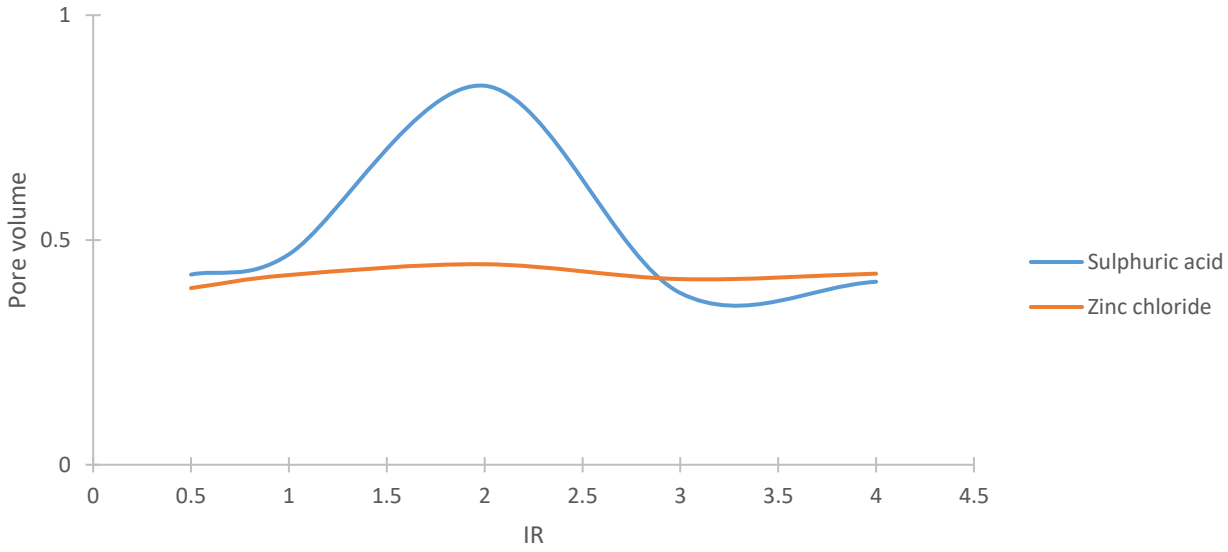

Figure 4.3: Effect of IR on pore volume

At low impregnation ratios, pore formation is dominating mechanism and pore widening becomes important as the ratio increases. Therefore, pore volume increases until the impregnation ratio of 2/1. Then, the total pore volume decreases at the impregnation ratio of 3/1. The maximal value ofthe total pore volume of WRAC prepared with impregnation ratio of 2/1 is found to be 0.84 cc/g for sulphuric acid and 0.446 cc/g for zinc chloride. The pore volume drastically reduced at 0.382 cc/g for sulphuric acid but only observed a slight reduction for zinc chloride at 0.413 mm/g. The reduction in pore volume as the IR increases shows that there opening of the micropores in mesopores under the effect of the temperature

and on the other hand the entities of the activating agent become more voluminous, accentuating further the hydrolysis and thus the swelling of the activating material (Naima *et al.*, 2009).

4.3.2 Influence of impregnation ratio on pore diameter of activated carbon

This section represents the average pore diameters of WRACs produced with the different As theimpregnation ratio was raised for all WRACs produced with sulphuric acid, the pore diameter increased until the impregnation ratio of 1/1 at 3.000e+00 nm but drastically reduced to 2.940e+00 nm at IR of 2/1.

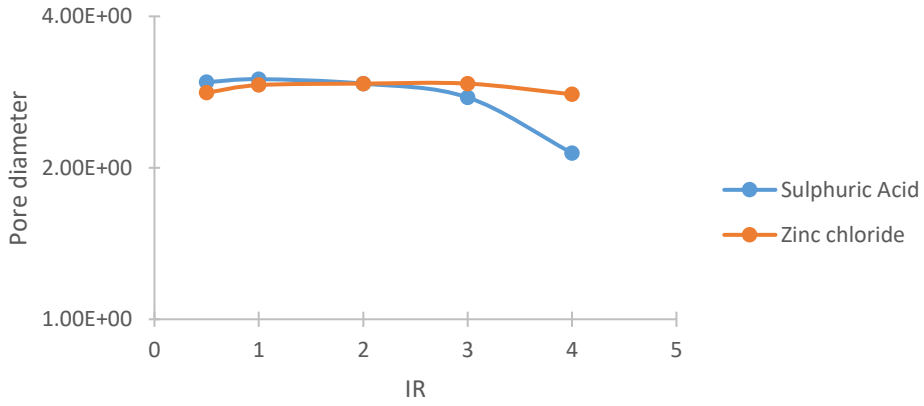

Figure 4.4: Effect of IR on pore diameter

As seen in Figure 4.4 in zinc chloride, the pore diameter peaked at 2/1 at 2.940e+00 nm and remained steady at IR of 3/1 with 2.940e+00 nm but finally reduced slightly at 4/1 with 2.800e+00 nm. It is possible that their observed pore widening at high activating agent -to-raw material ratios can be attributed to the fact that a significant faction of the activating agent would widen the pores due to large external localized decomposition (Naima *et al.*, 2009).

4.4 Characterization Of Activated Carbon

4.4.1 FTIR analysis of the activated carbon

The FTIR technique is an important tool to identify important functional groups, which are capableof adsorbing the pollutants. Watermelon contains pectin, polysaccharide, amino acid, coralline, cellulose, and water soluble low molecular weight components. FTIR spectra of WRAC preparedat different conditions were determined. At the spectrum of WRAC, the broad absorption band between 3200 and 3400 cm^{-1}shows the existences of OH groups and the vibration of NH stretching (Dagdelen *et al.*, 2014). The peaks of aromatic ring were observed at 1560.29 cm^{-1} (Gupta and Gogate, 2016). The bands in the range of 1300–1000 cm^{-1}can be assigned to the stretching vibration of carboxylic acids and alcohols (Uner *et al.*, 2015). The hydroxyl and carboxylic groups are important sorption sites as they work to bind hydrocarbon fractions to the active sites of the adsorbent.

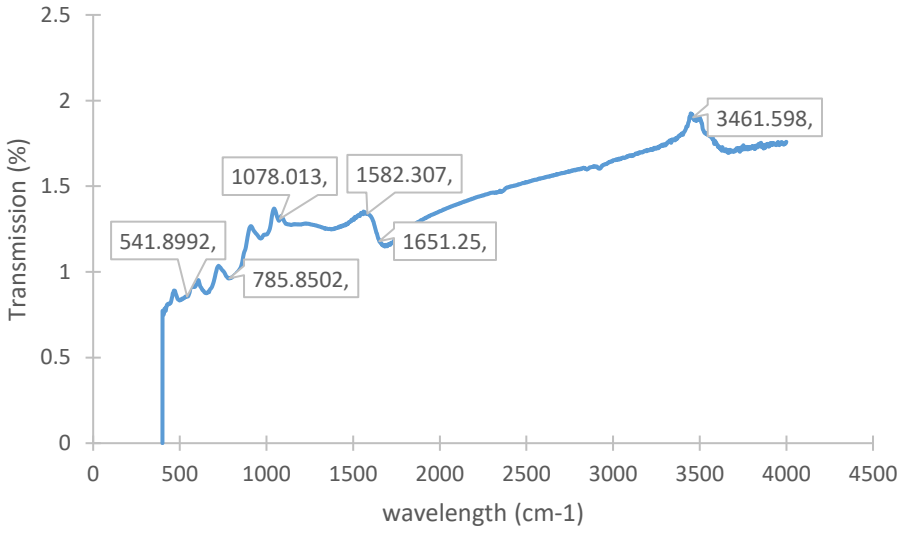

Figure 4.5: FTIR graph for activated carbon

4.4.2 SEM analysis of the activated carbon

The SEM images obtained for the raw WR and WRAC reveal the surface texture and morphologyof the both the raw material and adsorbent respectively. The SEM images of WR and WRAC at the operating condition with 22000x magnification as seen in Fig. 4.6. The SEM image of the activatedcarbon activated with H_2SO_4 when compared to the raw WR should distinct changes that occur because of the treatment with the reagent. After treatment, the SEM shows a change in the morphology of the WRAC when compared to the raw WR; this should provide better adsorption capacity.

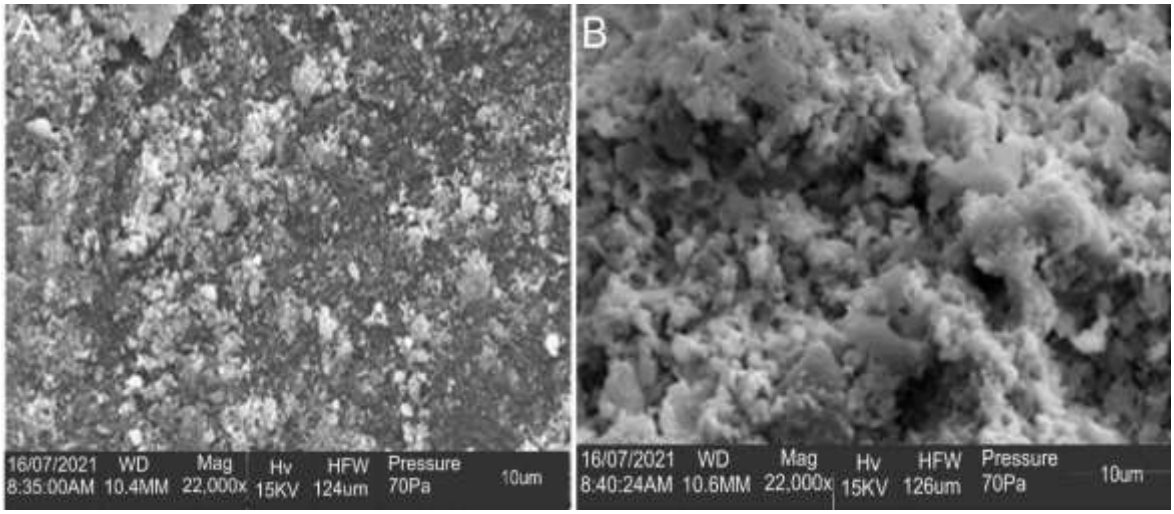

Figure 4.6: SEM micrograph of raw WR (A) and WR activated carbon (B)

4.5 Preliminary Analysis on Oil Wastewater

Primary analysis on the concentration of benzene and toluene show that they are well above the drinking water standards for the world health organization. WHO (2016) states that drinking water regulations for benzene and toluene must be around 0.01mg/L and 0.7 mg/L respectively. The initialconcentrations for benzene and toluene respectively were 8.826 mg/L and 137.65 mg/L. The results reported in this work were compared to the results

related to the literature (Stahelin *et al.,* 2018).By comparing the results, it is possible to observe that the behaviour in terms of adsorption capacitywas similar to literature at 51% (4.14 mg/L) for benzene 22% (113.79 mg/L) for toluene; this is as seen in (Stahelin, 2018).

4.6 Effect of Temperature on Adsorption Removal Efficiency

The effect of temperature on removal efficiency was studied for the removal of benzene and toluene in oil spill wastewater. Temperature ranging from 25^0C to 45^oC was used to determine theremoval efficiency of these soluble hydrocarbons. It was discovered that at lower temperatures, removal efficiency was higher than at higher temperatures, with the peak removal efficiency at 51% for benzene and 22% for toluene.

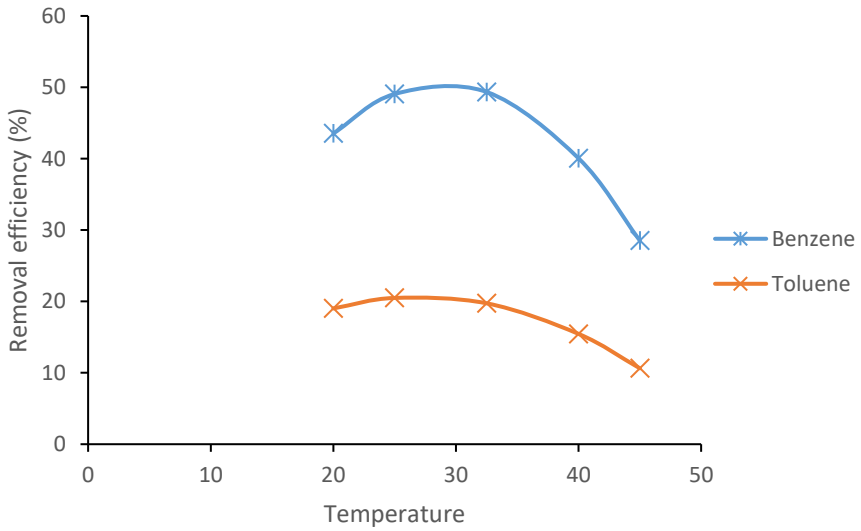

Figure 4.7: A plot of temperature vs removal efficiency

The removal efficiency was drastically reduced after the peak was achieved. This result is in line with (Nourmoradi *et al.,* 2013).

4.7 Effect of Time on Adsorption Removal Efficiency

The adsorption capacity of benzene and toluene using modified adsorbent was rapidly increased at the beginning of contact time, which could be due to the availability of more adsorption sites (Nourmoradi *et al.*, 2013). The contact time for the adsorbent on benzene and toluene was from 90-200 mins. The removal efficiency increases slowly up to about 120 mins and after that, the removal efficiency was slowed down.

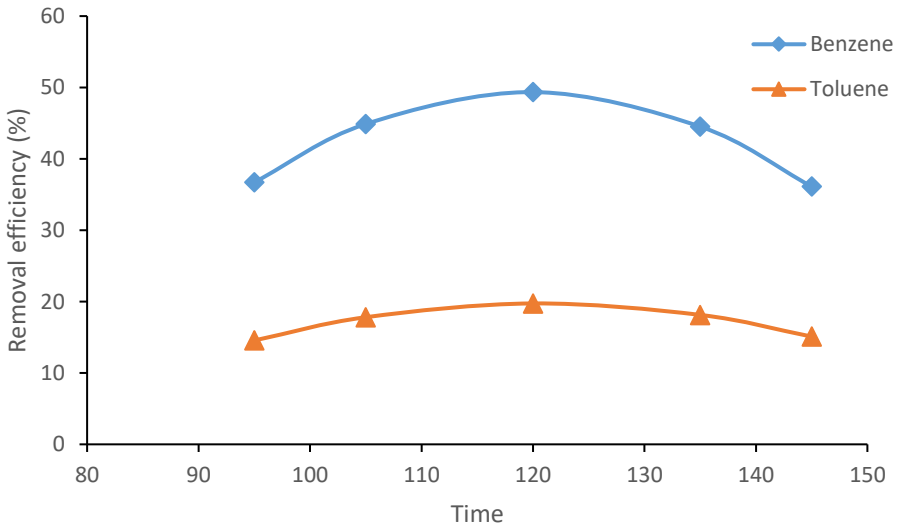

Figure 4.8: A plot of time vs removal efficiency

4.8 Effect of Adsorbent Dosage on Removal Efficiency

The adsorbent dosage is one of the important factors because it presented the capacity of the adsorbent for a given initial concentration of the adsorbate. To determine the influence of adsorbent dosage on removal efficiency, different adsorbent dosages (0.3-1 g) were used. The removal percentage of benzene and toluene increased as the adsorbent does was increased this could be as a result of the rise in adsorption sites. The peak removal efficiency was discovered at 0.7 g, and after this peak, the sorbent dosage was negligible because it

achieved the equilibrium adsorption capacity at higher adsorption dosages.

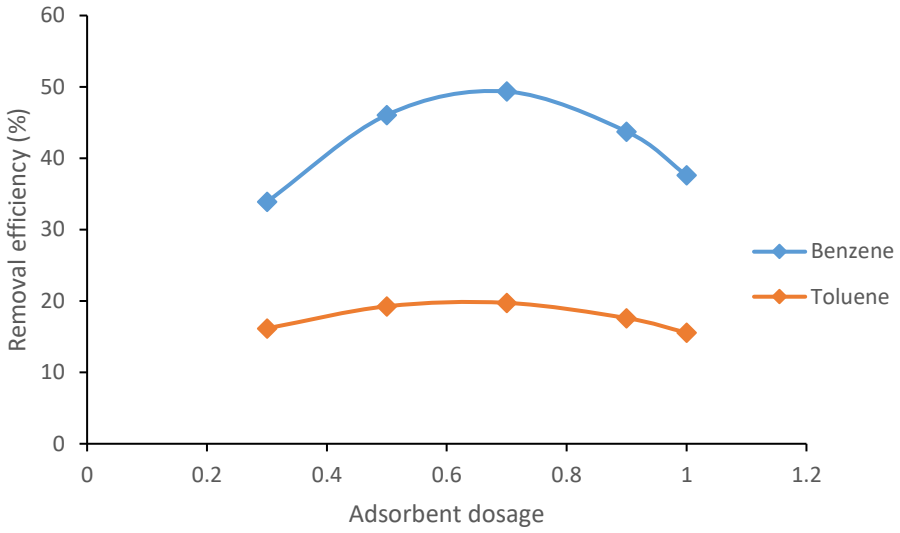

Figure 4.9: A plot of adsorbent dosage vs removal efficiency.

The reason that the removal efficient removal peaked at 0.7 g is because before then the adsorbent surface are completely uncovered which may accelerate the approachability of benzene and toluene molecules to a large number of the adsorbent active sites.Therefore, the adsorption on the surface active sites is reached to a saturated point, performing a high removal capacity. However, at higher adsorbent dosage, the accessibility of adsorbent active sites with higher energy decreases and a larger portion of the active sites with lower energy becoming occupied; leading to a decrease in adsorption process (Nourmoradi *et al.*, 2013).

4.9 Adsorption Isotherms

The equilibrium adsorption isotherm is known one of the most important data to understand the mechanism of the adsorption and describe how adsorbents interact with adsorbents. The experimental adsorption equilibrium data of benzene and toluene were fitted to the Langmuir and Tenkim isotherm models. These adsorption models give a representation of

the adsorption equilibrium between an adsorbate in solution and the surface active sites of the adsorbent.

Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature and adsorption is limited to monolayer coverage, and intermolecular forces decrease with the distance from the adsorption surface. On theother hand, the Temkim model supposes that the adsorption surface is heterogeneous, that interactions among adsorbed molecules can occur, and that multilayer adsorption is possible. The Langmuir and Temkim adsorption isotherms exhibit an approximately linear relationship for the WRAC. The data obtained from the WRAC revealed that the Langmuir isotherm model fitted the experimental data better than Temkim isotherm for benzene (Arshadi *et al*., 2016). Error analysis using the Chi_Square_Test (X^2) method was carried out for both the Langmuir and Temkin models and it was discovered that for benzene, the R^2 gave better results with the Langmuir model than the Chi_Square_Test (X^2) method. This shows that the Langmuir model is a better fit (Balarak and Salari, 2018). The error analysis for the Langmuir with the benzene pollutant gave slightly better result than the Temkin model.

Table 4.5: Values for Adsorption Isotherms.

Pollutant	Isotherm	Parameter	Value
Benzene	Langmuir	Q_o	0.132
		B	0.38
		R^2	0.9648
		X^2	0.24
	Temkin	A	3.3756
		B	81.0072
		R^2	0.9749
		X^2	0.23
Toulene	Langmuir	Q_o	-1.053
		B	-0.0069
		R^2	0.9862
		X^2	8.91
	Temkin	A	-0.587198
		B	0.073085
		R^2	0.9217
		X^2	0.061

4.10 Kinetic Studies

Benzene and toluene adsorption capacities were investigated as a function of time 0-120 min todetermine the adsorption equilibrium time for the adsorption of benzene and toluene onto WRAC at 0.7 g. It is easily seen that the amount of benzene and toluene adsorption were significantly increased onto the WRAC with increasing the contact time. Studies conducted on theadsorption kinetics of Benzene and toluene removal revealed that the removal efficiency reached equilibrium at 120 mins; there removal efficiency had minimal reduction. At 120 mins, theefficiency removal was 51% and 22% for benzene and toluene respectively. In order to determineand interpret the mechanism of benzene and toluene adsorption processes over the WRAC and major parameters governing sorption kinetics, kinetic sorption data obtained empirically were fitted to the pseudo-first-order and pseudo-

second-order, where k_1, and k_2 are the adsorption rateconstants of first and second order kinetic. The calculated kinetics parameters for adsorption of benzene and toluene at initial concentration of 8.826mg/l and 137.65mg/l respectively are tabulated in Table 4.6. As can be observed, the second-order equation appeared to be the best- fitting model than those for the other two equations (the correlation coefficient is extremely high for the second-order equation of WRAC; $R^2 > 0.97$ and 0.96 for benzene and toluene respectively.The pact of the experimental data with the pseudo second-order kinetic model is based on the sorption experiment and it indicates that the adsorption of benzene and toluene is controlled by chemisorption. This means that it exists as the rate-limiting step of the adsorption mechanism and no involvement of a mass transfer in solution (Arshadi *et al.,* 2016).

Table 4.6: Value for Pseudo-first order and Pseudo-second order kinetics

Pollutant	Pseudo-first order Parameters			Pseudo-second order Parameters			
	Qe (mg/g)	k_1(L min^{-1})	R^2	Qe (mg/g)	K_2	(Lmin^{-1})	R^2
Benzene	1.24	0.035	0.9391	0.0037	0.219		0.9797
Toluene	3.65	0.042	0.9105	0.0155	0.957		0.9813

4.11 Thermodynamics Studies

Table 4.7: Thermodynamic values for benzene and toluene pollutants

Pollutant	Temperature (K)	ΔHº (J mol-1)	ΔSº (J mol-1 K-1)	ΔGº (J mol-1)
Benzene	303	1107.325	-37.905	-10385.3
	313			-10763.1
	323			-11114.4
	333			-11504.6
	343			-11912.8
Toulene	303	13283.25	-66.7804	-6864.12
	313			-7637.06
	323			-8435.78
	333			-8995.07
	343			-9500.29

It can be observed that ΔGº values are the negative at all temperature indicate the feasibility of the process and the spontaneous nature of the adsorption of benzene and toluene onto WRAC. The negative value of ΔHº reveals that the adsorption process was exothermic and physical in nature (Nourmoradi *et al.*, 2013). Positive values of ΔSº indicates an irregular increase of randomness, mirrors the affinity towards the adsorbent and increased disorderliness at the solid-solution interface and the driving force during the adsorption process .

4.12 ANOVA Results for Benzene and Toluene

The Model F-value for benzene in the 3D plot of 4.10 implies the model is significant. P-values less than 0.0500 indicate model terms are significant. In this case A, AB, AC, BC, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value implies the Lack of Fit is not significant relative

to the pure error. There is a 26.73% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

Table 4.8: ANOVA table for benzene

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1527.98	9	169.78	30.22	< 0.0001	significant
A-Temp	276.97	1	276.97	49.30	< 0.0001	
B-time	0.4369	1	0.4369	0.0778	0.7860	
C-Adsorbent dosage	18.50	1	18.50	3.29	0.0997	
AB	54.60	1	54.60	9.72	0.0109	
AC	305.13	1	305.13	54.32	< 0.0001	
BC	97.40	1	97.40	17.34	0.0019	
A^2	331.52	1	331.52	59.02	< 0.0001	
B^2	312.39	1	312.39	55.61	< 0.0001	
C^2	284.65	1	284.65	50.67	< 0.0001	
Residual	56.17	10	5.62			
Lack of Fit	36.11	5	7.22	1.80	0.2673	not significant
Pure Error	20.06	5	4.01			
Cor Total	1584.16	19				

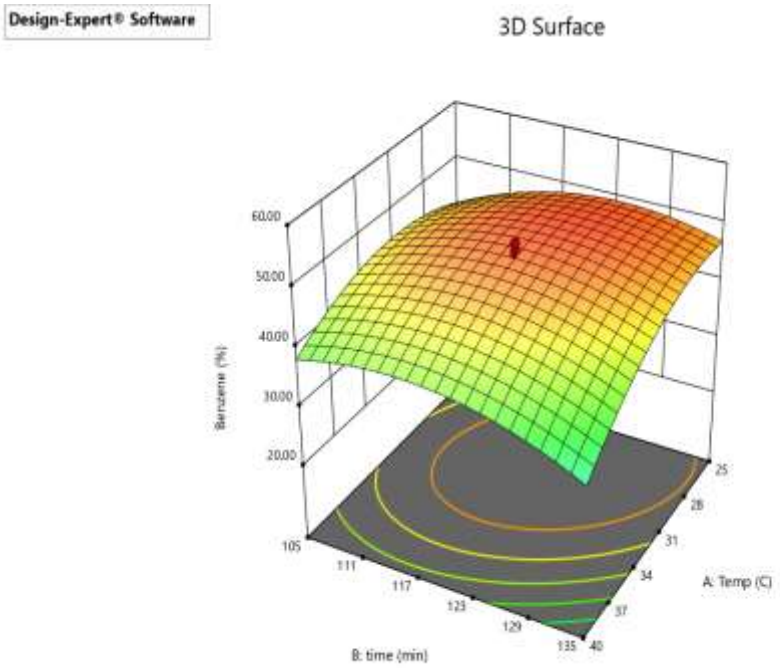

Figure 4.10: 3D plot of temperature and time vs removal efficiency for benzene

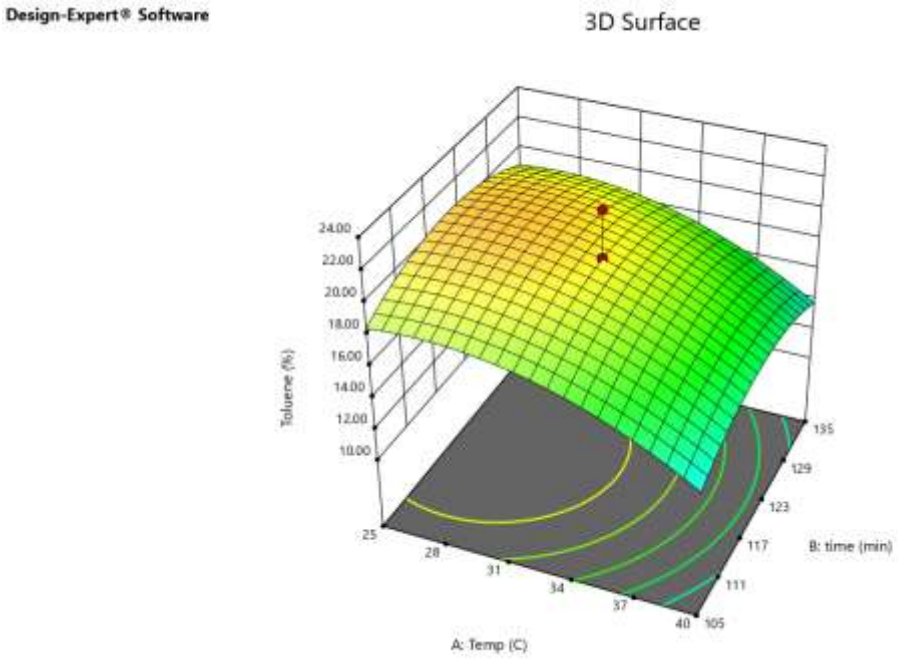

Figure 4.11: 3D plot of temperature and time vs removal efficiency for Toluene

The Model F-value for toluene in figure 4.11 above, implies the model is significant. There is only a 0.02% chance that an F-value this large could occur due to noise. P-values less than

0.0500 indicate model terms are significant. In this case A, C, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 0.15 implies the Lack of Fit is not significant relative to the pure error. There is a 97.13% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

Table 4.9: ANOVA table for Toluene

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	194.66	9	21.63	13.71	0.0002	Significant
A-Temp	86.53	1	86.53	54.84	< 0.0001	
B-time	0.3645	1	0.3645	0.2310	0.6411	
C-Adsorbent dosage	9.38	1	9.38	5.94	0.0350	
AB	0.0040	1	0.0040	0.0025	0.9608	
AC	1.75	1	1.75	1.11	0.3167	
BC	0.2743	1	0.2743	0.1738	0.6855	
A^2	45.10	1	45.10	28.58	0.0003	
B^2	45.10	1	45.10	28.58	0.0003	
C^2	24.62	1	24.62	15.61	0.0027	
Residual	15.78	10	1.58			
Lack of Fit	2.05	5	0.4105	0.1495	0.9713	not significant
Pure Error	13.72	5	2.74			

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, activated carbon was prepared from watermelon rind and the influence on certain parameters was investigated. Activated carbon was successfully prepared from biochar using chemical activation as a technique. The WR, BC and WRAC were characterized using proximate analysis. WR was characterized with SEM. The activated carbon was characterized with SEM, FTIR and BET. The morphology of the activated carbon when compared with WR confirmed that SEM shows change in structure when compared to the raw WR. FTIR confirmed the presence of –OH and carboxyl functional groups which are useful for adsorption of benzene and toluene.

The results of the adsorption showed that benzene and toluene removal largely depended on the operating parameter as the highest removal efficiency for benzene was 51% and toluene was 22% was recorded at optimal temperature, time and adsorbent dosage parameters which are 32.5^{o}C, 120 mins and 0.7 g . The results of obtained from this work, conclude that using watermelon rind as activated carbon for the adsorption of benzene and toluene shows promise. This method of adsorption removal is economical as it utilizes the use of agricultural waste and also because the production and utilization of WRAC is not expensive and does not need a lot of skill for implementation.

5.2 Recommendations

There should be further investigations:

I. Producing the activated carbon on appropriate support to provide an easy method for recovering the adsorbent. This investigation will also provide a platform for easier desorption studies.

II. On how using operating parameters separate from the parameters indicated in this study will affect fixed carbon for biochar. As biochar higher or equal to 60% is expected, a study on varying operating parameters for pyrolysis (nitrogen flow rate or heating capacity of pyrolysis equipment) is recommended

III. On how using operating parameters separate from the parameters indicated in this study will affect surface area and pore volume of the activated carbon. This would also inform other investigations on if a higher surface area than what was achieved in this project would improve removal efficiency of benzene and toluene on oil spill wastewater.

IV. Establishing a proper laboratory scale unit will enable proper investigation on these parameters.

5.3 Contribution to Knowledge

I. The removal of benzene and toluene from oil wastewater using activated carbon developed from watermelon rind at removal efficiencies of 51% and 22% respectively.

II. The optimization of biochar using Response surface methodology during production to study the influence of temperature and time with results showing optimal fixed

carbon of 37.46% values at 500^{o}C and 2.165 hrs.

III. The optimization of surface area of activated carbon by varying impregnation ratio and activating reagent (Sulphuric acid and Zinc chloride) to give optimal results of impregnation ratio of 2/1 with surface area of 900 m^2/g

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