# OPTIMIZATION OF ACTIVATED CARBON PREPARATION FROM CORNCOB WASTEWATER TREATMENT

**BY**

Akuso Samuel **ALKALI**

**DEPARTMENT OF CHEMICAL ENGINEERING,**
**FACULTY OF ENGINEERING**
**AHMADU BELLO UNIVERSITY, ZARIA**
**NIGERIA**

**SEPTEMBER, 2016**

# OPTIMIZATION OF ACTIVATED CARBON PREPARATION FROM CORNCOB FOR WASTEWATER TREATMENT

**BY**

**Akuso Samuel ALKALI, B.ENG (ABU) 2001**
**(MSc/Eng/6635/2010-2011)**

**A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER DEGREE IN CHEMICAL ENGINEERING**

**DEPARTMENT OF CHEMICAL ENGINEERING,**
**FACULTY OF ENGINEERING**
**AHMADU BELLO UNIVERSITY, ZARIA**
**NIGERIA**

**SEPTEMBER, 2016**

## DECLARATION

I declare that this dissertation work on titled "Optimization of Activated Carbon Preparation from Corncob" as carried out by me in the department of Chemical Engineering, Ahmadu Bello University, Zaria. The source of materials from the literature in the course of this work has been acknowledged and references provided. No part of this research work that has been presented for the award of another degree or diploma in this institution or elsewhere.

Akali Akuso Samuel
Name of student Signature Date

`

## CERTIFICATION

This dissertation titled "Optimization of activated carbon preparation from corncob" by Alkali Akuso Samuel has met the regulations governing the award of the degree of Master of Science in Chemical Engineering of the Ahmadu Bello University, Zaria, and has been certified and approved for its contribution to knowledge and its literary presentation.

| | | |
|---|---|---|
| Dr C. S. Ajinomoh<br>Chairman, Supervisory Committee | Signature | Date |
| Dr. A. S. Olawale<br>Member, Supervisory Committee | Signature | Date |
| Dr S. M. Waziri<br>Head of Department | Signature | Date |
| Prof. K. Bala<br>Dean, School of Postgraduate Studies | Signature | Date |

## DEDICATION

I dedicate this work to Almighty God, my late father Alkali Akuso and my beloved wife Elizabeth who stood by me in time of trials and challenges I encountered during the work.

## ACKNOWLEDGEMENT

First and foremost, I thank Almighty God; the giver of life, and knowledge for the wisdom and understanding given to me to undertake this work to completion. My profound gratitude goes to my project supervisors, Dr. C. S. Ajinomoh and Dr A. S. Olawale for their constructive comments to make this work what it is. I also wish to thank the management of National Research Institute for Chemical Technology (NARICT), Zaria for giving me the mandate and assistance in the course of my studies. I wish to appreciate the kind gesture of Dr S.M. Waziri and Dr B. Muktar of Chemical Engineering Department, Ahmadu Bello University, Zaria, Mr Ibrahim Wahala, Ephraim, Mrs S. Ibukun, Mrs B. Nworbi and Mr I. A. Raimi all staff of NARICT, Zaria. My hearty thanks go to my beloved wife and children for their endurance, tolerance and understanding during the course of my study.

## ABSTRACT

Corncob Activated Carbon (AC) was produced via chemical activation with phosphoric acid ($H_3PO_4$) for the hydrolysis step and potassium hydroxide (KOH) for the impregnation step. In this work, optimization and development of the model equations for the preparation conditions of AC, Design Expert 6.0.6 Stat-Ease, Inc USA software was used. For the optimization of the AC preparation conditions, a Central Composite Design (CCD) was used to investigate the effect of independent variables on the yield and adsorption capacity of the activated carbon samples. The independent variables used in this work were, phosphoric acid concentration, potassium hydroxide concentration, activation temperature ($^oC$) and activation time (minute). Response Surface Methodology (RSM) technique was used to optimize the preparation conditions ($H_3PO_4$, KOH, temperature and time); with percentage yields of hydrolysate and activated carbon and adsorption capacity of AC as the targeted responses. The optimal conditions for the preparation of AC using CCD software were 358.15 $^oC$, 116.90 minutes, 0.29 mg/l $H_3PO_4$, 0.09 mg/l KOH. This set of conditions gave hydrolysate yield of 76.9339 %, while activated carbon yield and Methylene Blue (MB) adsorption capacity were 21.84 % and 1.98 mg/g respectively. The specific surface area of the AC using Sear's method was 314.2 $m^2/g$. Analysis of Variance (ANOVA) for hydrolysate yield, AC yield and adsorption capacity showed the developed models equations were significant. The experimental and predicted values of the hydrolysate yield, AC yield and adsorption capacity of adsorbent on adsorbate MB were in close agreement and the correlation coefficients $R^2$-values of 0.9688, 0.9358 and 0.9134. The surface areas of selected ACs were 259.8 $m^2/g$ (AC8), 215 $m^2/g$ (AC9) and 314.2 $m^2/g$ (AC14) gave adsorption capacities of 1.92 gm/g, 1.97 mg/g and 1.98 mg/g of MB

respectively. The Fourier Transform Infra-Red (FTIR) analysis of the AC samples produced showed the presence of O-H, C-H, C-Br, N-H, C-C, C-N, C=C and C≡C functional groups which aid in adsorbing adsorbate onto the adsorbent. Adsorption isotherm data were used to model the following Langmuir and Freundlich isotherms; the adsorption of Chromium ions on the selected AC produced was predicted by Langmuir and Freundlich isotherm models with $R^2$ value of 0.9974 and 0.7691 respectively. The percentage chromium removal increases with increase in adsorbent dosage. The activated carbon samples produced can be effectively used for wastewater treatment.

## TABLE OF CONTENTS

DECLARATION ..... i
CERTIFICATION ..... ii
DEDICATION ..... iii
ACKNOWLEDGEMENT ..... iv
ABSTRACT ..... v
TABLE OF CONTENTS ..... vii
CHAPTER ONE: INTRODUCTION ..... 1
1.1 Background of Study ..... 1
1.2 Problem Statement ..... 3
1.3 Aim and Objectives ..... 3
1.4 Scope of the Work ..... 4
1.5 Justification ..... 5
CHAPTER TWO: LITERATURE SURVEY ..... 6
2.1 Corncob ..... 6
2.2 Economic Viability of Corncob ..... 7
2.3 Origin and History of Activated Carbon ..... 7
2.4 Processing Techniques ..... 8
2.5 Manufacture of Activated Carbon ..... 9
2.5.1 Thermal activation ..... 10
2.5.2 Chemical activation ..... 12
2.6 Properties of Activated Carbon ..... 13
2.6.1 Physical properties and pore structure ..... 13
2.7 Performance Evaluation of Activated Carbon using Methylene Blue (Mb) ..... 19
2.7.1 Determination of methylene blue concentration in solution ..... 19
2.7.2 Adsorption of methylene blue (MB) ..... 20
2.8 Chemical Properties ..... 23
2.9 Uses and Applications of Activated Carbon ..... 24
2.9.1 Gas phase application ..... 24
CHAPTER THREE: MATERIALS AND METHODS ..... 29
3.2 Materials ..... 29

3.3 Equipment ..... 29
3.4 Methodology ..... 30
3.4.1 Preparation of raw materials ..... 31
3.4.2 Hydrolysis, impregnation and activation of corncob ..... 31
3.4.3 Design of experiment ..... 32
3.4.4 Characterization of the corncob, hydrolysate corncob and activated carbon samples ..... 34
CHAPTER FOUR: RESULTS AND DISCUSSION ..... 37
4.1 Proximate Analysis of Corncob ..... 37
4.2 Yield and Adsorption Capacity of Activated Carbon ..... 37
4.2.1 Model validation ..... 38
4.2.2 Analysis of variance (ANOVA) ..... 42
4.2.3 Response surface analysis (RSA) plots for hydrolysate yield, activated carbon yield and adsorption capacity of activated carbon samples ..... 43
4.2.4 Optimization ..... 56
4.2.5 Fourier transform infrared (FTIR) spectroscopy ..... 57
4.2.6 Scanning electron microscope (SEM) ..... 59
4.3 Physical and Structural Characteristics of Selected Activated Carbon Samples ..... 62
4.4 Adsorption Isotherm Study ..... 64
4.4.1 Batch adsorption studies of chromium (VI) ions on AC ..... 64
4.4.2 Adjusted coefficient of determination ..... 67
CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS ..... 69
5.1 Conclusions ..... 69
5.2 Recommendations ..... 70
REFERENCES ..... 71
APPENDICES ..... 76
APPENDIX A ..... 76
APPENDIX B ..... 81

## LIST OF TABLES

Table 2.1: Surface areas of some activated carbon produced from corn cob (Sun *et al.*, 2007). ..... 15

Table 3.1 Materials used for the research work, their supplier and purity level ..... 29

Table 3.2: Equipment used for the experiment, their availability and model ..... 29

Table 3.3: Experimental range and levels of independent variables used in the activated carbon preparation from corncob..... 33

Table 3.4: Experimental design matrix using Central Composite Design expert (CCD) for the preparation of activated carbon. ..... 34

Table 4.1: Proximate analysis of corncob ..... 37

Table 4.2: The yield of samples and adsorption performance of activated carbon using central composite design (CCD)..... 38

Table 4.3: Properties of corncob and activated carbon samples ..... 63

Table 4.4: Elemental analysis of selected activated carbon samples..... 64

Table 4.5: Bulk density of selected activated carbon samples ..... 64

Table 4.6: Langmuir and Freundlich isotherm models for adsorption capacity of chromium ions in tannery effluent on activated carbon (AC14). ..... 65

Table A1: Surface areas of activated carbon, Sun et al., 2007. ..... 76

Table A2: Shows the experimental hydrolysate yield (%)..... 76

Table A3: Experimental and predicted hydrolysate yield (%) ..... 77

Table A4: Experimental and predicted response values for activated carbon yield ..... 77

Table A5: Experimental and predicted response values for adsorption capacity of activated carbon. ..... 78

Table A6: Analysis of variance (ANOVA) for the response of hydrolysate yield. ..... 78

Table A7: Analysis of variance (ANOVA) for activated carbon yield response. ..... 79

Table A8: Analysis of variance (ANOVA) for adsorption capacity of activated carbon response ..... 80

Table B1: Principal FTIR Absorptions for Certain Functional Groups ..... 81

Table B2: Characteristic FTIR Absorptions for Certain Functional Groups ..... 83

Table B3: Characteristic IR Absorptions ..... 84

Table B4: Characteristic Infrared Absorption Bands of Functional Groups ..... 85

## LIST OF FIGURES

Plate1: Images of (a) corn cob (b) prepared activated carbon (Hiremath et al., 2012)..... 7

Figure 2.1: Structure of Methylene Blue (MB). ..... 19

Figure 2.2: A general Freundlich isotherm curve. ..... 22

Figure 3.1: Flow diagram of research methodology ..... 32

Figure 4.1: Parity plot of hydrolysate yield (%) versus phosphoric acid concentration (mg/ml). ..... 39

Figure 4.2: Parity plot of experimental hydrolysate yield (%) versus predicted hydrolysate yield (%). ..... 40

Figure 4.3: Parity plot of experimental activated carbon yield versus predicted activated carbon yield. ..... 41

Figure 4.4: Parity plot of experimental adsorption capacity versus predicted adsorption capacity of activated carbon. ..... 42

Figure 4.5: Effect of phosphoric acid concentration (mg/l) and potassium hydroxide concentration (mg/l) on hydrolysate yield (%). ..... 44

Figure 4.6: Effect of phosphoric acid concentration (mg/l) and potassium hydroxide concentration (mg/l) on activated carbon yield (%). ..... 45

Figure 4.7: Effect of phosphoric acid concentration (mg/l) and activation temperature ($^{o}$C) on activated carbon yield (%). ..... 46

Figure 4.8: Effect of activation temperature ($^{o}$C) and potassium hydroxide concentration (mg/l) on activated carbon yield (%). ..... 47

Figure 4.9: Effect of activation temperature ($^{o}$C) and activation time (min) on activated carbon yield (%). ..... 48

Figure 4.10: Effect of potassium hydroxide concentration (mg/l) and activation time (min) on activated carbon yield (%). ..... 49

Figure 4.11: Effect of phosphoric acid concentration (mg/l) and activation time (min) on activated carbon yield (%). ..... 50

Figure 4.12: Effect of phosphoric acid concentration (mg/l) and potassium hydroxide concentration (mg/l) on adsorption capacity of activated carbon. ..... 51

Figure 4.13: Effect of phosphoric acid concentration (mg/l) and activation temperature ($^{o}$C) on adsorption capacity of activated carbon. ..... 52

Figure 4.14: Effect of potassium hydroxide concentration (mg/l) and activation temperature ($^{o}$C) on adsorption capacity of activated carbon. ..... 53

Figure 4.15: Effect of potassium hydroxide concentration (mg/l) and activation time (min) on adsorption capacity of activated carbon. ..... 54

Figure 4.17: Effect of activation temperature ($^{o}$C) and activation time (min) on adsorption capacity of activated carbon. ..... 56

Figure 4.18a: FTIR spectra of corncob, $cm^{-1}$ ..... 58

Figure 4.18b: FTIR spectra of hydrolysate corncob, $cm^{-1}$ ..... 59

Figure 4.18c: FTIR spectra of activated carbon, $cm^{-1}$ ..... 59

Figure 4.19c: SEM image of AC 14 at a magnification of 600x..... 62

Figure 4.22a: Effect of adsorbent dosage on chromium (VI) adsorption on activated carbon 14. ..... 65

Figure 4.21: Percentage removal of Chromium ions as a function of adsorbent dosage..... 66

## LIST OF SYMBOLS AND ABBREVIATIONS

### SYMBOLS

| | |
|---|---|
| b | affinity of adsorbent towards adsorbate |
| $C_e$ | equilibrium concentration |
| $C_o$ | initial concentration |
| $^oC$ | Degree Celcius |
| $^oF$ | Degree Fahrenheit |
| g | Gram |
| K | Kelvin |
| $k_F$ | adsorption capacity of the adsorbate |
| $m^2/g$ | meter square per gram |
| $m^3/g$ | meter cubic per gram |
| $M_a$ | weight of sample (activated carbon) |
| mg/l | milligram per litre |
| ml | Millilitre |
| $\Delta M_p$ | change in particle weight |
| n | favorability of adsorption process |
| nd | not determined |
| nm | nanometer ($1x10^{-9}$) |
| pH | hydrogen ion concentration in a solution |
| $q_e$ | amount of adsorbate adsorbed at equilibrium |
| $q_m$ | monolayer adsorption capacity |
| $R^2$ | coefficient of determination |

$R^2_{adj}$ Adjusted coefficient of determination

t adsorption time

UV Ultra Violet Spectrophotometer

V volume of solute

$V_a$ Volume of water displaced (by activated carbon)

$V_v$ pore or void volume

W amount of adsorbed used

% percentage

$\rho_l$ Density of liquid

$\mu_m$ micrometer ($1x10^{-6}$)

## ABBREVIATIONS

A Coded factor for phosphoric acid concentration (mg/l)

AC Activated carbon

ACs Activated carbons

AC8 Activated carbon eight

AC9 Activated carbon nine

AC14 Activated carbon fourteen

B Coded factor for potassium hydroxide concentration (mg/l)

BD Bulk density

C Coded factor for activation temperature ($^oC$)

CCD Central Composite Design

D Coded factor for activation time (minute)

FTIR Fourier Transform Infrared Spectrophotometer

| | |
|---|---|
| $H_2$ | Hydrogen gas |
| HCl | Hydrochloric acid |
| $H_2SO_4$ | Sulphuric acid |
| $H_3PO_4$ | Phosphoric acid |
| IAR | Institute of Agricultural Research |
| $K_2CO_3$ | Potassium Carbonate |
| KOH | Potassium hydroxide |
| MB | Methylene Blue |
| $N_2$ | Nitrogen gas |
| NaCl | Sodium Chloride |
| NaOH | Sodium Hydroxide |
| $O_2$ | Oxygen gas |
| RSM | Response Surface Methodology |
| SEM | Scanning Electron Microscope |
| $ZnCl_2$ | Zinc Chloride |

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background of Study

Activated Carbon (AC) is a versatile derivative of biomass predominantly amorphous (crystalline) solid that has extra ordinary large internal surface area and pore volume (Jamaludin, 2010). The unique structure of AC gives rise to its application ranges from liquid to gas phase because of their adsorptive properties.

Industrial ACs can be produced from any cheap material with a high carbon content, low inorganics as precursors such as coal, wood, coconut shell, corn cob, almond shells, peach stones, grape seeds, apricot stones, cherry stones, olive stones, peanut hull, nut shells, rice husk, oil palm shells, sugar cane bagasse (Tsai *et al*., 1997, and 2001; Jamaludin, 2010; Diya'udeen *et al*., 2011). Palm shell, rattan, mango stem peel, and corn cob (Mohd *et al*., 2011); canarium schevein furthii nutshell (and Ajayi and Olawale, 2009), groundnut shells, Palm Kernel shells, coconut shells, bamboo, wood chips, corn cob, seeds and saw dusts (Oloworise, 2006).

AC has been the most popular and widely used adsorbent in liquid and gas treatment throughout the world. Charcoal been the pioneer of AC has been recognized as the oldest adsorbent known in waste water treatment.

AC is produced by a process consisting of raw material dehydration and carbonization followed by activation. The product obtained has a very porous structure with a larger surface area ranging from 600 - 2000$m^2$/g.

AC has versatile uses ranging from domestic usage to large scale industrial applications which can remove diverse pollutants such as metallic ions, anions, dyes, phenols, detergents, odours and tastes from drinking water, pesticides, humid substances, chlorinated hydrocarbons, and many other chemicals and organisms (Siti, 2010).

AC is also used in corn and cane sugar refining, gas adsorption, dry cleaning recovery processes, pharmaceuticals, fat and oil removal, electroplating, alcoholic beverage production (Oloworise, 2006), Oil Spillage Clean-up (Diya'uddeen *et al*., 2008). Basically, there are two different processes for the production of AC from carbonaceous materials which are thermal and chemical activation action; physical (thermal) activation involves carbonization of a carbonaceous material followed by the activation of the resulting char at a high temperature between 700-1100$^{o}$C in the presence of suitable oxidizing gases such as carbon dioxide, Steam or nitrogen (Ajayi and Olawale, 2009).

In Chemical activation, the precursor is mixed with a chemical agent and then pyrolyzed at lower temperature of 400-600$^{o}$C in the absence of air. Chemical activation offers several advantages over thermal activation. It is carried out in a single step combining carbonization and activation, performed at lower temperatures and therefore, resulting in the development of a better porous structure (Tsai *et al*., 1997). During the 1980's, there was a tremendous expansion of corn plantations which was followed by the generation of large quantities of agricultural waste (corncob) in fields and factories (Tai *et al*., 1997). It was reported that, for every 100kg of corn grain, approximately18kg of corn cob is produced (Tsai *et al*., 2000).

Generally, production of AC with high specific surface area and pore size depend on the nature of the raw materials used as well as the methods and condition of production (Yusuf

*et al*., 2012). Past works have shown that high grade AC can be produced from locally sourced materials and the product could compete favourably with commercial AC. Agricultural waste materials such as corncob (Sun *et al*., 2007; Diya'uddeen *et al*., 2008; Tsai *et al*., 1997 and 2000; Mohd *et al*., 2011); canarrium *scheweinfurthii* nutshell (Adejonwo, 2006 and Ajayi and Olawale, 2009), coconut shell, palm kernel shell (Nurul'ain, 2007) and macademia nuts (Chipofya, 2000) have been investigated in previous researchers.

## 1.2 Problem Statement

Optimizing the process parameters for the preparation of activated carbon for an effective wastewater treatment would curtail the problem of environmental issues as a results of discharged of untreated wastewater into water bodies and the immediate environment would pose serious threat both human and aquatic life. There is no work previously carried out in literature using hybrid chemical activation (hydrolysis of the corncob sample with $H_3PO_4$ acid concentration then activating with KOH concentration in a muffle furnace) to optimize the operating conditions for activated carbon preparation from corncob using response surface methodology (RSM) for effective waste water treatment, to the best of my knowledge.

## 1.3 Aim and Objectives

The aim of this work is to investigate the optimal conditions for the preparation of activated carbon from corncob by hydrolysis and chemical activation method with the following objectives.

The objectives of this work are to:

- Produce and characterize activated carbon from corn cob by employing the chemical activation using co-activation process.
- Optimize the process parameters for the preparation of AC using CCD expert software.
- Determine the adsorption capacity of the activated carbon samples produced using batch adsorption experiment to verify its viability for commercial usage.
- Analyze the data obtained from the batch adsorption experiment via Langmuir and Freundlich isothermal studies.

## 1.4 Scope of the Work

The scope of the work includes:

- The production of activated carbon from agricultural waste (corncob).
- The optimization of the effective parameters such as phosphoric acid concentration, potassium hydroxide concentration as activating agents, variable activation temperature and variable activation time on the effects of the preparation of activated carbons by chemical activation method.
- Characterization of the resulting activated carbons for its specific surface area, adsorptive capacity, morphology of the AC using Scanning Electron Microscope (SEM), isotherm study and Fourier Transform Infrared (FTIR) spectroscope.
- Analysis of the data obtained from the batch adsorption experiment via Langmuir and Freundlich isotherms.
- Determination of the concentration of dyes and heavy metals concentration before and after adsorption.

## 1.5 Justification

Consumables such as water, beverages, pharmaceuticals, viable gases, chemicals, etc, are only fit for consumptions when they have been purified of contaminants like odours, tastes, or colours. The commonly used adsorbent (commercial activated carbon), which is often scarce and costly, thus posing limiting to households and industrial usages.

Agricultural materials particularly those containing cellulose, shows potential adsorption capacity for various pollutants, but some of these agricultural materials are either scarce or have very small adsorption capacity. Corncob was found to be a suitable material for the preparation of activated carbon owing to its high carbon content and low ash content, eco-friendly and availability (renewable in nature).

# CHAPTER TWO

# LITERATURE SURVEY

## 2.1 Corncob

The maize plant (*Zea mays L*) or corn is the most common important cereal crop in sub – Saharan Africa. Locally it is often called "Masara" in Hausa. It is widely spread and distributed in Nigeria, mostly in the northern parts of the country. According to Institute of Agricultural Research (IAR, 2011), annual production of maize as at 2011 stood at 9,300 metric tons, while corn cob stood at 1,550 metric tons. The annual production n worldwide is about $520\times10^9$ kg (Mohd *et al*., 2014) and 7,700,000 (World Corn Production.com, 2014) respectively. Considerable amounts of maize is cultivated in Nigeria, with Kaduna State being the highest with 770 metric tons, followed by Niger State with 660 metric tons and Plateau the third with 640 metric tons (world corn production.com, 2013). Corn cob is the hard cylindrical central core of maize on which are borne the grains or kernels of an ear of corn. Corn cob is the agricultural waste product obtained from maize or corn. As a result of the increase in corn production, large quantity of corn cob thus generated remains unused as cellulosic wastes in fields and factories. This poses a serious environmental problem not only to pollution and storage but also for disposal (Tsai *et al*., 1997).

Maize is grown twice in a year, between February – May and May – October. This agricultural waste can be utilized as a potential renewable source of energy. The most common routes for conversion of this waste to energy or disposal includes; combustion, gasification, liquefaction and carbonization. In all of these processes, combustion is

preferred. However, it has its own problem of air pollution from burning. Plate 1, shows corn cob and prepared activated carbon.



a



b

Plate1: Images of (a) corn cob (b) prepared activated carbon (Hiremath et al., 2012).

## 2.2 Economic Viability of Corncob

Researchers are focusing on the utilization of viable products from corn cob. Among the viable products that were successfully synthesized from corncob are; glucose, pentose, furfural, activated carbon, zeolites, fuels (like acetone, butanol and ethanol), cement silica bricks, etc.

In actualizing the by-products of corncob will create a challenge at sourcing for feed stocks from the hills of farms by-products that are left to waste away in fields (Oloworise, 2006).

## 2.3 Origin and History of Activated Carbon

Carbon has been in use as far back into history that its origin cannot be ascertained. However, the earliest known use of wood chars (charcoal) was by the Egyptians and Samarians for the reduction of copper, zinc, and tin ores in the manufacture of bronze, as well as domestic smokeless fuel for cooking (Oloworise, 2006).

Charcoal (carbon) has the ability to absorb vapours from organic chemicals, colorizing aqueous solutions. However, the wood charcoal at this time were not particularly effective in this role, presumably because their porosity had not been developed beyond the extent produced by carbonization, and thus, consequently attempts to increase the porosity of these charcoals gave birth to activated carbon (Oloworise, 2006).

The first method of producing activated carbon by a combination of thermal and chemical process was done by heating blood with potash to produce a carbon with 20 to 50 times the decolorizing power of bone char (Oloworise, 2006)

Thereafter, scholars and researchers started searching on ways of producing AC industrially from vegetable materials (agro wastes) with improve porosity (i.e. large surface area). In recent times, activated carbons production techniques employed the methods of incorporation of carbonaceous materials with an activants; such as phosphoric acid, carbonate, salts, metalic chlorides, sulphuric acid, hydrochloric acid, etc to yield activated carbons with superior/high adsorptive.

## 2.4 Processing Techniques

There are different processes/techniques used in the production of activated carbons:

**Nature and type of raw material available:** Studies have shown that, the production of AC from agricultural wastes included dates stones, corncob, coconuts shells, nuts shells and stones, oil palm stones and shells, apple pulp, chickpea husks, rice straw and palm tree branches (Yahia, 2006). Two distinct methods are described in the literature for the production of AC, namely, chemical activation (activation with mineral salts) and physical activation. In chemical activation, the precursor is impregnated with activating agents such as $H_2SO_4$, HCl, $H_3PO_4$, KOH, NaOH, $ZnCl_2$, and $K_2CO_3$ have been used followed by

carbonization in an inert atmosphere at temperatures ranging from 400 to 800 $^{O}$C (Yahia, 2006). Chemical activation method is energy and time saving and, yields good results of product than physical activation. The choice and manner of usage of activating agents depends on the nature of raw material and the effectiveness of the activating agent. Potassium hydroxide has been certified by other researchers as one of the best activating agent that enhances the development of good surface area and pores formation in the production of AC.

**The desired techniques for the preparation of AC:** Several methods have been employed. Some of these techniques are; chemical coagulation/flocculation, ozonation, sedimentation, cloud point extraction, oxidation processes, nanofiltration, chemical precipitation, ion-exchange, reverse osmosis and ultra filtration. All of these both have operationally expensive and creates disposal problems after adsorption of the desire adsorbate from the effluent. The most preferred technique according to Diya'udeen et al., 2011 is activated carbon adsorption compared to commercial activated carbon.

## 2.5 Manufacture of Activated Carbon

Activated Carbon are produced from different carbonaceous materials of organic origin that are rich in carbon such as wood, coal, peat, fruit stones, nutshells, husks of fruits, bones, synthetic polymers, etc followed by activation of the chars produced from them.

Choice of raw materials is an important factor in the production of activated carbon, so also the manufacturing process and intended application of the product are also important. There are two main methods of producing AC; thermal activation and chemical activation. Thermal activation of any carbonaceous material in absence of air involves decomposition of organic molecules, evolution of tarry and gaseous products (hydrogen, oxygen, traces of

sulphur and nitrogen) are first removed at relatively low temperature and finally a solid porous carbon is produced. While Chemical activation, the carbonaceous material is mixed with activating agents, which restrict the formation of tar and create more internal pores through dehydration reactions occurring at significantly lower temperatures.

The basic production processes can be combined in different ways. Sometimes the chemically activated carbon is subjected to additional activation with gaseous environment in order to change the pore structure of the final product (Nezih, 2004).

### 2.5.1 Thermal activation

This process takes place in two stages: thermal decomposition or carbonization of raw material followed by the activation of intermediate product (crude char) at different temperatures range (600- 1200 $^{o}$C) in the presence of oxidizing gases such as carbon dioxide, nitrogen or steam in a muffle furnace (Tsai *et al*., 1997; Diya'udeen et al., 2011).

#### *2.5.1.1 Carbonization*

In carbonization, the sample is decomposed by heat. Carbonization is used to reduce the volatile content of the raw material in order to convert it to a suitable form for activation.

By carbonization most of the volatile content (non-carbon elements), hydrogen ($H_2$) and Oxygen ($O_2$) are first removed in gaseous form by pyrolytic decomposition of the raw materials to elemental carbon skeleton.

During the phase of carbonization, carbon content attains a value of about 80 percent. The carbonization process converts the materials to char and opens the pore of the char for adsorption purposes (Adejonwo, 2006).

*2.5.1.2 Hydrolysis*

In hydrolysis, the sample is soaked in phosphoric acid. Hydrolysis dislodges soluble organic matter such as hydrogen; oxygen etc in the agro waste making the material porous and at the same time adds more strength to the material. Eric, 2010 produces AC using hybrid chemical activation via thermal activation at temperatures range of 480 to 800 $^{o}$C.

*2.5.1.3 Activation of carbonized intermediate product with gaseous agents*

A carbon with a large adsorption capacity can be produced by activating the carbonized intermediate with activating agents such as steam, carbon dioxide ($CO_2$) and nitrogen ($N_2$) at a temperature of 800 to 1100$^{o}$C in an electric furnace.

The activating agent burns away the more reactive portion of the carbon skeleton at high temperatures. The reaction between the activating agent and the carbonized intimidate takes place at the internal surface area, creating more sites for adsorption with liberation of $H_2$, $CO_2$, CO and $O_2$. The reactions below show how the reaction takes place between the activating agent and the carbonized intermediate; known as water-gas reaction in equation (2.1a to 2.1d).

$$C + H_2O \longrightarrow CO + H_2;\ (\text{at } 800 - 1100^{o}C) \qquad (2.1a)$$

$$2CO + O_2 \longrightarrow 2CO_2;\ (\text{at } 800 - 1100^{o}C) \qquad (2.1b)$$

$$2H_2 + O_2 \longrightarrow 2H_2O;\ (\text{at } 800 - 1100^{o}C) \qquad (2.1c)$$

$$C + CO_2 \longrightarrow 2CO;\ (\text{at } 800 - 1100^{o}C) \qquad (2.1d)$$

Carbonization and activation steps are usually carried out separately but recently there is an increasing tendency to conduct the two processes in one-step (Nezih, 2004).

### 2.5.2 Chemical activation

In chemical activation, the material is impregnated with chemical agents such as; $H_3PO_4$, Zn $Cl_2$, KOH, $K_2CO_3$, $H_2SO_4$, HCl, alkali metal compounds, etc, and pyrolyzed after that.

As a result of the pyrolysis process, a much richer carbon content material with a much more ordered structure is produced, and once the chemical agent is eliminated after the heat treatment, the porosity is highly developed.

Basically, there are two types of chemical activation; one-step chemical activation and two-step chemical activation.

In one-step chemical activation, the material is activated with the activating agent, mixed to paste and then heated to temperature of 400-600$^{o}$C in the absence of air to activate the carbon.

While in the two-step chemical activation, the raw material is first carbonized at a temperature range of 450-500$^{o}$C for 20 minutes to char, and the resulting char is treated with activating agent.

Chemical activation offers advantages; it is carried out in a single-step combining carbonization and activation performed at lower temperatures, reduces tar formation and by-products. Initiation of bond cleavage and create stronger cross-linked solid, and yield adsorbents with high surface area and a very pore size (Tsai *et al*., 2001; Adejonwo, 2006; Cuhadar, 2005).

The important factor in chemical activation is the degree of impregnation. For a small increase in impregnation amount to an increase in the total pore volume of the product showing an increase in the volume of small pores. When the degree of impregnation is

further raised, the number of larger diameter pores increases, and the volume of the smallest pores decreases (Nezih, 2004).

## 2.6 Properties of Activated Carbon

### 2.6.1 Physical properties and pore structure

The characteristics of AC that made it an excellent adsorbent are its, high porosity, internal surface area and pore volume. It may be visualized as foam solid that has a large surface area with rigid particle structure of relatively small volume. The large surface area results in a high capacity for absorbing chemical/contaminants from gases or liquids. The adsorptive property stems from the extensive internal pore structure that develops during the activation process (Cuhadar, 2005).

Activated carbon particles have two types of pores existing in it by which adsorption takes place; these are the macropores and the micropores. The macropores provide a passage way/transport to the particles interior (micropores) but do not contribute substantially to the particle surface area.

Nurul'ain, 2007 classified porosity into three different groups of pore sizes, they are: micropores (width less than 2nm), mosopores (width between 2nm – 50nm), and macropores (width greater than 50nm), (Gua and Lua, 2001).

The micropores, on the other hand, are responsible for the large surface area of activated carbon particles created during the activation process. It is in the micropores that adsorption largely takes place. Thus, two main parameters relevant to the performance of activated carbons are namely the surface area and the pore volume (Cuhadar, 2005).

Mechanical strength is also an important factor for preventing damage due to regeneration, recycling, etc, (Oloworise, 2006).

#### *2.6.1.1 Surface area*

The surface area of an adsorbent can be defined as the accessible or available area of a solid surface of an adsorbent material. It is the internal surface area of an adsorbent material accessible to physically adsorbed species. The size and the number of pores determine the internal surface area of an adsorbent (Oloworise, 2006). Generally, the larger the specific surface area of the adsorbents, the better its adsorption performance will be; i.e. the smaller the exposure or contact time required during an adsorption process and vice versa (Gua and Lua, 2001).

The most widely used commercial activated carbons have a specific surface area ranges from 600 to 1200$m^2$/g (Nurul'ain, 2007). The pore volume limit the size of the molecules that can be adsorbed, while, the surface area limits the amount of material which can be adsorbed (Lartley, 1999).

The most commonly employed method to measure the specific surface area of adsorbent is based on the interpretation of adsorption isotherm of nitrogen gas at 77K. Areas determined in this can be taken to represent the total surface area of the adsorbent.

Table 2.1: Surface areas of some activated carbon produced from corn cob (Sun *et al.*, 2007).

| Preparation Method | Carbonization | Surface Area ($m^2/g$) | Pore Volume ($m^3/g$) | References |
|---|---|---|---|---|
| Thermal | 450$^oC$, 4h | 2700 | - | Sun et al., 2003 |
| Thermal | 450 $^oC$, 1.5h | 2595 | 1.480 | Tseng et al., 2005 |
| Thermal | 450 $^oC$, 1.5h | 2844 | 1.533 | Tseng et al., 2006 |
| Chemical | 800 $^oC$, 1h | 1806 | 0.870 | Tsai et al., 2001 |
| Chemical | 750 $^oC$, 1h | 3290 | 1.450 | Sun et al., 2003 |
| Chemical | 800 $^oC$, 1h | 1975 | 0.945 | Sun et al., 2007 |
| Thermal | 350 $^oC$, 5min | 2880 | 1.664 | Sun et al., 2007 |

*2.6.1.2 Pore volume*

The word pore comes from the Greek word, meaning a passage (Nurul'ain, 2009). In this sense, a pore is a class of void which is connected to the external surface of a solid and will allow the passage of fluids out of, or through a material. Pore volume is the capacity of the void volume within a porous material where adsorption takes place in micropores and mesopores, with macropores acting as transport channels. Beside their significant contribution to adsorption, mesopores are serving as the main transport arteries for the adsorbate molecules.

The distribution of pores in adsorbents can vary significantly depending upon the raw material and the carbonization temperature.

Pore volume can be determined by boiling a known weight of the AC particle on its immersion into a liquid (say water); it will lose the air in its pore. When the sample is dried

and reweighed, it will experience an increase in weight. The weight increase divided by the density of the liquid gives the pore or void volume (Oloworise, 2006).

If $\Delta Mp$ is the weight difference or increase experienced by the AC particle and $\rho_L$ is the density of the liquid, then

Pore or Void Volume, Vv is given by Equation (2.2).

$$Vv = \Delta M_p/\rho_L \qquad (2.2)$$

*2.6.1.3 Moisture content*

Activated carbon is generally priced on a moisture free basis, although occasionally, some moisture content is stipulated in the range of 3-10%. Some adsorbents when stored under humid conditions still adsorb considerable moisture over a period time. They may absorb as much as 25 to 30% moistures still look or appear dry. Despite this moisture content does not affect the adsorptive power of the adsorbent Cuhadar, (2005). The method described by AOAC (1984) was used to determine the moisture. A washed crucible was dried to constant weight in an air oven at 105$^{o}$C, cooled in a desiccator and weighed ($W_1$). Two grammes of sample was weighed into the previously labeled crucible and reweighed ($W_2$). The crucible was dried in an oven to a constant weight ($W_3$). The percentage moisture content was calculated thus:

$$\% \text{ Moisture content} = \frac{W3-W1}{W2-W1} \text{ x } 100 \qquad (2.3)$$

*2.6.1.4 Ash content*

The ash content of a carbon is the residue that remains when the carbonaceous materials are burned off. Some activated carbons contain inorganic constituents derived from the source materials and from activating agents used during processing. The total inorganic constituents in activated carbons of high ash content in activated carbons can cause restructuring during regeneration of used activated carbon. The Association of Analytical Chemist (AOAC) 1984 method was used to determined ash content of the activated carbon. Porcelain crucible was washed and dried in an oven at 100 $^{o}$C for 10 minutes, cooled in a desiccator and weighed ($W_1$). Two grams of the sample was placed into the previously weighed porcelain crucible and weighed ($W_2$). The sample was first ignited and transferred into a furnace, which was then set at 550 $^{o}$C. The sample was left in the furnace for eight hours to ensure proper ashing. The crucible containing the ash was then removed cooled in the desiccator and weighed ($W_3$). The percentage ash content was calculated as:

$$\% \text{ Ash content} = \frac{W3-W1}{W2-W1} \times 100 \qquad (2.4)$$

*2.6.1.5 pH*

This is a measure of the hydrogen ion concentration of a solution. The pH of activated carbon produced is determined by the activation process, acid activation produces carbons with pH values below 5, and basic activation produces carbons with pH values between 5 and 7. The pH of the system can have marked effect on the performance of the activated carbon (the acidity or alkalinity). Adsorption usually increases as pH decreases; when pH

is lowered; many organic chemicals assume more stable adsorbable form (Oloworise, 2006).

*2.6.1.6 Temperature*

The rate of adsorption usually increases as temperatures decreases. Many contaminants assume a more adsorbable form when temperature decreases. The reason for this phenomenon is because contaminants assumed solubility state as temperature increases.

*2.6.1.7 Exposure time*

The process of adsorption is highly influenced by the length of time that the activated carbon is in contact with the contaminant in the solution. Increasing the contact time allows greater amounts of impurities to be removed from their sources.

*2.6.1.8 Bulk density*

The bulk density of the adsorbent (corncob powder) was carried out in the laboratory.

This was done by measuring the volume of water displaced when a known weight of the raw sample was dropped into a graduated measuring cylinder.

1g of the activated carbon was placed in a measuring cylinder. 20 ml of distilled water was measured and recorded as $C_1$. The distilled water measured was poured into the measuring cylinder containing the activated carbon. The increase in volume of water was recorded as $C_2$. The difference in volume ($C_2$-$C_1$) gives the volume of 1g of the activated carbon. The bulk density was calculated as the mass (weight) of a quantity of activated carbon divided

by the volume it occupies (including pore volume and interparticle voids).This is expressed in equation (2.5).

$$\text{Bulk Density (BD)} = \text{Ma}/\text{ Va g/cm}^3 \qquad (2.5)$$

Where, Ma = weight of sample (activated carbon), Va = volume of water displaced (occupied).

## 2.7 Performance Evaluation of Activated Carbon using Methylene Blue (Mb)

MB salt was chosen in this study for the preparation of the stock solution. The chemical formula and molecular weight for MB are $C_{16}H_{18}N_3SCl$, 319.85 g/mol, respectively; and the molecular structure of MB is shown in Fig.2.1 by Auta and Hameed, 2011.

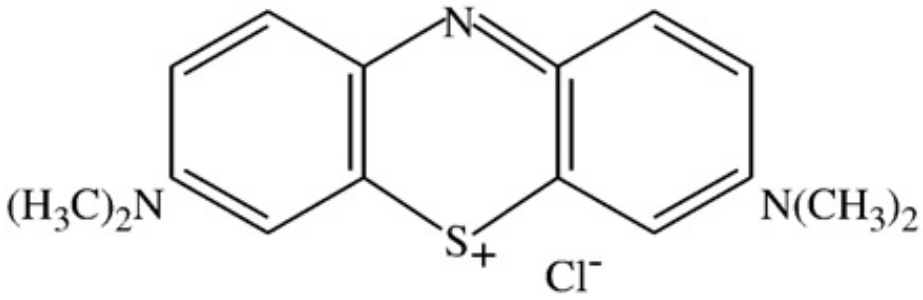



Figure 2.1: Structure of Methylene Blue (MB).

### 2.7.1 Determination of methylene blue concentration in solution

Standard solution of methylene blue can be prepared by dissolving 1g per litre of distilled water.

10ml of 1000mg/l was diluted with distilled water to a volume of 100ml. This is the 100mg/l MB standard solution.

The concentration of MB solutions was determined using UV spectrophotometer at maximum wavelength of 660nm.

### 2.7.2 Adsorption of methylene blue (MB)

Adsorption of MB may be carried out by dropping a known weight of the adsorbent into 100mg/l of MB standard solution of known concentration.

The mixture was maintained at room temperature of 25$^{o}$C-27$^{o}$C with continual agitation for a stipulated contact time.

After the elapse of the contact time, the MB uptake onto the adsorbent is determined from the differences between the initial MB concentrations after adsorption onto the surface of the adsorbent.

To obtain adsorption isotherm, replicate of the adsorption procedure described above need to be carried out, while the concentration of the MB are made to vary alongside with those of the adsorbent. Langmuir Isotherm show that the amount of species (MB) adsorbed onto the adsorbent increases as the concentration increases till it reaches a saturation point. Further increase of MB concentration has no any effect to increase adsorption of the species. This shows that there are no vacant sites for adsorption to take place.

As long as there are vacant sites, adsorption will increase with increasing MB concentration (Oloworise, 2006 and Fogler, 2006).

#### *2.7.2.1 Adsorption mechanism*

Adsorption is the process whereby an adsorbent attracts or removes contaminants from solvent. It is a process where contaminants are adhered to an adsorbent surface either by chemical or physical attraction. Adsorbents could be natural or synthetic materials or

amorphous or micro-crystaline structure; activated carbon, activated alumina, silica gel, molecular sieves such as zeolites, fuller's earth, and special clays (Oloworise, 2006). Activated carbon uses the physical adsorption process to drive solute out of solution onto its surface. Once a solute is adsorbed on the surface of the adsorbent, it is considered removed from the solution or solvent. Adsorption occurs when the attraction forces at the carbon surface overcome the attractive forces of the liquid.

Activated carbon adsorption takes place through different routes:

a. The adsorbate adsorbed to the exterior surface of the adsorbent.
b. The adsorbate moves into the pores cavities or active sites of the adsorbent.
c. The adsorbate adsorbed to the interior walls of the pores cavities or active sites of the adsorbent.

The efficiency of the adsorbent decreases over-time and consequently need to be replaced or reactivated. Reactivation is usually done by blowing hot steam or water at $145^{o}F/63^{o}C$ to flush out the adsorbed contaminants.

The phenomenon of adsorption is mostly expressed by the Langmuir and Freundlich Isotherms. Isotherms are empirical relationships which are used to predict how much solute can be absorbed by activated carbon. The extent of adsorption with concentration of the solute is usually represented by the Freundlich Isotherm Equation given by: The non-linear and linear forms of Freundlich isotherm model is given in Equations (2.6) and (2.7) respectively.

$$q_e = K_F C_e^{1/n} \quad (2.6)$$

$$\text{Log}q_e = \log K_F + 1/n \log C_e \quad (2.7)$$

where

$q_e$ = amount of absorbate per unit mass of adsorbent at equilibrium (mg/g)

$C_e$ = equilibrium concentration of the absorbate (mg/l)

$K_F$ (l/mg) and n are the Freundlich constants.

From Equation 2.4, a plot of log$q_e$ versus log $C_e$ will give a straight line with slope equal to 1/n and an intercept equal to log$K_F$ (Fig. 2.2).

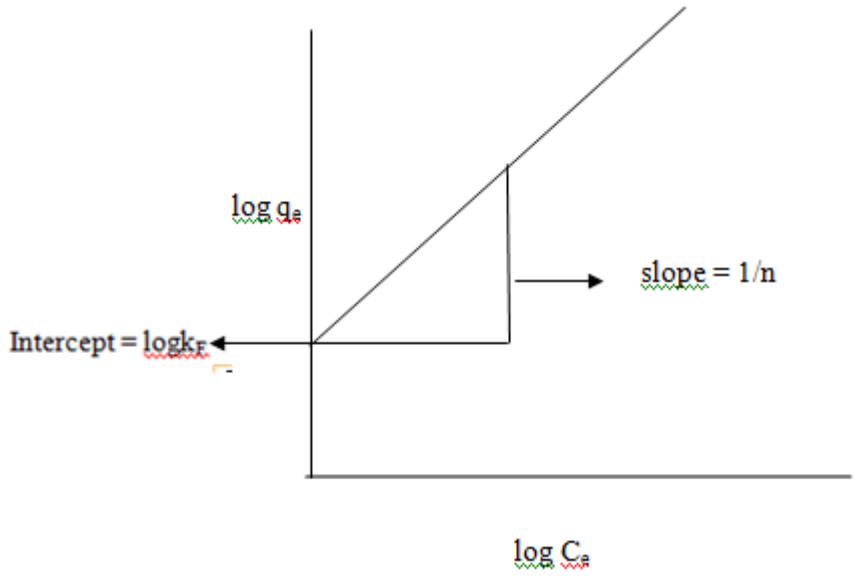



Figure 2.2: A general Freundlich isotherm curve.

The non-linear and linear forms of Langmuir isotherm model is given in Equations (2.8) and (2.9) respectively.

$$q_e = q_m b C_e/(1+bC_e) \quad (2.8)$$

$$C_e/q_e = C_e/q_m + 1/q_m b \quad (2.9)$$

where,

qe = amount of absorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).

b = a constant (l/mg)

$q_m$ = maximum adsorption capacity corresponding to monolayer coverage (mg/g)

$C_e$ = concentration of the adsorbing material at equilibrium (mg/l).

## 2.8 Chemical Properties

The properties of AC for adsorption are depended upon their surface chemistry, as well as their pore size distribution. Normally, the adsorptive surface of activated carbon is approximately neutral such as polar and ionic species less readily adsorbed than organic molecules. For many applications, it would be advantageous to tailor the surface chemistry of activated carbon in order to improve their effectiveness.

Activated carbons were used as adsorbent materials because of their extended surface area, microporous structure, high adsorption capacity, and degree of surface reactivity.

Furthermore, the presence of different functional groups on AC, especially oxygen and hydrogen, leads to the adsorption of ions of heavy metals (Malakootian *et al.*, 2009).

The chemical composition of the raw material influence the surface chemistry and offer a potentially lower cost method for adjusting the properties of activated carbons.

There are numerous methods of determining surface functional groups and attempts have been made to study the surface functional groups by spectroscopic methods, for examples by Fourier Transform Infrared (FTIR) spectroscopy. Figure 4.1(a-c) shows several IR active functional groups that may be found at the edges of and within the graphene layers of the carbon.

## 2.9 Uses and Applications of Activated Carbon

The importance and relevance of AC to an ever-growing society can never be exhausted or quantified. Its uses ranges from liquid to gaseous - phase applications such as in domestic, commercial and industrial settings.

### 2.9.1 Gas phase application

These include separation, gas storage and catalysis.

About 20% AC production is used for gas-phase application of which most is granulated or shaped (Adejonwo, 2006).

Separation processes is the main gas-phase applications of activated carbon which has the greatest influence upon gas adsorption. Adsorption in gas-phase is dependent on the molecular weight and size of the gas molecule to be adsorbed. Organic molecules with large molecular weight are not readily removed from air by activated carbon. The gaseous-phase applications include the following:

#### *2.9.1.1 Process stream application*

Activated carbon employed in industrial process gas streams adsorption differs from one gas stream to the other. Activated carbons in fixed beds have been used to separate aromatic compounds from lighter vapours in petroleum refining-process streams and in natural and manufactured gas production.

Molecular sieves activated carbons are especially made with restricted openings leading to micropores. These adsorbents can withstand high pressure gas streams. Larger molecules

are restricted from entrance into the pores of the adsorbent, and therefore not strongly adsorbed. The products of interest can either the adsorbed or unabsorbed gases.

*2.9.1.2 Solvent recovery*

Most of the activated carbon used in gas-phase separation is employed to prevent the release of volatile organic and inorganic compounds into the atmosphere. These trapped solvents can be recovered and recycled in future. Recovery and recycling of solvents from industrial processes such as electroplating refining, coatings, printing, etc., provides substantial economic benefits.

Micropores provide strong adsorption affinity to capture small vapour molecules at low concentrations in process air. However, recent years, more mesoporous carbons have become available and are giving good result for the adsorption of heavier vapours that are difficult to remove from micropores during regeneration.

*2.9.1.3 Protection against atmospheric contaminations*

Activated carbon is widely used to filter breathing air against variety of toxic vapour including industrial chemicals, solvents and odorous compounds. Activated carbons for this purpose are highly microporous with maximum adsorption capacity which hold adsorbate molecules on the surface. Inorganic vapours are usually not strongly adsorbed on activated carbon by physical forces, but protects against toxic agents by impregnating activated carbon with specific reactants or catalyst.

Alkali – impregnated carbon is effective against sulphur dioxide, hydrogen sulphide, and chlorine at low concentrations.

### 2.9.2 Liquid – phase application

Activated carbon for use in liquid – phase application differs from gas-phase carbons primarily in pore size distribution. In liquid-phase, adsorption takes place in mesopores which allows liquid to diffuse more rapidly into the mesopores and micropores. The larger pores in mesopores promote greater adsorption of large molecules, either impurities or products of interest.

Liquid – phase activated carbon; granular, powdered, or shaped form carbon can be applied. There is a significant factor in choosing either powder and non-powder carbon is the degree of purification required in the adsorption application. Granular or shaped carbons are used in continuous systems, where the liquid to be treated is passed through a fixed bed. Materials to be absorbed are absorbed by the carbon bed in the adsorption zone.

#### *2.9.2.1 Industrial and municipal wastewater treatment*

Wastewater may contain suspended solids, hazardous micro-organisms, and toxic organic and inorganic contaminants that must be removed or destroyed before discharge to the environment or water bodies. In advanced wastewater treatment systems, powdered, granular or shaped activated carbon can be used to remove residual toxic substances and other organic compounds after primary and secondary biological treatment.

#### *2.9.2.2 Drinking water treatment*

Water treatment account for about 24% of the total activated carbon used in liquid-phase applications (Adejonwo, 2006) The most common sources of drinking water are Ground water from wells and bore-hole, Rivers, Lakes. These are often contaminated with bacteria, volatile organic and inorganic compounds, etc. Normal water purification treatment steps

to remove or destroy these bulk contaminants are inaccurate compared to activated carbon. However, activated carbon is preferred in removing toxic and other organic and inorganic materials from water that is safe for drinking.

#### *2.9.2.3 Chemical processing*

Activated carbon is used to remove impurities/contaminants from chemical processing to achieve high quality products and safe environment.

#### *2.9.2.4 Decolourization of sweetener*

Sugar is made from raw sugar juice squeezed from sugar cane or sugar beets. The coloured liquor is decolourized using activated carbon.

Activated carbon is used to purify and remove undesirable tastes and odour compounds to improve the life of sweetener and storage.

#### *2.9.2.5 Other uses of activated carbon*

Activated carbon can find other applications in food, beverage, cooking oil, pharmaceuticals, petroleum refining, etc. Activated carbon absorbed oil, dyes and other organic in dry cleaning and recycling systems. It can also be used in medical applications for the removal of toxic from the blood of patients and recovery of poison by oral ingestion into the stomach.

## 2.10 Forms of activated carbon (AC)

Activated carbon could be in the form of Powdered Activated Carbon (PAC) and Granular Activated Carbon (GAC). Each of PAC and GAC are specifically used to deal with

varieties of undesirable contaminants in raw water (Siti, 2010). PACs are obtained by grinding GAC products.

PAC is basically used to remove taste and odour problems that are primarily an aesthetic quality of the water. After usage, PAC is recovered from the water by the process of coagulation, flocculation, filtration, settling, and sedimentation. Once PAC has been separated from the water it is disposed with sedimentation sludge.

GACs are produced directly from granular materials, such as agro residue, e.g. corn cob. When GAC is used for long term applications, it can be reactivated or regenerated following decreased adsorption efficiency, but in the case of PAC, regeneration may be impossible because PAC particles are too small to be effectively reactivated.

The choice between GAC and PAC depends on the size of the plant, its applications, and the degree of purification required. The use of GAC involves high capital investment but low running costs (Siti, 2010), while PAC involves low capital investment, but high running costs. The parameters for selecting the correct carbon for any particular process are; capacity, hardness, mechanical strength, permeability, solubility, filterability, bulk density, solubility, etc.

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Introduction

This chapter covers three sections namely Materials, Equipment and Methodology.

## 3.2 Materials

Table 3.1 Materials used for the research work, their supplier and purity level

| S/N | Material | Supplier | Purity Level |
|---|---|---|---|
| 1 | Corncob | NARICT, Zaria | - |
| 2 | Phosphoric acid | BDH chemical limited-England | 85% |
| 3 | Potassium hydroxide | BDH laboratory-England | 85% |
| 4 | Distilled water | NARICT, Zaria | - |
| 5 | Methylene Blue (MB) | Analytical grade | BDH chemical limited-England |
| 6 | Commercial activated carbon | BDH chemicals Ltd pools, England | - |

## 3.3 Equipment

Table 3.2: Equipment used for the experiment, their availability and model

| S/N | Equipment | Availability | Model |
|---|---|---|---|
| 1 | Laboratory mortar and pestle | NARICT, Zaria | - |
| 2 | Porcelain crucibles | NARICT, Zaria | - |
| 3 | Measuring cylinders (200 and 500 $cm^3$) | NARICT, Zaria | - |
| 4 | Set of beakers (100, 250 and 500 $cm^3$) | NARICT, Zaria | - |

| | | | |
|---|---|---|---|
| 5 | Glass rod stirrer | NARICT, Zaria | - |
| 6 | Mesh sieve ( 600μm) | ABU, Zaria | Endecotts Ltd, England |
| 7 | Whatman filter papers | NARICT, Zaria | - |
| 8 | Desiccators | NARICT, Zaria | - |
| 9 | Volumetric flasks (1000 $cm^3$) | NARICT, Zaria | - |
| 10 | Electric Muffle furnace | NARICT, Zaria | (LH 120/14, 3/4/PEV, Germany |
| 11 | Sealed ceramic oven | NARICT, Zaria | DZF – 6020 |
| 12 | Weighing Balance | | JA11003 |
| 13 | Centrifuge | NARICT, Zaria | 0412-1, Cole Medical Instrument Co.Ltd, England |
| 14 | Laboratory mill | NARICT, Zaria | |
| 15 | Magnetic stirrer hot plate | NARICT, Zaria | AHL-122226, Elektro Craft (India) Pvt. Ltd. Mumbai-63 |
| 16 | Fourier Transform Infrared Spectroscopy | NARICT, Zaria | FTIR-8400S, Shimadzu |
| 17 | Digital pH meter | NARICT, Zaria | PHS-3C, Jenway |
| 18 | Mechanical shaker | NARICT, Zaria | Stuart Flask Shaker, Stuart Scientific Co. Ltd, England |
| 19 | UV-vis Spectrophotometer | NARICT, Zaria | UV-2550, Shimadzu co-operation |
| 20 | Atomic Adsorption Spectrophotometer | NARICT, Zaria | AA-6800, Shimadzu co-operation |
| 21 | Electric Muffle furnace | ABU, Zaria | LH 120/14, 3/4/PEV, Germany |

### 3.4 Methodology

This section describes the methods used in producing activated carbon from agricultural wastes (corncob) and characterization of the products. A hybrid (or co-activation) method was employed: hydrolysis of the raw corn cob with phosphoric acid was followed by

impregnation of the hydrolysate corn cob with potassium hydroxide concentration (mg/l) as the activating agents and subsequent activation.

### 3.4.1 Preparation of raw materials

Corncob was collected at the National Research Institute for Chemical Technology (NARICT) farms in Zaria. They were washed with distilled water to remove dirt's and left to dry in an oven at 105 $^{o}$C for twelve hours. Thereafter, the dried corncob were crushed with mortar and pestle and ground by a laboratory mill type grinding machine.

The resulting particles were sieved and corncobs particles having sizes between 400 – 600 μm were used in the experimental work.

### 3.4.2 Hydrolysis, impregnation and activation of corncob

The corncob was first hydrolyzed with phosphoric acid on a magnetic stirrer at 85 $^{o}$C for one hour. The hydrolyzed corncob was washed with distilled water until the filtrate became neutral to pH paper and then dried in an oven at 105 $^{o}$C for twelve hours or overnight. The hydrolysate corncob was thereafter impregnated with potassium hydroxide activated in a muffle furnace at temperature range of 100 to 500 $^{o}$C, and activation time's of 15 to 150 minutes. The activated carbon was washed with distilled water to a neutral pH of 7 and dried in an oven at 105 $^{o}$C for twelve hours or overnight. The experimental conditions utilized were the template described in Section 3.2.3 and the methodology flow diagram is as presented in Figure 3.1.

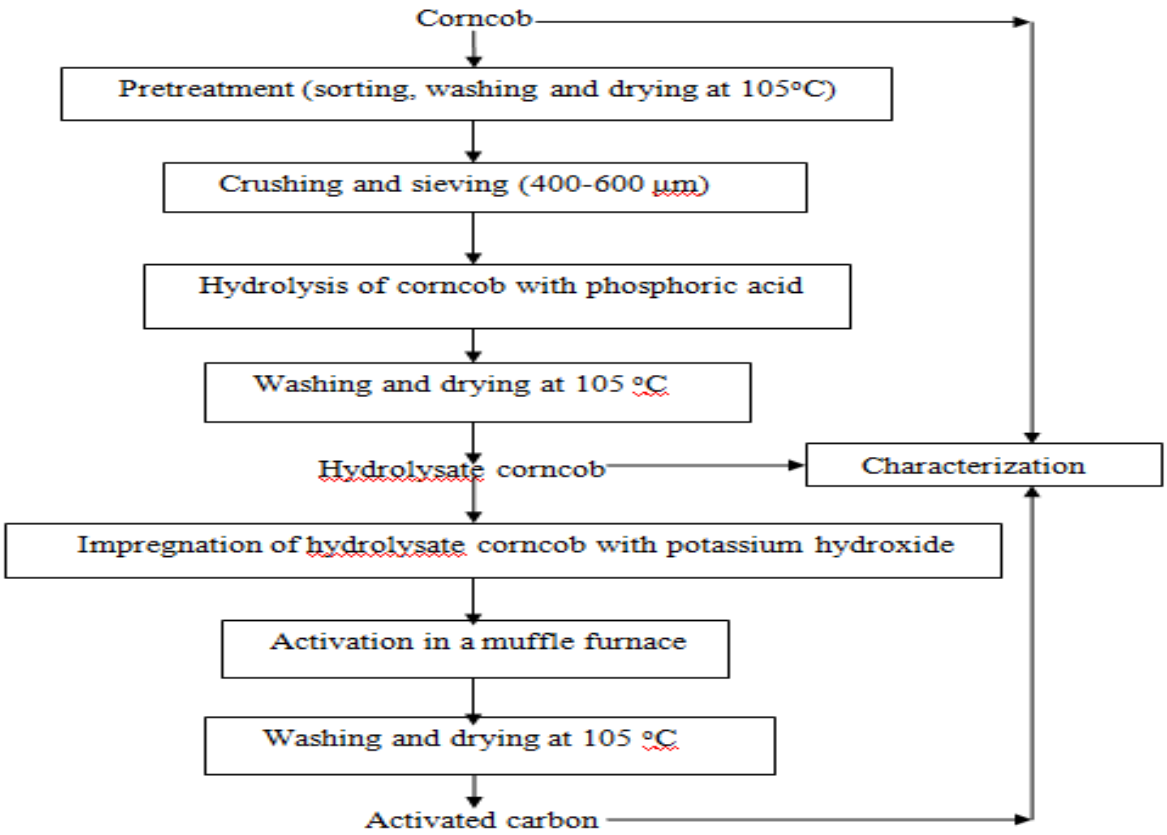



Figure 3.1: Flow diagram of research methodology

### 3.4.3 Design of experiment

The activation process was carried out following a standard Response Surface Method (RSM) design called Central Composite Design (CCD). This method can optimize the effective independent variables with a minimum number of experiments, as well as to analyze the interaction effect between those independent variables. The central composite design expert version 6.0.6 Stat-Ease, Inc (USA) was chosen to design the experiment. The design software reduces the number of experiments and minimizes errors in the course of the work as compared with ordinary method was employed.

The design consists of $F = 2^n$ factorial points, 2n axial points and $n_c$ centre points (6 replacates). The total number of design points (runs) N is given by equation (3.1) below.

$$N = 2^n + 2n + 6 \qquad (3.1)$$

Where, N is the total number of experimental runs and n is number of independent variables.

The independent variables optimized were phosphoric acid concentration, potassium hydroxide concentration, activation temperature ($^{o}$C), and activation time (minute). The responses were hydrolysate yield ($Y_H$), activated carbon yield ($Y_{AC}$) and adsorption capacity of the activated carbon samples ($Y_{ADS}$).

Therefore, the total number of experiments (*N*) required is as follows;

Putting n = 4 (variables) in Equation (3.1) gives

$$N = 2^4 + 2x4 + 6 = 30 \qquad (3.2)$$

Table 3.3: Experimental range and levels of independent variables used in the activated carbon preparation from corncob using CCD software.

| Independent Variables | Range and Level | | | | |
|---|---|---|---|---|---|
| | -2 | -1 | 0 | 1 | 2 |
| Phosphoric acid, $x_1$ (mg/l) | 0.07 | 0.29 | 0.50 | 0.72 | 0.93 |
| Potassium hydroxide, $x_2$ (mg/l) | 0.02 | 0.08 | 0.14 | 0.20 | 0.26 |
| Temperature, $x_3$ (°C) | 100 | 200 | 300 | 400 | 500 |
| Time, $x_4$ (minute) | 15 | 60 | 105 | 150 | 195 |

The resulting design of experiment (DOE) template is presented in Table 3.4.

Table 3.4: Experimental design matrix using Central Composite Design expert (CCD) for the preparation of activated carbon.

| S/N | Sample Code | $H_3PO_4$ (mg/l) | KOH (mg/l) | Temperature ($^oC$) | Time (minute) |
|---|---|---|---|---|---|
| 1 | AC1 | 0.72 | 0.20 | 400 | 150 |
| 2 | AC2 | 0.72 | 0.08 | 400 | 60 |
| 3 | AC3 | 0.50 | 0.02 | 300 | 105 |
| 4 | AC4 | 0.29 | 0.08 | 200 | 150 |
| 5 | AC5 | 0.29 | 0.08 | 400 | 60 |
| 6 | AC6 | 0.29 | 0.20 | 200 | 150 |
| 7 | AC7 | 0.50 | 0.14 | 300 | 195 |
| 8 | AC8 | 0.07 | 0.14 | 300 | 105 |
| 9 | AC9 | 0.72 | 0.20 | 200 | 60 |
| 10 | AC10 | 0.29 | 0.20 | 400 | 60 |
| 11 | AC11 | 0.50 | 0.14 | 300 | 105 |
| 12 | AC12 | 0.93 | 0.14 | 300 | 105 |
| 13 | AC13 | 0.72 | 0.08 | 200 | 60 |
| 14 | AC14 | 0.50 | 0.14 | 300 | 105 |
| 15 | AC15 | 0.50 | 0.14 | 300 | 15 |
| 16 | AC16 | 0.50 | 0.14 | 500 | 105 |
| 17 | AC17 | 0.50 | 0.15 | 300 | 105 |
| 18 | AC18 | 0.50 | 0.14 | 300 | 105 |
| 19 | AC19 | 0.50 | 0.14 | 300 | 105 |
| 20 | AC20 | 0.50 | 0.14 | 100 | 105 |
| 21 | AC21 | 0.29 | 0.08 | 400 | 150 |
| 22 | AC22 | 0.72 | 0.08 | 400 | 150 |
| 23 | AC23 | 0.29 | 0.08 | 200 | 60 |
| 24 | AC24 | 0.72 | 0.02 | 400 | 60 |
| 25 | AC25 | 0.50 | 0.26 | 300 | 105 |
| 26 | AC26 | 0.72 | 0.20 | 200 | 150 |
| 27 | AC27 | 0.29 | 0.20 | 400 | 150 |
| 28 | AC28 | 0.29 | 0.20 | 200 | 60 |
| 29 | AC29 | 0.72 | 0.08 | 200 | 150 |
| 30 | AC30 | 0.50 | 0.14 | 300 | 105 |

### 3.4.4 Characterization of the corncob, hydrolysate corncob and activated carbon samples

#### *3.4.4.1 Proximate analysis of corncob*

The proximate analysis of the corncob particles was determined in accordance with the Official Method of Association of Analytical Chemist (1984).

*3.4.4.2 Determination of yields of samples and adsorption capacity of activated carbon*

The yield of the hydrolysate and activated carbon produced as well as the adsorption performance of the activated carbon samples were carried out as follows: Hydrolysate yield – ratio of weight of hydroloysate to weight of corncob; Activated carbon yield – ratio of weight of activated carbon to weight of hydrolysate, and adsorption capacity of the activated carbon samples were determined using methylene blue concentration of 10 mg/l and 0.5 g of activated carbon samples were subjected to mechanical shaker at 120 revolution per minute (rpm) for time 20 minutes and centrifuged the cleared solutions at 400 rpm. The cleared solutions were used to determine the rate of adsorption capacity of the activated carbon samples using UV-vis spectrophotometer. The resulting yields of hydrolysate and activated carbon and adsorption capacity of activated carbon samples were presented in Chapter Four.

*3.4.4.3 Physical and structural characterization of selected activated carbon samples*

Moisture and Ash Contents: The moisture and ash content of the activated carbon samples were determined using the Methods of Association of Analytical Chemist (1990).

Specific Surface Area: In determining the specific surface area of the selected activated carbon samples, Sera's method was employed.

1.5 g of each of the activated carbon samples was acidified with dilute hydrochloric acid (HCl) in a drop – wise manner, until a pH of 3 – 3.5 was achieved. Thirty grams sodium chloride (NaCl) was added to the acidified activated carbon samples with constant stirring; then distilled water added to make up the volume to 150 ml. The solution was titrated with 0.1 M sodium hydroxide (NaOH) solution till a pH of 9 was achieved (Mohammed et al.,

2015). The volume of sodium hydroxide used was noted. The specific surface area was determined using Equation (3.3).

$$S = 32V - 25 \quad (3.3)$$

where, V is the volume of sodium hydroxide used to raise the pH of the solution to 9, and S is the specific surface area of the activated carbon.

Adsorption Isotherm Study: The equilibrium adsorption behaviour of the three best activated carbon was determined using methylene blue and tannery effluent containing 10 mg/l of chromium (VI) ions as the adsorbate. Ten ml of the methylene blue and chromium (VI) ions solutions were poured into each of five flasks containing 0.02, 0.04, 0.06, 0.08 and 0.10 g of the activated carbon samples (Ajinomoh and Salahudeen, 2013). The flasks were mechanically shaken for 20 minutes at a speed of 120 rpm, after which a cleared solution was collected with a needle and syringe. The solutions were centrifuged for 10 minute at 400 rpm. The cleared solutions from centrifuge were analyzed to obtain the ethylene blue and chromium (VI) ions concentrations using UV-vis and atomic adsorption spectrophotometer (AAS). Hence, the adsorption data generated were fitted to the Langmuir and Freundlich adsorption isotherm models. The resulting isotherm study models are presented in Chapter Four.

# CHAPTER FOUR

# RESULTS AND DISCUSSION

The results obtained in this work with detailed discussion are presented in this chapter.

## 4.1 Proximate Analysis of Corncob

The result of the proximate analysis of corncob is presented in Table 4.1.

Table 4.1: Proximate analysis of corncob

| Characteristics | Value, % |
|---|---|
| Moisture content | 5.8 |
| Ash content | 3.9 |
| Crude protein | 2.84 |
| Fibre | 14 |
| Lipid | 9 |
| Carbohydrate (by difference) | 64.46 |

## 4.2 Yield and Adsorption Capacity of Activated Carbon

The yield of hydrolysate and activated carbon and adsorption capacity of activated carbon samples produced using the design of experiment (DOE) template are presented in Table 4.2.

Table 4.2: The yield of samples and adsorption performance of activated carbon using central composite design (CCD)

| S/N | Sample Code | $H_3PO_4$ (mg/l) | KOH (mg/l) | Temperature ($^oC$) | Time (minute) | Hydrolysate yield (%) | Activated carbon yield (%) | Adsorption capacity of AC (mg/g) |
|---|---|---|---|---|---|---|---|---|
| 1 | AC1 | 0.72 | 0.20 | 400 | 150 | 48.15 | 7.12 | 1.22 |
| 2 | AC2 | 0.72 | 0.08 | 400 | 60 | 48.70 | 5.00 | 1.25 |
| 3 | AC3 | 0.50 | 0.02 | 300 | 105 | 67.03 | 19.32 | 1.30 |
| 4 | AC4 | 0.29 | 0.08 | 200 | 150 | 76.59 | 18.87 | 1.72 |
| 5 | AC5 | 0.29 | 0.08 | 400 | 60 | 77.67 | 18.73 | 1.91 |
| 6 | AC6 | 0.29 | 0.20 | 200 | 150 | 74.60 | 8.99 | 1.28 |
| 7 | AC7 | 0.50 | 0.14 | 300 | 195 | 70.14 | 14.20 | 1.90 |
| 8 | AC8 | 0.07 | 0.14 | 300 | 105 | 85.27 | 18.30 | 1.92 |
| 9 | AC9 | 0.72 | 0.20 | 200 | 60 | 47.72 | 15.69 | 1.97 |
| 10 | AC10 | 0.29 | 0.20 | 400 | 60 | 70.27 | 18.78 | 1.88 |
| 11 | AC11 | 0.50 | 0.14 | 300 | 105 | 67.01 | 19.00 | 1.74 |
| 12 | AC12 | 0.93 | 0.14 | 300 | 105 | 41.98 | 6.67 | 1.71 |
| 13 | AC13 | 0.72 | 0.08 | 200 | 60 | 47.42 | 15.72 | 1.67 |
| 14 | AC14 | 0.50 | 0.14 | 300 | 105 | 67.04 | 18.52 | 1.98 |
| 15 | AC15 | 0.50 | 0.14 | 300 | 15 | 68.21 | 13.57 | 1.89 |
| 16 | AC16 | 0.50 | 0.14 | 500 | 105 | 69.41 | 7.33 | 1.91 |
| 17 | AC17 | 0.50 | 0.15 | 300 | 105 | 68.16 | 18.50 | 1.79 |
| 18 | AC18 | 0.50 | 0.14 | 300 | 105 | 70.27 | 18.78 | 1.88 |
| 19 | AC19 | 0.50 | 0.14 | 300 | 105 | 68.18 | 18.66 | 1.88 |
| 20 | AC20 | 0.50 | 0.14 | 100 | 105 | 68.41 | 18.67 | 1.83 |
| 21 | AC21 | 0.29 | 0.08 | 400 | 150 | 73.67 | 20.48 | 1.87 |
| 22 | AC22 | 0.72 | 0.08 | 400 | 150 | 47.89 | 7.83 | 1.47 |
| 23 | AC23 | 0.29 | 0.08 | 200 | 60 | 74.34 | 25.39 | 1.73 |
| 24 | AC24 | 0.72 | 0.02 | 400 | 60 | 48.55 | 7.65 | 1.73 |
| 25 | AC25 | 0.50 | 0.26 | 300 | 105 | 67.52 | 10.00 | 1.17 |
| 26 | AC26 | 0.72 | 0.20 | 200 | 150 | 47.56 | 12.05 | 1.66 |
| 27 | AC27 | 0.29 | 0.20 | 400 | 150 | 74.91 | 15.00 | 1.90 |
| 28 | AC28 | 0.29 | 0.20 | 200 | 60 | 75.39 | 13.83 | 1.23 |
| 29 | AC29 | 0.72 | 0.08 | 200 | 150 | 47.00 | 11.59 | 1.90 |
| 30 | AC30 | 0.50 | 0.14 | 300 | 105 | 68.93 | 18.69 | 1.89 |

### 4.2.1 Model validation

The predicted hydrolysate yield was calculated using the model equation generated from the plot of experimental hydrolysate yield versus phosphoric acid concentration to determine the validity of the developed model. The model equation for hydrolysate yield is given by Equation (4.1)

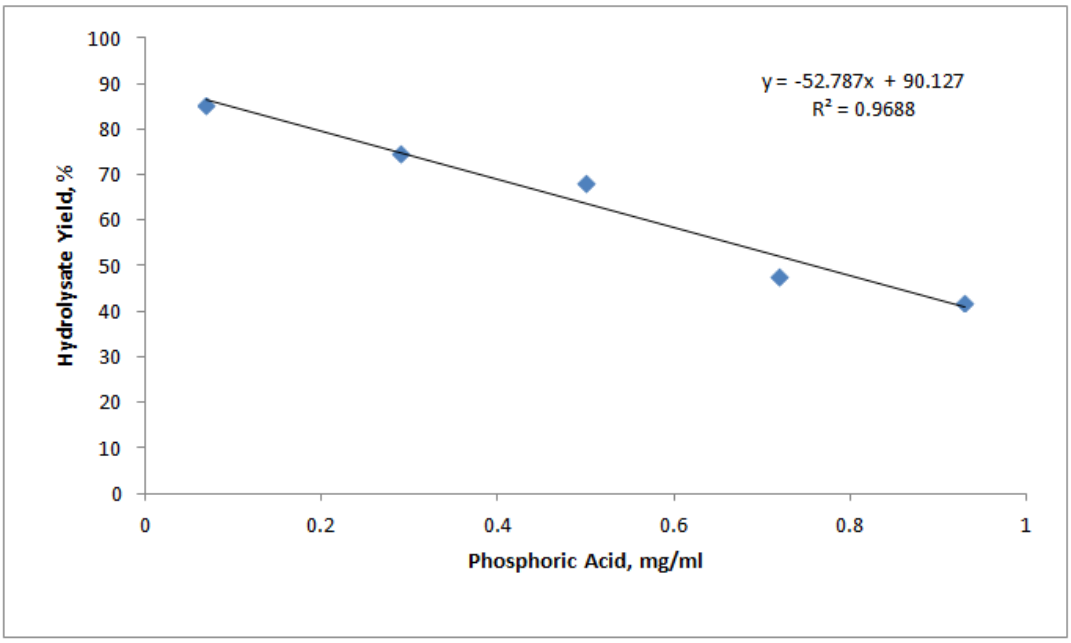
$$Y = 90.127 – 52.787X \quad (4.1)$$

where:

Y – Predicted hydrolysate yield (%) and X is the experimental yield.

Table A2 in appendix A (Experimental hydrolysate yield)

Figure




4.1:

Parity plot of hydrolysate yield (%) versus phosphoric acid concentration (mg/ml).

Substituting values of experimental hydrolysate yield into the model Equation 4.1, predicted hydrolysate yield which was determined as shown in Table A3 in Appendix A.

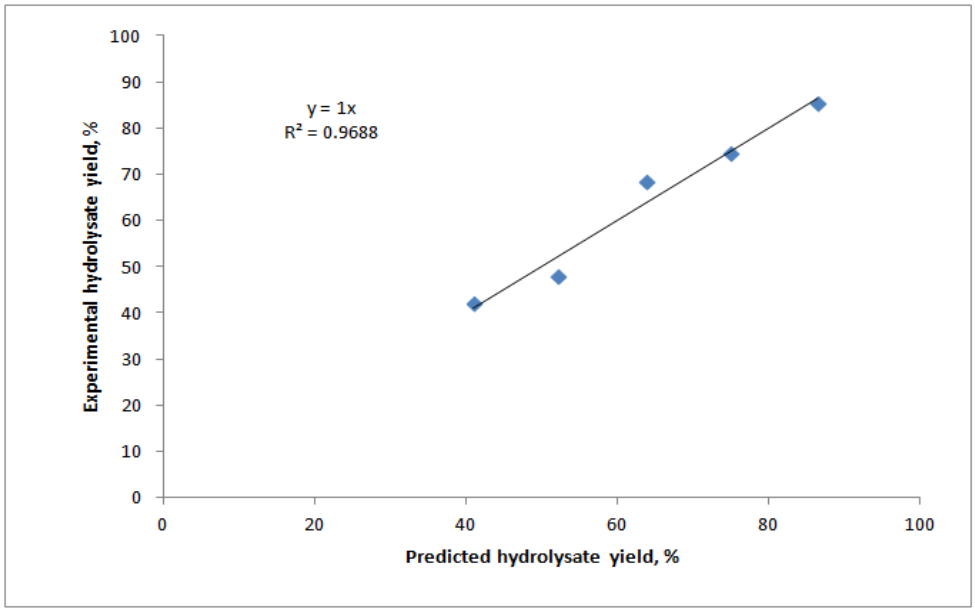



Figure 4.2: Parity plot of experimental hydrolysate yield (%) versus predicted hydrolysate yield (%).

The model equation for activated carbon yield was given in Equation (4.2) by the software.

$$\text{AC yield} = 18.62 - 3.38A - 1.78B - 1.86C - 1.48A^2 - 0.93B^2 - 1.34C^2 + 1.83AB - 2.07AC + 1.10BC + 1.21CD \quad (4.2)$$

Where, A is phosphoric acid concentration (mg/l), B is potassium hydroxide concentration (mg/l), C is activation temperature ($^oC$), and D is activation time (minute).

The terms D, $D^2$, AD and BD were insignificant and excluded in the model equation.

Table A4 for experimental design matrix and response values for activated carbon yield (experimental and predicted) in appendix A

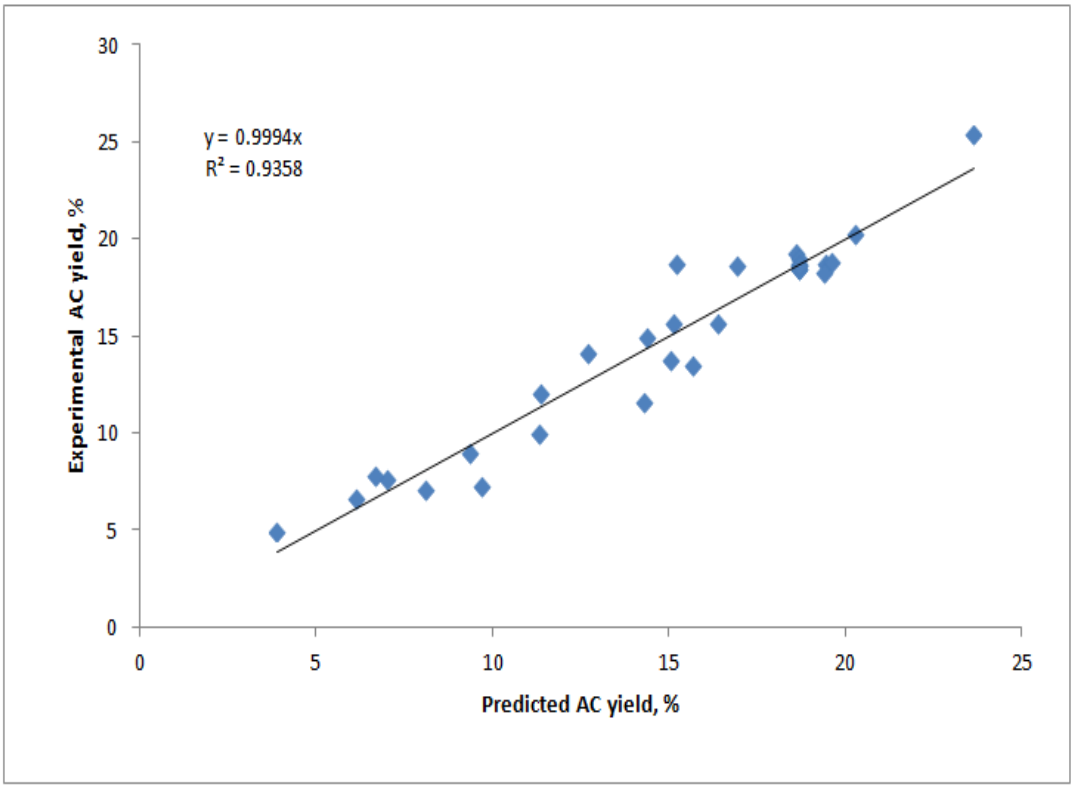



Figure 4.3: Parity plot of experimental activated carbon yield versus predicted activated carbon yield.

The R-square value of 0.9358 indicates a good correlation between the predicted and the experimental activated carbon yield.

The model equation for the adsorption capacity of activated carbon is given by Equation (4.3). Where, the parameters D, $C^2$, $D^2$, AD and CD were insignificant terms.

$$\text{Adsorption capacity} = 1.84 - 0.053A - 0.049B - 0.16B^2 + 0.074AB - 0.19AC + 0.072BC - 0.069BD \quad (4.3)$$

Table A5 for experimental design matrix and response values for adsorption capacity of AC

( experimental and predicted)

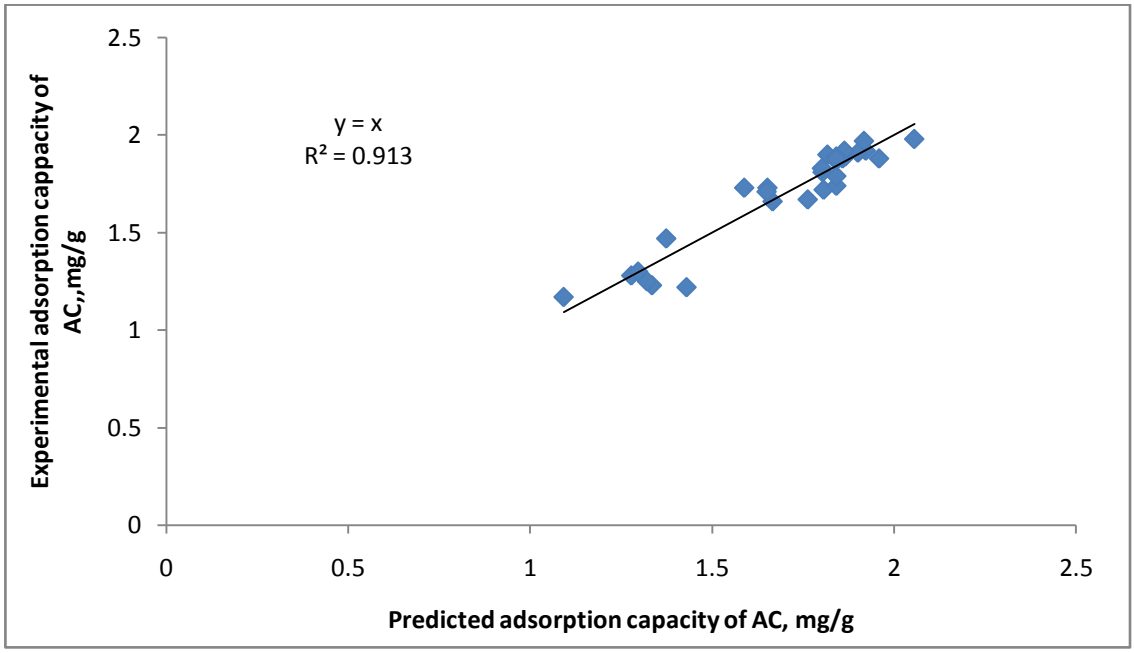



Figure 4.4: Parity plot of experimental adsorption capacity versus predicted adsorption capacity of activated carbon.

The R-square value of 0.9134 shows there was a quality agreement between the predicted and the experimental adsorption capacity (mg/g) of the AC.

### 4.2.2 Analysis of variance (ANOVA)

The responses obtained from Table 4.2 were subjected to Analysis of Variance (ANOVA), $R^2$ and lack of fit (LOF). Table A6 ANOVA response of hydrolysate yield is in Appendix A.

The model for yield of hydrolysate revealed that only term A was significant, since it is a single factor interaction, while other terms are insignificant. A good correlation existed between the experimental and the predicted yield with R-square value of 0.9045. The higher the F-value, the greater the significance of the independent variables to cause effect. Also, if the Prob-F is less than 0.05, the model terms are considered significant. The model

F-value of 59.22 and Prob-F of <0.0001 implied that the model is significant. The ANOVA for the quadratic model for activated carbon yield preparation is shown in Table A7 in Appendix A.

The model F-value of 15.66 and Prob-F of 0.0001for AC yield implied that the model was significant with R-square of 0.9360. The higher the F-value, the greater the significance of the independent variables to cause effect. In this case, A, B, C, $A^2$, $B^2$, $C^2$, AB, AC, BC, and CD were significant terms, whereas D, $D^2$, AD, and BD were insignificant terms to the response. ANOVA for adsorption capacity of AC response in Table A8 in Appendix A.

From Table A8, the model F-value of 11.31 and Prob-F of 0.0001 implies the model is significant. In this case, A, B, $B^2$, AB, AC, BC, and BD were significant terms, whereas C, D, $A^2$, $C^2$, $D^2$, AD, and CD were insignificant terms. The coefficient of determination R-square of 0.9134 was statistically high which reflects a good correlation. The higher the F-value, the greater is the significance of the independent variables to cause effect.

### 4.2.3 Response surface analysis (RSA) plots for hydrolysate yield, activated carbon yield and adsorption capacity of activated carbon samples

Figures 4.5 to 4.17 are response surface plots for hydrolysate corncob, AC yield and adsorption capacity of AC samples produced. The response surface plot is a Three-Dimensional (3-D) graphical representation of the regression equation. Each Figure showed an interaction effect of two variables on the yield and adsorption capacity of the AC samples, while, the other were held constant. For this research work, phosphoric acid concentration was in the range 0.07 to 0.93 mg/l, potassium hydroxide concentration was

in the range 0.02 to 0.26 mg/l, activation temperature 100 to 500 $^{o}$C, activation time 15 to 195 minute and weight of corncob used for sample was 30 g.

Hydrolysate Yield: The model yield of hydrolysate revealed that only A was significant, whereas, B, C and D were insignificant.

Where, Terms A, B, C and D represent phosphoric acid concentration, potassium hydroxide concentration, activation temperature and activation time.

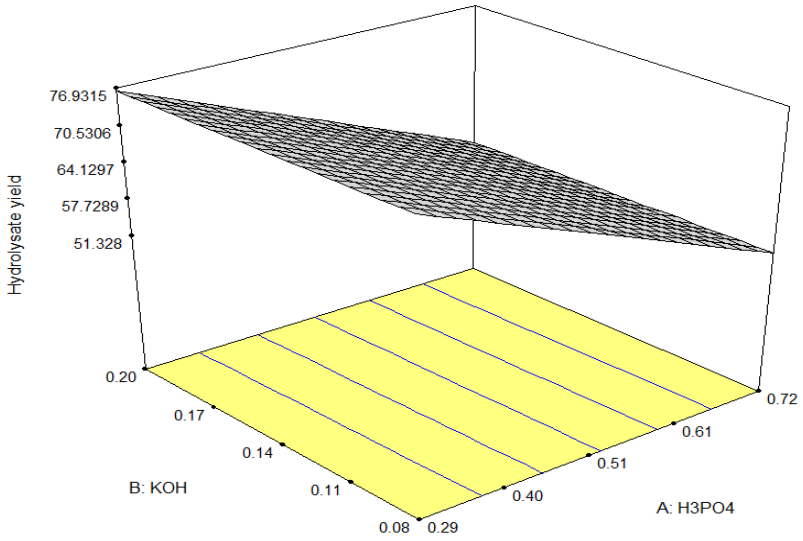



Figure 4.5: Effect of phosphoric acid concentration (mg/l) and potassium hydroxide concentration (mg/l) on hydrolysate yield (%).

The interaction term of phosphoric acid concentration showed a significant effect on hydrolysate corncob yield as illustrated in Figure 4.5.

The model yield of hydrolysate corncob revealed that only phosphoric acid concentration was significant, whereas, potassium hydroxide concentration, activation temperature and activation time were insignificant. This was because the process involved only one factor.

The interaction effect of phosphoric ($H_3PO_4$) acid concentration (mg/l) on the yield (%) of hydrolysate corncob shows that the yield decreases as concentration of $H_3PO_4$ increases

from 0.29 to 0.72 mg/l. From the 3-D plot, it shows that high yield of hydrolysate was achieved at lower phosphoric acid concentration. The maximum yield is at 0.29 mg/l.

Activated Carbon Yield: The four variables, potassium hydroxide concentration, phosphoric acid concentration, activation temperature and time all contributed either individually or by way of interaction to the yield of the activated carbon, although their level of interactions differed from one another. Temperature and potassium hydroxide concentration imposed the most significant effect on the yield of activated carbon. This can be seen from their large F-values. Temperature and potassium hydroxide concentration plays a vital role in pores development than time and phosphoric acid.

The yield of activated carbon depends on the interaction either by one or more factors AB, AC, AD etc.

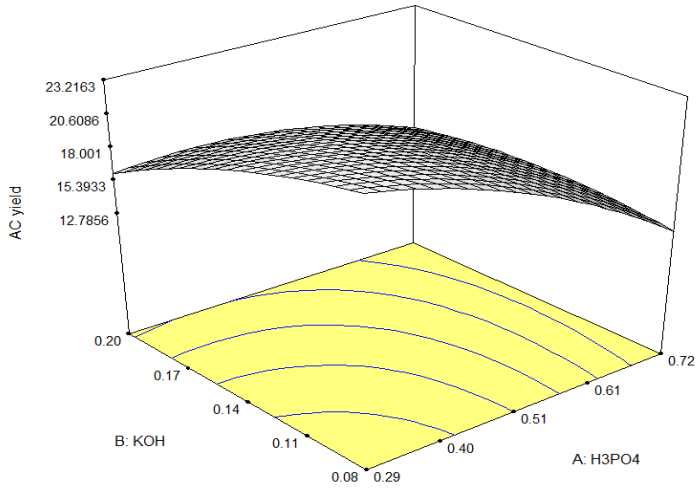



Figure 4.6: Effect of phosphoric acid concentration (mg/l) and potassium hydroxide concentration (mg/l) on activated carbon yield (%).

Figure 4.6 showed the interaction of phosphoric acid concentration and potassium hydroxide concentration on the yield of activated carbon. As potassium hydroxide

concentration and phosphoric acid concentration were increased, the yield of AC increases. The maximum yield was obtained at around 0.14 mg/l potassium hydroxide and 0.66 mg/l phosphoric acid concentrations.

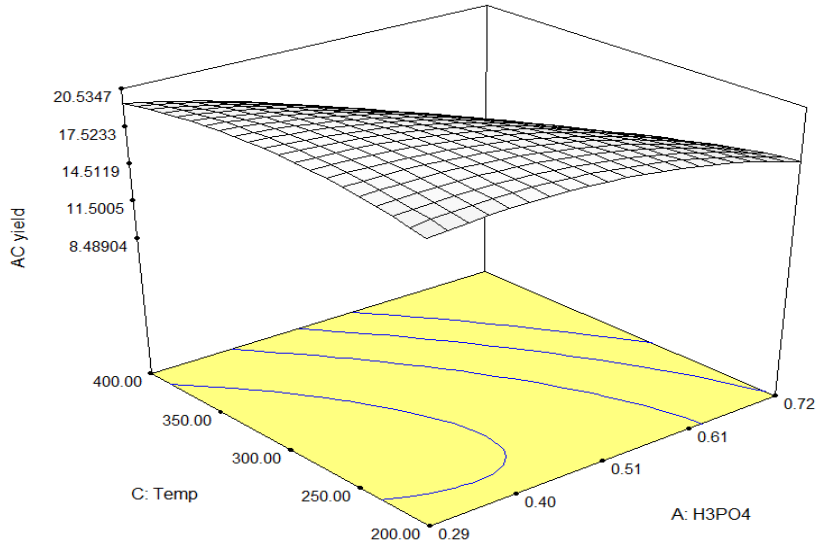



Figure 4.7: Effect of phosphoric acid concentration (mg/l) and activation temperature ($^{o}$C) on activated carbon yield (%).

Figure 4.7 shows the interaction effects between activation temperature and phosphoric acid concentration. As activation temperature increased, AC yield increases at any given phosphoric acid concentration from 0.29 to 0.72 mg/l. This can be seen from their F-values of 81.74 ($H_3PO_4$) and 24.68 (Temperature).

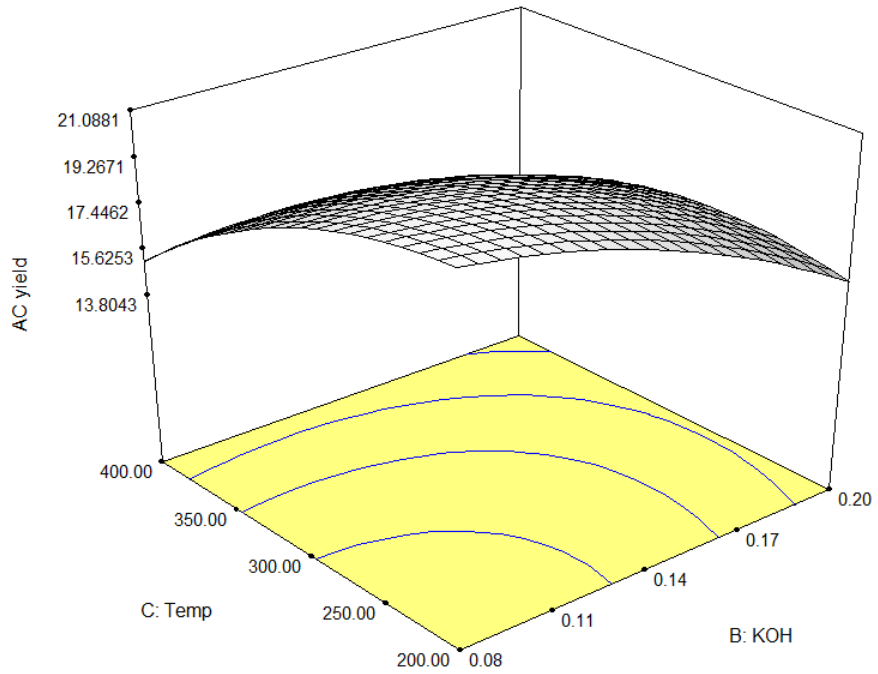



Figure 4.8: Effect of activation temperature ($^{o}$C) and potassium hydroxide concentration (mg/l) on activated carbon yield (%).

Figure 4.8 showed the interaction effect of activation temperature and potassium hydroxide concentration on the yield of activated carbon. As potassium hydroxide concentration and activation temperature were increased, the yield increases. This can be seen in their F-values of 81.54 and 24.64, respectively. Maximum yield was obtained at around 250 $^{o}$C and 0.19 mg/l potassium hydroxide concentration. This finding was in agreement with the findings of Auta and Hameed, 2011; Auta, 2012, yield of AC increases with decrease in activation temperature.

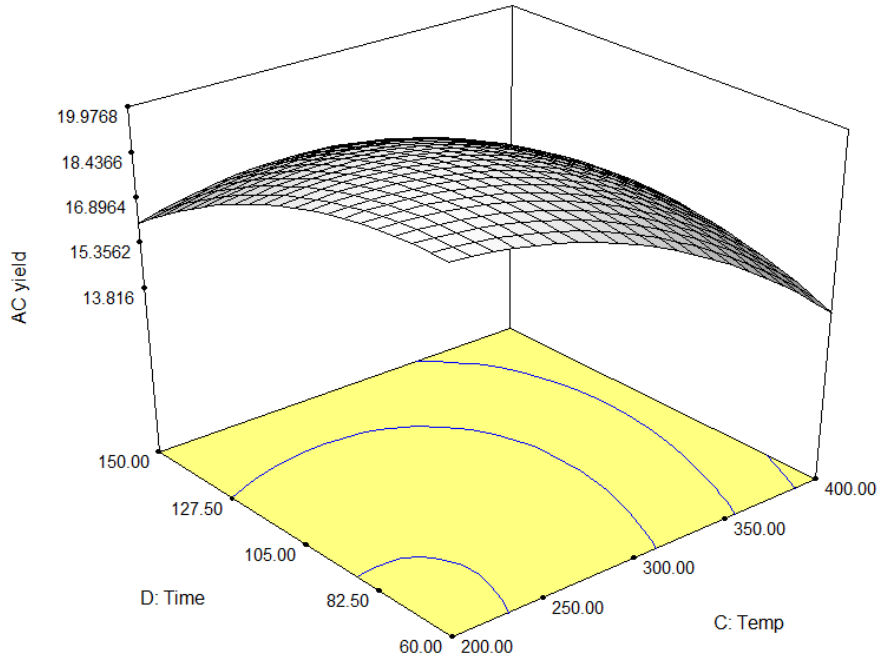



Figure 4.9: Effect of activation temperature ($^{o}$C) and activation time (min) on activated carbon yield (%).

Figure 4.9 shows the interaction effects of activation temperature and activation time on the yield of activated carbon. Activation temperature and activation time had little effect on the yield, since it was only dehydration operation that occurred without any process due to the absence of activating agent to ignite the reaction. At higher activation temperature the yield of AC decreases. Ahmad *et al*., 2011; Auta and Hameed, 2011; Auta, 2012 reported similar findings for the preparation of activated carbon from mango-steen peel.

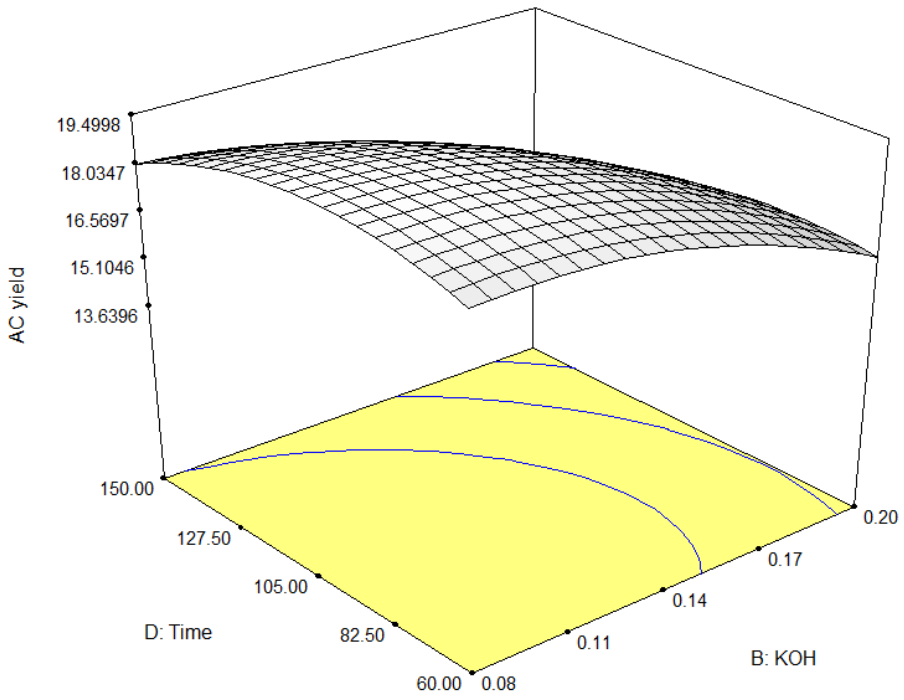



Figure 4.10: Effect of potassium hydroxide concentration (mg/l) and activation time (min) on activated carbon yield (%).

Figure 4.10 shows the interaction of potassium hydroxide concentration and activation time on the yield of AC. It can be seen that at any given potassium hydroxide concentration, yield increases as time was increased. The maximum activation time was around 82.50 minute and potassium hydroxide concentration of 0.20 mg/l.

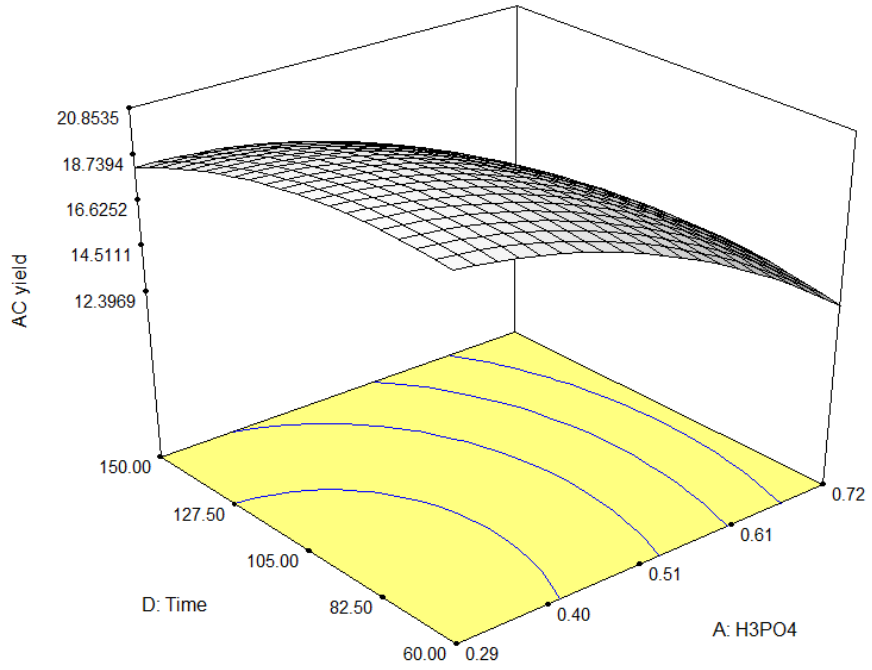



Figure 4.11: Effect of phosphoric acid concentration (mg/l) and activation time (min) on activated carbon yield (%).

Figure 4.11 shows the interaction effect of activation time and phosphoric acid concentration on the yield of AC at constant activation temperature and potassium hydroxide concentration. At any given phosphoric acid concentration, yield of AC increased with increasing activation time from 60 to 150 minute. However, beyond 105 minute, yield decreased.

Adsorption Capacity of Activated Carbon: Adsorption capacity is to test the performance of the AC samples produced to satisfy its viability for commercial usage.

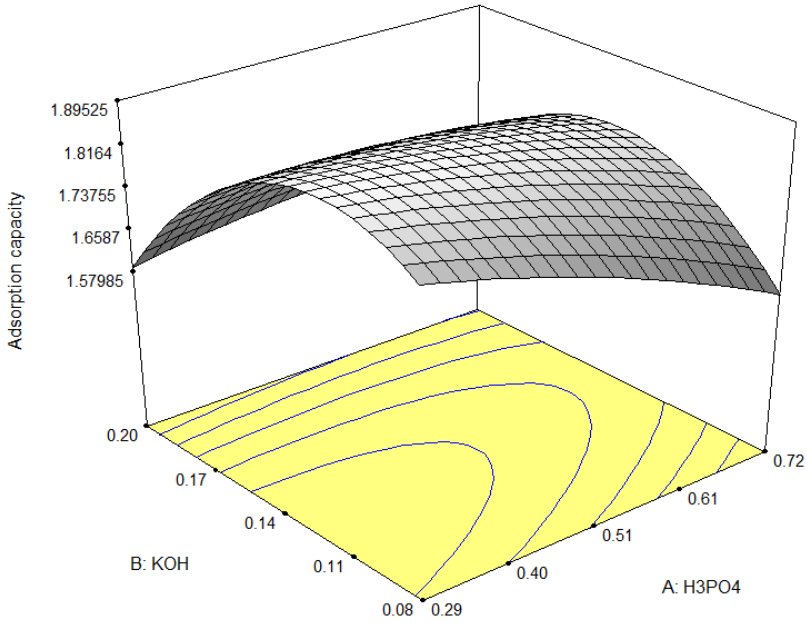



Figure 4.12: Effect of phosphoric acid concentration (mg/l) and potassium hydroxide concentration (mg/l) on adsorption capacity of activated carbon.

Figure 4.12 illustrate the effect of potassium hydroxide concentration and phosphoric acid concentration on the adsorption capacity of AC sample. At any given phosphoric acid concentration, adsorption capacity increased with increasing potassium hydroxide concentration. However, at concentration beyond 0.13 mg/l of potassium hydroxide, adsorption capacity of AC on methylene blue decreased. Thus, implies phosphoric acid concentration has little effect on the adsorption capacity of AC on MB adsorption.

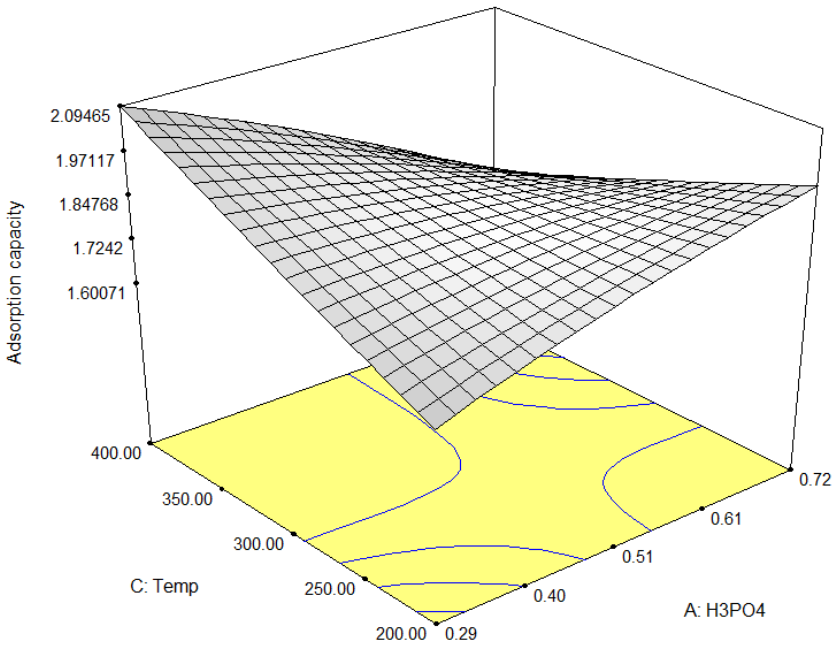



Figure 4.13: Effect of phosphoric acid concentration (mg/l) and activation temperature ($^{o}$C) on adsorption capacity of activated carbon.

Figure 4.13 shows the interaction effect of phosphoric acid concentration and activation temperature on the adsorption capacity of activated carbon on methylene blue. It can be seen that both activation temperature and $H_3PO_4$ acid concentration had significantly effect on the adsorption capacity of the AC. As activation temperature and $H_3PO_4$ concentration were increased the adsorption capacity increased. This was in conformity with the findings of Auta and Hameed, 2011and Auta, 2012. The maximum adsorption capacity takes place at lower activation temperature of 270 $^{o}$C and about 0.51 mg/l phosphoric acid concentration.

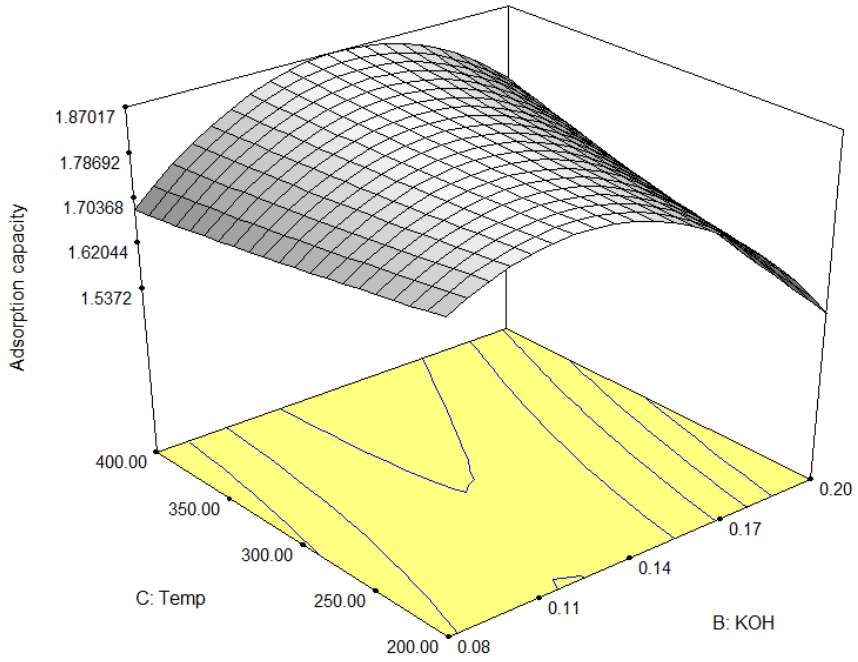



Figure 4.14: Effect of potassium hydroxide concentration (mg/l) and activation temperature ($^{o}$C) on adsorption capacity of activated carbon.

Figure 4.14 shows that adsorption capacity was significant with increased in potassium hydroxide concentration and activation temperature as can be seen in their F-value of 7.55. However, at any designate potassium hydroxide concentration, adsorption capacity slightly affected by any change in activation temperature. This result was in agreement with the findings of Auta and Hameed, 2011; Auta, 2012 and Ahmad et al., 2011, that at higher temperature more pores were developed hence surface area increases.

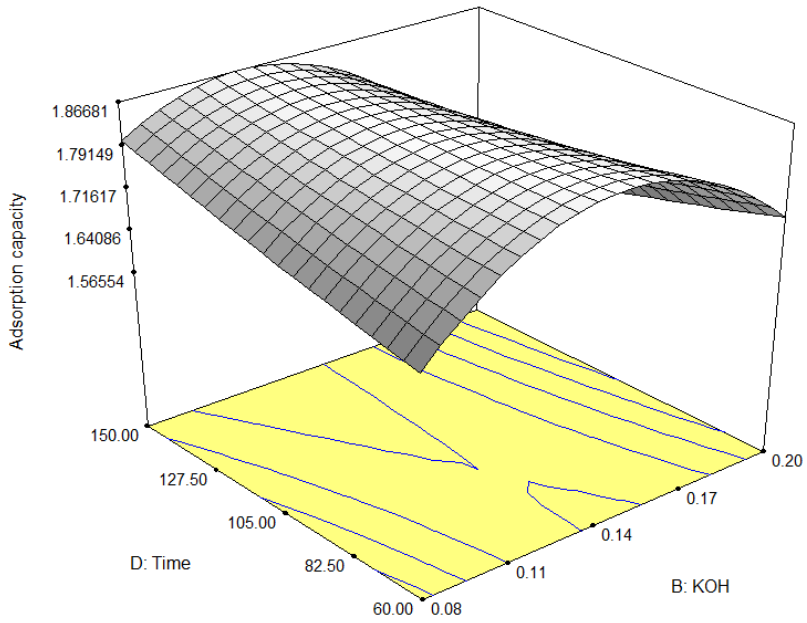



Figure 4.15: Effect of potassium hydroxide concentration (mg/l) and activation time (min) on adsorption capacity of activated carbon.

While Figure 4.15 showed the effect of KOH concentration and activation time on adsorption capacity of AC on methylene blue. As KOH concentration increased, adsorption capacity increases at any given activation time from 60 to 150 minute. But at higher KOH concentration, adsorption decreases. This was as a result of larger pore size of the AC.

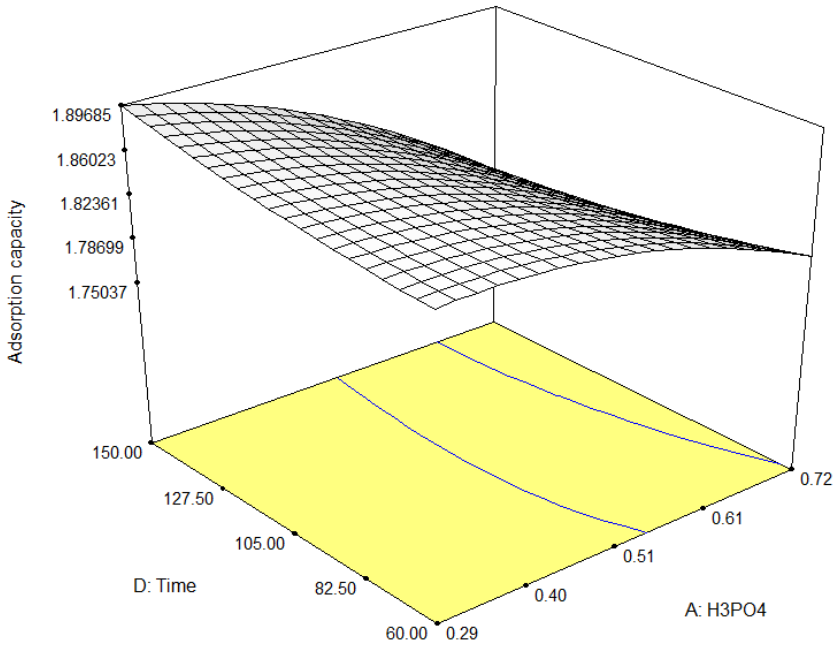



Figure 4.16: Effect of phosphoric acid concentration (mg/l) and activation time (min) on adsorption capacity of activated carbon.

Figure 4.16 shows the interaction effect of $H_3PO_4$ concentration and activation time on adsorption capacity of AC. It can be seen that at any given $H_3PO_4$ concentration, adsorption capacity of AC increased with slightly increased in activation time from 60 to 150 minute.

The interaction effect of activation time and activation temperature on the adsorption capacity of AC on methylene blue is presented in Figure 4.17.

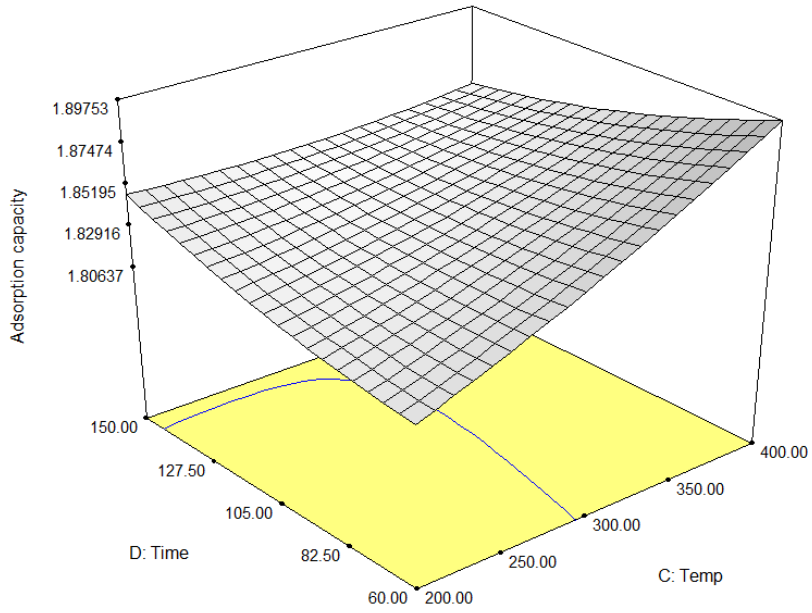



Figure 4.17: Effect of activation temperature ($^{o}$C) and activation time (min) on adsorption capacity of activated carbon.

Figure 4.17 shows the interaction effect of activation temperature and activation time on adsorption capacity of AC. Adsorption capacity of AC is enhanced by an increased in activation temperature from 200 to 400 $^{o}$C with an increase in activation time from 60 to 150 minute which resulted to high surface area of the adsorbent.

### 4.2.4 Optimization

The results for the optimal conditions for the preparation of activated carbon using Design expert Software Version 6.0.6 (STAT-EASE Inc., Minneapolis USA) were 76.93 % hydrolysate yield, 21.84 % activated carbon yield and 1.98 mg/g adsorption capacity of activated carbon, respectively. The optimal conditions obtained by the variables studied

were 0.29 mg/l phosphoric acid, 0.09 mg/l potassium hydroxide, 358.15 $^{o}$C activation temperature and 116.90 minutes activation time, respectively.

### 4.2.5 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra analysis results indicate that only minor differences between corncob, hydrolysate corncob and activated carbon samples could be established. However, shift in bands and changes in wavelength between the untreated and treated samples indicate that chemical transformation would have taken place during chemical treatment or during pyrolysis.

Figures 4.18 (a – c) spectrum shows adsorption bands at 3394.83 $cm^{-1}$, 3398.69 $cm^{-1}$ and 3425.69 $cm^{-1}$ which are associated with the stretched vibration of the O-H groups in alcohols, phenols and carboxylic acids, N-H groups in amines and amides. Also, bands at 2916.47 $cm^{-1}$, 2918.40 $cm^{-1}$ and 2939.61 $cm^{-1}$ are associated with the stretched vibration of the C-H in alkanes and alkyl groups and O-H in carboxylic acids. While bands of 2266.43 $cm^{-1}$, 2276.08 $cm^{-1}$ and 2291.51 $cm^{-1}$ are associated with the stretched vibration of the C≡C and C≡N in alkynes and nitriles. Spectrum bands at 1583.61 $cm^{-1}$, 1641.48 $cm^{-1}$ and 1645.83 $cm^{-1}$ are associated with the stretched vibration of the N-H groups in amines and amides bend, C-C and C=C in alkenes and aromatics and C=O in inorganic carbonate. While bands at 1045.45 $cm^{-1}$, 1055.10 $cm^{-1}$ and 1047.38 $cm^{-1}$ which are associated with stretched vibration of the O-H groups in alcohols, esters, carboxylic acids, aromatics and ethers, and C-N stretched in amines. While bands of 534.30 $cm^{-1}$, 570.95 $cm^{-1}$ and 580.59 $cm^{-1}$ are associated with the stretching vibration of C-Br groups in alkyl halides. Bands at 781.20 $cm^{-1}$ and 1120.68 $cm^{-1}$ are associated with stretched of C-O in aromatic, esters and ethers. Bands at 686.68 $cm^{-1}$, 781.20 $cm^{-1}$ and 1487.17 $cm^{-1}$ are associated with stretched

of C-H in alkanes, alkynes and aromatic. The spectral assignment is shown in Figures 4.18 (a-c).

The presence of these functional groups and their enhancement in adsorption abilities of activated carbons agree with the findings of Auta and Hameed, (2011) and Manase, (2012).

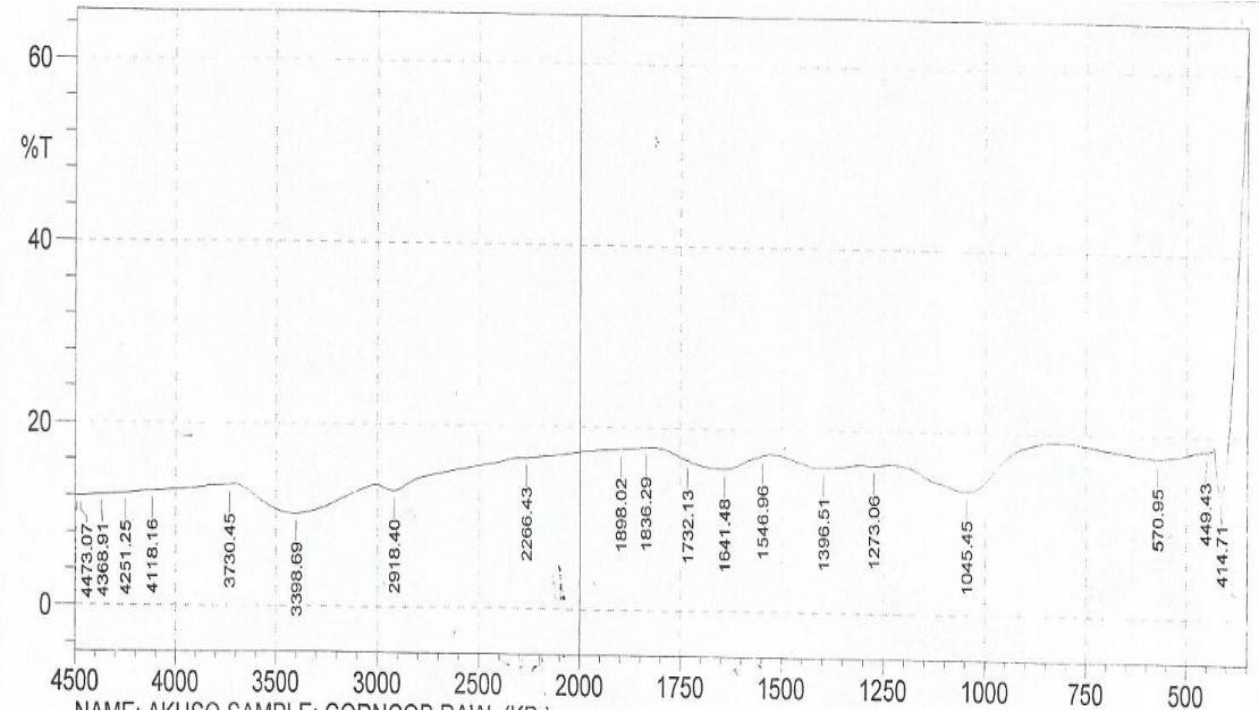



Figure 4.18a: FTIR spectra of corncob, $cm^{-1}$

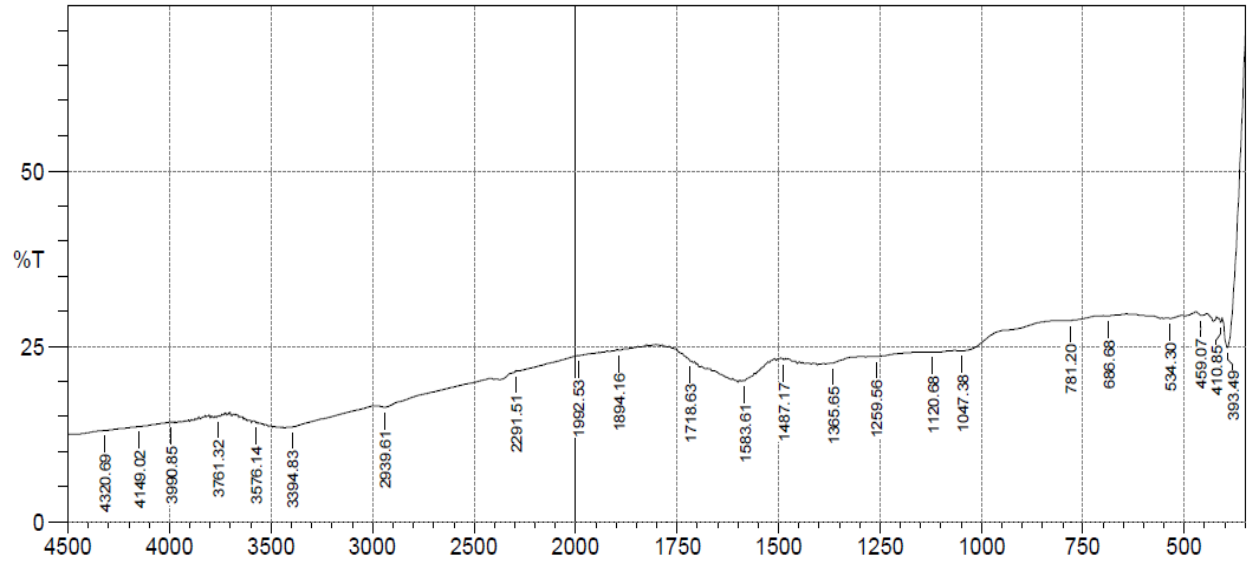


Figure 4.18b: FTIR spectra of hydrolysate corncob, $cm^{-1}$

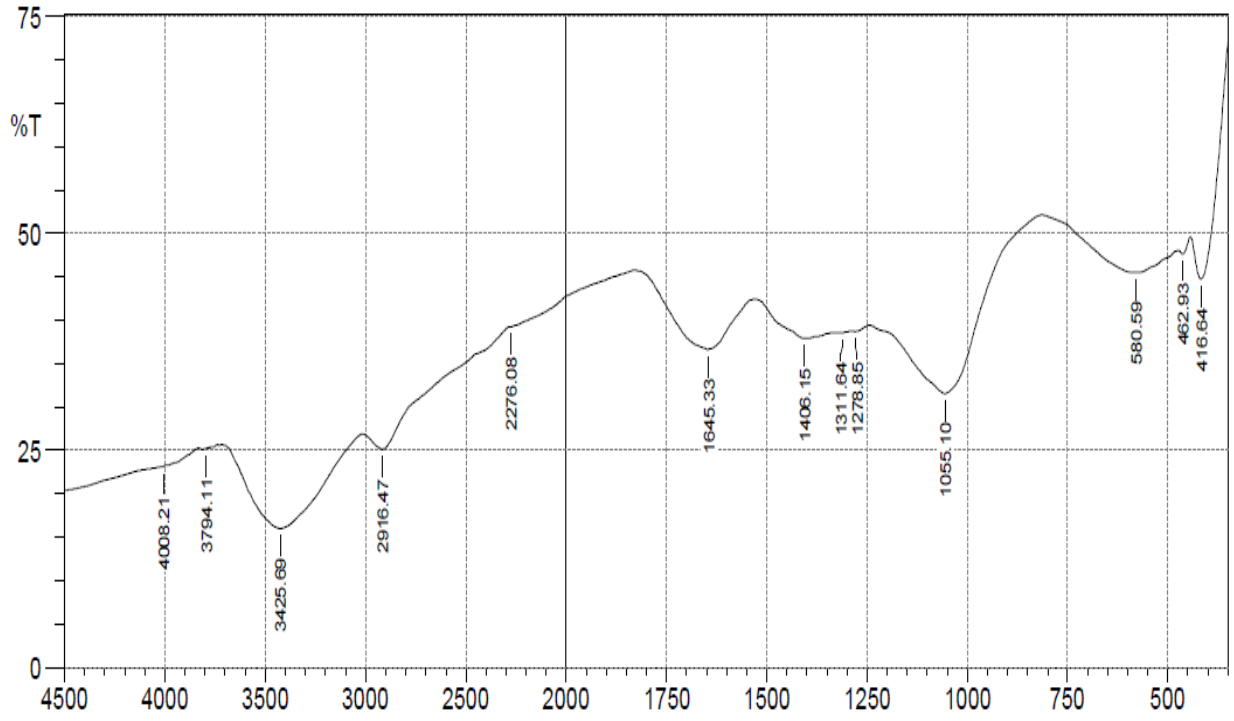



Figure 4.18c: FTIR spectra of activated carbon, $cm^{-1}$

### 4.2.6 Scanning electron microscope (SEM)

SEM images of the best activated carbon samples produced showed the surface texture and porosity with holes and small openings found on the surfaces which facilitate pore diffusion of adsorbate during adsorption. Figures 4.19 (a-c) showed the SEM images of the best AC samples 8, 9 and 14 produced.

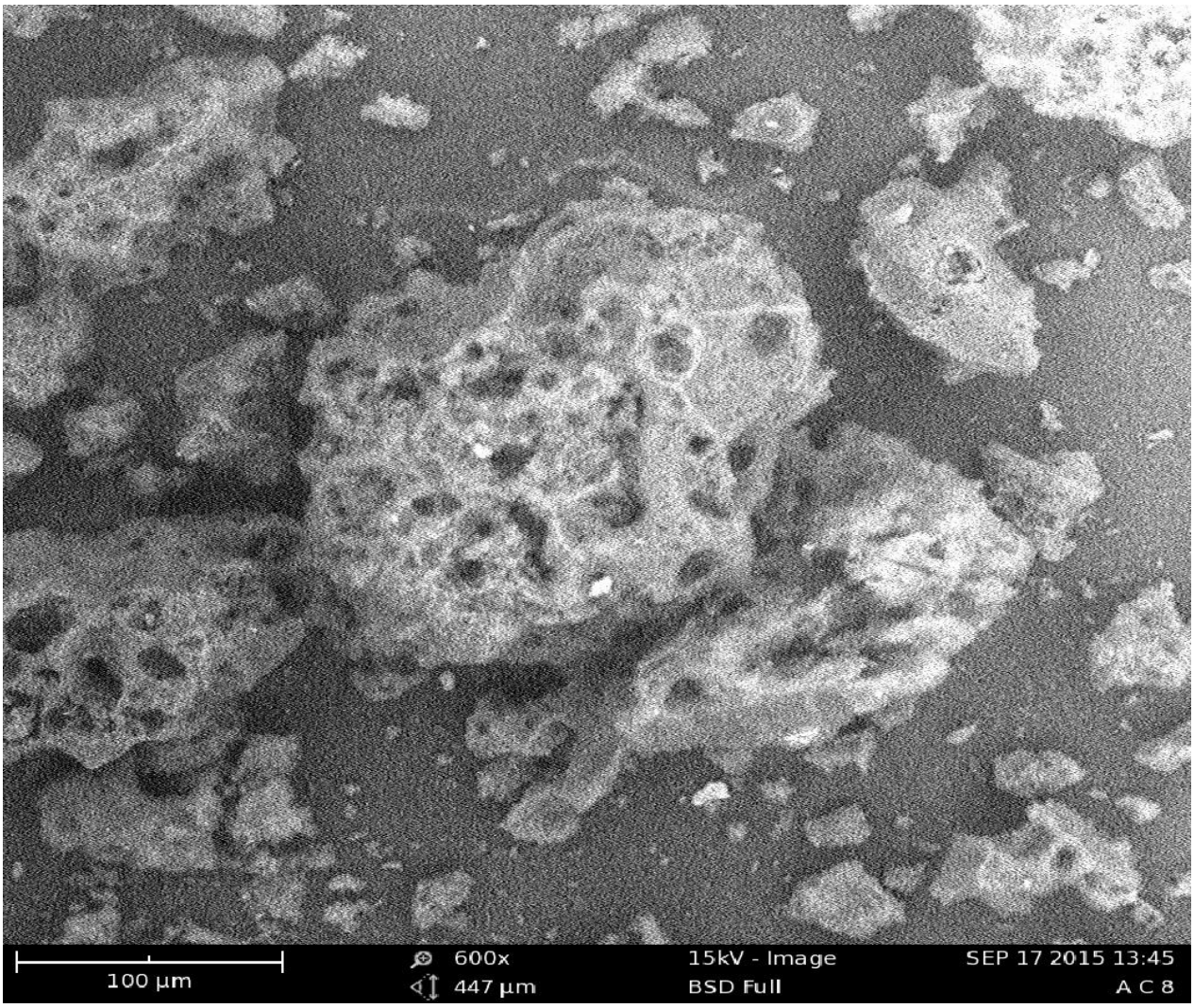



Figure 4.19a: SEM image of AC 8 at a magnification of 600x

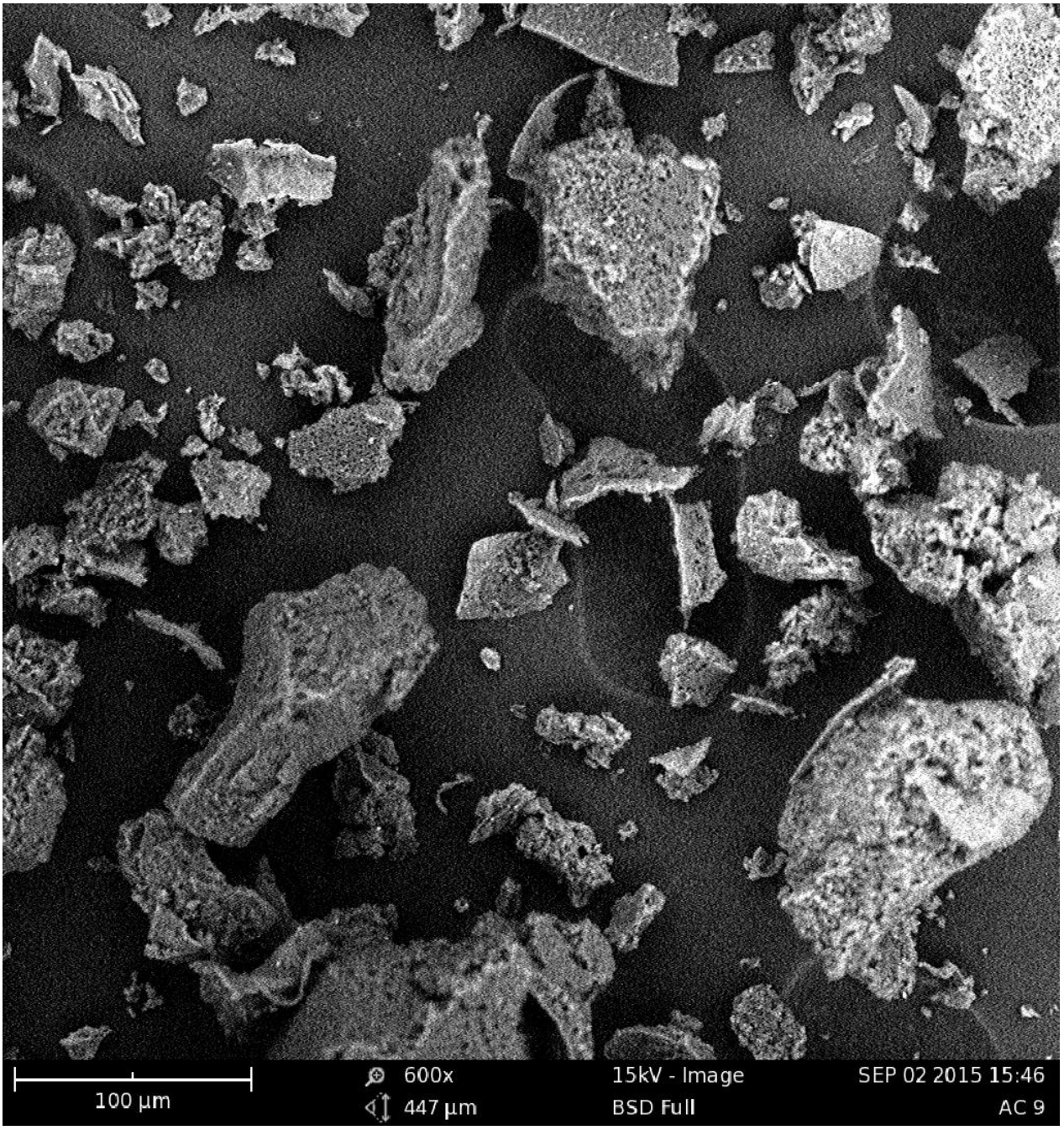



Figure 4.19b: SEM image of AC 9 at a magnification of 600x

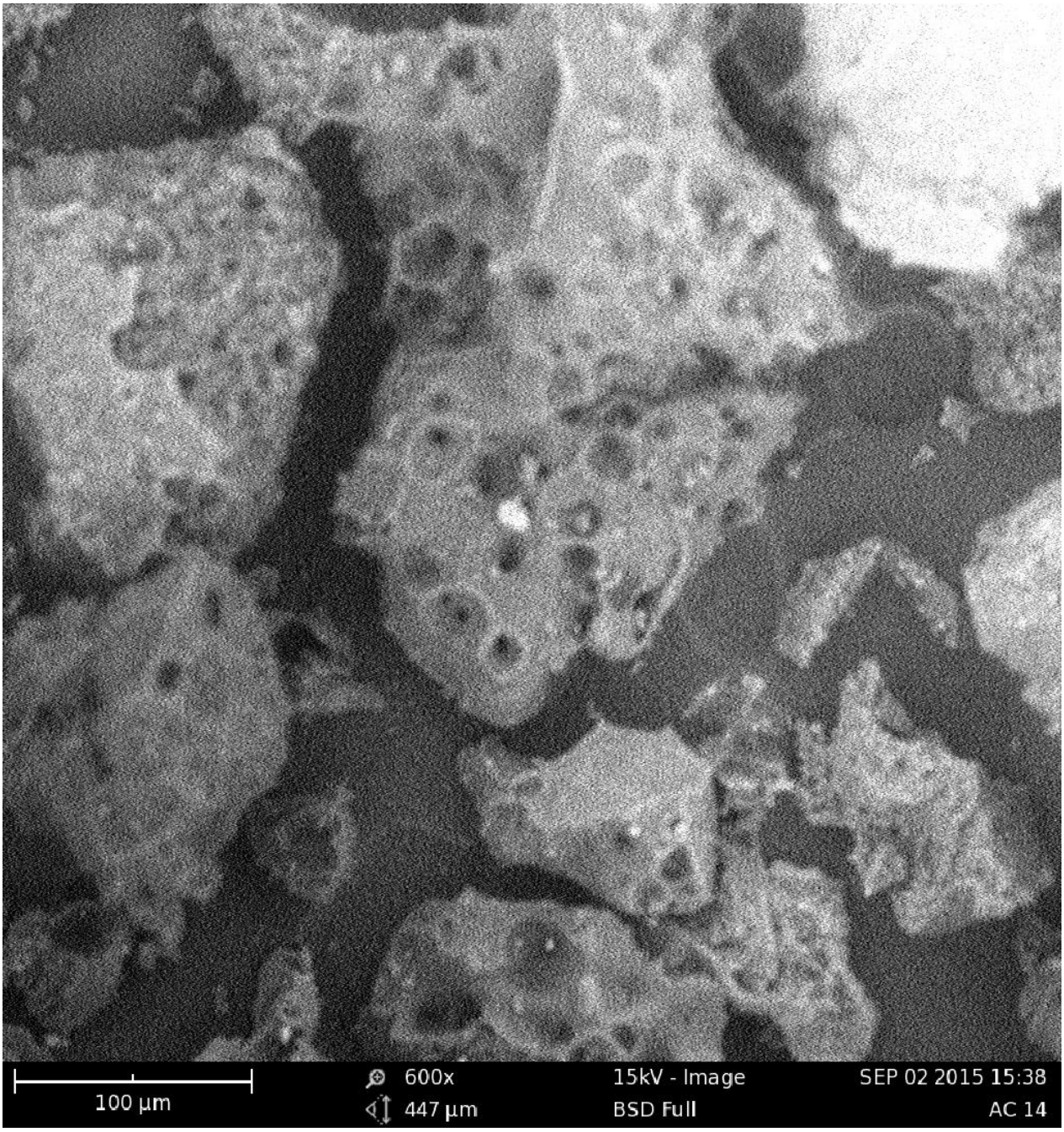



Figure 4.19c: SEM image of AC 14 at a magnification of 600x

### 4.3 Physical and Structural Characteristics of Selected Activated Carbon Samples

The moisture, elemental analysis and ash contents were determined for the selected activated carbon samples using the Method of Association of Analytical Chemist (1990).

In determining the surface area of selected activated carbon samples, Sear's method was employed as given in Equation 3.2. The bulk density of the selected activated carbon samples were determined using Equation 2.6.was calculated as the weight of a quantity of activated carbon divided by the volume it occupies. Properties of corncob, elemental analysis and bulk density of the selected activated carbon samples are presented in Table 4.3, Table 4.4 and Table 4.5.

Table 4.3: Properties of corncob and activated carbon samples

| Properties | Corncob | Activated carbon | | | |
|---|---|---|---|---|---|
| | | AC8 | AC9 | AC14 | Commercial activated carbon |
| Moisture content, wt% | 5.8 | 5.8 | 4.2 | 5.3 | nd |
| Ash content, wt% | 3.9 | 9.3 | 8.2 | 12.3 | nd |
| Crude fibre, wt% | 14 | - | - | - | - |
| Crude lipid, wt% | 9.0 | - | - | - | - |
| Crude protein, wt% | 2.84 | - | - | - | - |
| Carbohydrate (by difference), wt% | 64.46 | - | - | - | - |
| Specific surface area, $m^2/g$ | nd | 259.8 | 215.0 | 314.2 | 109.4 |

Table 4.4: Elemental analysis of selected activated carbon samples

| Composition | Activated carbon - This work | | | Mass fraction, wt% | |
|---|---|---|---|---|---|
| | 8 | 9 | 14 | Heriemath et al., 2012 | Sun et al., 2007 |
| Carbon | 37.64 | 39.95 | 41.54 | 44.0 | 43.41 |
| Hydrogen | nd | nd | nd | 7.0 | 5.83 |
| Nitrogen | 1.19 | 0.95 | 0.84 | 0.40 | 0.56 |
| Oxygen | nd | nd | nd | 47.0 | 50.20 |

nd – not determined

Table 4.5: Bulk density of selected activated carbon samples

| Sample code | Weight of sample (g) | Volume of water displaced ($cm^3$) | Bulk density ($g/cm^3$) |
|---|---|---|---|
| AC 8 | 1 | 4.0 | 0.25 |
| AC9 | 1 | 4.5 | 0.22 |
| AC 14 | 1 | 6.0 | 0.17 |

## 4.4 Adsorption Isotherm Study

### 4.4.1 Batch adsorption studies of chromium (VI) ions on AC

The adsorption data obtained from the batch adsorption experiment for the best AC sample based on MB uptake was used to analyze Langmuir and Freundlich isotherm models using Equations (2.5) and (2.7) for chromium (VI) ions from tannery effluent. Table 4.6 is the Langmuir and Freundlich isotherm models for chromium (VI) ions adsorption on AC 14.

Table 4.6: Langmuir and Freundlich isotherm models for adsorption capacity of chromium ions in tannery effluent on activated carbon (AC14).

| Adsorbent dosage(g) | $C_o$ (mg/l) | $C_e$ (mg/l) | $q_e$ (mg/g) | $C_e/q_e$ (g/l) | log$C_e$ (mg/l) | log$q_e$ (mg/g) | %removal |
|---|---|---|---|---|---|---|---|
| 0.02 | 0.1634 | 0.1392 | 0.0242 | 5.752066 | -0.85636 | -1.61618 | 14.81028 |
| 0.04 | 0.1634 | 0.1168 | 0.0233 | 5.012876 | -0.93256 | -1.63264 | 28.51897 |
| 0.06 | 0.1634 | 0.0943 | 0.023033 | 4.094067 | -1.02549 | -1.63764 | 42.28886 |
| 0.08 | 0.1634 | 0.0733 | 0.022525 | 3.254162 | -1.1349 | -1.64734 | 55.14076 |
| 0.1 | 0.1634 | 0.0505 | 0.02258 | 2.236492 | -1.29671 | -1.64628 | 69.09425 |

Figures 4.20 (a-b) are Langmuir and Freundlich and Figure 4.2 percentage removal of chromium

(VI) ions from tannery effluent.

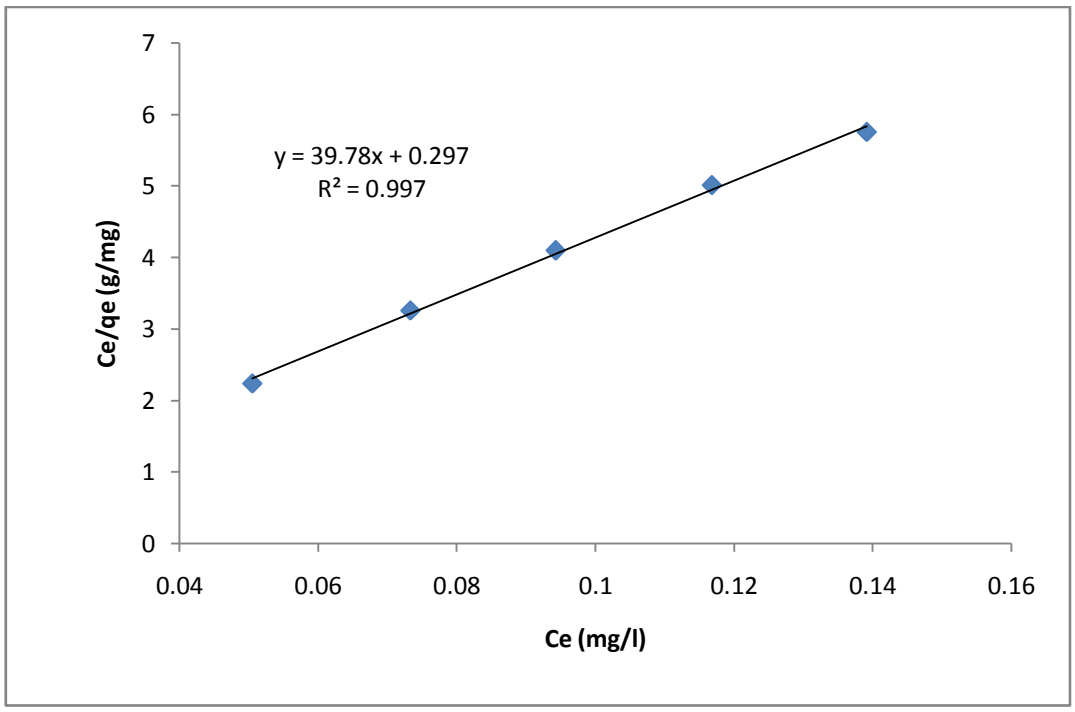



Figure 4.20a: Effect of adsorbent dosage on chromium (VI) adsorption on activated carbon 14.

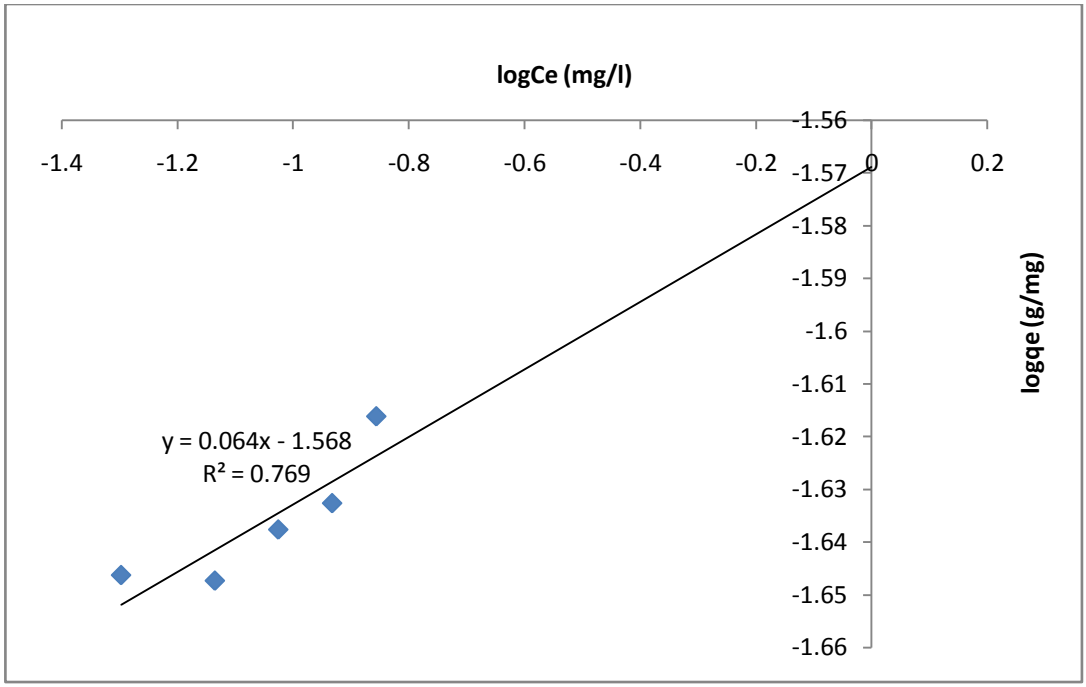



Figure 4.20b: Effect of adsorbent dosage on chromium (VI) adsorption on activated carbon 14.

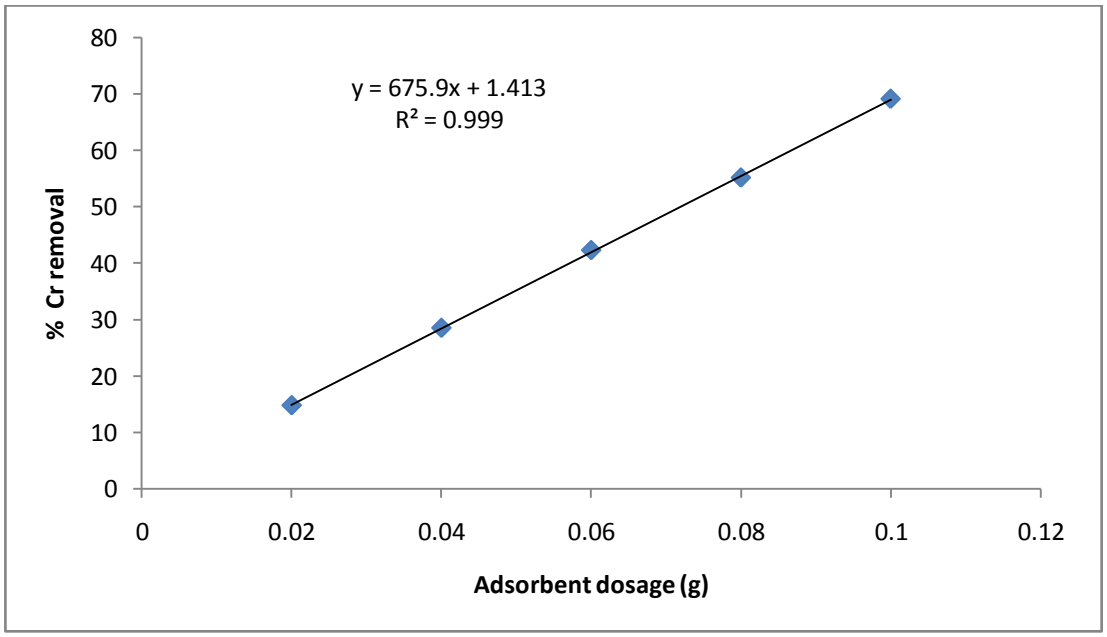



Figure 4.21: Percentage removal of Chromium ions as a function of adsorbent dosage.

Study was carried out on the best activated carbon sample produced to establish the appropriate isotherm model for the sample. The adsorption isotherm studied showed that Langmuir isotherm gave a better correlation than Freundlich isotherm. However, the coefficient of determination $R^2$ for the Langmuir isotherm was 0.9974, while that of Freundlich isotherm was 0.7691. The AC 14 formulation showed the best correlation with Langmuir isotherm. Isotherm plot for chromium (VI) adsorption on the activated carbon produced as shown in Figure 4.20 above using Langmuir and Freundlich models gave the following parameters: b (0.0251, l/mg) is a constant related to the affinity of adsorbent towards adsorbate, $q_m$ (133.88, mg/g) is the maximum monolayer adsorption capacity on the surface of the adsorbent and coefficient of determination $R^2$ (0.9974); n (0.0670) is Freundlich constant, $k_F$ (15.601, mg/g) is the adsorption capacity of adsorbate and coefficient of determination $R^2$ (0.7691), respectively. It can be observed that, % removal of chromium (VI) ions increases with increase in adsorbent dosage

### 4.4.2 Adjusted coefficient of determination

The adjusted coefficient of determination of a multiple linear regression model is defined in terms of the coefficient of determination as follows, where n is the number of experimental runs and p is the number of independent variables (*support @ easycalculation.com*). The independent variables are phosphoric acid concentration (mg/l), potassium hydroxide concentration (mg/l), activation temperature ($^oC$) and activation time (minute), respectively.

Adjusted R-square is nothing but the change of R-square that adjusts the number of terms (variables) in a model. Adjusted R-square calculates the proportion of the variation in the independent variable accounted by the explanatory variables. Adjusted R-square Equation is given in Equation 4.4 below.

$$R^2\text{Adjusted} = 1 - \frac{(1-R\hat{}2)(n-1)}{(n-p-1)} \quad (4.4)$$

Where, $R^2$ is model correlation coefficient, n is the number of experimental runs, and p is the number of independent variables.

# CHAPTER FIVE

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

The preliminary studies on corncob activated carbon preparation was used to investigate the effect of four independent variables; phosphoric acid concentration, potassium hydroxide concentration, activation temperature and activation time on the yield of hydrolysate, activated carbon yield and adsorption capacity of activated carbon samples produced. The following conclusions were drawn from the results of the experiments:

Central Composite Design (CCD) expert was used to investigate the effects of independent variable parameters such as phosphoric acid concentration, potassium hydroxide concentration, and activation temperature and time on the yield of hydrolysate, yield of activated carbon and adsorption capacity of the activated carbon samples produced.

Optimization was carried out using RSM to obtain the optimal process parameters for the preparation of AC and their responses were 0.29 mg/l phosphoric acid concentration, 0.09 mg/l potassium hydroxide concentration, 358.15 $^{o}$C activation temperatures and 116.9 minute activation time resulting in 76.93 % hydrolysate yield, 21.84 % AC yield and 1.98 mg/g adsorption capacity of the activated carbon.

FTIR spectra analysis for corncob sample, hydrolysate corncob sample and activated carbon (AC) sample showed the presence of O-H, C-H, C-C, C-N, C=C, C-I, C≡N and C≡C functional groups which influence enhancement in adsorption abilities of activated carbon onto the adsorbent. SEM images of the selected best AC samples 8, 9 and 14 showed the surface texture and porosity with holes and small openings found on the surfaces which facilitate pore diffusion of adsorbate during adsorption.

The isotherm studied for the best activated carbon 14 showed Langmuir isotherm model gave a fitted curve of the adsorption data obtained from batch adsorption experiments for chromium (VI) ions adsorption on activated carbon sample with a coefficient of determination of 0.9974.

## 5.2 Recommendations

1. Effect of high activation temperature above 500$^{o}$C on corncob using hybrid chemical activation should be investigated to compare the yield and its adsorption capacity of the activated carbon.

2. Kinetics study of the activated carbon samples should be investigated.

3. Comparison of economic analysis of hybrid chemical activation and one activating agent should be investigated.

4. Activated carbons produced from lingo-cellulosic waste biomass (corncob) can be used as adsorbents (low ash content of 4.01 wt %) for various environmental applications such as drinking water, removing colour from industrial effluents and removal of dyes and heavy metals.

## REFERENCES


Abia, A.A. & J.C. Igwe (2005). "Sorption Kinetics and Intraparticulate Diffusivities of Cd, Pb And

Zn Ions on Maize Cob". African Journal of Biotechnology, Vol. 4 (6): 509-512, June 2005.

Adejonwo H. (2006). Production of Activated Carbon from Elemi (Canarium

Schweinfuthii) Nutshell Using Chemical Method. Final Year Research Project. Ahmadu Bello University, Zaria.

Al-Asheh S, Banat F, Al-Hamed N (2003). Adsorption of Pollutants from Aqueous Solutions

Using Activated and Non-Activated Oak Shells: Parametric and Fractional Factorial Design Study, Part 1, and Removal of Copper. Adsorption, 21: 177-188. African Journal of Pure and Applied Chemistry Vol. 6(11), pp. 149-156, 13 June, 2012.

Ajayi. O. A and Olawale. A. S.( 2009). Comparison Study of Thermal and Chemical Activation

of *Canarium scheweinfurthii* Nutshell. Journal of Applied Sciences Research, 5(12) 2148-2152.

Ajinomoh C.S and Nurudeen S. (2013). Production of Activated Carbon from

Sugar Cane Bagasse. Australian Journal of Industry research.

Auta M and Hameed B. H. (2011). "Optimized Waste tea Activated Carbon for Adsorption Of

Methylene Blue And Acid Blue 29 Dyes Using Response Surface Methodology". Chemical Engineering Journal Vol 125 pp.233-243.

Auta M. (2012). "Optimizationof Tea Waste Activated Carbon Preparation Parameters for

Removal Cibacron Yellow Dye from Textile Waste Waters". International Journal of

Advanced Engineering Research Studiesvol 1 (4) July-September pp. 50-56.

Chipofya V. H and Mcconnachie. G. L. (2000).Characterisation Of Activated Carbon Produced from Agricultural Waste Materials for Taste and Odour Removal in Drinking Water Supplies. Journal of Sustainable Use of Water Resources, Maputo, 1-2.

Cuhadar, C.(2005). Production and Characterization of Activated Carbon from Hazelnut Shell And Hazelnut Husk (Msc Thesis) The Graduate School Of Natural and Applied Sciences Of Middle East Technical University *aav.mehmetakif.edu.tr/index.php/.../52?...*

Diya'Udeen, B. H., Mohammed, I. A., Ahmed, A. S and Jibril, B. Y. (2008). Production of Activated Carbon From Corncobs and Its Utilization in Crude Oil Spillage Clean Up. Agricultural Engineering International CIGR journal EE 08 004. Vol. X.

Diya'uddeen B. H., Mohammed, I.A, Jibril, B.Y. (2011). Kinetics of Methylene Blue Adsorption on KOH-activated Carbon Using Corn Cobs. Malaysian Journal of Science 30 (3): 196-207.

Eric P. L. (2010). Production, Characterization, and Applications of Activated Carbon. An M.Sc Thesis.

Hiremath M. N.1, Shivayogimath C.B.2, Shivalingappa S.N. (2012). Preparation and Characterization of Granular Activated Carbon from Corn Cob by KOH Activation. International Journal of Research in Chemistry and Environment Vol. 2 Issue 3 (84-87).

Institute of Agricultural Research, Ahmadu Bello University, Zaria (2011) bulletin.

Jamaludin S. R. B. (2010). "A Production of Activated Carbon Using Local Agricultural Waste for Groundwater Treatment in Universiti Malaysia, Pahang". Thesis

Submitted to University of Malaysia, Pahang.

Lartey R. B., Francis A. and Mr Nketia N. S. (1999). Developing National Capability For Manufacture Of Activated Carbon From Agricultural Wastes. The Journal of Ghana Engineer.

Lua and Gua, 2001. Korean J. Chem. Eng., 23(6), 1046-1054.

Malakootian M., Nouri J and Hossaini H. (2009). "Removal of Heavy Metals from Paint Industry's Wastewater Using Leca as an Available Adsorbent". International Journal of Environment Science and Technology, 6 (2), 183-190, Spring.

Mohammed M. A., Babagana G. and Bitrus K. H. (2015) Production And Characterization Of Activated Carbon From Groundnut Shell Sourced In Maiduguri. Columbia Journal of Life Science Vol 17 (1) pp 18-24.

Mohd A. A., Evelyn T. C. Y., Ismail A., Nazwin A. and Shamsul K. S. (2011). Optimization of Preparation Conditions For Corncob Based Activated Carbons For The Removal Of Remazol Brilliant Blue R-Dye. International Journal of Engineering and Technology IJET-IJENS Vol: 11 No: 01.

Mohd A. A., Olugbenga S. B., and Mohd A. A. (2014). Adsorption Studies of Remazol Brilliant Blue R Dye on Activated Carbon Prepared from Corncob American Journal of Modern Chemical Engineering (2014) Vol. 1 No. 1 pp. 1-12

Nazar A. E., Mutaz A. E. and Mohammed A. E. (2013).

Physico-ChemicalCharacterizationand and Freundlich Isotherm Studies of Adsorption of

Fe (II) from aqueous solution by using AC Prepared from Doum Fruit Waste. Archieves

of Applied Sciences Research, vol. 5 (5), pp 149-158.

(http//scholarresearchlibrary.com/archieve.html).

Nezih U. Y. (2004). Production and Characterization of Activated Carbon from Apricot Stones. An MSc Thesis Submitted To The Graduate School Of Natural And Applied Sciences Of The Middle East Technical University.

Nurul'Ain B. J. (2007).The Production and Characterization osf activated Carbon Using Local Agriculturalwaste through Chemical Activation Process. MSc Thesis**.** http://Prints. Usm.my/9576/1/Nurul'Ain Binti Jabit.PDF.s

Oloworise F. J. (2006). Production and Characterization of Activated Carbon from Rice Husk. A Final Year Research Project, Federal University of Technology, Minna.

Tseng R-L., Wu F-C and Juang R-S. (2005). J Colloid Interface Sci. Mar 1;

283 (1):49-56.

Sun Y., Zhang J. P., G. Yang G and Li Z. H. (2003). Journal of Chemical and Biochemical Engineering.

Siti R. B. J. (2010). A Production of Activated Carbon Using Local Agricultural Waste for Ground Water Treatment in University of Malaysia, Pahang. An Under Graduate Thesis for the Award of Bachelor of Civil Engineering.

Sun Y., Zhang J. P., Yang G and Li Z. H. (2007). An improved Process for Preparing Activated

Carbon with Large Specific Surface Area from Corncob. "Journal of Chemical and Biochemical Engineering Q. 21 (2) 169-174".

Tsai W.T., Chang C.Y and Lee S. L. (1997). Preparation and Characterization of Activated Carbons from Corncob. http//ntur.lib.edu/bitstream/246246/96109/1/14.pdf.

Tsai W. T., Chang C. Y., Wang S. Y., Chien S. F and Sun H. F. (2001). Preparation of Activated Carbons from Corncob Catalyzed by Potassium Salts and Subsequent Gasification with $CO_2$. "Journal of Bioresource Technology (78) 203-208."

Tsai, W.T., Chang, C.Y., Wang, S. Y., Chang, C. F., Chien, S. F and Sun, H. F. (2000). Cleaner production of carbon adsorbents by utilizing agricultural waste corn cob. "Journal of Resources, Conservation and Recycling (32) 43."

World corn production.com (2013; July, 2014).

Yahia A.A. (2006). Journal of Engineering and Science Vol.17, pp. 75-100. Activated Carbon from Dates' Stone by Zinc(II)Chloride Activation.

Yusufu M. I., Ariahu C. C. and Igbabul B. D.(2012). Production and characterization of activated carbon from selected local raw materials. African Journal of Pure and Applied Chemistry Vol. 6(9), pp. 123-131.

# APPENDICES

## APPENDIX A

Table A1: Surface areas of activated carbon, Sun et al., 2007.

| Preparation Method | Carbonization | Surface Area ($m^2/g$) | Pore Volume ($m^3/g$) | References |
|---|---|---|---|---|
| Thermal | 450°C, 4h | 2700 | - | Sun et al., 2003 |
| Thermal | 450 °C, 1.5h | 2595 | 1.480 | Tseng et al., 2005 |
| Thermal | 450 °C, 1.5h | 2844 | 1.533 | Tseng et al., 2006 |
| Chemical | 800 °C, 1h | 1806 | 0.870 | Tsai et al., 2001 |
| Chemical | 750 °C, 1h | 3290 | 1.450 | Sun et al., 2003 |
| Chemical | 800 °C, 1h | 1975 | 0.945 | Sun et al., 2007 |
| Thermal | 350 °C, 5min | 2880 | 1.664 | Sun et al., 2007 |

Table A2: Shows the experimental hydrolysate yield (%)

| S/N | Phosphoric acid, mg/ml | Hydrolysate yield, % |
|---|---|---|
| 1 | 0.07 | 85.27 |
| 2 | 0.29 | 74.68 |
| 3 | 0.50 | 68.34 |
| 4 | 0.72 | 47.87 |
| 5 | 0.93 | 41.98 |

Table A3: Experimental and predicted hydrolysate yield (%)

| S/N | Experimental hydrolysate yield, % | Predicted hydrolysate yield, % |
|---|---|---|
| 1 | 85.27 | 86.43 |
| 2 | 74.64 | 74.82 |
| 3 | 68.34 | 63.73 |
| 4 | 47.87 | 52.12 |
| 5 | 41.98 | 41.04 |

Table A4: Experimental and predicted response values for activated carbon yield

| S/N | Experimental AC yield, % | Predicted AC yield, % |
|---|---|---|
| 1 | 25.39 | 23.64 |
| 2 | 15.72 | 16.39 |
| 3 | 13.83 | 15.06 |
| 4 | 15.69 | 15.14 |
| 5 | 18.73 | 19.45 |
| 6 | 5.00 | 3.91 |
| 7 | 18.78 | 15.25 |
| 8 | 7.65 | 7.04 |
| 9 | 18.87 | 19.63 |
| 10 | 11.59 | 14.31 |
| 11 | 8.99 | 9.36 |
| 12 | 12.05 | 11.38 |
| 13 | 20.28 | 20.29 |
| 14 | 7.83 | 6.68 |
| 15 | 15.00 | 14.41 |
| 16 | 7.12 | 8.13 |
| 17 | 18.30 | 19.42 |
| 18 | 6.67 | 6.17 |
| 19 | 19.32 | 18.64 |
| 20 | 10.00 | 11.34 |
| 21 | 18.67 | 16.95 |
| 22 | 7.33 | 9.71 |
| 23 | 13.57 | 15.70 |
| 24 | 14.20 | 12.73 |
| 25 | 19.00 | 18.70 |
| 26 | 18.50 | 18.70 |
| 27 | 18.52 | 18.70 |
| 28 | 18.78 | 18.70 |
| 29 | 18.69 | 18.70 |
| 30 | 18.66 | 18.70 |

Table A5: Experimental and predicted response values for adsorption capacity of activated carbon.

| S/N | Experimental adsorption capacity, mg/g | Predicted adsorption capacity, mg/g |
|---|---|---|
| 1 | 1.73 | 1.59 |
| 2 | 1.67 | 1.76 |
| 3 | 1.23 | 1.34 |
| 4 | 1.81 | 1.80 |
| 5 | 1.92 | 1.92 |
| 6 | 1.25 | 1.32 |
| 7 | 1.88 | 1.96 |
| 8 | 1.73 | 1.65 |
| 9 | 1.72 | 1.81 |
| 10 | 1.91 | 1.90 |
| 11 | 1.28 | 1.28 |
| 12 | 1.66 | 1.67 |
| 13 | 1.98 | 1.06 |
| 14 | 1.47 | 1.37 |
| 15 | 1.90 | 1.82 |
| 16 | 1.22 | 1.43 |
| 17 | 1.88 | 1.86 |
| 18 | 1.71 | 1.65 |
| 19 | 1.30 | 1.30 |
| 20 | 1.17 | 1.09 |
| 21 | 1.83 | 1.80 |
| 22 | 1.97 | 1.92 |
| 23 | 1.89 | 1.87 |
| 24 | 1.92 | 1.86 |
| 25 | 1.74 | 1.84 |
| 26 | 1.79 | 1.84 |
| 27 | 1.87 | 1.84 |
| 28 | 1.88 | 1.84 |
| 29 | 1.89 | 1.84 |
| 30 | 1.88 | 1.84 |

Table A6: Analysis of variance (ANOVA) for the response of hydrolysate yield.

| Source | Sum of Squares | DF | Mean Square | F-Value | Prob>F |
|---|---|---|---|---|---|
| Model | 3805.00 | 4 | 951.25 | 59.22 | <0.0001 |
| A | 3803.11 | 1 | 3803.11 | 236.77 | <0.0001 |
| B | 1.11 | 1 | 1.11 | 0.069 | 0.7952 |
| C | 0.059 | 1 | 0.059 | 3.673E-003 | 0.9522 |
| D | 0.79 | 1 | 0.79 | 0.045 | 0.8335 |
| Residual | 401.57 | 25 | 16.06 | | |
| Lack of Fit | 394.01 | 20 | 19.70 | 13.04 | 0.0049 |
| Pure Error | 7.56 | 5 | 1.51 | | |
| Cor Total | 4206.56 | 29 | | | |

| | | | |
|---|---|---|---|
| Std. Dev. | 4.01 | R-Squared | 0.9045 |
| Mean | 64.27 | Adj R-Squared | 0.8893 |
| C.V. | 6.24 | Pred R-Squared | 0.8620 |
| PRESS | 580.37 | Adeq Precision | 30.772 |

Table A7: Analysis of variance (ANOVA) for activated carbon yield response.

| Source | Sum of Squares | DF | Mean Square | F-Value | Prob-F |
|---|---|---|---|---|---|
| Model | 736.32 | 14 | 52.59 | 15.66 | <0.0001 |
| A | 274.52 | 1 | 274.52 | 81.74 | <0.0001 |
| B | 76.32 | 1 | 76.32 | 22.72 | 0.0002 |
| C | 82.90 | 1 | 82.90 | 24.68 | 0.0002 |
| D | 12.77 | 1 | 12.77 | 3.80 | 0.0701 |
| $A^2$ | 59.74 | 1 | 59.74 | 17.79 | 0.0007 |
| $B^2$ | 23.57 | 1 | 23.57 | 7.01 | 0.0182 |
| $C^2$ | 49.40 | 1 | 49.40 | 14.71 | 0.0016 |
| $D^2$ | 34.45 | 1 | 34.45 | 10.26 | 0.0059 |
| AB | 53.79 | 1 | 53.79 | 16.02 | 0.0012 |
| AC | 68.78 | 1 | 68.78 | 20.48 | 0.0004 |
| AD | 3.76 | 1 | 3.76 | 1.12 | 0.3069 |
| BC | 19.18 | 1 | 19.18 | 5.71 | 0.0304 |
| BD | 2.82 | 1 | 2.82 | 0.84 | 0.3738 |
| CD | 23.52 | 1 | 23.52 | 7.00 | 0.0183 |
| Residual | 50.38 | 15 | 3.36 | | |
| Lack of Fit | 50.21 | 10 | 5.02 | 247.60 | <0.0001 |
| Pure Error | 0.17 | 5 | 0.032 | | |
| Cor Total | 786.70 | 29 | | | |

| | | | |
|---|---|---|---|
| Std. Dev. | 1.83 | R-Squared | 0.9360 |
| Mean | 14.76 | Adj R-Squared | 0.8762 |
| C.V. | 12.41 | Pred R-Squared | 0.6322 |

| | | | |
|---|---|---|---|
| PRESS | 289.31 | Adeq Precision | 15.227 |

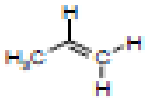
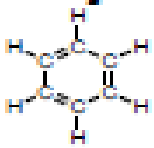
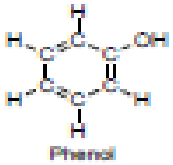
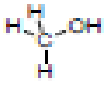
Table A8: Analysis of variance (ANOVA) for adsorption capacity of activated carbon response

| Source | Sum of Squares | DF | Mean Square | F-Value | Prob-F |
|---|---|---|---|---|---|
| Model | 1.76 | 14 | 0.13 | 11.31 | <0.0001 |
| A | 0.068 | 1 | 0.068 | 6.09 | 0.0262 |
| B | 0.059 | 1 | 0.059 | 5.26 | 0.0366 |
| C | 0.014 | 1 | 0.014 | 1.28 | 0.2765 |
| D | 3.348E-5 | 1 | 3.348E-5 | 2.108E-3 | 0.9640 |
| $A^2$ | 0.013 | 1 | 0.013 | 1.17 | 0.2965 |
| $B^2$ | 0.72 | 1 | 0.72 | 64.37 | <0.0001 |
| $C^2$ | 5.706E-4 | 1 | 5.706E-4 | 0.051 | 0.8240 |
| $D^2$ | 9.263E-4 | 1 | 9.263E-4 | 0.083 | 0.7770 |
| AB | 0.087 | 1 | 0.087 | 7.77 | 0.0138 |
| AC | 0.60 | 1 | 0.60 | 53.97 | <0.0001 |
| AD | 6.461E-3 | 1 | 6.461E-3 | 0.58 | 0.4581 |
| BC | 0.084 | 1 | 0.084 | 7.55 | 0.0150 |
| BD | 0.076 | 1 | 0.076 | 6.79 | 0.0199 |
| CD | 7.225E-3 | 1 | 7.225E-3 | 0.65 | 0.4332 |
| Residual | 0.17 | 15 | 0.011 | | |
| Lack of Fit | 0.15 | 10 | 0.015 | 3.88 | 0.0739 |
| Pure Error | 0.019 | 5 | 3.817E-3 | | |
| Cor Total | 1.93 | 29 | | | |

| | | | |
|---|---|---|---|
| Std. Dev. | 0.11 | R-Squared | 0.9134 |
| Mean | 1.70 | Adj R-Squared | 0.8326 |
| C.V. | 6.20 | Pred R-Squared | 0.5438 |
| PRESS | 0.88 | Adeq Precision | 12.904 |

## APPENDIX B

Table B1: Principal FTIR Absorptions for Certain Functional Groups

| **Functional Group Names** & Example compounds | **Absorption Ranges ($cm^{-1}$)** (Look for a single absorption in these regions, unless stated otherwise.) | **Type of Vibration** causing IR absorption |
|---|---|---|
| **Alkanes:**  Methane | **3000-2800** (Note: The absorptions can be seen as several distinct peaks in this region.) | H-C-H Asymmetric & Symmetric Stretch |
| | **1500-1440** | H-C-H Bend |
| **Alkenes:**  1-Propene | **3100-3000** | C=C-H Asymmetric Stretch |
| | **1675-1600** | C-C=C Symmetric Stretch |
| **Alkynes:**  Propyne | **3300-3200** | ≡C—H Stretch |
| | **2200-2100** | C≡C Stretch |
| **Aromatic Rings:**  Benzene | **3100-3000** | C=C-H Asymmetric Stretch |
| | **1600-1580** | C-C=C Symmetric Stretch |
| | **1500-1450** | C-C=C Asymmetric Stretch |
| **Phenols & Alcohols:**  Phenol  Methanol (Alcohol) | **3600-3100** (Note: Phenols MUST have Aromatic Ring Absorptions too.) | Hydrogen-bonded O-H Stretch (This peak usually appears much broader than the other IR absorptions. |
| **Carboxylic Acids:**  Formic Acid | **3400-2400** *(This peak always covers the entire region with a VERY BROAD peak.)* | Hydrogen-bonded O-H Stretch *(Note: This peak can obscure other peaks in this region.)* |
| | **1730-1650** | C=O Stretch |
| **Ketones:**  Acetone | **1750-1625** | C=O Stretch |
| **Aldehydes:**  Ethanal | **1750-1625** | C=O Stretch |
| | **2850-2800** | C-H Stretch off C=O |
| | **2750-2700** | C-H Stretch off C=O |

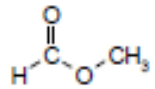
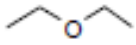
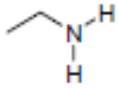
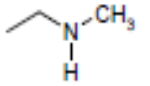
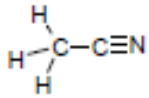
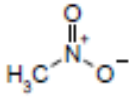
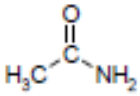
| **Functional Group Names** & **Example compounds** | **Absorption Ranges($cm^{-1}$)** [Look for a single absorption in these regions, unless stated otherwise.] | **Type of Vibration** causing IR absorption |
|---|---|---|
| **Esters:**  Methyl Formate | 1755-1650 | C=O Stretch |
| | (1300-1000) | (C-O Stretch) |
| **Ethers:**  Diethyl Ether (aka-Ethyl Ether) | (1300-1000) | (C-O Stretch) |
| **Amines—Primary:**  Ethylamine | 3500-3100 (TWO PEAKS!) | N-H Stretch |
| | 1640-1560 | N-H Bend |
| **Amines—Secondary:**  N-Methylethylamine | 3500-3100 (ONE PEAK!) | N-H Stretch |
| | 1550-1450 | N-H Bend |
| **Nitriles:**  Methanenitrile | 2300-2200 | C≡N Stretch |
| **Nitro Groups:**  Nitromethane (Note: Both peaks are <200 cm-1 apart.) | 1600-1500 | N=O Stretch |
| | 1400-1300 | N=O Bend |
| **Amides:**  Methanamide | 3500-3100 | N-H Stretch (similar to amines) |
| | 1670-1600 | C=O Stretch |
| | 1640-1550 | N-H Bend |

Table B2: Characteristic FTIR Absorptions for Certain Functional Groups

| Functional Group | Characteristics Adsorption ($cm^{-1}$) | Notes |
|---|---|---|
| Alkyl C–H stretch | 2950–2850 (m or s) | Alkane, C–H bonds are fairly ubiquitous and therefore usually less useful in determining structure. |
| Alkenyl C–H stretch<br>Alkenyl C=C stretch | 3100–3010 (m) | Absorption peaks above 3000 $cm^{-1}$ are frequently diagnostic of unsaturation |
| Alkynl C–H stretch | ~3300 (s) | |
| Alkynl C≡C strech | 2260–2100 (v) | |
| Aromatic C–H stretch | ~3030 (v) | |
| Aromatic C–H bending | 860–680 (s) | |
| Aromatic C=Cbending | 1700–1500 (m, m) | |
| Alcohol/Phenol O–H stretch | 3550–3200 (broad, s) | See “free vs Hydrogen–bonded Hydroxyl groups” in the introduction in IR spectra for more information |
| Carboxylic acid O–H stretch | 3000–2500 (broad, v) | |
| Amine N–H stretch | 3500–3300 (m) | Primary amine produce two N–H stretch absorptions, secondary amides only one and tertiary none |
| Nitrile C≡N stretch | 2260–2220 (m) | |
| Aldehyde C=O stretch | 1740–1690 (s) | |
| Ketone C=O stretch | 1750–1680 (s) | |
| Ester C=O stretch | 1750–1735 (s) | |
| Carboxylic acid C=O stretch | 1780–1710 (s) | |
| Amide C=O stretch | 1690–1630 (s) | |
| Amide N–H stretch | 3700–3500 (m) | As with amines, an amide produces zero to two N–H absorptions depending on its type |

Table B3: Characteristic IR Absorptions

| Frequency, $cm^{-1}$ | Bond | Functional Group |
|---|---|---|
| 3640–3610 (s, sh) | O–H stretch, free hydroxyl | alcohols, phenols |
| 3500–3200 (s,b) | O–H stretch, | H–bonded alcohols, phenols |
| 3400–3250 (m) | N–H stretch | 1°, 2° amines, amides |
| 3300–2500 (m) | O–H stretch | carboxylic acids |
| 3330–3270 (n, s) | –C≡C–H: C–H stretch | alkynes (terminal) |
| 3100–3000 (s) | C–H stretch | aromatics |
| 3100–3000 (m) | =C–H stretch | alkenes |
| 3000–2850 (m) | C–H stretch | alkanes |
| 2830–2695 (m) | H–C=O: C–H stretch | aldehydes |
| 2260–2210 (v) | C≡N stretch | nitriles |
| 2260–2100 (w) | –C≡C– stretch | alkynes |
| 1760–1665 (s) | C=O stretch | carbonyls (general) |
| 1760–1690 (s) | C=O stretch | carboxylic acids |
| 1750–1735 (s) | C=O stretch | esters, saturated aliphatic |
| 1740–1720 (s) | C=O stretch | aldehydes, saturated aliphatic |
| 1730–1715 (s) | C=O stretch | α,β–unsaturated esters |
| 1715 (s) | C=O stretch | ketones, saturated aliphatic |
| 1710–1665 (s) | C=O stretch | α,β–unsaturated aldehydes, ketones |
| 1680–1640 (m) | –C=C– stretch | alkenes |
| 1650–1580 (m) | N–H bend | 1° amines |
| 1600–1585 (m) | C–C stretch (in–ring) | aromatics |
| 1550–1475 (s) | N–O asymmetric stretch | nitro compounds |
| 1500–1400 (m) | C–C stretch (in–ring) | aromatics |
| 1470–1450 (m) | C–H bend | alkanes |
| 1370–1350 (m) | C–H rock | alkanes |
| 1360–1290 (m) | N–O symmetric stretch | nitro compounds |
| 1335–1250 (s) | C–N stretch | aromatic amines |
| 1320–1000 (s) | C–O stretch | alcohols, carboxylic acids, esters, ethers |
| 1300–1150 (m) | C–H wag | (–CH2X) alkyl halides |
| 1250–1020 (m) | C–N stretch | aliphatic amines |
| 1000–650 (s) | =C–H bend | alkenes |
| 950–910 (m) | O–H bend | carboxylic acids |
| 910–665 (s, b) | N–H wag | 1°, 2° amines |
| 900–675 (s) | C–H “oop” | aromatics |
| 850–550 (m) | C–Cl stretch | alkyl halides |
| 725–720 (m) | C–H rock | alkanes |
| 700–610 (b, s) | –C≡C–H: C–H bend | alkynes |
| 690–515 (m) | C–Br stretch | alkyl halides |

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Table B4: Characteristic Infrared Absorption Bands of Functional Groups

| Class of Compounds | Adsorption, $cm^{-1}$ | Intensity | Assignment |
|---|---|---|---|
| **Alkanes** & **Alkyls** | 2850-3000 | s | C-H, stretch |
| | 1450-1470 | s | C-H, bend |
| | 1370-1390 | m | $CH_3$C-H, bend |
| | 1365+1390 (two bands) | m | –CH($CH_3$) or –($CH_3$)$_3$, bend |
| | 715-725 | w | |
| **Alkenes** | 3020-3140 | w-m | =C-H, stretch |
| | 1640-1670 | w-m | C=C, stretch |
| $RCH=CH_2$ | 910+990 (two bands) | m+s | =C-H, stretch |
| $RR'C=CH_2$ | 885-895 | s | =C-H, bend |
| cis –RCH=CHR' | 665-730 | m-s, broad | =C-H, bend |
| trans-RCH=CHR' | 960-980 | s | =C-H, bend |
| RCH=CR'R" | 790-840 | s | =C-H, bend |
| **Alkynes** | | | |
| R-C≡C-H | 3265-3335 | s,sharp | ≡C-H, stretch |
| | 2100-2140 | m | C≡C, stretch |
| | 610-700 | s, broad | ≡C-H, bend |
| R-C≡C-R' | 2190-2260 | vw-w | C≡C, stretch |
| **Alkyl halides** | | | |
| R-F | 1000-1350 | vs | C-F, stretch |
| R-Cl | 750-850 | s | C-Cl, stretch |
| R-Br | 500-680 | s | C-Br, stretch |
| C-I | 200-500 | s | C-I, stretch |
| **Alcohols** | 3300-3400 | S, broad | O-H, stretch |
| $C=C-CH_2$-OH | 1035-1050 | m,s | C-O, stretch |
| $R-CH_2$-OH ($1^o$) or C=C-CH(R)-OH | 1050-1085 | m-s | C-O, stretch |
| RR'CH-OH($2^o$) or C=C-CRR'-OH | 1085-1125 | m-s | C-O, stretch |
| RR'R"C-OH($3^o$) | 1125-1205 | m-s | C-O, stretch |
| Ar-O-H | 1180-1260 | m-s | C-O, stretch |
| **Ethers** | | | |
| R-O-R' | 1085-1150 | s | C-O-C, stretch |
| Ar-O-R | 1020-1075 and 1200-1275 (two bands) | m-s | =C-O-C, symmetric & asymmetric, stretch |
| **Aldehydes** | 2700-2725 | m | H-C=O, stretch |
| R-CH=O | 1720-1740 | s | C=O |
| C=C-CH=O or Ar-CH=O | 1685-1710 | s | C=O, stretch |
| **Ketones** | | | |
| RR'-C=O | 1710-1720 | s | C=O, stretch |
| C=C-C(O)-R | 1665-1685 | s | C=O, stretch |
| Ar-C(O)-R | 1675-1695 | s | C=O, stretch |

| | | | |
|---|---|---|---|
| four member cyclic | 1770-1780 | s | C=O, stretch |
| five member cyclic | 1740-1755 | s | C=O, stretch |
| six member cyclic | 1710-1720 | s | C=O, stretch |
| **Carboxylic Acids** | 2500-3500 | s, broad | O–H, stretch |
| R-C(O)-OH | 1710-1715 | s, broad | C=O, stretch |
| C=C-C(O)-OH or Ar-C(O)-OH | 1680-1710 | s | C=O, stretch |
| **Esters** | aliphatic 1160-1210<br>acetic ~1240<br>aromatic 1250-1310 | s-vs | O=C-O-C, stretch |
| R-C(O)-O-R | 1735-1750 | s | C=O,stretch |
| C=C-C(O)-O-R or Ar-C(O)-O-Ar | 1715-1730 | s | C=O,stretch |
| R-C(O)-O-Ar | 1760-1790 | s | C=O,stretch |
| **Acyl Chlorides** | | | |
| R-C(O)-Cl | 1785-1815 | s | C=O,stretch |
| Ar-C(O)-Cl | 1770-1800 | s | C=O,stretch |
| **Anhydrides** | | | |
| R-C(O)-O-C(O)-R | ~1750+~1815 | s,s | CO, symmetric, stretch |
| Ar-C(O)-O-C(O)-R | ~1720+~1775 (both two bands) | s,s | C=O, asymmetric strech |
| **Nitiles** | | | |
| R-C≡N | 2240-2260 | m,s | C≡N, stretch |
| C=C-C≡N or Ar-C≡N | 2220-2240 | s | C≡N, stretch |
| **Amines** | | | |
| R-$NH_2$ | ~3400+~3500 (two bands) | w | N-H, symmetric & asymmetric stretch |
| | 1580-3350 | w-m | N-H, bend |
| RR'N-H | 3310-3350 | w | N-H, stretch |
| **Amides** | | | |
| R-C(O)-$NH_2$ | 3200-3400 and 3400-3500 | w-m | N-H, symmetric & asymmetric stretch |
| | 1650-1690 | s, broad | C=O, stretch |
| | 1590-1655 | m-s | N-H, bend |
| R-C(O)-NH-R | 3400-3500 | w-m | N-H, stretch |
| | 1640-1690 | s, broad | C=O, stretch |
| | 1510-1560 | m-s | N-H, bend |
| R-C(O)-NR'R" | 1630-1680 | m-s | C=O, stretch |
| **Nitro Compounds** | | | |
| R-$NO_2$ | ~1550 & 1370 | s | N-O, symmetric & asymmetric, stretch |
| C=C-$NO_2$ or Ar_$NO_2$ | 1525 and 1335 (both two bands) | s | N-O, symmetric and asymmetric, stretch |
| **Aromatic** | 3010-3100 | m | ArC-H, stretch |

| | | | |
|---|---|---|---|
| **Compounds** | 1450-1600 (two to four bands) | m-s sharp | ring C=C, stretch |
| monosubstituted | 735-770 | s | C-H, bend |
| | 690-710 (two bands) | s | C-H, bend |
| o-disubstituted | 735-770 | s | C-H, bend |
| m-disubstituted | 750-810 and | s | C-H, bend |
| | 690-710 | s | C-H, bend |
| P-disubstituted | 810-840 | s | C-H, bend |

**Intensity abbreviations:** vw=very weak, w=weak, m=medium, s=strong, vs=very strong