KINETICS AND OPTIMIZATION OF PHENOL UPTAKE FROM AQUEOUS SOLUTION USING AGRICULTURAL WASTES

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CERTIFICATION

This is to certify that Iheanacho, Chamberlain Ositadinma,NAU/2014217013P carried out this research work titled "*kinetics and optimization of phenol uptake from aqueous solution using agricultural wastes*" and that this work is original and has not been submitted anywhere before for award of any degree or diploma.

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APPROVAL PAGE

This research work was duly supervised and approved having met the requirement of the Department of Chemical Engineering, Faculty of Engineering, NnamdiAzikiwe University Awka, for the award of Doctor of Philosophy (PhD) in Chemical Engineering.

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DEDICATION

This work is dedicated to the one and only Almighty God who has been the source of my strength throughout this research work.

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ABSTRACT

The uptake of phenol from simulated aqueous solution using agricultural wastes as adsorbents is the focus of this research work. The agricultural wastes used were corn cob and rice husk which were modified with tetraoxophosphate V acid (H₃PO₄) and carbonized to give corn cob activated carbon (CCAC) and rice husk activated carbon (RHAC) respectively. The surface area of the adsorbents was determined using the Brunauer-Emmett-Teller (BET) nitrogen absorption method. Other physical properties of the adsorbents such as fixed carbon, bulk density, moisture content, volatile matter etc were determined using the method of Association of Analytical Chemistry (AOAC). Instrumental characterization was carried out using the Scanning electron microscopy (SEM) to examine the surface morphology and the Fourier Transform Infra-Red (FTIR) spectrophotometer to determine the functional groups present in the adsorbents. The effects of batch adsorption operational parameters such as contact time, initial phenol concentration, temperature, adsorbent dosage and pH on the phenol uptake were investigated. The adsorption equilibrium was evaluated by fitting the experimental data to nine linear isotherms and tennon linear isotherms. Nine linear and non linear kinetic models were employed in the kinetic study. Eight error terms were used to determine the significance of the errors associated with these models. Three mechanistic models were used to determine the adsorption mechanism. Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH), entropy change (ΔS) and the activation energy (E_a) were evaluated. The adsorption process was optimized using the response surface methodology (RSM) and the artificial neural network (ANN). Packed bed adsorption column was performed to determine the effects of influent concentration, flowrate, particle size and bed height. Seven kinetic models were employed in describing the kinetics of the continuous adsorption process. BET surface area of CCAC was 903.7 m²/s while that of RHAC was 417.7 m^2/s . Effects of operational parameters showed that the removal efficiency of phenol increased with increase in adsorbent dosage and contact time but decreased with temperature and initial phenol concentration. Adsorption kinetic process was best described by pseudo-second-order. The Langmuir and Flower-Guggenhein best fitted the adsorption equilibrium data. Mechanistic modeling showed that external mass transport mechanism was the rate controlling step. The ΔG ranged from -7.7 to -11.2 K/mol while ΔH ranged from 13.96 to 14.83KJ/molfor the adsorbents, suggesting that the adsorption process is spontaneous and endothermic respectively. The optimum conditions for the uptake of phenol for RHAC were dosage of 0.8g, contact time of 70.8 minutes, phenol concentration of 150 mg/l and temperature of 50 °C while for CCAC, the optimum conditions were dosage of 1.5g, temperature of 50 °C, contact time of 90 minutes and phenol concentration of 100 mg/l. This gave maximum adsorption efficiency of 92.6% and 93.5% for RHAC and CCAC respectively. Quadratic model best fitted the optimization process. ANN gave a good correlation of 0.9959 for validation of the optimum result with predicted maximum adsorption of 92.3% using CCAC and 93.4 for RHAC. Flowrate, influent phenol concentration and bed height affect the removal of phenol in the column adsorption. Wolborska and Clark kinetic models best described the column adsorption process. The study has shown that CCAC and RHAC can effectively be used as adsorbents in the uptake of phenol from aqueous solution.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

a	Elovich and power function constants
А	Temkin constant, l/g
$A_{\rm f}$	Frequency factor, min ⁻¹
b	Langmuir constants, l/mg.
Co	Initial concentration, mg/l
C _e	Equilibrium concentration, mg/l
Ct	Concentration at time t, mg/l
E	Mean free energy, KJ/mol
E _a	Activation energy, KJ/mol
K ₂	Second-order and Pseudo second-order kinetic constant
K _d	Intra-particle diffusion rate constant, mg/gmin ^{1/2}
K _B	Bhttacharya-Venkobachor rate constant
Μ	Total mass of the adsorbent, g
R _L	Dimensional separation factor.
K _f	Freundlich constants, l/g
K ₁	First-order and Pseudo first order kinetic constant
n	Freundlich constants
q	Adsorption capacity, mg/g.
q _e	Adsorption capacity at equilibruim, mg/g.
q _t	Adsorption capacity at time t, mg/g.
q _{max}	Maximum adsorption capacity
Qo	Langmuir constant, mg/g.
R	Universal gas constants, J/mol K
Т	Temperature, °C, K
q _D	Dubinin-Radushkevich constant, mg/g
q _m	Dubinin-Radushkevich monolayer capacity, mol/g
t	Time, min

Т	Temperature (k)
Ut	Fractional attainment of equilibrium
W	Weight of adsorbent
pHzpc	pH of zero point charge
ΔG	Free energy change, KJ/mol
ΔH	Free enthalpy change, KJ/mol
ΔS	Free entropy change, J/mol K
D ₂	Effective diffusion coefficients
β	Constant related to sorption energy, mol ²

Abbreviations

ANOVA	Analysis of variance
CCAC	Activated carbon prepared from corn cob
CCD	Central Composite Design
DOE	Design of experiment
HCl	Hydrochloric acid
H_2SO_4	Tetraoxosulphate VI acid
OFAT	One factor at a time
RHAC	Activated carbon prepared from rice husk
RSM	Response surface method
SEM	Scanning electron microscopy

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

When wastewaters are discharged directly or indirectly into water bodies without adequate treatment, they constitute water pollution. Most wastewater contains varying degrees of pollutants which makes it unsuitable for man and his environment. Pollutants are substances that are introduced in the environment in quantities that are beyond their minimum acceptable standard. Since the beginning of the industrial age, environmental pollution has been on the increase with its adverse effects on man and the environment. This has created a global concern in recent years (Afshin et al, 2010).

The wastewater that results from the industries is called industrial wastewater. Industrial wastewater represents the main source of water pollution. This is because they constitute a large chunk of the wastewater and usually contain substances in large proportions that make them harmful to man and the environment. Industrial wastewater is categorized according to its source. These are textile wastewater, pharmaceutical wastewater, refinery wastewater, paint wastewater etc.

Refinery wastewater consists of all the effluents from petroleum refining industries and other related industries. Petroleum wastewater constitutes one of the major sources of industrial wastewater in Nigeria. This is due to the exploration of huge and abundant crude oil and gas deposits in Nigeria (Nduka and Orisakwe, 2009). The refinery and petrochemical plants generate wastewater that is composed of heavy metals, organic and inorganic compounds (Suleimanov, 1995). Furthermore, the frequency of oil spill and untreated wastewater being discharged into water bodies is very high in Nigeria.

Refinery wastewater is very harmful because the substances that are contained in it when discharged into the water bodies cause serious danger to man, aquatic life, plants etc. Pollution from wastewater depreciates land values, increases municipal costs, escalates

conflicts between communities and causes numerous adverse biological and human health effects (Nwabanne and Igbokwe, 2012).

Phenols are common but dangerous pollutants that are associated with effluents of some industries such as petroleum, coal, paper, textile, petrochemicals, pharmaceuticals, and other phenol producing industries and plants, which are processing phenols to plastics. Phenol is one of the major pollutants in refinery wastewater. Many phenolic compounds have been classified as hazardous pollutants because of their potential toxicity to human health. It has a severe effect on human being, both short term and long term. Human consumption of phenol contaminated water can cause severe pain leading to damage of the capillaries, ultimately causing death. (Uddin, et al, 2007). Phenols are considered as one of the priority pollutants since they are harmful to organisms at low concentrations (Ahmaruzzaman, 2008). Phenol is a major pollutant in the wastewater because of its presence in the effluent of major processing and refining plants such as petrochemical industries, petroleum refineries, coal gasification operations, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. It is a highly corrosive and nerve poisoning agent. Phenol causes harmful side effects such as sour mouth, diarrhoea, impaired vision, excretion of dark urine. It is also toxic for fishes. The toxic levels usually range between the concentrations of 10-24 mg/l for human and the toxicity level for fish between 9-25 mg/l. Lethal blood concentration of phenol is around 150-mg/100 ml (Sunil and Jayant, 2013).

The technologies for treating the industrial wastewater are broadly classified into three: biological, chemical and physical methods (Robinson et al, 2001; Kayode and Olugbenga, 2015). Each of these methods has its inherent advantages and drawbacks. The considerations given in using each method include cost, efficiency, generation of toxic products, ability to re-generate the starting materials and the sludge volume generated (Ehssan and Yehia, 2012).

Adsorption is the most widely used and it is a highly efficient technique for treating industrial effluents (Al-Sultani and Al-Seroury, 2011; Salim, and Abdeslam, 2014). Adsorption has been preferred mainly because it is cost-effective and gives high quality treated effluents especially for well-designed adsorption process (Qadeer, 2007). In adsorption, the gas, liquid or solid adheres to the surface of a solid but does not penetrate it. The adsorbing phase is the adsorbent and the material adsorbed or concentrated at the surface of the phase is the adsorbate (Klaus, 2010). The efficiency of the adsorption process is mainly due to the characteristics of the adsorbent such as high surface area, high adsorption capacity, micro-porous structure and special surface reactivity (Al-Sultani and Al-Seroury, 2011).

The most commonly used adsorbent is activated carbon which has a high affinity for pollutants in wastewater mainly because of their high surface area, micro porous structure and a high degree of surface reactivity. Activated carbons are usually obtained from materials with high carbon content. The inherent nature of the precursor, as well as the method employed for carbon synthesis strongly, affects the final pore size distribution and the adsorption properties of the activated carbons. Commercial activated carbon is quite expensive hence there is extensive research on the preparation of activated carbon from several materials especially agricultural wastes.

Researchers have studied the production of activated carbon from agricultural biomass such as Palm tree cobs (Avom et al., 1997), plum kernels (Wu et al., 1999), cassava peel (Rajeshwarisivaraj, et al., 2001), jute fibre (Senthilkumaar, et al., 2005), rice husks (Yalein and Sevine, 2000), olive stones (El – sheikh and Newman, 2004), date pits (Girgis and El – Hendawy, 2002) fruit stones and nutshells (Aygun, et al., 2003). The merits of using agricultural biomass as raw materials for activated carbon production are that these raw materials are renewable and potentially less expensive to develop.

Corn cob and rice husk are waste products of agricultural processes in Nigeria. Corn cobs are the long rounded parts of the maize or corn plant on which small yellow seeds grow.

Rice husks are the hard protecting coverings of grains of rice. When the maize and rice grains are detached, the corn cob and the maize husks are usually thrown away as waste. Hence, corn cobs and rice husks running into millions of tons are dumped as waste annually. They are usually discarded and burnt or dumped as refuse. Sometimes, they even constitute environmental pollution. According to Amudalat and Ephraim (2004), Nigeria produces about 5.5 million tons of maize in 2004. This number is estimated to have grown up to 8.0 million tons in 2017. On the other hand, rice production in Nigeria was estimated at over 5.8 million tons in 2017 (Udemezue et al, 2018).

Adsorption process can be carried out in a batch or continuous process. The batch process is used mainly for treating a small amount of effluents such as domestic wastewater. The continuous process is usually applied for large scale industrial treatment of effluents. It is usually carried out in a packed-bed column. Some works have been reported on the use of batch adsorption process in the treatment of phenolic industrial effluent using some local wastes (Uddin et al, 2007; Ihsan, 2013; Salim and Abdeslam, 2014) but little has been reported on the use of packed-bed column in removing phenol from oil refinery wastewater. Equally, there is little or no available report on the comparison of the response surface methodology (RSM) and artificial neural network (ANN) in optimizing the uptake of phenol from aqueous solution. Hence, this present study focuses on evaluating the effectiveness of rice husks and corn cobs in the uptake of phenolic ions from simulated wastewater through batch and packed-bed adsorption processes.

1.2 Problem Statement

The impact of environmental degradation caused by the adverse effects of the oil refinery effluents cannot be over-emphasized. Refinery effluents contain phenol which is a dangerous pollutant. Phenols are considered as primary pollutants because they are harmful to man even at low concentration both in the short term and the long term. These effluents containing phenol, when discharged without adequate treatment cause severe harmful effects to man and the environment. Phenol wastewater are extremely toxic to aquatic life hence, the removal of phenol from wastewater before discharging is the crux of this work.

On the other hand, corn cob and rice husk are wastes generated from agricultural processes. These wastes, running into millions of tons are discarded and dumped indiscriminately constituting environmental pollution. Hence, the need to convert these wastes into useful products.

Most of the works on phenol removal from petroleum wastewater focused on linear isotherm and kinetic models, but this work will involve both linear and non linear models. The comparison of response surface methodology and artificial neural network in the uptake of phenol from wastewater using corn cob and rice husk has not received adequate attention. Most of the works on the adsorption of phenol focused on batch method of treatment. Equally, few column kinetic models have been investigated in phenol adsorption using packed bed. Furthermore, the regeneration of spent activated carbon in the treatment of phenol wastewater has not been widely reported. Therefore, this work will focus on the removal of phenol from stimulated wastewater using activated carbons produced from rice husks and corn cobs.

1.3 Aim and Objectives

This work is aimed at studying the kinetics and optimization of phenol uptake from aqueous solution using agricultural wastes.

The specific objectives of this research work include to:

- optimize the production of activated carbon from rice husk and corn cob using Response Surface Methodology and characterize the activated carbons produced using proximate analysis, SEM and FTIR
- ii. study the effects of process parameters such as temperature, dosage, concentration, time, dosage, and particle size on the efficiency of the adsorption
- iii. evaluate the adsorption isotherms, kinetics and thermodynamics of the adsorption process using linear and nonlinear models
- iv. optimize the adsorption process using Response Surface Methodology (RSM) and Artificial Neural Network (ANN)

v. carry out the column studies in a packed bed and determine the breakthrough curves and evaluate the kinetics of the column adsorption process using different column kinetics models

1.4 Significance of the study

Rice husks and corn cobs affect the environment negatively because most times they are disposed of indiscriminately in such a way that they constitute environmental pollution. Therefore, producing activated carbon from these agricultural wastes is an alternate method of waste reduction which equally complies the waste to wealth initiative of the federal government.

The discharge of untreated petroleum effluent into water-bodies has greatly impacted the domestic and economic values of such water-bodies. Petroleum effluent contains phenol which is a toxic pollutant that damages the human capillaries, causes diarrhoea, impaired vision, etc. Removal of phenol from petroleum wastewater before discharge will help to reduce the contamination of water-bodies.

The activated carbons are usually land filled or disposed off indiscriminately after use. This constitutes solid waste pollution on its own. Regeneration of the spent activated carbon for reuse will help to solve the problem of solid waste pollution.

1.5 Scope of the study

The scope of this research work includes the production of activated carbons from rice husk and corn cob and the adsorption of phenol using batch and packed bed adsorption processes. The research work also includes the linear and non linear isotherm and kinetics of the process and the regeneration of the spent activated carbon. The research work is limited to the optimization of the adsorption process using response surface methodology and artificial neural network.

CHAPTER TWO

LITERATURE REVIEW

2.1 Industrial effluent

Increase in technology has positively affected the life of man on earth, making life easier and enjoyable because technologies together with its industrialization are the bedrock of the modern age. But these industries also came with their own problems especially as regards pollution. Industrial wastewater is one of the important pollution sources in the pollution of the water environment. Until the mid 18th century, water pollution was essentially limited to small, localized areas. The emergence of the industrial revolution and the development of the various heavy industries resulted in the use of huge amount of fresh water as production raw materials and for cooling purposes. However, large amount of this industrial wastewater is constantly discharged into rivers, lakes and coastal areas. This usually results in a serious pollution problem in the aquatic environment and cause negative effects on the ecosystem and human life. Industrial discharge of this untreated or inadequately treated wastewater into the water bodies has become a major global concern (Amuda and Ibrahim, 2006).

This industrial wastewater contains harmful and toxic substances in the form of organic and inorganic substances. The inorganic substances are mainly in the form of heavy metals such as lead II ions (Pb^{2+}), Copper II ions (Cu^{2+}), chromium ions etc, while the organic pollutants include phenol, dyes, resorcinol etc. Heavy metals-polluted wastewater has posed a serious and complex problem because of its poisonous nature and its capacity to bio-accumulate to higher levels. They usually find their sources from industries such as electroplating industries, mining industries, paint industry, refinery etc. On the other hand, the inorganic pollutants in water bodies are considered critically dangerous because they are toxic even at low concentration and mostly do not undergo degradation (Agnieszka et al., 2011). They are undesirable because they are harmful, create odor and
unsightly colour, foaming etc (Sofia et al, 2005). There are many types of industrial effluent based on different industries and contaminants with each sector producing its own particular combination of pollutants. Because of these deadly effects, treatment of industrial effluent has become of great importance.

2.1.1 Refinery effluent

While the petroleum refinery and petrochemical industries are most desirable for national development and improved quality of life, the unwholesome and environmentally unacceptable pollution effects of the effluent from these industries generate reasons for worry. This is because, in the process of converting crude oil into petroleum products (liquefied petroleum gas, naphtha, kerosene, diesel oil and residual oil) and petrochemical products (polypropylene, polyethylene), wastes of different kinds are generated. The wastes can be broadly categorized into oily materials, spent chemicals, spent catalyst and other residuals. These wastes are released to the environment in the form of gases, particles, and liquid effluent (liquid consisting of surface runoff water, sanitary wastewater, solid waste and sludge). The wastewater released from the refineries is characterized by the presence of large quantity of crude oil products, polycyclic and aromatic hydrocarbon, phenols, metal derivatives, surface-active substances, sulfides, naphthalene acids and other chemicals (Suleimanov, 1995).

Kuehn et al (1995) observed that refinery effluent contaminated with aromatic hydrocarbons produces poor health and lethal toxicity in fishes and two species of tilapia. Onwumere and Oladimeji (1990) earlier demonstrated accumulation of heavy metals with accompanying histopathology in Oreochromisniloticus exposed to treated petroleum refinery effluent from the Kaduna refining and petrochemical company. These and other studies are in agreement that petroleum refinery effluents pose a serious problem to both aquatic and human life form.

Oil prospecting in Nigeria has brought with it untold hardship to the environment. Dwellers of oil producing areas generally suffer from scarcity of farmlands as their land has been made unproductive due to constant oil spillages and waste dump (FEPA, 1991). One of the most visible consequences of numerous oil spills had been the loss of mangrove trees. The mangrove was a source of both fuel for the indigenous people and a habitat for the area's biodiversity but is now unable to be sourced due to the oil toxicity of its habitat. Oil spills pose serious health risks to people when they consume contaminated seafood (Bogardy, 2004; Onuoha, 2007). Refinery effluent contains phenol and its derivatives.

2.1.2 Phenol

Phenol is an aromatic organic compound with the molecular formula C_6H_5OH . It is a white crystalline solid that is volatile. The phenol molecule consists of a phenyl group ($-C_6H_5$) bonded to a hydroxyl group (-OH). It is mildly acidic and requires careful handling due to its propensity for causing chemical burns.

Phenol was first extracted from coal tar, but today is produced on a large scale (about 7 billion kg/year) from petroleum. It is an important industrial commodity as a precursor to many materials and useful compounds. It is primarily used to synthesize plastics and related materials. Phenol and its chemical derivatives are essential for the production of polycarbonates, epoxies, Bakelite, nylon, detergents, herbicides such as phenoxy herbicides, and numerous pharmaceutical drugs

2.1.2.1 Structure and properties of phenol

The structure of phenol is that of a hydroxyl group bonded to an aromatic ring structure (benzene structure) as shown in figure 2.1.



Figure 2.1 Structure of phenol (Osei, 2015)

Phenol is an organic compound appreciably soluble in water, with about 84.2 g dissolving in 1000 mL (0.895 M). Homogeneous mixtures of phenol and water at phenol to water mass ratios of ~2.6 and higher are possible. Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenols occur either as colourless liquids or white solids at room temperature and may be highly toxic and caustic. Some other properties of phenol are given in Table 2.2

Chemical formula	C ₆ H ₆ O
Molar mass	94.113 g/mol
Appearance	Transparent crystalline solid
Odour	Sweet and tarry
Density	1.07 g/cm^3
Melting point	40 °C / 313.6 K
Boiling point	181.7 °C / 454.8K
Solubility in water	8.3g/100mL (20 °C)

Log P	1.48	
Vapour pressure	0.4 mmHg (20 °C)	
Acidity (pK _a)	9.95 (in water)	
	29.1 (in acetonitrile)	
Conjugate base	Phenoxide	
UV-vis (λ_{max})	270.75 nm	
Dipole moment	1.224D	

(Wikipedia, 2018)

Phenol is a toxic weak acid with an unpleasant taste and odour even at low concentrations in water. The major sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coal conversion, polymeric resin, petroleum and petrochemicals industries.

Phenols are considered as one of the priority pollutants in wastewater because they are harmful to organisms even at low concentrations (Bousba and Meniai, 2014). Many phenols have been classified as hazardous pollutants because of their potential toxicity to human health. Human consumption of phenol contaminated water can cause severe pain leading to damage of the capillaries ultimately causing death. Their presence in water supplies is noticed as bad taste and odor. In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste and which is quite pronounced and objectionable (Uddin et al, 2007).

2.1.3 Need for treated and safe industrial effluent

As a result of the ineffectiveness of purification systems, wastewater may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem (Beg et al, 2003; Aghalino and Eyinla, 2009). The uncontrolled discharge of contaminated industrial effluent into water bodies renders water unsafe for economic use, recreational use and poses a threat to human life and it is also against the ethics of principles of sustainable development. Water borne diseases and water caused health problems are mostly due to incompetent management of water resources. Safe water for all can only be assured when accessibility and sustainability quality can be guaranteed. Drinking contaminated water can cause various diseases such as typhoid fever, dysentery, cholera and other intestinal diseases (Adeyemi, 2004). According to Gore (1993), human beings are made up of water, in roughly the same percentage as water on the surface of the earth. Our tissues and membranes, brains, and hearts, our sweat and tears, all reflect the same recipe for life. Water is essential for the development and maintenance of the dynamics of every ramification of society. Water is indeed life and thus is the most important natural resource, without which life would be non-existent. Availability of safe and reliable source of water is an essential pre-requisite for sustained development (Asonye et al, 2007).

2.1.4 Methods of industrial effluent treatment

It is a known fact that the waste water from the industries must be treated before discharging it. Wastewater treatment involves using known technology to improve or upgrade the quality of wastewater. The principal objective of wastewater treatment is generally to allow industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment (Robinson, et al., 2001). Over the years, several methods have been used for this purpose of wastewater treatment. Each treatment methods offer varying cost-effectiveness, operational efficiency, availability of raw materials et.c. Wastewater treatment can be organized or categorized by the nature of the treatment process operation being used. The categories are biological, chemical and physical treatment methods.

2.1.4.1 Biological treatment method

Biological treatment involves the use of microorganisms, mostly bacteria, in the biochemical decomposition of wastewaters to stable end products. More microorganisms, or sludges, are formed and a portion of the waste is converted to carbon

dioxide, water and other end products. Treatment to control odors, to retard biological activity, or destroy pathogenic organisms may also be needed.Biological methods of removing waste water pollutants include biodegradation methods such as microbial degradation, fungal decolourization, absorption by living or dead microbial biomass, reverse osmosis, bioremediation and liquid membrane permeation (Sofia, et al, 2005).

Generally, biological treatment methods can be divided into aerobic and anaerobic methods, based on availability of dissolved oxygen. Aerobic treatment methods include; activated sludge treatment method, trickling filtration, oxidation ponds, lagoons and aerobic digestion while the anaerobic treatment methods are; anaerobic digestion, septic tanks and lagoons.

These methods are commonly applied to the treatment of industrial effluents because many micro organisms such as bacterial, yeasts, algae and fungi are able to accumulate and degrade different pollutants. Biological treatment is often the most economic alternative when compared to chemical and physical methods. However, their applications are often restricted because of technical constraints. It usually requires a long time to achieve great efficiency. Biological treatment requires a large land area and is constrained by sensitivity towards diurnal variation as well as the toxicity of chemicals which may be generated or released during the biological treatment process, and less flexibility in process design and operation (Sofia, et al., 2005). Further, biological treatment is incapable of obtaining satisfactory removal with current conventional biodegradation processes. Production of large sludge volume is an undesirable factor. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin (Robinson et al, 2001).

2.1.4.2 Chemical treatment method

This involves the treatment of industrial effluents using chemicals or chemical reactions so as to enhance the quality of the wastewater before discharge. The chemical methods employed in removing wastewater pollutants include electrochemical oxidation by an oxidizing agent, coagulation/flocculation, ozonation, precipitation (Afshin et al, 2012). Others are neutralization, solvent extraction, electrochemical processes, chlorination, ion exchange etc (Ehssan and Yehia, 2011).

Probably the most commonly used chemical process is chlorination (Afshin, et al., 2012). Chlorine, a strong oxidizing chemical, is used to kill bacteria and to slow down the rate of decomposition of the wastewater. The Bacterial kill is achieved when vital biological processes are affected by the chlorine. Another strong oxidizing agent that has also been used as an oxidizing disinfectant is ozone. Neutralization is a chemical process commonly used in many industrial wastewater treatment operations (Ehssan and Yehia, 2011). Neutralization consists of the addition of acid or base to adjust pH levels back to neutrality. Since lime is a base it is sometimes used in the neutralization of acid wastes. Coagulation consists of the addition of a chemical that, through a chemical reaction, forms an insoluble end product that serves to remove substances from the wastewater. Polyvalent metals are commonly used as coagulating chemicals in wastewater treatment and typical coagulants would include lime (that can also be used in neutralization), certain iron-containing compounds (such as ferric chloride or ferric sulfate) and alum aluminium sulfate) (Ehssan and Yehia, 2011). Processes such as ion exchange, which involves exchanging certain ions for others, are not used to any great extent in wastewater treatment (Afshin, et al., 2012).

These chemical techniques are often expensive, and although the pollutants are sufficiently removed, accumulation of concentrated sludge creates another problem— a disposal problem. There is also the possibility of a secondary pollution problem arising because of excessive chemicals used. Recently, other emerging techniques such as advanced oxidation processes which are based on the regeneration of powerful oxidizing agents such as hydroxyl radical have been applied with success for the pollutant degradation. Although these methods are more efficient for the treatment of waste water contaminated with pollutants, some of them are costly and commercially unattractive.

The high electrical energy demand and the consumption of chemical are common problems.

2.1.4.3 Physical treatment method

Treatment of wastewater using physical treatment methods involves using physical phenomena to improve or treat the wastewater with no chemical or biological changes.Examples of physical techniques mostly used in the treatment of wastewater effluents include nanofiltration, electrodialysis, membrane filtration, sedimentation, screening, aeration, flotation and skimming, degasification, equalization and adsorption technique.

In the process of sedimentation, physical phenomena relating to the settling of solids by gravity are allowed to operate (Ehssan and Yehia, 2011). Usually, this consists of simply holding wastewater for a short period of time in a tank under quiescent conditions, allowing the heavier solids to settle, and removing the "clarified" effluent. Sedimentation for solids separation is a very common operation and is routinely employed at the beginning and end of wastewater treatment operations. While sedimentation is one of the most common physical treatment processes that is used to achieve wastewater treatment, another physical treatment process consists of aeration which is the process of physically adding air, usually to provide oxygen to the wastewater. Still, another physical phenomenon used in wastewater treatment is the filtration. Here wastewater is passed through a filter medium to separate solids. An example would be the use of sand filters to further remove entrained solids from treated wastewater. Recently, emphasis has been shifted to the use of adsorption technique for the removal of pollutants from wastewater, hence making adsorption technique the most widely used for the removal of pollutants from wastewater (Ehssan and Yehia, 2011). Equally, certain processes may actually be physical and chemical in nature. The use of activated carbon to "adsorb" or remove organics, for example, involves both chemical and physical processes.

2.2 Adsorption

Generally, adsorption is the process that involves the transfer of mass of a fluid to the surface of an adsorbing solid. The molecules that diffuse from the bulk of the fluid to the surface of the solid adsorbents form a distinct adsorbed phase (Richardson and Harker, 2002). The fluid (either a gas or a liquid) that is transferred is called the Adsorbate while the solid that adsorbs them is called the Adsorbent. Adsorption is also a process by which fluid molecules become attached to a surface by physical or chemical forces or a combination of both (Salil et al, 2005). Although adsorption has been used as a physical-chemical process for many years, it is only in the last few decades that the process has developed to a stage where it is now a major industrial separation technique (Richardson and Harker, 2002).

Adsorption is now a well established, powerful and highly efficient technique for treating domestic and industrial effluents (Afshin et al, 2012). Adsorption techniques have gained acceptance recently due to their efficiency in the removal of pollutants too stable for conventional methods. Adsorption produces a high-quality product and is a process which is economically feasible. Adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available (Ozacar and Sengil, 2003). Furthermore, this process has the edge on the other method due to its sludge free clean operation and complete removal of the organic matter even from a dilute solution (Malik, 2003).

Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. Adsorption of atoms or molecules on a solid from a fluid takes place when the sorbed molecules or atoms are concentrated on the surface only. Thus, a substance contained in a fluid phase is said to be adsorbed on solid phase when its mass moves from the fluid phase to the surface of the solid adsorbing phase. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption occurs when molecules diffusing in the fluid phase are held for a period of time by forces emanating from an

adjacent surface (Richardson and Harker, 2002). Separation by adsorption depends on one component being more readily adsorbed than the other. Similar to Surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be it ionic, covalent or metallic) of the constituent atoms of the material are all filled. But atoms on the clean surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus, it is energetically favourable to them to be bond with whatever happens to be available. When molecules move from a bulk fluid to an adsorbed phase, they lose degrees of freedom and the free energy is reduced. Equilibrium adsorption occurs when the rate of adsorption of the fluid molecules unto the solid surface is equal to the rate of desorption of the fluid molecules from the solid surface. Adsorption is always accompanied by the liberation of heat (Richardson and Harker, 2002). Adsorption must not be confused with absorption as the two are different processes.

The driving force for adsorption is the reduction in inter-facial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid. The surface or interfacial tension is the change in free energy, G. resulting when the area between two phases, A, is increased.

2.2.2.1 Physical adsorption

This is also known as physisorption. Physical adsorption is a type of adsorption in which the adsorbate fluid (gas or liquid) adheres to the surface of the adsorbent and remain attached without any chemical bonding of any type. The mechanism of physisorption may be intermolecular, electrostatic or the weak Van der Waals intermolecular forces. These also depend on the physical configuration of the adsorbent such as the pore structure of the adsorbent.

Physical adsorption may be easily reversed since the forces are not strong (Richardson and Harker, 2002). Physical adsorption usually involves adsorbent with large surface areas. The properties of the surface of the adsorbent (pore size, polarity and spacing)

together serve to determine the quality of adsorption. The following parameters can have effects on physical adsorption: initial adsorbent concentration, adsorbent surface area, the adsorption temperature, adsorption contact time, and selection of the best adsorbent for the specific gas or liquid adsorption. The amount of heat involved in physical adsorption is similar in magnitude to the heat of condensation (Richardson and Harker, 2002).

2.2.2.2 Chemical adsorption

This is also known as Chemisorption. It is a type of adsorption where gaseous or liquid molecules adhere to the surface of the adsorbent by means of chemical reaction and the formation of chemical bond. These are chemical in nature involving the exchange of or sharing of electrons, or possibly molecules forming atom or radicals. It involves valence forces in which electrons are covalently shared or exchanged between sorbent and sorbate (Yuh-Shan, et al. 2001). Chemisorption is restricted to just one layer of molecules on the surface although it may be followed by additional layers of physically adsorbed molecules. It normally occurs at temperatures greater than 200⁰C when the activation energy is available to break and make chemical bonds. The heat released is about 10 to 100 Cal/gmol in chemisorptions, which is much higher than the heat released in physisorption. This heat released is of the order of magnitude normally associated with chemical reaction (Richardson and Harker, 2002). In chemisorptions, regeneration is very difficult if not impossible. Table 2.1 below shows a summary of the differences between physisorption and chemisorptions.

Parameter	Physical adsorption	Chemical adsorption
Adsorbent	All solids	Some solids
Adsorbate	All gasses below critical	Some chemical reactive
	temperature	gasses
Temperature range	Low temperature	Generally high

Table 2.1 Physical adsorption versus Chemical adsorption

		temperature
Heat adsorption	Low (ΔH cond.)	High order of heat
		reaction
Rate, activation	Very rapid, low E	Non activated, low
energy		activated, high E
Coverage	Multilayer possible	Monolayer
Reversibility	High reversibility	Often irreversible
Importance	For determination of surface area	For determination of
	and pore size	active centre, area and
		elucidation of surface
		reaction kinetics.

(Richardson and Harker, 2002)

2.2.3 Classes of adsorption

Adsorption process can be classified into two, depending on the type of the process used.

- 1) Batch Adsorption:
- 2) Column Adsorption:

2.2.3.1 Batch adsorption process

Majority of the works so far on adsorption has centred on batch adsorption because it is the earliest type that has been used. It works on the principles of batch operations where one system is loaded and the process is carried out completely before loading another one. In batch adsorption, equilibrium adsorption is attained when the rate of adsorption onto the adsorbent is equal to the rate of desorption from the adsorbent (Onu and Nwabanne, 2014).

2.2.3.2 Column adsorption process

This works on the principles of continuous operation. An example is the packed-bed adsorption. It is a flow process in which the column is packed with the adsorbent to a

certain height and the waste water is introduced from the top and allowed to flow down the column through the adsorbent in the column. In the process, some of the pollutants will be adhered to the surface of the adsorbent. Equilibrium is attained when the concentration of the effluent from the column is the same as the concentration of the influent into the column (Nwabanne and Igbokwe, 2012).

2.2.4 Factors affecting adsorption processes

There are many factors affecting adsorption and the effectiveness of the adsorption process depends on them. They include solubility of solute, degree of ionization, contact time, particle size, pH, concentration, dosage, etc

i. Solubility of solute (adsorbate) in liquid (wastewater):

Substances slightly soluble in water will be easily removed from water than substances with high solubility. Also, non-polar substances will be easily removed than polar substances since the latter have greater affinity for water.

ii. Degree of Ionization of the adsorbate molecule:

More highly ionized molecules are adsorbed to smaller degree than neutral molecules. This is because it takes greater amount of energy to separate the ions from their molecules

***** Contact time:

This is the adsorption time. That is, the duration the adsorbate and the adsorbent are mixed together. Sufficient contact time is required to reach adsorption equilibrium and to maximize adsorption efficiency. It was found out that as the contact time between the adsorbent and the adsorbate increases, the percentage removal of the adsorbate increases and also its residual concentration decreases. These happen until equilibrium adsorption is reached where further increase in time no longer has an effect on the percentage removal (Ehssan and Yehia, 2012).

iii. Particle size:

The size of the adsorbent particle also affects the adsorption capacity as it relates to the surface area. The smaller the particle size, the greater the surface area and this will result to increase in the adsorption capacity. Smaller particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained).

However, wastewater drop across columns packed with powdered material is too high to be used in packed beds. Large surface area is necessary to facilitate the adsorption process by providing adsorption sites on the appropriate channels to transport the adsorbate. In an ideal adsorption situation--where all other conditions (such as pore size, surface chemistry and adsorbent-adsorbate interactions) are optimal for contaminant removal- the surface area will serve as the limiting factor for the adsorption process. The smaller the particle size of the adsorbent for a given mass, the more surface area is available and as a consequence the greater the number of binding sites available, hence the greater the adsorption capacity (Yuh-Shan et al, 2001).

iv. pH

The initial pH of the adsorbate solution significantly affects the adsorption efficiency. The pH of the solution can be reduced by adding drops of an acid such as HCl, H_2SO_4 or it can be increased by adding drops of an alkali such as NaOH. The effect of pH affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species (Afshin et al, 2012). Most previous works showed that increase in the pH (from 2 upwards) of the adsorbate solution increases the adsorption efficiency until a pH of about 5-7 where it remains constant and in some cases, will start to decrease again. This may be because, at very low pH, the negative charges on the adsorbate ions; but as the pH is increased, the adsorbent surface becomes more negatively charged thereby supporting more adsorbate ion adsorption by electrostatic attraction due to columbic forces. At

higher pH of beyond 7, there is the formation of anionic hydroxides complexes which decreases the concentration of the adsorbate ions, thereby resulting in decrease of the adsorption capacities (Njoku et al, 2011; Djebbar et al, 2012; Afshin et al, 2012).

✤ Initial concentration:

This is the initial amount of the adsorbate in the solution and it has an effect on the amount of the adsorbate removed from the solution. An increase in the initial adsorbate concentration increases the adsorption capacity but not necessarily the adsorption efficiency. The increase is because of the increase in the concentration gradient which acts as a driving force for the adsorption process. But at high concentration, the active sites on the adsorbent become easily saturated and subsequent increase in the concentration does not affect the adsorption capacity. This is because the available sites of adsorption have become fewer (Njoku et al, 2011; Ehssan and Yehia, 2012).

v. Adsorbent dosage:

The amount or mass of the adsorbent has an effect on the adsorption capacity. This also relates to the adsorbent (solid)/adsorbate (liquid) ratio. Results show that as the amount of the adsorbent increases, the removal efficiency increases up to the optimum dosage beyond which the removal does not increase again. This may be because larger amounts of adsorbent mean more availability of large surface area or a larger number of adsorption sites, and therefore higher capacity for adsorption (Ehssan and Yehia, 2012; Omar, 2012; Afshin et al, 2012).

vi. Temperature:

From previous works, temperature has some effect on the adsorption capacity. Adsorption is normally carried out at room temperature or even below it. A low temperature favours the adsorption capacity while temperature will reduce the adsorption capacity. This is because an elevation temperature increases the escaping tendency of the adsorbate from the surface (Yuh-Shan et al, 2001).

vii. Solvent:

The solvent of the adsorbate has an important effect since it competes with the adsorbent surface in attracting the solute. Thus, adsorption of an organic solute out of an organic solvent is much less than its adsorption out of an aqueous solution. But in most cases of interest, the solvent would be water (Cooney, 1998).

viii. Surface area of adsorbent:

This is one of the main factors that determine the efficiency of the adsorption process. Larger surface area implies a greater adsorption capacity while lower surface area will imply a lower adsorption capacity.

ix. Number of carbon atoms.

For substances in the same homologous series a large number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption in gases in the sequence formic-aceticpropronic-butyric acid).

x. Size of molecules with respect to size of the pores:

Larger molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.

2.2.5 Adsorbent

An adsorbent is a material that is capable of the binding the collection of substances or particles on its surface without chemically altering them. It is a substance, usually porous that allows the molecules of a gas or liquid to adhere to its large surface area. Adsorbent absorbs molecules or gases and dissolves substances in a thin layer on the surface, as in the case of belt or disk. It is also a highly porous solid with the ability to concentrate and hold gases and vapours in contact with the solid. This includes moisture, as well as many other organic and inorganic molecules.

Adsorbents have been used for various processes such as filtration, adsorption, purification, deodorization, decolourization, and separation. The existing adsorbents used for adsorption includes; activated plantain peel ash (APPA), activated clay, activated carbon, saw dust, and so on.

2.2.5.1 Properties of adsorbents

The efficiency of the adsorption process depends mainly on the characteristics of the adsorbent (Al-Sultani and Al-Seroury, 2012). Adsorbents are available in irregular granules, extruded pellets and formed spheres. To be attractive commercially, an adsorbent should embody a number of features such as:

i) It should have a large surface area

ii) The area should be accessible through pores big enough to admit the molecules to be adsorbed. It is a bonus if the pores are also small enough to exclude molecules which it is desired not to adsorb.

iii) The adsorbent should be capable of being easily regenerated

iv) The adsorbent should not age rapidly, that is, not lose its adsorptive capacity through continual recycling.

v) The adsorbent should be mechanically strong enough to withstand the bulk handling and vibration that are a feature of any industrial unit (Richardson et al,2002).

vi) It should be cheap and readily available

vii) The adsorbent should have a microporous structure.

viii) The adsorbent should have special surface reactivity (Al-Sultani and Al-Seroury, 2012).

2.2.6 Corn cob and rice husk

Corn cob

Corn cobs are the long rounded parts of the maize or corn plant on which small yellow seeds grow (figure 2.2). It is the part of the ear on which the kernels/grains grow. A corncob, also called cob of corn, is the central core of an ear of corn. The ear is also considered a "cob" or "pole" but it is not fully a "pole" until the ear is shucked, or removed from the plant material around the ear. The innermost part of the cob is white and has a consistency similar to foam plastic.



Figure 2.2 Image of corn cobs

In recent times, corncobs find usage in the following applications:

- i. Industrial source of the chemical furfural
- ii. Fiber in fodder for ruminant livestock (despite low nutritional value)
- Water in which corncobs have been boiled contains thickeners and can be added to soup stock or made into traditional sweetened corncob jelly
- iv. Bedding for animals cobs absorb moisture and provide a compliant surface
- v. Ground up and washed (then re-dried) to make cat litter

- vi. A mild abrasive for cleaning building surfaces, when coarsely ground
- vii. Raw material for bowls of corncob pipes

viii. As a biofuel

- ix. Charcoal production
- x. Environmentally-friendly rodenticide (powdered corn cob)
- xi. Soil conditioner, water retainer in horticulture
- xii. Absorbent media for safe disposal of liquid and solid effluents
- xiii. Diluent/carrier/filler material in Animal health products, Agro-chemicals, Veterinary formulations, Vitamin premixes, Pharmaceuticals, etc.

xiv. Xylose - a sweetener

Tsai et al, (2007) even reported of an attempt in utilizing corn cob to produce activated carbon.

Rice husk

Rice husks are the hard protecting coverings of grains of rice (figure 2.3). It is the coating on a seed or grain of rice. The rice husk protects the seed during the growing season and is formed from hard materials, including opaline silica and lignin. The hull is hard to eat or swallow and mostly indigestible to humans because of its enriched fibre components. It is a major by-product of the rice milling and agro-based biomass industry. Rice husk is a cellulose-based fiber and contains approximately 20% silica in amorphous form. The ash of rice husk contains approximately 90% silica, which is a highly porous structure and is lightweight, with high specific surface area.



Figure 2.3 Image of rice husk

Though rice husk is agricultural waste, it has found useful applications such as:

- i. Industries use rice husk as fuel in boilers and for power generation.
- ii. Rice hulls can be put to use as a building material, fertilizer, insulation material, or fuel.
- iii. Rice hulk ash has been applied as an additive in many materials and applications, such as refractory brick,
- iv. manufacturing of insulation, and
- v. materials for flame retardants

In most parts of Nigeria, corn cobs and rice husks are not being utilized at all instead they are still considered as agricultural waste. Sometimes, because of improper disposal, they constitute pollutants to the environment.

2.2.7 Review of works on carbonization of rice husk and corn cob precursors

Arunrat and Sukjit (2014) reported on the preparation of activated carbon from Thailand rice husk. The aim of the research was to make value-added activated carbons of rice husk and to study the optimum conditions for gasoline adsorption using the rice husk activated carbon as adsorbents. The 20 g of rice husk samples were carbonized at 200 and 400 °C for 1 hr in a muffle furnace in order to produce charcoal. The sample was

crushed with blender and sieved to a size smaller than 850 μ m to obtain the charcoal of rice husk (CRH). The rice husk was subjected to impregnation in 1 dm³ of 3 M H₃PO₄ at 80 °C for 3 hr. After that, it was washed with distilled water until its pH value was 7. The sample was dried at 100 °C for 24 hr. The dried samples were carbonized at 450 and 700 °C for 2 hr in a muffle furnace. The charcoal was crushed and sieved to a size smaller than 850 μ m to obtain the activated carbon of rice husk (ACRH). The activated carbon produced from rice husk at a temperature of 450 °C, has the highest adsorption capacity. According to gasoline adsorption study, the optimum conditions were 0.1 g of activated carbon, 70 °C of adsorption temperature and 30 minutes of adsorption time. Physical characterization of the activated carbon obtained was performed by scanning electron microscopy (SEM). BET surface area was determined. The results present that the activated carbon of rice husk possesses a high apparent surface area (SBET = 336.35 m2/g). They thus encourage the use of activated carbon of rice husk as an adsorbent for the qualitative analysis of gasoline in order to apply for gasoline sampling in the arson case and to reduce the analysis cost from commercial adsorbent.

Esra (2015) reported on the production of low-cost activated carbon from rice husks by chemical activation using zinc chloride (ZnCl2) at 700 °C in N₂ atmosphere. Rice husk was milled to a particle size of around 1 mm. It was then washed thoroughly with distilled water and then dried in air at 100 °C in an oven for 24 h. 150 g of this air dried biomass was mixed in a beaker with varying concentrations of ZnCl₂ solution, which resulted in impregnation ratios of 1:1, 1:2, 1:3, 1:4 (weight of biomass to be impregnated / weight of reagent). The slurry was then dried in an oven at 105 °C. The impregnated sample was pyrolyzed in a stainless steel fixed bed reactor. The system was heated at a rate of 7 °C/min to 700 °C, and held at that temperature for 2 h. The reactor was continuously purged with nitrogen at a flow rate of 10 mL/min. After pyrolysis, the furnace was cooled down to room temperature in a nitrogen atmosphere. The sample was boiled with 200 mL of 10% HCl solution for 1 h, filtered and washed with hot water and finally cold water to remove the chloride ions and other inorganic contaminants.

Activated carbon samples were dried at 110 °C for 24 h and weighed. They were then characterized using Scanning electron microscopy (SEM) photos, X-ray diffractometer (XRD), Brunauer-Emmett-Teller (BET) surface analysis and Fourier transform infrared spectra (FTIR) methods. The BET surface area of the highest yield activated carbon was found to be 922.319 m²/g. Results showed that carbonization impregnation ratio hasa significant effect on the surface area and pore structure of the prepared activated carbon. The whole process can be summarized in the following steps; activation of the rice husk, carbonization, washing, preparing the RHC/Zn mixtures and characterization.

Hanum et al, (2017) evaluated the effects of carbonization time and temperature on activated carbon production from rice husk and its application for lead (Pb) adsorption in car battery wastewater. Rice husks were repeatedly washed using distilled water to remove existing impurities on the surface and dried in an oven at 110 °C for 3 hours. After that, 25 g dried rice husk was carbonized in the furnace at 400, 450, 500, 550, and 600 °C for 90, 120, and 150 minutes. Then, it was impregnated with hydrochloric acid 5% (v/v) at carbon to acid ratio of 1:10 (w/v) for 24 hours. Afterwards, it was filtered and oven dried at 110°C for 3 hours, followed by sieving to 100 meshes. The result indicated that the maximum carbon yield of 49.33% was obtained at carbonization temperature of 500 °C and carbonization time of 150 minutes. The activated carbon contained 4.86% moisture, 30.04% ash, and 15.76% volatile matter. The adsorption capacity was found to be 0.56731mg/g with percentage removal of 54.85%.

Korobochkin et al, (2016) reported on the production of activated carbon from rice husk from Delta of the Red River in Vietnam. At the first stage, carbonization of a rice husk was carried out to obtain material containing 43.1% carbon and 25 % silica with a specific surface area of 51.5 m²/g. The process of carbonization of a rice husk was carried out in the Flow Reactor with a volume capacity of 500 cm3 at 600 °C. Aprioristic information about the process was obtained by Differential Thermal Analysis. After separating of silica (the second stage), the specific surface area of the product increased to 204 m2/g and the silica content decreased to 1.23% by weight as well. The most important stage in the formation of the porous structure of the material is the activation. The products with the high specific surface area in the range of 800-1345 m2/g were obtained by activation of carbonized product with water vapour or carbon dioxide at temperatures of 700 °C and 850 °C, with varying the flow rate of the activating agent and activation time. The best results were achieved by activation of carbon material with water vapour at the flow rate of 0.08 dm3/min per 500 g of material and the temperature of 850 °C.

Khu et al, (2014) reported on the production of activated carbon derived from rice husk by NaOH activation and its application in supercapacitor. Firstly, the rice husks were washed with water to remove dirt and other contaminants, oven-dried at 110 °C for 12h, grounded and sieved to fractions with an average particle size of 1.0 mm. Then, the prepared husks were carbonized at 4001C under nitrogen flow (300 mL min1) for 90 min. The resulting samples were impregnated with NaOH (weight ratio 1/3) and dried at 120 °C for 12 h. Heating at 4001C for 20 min under nitrogen atmosphere at a flow rate of 300 mL/min was followed; thereafter the temperature was raised to the pre-determined temperatures (650-8001C) at a heating rate of 101 °C and maintained at the final temperature for 60 min to activate the obtained material. Finally, the activated product was grounded, neutralized by 0.1 M HCl solution and washed several times with hot distilled water to a constant pH (6.6-7.0). The washed activated carbon samples were dried under vacuum at 1201C for 24 h and stored in a desiccator. The specific surface area of the AC sample reached 2681 m^2/g under activation temperature of 8001C. The AC samples were then tested as electrode material; the specific capacitance of the asprepared activated carbon electrode was found to be 172.3 F/g using cyclic voltammetry at a scan rate of 5 mV s1and 198.4 F/g at current density 1000 mA/g in the charge/discharge mode.

Williams and Jennifer (2016) carried out a research that was aimed at the development of activated Carbons from Corn Cobs and the assessment of their efficiency for removing heavy metals like lead Pb, Cadmium Cd, mercury Hg, Arsenic. The Corn Cobs were

washed thoroughly, dried at 11[°]C in an oven till constant weigh was achieved. Pyrolysis - activation reactor was used at 900[°]C temperature. The Pyrolysis derived char kept at 900[°]C for 60 minutes and allowed to cool. The second step involved physical activation using steam as the activated agent at interval hours from 1hr, 2hr, 2.5hr ana d 3hrs at flow rate of 0.2mol/hlg. BET Method was used to determine the Specific surface area. Micropore Volume was determined using the DubininRadushkevich (DR) equation to the nitrogen adsorption Isotherms of the activated Carbons of each sample. The BET surface area of the activated Carbons ranged between 510.10m8/g ad 631.15m²/g for various durations ranging from 1hr to 3hr which are well within range reported in the literature from various precursors. Micropore volumes of the derived activated carbons ranging between 0.25-0.6 cm³/g were recorded. The metal ions in the waste water analyzed during this research were Pb²⁺, Cu²⁺, Cd²⁺ with initial concentrations 1.57, 1.87 and 0.69mg/L. The Pb²⁺ Concentration in solution decreased sharply and adsorbed up to 99.6% after 30minutes, 97.1% within 1hr, 98.6% at 3hr. The Cu²⁺ Concentration in solution 1.87mg/l to less than 0.03mg/L in 15min, attaining 98.4-99.0% adsorption. The Cd²⁺Concentration from the waste water at initial concentration 0.69mg/L decreased sharply in the first 15min, absorption of 99.7% was achieved after 45minutes.

Ketcha et al, (2012) reported on the preparation and characterization of activated carbons obtained from maize cobs by zinc chloride activation. The maize cobs were washed, dried in open air in order to remove residual water, crushed and sieved into different sizes of particles, one part of 1.25mm - 1.75mm, which is the soft part while the hard part is 1.75mm above in size. The soft sample was activated with 10% of zinc chloride Zncl₂ for 60minutes and 24hours respectively which the other part were activated with solid Zncl₂ (2g, 3g and1g respectively) for 60 minutes. The activated samples were weighed in desiccators and dried at a temperature of 120^{0} C for 24 hours. The activating agent was mixed with the matter by agitating for one hour to ensure access of Zncl₂ Carbonization was carried out using continuous steel pipe which can reach a temperature of 1200^{0} C, with a regulatory device of temperature at time (TC) the speed of heating was maintained

at a temperature of 10^{9} C/min. The duration of impregnation was maintained at 1hour and maximum temperature of 500^{9} C for all the samples washing with a solution of HCL 1% then Hot distilled water and finally, cold distilled water drying follows with oven $(120^{9}$ C). The resultant activated carbon samples of corn cobs were characterized using SEM analysis using field Emission Gun at 15-20KV, the detection unit was about 100% and the penetration 14m. Physical absorption was carried out using Nitrogen N₂ on the activated carbon surface. The pH of each sample was measured and found to be between 2 and 12.5. The results show that the cob used, the residence time, quantity and the state of the activating agent affected the activated carbon produced. the hard part showed the most significant properties with a BET surface area of 701.68m²/g and a porous volume of about 0.39cm³/g. On the other hand, samples obtained from the soft part of the cob gave low specified surface area (0.43-11.6²m²g/g) and pore volume (0.00028-0.11cm³/g). The experimental results indicated that this method of preparation shows that activated carbon is non-corrosive and can be used for purification of water.

Mohammad and Zamam (2016) prepared and utilized corn cob Activated Carbon for Dyes Removal from Aqueous Solutions. The Corn Cobs were cut/sieved to the size of 1mm, washed, dried for 2 hours at 110° C. It was then soaked with 0.85% solution of H₃PO₄ for 2hours. Heating of the soaked corncob took place for another 2hours in an oven at 400°C. The activated carbon was washed with distilled water until pH reached 6. Finally, the produced activated carbon was dried at110°C for two hours. The Activated Carbons so produced were used for the adsorption of methylene blue dye from aqueous solution. Batch processes were conducted to study the effects of solution pH, Contact time, adsorbent close, agitation speed and initial dye concentration. The optimum value for methylene blue dye adsorption was: solution pHs of 6 and 7, Contact times of 8 and 5hr, adsorbent dosage of 1.5, and 0.5g, agitation speed of 200 and 250rpm and initial dye concentration of 50mg/L. Two isotherm models, Freundlich and Langmuir fitted well with the experimental data found from batch processes with R² of 0.952 and 0.992. The maximum adsorption capacities of 16.12 and 30.95mg/g were obtained by commercial

activated carbon and corncob activated carbon respectively. The chemically activated corncob shows gold adsorption capacities in comparison with commercial activated carbon.

Nethaji et al, (2013) investigated the efficiency of activated carbon preparation from a precursor corn cob bio-mass, magnetized by magnetite nanoparticles (MCC AC) and used for the adsorption of hexavalent chromium from aqueous solution. The adsorbent was characterized by SEM, TEM, XRD, VSM and zero point charge. The iron oxide nanoparticles were of 50mm sizes and the saturation magnetization value for the adsorbent was 48.43 emu/g. Adsorption was maximum at pH of 2. Isotherm data were modeled using Langmuir, Freundlich and Temkin isotherm. The prepared MCCAC had a heterogeneous surface. The maximum monolayer adsorption capacity was 57.37 mg/g. Kinetic studies were carried out and the data fitted the pseudo-second order equation. The mechanism of the adsorption process was studied by incorporating the kinetic data with intra-particles diffusion model, Bangham equation and Boyd plot. The adsorption was by chemisorptions and the basic column parameters were estimated.

Shuxioing et al, (2016) reported on the preparation of activated carbon from corn cob and its adsorption behaviour Cr (VI). Optimization was carried out on the preparation of activated carbons from corn cob. The Cr(VI) adsorption capacity of the produced activated carbons was also evaluated. The impact of adsorbent dosage, contact time, initial solution pH and temperature were studied. The results showed that the produced corn activated carbon had a good Cr(VI) adsorptive capacity. The theoretical maximum adsorption was 34.48mg g⁻¹ at 298k. The Brunnet-Emmet-Teller surface area and iodine adsorption value of the produced activated carbon were 924.9m²/g and 1,188mg/g respectively. Under an initial Cr(VI) concentration of 10mg/L and original solution pH of 5.8, an adsorption equilibrium was reached after 4hr, with the Cr(VI) removal efficiency ranging from 78.9 to 100% as the adsorbent's dosage increased from 0.5 to

0.7g/L. The kinetic and equilibrium data agreed well with the Langmuir Isotherm model. The equilibrium adsorption capacity improved with increment of the temperature.

2.3 Adsorption equilibrium/isotherms and error functions

The adsorption isotherm is a relationship between the amount of a substance removed from liquid phase by unit mass of adsorbent and its concentration at a constant temperature. It shows how the quantities of molecules are distributed between the liquid and solid phase when the adsorption process must have reached equilibrium. It is equally used to suggest the maximum adsorption capacity of the adsorbate onto the surface of the adsorbents and is usually expressed in terms of quantity adsorbed per unit mass of adsorbent (mg/g).

Upon contacting an amount of adsorbent with an adsorbate, some molecules of the adsorbate will stick to the surface of the adsorbent while others rebound. The initial high rate of this adsorption will decrease gradually as more and more surface of the adsorbent becomes covered by the molecules of the adsorbent and the available bare surface decreases. However, the rate of desorption, which is the rate at which adsorbed molecules rebound from the surface increases because desorption takes place from the covered surface.

At a time, the rate of adsorption becomes equal to the rate of desorption. At that time, equilibrium is said to have been reached because no further relative adsorption takes place even as the time increases. The rate of adsorption is equal to the rate of desorption (Bansal and Goyal, 2005). At equilibrium, a relationship exists between the concentration of the species on solution and the "concentration" of the same species in the adsorbed state (i.e., the amount of species adsorbed per unit mass of adsorbent q_e).

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants (Uddin et al, 2017).

2.3.1 Development of adsorption isotherm

Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb on to a surface is equal to the rate at which they adsorb from the surface ((Richardson and Harker, 2002)). The capacity of an adsorbent for a particular adsorbate involves the interaction of three properties – the concentration C of the adsorbate in the fluid phase, the concentration Cs of the adsorbate in the solid phase and the temperature T of the system. If one of these properties is kept constant, the other two may be graphed to represent the equilibrium. Therefore, the quality of adsorbate that can be taken up by an adsorbent is a function of both characteristics and concentration of adsorbate and the temperature. Adsorption isotherm refers to the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature (Metcalf and Eddy, 2003). Generally, the amount of material adsorbed is a function of the initial concentration at a constant temperature, and the resulting function is called an adsorption isotherm.

Therefore, the adsorption equilibrium relationship at a given temperature is typically referred to as adsorption isotherm in equation 2.1:

$$\mathbf{q} = \mathbf{f} \left(\mathbf{C} \right) \tag{2.1}$$

where:

q = mass of species adsorbed/mass adsorbent (i.e., equilibrium concentrationadsorbable species in solid adsorbent).

C = equilibrium concentration of adsorbable species in soluble.

The amount of adsorbate adsorbed by the adsorbent after equilibrium is given by equation 2.2 (Djebber, et al, 2012)

$$q = \frac{(C_i - C_e)V}{m}$$
(2.2)

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Where q = amount of phenol adsorbed by adsorbent, mg/g, $C_i = initial$ liquid phase concentration of adsorbate, mg/l, $C_e = equilibrium$ liquid phase concentration of adsorbate, mg/l, v = initial volume of the absorbate solution, and m = mass of the adsorbent, g

The percentage adsorption (%) is given by equation 2.3

Percent adsorbed
$$\% = \left(\frac{C_i - C_e}{C_i}\right) X \ 100$$
 (2.3)

Where

 C_i = initial concentration of absorbate, and C_e = equilibrium concentration at any time t

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its concentration at a constant temperature. The quality adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Some of the equation used to describe adsorption isotherm were those of Halsay, Freundlich, Langmuir, Harkins-Jura, Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, Flory-Huggins, Kiselev isotherm models, etc.

2.3.2 Langmuir isotherm model

The Langmuir isotherm is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions (Njoku, et al., 2011):

- i. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
- ii. Adsorbed molecules do not interact.
- iii. All adsorption occurs through the same mechanism.
- iv. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

These four assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last. The fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the Brunauer-Emmett-Teller (BET) isotherm for relatively flat (non-microporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics and thermodynamics. Langmuir suggested that adsorption takes place through this mechanism:

$$\mathbf{A}_{\mathbf{l}} + \mathbf{S} \rightleftharpoons \mathbf{A} \tag{2.4}$$

Where A is an adsorbate molecule and S is an adsorption site. The direct and inverse rate constants are k_1 and k_{-1} . If we define surface coverage $\boldsymbol{\theta}$, as the fraction of the adsorption sites occupied in the equilibrium, we have

$$\mathbf{\theta} = \frac{\mathbf{K}\mathbf{C}_{\mathbf{e}}}{1 + \mathbf{K}\mathbf{C}_{\mathbf{e}}} \tag{2.5}$$

Where C_e is the equilibrium concentration of the solution.

For very low concentrations, $\theta \approx KC_e$ and for high concentrations, $\theta \approx 1$. If q_{max} is the maximum adsorption needed for complete monolayer coverage of available adsorption sites, then

$$\theta = \frac{q_e}{q_m} \tag{2.6}$$

Combing the two equations gives the nonlinear Langmuir model in equation 2.8 (Njoku et al, 2011)

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2.7}$$

Where K_L is the Langmuir constant equivalent to the equilibrium constant at a given temperature. q_{max} is related to the number of adsorption sites, q_e is the amount adsorbed in

mg/g. If we assume that the number of sites is just the whole area of the solid divided into the cross section of the adsorbate molecules, we can easily calculate the surface area of the adsorbent. The surface area of an adsorbent depends on its structure; the more pores it has, the greater the surface area, which has a big influence on reactions on surfaces. The linear form of the Langmuir isotherm is given in equation 2.8

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \left(\frac{1}{q_m}\right) C_e \tag{2.8}$$

where

 q_e = equilibrium amount of solute adsorbed per unit weight of adsorbent in (mg/g)

 C_e = equilibrium concentration in aqueous phase (mg/l)

 q_m = maximum adsorbed per unit mass of adsorbent (mg/g)

 K_L = Langmuir constant related to the affinity of the binding sites and energy of adsorption in (l/mg).

A linear plot of C_e/q_e against C_e can be used to evaluate q_m from the slope and then evaluate K_L from intercept (Djebbar et al, 2012).The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor, R_L defined by equation 2.9

$$R_L = \frac{1}{1 + K_L C_o}$$
(2.9)

Where,

C_o is the highest initial solute concentration (mg/L), K_L is the Langmuir constant.

The value of R_L indicates whether the adsorption isotherm is unfavourable ($R_L > 1$),

linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.3.3 Freundlich Isotherm model

1.

The Freundlich isotherm involves an adsorption isotherm that gives an expression describing surface heterogeneity and the exponential distribution of active sites and energies. It is a brief empirical equation often used to represent adsorption data. It does not predict any saturation of adsorbent by the adsorbate. Thus, infinite surface coverage predicted mathematically, indicating multilayer adsorption on the surface (Njoku et al, 2011). The Freundlich isotherm describes physical adsorption from liquids.

The empirical Freundlich isotherm in its nonlinear form is given in equation 2.10

$$q_e = K_F C_e^{1/n}$$
 (2.10)

Taking the natural logarithm of both sides, the Freundlich isotherm can be linearized as given in equation 2.11

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2.11}$$

where

 q_e = the amount adsorbed at equilibrium (mg/g)

 C_e = the equilibrium concentration of the adsorbate (mg/l)

K_f=Freundlich adsorption intensity capacity factor

1/n = Freundlich adsorption intensity factor

Hence, the Freundlich isotherm can be investigated by plotting lnq_e and lnC_e . The value of K_fand 1/n can be from the intercept and the slope respectively (Djebbar, et al, 2011). K_fand 1/n are constants related to the adsorbent as defined above. K_f is sensitive to temperature while n is a constant characteristic of the adsorption system under study (Njoku, et al, 2011).

The exponent 1/n is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent. When 1/n <1, the isotherm is concave and adsorbates are bound with weaker and weaker free energies. On the other hand, when 1/n >1, the isotherm is convex and more adsorbate presence in the adsorbent enhance the free energies of further adsorption.

Results showed that the numerical values of n (between 2 and 10) indicate that the adsorption capacity was only slightly suppressed at lower equilibrium concentration (Njoku et al, 2011). The good fit of Freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed and there is a multilayer adsorption (Abasi, et al., 2011).

2.3.3.1 Comparison between Langmuir Isotherm and Freundlich Isotherm.

- i. The Langmuir isotherm has a theoretical justification while the Freundlich isotherm represents an empirical model.
- ii. The Langmuir isotherm assumes reversible adsorption and desorption of the adsorbate molecules. No assumption is made for the Freundlich isotherm.
- iii. The Langmuir isotherm typically represents well data for single components. The Freundlich isotherm can be used also for mixtures of compounds.

2.3.4 Halsay Isotherm model

The Halsey isotherm was proposed based on the assumption that the multilayer adsorption is at a relatively large distance from the surface (Vicente et al, 2011; Soheila and Hasan 2017;).

The nonlinear Halsay adsorption isotherm is given in equation 2.11

$$q_e = \exp\left(\frac{\ln K_H - \ln C_e}{n_H}\right) \tag{2.11}$$

Taking the natural logarithm and linearizing the equation gives the linear Halsay isotherm model as in equation 2.12

$$\ln q_{e} = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_{e}}{n_{Ha}}$$
(2.12)

Where K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants.

2.3.5 Harkins-Jura Isotherm model

Harkin-Jura isotherm model equally assumes the possibility of multilayer adsorption on the surface of absorbents having heterogeneous pore distribution (Nimibofa et al, 2017).

The Harkins-Jura adsorption isotherm can be expressed as (Itodo and Itodo, 2010):

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \tag{2.13}$$

The linear form of the Harkins-Jura isotherm model is given by equation 2.14

$$\frac{1}{q_{e}^{2}} = \frac{B_{H}}{A_{H}} - \frac{1}{A_{H}} \log C_{e}$$
(2.14)

Where A_H (g²/L) and B_H (mg²/L) are two parameters characterizing the adsorption equilibrium.

2.3.6 Temkin Isotherm model

The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather logarithmic as stated by Freundlich (Sivakumar and Palanisamy, 2009). It involves a study of the heat of adsorption and the adsorbent-adsorbate interaction.

The general form of the Temkin isotherm is given in equation 2.15

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \tag{2.15}$$

Linearizing the Temkin isotherm gives equation 2.16

$$q_e = \left(\frac{RT}{b}\right) \ln A + \left(\frac{RT}{b}\right) \ln C_e \tag{2.16}$$

Hence, plotting q_e against lnC_e enables the constants b and A to be determined and RT/b = B which is the heat of adsorption.

2.3.7 Dubinin-Radushkevich Isotherm model

Not only that the Dubinin-Radushkevich isotherm is based on physical parameters and has easy applications but, much importantly, it includes temperature effects and quite fairly predicts the experimental data over a wide concentration range (Inglezakis and Poulopoulos, 2006).

The general form of Dubinin-Radushkevich isotherm equation is in equation 2.17

$$q_e = q_m \exp(-B\epsilon^2)$$
(2.17)

Linearizing the Dubinin-Radushkevich equation gives equation 2.18

$$\ln q_e = \ln q_m - B\epsilon^2 \tag{2.18}$$

where

 β is a constant related to the sorption energy

 q_m is the Dubinin-Radushkevich monolayer capacity (mmol/g) and

 ε is the Polanyi potential which is related to the equilibrium Concentration (Sivakumar and Palanisamy, 2009) and is given by equation 2.19

$$\varepsilon = \operatorname{RT}\ln(1 + (\frac{1}{C_e})) \tag{2.19}$$

Where,

R is the gas constant = 8.314 J/mol K

T is the absolute temperature (K)

The constant β gives the mean free energy E, of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship in equation 2.20 (Lin and Juang, 2002).

$$E = \frac{1}{(2\beta)^{\frac{1}{2}}}$$
(2.20)

2.3.8 Fowler-Guggenheim isotherm model

The linear form of the Fowler-Guggenheim isotherm model is given by Soheila and Hasan (2017) and Sampranpiboon et al (2014) in equation 2.21

$$\ln\left[\frac{C_{e}(1-\Theta)}{\Theta}\right] = -\ln K_{FG} + \frac{2w\Theta}{RT}$$
(2.21)

where K_{GF} is the Fowler-Guggenheim equilibrium constant (L mg⁻¹); $\theta = (1-C_e/C_o)$ is the degree of surface coverage; W is the interaction energy between adsorbed molecules (kJ mol⁻¹); R is the universal gas constant and is equal to 8.314 J mol⁻¹ K⁻¹, and T is the absolute temperature (K)

2.3.9 Flory-Huggins isotherm model

The Flory-Huggins isotherm equation is given by equation 2.22

$$\ln\left(\frac{\Theta}{C_{o}}\right) = \ln K_{FH} + n_{FH} \ln (\theta - \Theta)$$
(2.22)

Where Θ is degree of surface coverage, C_o is initial concentration, n_{FH} and K_{FH} are Flory-Huggins isotherm constants describing number of adsorbates occupying adsorption sites (model exponent) and the equilibrium constant (Lmol⁻¹) respectively (Nimibofa et al, 2017; Foo and Hameed, 2010).

2.3.10 Kiselev adsorption isotherm model

The Kiselev adsorption isotherm equation is expressed as in equation 2.23
$$\frac{1}{C_{e}(1-\Theta)} = \frac{1}{\Theta}K_{1} + K_{1}K_{n}$$
(2.23)

where K_1 is Kiselev equilibrium constant (Lmg-1) and K_n is equilibrium constant of the formationa of a complex between adsorbed molecules (Nimibofa et al, 2017)

2.3.11 Non linear isotherm models

Accuracy of an isotherm model is generally a function of the number of independent parameters, while its popularity in relation to the process application is an indicative of its mathematical simplicity (Malek and Farooq, 1996). Undoubtedly, linear regression analysis has frequently been employed in accessing the quality of fits and adsorption performance, primarily owing to its wide usefulness in a variety of adsorption data and partly reflecting the appealing simplicity of its equations. However, during the last few years, a development interest in the utilization of nonlinear optimization modeling has been noted (Prasad and Srivastava, 2009). These researches have advocated for investigating the applicability of linear or nonlinear isotherm models in describing the adsorption of dyes, heavy metals and organic pollutants onto activated carbons, zeolites, chitosans, bentonites, montmorillonites, kaolinites and a list of low-cost adsorbents.

The linearized equations apparently generate real problems and errors arising from the complexities and complications for simultaneous transformation of data, leading to the violation of theories behind the isotherms. Moreover, linear analysis method assumes that the scatter vertical points around the line follows a Gaussian distribution, and the error distribution is uniform at every value of the liquid-phase residual concentration (X-axis) (Kumar and Sivanesan, 2006).Nonetheless, such behavior is practically impossible with the equilibrium relationships (since isotherm models had a nonlinear shape) as the error distribution tends to get altered after transforming into a linearized order.

In another study, linearized isotherms models (Langmuir and Freundlich isotherm models) have been found inappropriate in predicting the goodness of fit for a particular set of conditions (Mane et al, 2007) and unable for provide a fundamental understanding

of the adsorption systems, resulting in an improper conclusion. On the contrary, the nonlinear isotherm models are conducted on the same abscissa and ordinate, thus avoiding such drawbacks of linearization. This has led to the utilization of nonlinearized models in conjunction with a number of error analysis techniques (Han et al, 2007; Kumar and Sivanesan, 2007).

Nevertheless, a few researchers (Mane, et al, 2007; Han, et al, 2009; Ofomaja and Ho, 2008) also indicated the similarities and consistency of both linear and nonlinear isotherms, lying into the same error distributions and structures. Under such conditions, it would be more rational and reliable to interpret adsorption data through a process of linear and nonlinear regressions which should represent efficient and complete isotherm models.

2.3.12 Multi-parametric isotherm models

These isotherm models involve more than two parameters.

2.3.12.1 Redlich-Peterson Isotherm model

This isotherm model is an empirical isotherm incorporating three parameters (A, B and β). It combines elements from both Langmuir and Freundlich equations; therefore the mechanism of adsorption is a mix and does not follow ideal monolayer adsorption (Brouers and Al-Musawi, 2015).

This model is defined by the following expression in equation (2.24)

$$q_e = \frac{AC_e}{1+BC_e^{\beta}} \tag{2.24}$$

where *A* is Redlich-Peterson isotherm constant (Lg-1), *B* is constant (Lmg-1), β is exponent that lies between 0 and 1, *Ce* is equilibrium liquid-phase concentration of the adsorbent (mgl-1), and *qe* is equilibrium adsorbate loading on the adsorbent (mg g-1).

2.3.12.2 Radke-Prausniiz Isotherm model

The isotherm is given by the following expression in equation (2.25)

$$q_e = \frac{q_{RP} K_{RP} C_e}{(1 + K_{RP} C_e)^m}$$
(2.25)

Where q_{RP} is Radke-Prausnitz maximum adsorption capacity (mg g-1), K_{RP} is Radke-Prausnitz equilibrium constant, and m isRadke-Prausnitz model exponent.

This model isotherm gives a good fit over a wide range of adsorbate concentration. Also, at high adsorbate concentration, this isotherm model reduces to Freundlich isotherm (Al-Jlil and Latif, 2013).

2.3.12.3 Sips Isotherm model

Sips isotherm is a combination of the Langmuir and Freundlich isotherms and it is given by the following general expression in equation 2.26 (Jeppu and Clement, 2012):

$$q_e = \frac{K_s C_e^{\beta s}}{1 - a_s C_e^{\beta s}} \tag{2.26}$$

Where *Ks* is Sips isotherm model constant (Lg–1), βs is Sips isotherm exponent, and a_s is the monolayer adsorption capacity of the composite (mg/g)

2.3.12.4 Toth Isotherm model

This isotherm model has been applied for the modeling of several multilayers and heterogeneous adsorption systems (Benzaoui et al, 2017).

The Toth isotherm model is expressed as given in equation (2.27)

$$q_e = \frac{q_{m K_T C_e}}{\left[1 + (K_T C_e)^n\right]^{1/n}}$$
(2.27)

where q_m is the Toth's maximum adsorption capacity, K_L is Toth isotherm constant (mg/g) and *n* is Toth isotherm exponent (mg g-1).

The values of parameters of the Toth model can be evaluated by nonlinear curve fitting method.

2.3.12.5 Kahn Isotherm model

This isotherm model is expressed as follows in equation 2.28 (Amrhar et al, 2015)

$$q_e = \frac{q_{\rm m \ b_k \ c_e}}{(1+b_k \ c_e)^{a_k}} \tag{2.28}$$

where a_k is Kahn isotherm model exponent, bk is Khan isotherm model constant, and q_m is Khan isotherm maximum adsorption capacity (mg/g).

Nonlinear methods have been applied by several researchers to obtain the Khan isotherm model parameters (Varank et al, 2011).

2.3.12.6 Koble-Carrigan Isotherm model

Koble-Carrigan isotherm model is a three-parameter equation which incorporates both Langmuir and Freundlich isotherms for representing equilibrium adsorption data (Alahmadi et al, 2014).

This isotherm model is expressed in equation 2.29

$$q_e = \frac{A_{kc} C_e^{p} B_{kc}}{1 + B_{kc} C_e^{p}}$$
(2.29)

where A_{kc} is Koble-Carrigan's isotherm constant, Bk is also Koble-Carrigan's isotherm constant, and p is Koble-Carrigan's isotherm exponent. All three Koble-Carrigan isotherm constants can be evaluated with the use of a solver add-in function of the Microsoft Excel (Khan et al, 1997).

2.3.12.7 Fritz-Schlunder Isotherm model

Fritz and Schlunder derived an empirical equation which can fit a wide range of experimental results because of the large number of coefficients in the isotherm (Yeneva et al, 2013).

This isotherm model has the following equation in equation 2.30

$$q_e = \frac{q_F K_F C_e}{1 + q_m C_e^m} \tag{2.30}$$

where q_F is Fritz-Schlunder adsorption capacity (mg g-1), K_F is Fritz-Schlunder equilibrium constant (mg g-1), q_m is equilibrium maximum adsorption capacity and m is Fritz-Schlunder model exponent.Nimibofa et al, (2017) reported that the Fritz-Schlunder isotherm parameters can be determined by nonlinear regression analysis.

2.3.12.8 Baudu isotherm model

Baudu isotherm model was developed mainly due to the discrepancy in calculating Langmuir constant and coefficient from slope over a broad range of concentrations. Baudu isotherm model is the transformed form of the Langmuir isotherm (Ramsenthil and Dhanasekaran, 2018). It is given by equation 2.31

$$q_e = \frac{q_m b \, C_e^{1+x+y}}{1+b \, C_e^{1+x}} \tag{2.31}$$

where q_m is Baudu maximum adsorption capacity (mg/g), b is equilibrium constant, x is Baudu parametric constant, and y is also Baudu parametric constant.

Due to the inherent bias resulting from linearization, the Baudu isotherm parameters are determined by nonlinear regression analysis (Hamdaoui and Naffrechoux, 2007; Van-Vilt et al, 1980).

2.3.12.9 Marczewski-Jaroniec Isotherm model

The Marczewski-Jaroniec isotherm is also known as the four-parameter general Langmuir equation. It is the resemblance of Langmuir isotherm model and was recommended on the basis of the supposition of local Langmuir isotherm and adsorption energies distribution in the active sites on adsorbent (Ramsenthil and Dhanasekaran, 2018).

The isotherm equation is expressed as given in equation 2.32:

$$q_e = q_m \left[\frac{(KC_e)^n}{1 + (KC_e)^n} \right]^{m/n}$$
(2.32)

Where q_m is Marczewski-Jaroniec maximum adsorption capacity (mg/g), K is Marczewski-Jaroniec constant, n and m are parameters that characterize the heterogeneity of the adsorbent surface with m describing the spreading of distribution in the path of higher adsorption energy, and n describing the spreading in the path of lesser adsorption energies.

2.3.12.10 Fritz-Schlunder-V isotherm model

Fritz and Schlunder developed a five-parameter empirical model that is capable of simulating the model variations more precisely for application over a wide range of equilibrium data.

The isotherm equation is expressed in equation 2.33

$$q_e = \frac{q_m K_1 C_e^{\alpha}}{1 + K_2 C_e^{\beta}} \tag{2.33}$$

where q_m is Fritz-Schlunder maximum adsorption capacity (mg g-1) and K₁, K₂, are Fritz-Schlunder parametric constants, α and β are Fritz-Schlunder exponents (Nimibofa et al, 2017).

2.3.13 Error analysis functions

Different error analyses were employed in the nonlinear studies of both isotherm and kinetic models. Studies have shown that the error structure of experimental data is usually changed during the transformation of adsorption models into their linearized forms (Kumar, 2006). It is against this backdrop that nonlinearized regression analysis became inevitable since it provides a mathematically rigorous method for determining adsorption parameters ustheingthe original form of the equations. During the last few decades, linear regression was one of the most viable tools, defining the best-fitting relationship and quantifying the distribution of adsorbates on the adsorbents. It was used to mathematically analyze the adsorption systems and verify the consistency and theoretical assumptions of an adsorption model.

Due to the inherent bias resulting from the transformation which riding towards a diverse form of parameters estimation errors and fits distortion, several mathematically rigorous error functions (sum square error, Hybrid fractional error function, sum of absolute errors, average relative error, Marquardt's percent standard deviation, coefficient of determination, Spearman's correlation coefficient, standard deviation of relative errors, nonlinear chi-square test, coefficient of non-determination and sum of normalized errors) will be employed in determining the best fit model.

2.3.13.1 The Sum Square of Errors

The sum of square of errors (SSE) is said to be the most widely used error function. This method can be represented by the following expression in equation 2.34 (Ng, et al, 2002).

$$SSE = \sum_{i=1}^{n} (q_{e,cal} - q_{e,exp})^{2}$$
(2.34)

where *qe*, calc is the theoretical concentration of adsorbate on the adsorbent, which has been calculated from one of the isotherm models.

 $q_{e,exp}$ is the experimentally measured adsorbed phenol concentration on the adsorbent. One major disadvantage of this error function is that at higher end of liquid-phase adsorbate concentration ranges, the isotherm parameters derived using this error function will provide a better fit as the magnitude of the errors and therefore the square of errors tend to increase, illustrating a better fit for experimental data obtained at the high end of concentration range.

2.3.13.2 Hybrid Fractional Error Function

The hybrid fractional error function (HYBRID) was developed to improve the fit of the sum square of errors (SSE) at low concentrations by dividing it by the measured value (Kapoor and Yang, 1989)

This function includes the number of data points (n), minus the number of parameters (p) or isotherm equation as a divisor. The equation for this error function is given in equation 2.35

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{(q_{e,i,exp} - q_{e,i,cal})^2}{q_{e,i,exp}} \right]$$
(2.35)

2.3.13.3 Average Relative Error

The average relative error (ARE) was developed by Marquardt with the aim of minimizing the fractional error distribution across the entire concentration range. It is given by the following expression in equation 2.36

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left[\frac{q_{e,cal} - q_{e,exp}}{q_{e,exp}} \right]$$
(2.36)

2.3.13.4 Marquardt's Percent Standard Deviation

The Marquardt's percent standard deviation (MPSD) error function is similar to a geometric mean error distribution modified according to the degree of freedom of the system (Ng et al, 2003). It is given by the following expression in equation 2.37:

$$MPSD = \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left(\frac{(q_{e,exp} - q_{e,cal})}{q_{e,exp}}\right)^2}$$
(2.37)

2.3.13.5 Sum of Absolute Errors (EABS)

The Sum of Absolute Errors (EABS) is similar to the sum square error (SSE) function. In this ,case, isotherm parameters determined using this error function would provide a better fit as the forward high concentration data (Kundu and Gupta, 2006). It is represented by the following equation in equation 2.38.

$$EABS = \sum_{i=1}^{p} (q_{e,exp} - q_{e,cal})$$
(2.38)

2.3.13.6 Nonlinear Chi-Square Test

Nonlinear Chi-Square Test (X2) function is very important in the determination of the best fit of an adsorption system. It can be obtained by judging the sum square difference between experimental and calculated data, with each square difference divided by its corresponding values. The value of this function can be obtained from equation 2.39

$$X^{2} = \sum_{i=1}^{n} \frac{(q_{e,cal} - q_{e,exp})^{2}}{q_{e,exp}}$$
(2.39)

2.3.13.7 Standard deviation of relative errors

Standard deviation of relative errors (S_{RE}) function involves the average relative error (ARE) which is subtracted from the difference between the calculated and the experimental values. The denominator is the number of data points minus one. It is given by equation 2.40

$$S_{RE} = \sqrt{\frac{\sum_{i=1}^{n} [(q_{e,exp} - q_{e,cal}) - ARE]^2}{n-1}}$$
(2.40)

2.3.13.8 Root mean square error

Root mean square error (RMSE) function includes the number of data points (n), minus one. The equation for this error function is in equation 2.41.

RMSE =
$$\sqrt{\frac{1}{n-1}\sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2}$$
 (2.41)

2.4 Point of zero charge

The adsorption mechanism is not always an electrostatic interaction between the adsorbate and the adsorbent. The pH of zero point charge (pHzpc) is usually used to explain either the adsorption mechanism follows an electrostatic or another mechanism. Nuria and Isabel (2009) defined the point of zero charge as the pH at which the sorbent surface charge takes a zero value. This means that it is the pH at which the surface of the adsorbent is neutral, that is, it contains as much positively charged as negatively charged surface functions. At this pH, the charge of the positive surface sites is equal to that of the negative ones.

pHpzc provides information about the possible attraction and repulsion between sorbent and sorbate. The knowledge of pHpzc also allows one to hypothesize on the ionization of functional groups and their interaction with adsorbate species in solution. At solution pHs higher than pHpzc, sorbent surface is negatively charged and could interact with positive species while at pHs lower than pHpzc, solid surface is positively charged and could interact with negative species

So normally, it is always easier to adsorb a cation on a negatively charged surface, and an anion on a positively charged surface. However, other interactions may be stronger than purely electrostatic forces, making the effect of surface charge not so important. Additionally, a cation is often complexed with ligands, some of them being possibly negatively charged. Therefore, in such a case, the cation is, in fact, a negative complex, which may adsorb very well on a positively charged surface.

2.5 Adsorption kinetics and thermodynamics

Kinetics of adsorption, a standard analysis in defining adsorption efficiency, describes the solute uptake rate, which in turn governs the residence time of adsorption reaction (Srihari and Ashutosh, 2009). The adsorption rate in a batch adsorption process is useful when designing an adsorption system. Consequently, the time dependence of such adsorption system should be established at various process conditions (Ekpette and Horsfall, 2011). In other to investigate the mechanism of the process and the potential rate controlling steps such as mass transport, pore diffusion and chemical reaction processes, kinetic models have been used to fit experimental data (Ekpette and Horsfall, 2011).

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. The rate and mechanism of adsorption are controlled by various factors like physical and/or chemical properties of absorbent, ambient temperature, solution ph and nature of adsorbate. Kinetics of adsorption is controlled by severally independent processes/factors which include intra-particle diffusion, pH, film diffusion, temperature, bulk diffusion etc which influence the adsorption mechanism and dynamics of the adsorption process (Abia and Asuquo, 2006). It reveals the solute uptake rate of the reaction. It is one of the important characteristics in defining the efficiency of adsorption (Arivoli et al, 2009). These kinetics models are useful for the design and optimizations of the effluent treatment process. The kinetic models are discussed below:

2.5.1 Bangham's kinetic model

The kinetic model is given Rajendran and Namasivayam (2008) in equation 2.42

$$\log\left\{\frac{C_{o}}{C_{o}-q_{m}}\right\} = \log\left(\frac{K_{o}M}{2.30V}\right) + \alpha\log t$$
(2.42)

where C_o is initial concentration (mM), V is volume of the solution (mL), M is weight of the adsorbent (gL⁻¹), qm is amount of adsorbate retained at time 't' (mmol g-1) while α and K_o are Bangham constants.

2.5.2 Natarajan and Khalaf kinetic model

Natarajan and Khalaf kinetic model is given in equation 2.43 by Yilmaz et al. (2015).

$$\log\left(\frac{C_{o}}{C_{t}}\right) = \left(\frac{K_{N}}{2.303}\right) t$$
(2.43)

where Co = initial concentration (mg/L); Ct = concentration (mg/L) at time t. The value of K_N was calculated from the slope of the plot of log (Co/Ct) against time (minutes)

2.5.3 Elovich model

The Elovich model equation which is used for systems in which the adsorbing surface is heterogenous applicable is mainly for chemisorptions kinetics and is given by (Noroozi et al, 2007) in equation (2.44)

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}\mathrm{t}} = \alpha \exp(-\beta q_{\mathrm{t}}) \tag{2.44}$$

Where α is the initial adsorption rate (mg/min). β is related to the extent of surface coverage and the activation energy for chemisorption (g/min).

Integrating this equation (2.44) at the appropriate boundary conditions and simplifying to a linear equation gives equation (2.45)

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t$$
(2.45)

Hence, a plot of q_t against ln t will give a linear plot which can then be used to calculate β and α from the slope and intercept respectively.

2.5.4 Pseudo–first order kinetic model

The pseudo - first order kinetic model was proposed by Lagergren in equation 2.46

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}\mathrm{t}} = \mathrm{K}_{1}(\mathrm{q}_{\mathrm{e}} - \mathrm{q}_{\mathrm{t}}) \tag{2.46}$$

Rearranging and integrating the above equation between the limits from t = 0 to t = t and from $q_t = 0$ to obtain the linear form gives equation 2.47 (Srihari and Ashutosh, 2009).

$$\log(q_e - q_t) = \log q_e - \left(\frac{\kappa_1}{2.303}\right)t$$
 (2.47)

Where,

 q_e = is the amount of adsorbate adsorbed at equilibrium (mg/g)

 q_t = is the amount of adsorbate at time t (mg/g)

 $K_1 = is$ the first order rate constant (mm⁻¹) and t is time (min)

For an adsorption process that follows this first order model, the straight line plot of log $(q_e - q_t)$ against time (t) should give a linear relationship from which the values of K₁ and q_e can be calculated from the slope and intercept respectively (Ekpette and Horsfall, 2011).

2.5.5 Pseudo – second order kinetic model

The pseudo second order kinetic model was by Ho and Mckay and expressed in equation 2.48 as (Srihari and Ashutosh, 2009).

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \tag{2.48}$$

Integrating the above equation between the boundary condition of t = 0 to t = t and $q_t = 0$ to $q_t = q_t$ will yield equation 2.49

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} - K_2 t \tag{2.49}$$

which on linearizing will yield equation 2.50

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$
(2.50)

Where,

 K_2 = rate constant of the pseudo second order adsorption (g/mg.min)

$$q_e$$
 = equilibrium adsorption capacity (mg/g).

If the adsorption follows pseudo second-order, the plot of t/q_t against t gives linear relationship from which the constants q_e and K_2 will be determined from the slope and intercept (Srihari and Ashutosh, 2009; Nwabanne and Igbokwe, 2008)

2.5.6 Battacharya-Venkobachor kinetic model

The Bhattacharya-Venkobachor model is given as in equation 2.51 (Goswami and Ghosh, 2005)

$$\ln(1 - U_{\rm t}) = K_{\rm B} t \tag{2.51}$$

Where,

$$U_t = \frac{c_e - c_t}{c_o - c_e}$$
(2.52)

 C_{o} and C_{e} are the initial and equilibrium concentration respectively and C_{t} is the concentration at time t.

The effective diffusion coefficient D_2 is given by

 $D_2 = (K_B r^2)/\pi^2$ where r is the particle radius

2.5.7 Power function model

Power function equation is given by equation 2.53 (Goswami and Ghosh, 2005)

$$\log q_t = \log a + b \log t \tag{2.53}$$

Where a and b are power function equation constants

2.5.9 The intra-particle diffusion model

There is a possibility of the adsorbate diffusing into the interior pores of the adsorbent after initially being adsorbed on the surface of the adsorbent (Sivakumar and Palanisamy,

2009). Hence, the following kinetic model in equation 2.54 propounded by Weber and Morris is used to investigate the adsorption for intra-particle diffusion (Oladoja and Asia, 2008).

$$q_t = K_d t^{\frac{1}{2}} + \partial \tag{2.54}$$

where K_d is the intra-particle diffusion constant

 δ is the intercept of the line which is proportion to the boundary layer thickness

2.5.10 Second-order Lagergren kinetics model

The second-order kinetic equation is given by equation 2.55

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} - K_2 t \tag{2.55}$$

Where K_2 is Langergren 2^{nd} – order rate constant

A plot of $1/(q_e - q_t)$ versus t is used to calculate K_2 and q_t from the slope and the intercept respectively (Goswami and Ghosh, 2005).

2.5.11 Boyd kinetic model

It also determines if the adsorption mechanism was governed by external mass transport.

The Boyd model is given as expressed by Tsibranska, and Hristova (2011) in equ. 2.56

$$\ln (1 - F) = -kt \tag{2.56}$$

where F represents the fraction of solute adsorbed at any time given by q_t/q_e and t is the time in minutes and k denotes the external mass transfer coefficient.

2.5.12 Thermodynamics parameters

2.5.12.1 Process Thermodynamics

The knowledge of the kinetics ((how fast) and the thermodynamics (heat changes) are very important in any adsorption experiment. The fastness of the adsorption process can be calculated from the knowledge of kinetic studies, but the heat change during the adsorption process requiares a brief idea of thermodynamic parameters. The thermodynamic parameters that must be considered to determine the heat change of the adsorption process are enthalpy of adsorption (Δ H), free energy change (Δ G) and entropy change (Δ S) due to transfer of unit mole of solute from solution onto the solid–liquid interface. The thermodynamic function Δ His very useful whenever a differential change occurs in the system. Change in entropy Δ S, relates to the randomness of the adsorption process. The parameter Δ G is used to identify the spontaneity and feasibility of the adsorption process.

Since K_e is equilibrium constant, it can be changed with temperature and therefore it can be used to deduce the thermodynamics parameters such as the Gibbs free energy (ΔG), enthalpy charges (ΔH^o) and entropy changes (ΔS) associated to the adsorption process (Djebbar et al, 2012). These parameters are used to gain insight into the mechanism involved in the adsorption. They are given by equations 2.57 to 2.59 (Onu and Nwabanne,2014)

$$\Delta G^o = -RT \ln K_L \tag{2.57}$$

$$\ln K_{\rm L} = \frac{\Delta S^{\rm o}}{R} - \frac{\Delta H^{\rm o}}{RT}$$
(2.58)

$$\Delta S^{o} = \Delta H^{o} - \frac{\Delta G^{o}}{T}$$
(2.59)

Where,

R = the universal gas constant

T = the temperature (K)

K_L = Langmuir equilibrium constant

The plot of ln K_L as a function of 1/t yields a straight line from which ΔH ° and ΔS ° can be calculated from the slope and intercept respectively.

The variation of Gibbs free energy with temp can be calculated using the equations above (Djebbar et al, 2012). A negative value of the Gibbs free energy change (ΔG) means that the adsorption is spontaneous while a positive value of ΔG° means the adsorption is not spontaneous. Results showed that ΔG° for physisorption is generally between -20 and 0KJ mol⁻; the physisorption together with chemisorptions is at range of – 80 to – 400KJmol⁻¹.

A negative value of the energy change (Δ H) shows that the process is exothermic i.e giving out heat whereas a positive value of Δ H^o shows the process to be endothermic and also indicates the process may be due to chemical bonding or chemisorptions (Tabrez et al, 2004).A positive value of Δ S shows that the adsorption is spontaneous in nature and there is increased randomness at the solid solution interface during adsorption. It also reflects the affinity of the clay for the dyes and suggests some structural changes in the dye (Atef and Waleed, 2009).

2.5.12.2 Activation energy

The activation energy can be calculated using the Arrhenius equation in equation 2.61

$$K = A \exp\left(-\frac{E_a}{RT}\right) \tag{2.61}$$

The linear form of the Arrhenius equation can be expressed in equation 2.62

$$\ln K = \ln A - \frac{E_a}{RT} \tag{2.62}$$

Where,

A is the frequency factor (\min^{-1})

E_a is the activation energy (KJ/mol)

T is the absolute temperature (K)

2.6 Optimization process

2.6.1 Surface Response Methodology

Response surface methodology (RSM) is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously. A full factorial design, which includes all possible factor combinations in each of the factors, is a powerful tool for understanding complex processes for describing factor interactions in multifactor systems. (Rajeshkannan et al, 2010). The relationships which link inputs with outputs are complex and difficult to describe with elemental mathematical models. Therefore, the need arises for tools that are capable of more complex modeling and that achieve maximum refinement of the role of each variable in the system as well as the synergetic and/or antagonistic interrelationships between the same variables.

The Response Surface Methodology (RSM) emerged in the 1950s within the context of Chemical Engineering in an attempt to construct empirical models able to find useful statistical relationships between all the variables making up an industrial system. This methodology is based on experimental design with the final goal of evaluating optimal functioning of industrial facilities, using minimum experimental effort. Here, the inputs are called factors or variables and the outputs represent the response that generatesthe system under the causal action of the factors. Afterwards, the use of RSM was shown in the design of new processes and products. In recent years it is being applied successfully in other scientific fields such as biology, medicine, and economy. (Myers et al, 2004) has exhaustively reviewed the literature in the sense, describing the

developments and applications of this methodology. Very recently, RSM has been used even to validate new experimental methods (Jurado et al, 2003)

For example, the growth of a plant is affected by a certain amount of water x1 and sunshine x2. The plant can grow under any combination of treatment x1 and x2. Therefore, water and sunshine can vary continuously. When treatments are from a continuous range of values, then a Response Surface Methodology is useful for developing, improving, and optimizing the response variable. In this case, the plant growth y is the response variable, and it is a function of water and sunshine. It can be expressed as

$$y = f(x_1, x_2) + e$$
 (2.63)

The variables x1 and x2 are independent variables where the response y depends on them. The dependent variable y is a function of x1, x2, and the experimental error term, denoted as e. The error term e represents any measurement error on the response, as well as another type of variations not counted in f. It is a statistical error that is assumed to distribute normally with zero mean and variance s2. In most RSM problems, the true response function f is unknown. In order to develop a proper approximation for f, the experimenter usually starts with a low-order polynomial in some small region. If the response can be defined by a linear function of independent variables, then the approximating function is a first-order model. A first-order model with 2 independent variables can be expressed as in equation (2.64)

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \varepsilon$$
 (2.64)

If there is a curvature in the response surface, then a higher degree polynomial should be used. The approximating function with 2 variables is called a second-order model, it is given by equation (2.65)

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_{11}^2 + \beta_{22} X_{22}^2 + \beta_{12} X_1 X_2 + \varepsilon$$
(2.65)

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In general, all,RSM problems use either one or the mixture of both of these models. In each model, the levels of each factor are independent of the levels of other factors. In order to get the most efficient result in the approximation of polynomials, the proper experimental design must be used to collect data. Once the data are collected, the Method of Least Square is used to estimate the parameters in the polynomials. The response surface analysis is performed by using the fitted surface. The response surfacedesigns are types of designs for fitting the response surface. Therefore, the objective of studying RSM can be accomplished by

(1) Understanding the topography of the response surface (local maximum, localminimum, ridge lines), and

(2) Finding the region where the optimal response occurs. The goal is to move rapidly and efficiently along a path to get to a maximum or a minimum response so that the response is optimized.

2.6.2 Central Composite Design (CCD)

Two major Response Surface optimization designs are the Central Composite Design (CCD) and Box-Behnken Design (BBD). They are available to generate standard response-surface designs. The most popular response-surface design is the central-composite design (CCD), due to Box and Wilson. A simple example is a chemical-reaction experiment presented in the preceding section. These designs allow for sequential augmentation, so that we may first experiment with just one block suitable for fitting a first-order model, and then add more block(s) if a second-order fit is needed.

The blocks in a CCD are of two types----one type, called a "cube" block, contains design points from a two-level factorial or fractional factorial design, plus center points; the other type, called a "star" block, contains axis points plus center points. In the following discussion, the term "design points" refers to the non-center points in a block. The levels of the factors are coded, so that the cube blocks contain design points with coordinate values all equal to ± 1 , and center points at $(0, 0, \ldots, 0)$. The design points in the star blocks are at positions of $\pm \alpha$ along each coordinate axis. The value of α , and choices of replications of design points and center points, are often selected based on considerations of rotatability (i.e., the variance of the prediction depends only on the distance from the center) and orthogonality of blocks (so that the coefficients of the fitted response-surface equation are not correlated with block effects).

2.6.3 Coding of data

An important aspect of the response-surface analysis is using an appropriate coding transformation of the data. The way the data are coded affects the results of canonical analysis and steepest-ascent analysis; for example, unless the scaling factors are all equal, the path of steepest ascent obtained by fitting a model to the raw predictor values will differ from the path obtained in the coded units, decoded to the original scale. Using a coding method that makes all coded variables in the experiment vary over the same range is a way of giving each predictor an equal share in potentially determining the steepest-ascent path. Thus, coding is an important step in response-surface analysis (Russell, 2009).

2.6.4 Artificial Neural Network

Artificial neural networks (ANN's) are inspired by biological neural systems. In this approach weighted sum of inputs arriving at each neuron is passed through an activation function (generally nonlinear) to generate an output signal (Manpreet *et al.*, 2011; Haykyn, 2003). The neural network was required to map between a data set of numeric inputs of the various process parameters (such as time, slice thickness, air speed and temperature) influencing the drying process and a set of numeric targets. Neural network function fitting is used to select data, create and train a network, and evaluate its performance using mean square error and regression analysis. Interest in using artificial

neural networks (ANNs) for predicting has led to a tremendous surge in research activities in the past two decades (Omid *et al.*, 2009; Aghbashlo *et al.*, 2011).

2.7 Column Adsorption process

The knowledge of the main principles of column adsorption is important in the design of adsorption column. The concentration-time curves are also known as the breakthrough curves. The breakthrough time is the time at which the effluent concentration reaches the threshold value. The analysis of the fixed bed adsorption column is very useful but usually complex. This is probably because it is found that equilibrium parameters and/or solid diffusion coefficients seem to be unexpectedly influenced by contact time, thereby making the modeling of the operation more complex.

The packed-bed operation is influenced by equilibrium (isotherm and capacity), kinetic (diffusion and convection coefficients) and hydraulic (liquid hold up geometric analysis) factors (Nwabanne and Igbokwe, 2012). The process of adsorption of the material through a fluid mixture flowing into a packed column has become of great interest to researchers in recent time. This is because of the fact that most adsorption processes that are directly carried out in the industries are of the continuous process mode (Mahsa et al, 2014).

The major requirements when sizing absorptive column is to determine the service time (or total effluent volume) until the column effluent reaches the breakpoint concentration, the flow rate, and the bed height for maximum adsorption process (Inglezakis, 2010).

A fixed-bed column is used commonly for contacting wastewater with GAC. Fixed bed columns can be operated singly, in series, or in parallel. The water to be treated is applied to the top of the column and withdrawn at the bottom (Sorour et al, 2006).

2.7.1 Column kinetic models

In modeling any column adsorption process, the knowledge of the kinetic process is important in describing the adsorption process. Some of the kinetic models include Thomas BDST model, Yoon–Nelson model, Adam Bohart kinetics model, Wolborska model, Clark kinetic model, Yan kinetic model, Modified dose-response, etc.

2.7.2 Thomas BDST model

The Thomas kinetic model is also referred to as the bed-depth service time (BDST) model which is based on the irreversible isotherm model by Bohart and Aams (Inglezakis and Poulopoules, 2006). This simplified design model ignores the intra particle (solid) mass transfer resistance and the external (liquid film) resistance such that the adsorbate is adsorbed onto the surface of the solid directly. Thomas kinetic model is given by equation 2.66

$$\frac{c_e}{c_o} = \frac{1}{1 + \exp\left[\frac{K_T}{Q}(q_{max} \ M - c_o t)\right]}$$
(2.66)

Where C_e and C_o = the effluent and inlet solute concentrations

 q_{max} = the maximum adsorption capacity, M = the total mass of the adsorbent

Q = inlet volumetric flow rate, t = the breakthrough time

 K_T = the Thomas rate constant, volume/mass time

The Thomas equation constants q_{max} and Q values can be obtained from the column data and can be used in the design of a full-scale adsorption bed. The linear form of equation 2.67 is given as:

$$\operatorname{In}\left[\frac{C_e}{C_o} - 1\right] = \frac{K_T q_{max} M}{Q} - \frac{K_T C_o}{Q} t$$
(2.67)

2.7.3 Yoon–Nelson kinetic model

The Yoon–Nelson model not only is less complicated than other models but also requires no detailed data concerning the characteristics of adsorbate, (Runping et al, 2009).(Zhe et al, 2013). It can be represented by equation 2.68

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp\left[\frac{W(\tau - t)}{T}\right]} \tag{2.68}$$

Where K is the rate constant (1/min), τ the time required for 50% adsorbate breakthrough (min) and t is the breakthrough (sampling) time (min).

The linearized form of the Yoon and Nelson model is in equation 2.69:

$$ln\frac{c_e}{c_o - c_e} = kt - \tau k \tag{2.69}$$

Equation (2.60) gives the linear relationship between adsorption inlet concentration (C_o) and the 50% breakthrough time (τ).

2.7.4 Adam Bohart kinetics model

The Adam Bohart kinetic model is as given by equation 2.70

$$ln\frac{c_t}{c_o} = K_{AB}C_ot - K_{AB}N_o\frac{Z}{U_o}$$
(2.70)

The Adam-Bohart kinetic model was investigated by plotting the graph of $\ln(C_t/C_o)$ against t at different adsorption conditions as given in figures 4.5 to 4.8. Respective values of K_{AB} and *N0*, were calculated from the slope and the intercept respectively

2.7.5 Wolborska kinetic model

The column kinetic model given byWolborska generally describes the concentration distribution in the packed bed for the low concentration region of the breakthrough curve (Yanhong et al, 2018). The model equation is represented in equation 2.71

$$ln\frac{c_t}{c_o} = \frac{\beta c_o}{N_o} t - \frac{\beta Z}{U_o}$$
(2.71)

2.7.6 Clark kinetic model

The Clark kinetic model was developed based on the use of a mass-transfer concept in combination with the Freundlich isotherm (Nouri and Ouederni, 2013). The Clark kinetic model is as given in equation 2.72

$$ln\left[\left(\frac{C_t}{C_o}\right)^{1-n} - 1\right] = \ln A - rt$$
(2.72)

Linear regression involving the plot of $\ln((C_t/C_o)^{1-n} - 1)$ against the time of adsorption t can be used to fit the Clark model with the experimental result under conditions of experiment.

2.7.7 Yan kinetic model

Yan proposed a kinetic model that can give a good description of the breakthrough curve of the fixed bed column study. The Yan kinetic model is given by Shreyashi and Sudip (2006) as equation 2.73

$$ln\left(\frac{C_t}{C_o - C_t}\right) = \frac{K_y}{Q}C_o ln\left(\frac{Q^2}{K_y q_y m}\right) + \frac{K_y C_o}{Q}ln t$$
(2.73)

The adsorption parameters, that is, the Yan rate constant K_y and the adsorption capacity q_y were evaluated from the slope and the intercept respectively of the plot.

2.7.8 Modified dose-response

The Modified dose-response kinetic model is based on mathematical issues instead of mechanistic fundamentals. How, ever, its final form is similar to Thomas and Yoon– Nelson models and is given by Shanmugam et al, (2016) in equation 2.74

$$ln\left(\frac{C_t}{C_o-C_t}\right) = a ln(C_o Q t) - a ln(q_{md} m)$$
(2.74)

In fitting the experimental data to the modified dose-response model, the plot of $\ln(C_t/(C_0 - C_t))$ is drawn against $\ln(q_m m)$ at different conditions of flowrate, bed height, influent phenol concentration and particle size.

2.8 Review of previous works on phenol adsorption using activated cabon

Salim and Abdeslam (2014) studied the adsorptive performance of phenol removal from water using sewage sludge based adsorbent (SSBA). The SSBA was prepared by chemical activation with H2SO4 in a mass ratio of 1:1, followed by pyrolysis at 650°C for 1 h under inert atmosphere. Phenol removal by SSBA was investigated using kinetic and equilibrium experiments. The results demonstrate that phenol sorption to the SSBA reached equilibrium at 2 h with the maximum sorption capacity of 26.16 mg/g under given experimental conditions (initial Phenol concentration range = 40–200 mg/l; adsorbent dose = 5.0g/l and temperature = 20°C). The phenol removal was high and relatively constant at (pH <pKa), whereas the phenol removal decreased sharply as the solution pH approached a highly alkaline condition (pH > pKa). The results indicate that the pseudo second order model was suitable for describing the kinetic data. Regarding the equilibrium data, the Freundlich isotherm was fitted well. This study concluded that SSBA could be used for phenol removal from water.

Uddin, et al, (2007) investigated the phenol adsorption from aqueous solution using water hyacinth ash. Batch kinetic and isotherm studies were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dosage and pH. The adsorption of phenol decreased with increasing pH. The Freundlich and Langmuir adsorption models were used for the mathematical description of adsorption equilibrium and it was found that the experimental data fitted very well to the Langmuir model. Batch adsorption models, based on the assumption of the pseudo-first-order and pseudo-second-order models, were applied to examine the kinetics of the adsorption. The results showed that kinetic data followed closely to the pseudo-second-order model.

Ihsan (2013) carried out a research to study the removal of phenol presents in industrial wastewater using the local sawdust. Four factors namely initial phenol concentration, adsorbent dose, pH and contact time were considered for their removal capacity in the range of (100-500) mg/l, (0.1-1) gm, (3-9) and (20-180) min respectively. Statistical

analysis of the results showed the significance of the individual factors and their interactions on the adsorption process. Box-Wilson design of experiments was adopted to find a useful relationship between the four variables and the removal efficiency. The experimental data collected by this method is successively fitted to a second order polynomial mathematical model. The optimum conditions for the removal of phenol within the experiment range of variables studies were 130 mg/l of initial phenol concentration, 0.82 gm of adsorbent dose, natural pH value of 6.7 and 120 min of contact time. Under these conditions, the maximum removal efficiency was 91.6%. Batch kinetic and isotherm studies were carried out to evaluate the effect of initial phenol concentration, adsorbent dose, pH and contact time. A comparison of the mathematical model applied to the adsorption of phenol was evaluated for the Langmuir and Freundlich adsorption models. It was found that the equilibrium data agree very well with the Langmuir and Freundlich models.

Jolanta et al, (2012) presented the sorption potential of activated carbon for the removal of phenolic compounds from municipal wastewater. The structural property of carbon was characterized by nitrogen adsorption-desorption isotherms. The sorption experiments were carried outa ina batch system for raw and biologically treated wastewater, namely influent and effluent respectively. The effectiveness of phenols removal was determined by measurement of phenolic index and was in the range 20.7-60.5%; 49.6-94% for influent and effluent respectively. Lower removal of phenols from influent resulted from higher competition with other pollutants for the sorption sites than in effluent. The experimental data fitted slightly better Freundlich model than Langmuir which indicates favorable adsorption and heterogeneity of the sorbent adsorption sites.

Nour et al (2015) investigated the uptake of phenol and nickel in Individual and competitive adsorption processes using multiwalled carbon nanotubes (MWCNTs). The carbon nanotubes were characterized by different techniques such as X-ray diffraction, scanning electron microscopy, thermal analysis and Fourier transformation infrared spectroscopy. The different experimental conditions affecting the adsorption process

were investigated. Kinetics and equilibrium models were tested for fitting the adsorption experimental data. The characterization experimental results proved that the studied adsorbent possess different surface functional groups as well as typical morphological features. The batch experiments revealed that 300 min of contact time was enough to achieve equilibrium for the adsorption of both phenol and nickel at an initial adsorbate concentration of 25 mg/l, an adsorbent dosage of 5 g/l, and a solution pH of 7. The adsorption of phenol and nickel by MWCNTs followed the pseudo-second-order kinetic model and the intraparticle diffusion model was quite good in describing the adsorption mechanism. The Langmuir equilibrium model fitted well the experimental data indicating the homogeneity of the adsorbent surface sites. The maximum Langmuir adsorption capacities were found to be 32.23 and 6.09 mg/g, for phenol and Ni ions, respectively. The removal efficiency of MWCNTs for nickel ions or phenol in real wastewater samples at the optimum conditions reached up to 60% and 70%, respectively.

Hamdaoui, et al, (2018) studied the adsorption of phenol onto natural and organically modified Moroccan clay named Rhassoul using the batch equilibrium method. Several techniques, such as X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermal analysis (TGA/DTG) were used for clays characterization. Adsorption experiments were carried out varying initial phenol concentration, pH and contact equilibrium time. The adsorption isotherms of phenol on Rhassoul and modified Rhassoul by the HDTMA surfactant molecules were determined and modeled by Langmuir equation. The experimental results indicate that the adsorption was improved by increasing pH and initial concentration of phenol in the solution. Experimental and calculated kinetic data for equilibrium are well fitted with the pseudo second order kinetic model. The adsorption isotherm was described satisfactorily using the mathematical model of Langmuir with a maximum monolayer adsorption capacity of 25 mg/g for organically Rhassoul. The results indicate that raw and organically modified Rhassoul could be used as a low cost adsorbent in wastewater treatment for the elimination of phenolic compounds

Girish and Ramachandra (2014) carried out research on the potential of Lantana Camara, a forest waste, as an adsorbent for the phenol reduction in wastewater. Batch studies were conducted with adsorbent treated with HCl and KOH to determine the influence of various experimental parameters such as pH, contact time, adsorbent dosage, and phenol concentration. The experimental conditions were optimized for the removal of phenol from wastewater. Equilibrium isotherms for the adsorption of phenol were analyzed by Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich isotherm models. Thermodynamic parameters like the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were also determined and they showed that the adsorption process was feasible, spontaneous, and exothermic in the temperature range of 298–328 K. The kinetic data were fitted with pseudo-second-order model. The equilibrium data that followed Langmuir model with the monolayer adsorption capacity was found to be 112.5 mg/g and 91.07 mg/g for adsorbent treated with HCl and KOH, respectively, for the concentration of phenol ranging from 25 to 250 mg/L. This indicates that the Lantana camara was a promising adsorbent for the removal of phenol from aqueous solutions.

Mihoc, et al, (2014) reported on the adsorption of phenol and p-chlorophenol from aqueous solutions by magnetic nanopowder. The magnetic iron oxide nanopowder (MNM) was prepared, characterized and tested as adsorbent for the removal of phenol and p-chlorophenol (PCP) from aqueous solution. The iron oxide was obtained by a new combustion method which allows the direct obtaining of magnetic nanopowder covered with some organic residues resulting from fuel combustion. The magnetic powder was characterized in terms of phase composition, structure, texture, magnetic properties and carbon content. The adsorption kinetics was examined by the pseudo-first-order and pseudo-second-order models and the equilibrium data were fitted with Langmuir and Freundlich isotherms. The results confirmed the good adsorption capacity of the new magnetic nanopowder for the removal of phenol and PCP from aqueous solutions and its great potential for practical applications.

Asgari et al, (2013) studied phenol removal from a synthetic solution using modified zeolite (clinoptilolite) with FeCl₃ as an adsorbent. The zeolite samples were crushed and granulated using standard ASTM sieves (mesh size of 20). The prepared zeolite then was modified by FeCl₃. The chemical composition and the surface area of the zeolite were analyzed using XRF and N₂ gas via BET isotherm and Belsorb software. In this study, different parameters including pH (3, 7, and 12), initial concentration of phenol (25-200 mg/l), contact time (20-240 min) and the amount of modified zeolite (0.25-3 g/l) were examined in a batch reactor. The concentration of phenol was measured aata wavelength of 500 nm by a spectrophotometer. The results of this study showed that as the initial concentration of phenol, the adsorbent dose and the pH in the range of 3-12 increased the adsorption/removal of phenol increased. Phenol adsorption equilibrium was achieved within 100 min contact time and the optimum pH for adsorption of phenol using zeolite was found as 3. The adsorption data complied with Langmuir isotherm (r 2 =0.98). The results showed that modified zeolite can be used effectively in removing phenol. The removal efficiency of phenol in lower pH was more than in higher pH. Also, due to the low price of the zeolite and its simple modification, it can be used for removing hazardous pollutants in water and wastewater.

Gundogdu, et al, (2012) investigated the ability of activated carbon which was produced by chemical activation using zinc chloride from tea industry wastes (TIWAC) to adsorb phenol molecules from aqueous solution. The phenol adsorption on TIWAC took place with a high yield at pH values in the range 4 to 8. The optimum contact period was observed as 4.0 h and from the adsorption graphs plotted as a function of time; it was established that phenol adsorption on TIWAC conformed more to a pseudo-second-order kinetic model. Additionally, it was determined that the adsorption rate is controlled by intraparticle diffusion as well as film diffusion. It was established that phenol adsorption on TIWAC can be better defined by the Langmuir adsorption model and its adsorption capacity was 142.9 mg·g⁻¹ from the linear Langmuir equation. Temperature had an adverse effect on adsorption yield, and hence, the adsorption process was exothermic in our case. Moreover, increasing electrolyte concentration in the medium has a positive

effect on adsorption yield. From the data obtained, it was concluded that the removal of phenol from aqueous solution by TIWAC produced from tea industry wastes with a very low cost took place with extremely high performance.

2.9 Summary of literature review and knowledge gap

From literature, there is limited work on the optimization of activated carbon production from rice husk and corn cob. Equally, the comparison of response surface methodology and artificial neural network in the uptake of phenol from wastewater using corn cob and rice husk has not received adequate attention. Furthermore, there is scanty research work on phenol uptake that involved both linear and non linear isotherm and kinetic modeling. Few column kinetic models have been investigated in phenol adsorption using packed bed. Hence, this work aims to bridge these knowledge gaps and equally provide additional information on regeneration of adsorbents and point of zero charge.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Raw material collection and preparations

The raw materials used in the preparation of activated carbon were Rice husk and Corn cob. Rice Husk was obtained from Wisdom Pack Gloal Rice Mills at Agu-Awka, Anambra State. Corn cob was obtained from Maize farms at Okpuno in Awka, Anambra State. They were washed several times using de-ionised water to remove all traces of impurities and dried in the sun to reduce the moisture content to below 10% (db). The samples were ground into fine particles using a grinding machine and sieved in different particle sizes. The aqueous wastewater was prepared by dissolved calculated amount of phenol in distilled water.

3.2.1 Carbonization process

The aim of the carbonization process was to remove excess of the volatile matters. The activated carbons were prepared according to the method of Nwabanne et al (2017). The corn cob and rice husks were washed to remove dirt, ground using laboratory pestle and mortar and sun dried to reduce the moisture content to below 10% (db). The dried samples were impregnated with an appropriate concentration (depending on the design matrix in Table 3.2) of tetraoxo-phosphate V acid (H_3PO_4) and kept in an oven (Memmert Oven Din 40050-1p20) at 383K for 24 hours. The samples were washed many times with deionized water till a pH of 7 was obtained and leached with warm water to remove any trace of metal present in the sample. The samples were stored in crucibles and placed in a furnace at appropriate temperature and for a specified contact time given in the experimental design matrix in Table 3.2. The samples were then cooled, ground using mortar and pistil and then sieved to particle size of 75µm. The experiment was repeated with different percentage concentration of acid, carbonization temperature and time according to the experimental design matrix. The activated carbons were placed in airtight containers which were labeled and stored in desiccators, ready for use. The

activated carbon prepared from corn cob was abbreviated as CCAC while the one prepared from rice husk was abbreviated RHAC.

3.2 Optimization of the carbonization process

The central composite design (CCD) of the RSM was used to optimize the carbonization process involved in the production of the activated carbon. This method is suitable for fitting a quadratic surface and it helps to optimize the parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters.

The different levels and the experimental ranges of the independent variables are given in Table 3.1. The regression analysis was performed to estimate the response function as a second-order polynomial. The percentage adsorbed was the dependent variable or the response. This experiment was made of 20 runs which consisted of 8 core points, 6 starlike points and 6 center/null points. Each independent variable has five levels which were $-\alpha$, -1, 0, +1, and $+\alpha$. The alpha value α (which is the distance of the star like points from the core point) used was 1.68.

Table 3.1: Factor levels of the independent variables for activated carbon preparation

Independent variable	-α	-1	0	-1	-a
Concentration of acid (%)	10	20	35	50	60
Carbonization temperature (°C)	19	60	120	180	221
Carbonization time (mins)	298	400	550	700	802

Design Expert 8.0.1.7 software was used for the statistical analysis. Analysis of variance (ANOVA) and the coefficients of the regression models were carried out. Response surface was used to determine the individual and interactive effects of the independent variables on the percentage of the phenol adsorbed.

Standard	Acid Concentration	Carbonization	Carbonization
Run	(%)	time (minutes)	temperature (°C)
1	20	60	400
2	50	60	400
3	20	180	400
4	50	180	400
5	20	60	700
6	50	60	700
7	20	180	700
8	50	180	700
9	10	120	550
10	60	120	550
11	35	19	550
12	35	221	550
13	35	120	298
14	35	120	802
15	35	120	550
16	35	120	550
17	35	120	550
18	35	120	550
19	35	120	550
20	35	120	550

Table 3.2: Design matrix for optimum production of activated carbon



Figure 3.1 Block diagram for the activated carbon production.

3.3 Characterization of the adsorbents

The adsorbents were characterized for their physical properties, surface area and pore size distribution, Fourier Transform Infra-Red (FTIR) and Scanning Electron Microscope (SEM).

3.3.1 Physical properties of the adsorbents

The physical properties of the activated carbon were determined using standard methods of Association of Analytical Chemistry (AOAC). pH was determined using a pH meter (Elico model L1 -120). The bulk density was determined using the water displacement method (Dipa et al, 2015). Moisture content, ash content, volatile matter, fixed carbon, porosity, iodine number were analyzed as per standard procedures used by Nwabanne et al, (2017).

3.3.2 Surface area and Pore size distribution analysis

The surface area and the pore volume were determined using the BET nitrogen (N_2) adsorption-desorption isotherms measured at 77K using N_2 gas sorption analyzer. The Quantachrome NOVA Win version 11.03 was used. The total pore volume estimated using liquid volume of adsorbate (N_2) at a relative pressure of 0.99. All the surface areas were calculated from the nitrogen adsorption isotherms by assuming the surface area of a nitrogen molecule is 0.162 nm².

3.3.3 FourierTransform Infra-Red (FTIR) spectrophotometry

An FTIR-8400S Fourier Transform Infrared Spectrophotometer, made by SHIMADZU is a effective tool for identifying types of chemical bonds (functional group) in a molecule by producing an intra-red absorption spectrum that is like a molecular "finger print". The solid samples were dissolved in a methylene chloride solvent, and the solution placed onto the plate and analyzed in a liquid cell. This is a small container made from NaCl (or other IR-transparent material) which is filled with liquid, such as the extract for EPA 418.1 analysis. This creates a longer path for the sample, which leads to increased
sensitivity. Sampling methods include making a null of a powder with hydrocarbon oil (Nujol) or pyrolyzing insoluble polymer and using the distilled pyrolyzate to cast a film.

3.3.4 Scanning Electron Microscopy (SEM)

SEM is a type of microscope that uses electrons rather than light to form an image. The observation was done using a JOEL scanning electron microscope model JSM 6400. To prepare for the observation, the solid samples were placed on a brace stub sample holder using double stick carbon tape. Then, the samples were coated with layers of gold approximately 20-25A thick using Blazer sputtering coater. The micrograph was recorded with 12 KV, 500x and 1000x magnification. Morphology of the solid samples could be seen through the microscopy. Crystal shape size of the crystalline solid phase could be identified from the micrograph.

3.4 Batch Adsorption procedure

The efficiency of the activated carbon was determined by carrying out batch studies. The simulated aqueous phenol solution was prepared by dissolving 0.1g of the phenol in 1000ml of distilled water each to get a solution of 100mg/l. After the adsorption, the solution was filtered and the absorbance measured at its wavelength of 290nm using UV spectrophotometer. The amount of equilibrium adsorption, q_e (mg/g) was calculated using equation (3.4)

$$q = \frac{(C_i - C_e)V}{m} \tag{3.4}$$

Where C_i and C_e (mg/L) are the liquid – phase concentrations of phenol at initial and equilibrium respectively. V is the volume of the solution (L) and W is the mass of active activated carbon used (g)

The percentage adsorbed % was calculated using equation 3.2 (Djebbar et al, 2012)

Percent adsorbed
$$\% = \left(\frac{C_i - C_e}{C_o}\right) X \ 100$$
 (3.2)

Effect of pH

The effect of initial solution pH was determined by agitating 0.5g of activated carbon produced with 100ml of phenol solution of initial phenol concentration of 100mg/L in a magnetic stirrer at different pH values ranging from 2 to 10. Agitation was provided for 60 minutes contact time which is sufficient to reach equilibrium with a constant agitation speed of 200 rpm. The pH was adjusted by adding a few drops of diluted 1.0M NaOH or 1.0 HCl before each experiment. The pH was measured using a pH meter.

Effect of initial phenol concentration

Stock solution of phenol was prepared by dissolving 500mg of phenol crystal in 1 liter of distilled water. Various concentrations of phenol (50, 100, 150, 200, 300, and 600mg/l) were prepared by diluting the stock solution to the desired concentration using distilled water. Then 0.5g of the activated carbon produced was added into 250ml Erlenmeyer flasks containing 50ml of the different concentration of the phenol solutions.

Effect of contact time

The effect of contact time was determined by agitating 0.5g of activated carbon produced and 100ml of phenol solution of initial concentration (100mg/L) in a magnetic stirrer at different contact time intervals (5, 10, 20, 30, 45, 60mins) with a constant agitation speed of 200rpm.

Effect of adsorbent dosage

The effect of adsorbent dosage was determined by agitating different masses (0.1, 0.2, 0.3, 0.4 0.5g) of the activated carbon produced with 100ml of phenol solution of initial concentration 100mg/L in a magnetic stirrer. Agitation was provided for 60mins contact time which is sufficient to reach equilibrium with a constant agitation speed of 120rpm.

Effect of particle size

Samples of activated carbon of different sizes used to determine the effect of the particles size. The sizes used were $600\mu m$, $300\mu m$, $150\mu m$ and $75\mu m$. Laboratory sieves were used to segregate the sizes into the required μm . 0.5g of each of these particles sizes of activated carbon were agitated with 100ml of phenol solution of 100mg/l concentration in a magnetic stirrer for 60minutes.

Effect of temperature

The effect of temperature was determined by agitating 0.5g of activated carbon produced and 100ml of phenol solution of 100mg/l concentration in a magnetic stirrer for 60minutes with a constant agitation speed of 200 rpm at different temperatures of 303K, 308K, 313K, 323K and 333K.

3.5 Isotherm, kinetic and thermodynamic studies

The isotherm study was carried out by fitting the experimental data obtained at different concentrations to different isotherm models such as Halsay, Freundlich, Langmuir, Harkins-Jura, Temkin, Dubinin-Radushkevich, Fowler-Guggenheim, Flory-Huggins, and Kiselev isotherm models. The nonlinear isotherm models were equally evaluated.

The kinetic analysis involves correlating the experimental data to different kinetic models to determine if there is a good correlation or not. The kinetic models tested include Bangham's kinetic models, Natarajan andKhalaf kinetic models, Elovich kinetic models, Pseudo–first order kinetic models, Pseudo–second order kinetic models, Battacharya-Venkobachor kinetic models, intra-particle diffusion model, Boyd kinetic models etc

In the thermodynamics study, thermodynamics parameters such as enthalpy change (Δ H), entropy change (Δ S) and Gibbs free energy change (Δ G) were evaluated using the Vant Hoff's equation. The activation energy E_a was equally determined using the Arrhenius equation.

3.6 Optimization of the batch adsorption process

The Central Composite Design (CCD) was used to study the effects of the process variables with respect to their responses. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters.

Optimization usually involves the combined effect of the main important independent variables (temperature, initial concentration, contact time and adsorbent dosage) in relation to the response (percentage adsorbed).Using the CCD involves varying the independent variables at five different levels (- α , -1, 0, +1, + α). CCD is best for the development of the polynomial regression equations in order to effectively determine the best conditions for optimum removal of phenol ions from solution.

The process parameters used include the temperature, initial concentration, contact time and adsorbent dosage. These serve as the independent variables while the percentage adsorbed serve as the response or dependent variable.

The coded values of the process parameters were determined by the following equation 3.3 (Rajeshkannan et al, 2012)

$$x_i = \frac{X_i - X_o}{\Delta X} \tag{3.3}$$

where x_i – coded value of the ith variable, X_i – uncoded value of the ith test variable and X_o – uncoded value of the ith test variable at center point. The range and levels of individual variables are given in Tables 3.3 and 3.4 for CCAC and RHAC respectively. The regression analysis was performed to estimate the response function as a second order polynomial.

Independent	-α	Low level	Medium level	High level	+α
Factors		(-)	(0)	(+)	
Temp, °C	37.93	40	45	50	52.07
Concentration,	79.29	100	150	200	220.71
mg/l					
Contact time,	17.57	30	60	90	102.43
mins					
Dosage, g	0.896	1.0	1.25	1.5	1.60

Table 3.3: Factor levels of independent variables for CCAC

Table 3.4: Factor levels of independent variables for RHAC

Independent	-α	Low level (-)	Medium level (0)	High lev	el +α
Factors				(+)	
Temp, °C	32.81	40	50	60	67.19
Concentration,	60.06	100	150	200	235.94
mg/l					
Contact time,	19.22	30	45	60	70.78
mins					
Dosage, g	0.46	0.6	0.8	1.0	1.14

A statistical program package, Design Expert 10.7.0.1 was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by ANOVA. The significance of each term in the equation was estimated by the goodness of fit in each case. Response surfaces were drawn to determine the individual and interactive effects of the test variable on the percentage removal. The optimum conditions were validated.

The optimal values of the test variables were first obtained in coded units and then converted to the actual values. Using four factor variables and six centre points, the CCD gave the following design matrix in Tables 3.6 and 3.7.

Std Run	Temperature	Concentration	Contact	Dosage	Percentage
	(°C)	(mg/l)	time (mins)	(g)	adsorbed (%)
1	40	100	30	1.0	
2	50	100	30	1.0	
3	40	200	30	1.0	
4	50	200	30	1.0	
5	40	100	90	1.0	
6	50	100	90	1.0	
7	40	200	90	1.0	
8	50	200	90	1.0	
9	40	100	30	1.5	
10	50	100	30	1.5	
11	40	200	30	1.5	
12	50	200	30	1.5	
13	40	100	90	1.5	
14	50	100	90	1.5	
15	40	200	90	1.5	
16	50	200	90	1.5	
17	37.93	150	60	1.25	
18	52.07	150	60	1.25	
19	45	79.29	60	1.25	
20	45	220.71	60	1.25	
21	45	150	17.57	1.25	
22	45	150	102.43	1.25	
23	45	150	60	0.896	
24	45	150	60	1.603	
25	45	150	60	1.25	
26	45	150	60	1.25	
27	45	150	60	1.25	
28	45	150	60	1.25	
29	45	150	60	1.25	
30	45	150	60	1.25	

Table 3.6 Experimental design matrix for adsorption of phenol using CCAC

Std Run	Temperature	Concentration	Contact time	Dosage	Percentage
	(°C)	(mg/l)	(mins)	(g)	Adsorbed (%)
1	40	100	30	0.6	
2	60	100	30	0.6	
3	40	200	30	0.6	
4	60	200	30	0.6	
5	40	100	60	0.6	
6	60	100	60	0.6	
7	40	200	60	0.6	
8	60	200	60	0.6	
9	40	100	30	1.0	
10	60	100	30	1.0	
11	40	200	30	1.0	
12	60	200	30	1.0	
13	40	100	60	1.0	
14	60	100	60	1.0	
15	40	200	60	1.0	
16	60	200	60	1.0	
17	32.81	150	45	0.8	
18	67.19	150	45	0.8	
19	50	60.06	45	0.8	
20	50	235.94	45	0.8	
21	50	150	19.22	0.8	
22	50	150	70.78	0.8	
23	50	150	45	0.46	
24	50	150	45	1.14	
25	50	150	45	0.8	
26	50	150	45	0.8	
27	50	150	45	0.8	
28	50	150	45	0.8	
29	50	150	45	0.8	
30	50	150	45	0.8	

Table 3.7 Experimental design for adsorption of phenol using RHAC

3.7 Artificial Neural Network

Artificial Neural Networks (ANNs) are mathematical models that loosely approximate the function of biological neural networks. The network was trained with Levenberg-Marquardt (LM) back propagation algorithm which is one of the Multi-Layer Perceptron (MLP). It consists of three or more layers of neurons, with the first layer of neurons representing the independent variable inputs. Each of the neurons in the first layer is connected to one or more layers of hidden neurons that represent nonlinear activation functions. These neurons are in turn connected to a final level of output neurons and, through the use of learning algorithms, the relative influence of each input neuron and their complex interactions on the observed result can be discerned.

An MLP was developed in MATLAB software with four input neurons representing the contact time, adsorbent dosage, temperature and initial phenol concentration, and an output neuron representing the percentage adsorbent. The number of neurons required in the hidden layer was determined by trial and error to minimise the deviation of predictions from experimental results and reduce the possibility of over-fitting the model. A total of 20 (70%) of experimental results were used to train the network, with the remaining results split evenly between network validation and testing. The ANN architecture for the adsorption process is given in figure 3.2



Fig 3.2: The ANN architecture for the adsorption process

3.8 Adsorbent Regeneration/desorption.

Phenol is readily soluble in an alkaline solution due to the presence of hydroxyl group. The spent adsorbent was digested in a 2M solution of sodium hydroxide where it becomes completely soluble. This solution was further acidified with concentrated Hydrochloric acid until pH 2.0. The solid precipitate as a result of the acidification was then stirred for 2 hours and finally filtered off. The residue was washed with distilled water to pH 7 and air dried.

3.9 Packed bed column studies

A laboratory packed bed column was constructed for the purpose of this study. A glass column of 30cm high and internal diameter of 30mm was used. The schematic diagram is given in figure 3.4. The particle size of the adsorbents ranged from 300µm. The adsorbents were separately packed in the column with glass wool at the bottom of the column. A peristaltic pump (BQ 50-IJ-A) was used to regulate the flow rate of the

influent phenol solution. A flow controller was used to vary and regulate the flowrate. Different flowrates of 9ml/min, 13ml/min, and 18ml/min were used.

The heights of packed bed used include 5cm, 7.5cm and 10cm. The influent phenol concentrations of 100mg/l, 200mg/l and 300mg/l were investigated. The phenol solution was placed at an elevation in a small cylindrical tank and connected to the column for delivery. The effluent samples were collected at different time intervals of 1 hour for about 24 hours until the adsorbents became saturated. The absorbance of the samples was determined and converted to concentration. When equilibrium concentration was reached, the experiment was stopped. The effects of flow rate, bed height influent concentrations were evaluated. Different column kinetic models such as Thomas model, Yoon Nelson kinetic model, Adam-Bohart model, Wolborska model, Clark model, Yan model etc were evaluated using the experimental data.



Figure 3.4 Schematic diagram for packed bed adsorption process

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Activated carbon production

The production of the adsorbents was optimized in order to determine the optimum conditions that will be used in mass production of the adsorbents for both the batch and column analysis. Design Expert was employed in carrying out the multiple regression analysis of the experimental data obtained with the central composite design. The summary of the P-values indicated that a quadratic model fitted the ANOVA analysis and hence it was suggested.

The model summary tests for the production of the activated carbons were presented in Tables 4.1 and 4.2. The coefficient of regression (\mathbb{R}^2) was used to validate the fitness of the quadratic model. This is probably because the correlation coefficient (\mathbb{R}^2) of the quadratic model was closer to unity. The R-squared value is a measure of how efficient the variability in the actual response values can be explained by the experimental variables and their interactions. For production of CCAC, the \mathbb{R}^2 has a high value of 0.9705 showing that 97.05% of the variability in the response can be explained by the model while for production of RHAC, the \mathbb{R}^2 was 0.9546 indicating that 95.46% of the variability in the response can be explained by the model. This suggests that the prediction of experimental data was quite satisfactory.

Source	Std. Dev.	R.	Adjusted	Predicted	PRESS	Remark
		squared	R-squared	R-squared		
Linear	23.21	0.0270	-0.1554	-0.7451	15454	Not suggested
2FI	24.30	0.1331	-0.2670	-0.7891	15844	Not suggested
Quadratic	5.11	0.9705	0.9440	0.7984	1785	Suggested
Cubic	5.98	0.9758	0.9233	-0.5829	40586	Aliased

Table 4.1: Model Summary Statistics for production of CCAC

Source	Std. Dev.	R-	Adjusted	Predicted	PRESS	Remark
		squared	R-sq	R-sq		
Linear	20.48	0 1550	-0.0035	-0.4966	11887 43	Not
	20.40	0.1550	-0.0055	-0.+700	11007.45	suggested
2FI	22 11	0 1757	0.2047	0 8208	14522 60	Not
	22.44	0.1757	-0.2047	-0.8298	14555.00	suggested
Quadratic	6.01	0.9546	0.9137	0.6717	2607.29	Suggested
Cubic	6.43	0.9688	0.9012	-5.2957	50005.71	Aliased

 Table 4.2: Model Summary Statistics for production of RHAC

4.1.1 ANOVA of the production process

The ANOVA table was given in Table 4.3 and 4.4. The model regression F-values of 36.57 for CCAC production and 23.35 for RHAC production implies that the models are significant which was validated by the P-values being less than 0.0001. The tests for adequacy of the regression models, significance of individual model coefficients and the lack of fit test were performed with the design expert.

The P-values were used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the test variables (Shrivastava et al, 2008). A significance level of 5% was used implying that all terms whose P-value are less than 0.05 are considered significant. The larger the magnitude of F-test value and the smaller the magnitude of P-values, the higher the significance of the corresponding coefficient (Iheanacho et al, 2019; Alam et al, 2008). Percentage concentration of the acid is represented by A, Carbonization time by B while Carbonization temperature is C.

Source	Sum of	df	Mean	F-value	p-value
	squares		square		Prob>F
Model	8594.95	9	954.99	36.57	< 0.0001
А	37.64	1	37.64	1.44	0.0257
В	58.83	1	58.83	2.25	0.0164
С	142.64	1	142.64	5.46	0.0416
AB	41.86	1	41.86	1.60	0.2342
AC	556.11	1	556.11	21.29	0.0010
BC	341.91	1	341.91	13.09	0.0047
A^2	5075.34	1	5075.34	194.34	< 0.0001
B^2	1634.33	1	1634.33	62.58	< 0.0001
C^2	111.84	1	111.84	4.28	0.0653
Residual	261.16	10	26.12		
Lack of Fit	230.47	5	46.09		
Pure Error	30.69	5	6.14		
Cor Total	8856.11	19			

Table 4.3: ANOVA a	analysis for	production	of CCAC
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C.V. (%) = 10.79 PRESS = 1785.82 Adeq Precision = 24.763

Source	Sum of	df	Mean	F value	p-value
	squares		square		(Prob>F)
Model	7582.08	9	842.45	23.35	< 0.0001
A-Acid	580.05	1	580.95	16 10	0.0025
Concentration	500.75	1	500.75	10.10	0.0025
B -Carbonization	268 53	1	268 53	7 11	0.0213
time	208.33	1	200.33	/.44	0.0213
C-Carbonization	281.26	1	201 26	10.57	0.0087
temperature	301.20	1	361.20	10.37	0.0087
AB	1.45	1	1.45	0.040	0.8454
AC	22.44	1	22.44	0.62	0.4485
BC	141.12	1	141.12	3.91	0.0761
A^2	5180.95	1	5180.95	143.62	< 0.0001
B^2	585.03	1	585.03	16.22	0.0024
C^2	0.41	1	0.41	0.011	0.9169
Residual	360.73	10	36.07		
Lack of Fit	339.73	5	67.95		
Pure Error	21.00	5	4.20		
Cor Total	7942.81	19			

Table 4.4: ANOVA analysis for production of RHAC

C.V. = 11.07%; PRESS = 2607.29 Adeq Precision = 21.210

The adequate precision was 24.76 and 21.21 for production of CCAC and RHAC respectively. The adequate precision measures the signal to noise ratio and compares the range of the predicted value at the design points to the average prediction error. The adequate prediction ratio above 4 indicates adequate model efficacy (Kumar et al, 2007).

Also, a high PRESS value indicates an adequate signal implying that the model can be used to navigate the design space. The Coefficient of variance (C.V.) is defined as the ratio of the standard deviation of the estimate to the mean value of the observed response. According to Chen et al (2011), a C.V value of more than 10% can be considered reasonably reproducible. The initial quadratic models obtained for the adsorption process were given in equations 4.1 and 4.2

Percentage of CCAC adsorbed (%) =
$$+54.80 - 1.66A + 2.08B + 3.23C - 2.29AB + 8.34AC + 6.54BC - 18.77A^{2} + 10.65B^{2} - 2.79C^{2}$$
 (4.1)

Percentage of RHAC adsorbed (%) = $+62.97 - 6.52A + 4.43B + 5.28C + 0.43AB - 1.67AC + 4.20BC - 18.96A^2 + 6.37B^2 - 0.17C^2$ (4.2)

According to Kumur et al, (2008), the positive sign of a factor indicates that there will be an increase in the response while negative sign shows that there will be a decrease in the response when the factor is increased. Increase in carbonization temperature will show the most significant increase in the response on the account that its coefficient is highest.

Since a significant level of 5% was used, all factors with P-values greater than 0.05 were eliminated, giving the final models as in equations 4.3 and 4.4

Percentage of CCAC adsorbed (%) = $+54.80 + 2.08B - 2.29AB + 8.34AC + 6.54BC - 18.77A^{2} + 10.65B^{2} - 2.79C^{2}$ (4.3)

Percentage of RHAC adsorbed (%) = $+62.97 - 6.52A + 4.43B + 5.28C + 4.20BC - 18.96A^2 + 6.37B^2$ (4.4)

4.1.2 Comparism of predicted and experimental values

The experimental response was compared with the predicted response from the model equations (Tables 4.5 and 4.6). This showed a close correlation between the experimental and the predicted values confirming the acceptability of the suggested model. The maximum percentage adsorption of 95.1% was obtained at percentage

concentration of 35%, carbonization time of 221 minutes and carbonization temperature of 550°C for CCAC. In the case of RHAC production, maximum percentage adsorption was 96.5% at an acid concentration of 45%, time of 240 minutes and carbonization temperature of 575 °C.

Standard	Acid	Carbonization	Carbonization	Experimental	Predicted
Run	Concentration	time	temperature	Percentage	Percentage
	(%)	(minutes)	(°C)	Adsorbed (%)	Adsorbed (%)
1	20	60	400	52.5	52.8
2	50	60	400	35.7	37.4
3	20	180	400	46.0	48.5
4	50	180	400	20.3	23.9
5	20	60	700	27.1	29.6
6	50	60	700	43.9	47.5
7	20	180	700	47.0	51.4
8	50	180	700	54.4	60.1
9	10	120	550	7.3	4.51
10	60	120	550	4.7	1.1
11	35	19	550	83.3	81.4
12	35	221	550	95.1	88.4
13	35	120	298	43.7	41.4
14	35	120	802	59.0	52.4
15	35	120	550	51.0	54.8
16	35	120	550	55.3	54.8
17	35	120	550	52.9	54.8
18	35	120	550	54.4	54.8
19	35	120	550	58.3	54.8
20	35	120	550	55.4	54.8

Table 4.5: Experimental and predicted values for CCAC production

Standard	Acid	Carbonization	Carbonization	Experimental	Predicted
Run	Concentration	time	temperature	Percentage	Percentage
	(%)	(minutes)	(°C)	Adsorbed (%)	Adsorbed (%)
1	30	80	400	51.3	49.9
2	60	80	400	35.7	39.4
3	30	200	400	46.6	49.6
4	60	200	400	35.8	40.7
5	30	80	750	53.7	55.5
6	60	80	750	34.5	38.2
7	30	200	750	68.9	71.9
8	60	200	750	48.3	56.4
9	19.8	140	575	20.9	20.3
10	70.2	140	575	7.3	-1.6
11	45	39.1	575	75	73.5
12	45	240.9	575	96.5	88.5
13	45	140	280.7	56.5	53.6
14	45	140	869.3	78	71.4
15	45	140	575	61.1	62.9
16	45	140	575	63.5	62.9
17	45	140	575	62.6	62.9
18	45	140	575	63.6	62.9
19	45	140	575	60.6	62.9
20	45	140	575	61.4	62.9

Table 4.6: Experimental and predicted values for RHAC production

4.1.3 Error analysis of carbonization process

The Normal plots of Residuals in Figures 4.1 and 4.2 were used to determine whether the points will follow a straight line when plotted against the normal probability. In that case, it is concluded that the residuals follow a normal distribution and that the selected model was adequate in predicting the response variables in the experimental values (Onu and Nwabanne, 2014). Figures 4.1 and 4.2 showed that the points were closely distributed to the straight line of the plot, hence confirming the good relationship between the experimental values and the predicted values of the response though some small scatter like an "S" shape is always expected.



Figure 4.1: Normal Plot of Residuals for the CCAC process



Figure 4.2: Normal Plot of Residuals for the RHAC process

4.1.4 The Three Dimensional (3-D) response surface plots

Three dimensional (3-D) surface plots generated from the quadratic model predicted by the software and used to visualize the relationship between the experimental variables and the responses, The 3-D response surface plots are graphical representation of the interactive effects of any two variables or factors. It involves two varying factors at a time while keeping all other factors constant as shown in Figures 4.3 to 4.8. The surface plots were plotted as a function of two factors at a time maintaining all other factors at fixed levels. They are helpful in understanding the single and interaction effects of all the factors. The nature of the response surface curves shows the interaction between the

variables. The elliptical shape of the curve indicates good interaction of the two variables and circular shape indicates no interaction between the variables. The elliptical nature of the contour in the figures depicted mutual interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted percentage adsorbed as indicated by the surface-confined in the smallest ellipse in the contour diagrams.



Figure 4.3: 3D Surface plot for combined effects of carbonization temperature and percentage concentration using CCAC



Figure 4.5: 3D Surface plot for combined effects of carbonization time and Temperature using CCAC



Figure 4.4: 3D Surface plot for combined effects of carbonization time and percentage concentration using CCAC



Figure 4.6: 3D Surface plot for combined effects of carbonization time and temperature using RHAC





Figure 4.7: 3D Surface plot for combined effects of carbonization temperature and acid concentration using RHAC

Figure 4.8: 3D Surface plot for combined effects of carbonization time and acid concentration using RHAC

4.1.5 Validation of the production process

The adsorption experiment was validated by repeating the process at the optimum conditions of 35% percentage concentration, carbonization time of 221 minutes and carbonization temperature of 550°C for CCAC adsorbent. A value of 94.7 % was obtained which is in close agreement to the initial 95.1% obtained at the same conditions for CCAC production. For RHAC production, the adsorption was repeated at a percentage acid concentration of 45%, time of 240 minutes and carbonization temperature of 575 °C, percentage adsorption of 95.7% was obtained which is equally in close agreement to the 96.5% obtained.

4.2 Characterization of the adsorbents

4.2.1 Physical properties of the adsorbents

The physical properties of the adsorbents were presented in Table 4.7. For the RHAC, the fixed carbon was not very high at 10.14% while the CCAC gave 33.47%. This indicates that the carbon content of corn cob is higher than that of rice husk. The carbon content in CCAC and RHAC were relatively high because according to Dipa, et al, (2015), during the carbonization and activation processes, the hydrogen, nitrogen, sulphur and oxygen contents decreased considerably by decomposing leaving the carbonaceous product very richer in carbon. Sivakumar and Palanisamy (2009) reported a fixed carbon of 57.94% foractivated carbon produced from Euphorbia Antiquorum L while Lua and Guo (1998) reported values ranging from 23.7 to 87.13.

Moisture content was measured from loss of water over initial mass of raw materials. As temperature increased, moisture content usually decreases. The moisture content was less than 7.0% for both adsorbents as seen in Table 4.7. This is as expected because carbonization involves great loss of moisture. Maheswari et al (2008) obtained a moisture content of 4.33% while Okpe et al (2018) obtained a moisture content of 5.8% in activated carbon prepared from kola nut shell.

The iodine number was high at 461 mg/g for RHAC and 888.34mg/g for CCAC. Iodine number is used as an index to investigate the internal structure and surface area of the activated carbon. In the production of activated carbon from pinecone, Samarghandi et al (2009) obtained an iodine number of 483.54mg/g. A high value of iodine number corresponds to high surface area of the activated carbon. Activated carbons with very high iodine numbers can be attractive for waste water treatment. Each 1.0mg of iodine

adsorbed is considered to represent 1.0m² of activated carbon internal area (Al-Quodah and Shawabkah, 2009).

The pH of activated carbon can be defined as the pH of a suspension of carbon in distilled water. The chemical nature of the carbon surfaces was globally inferred from the acidity or pH of the carbon. The pH was 6.8 and 6.3 for RHAC and CCAC respectively suggesting weak acidic surface properties. Valix et al (2004) obtained pH between 6.4 and 7.4 for activated carbon prepared from bagasse while Okpe et al (2018) reported a pH of 7.4 which is slightly alkaline.

The porosity index was 0.339 for RHAC and 0.235 for CCAC. The volatile matter obtained in RHAC was 30.82% which was almost twice that in CCAC at 18.01%. Lua and Guo (1999) reported values ranging from 4.08 to 74.86% for palm waste.

Property	RHAC	CCAC
Bulk density (g/ml)	0.448	0.625
рН	$6.8~\pm~0.2$	6.3 <u>+ 0</u> .2
Ash content (%)	5.79	5.82
Iodine Number (mg/g)	461.84	888.34
Moisture content (%)	6.5	5.5
Porosity(η)	0.339	0.235
Volatile matter (%)	30.82	18.01
Fixed Carbon (%)	10.14	33.47

Table 4.7: Physical properties of the activated adsorbents

4.2.2 BET surface area and pore size distribution

The N₂ adsorption isotherm of the activated carbon at 77K was used to obtain the surface area. For the RHAC, the BET surface area was $471.7m^2/s$ and for CCAC, the BET surface area was $903.7m^2/s$ as shown in Table 4.8. Parimalam, et al (2011) obtained a BET surface area of 807 m²/s for activated carbon derived from *ananascomosus*.

The surface area was high as a result of the presence of excess pores that developed during the activation and carbonization process. The larger the surface area, the better the adsorption potentials of the adsorbents. The micropore volume was $0.179 \text{ cm}^2/\text{g}$ and $0.389 \text{ cm}^2/\text{g}$ for RHAC and CCAC respectively. These values are similar to those reported by Adegboyega, et al (2015) and Dipa, et al (2015). The pore radius was 16.20A° for both adsorbents. The values obtained provide qualitative information on the adsorption mechanism and the pore structure of the activated carbons.

Property	RHAC	CCAC
Multipoint BET surface area	471.67	903.7
(m^2/s)		
Average pore width (nm)	6.247	5.55
Micropore volume (cm ² /g)	0.179	0.389
Adsorption energy (KJ/mol)	4.162	4.68
Pore radius (A ^o)	16.20	16.20

Table 4.8 BET surface area	a
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4.2.3 Scanning electron microscope (SEM)

SEM images were used to study the morphology of the adsorbents. It was obtained using a magnification of 500x and 1000x for the adsorbents sieved at 200µm. The figures of the SEM images were shown in Figures 4.9 to 4.14. The images of CCAC and RHAC indicate clear textural and morphological changes between the raw rice husk and corn cob and the activated carbons produced from them.

Figures 4.11 to 4.14 showed that the surface morphologies and texture of the activated carbons were characterized by ragged and rough surfaces. Prominent interspatial pores could also be observed within the matrix of the activated adsorbent. These pores are an index of good adsorption properties. There are large pores of different shapes as can be observed in figures 4.13 and 4.14. This is probably because the activating agents increased the surface area and porosity of activated carbon

The corn cob particles were seen to have disintegrated by the effect of carbonization. This is likely as a result of intensive heat or a chemical acid used in the carbonization. Figures 4.10, 4.13 and 4.14 show the difference in the morphology of the rice husk and the activated carbon produced from it. It indicated that the texture and surface morphology of the activated carbon were characterized by rough surfaces. Interspatial pores were seen within the matrix of the adsorbent indicating good adsorption properties. The large pores observed is due to the fact that the activating agents increases the contact area between the carbon and the activating agent.

The result ascertained that the macro pores were clearly visible after activation facilitating the easy diffusion of more number of phenol molecules into the pore structure and also adsorbed on the surface of the adsorbent.





Figure 4.9 SEM image of unactivated corn cob

Figure 4.10 SEM image of unactivated rice husk



Figure 4.11 SEM image of CCAC at 500x



Figure 4.12 SEM image of CCAC at 1000x



Figure 4.13 SEM image of RHAC at 500x

Figure 4.14 SEM image of RHAC at 1000x

4.2.4 Fourier Transform Infra-Red

The Fourier Transform Infra-Red (FTIR) technique is an important tool to identify the characteristic functional groups, which are instrumental in the adsorption of aromatic compounds. The chemical structure of the adsorbent is of vital importance in understanding the adsorption process.

FTIR Spectroscopy analyses result of the unactivated and activated samples are presented in Tables 4.9 to 4.12 while the FTIR spectrums are given in the appendix. The wave number ranged from 3693.8 to 670 cm⁻¹ with peaks from 96.68 to 83.45 cm⁻² for the CCAC and RHAC adsorbents as seen in the appendix. These FTIR spectra results were compared with known signature of identified materials in the FTIR library (Stuart, 2004; Vyazovkin, 2012). Some compounds such as carboxylic acids, ethers, esters and nitro compounds were more visible to the spectroscopy only after the activation. These may probably be due to the high temperature involved and the chemical activities of the inorganic acid used in the activation which revealed the presence of these compounds.

The absorption band in the 3600 cm⁻¹ region is due to O-H stretching of carboxylic acids group; while in the region of 3200 to 3300 cm⁻¹ is due to O-H bending of the alkanol groups. The alkanes and alkyls were in the region of 2900 – 3000 cm⁻¹ due to C – H stretching while esters corresponds to C – O – C stretching in the wavelength of 2200 to 2210 cm⁻¹. The nitro compounds which were not visible in the unactivated compounds correspond to C – N stretching in the region of 1000 to 1020 cm⁻¹. N-H bending of amides group while in the region of 1050-1035 cm⁻¹ is due to C-O stretching of alcohols group. The coupled vibrations are appreciable due to the availability of various constituents (Preeti and Singh, 2007). The –C=C- stretch indicates the presence of alkenes while the C-Cl stretch and vibration suggest the presence of alkyl halides. The FTIR analysis revealed that the corn cob can be a good source of some hydrocarbons such as alkenes, alkyl halides, alcohols etc.

Wave number (cm ⁻¹)	Peak Area (cm ⁻²)	Bond Source	Compound
3186.9	76.0	O – H bending	Alkanols
2374.3	76.6	C- H vibration	Alkanes
2109.7	77.9	$-C \equiv C - stretching$	Alkynes
1994.1	79.7	-C = C - stretching	Alkenes
1908.4	79.2	- O – H – bending	Alkanols
1684.8	76.4	N – H bending	Amides
1561.8	70.3	N – H bending	Amides
1058.7	61.2	C - O - H stretching	Alcohols
670.9	60.3	C – Cl stretching	Alkyl halides

Table 4.9. FTIR analysis result of unactivated rice husk

Wave number (cm ⁻¹)	Peak Area (cm ⁻²)	Bond Source	Compound
3693.8	96.7	-C = O - stretching	Carboxylic acid
3272.6	90.66	O – H bending	Alkanols
3008.0	93.0	- C – H stretching	Carboxylic acid
2922.0	85.1	- C – H stretching	Alkanes and Alkyls
2855.1	88.1	- C – H bending	Alkanes
2202.9	95.6	- C - O - C	Ethers
		stretching	
2035.1	95.2	N – H bending	Amides
1744.4	90.7	C = O - C bending	Esters
1707.1	92.8	C - O - C bending	Esters
1640.0	89.5	N – H bending	Amides
1464.1	91.1	-C = C - stretching	Alkenes
1375.4	91.1	- C – O – H bending	Alkanols
1233.7	90.2	- C – O – H bending	Alkanols
1021.3	77.3	- C – N stretching	Nitro compounds
853.6	87.8	- C – N stretching	Nitro compounds
670.9	83.5	C – Cl bending	Alkyl halides

Table 4.10 FTIR analysis result of RHAC

Table 4.11 FTIR analysis result of unactivated corn cob

Wave number (cm ⁻¹)	Peak Area (cm ⁻²)	Bond Source	Compound
3220.4	89.3	O – H stretching	Alkanols
2094.8	90.9	O – H stretching	Alkanols
11684.8	89.1	N – H bending	Amides
1561.8	86.4	-C = C - stretching	Alkene
1420.1	87.5	O – H bending	Carboxylic acid
1062.3	77.4	C – Cl stretching	Alkyl halides
782.7	69.4	C – Cl stretching	Alkyl halides

Wave number (cm ⁻¹)	Peak Area (cm ⁻²)	Bond Source	Compound
3267.5	78.1	- O – H bending	Alkanols
2922.2	80.7	C – H stretching	Alkanes and Alkyls
2855.1	84.1	C – H stretching	Alkanes
2109.7	93.7	O – H bending	Carboxylic acid
1736.9	88.3	C - O - C stretching	Esters
1636.3	62.7	N – H bending	Amides
1513.3	87.5	-C = C - bending	Alkenes
1420.1	84.2	-C = C - bending	Alkenes
1364.2	83.2	C - O - H stretching	Alkanols
1241.2	91.2	C - O - H stretching	Alkanols
1151.7	76.9	C – H bending	Alkanes
1017.6	56.0	C – N stretching	Nitro compounds
667.2	69.8	C – Cl bending	Alkyl halides

Table 4.12 FTIR analysis result of CCAC

4.3 Batch adsorption studies

The effects of process parameters such as solution temperature, contact time, initial phenol concentration, solution pH, adsorbent dosage and adsorbent particle size on the adsorption process were evaluated

4.3.1 Effect of contact time on the adsorption process

The effect of contact time on the percentage adsorption of phenol was investigated at different initial concentration as depicted in figures 4:15and 4.16. The result showed that most of the adsorption took place at a contact time of about 60 minutes. The contact time of 120 minutes chosen for other batch studies because it was sufficient to attain equilibrium. Some authors reported the same time of 120 minutes in reaching equilibrium

for phenol adsorption (Ihsan,2013; Abdelkreem, 2013; Bazrafshan et al, 2016). Maximum adsorption of about 66% was obtained using rice husk activated carbon (RHAC) while 89% was obtained using corn cob activated carbon (CCAC).

The results obtained from the batch studies indicated that as the sorption time increased, the phenol uptake was characterized by initial rapid and steep adsorption phase, followed by a less steep phase and then a constant phase indicating equilibrium phase. This means that most of the adsorption of phenol took place during the initial 60 minutes of the process. This is probably due to an increased number of vacant sites on the adsorbent available at the initial stage which resulted to increased concentration gradient between the adsorbate in solution and the adsorbate on the adsorbent surface and therefore increased driving force for the mass transfer (Uddin et al, 2007). The implication of this is a high rate of phenol adsorption at the initial stages which decreases as the time increase due to the accumulation of more phenol particles forming a monolayer on the surface of the adsorbent (Onu and Nwabanne, 2014). Goswani and Ghosh (2006) reported that the initial rapid adsorption was probably due to the availability of the micro pore spaces on the surface of the adsorbents for the adsorption. After a lapse of about 60 minutes, the number of active vacant sites decreases and the adsorbent becomes crowded inside the particles and thus impeding the movement of the adsorbate (Kennedy et al, 2007; Nurulhuda et al, 2009).

Equally, it is seen that an increase in initial phenol concentration resulted in a decrease in adsorption efficiency but increase in adsorption capacity (mg/g). This is because the increase in the initial concentration of phenol leads to larger mass transfer driving force which enhances the interaction between the adsorbent and the phenol resulting in higher adsorption capacity (Salim and Abdeslam, 2014).



Figure 4.15 Effect of contact time on adsorption efficiency of phenol for RHAC



Figure 4.16 Effect of contact time on adsorption efficiency of phenol for CCAC

4.3.2 Effect of initial phenol concentration on the adsorption process

Figures 4.17 and 4.18 show the effect of initial phenol concentration on the percentage adsorption of phenol for different temperatures/dosages at a constant pH value of 7.0 and contact time of 120 minutes.

It was observed that as initial phenol concentration increased, there was a decrease in the percentage removal of phenol. According to Ihsan (2013), this can be attributed to the accumulation of phenol particles on the surface of the adsorbate. A fixed mass of adsorbent contains a fixed number of active vacant sites therefore if the initial phenol concentration increases, then the number of phenol ions to be removed will increase with respect to the number of active vacant sites. This factor results in a decrease in the percentage of phenol adsorbed. Furthermore, a higher initial phenol concentration provides an important driving force to overcome all resistance for the phenol between the aqueous and solid phases thus, increasing the phenol uptake (Abdelkreem, 2013). This trend was reported by some authors such as Ekpete et al, (2010) and Maharvi et al, (2004).

The amount of phenol adsorbed per gram of the activated carbons increased from 3.32 to 5.96 mg/g and 4.72 to 15.33 mg/l for corn cob and rice husk adsorbents respectively as the initial phenol concentration increased from 100 to 500 mg/l. This enhances the interaction between the phenol and the prepared activated carbon leading to an increased number of phenol adsorbed per gram of the adsorbent. At higher concentration, the ratio of the initial number of the phenol molecules to the available surface is high (Onu and Nwabanne, 2014; Jadhav and Vanjara, 2004).



Figure 4.17 Effect of initial phenol concentration on adsorption efficiency of phenol for CCAC



Figure 4.18 Effect of initial phenol concentration on adsorption efficiency of phenol for RHAC

4.3.3 Effect of solution pH on the adsorption process

The pH of the solution is one of the most important factors that can affect the adsorption process of phenol in aqueous solution. Generally, solution pH affects the surface charge of adsorbent and degree of ionization of the adsorbate (Bazrafshan et al, 2016). The effect of the pH was determined by varying the pH from 2 to 10 as shown in figures 4.19 to 4.23. The results indicate that the percentage adsorption increased as the pH increased from 2 to 6 and then slightly decreased from pH of 6 to 10. The maximum percentage removal of phenol was obtained at pH of 6 though it is likely to increase at pH of 7 before decreasing. Some researchers indicated that the maximum phenol adsorption can be obtained within the pH range of 6 to 8 (Saravanakumar and Kumar, 2013; Magda et al, 2014; Ihsan, 2013).

At low pH values, the removal of phenol was low mainly due to the presence of hydrogen ions (H^+) that is responsible for suppressing the ionization of phenol. This, therefore, reduces its uptake on polar solvent (Ihsan, 2013; Djebbar et al, 2012). It was also reported that as pH decreased, there is a formation of positive charge on both the adsorbate and adsorbent systems which results in net reduction of phenol removed (Jadhav and Vanjara, 2004).

At higher pH (above 8), the percentage removal of phenol decreased as the pH increased. This is because there is increase in the hydroxide ion (OH⁻) concentration at a high pH which causes a repulse with the negative active sites on the adsorbent thereby decreasing the uptake of phenol and subsequently its percentage adsorbed (Magda et al, 2014). Equally, at high pH, phenol forms salts which are readily ionized leaving negative charges on the phenolic group. These negative charges prevent the uptake of phenol ions (Ihsan, 2013).





Fig 4.19 Effectof solution pH on adsorption efficiency of phenol at initial phenol concentration of 100mg/l

Fig 4.20 Effectof solution pH on adsorption efficiency of phenol at initial phenol concentration of 150mg/l ¹¹⁴



Fig 4.21Effectof solution pH on adsorption efficiency of phenol at initial phenol concentration of 200mg/l



Fig 4.22 Effectof solution pH on adsorption efficiency of phenol at initial phenol concentration of 300mg/l



Fig 4.23 Effectof solution pH on adsorption efficiency of phenol at initial phenol concentration of 500mg/l
4.3.4 Effect of Adsorbent Particle size on the adsorption process

Another factor that can affect the percentage of phenol adsorbed is the particle size of the adsorbent. This was investigated by varying the particle size of the adsorbent from 70 μ m to 850 μ m at constant time of 120 minutes and dosage of 1.5g as shown in figures 4.24 and 4.25.

It was observed that the percentage of phenol adsorbed decreased with increase in particle size. This is because, at constant dosage, the smaller/finer particles tend to yield larger surface area. One of the major properties of every material that must serve as adsorbent is that it must have a large surface area (Onu and Nwabanne, 2014). Equally, the breaking of larger particles tends to open tiny cracks and channels on the surface of the adsorbent resulting in more accessibility to better diffusion. A similar result in adsorption of phenol was reported by Vikrant and Deshmukh (2012).



Fig 4.24 Effect of adsorbent particle size on adsorption efficiency of phenol for CCAC



Fig 4.25 Effect of adsorbent particle size on adsorption efficiency of phenol for RHAC

4.3.5 Effect of adsorbent dosage on the adsorption process

The effect of adsorbent dosage on the removal of phenol is shown in figure 4.26 and 4.27. The adsorbent dosage used varied from 0.4 to 2.0g. The percentage of phenol adsorbed was observed to increase as the adsorbent dosage increased. This is mainly attributed to the increased adsorbent surface area and the availability of more adsorption sites resulting from the increase in the number of the adsorbents that are competing for the same number of phenolic ions. Therefore, the percentage adsorption of phenol increased as the adsorbent dosage increased (Ihsan, 2013; Uddin et al, 2007).

This trend is in agreement with the works of Abdelkreem, (2013); Saravanakumar and Kumar, (2013) and Marwa et al, (2017). The result also indicated that highest adsorption was obtained at adsorbent dosage of 1.5g, above which was no relative significant increase in the removal rate of phenol. Ihsan (2013) and Abdelkreem (2013) obtained maximum adsorption of phenol at a dosage of 1.0g; Uddin et al (2007) obtained maximum adsorption of phenol at an adsorbent dosage of 1.5g while Saravanakumar and Kumar (2013) obtained maximum adsorption of phenol at a dosage of 2.0g.

It was observed that as the adsorbent dosage increased, the quantity of phenol adsorbed onto the unit mass of the adsorbent reduces therefore, the adsorptive capacity (mg/g) of

the adsorbent decreased. This is because increase in adsorbent dosage increases the availability of more active vacant sites competing for the same number of phenol ions (Marwa et al, 2017). Hence the adsorptive capacity of the adsorbent decreases.



Fig 4.26 Effect of adsorbent dosage on adsorption efficiency of phenol for CCAC



Fig 4.27 Effect of adsorbent dosage on adsorption efficiency of phenol for RHAC

4.3.6 Effect of solution temperature on the adsorption process

Temperature influence on the percentage adsorption of phenol was studied for different temperature ranges of 30, 40, 50 and 60°C as shown in figures 4.28 to 4.32. It was observed that the percentage of phenol adsorbed decreased with increase in temperature. The results suggest that the phenol uptake was favoured at a lower temperature. This is because as the temperature increases, the adsorptive force between the active sites of the adsorbent and the phenol ions were weakened resulting in a decrease in the percentage of phenol adsorbed (Bazrafshan et al, 2016; Mota and Lyubchik, 2018).

Equally, higher temperature enhances the thermal energies of the adsorbate, hence making the attractive force between the phenol species and the adsorbent insufficient to retain the adsorbed molecules at the binding sites (Jadhav and Vanjara, 2004). Similar trend were obtained by some researchers such as Mota and Lyubchik (2008), Bazrafshan et al (2016) though Marwa et al (2017) in using magnetic zinc oxide nanotubes in adsorbing phenol reported that increase in temperature enhances the phenol adsorption on account of the chemical interaction between phenol and the magnetic zinc oxide material.



Fig 4.28Effectof solution temperature on adsorption efficiency of phenol at initial phenol concentration of 100 mg/l

Fig 4.29Effectof solution temperature on adsorption efficiency of phenol at initial phenol concentration of 150 mg/l





Fig 4.30Effectof solution temperature on adsorption efficiency of phenol at initial phenol concentration of 200 mg/l

Fig 4.31 Effectof solution temperature on adsorption efficiency of phenol at initial phenol concentration of 300 mg/l



Fig 4.32Effectof solution temperature on adsorption efficiency of phenol at initial phenol concentration of 500 mg/l

4.4 Isotherm Studies

The adsorption isotherm is the basic requirement for designing any adsorption system (Rajeshkannan et al, 2010). Results of several adsorption isotherms were reported.

4.4.1 One-Parameter Isotherm

4.4.1.1 Henry's Isotherm model

This is the simplest adsorption isotherm, model. It assumes that the amount of surface adsorbate is proportional to the partial pressure of the adsorptive gas (Nimibofa et al, 2017).

Hence, a linear expression is used to relate the equilibrium adsorbate concentrations in the liquid and adsorbed phases in equation 4.3

$$q_e = K_{He}C_e \tag{4.3}$$

where q_e is amount of the adsorbate at equilibrium (mg/g), K_{He} is Henry's adsorption constant, and C_e is equilibrium concentration of the adsorbate on the adsorbent (mg/l).

By plotting q_e against C_e (see appendix C), Henry's adsorption constant K_{Ha} was calculated at a different temperature where it was seen to decrease as the temperature increases.

The correlation coefficients obtained were very high indicating the adsorption of phenol unto these adsorbents agreed with Henry's isotherm model. The Henry's constant K_H was within the range of 0.015 to 0.008 l/g and 0.036 to 0.014 l/g using corn cob and rice husk adsorbents respectively.

4.4.2. Two-Parameter Isotherm

Several two-parameter isotherm models were investigated using the experimental data obtained.

4.4.2.1 Freundlich isotherm model

The plot of $\ln q_e$ against $\ln C_e$ was used to fit the Freundlich isotherm to the experimental data as shown in appendix C. The values of the Freundlich constants K_f and n were calculated from the intercept and the slope respectively and shown in Tables 4.13 and 4.14. The constant K_f is a measure of the adsorption capacity while constant n is a measure of the intensity or favorability of adsorption. The values of K were relatively constant as temperature was varied for both corn cob and rice husk adsorbents. For beneficial adsorption, the value of n will be between 1 and 10 (Ladhe et al, 2011). The values of n obtained generally increased from 3.2 to 5.8 for RHAC and from 4.5 to 6.5 for CCAC as the temperature increased showing beneficial adsorption of phenol on these adsorbents.

Salim and Abdeslam (2014) reported that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics. Hence both activated carbons showed good adsorption characteristics at low temperature based on the n values being less than 10 at low temperature. It was observed that at a relatively high temperature of 60°C, that the value of n increased up to 23.8 for CCAC suggesting that at high temperature, beneficial adsorption was not obtainable.

The correlation coefficient (\mathbb{R}^2) values of about 0.7 for adsorption using CCAC and 0.9 for adsorption using RHAC shows that RHAC performed better than CCAC. A similar result was obtained by Ladhe et al, (2011). This emphasized the heterogeneity of the surface binding sites on the matrix of the adsorbent towards phenol molecules. Freundlich isotherm is empirical and describes heterogeneous surface energy system (Jolanta et al, 2012; Ihsan 2013).

As the temperature increased the R^2 values of both adsorbents decreased confirming that high temperature did not favour the Freundlich isotherm. However, in adsorption using clay, Xiangliang and Dayong (2009) reported that the Freundlich isotherm analysis favoured high temperature.

4.4.2.2 Langmuir isotherm model

In fitting the Langmuir isotherm, the values of $1/q_e$ were plotted against $1/C_e$ as indicated in appendix C. q_e is the equilibrium adsorption capacity (mg/g) while C_e is the equilibrium concentration in the solution (mg/l). The Langmuir model assumes that uptake of molecules occurs on a homogeneous surface by monolayer adsorption (Sharma, 2009). The constants q_o and b were determined from the intercept and the slope respectively of the linear plot of C_e/q_e against C_e and tabulated in Tables 4.13 and 4.14. Ihsan (2013) and Uddin et al (2007) reported that q_o and b are Langmuir parameters related to maximum adsorption capacity (mg of solute per gm of adsorbent) and free energy of adsorption, respectively. It was seen that the maximum adsorption capacity q_o decreased from 6.4 to 3.6 mg/g and from 16.9 to 8.2 mg/g for CCAC and RHAC respectively as the temperature increased.

It was observed that the equilibrium data fitted very well to the Langmuir isotherm model than when compared to the Freundlich model because the correlation coefficients were all greater than 0.9. The correlation coefficients values ranged from 0.97 to 0.99 and from 0.92 to 0.97 adsorption using CCAC and RHAC respectively. This shows that CCAC was better in describing Langmuir isotherm than RHAC. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on the activated clay. The Langmuir theory is based on the assumption of monolayer adsorption, where molecules interact only with the surface of sorbent. Moreover, it is assumed that the surface is completely smooth and homogeneous, and there is no interaction between adsorbate molecules on adjacent sites (Jolanta et al, 2012).

The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor, R_L defined by equation 4.4

$$R_{\rm L} = \frac{1}{1 + bC_{\rm o}} \tag{4.4}$$

where C_o is the highest initial solute concentration(mg/L), b is the Langmuir constant.

The value of R_L indicates whether the adsorption isotherm is unfavourable ($R_L>1$), linear ($R_L=1$), favourable ($0 < R_L < 1$), or irreversible ($R_L=0$). The values of R_L were calculated and presented in Tables 4.13 and 4.14.

For the adsorption of phenol on both adsorbents, the R_L values were less than 1 and greater than zero showing that adsorption was favorable. Also, the smaller R_L value indicates highly favourable adsorption (Salim and Abdeslam, 2014). In the dephenolation of wastewater, some authors reported Langmuir isotherm fitted the experimental data very well with a high correlation coefficient (Salim and Abdeslam, 2014, Uddin et al, 2013).

4.4.2.3 Halsay Isotherm Model

The Halsay isotherm was proposed based on the assumption that the multilayer adsorption is at a relatively large distance from the surface (Vicente et al, 2011; Soheila and Hasan 2017; Muhammad, 2015).

The linear form of the Halsay Isotherm is given by equation 4.5

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}}$$
(4.5)

The Halsay constant K_{Ha} and n_{Ha} were determined by using the slope and intercept of the linear plot of lnq_e against lnC_e (see appendix C) and presented in Tables 4.13 and 4.14.

The fitting of the experimental data to the Halsey isotherm model attests to the heterogeneous nature of the adsorbent (Soheila and Hasan, 2017; Vicente et al, 2011).

The correlation coefficient of the adsorption of phenol using rice husk was much higher than that using corn cob suggesting that after carbonization, the rice husk adsorbent was more heterogeneous in nature. Vicente et al (2011) reported that in using activated coconut to remove copper II ions, the experimental data fitted the Halsay isotherm suggesting that the coconut adsorbent has heterogeneous surface.

4.4.2.4 Harkins-Jura isotherm model

The Harkin-Jura isotherm model was also investigated. The model assumes the existence of a heterogeneous pore distribution in the surface of the adsorbents (Soheila and Hasan, 2017).

The linear form of the Harkins-Jura isotherm model is given by equation 4.6

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e$$
(4.6)

The Harkins-Jura isotherm model was evaluated by plotting $1/qe^2$ against log Ce (see appendix C) from which the parametric constants, n_{Ha} and K_{Ha} were evaluated.

The values of the Harkins-Jura constants obtained using both adsorbents in adsorbing phenol are shown in Tables 4.13 and 4.14 together with their regression coefficients. It was seen that the Harkins-Jura isotherm model fitted the adsorption of phenol using rice husk adsorbent more than using corn cob adsorbent. The general low regression coefficients obtained from both adsorbents show the inapplicability of Harkins-Jura isotherm model for phenol adsorption unto these adsorbents.

Foo and Hameed (2010) reported that the Harkin-Jura isotherm model showed a better fit than most other isotherm models in the adsorptive removal of reactive black 5 from wastewater using Bentonite clay.

4.4.2.5 Temkin isotherm model

The Temkin isotherm was analyzed by plotting q_e against lnC_e as shown in appendix C. The assumption of the Temkin isotherm is that the fall in the heat of adsorption is linear rather logarithmic (Sivakumar and Palanisamy, 2009). It involves a study of the heat of adsorption and the adsorbent-adsorbate interaction. The values of the constants b_T and A were calculated from the slope and intercept respectively and tabulated in Tables 4.13 and 4.14.

The values of the adsorbent-adsorbate interaction constant A were all less than 20 l/g showing that there were not sufficient interaction between the adsorbent and the adsorbate. The Temkin constant b_T is related to the variation of adsorption energy (Hadi et al, 2010). It was observed to increase from 2.833kJ/mg to 18.706 kJ/mg for CCAC and 0.837 kJ/mg to 2.309kJ/mg for RHAC as the temperature increased. Rajeshkannan et al, (2010) reported that a decrease in the value of b_T as the temperature increased. The b_T increased with temperature indicating that the adsorption was more favoured at a lower temperature. The correlation coefficient R² was between 0.7 and 0.4 for CCAC while for RHAC, it was between 0.8 and 0.6. This shows that the experimental data did not follow the Temkin isotherm.

4.4.2.6 Fowler-Guggenheim isotherm model

Fowler-Guggenheim isotherm takes into consideration the lateral interaction of the adsorbed molecules. The linear form of the Fowler-Guggenheim isotherm model is given by Soheila and Hasan (2017) and Sampranpiboon et al (2014) in equation 4.7

$$\ln\left[\frac{C_{e}(1-\theta)}{\theta}\right] = -\ln K_{FG} + \frac{2w\theta}{RT}$$
(4.7)

where K_{GF} is the Fowler-Guggenheim equilibrium constant (L mg⁻¹); $\theta = (1-C_e/C_o)$ is the degree of surface coverage; W is the interaction energy between adsorbed molecules (kJ mol⁻¹); R is the universal gas constant and is equal to 8.314 J mol⁻¹ K⁻¹ and T is the absolute temperature (K). The values of K_{FG} and W were evaluated from the intercept and the slope respectively, of the linear plot of $\ln Ce(1-\theta)/\theta$ versus θ based on the experimental data (see appendix C) and summarized in Tables 4.13 and 4.14.

This isotherm model is predicated on the fact that the heat of adsorption varies linearly with loading. The sign of the interaction energy W determines the interactions between the adsorbed molecules. If W is positive, the interaction between the adsorbed molecules is attractive and the heat of adsorption due to the increased interaction between the adsorbed molecules increases with the loading of adsorbates. Additionally, if W is negative, the heat of adsorption decreases with the loading of adsorbates, and hence, the interaction among the adsorbed molecules is repulsive (Soheila and Hasan, 2017). When there is no interaction between adsorbed molecules, W=0 and the Fowler-Guggenheim isotherm reduces to the Langmuir equation (Nimibofa et al, 2017).

The correlation coefficients were very high indicating that the experimental data agreed with the Fowler-Guggenheim isotherm. The negative values of the interaction energy (W) for both adsorbents indicate the presence of repulsion between the adsorbed molecules. Soheila and Hasan (2017) obtained a similar trend in Fowler-Guggenheim isotherm. It is important to note that this model is only applicable when surface coverage is less than 0.6 (i.e $\Theta < 0.6$) (Nimibofa et al, 2017).

4.4.2.7 Flory-Huggins Isotherm model

Flory-Huggins isotherm describes the degree of surface coverage characteristics of the adsorbate on the adsorbent (Amin et al, 2015). It can express the feasibility and spontaneous nature of an adsorption process (Horsfall and Spiff, 2005).

The Flory-Huggins isotherm equation is given by equation 4.8

$$\ln\left(\frac{\theta}{C_0}\right) = \ln K_{\rm FH} + n_{\rm FH} \ln (1 - \theta)$$
(4.8)

Where Θ is degree of surface coverage, C_o is initial concentration, n_{FH} and K_{FH} are Flory-Huggins isotherm constants describing number of adsorbates occupying adsorption sites (model exponent) and the equilibrium constant (Lmol⁻¹) respectively (Nimibofa et al, 2017; Foo and Hameed, 2010). The Flory-Huggins isotherm constants (n_{FH} and K_{FH}) were evaluated by using the slope and intercept of the linear plot of ln (Θ / C_o) against ln (1- Θ) in appendix C and expressed in Tables 4.13 and 4.14

The correlation coefficient was very high indicating that the experimental data fitted the Flory-Huggins isotherm. Hamdaoui and Naffrechoux (2007) reported a similar trend in their study of the biosorption of Zinc from aqueous solution using coconut coir dust. Flory-Huggins isotherm equilibrium constant, K_{FH} was used to also calculate spontaneity Gibbs free energy as related by equation 4.7 (Vijayaraghavan et al, 2006)

$$\Delta G^{o} = -RT \ln(K_{FH}) \tag{4.7}$$

where ΔG^0 is standard free energy change, R is universal gas constant 8.314 Jmol⁻¹ K⁻¹, and T is absolute temperature.

The ΔG^0 calculated was negative and increased slightly as temperature increased suggesting that the adsorption of phenol unto these adsorbents was spontaneous.

4.4.2.8 Dubinin-Radushevich isotherm model

The Dubinin-Radushevich Isotherm plots of $\ln q_e$ versus \mathcal{E}^2 are shown in appendix C. ε is the Polanyi potential which is related to the equilibrium concentration (Sivakumar and Palanisamy, 2009). The Dubinin-Radushkevich isotherm is based on physical parameters and with easy applications. Though much importantly, it includes temperature effects and quite fairly predicts the experimental data over a wide concentration range (Inglezakis and Poulopoulos, 2006). The constant β is a constant related to the sorption energy while q_m is the Dubinin-Radushkevich monolayer capacity (mmol/g).

These constants were calculated from the slope and intercept of the plot (see appendix C) and summarized in Tables 4.13 and 4.14 together with the correlation coefficients. The correlation coefficient was very low in the range of 0.34 to 0.58 for adsorption using CCAC and 0.52 to 0.58 for adsorption using RHAC.

The sorption energy was very low ranging from 5×10^{-5} to 8×10^{-6} kJ/mg and from 1×10^{-5} to 2×10^{-5} kJ/mg for adsorption using CCAC and RHAC respectively. Maximum monolayer capacity of 5.66 mol/g was obtained in adsorption using CCAC while the maximum was 10.46 mol/g in adsorption using RHAC. The Dubinin-Radushkevich monolayer capacity was found to steadily decreased as the temperature increased suggesting that less adsorbate was adsorbed at a higher temperature.

The Dubinin-Radusherich Isotherm constant β was used to calculate the mean energy of the adsorption E which could involve the transfer of the free energy of one mole of solute from infinity (in solution) to the adsorbent surface. The results of E greater than 8KJ/mol obtained indicate that the adsorption is predominantly chemisorptions (Arh-Hwang and Yao-Yi, 2010).

4.4.2.9 Jovanovic isotherm model

The Jovanovic model is predicated on the assumptions contained in the Langmuir model but in addition the possibility of some mechanical contacts between the adsorbate and adsorbent (Knaebel, 2004). Jovanovic model can be shown using the following relationship given by Nimibofa et al, (2017) and Samarghandi et al, (2009) in equation 4.8

$$q_{e} = q_{max} \left[1 - e^{(K_{j}C_{e})} \right]$$
(4.8)

This equation can be expressed in linear form as given in equation 4.9

$$\ln q_e = \ln q_{max} - K_j C_e \tag{4.9}$$

where q_e is amount of adsorbate in the adsorbent at equilibrium (mg g-1), q_{max} is maximum uptake of adsorbate obtained from the plot of lnq_e versus C_e , and K_j is Jovanovic constant as shown in appendix C

The correlation coefficients obtained in figures 4.51 and 4.52 suggested that the experimental data did not agree with the Jovanovic isotherm model as such because its

value was not very high as seen in Tables 4.13 and 4.14. Equally, the Jovanovic maximum amount of adsorbate adsorbed (q_{max}) was much lower than the experimentally determined maximum amount of adsorbate adsorbed

4.4.2.10 Kiselev Isotherm model

The Kiselev adsorption isotherm model is also known as localized monomolecular layer model because it assumes that the adsorption is on monolayer only (Kumara et al, 2010).

The Kiselev adsorption isotherm equation is expressed in equation 4.9

$$\frac{1}{C_{e}(1-\theta)} = \frac{1}{\theta} K_{1} + K_{1} K_{n}$$
(4.9)

where K_1 is Kiselev equilibrium constant (Lmg-1) and K_n is equilibrium constant of the formation of a complex between adsorbed molecules (Nimibofa et al, 2017)

The Kiselev equilibrium data from adsorption processes are modelled by plotting $1/(1 - \Theta)$ versus $1/\Theta$ as given in appendix C and then determining k_1 and k_n from the slope and intercept respectively.

It was observed that the equilibrium data did not fit the Kiselev isotherm model because the correlation coefficients were all less than 0.9 as presented in Tables 4.13 and 4.14. Song et al, (2014) and Israel et al, (2013) reported that the Kiselev isotherm model is only valid when surface coverage Θ is less than 0.68.

Isotherm	Temperature					
model						
	30°C	35°C	40° C	50°C	60°C	
Freundlich						
R^2	0.778	0.793	0.564	0.771	0.424	
n	5.848	4.808	4.566	6.494	23.809	
$ m K_{f}$	2.268	1.809	2.430	1.954	2.740	
Langmuir						
\mathbf{R}^2	0.989	0.984	0.984	0.993	0.973	
q _o	6.410	6.494	5.128	5.050	3.584	
b	21.712	36.091	20.779	41.298	35.416	
В	4.60 x 10 ⁻⁴	2.77 x 10 ⁻⁴	4.81 x 10 ⁻⁴	2.42 x 10 ⁻⁴	2.82 x 10 ⁻	
Halsay						
\mathbf{R}^2	0.778	0.793	0.564	0.771	0.424	
n _{Ha}	5.848	4.587	7.752	6.494	23.810	
K _{Ha}	120.24	15.18	976.25	77.53	2.65	
Harkins-Jura	ı					
\mathbb{R}^2	0.829	0.831	0.601	0.756	0.403	
A _H	33.33	23.81	34.48	23.26	62.50	
B _H	3.40	3.14	3.83	3.54	7.63	
Tempkin						
R^2	0.744	0.764	0.537	0.774	0.435	
b	2833	2508	4403	4229	18,706	
А	3.005	1.119	18.867	5.662	18.901	
Flower-						
Guggenhein						
R^2	0.994	0.988	0.996	0.989	0.981	
$- W (x 10^3)$	12.476	11.566	12.786	11.905	12.837	
$K_{ar}(x10^{-5})$	9.9	12.09	7.67	8.47	4.88	
ΔG (KJ)	23.218	23.097	24.656	24.788	26.660	
Flory-						
Huggins						
R^2	0.900	0.895	0.909	0.907	0.913	

Table 4.13 Isotherm parameters	for phenol	adsorption	using CCAC
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n_{FH} 3.3780.2693.5143.436 $K_{FH} \times 10^{-3}$ 2.762.792.242.12	3.762 1.45
$K_{FH} \ge 10^{-3}$ 2.76 2.79 2.24 2.12	1.45
Dubinin –	
Radushkevich	
R^2 0.557 0.584 0.343 0.479	0.075
$B_D 7.0 x 10^{-5} 8.0 x 10^{-5} 5.0 x 10^{-5} 6.0 x 10^{-5}$	8.0 x 10 ⁻⁶
q _D 5.663 5.496 4.821 4.424	3.404
Jovanovic	
R^2 0.980 0.976 0.871 0.886	0.654
K _j 0.002 0.003 0.002 0.002	0.001
q _{max} 3.76 3.36 3.45 3.13	3.18
Kiselev	
R^2 0.847 0.836 0.871 0.875	0.886
K ₁ 0.045 0.036 0.032 0.025	0.022
K _n 3.044 3.083 3.125 3.160	3.227

Table 4.14 Isotherm parameters for phenol adsorption using RHAC

Isotherm			Temperature		
model					
	$30^{\circ}C$	35°C	$40^{\circ}C$	50°C	60°C
Freundlich					
R^2	0.936	0.941	0.921	0.732	0.893
n	3.155	3.831	4.310	5.814	4.629
$ m K_{f}$	2.337	2.707	2.818	3.152	2.583
Langmuir					
R^2	0.922	0.971	0.959	0.926	0.952
q_{o}	16.949	11.905	10.101	7.092	8.197
b	53.797	36.988	41.596	35.681	56.254
В	1.86 x 10 ⁻³	2.70 x 10 ⁻³	2.40 x 10 ⁻³	2.80 x 10 ⁻³	1.78 x 10 ⁻³
Halsay					
R^2	0.936	0.941	0.921	0.732	0.898
n _{Ha}	3.155	3.831	4.310	5.882	4.629
K _{Ha}	14.559	45.426	86.96	85.66	80.93
Harkins-Jura					

\mathbf{R}^2	0.945	0.944	0.956	0.771	0.939
A_{H}	125	125	125	125	100
B _H	6.50	6.50	6.88	7.50	7.50
Tempkin					
\mathbf{R}^2	0.861	0.891	0.864	0.698	0.836
b	836.9	1157.6	1429.0	2309.1	1898.9
А	2.945	1.466	1.035	4.526	1.381
Flower-					
Guggenhein					
\mathbf{R}^2	0.987	0.981	0.976	0.995	0.984
$- W (x 10^3)$	14.699	15.505	15.444	15.228	13.937
$K_{ar} (x10^{-5})$	1.54	8.29	7.07	5.62	1.06
$\Delta G (KJ)$	27.91	29.96	30.86	31.96	30.75
Flory-					
Huggins					
R^2	0.916	0.908	0.916	0.913	0.918
n _{FH}	1.59	1.70	1.77	1.89	1.80
$K_{FH} \ge 10^{-3}$	4.82	3.89	3.32	2.49	2.74
Dubinin -	_				
Radushkevich	1				
\mathbf{R}^2	0.557	0.582	0.539	0.523	0.522
B _D	$2.0 \ge 10^{-5}$	$2.0 \ge 10^{-5}$	$2.0 \ge 10^{-5}$	$1.0 \ge 10^{-5}$	$2.0 \ge 10^{-5}$
$q_{\rm D}$	10.46	9.34	8.42	7.16	7.17
Jovanovic					
\mathbf{R}^2	0.912	0.890	0.914	0.899	0.899
$\mathbf{K}_{\mathbf{j}}$	0.003	0.002	0.002	0.002	0.002
q _{max}	6.19	6.07	5.74	4.99	4.99
Kiselev					
\mathbf{R}^2	0.883	0.874	0.833	0.879	0.869
\mathbf{K}_1	0.088	0.067	0.050	0.040	0.032
K _n	2.193	2.194	2.240	2.225	2.281

4.5 Non linear parametric isotherm models and error analysis

4.5.1 Two Term parametric isotherm models

Non linear isotherm analysis was carried out using the non linear form of some of the linear isotherm models that have already been discussed in the linear section. These isotherm models include Freundlich model, Langmuir model, Tempkin model, Harkins Jura model, Halsay model and DubininRaduvechi model.

4.5.1.1 Non linearFreundlich isotherm model

The non linearFreundlich model is given in equation 4.10

$$q_e = K_f C_e^{1/n} \tag{4.10}$$

The non linearFreundlich isotherm model was analysed using the add-in solver in excel software. The values of the correlation coefficient were very high ranging from 0.995 to 0.999 as seen in Tables 4.15 and 4.16.

The values of K ranged from 1.38 to 1.03 while the values on n ranged from 4.12 to 4.75 increasing slightly as temperature increased for both corn cob and rice husk adsorbents showing beneficial adsorption of phenol on these adsorbents. Ladhe et al, (2011) reported that for beneficial adsorption, the value of n will be between 1 and 10. Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. The amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites are occupied first until adsorption energy is exponentially decreased upon the completion of the adsorption process.

This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of a monolayer. The different error terms seem to indicate that the adsorption using CCAC is more favoured that the adsorption of phenol using RHAC. This is because the error terms have lower values for the adsorption using CCAC.

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
К	1.38	1.37	1.25	1.23	1.03	
n	4.12	4.12	4.4	4.5	4.75	
R^2	0.999339	0.993289	0.999787	0.998795	0.998089	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.002655	0.036591	0.000264	0.004311	0.002784	
MPSD	0.00211	0.007913	0.000731	0.003013	0.002742	
RMSE	0.008897	0.032696	0.002554	0.010119	0.00718	
ARE	0.059679	-0.22382	-0.02066	0.085209	-0.07755	
SSE	0.000317	0.004276	2.61E-05	0.00041	0.000206	
X2	5.31E-05	0.000732	5.28E-06	8.62E-05	5.57E-05	
EABS	0.017794	-0.06539	-0.00511	0.020237	-0.01436	
Sre	0.041885	0.158428	0.015555	0.064972	0.063194	

 Table 4. 15:Nonlinear Freundlich isotherm parameters using CCAC

Table 4. 16: Nonlinear Freundlich isotherm parameters using RHAC

Parameter	TEMPERATURE (° C)				
	30	35	40	50	60
K	3.8	3.45	3.22	2.63	2.74
n	4.1	4.4	4.6	4.75	4.77
\mathbf{R}^2	0.994164	0.99902	0.999458	0.999917	0.997829
Mean	9.48733	8.516067	7.770733	6.677933	6.640733
HYBRID	0.650411	0.064602	0.029626	0.002715	0.095096
MPSD	0.020596	0.007163	0.005124	0.001725	0.009989
RMSE	0.223304	0.06377	0.040883	0.011127	0.067315
ARE	0.582533	-0.20261	-0.14493	0.048802	0.28254
SSE	0.19946	0.016267	0.006686	0.000495	0.018125
X2	0.013008	0.001292	0.000593	5.43E-05	0.001902
EABS	0.446609	-0.12754	-0.08177	0.022254	0.13463
Sre	0.135924	0.075066	0.063166	0.026548	0.147909

4.5.1.2 Non linear Langmuir isotherm model

The Langmuir model assumes that uptake of MG molecules occurs on a homogeneous surface by monolayer adsorption (Sharma, 2009). The Langmuir isotherm in its non linear form is given as in equation 4.11

$$q_e = \frac{q_m K_1 C_e}{1 + K_1 C_e} \tag{4.11}$$

The correlation coefficients obtained in the non linear Langmuir isotherm analysis were high but the value of the experimental values of the amount of phenol adsorbed per gram of adsorbent (4.1 mg/g to 5.9 mg/g) were much lower than the calculated Langmuir value which ranged from 10 mg/g to 20 mg/g as seen in Tables 4.17 and 4.18.

According to Jolanta et al, (2012), it is assumed that the surface is completely smooth and homogeneous, and there is no interaction between adsorbate molecules on adjacent sites. The Langmuir theory is based on the assumption of monolayer adsorption, where molecules interact only with the surface of sorbent.

Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered.

Parameter	TEMPERATURE (° C)						
	30	35	40	50	60		
K	0.001	0.001	0.001	0.00093	0.00093		
$q_{\rm m}$	20.4	20.1	16.6	16.6	12.7		
\mathbf{R}^2	0.998612	0.999014	0.998282	0.999063	0.998909		
Mean	5.271467	5.045067	4.5938	4.166933	3.374867		
HYBRID	0.005571	0.005377	0.002123	0.003352	0.00159		
MPSD	0.003057	0.003033	0.002072	0.002657	0.002072		
RMSE	0.018227	0.017725	0.010245	0.012618	0.007672		
ARE	0.086452	-0.0858	-0.05862	0.075137	-0.0586		
SSE	0.000664	0.000628	0.00021	0.000318	0.000118		
X2	0.000111	0.000108	4.25E-05	6.7E-05	3.18E-05		
EABS	0.025777	-0.02507	-0.01449	0.017845	-0.01085		
Sre	0.030337	0.030365	0.022065	0.028646	0.023874		

 Table 4.17: Nonlinear Langmuir isotherm parameters using CCAC

Table 4. 18: Nonlinear Langmuir isotherm parameters using RHAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
К	0.007	0.0058	0.0051	0.0046	0.0046	
$q_{\rm m}$	23.2	19.7	18.2	14.5	15.2	
\mathbf{R}^2	0.999241	0.999554	0.998346	0.999593	0.999189	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.084541	0.029373	0.090454	0.013297	0.03552	
MPSD	0.007425	0.00483	0.008954	0.003818	0.006105	
RMSE	0.113855	0.060812	0.101026	0.034823	0.058181	
ARE	0.21002	-0.13662	-0.25324	0.107999	0.172678	
SSE	0.025926	0.007396	0.020412	0.002425	0.00677	
X2	0.001691	0.000587	0.001809	0.000266	0.00071	
EABS	0.161015	-0.086	-0.14287	0.049248	0.082281	
Sre	0.024502	0.025308	0.055186	0.029376	0.045198	

4.5.1.3 Non linearTempkin isotherm model

The Temkin isotherm describes the heat of adsorption and the adsorbent-adsorbate interaction. Its non linear form is given in equation 4.12

$$qe = \frac{RT}{b} \ln(AC_e)$$
(4.12)

The assumption of the Temkin isotherm is that the fall in the heat of adsorption is linear rather logarithmic (Sivakumar and Palanisamy, 2009).

Hadi et al, (2010) reported that the Temkin constant b is related to the variation of adsorption energy. The adsorption energy obtained when using corn cob activated carbon ranged from 1.6 to 2.3 KJ/mg which is less than that obtained when using rice husk activated carbon which ranged from 0.5 to 0.69 KJ/mg as summarized in Tables 4.19 and 4.20. These values were less than the adsorption energy obtained in the linear Temkin isotherm analysis. They increased with temperature indicating that the adsorption was more favoured at lower temperature.

The values of the adsorbent-adsorbate interaction constant A were all less than 20 l/g showing that there were not sufficient interaction between the adsorbent and the adsorbate.

The correlation coefficient R^2 was not as high as what was obtained in other isotherm models. This shows that the experimental data did not follow the Temkin isotherm.

According to Soheila and Hasan (2017), the heat of adsorption of all molecules linearly decreases with the surface coverage due to adsorbent-adsorbate interactions. In addition, it assumes that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy.

Parameter	TEMPERATURE (° C)				
	30	35	40	50	60
Α	0.082	0.082	0.068	0.0645	0.051
b (J/mg)	1640	1630	1880	1930	2332
\mathbf{R}^2	0.998474	0.970622	0.998545	0.999563	0.999969
Mean	5.271467	5.045067	4.5938	4.166933	3.374867
HYBRID	0.00612463	0.16018602	0.00179848	0.0015643	4.4922E-05
MPSD	0.003205	0.016557	0.001907	0.1629354	0.000348
RMSE	0.013514	0.068411	0.006667	0.006095	0.000912
ARE	0.090644	-0.4683	6.46402572	-0.05133	-0.00985
SSE	0.0007305	0.0187204	0.0001778	0.0001486	3.327E-06
X2	0.000122	0.003204	3.6E-05	3.13E-05	8.98E-07
EABS	0.027027	-0.13682	-0.01333	-0.01219	-0.00182
Sre	0.031809	0.16574	0.020308	0.019569	0.004013

Table 4.19:Nonlinear Tempkin isotherm parameters using CCAC

Table 4.20:Nonlinear Tempkin isotherm parameters using RHAC

Parameter	TEMPERATURE (° C)				
	30	35	40	50	60
b (J/mg)	520	603	658	711	691
Α	0.067	0.051	0.046	0.029	0.029
\mathbf{R}^2	0.999803	0.999373	0.99764	0.999611	0.996743
Mean	9.487333	8.516067	7.770733	6.677933	6.640733
HYBRID	0.02193473	0.04129944	0.12903212	0.01271697	0.14267017
MPSD	0.003782	0.005727	0.010694	0.003734	0.012235
RMSE	0.041008	0.050988	0.08532	0.024081	0.082451
ARE	-0.10698	-0.162	-0.30247	-0.10562	0.346071
SSE	0.0067266	0.0103992	0.0291182	0.0023196	0.0271929
X2	0.000439	0.000826	0.002581	0.000254	0.002853
EABS	-0.08202	-0.10198	-0.17064	-0.04816	0.164903
Sre	0.012481	0.03001	0.065912	0.028728	0.090584

4.5.1.4 Non linear Harkins-Jura isotherm model

The Harkins-Jura non linear is given by equation 4.13

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}}$$
(4.13)

The correlation coefficients obtained were all very high (above 0.9) suggesting good fitting. The Harkins-Jura constant A ranged from 111 to 47mg/l for corn cob adsorbent. This is much lower than the values obtained when using rice husk adsorbent which ranged from 655 to 297 mg/l. These values decreased with increase in temperature for both adsorbents as given in Tables 4.21 and 4.22.

Harkin-Jura isotherm model equally assumes the possibility of multilayer adsorption on the surface of absorbents having heterogeneous pore distribution (Nimibofa et al, 2017). The values of the Harkins-Jura constants together with the regression coefficients are presented in Tables 4.21 and 4.22 for the adsorption of phenol onto RHAC and CCAC. The model assumes the existence of heterogeneous pore distribution in the surface of the adsorbents (Soheila and Hasan, 2017).

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
Α	111	107	86	80.13	47.2	
В	0.54	0.54	0.88	0.87	0.82	
\mathbf{R}^2	0.998078	0.999374	0.999589	0.99674	0.998172	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.00771511	0.00341239	0.00050733	0.01166653	0.00266348	
MPSD	0.003597	0.002417	0.001013	0.004956	0.002682	
RMSE	0.015167	0.009985	0.003541	0.016646	0.007023	
ARE	0.101735	0.068351	-0.02865	-0.14017	0.075853	
SSE	0.0009202	0.0003988	5.016E-05	0.0011083	0.0001973	
X2	0.000154	6.82E-05	1.01E-05	0.000233	5.33E-05	
EABS	0.030334	0.01997	-0.00708	-0.03329	0.014045	
Sre	0.0357010.	0.02419	0.010786	0.053442	0.030904	

Table 4.21: Nonlinear Harkin Jura isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
Α	655	503	413	286	297	
В	0.45	0.58	0.65	0.799	0.82	
\mathbf{R}^2	0.998081	0.997494	0.998593	0.998074	0.997446	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.2138743	0.16520242	0.07693658	0.06296987	0.11185287	
MPSD	0.01181	0.011455	0.008257	0.008309	0.010834	
RMSE	0.128051	0.101978	0.065883	0.053586	0.073005	
ARE	0.334046	-0.324	-0.23356	-0.23502	0.306424	
SSE	0.0655881	0.041598	0.017362	0.0114857	0.0213192	
X2	0.004277	0.003304	0.001539	0.001259	0.002237	
EABS	0.256102	-0.20396	-0.13177	-0.10717	0.146011	
Sre	0.038972	0.06002	0.050896	0.063927	0.080206	

Table 4.22: Nonlinear Harkin Jura isotherm parameters using RHAC

4.5.1.5 Non linear Halsay isotherm model

The Halsey isotherm was used to investigate the multilayer adsorption at a relatively large distance from the surface (Nimibofa et al, 2017). The non linear form is given as

$$q_e = \exp\left(\frac{\ln K_H - \ln C_e}{n_H}\right) \tag{4.14}$$

The values of the correlation coefficient were very high for both adsorbents.

The Halsay constant K_{Ha} decreased as the temperature increased while n_{Ha} increased with increased temperature. The correlations coefficients together with the Halsay isotherms are summarized in Tables 4.23 and 4.24. The values of K_{Ha} and n_{Ha} were in the range of 28.31 to 25.26 l/g and 8.65 to 8.33 respectively for adsorption using RHAC. For adsorption using CCAC, the values of K_{Ha} and n_{Ha} ranged from 19.85 to 16.4 l/g and 7.75

to 7.72 respectively. The Halsey isotherm was proposed based on the assumption that the multilayer adsorption is at a relatively large distance from the surface (Vicente et al, 2011; Soheila and Hasan 2017; Muhammad, 2015).

The fitting of their experimental data to the Halsey isotherm model attests to the heteroporous nature of the adsorbent and the heterogeneous distribution of activated sites and multilayer adsorption on coconut shell carbons. Song et al. (2015) applied the Halsey isotherm for the study of coconut shell carbon prepared by KOH activation for the removal of Pb^{2+} ions from aqueous solutions.

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
K _H	19.85	19.83	18.4	18.2	16.4	
n	7.75	7.79	7.72	7.81	7.88	
\mathbf{R}^2	0.999954	0.997168	0.999725	0.999026	0.999622	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.00018622	0.01544245	0.00033969	0.00348705	0.00055029	
MPSD	0.000559	0.005141	0.000829	0.002709	0.001219	
RMSE	0.002356	0.021241	0.002898	0.0091	0.003192	
ARE	0.015806	-0.1454	-0.02345	0.076635	0.034478	
SSE	2.221E-05	0.0018047	3.358E-05	0.0003313	4.076E-05	
X2	3.72E-06	0.000309	6.79E-06	6.97E-05	1.1E-05	
EABS	0.004713	-0.04248	-0.0058	0.018201	0.006384	
Sre	0.005547	0.05146	0.008826	0.029217	0.014047	

Table 4.23: Nonlinear Halsay isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
K _H	28.31	27.3	26.53	25.17	25.26	
n	8.33	8.52	8.59	8.68	8.65	
\mathbf{R}^2	0.999914	0.999944	0.998934	0.998546	0.997975	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.00962309	0.00367377	0.05826084	0.04752991	0.08868907	
MPSD	0.002505	0.001708	0.007186	0.007219	0.009647	
RMSE	0.027162	0.015207	0.057331	0.046555	0.065008	
ARE	0.070857	0.048316	0.203243	-0.20419	0.272856	
SSE	0.0029511	0.0009251	0.0131475	0.0086695	0.0169041	
X2	0.000192	7.35E-05	0.001165	0.000951	0.001774	
EABS	0.054324	0.030415	0.114663	-0.09311	0.130016	
Sre	0.008267	0.00895	0.04429	0.055539	0.07142	

Table 4.24: Nonlinear Halsay isotherm parameters using RHAC

4.5.1.6 Non linearDubininRadushkevich isotherm model

According to Inglezakis and Poulopoulos, (2006) the Dubinin-Radushkevich isotherm is based on physical parameters and with easy applications. It includes temperature effects and quite fairly predicts the experimental data over a wide concentration range. The non linearDubinin-Radushkevich isotherm is expressed as in equation 4.15

$$q_e = D_q \exp(B_D E^2) \tag{4.15}$$

As observed in Tables 4.25 and 4.26, the correlation coefficient was high suggesting that the experimental values obtained fitted the Dubinin-Radushkevich isotherm.

The values of constant β related to the sorption energy were relatively constant as temperature increases.

Benzaoui et al, (2017) reported that the Dubinin-Radushkevich isotherm is used to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well, but has unsatisfactory asymptotic properties and does not predict Henry's law at low pressure ((Alahmadi et al, 2014).

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _d	2.77	2.74	2.62	2.56	2.33	
В	0.017	0.0169	0.015	0.015	0.012	
\mathbf{R}^2	0.998542	0.999622	0.998893	0.997711	0.99981	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.0058521	0.0020604	0.0013678	0.0081907	0.0002771	
MPSD	0.001981	0.001188	0.001052	0.002626	0.000547	
RMSE	0.013209	0.007759	0.005814	0.013947	0.002265	
ARE	-0.0886	-0.05311	0.047049	-0.11745	-0.02447	
SSE	0.000698	0.000241	0.000135	0.000778	2.05E-05	
X2	0.000117	4.12E-05	2.74E-05	0.000164	5.54E-06	
EABS	-0.02642	-0.01552	0.011629	-0.02789	-0.00453	
Sre	0.031093	0.018797	0.01771	0.044778	0.009969	

Table 4.25: Nonlinear DubininRadushkevich isotherm parameters using CCAC

	Table 4.26:Nonlinear	DubininRadushkevich	isotherm parameters	using RHAC
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Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
$\mathbf{q}_{\mathbf{d}}$	3.5	3.8	4	3.6	3.6	
В	0.014	0.015	0.015	0.016	0.0161	
\mathbf{R}^2	0.999221	0.998119	0.998785	0.99992	0.999272	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.0867693	0.124005	0.0664255	0.0026249	0.0318782	
MPSD	0.004758	0.006277	0.004853	0.001073	0.003658	
RMSE	0.081562	0.088352	0.061217	0.01094	0.038974	
ARE	0.21277	0.280706	-0.21702	0.047985	0.163586	
SSE	0.026609	0.031224	0.01499	0.000479	0.006076	
X2	0.001735	0.00248	0.001329	5.25E-05	0.000638	
EABS	0.163123	0.176704	-0.12243	0.021881	0.077949	
Sre	0.024823	0.052001	0.047292	0.013052	0.042819	

4.5.2 Three term parametric isotherm models

Some three term parametric isotherm models were equally investigated. They include the Redlich-Peterson isotherm, the Radke-Prausniiz Isotherm, the Sips Isotherm, the Toth isotherm, the Khan isotherm and the Koble-Carrigan Isotherm. Most of these isotherm models were explained in chapter two.

4.5.2.1 The Redlich-Peterson isotherm

The nonlinear analysis of the Redlich-Peterson isotherm was carried out using the Solver add-in function of the Microsoft excel in an iteration method. Redlich–Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation (Prasad and Srivastava, 2009). A minimization procedure was adopted in solving the equation by maximizing the correlation coefficient between the experimental data points and theoretical model prediction.

The results are given in Tables 4.27 to 4.28. It was observed that the Redlich-Peterson isotherm constant A, decreased as the temperature increased for the adsorption of phenol using both CCAC and RHAC. The Redlich-Peterson isotherm exponent β was gradually decreasing to zero as the temperature increased indicating that at very high temperature the Redlich-Peterson isotherm will approach Henry's isotherm (Nimibofa et al, 2017). This was observed when using RHAC. The correlation coefficients were all high (>0.99) using both CCAC and RHAC adsorbents.

When $\beta = 1$, The Redlich-Peterson isotherm reduces to Langmuir equation with b = B that is, Langmuir adsorption constant (Lmg⁻¹) which is related to the energy of adsorption while $A = b_{qml}$ where qml is Langmuir maximum adsorption capacity of the adsorbent (mg g–1). When $\beta = 0$, the Redlich-Peterson isotherm reduces to Henry's equation with 1/(1 + b) representing Henry's constant (Nimibofa et al, 2017).

Gimbert et al, (2008) reported that The Redlich-Peterson isotherm model has a linear dependence on concentration in the numerator and an exponential function in the denomination representing adsorption equilibrium over a wide range of concentration of adsorbate which is applicable in either homogenous or heterogeneous systems due to its versatility.

The Redlich-Peterson isotherm is a mix of the Langmuir and Freundlich isotherms. The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution (Davoundinejad and Gharbanian, 2013). According to Soheila and Hasan (2017), the Redlich-Peterson isotherm approaches Freundlich isotherm model at high concentration and is in accordance with the low concentration limit of the ideal Langmuir condition.

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
Α	0.03	0.03	0.025	0.024	0.021	
В	0.23	0.25	0.26	0.26	0.3	
У	0.26	0.25	0.25	0.25	0.27	
\mathbf{R}^2	0.980347	0.998922	0.968333	0.996073	0.975062	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.078877	0.005877	0.039133	0.014052	0.036327	
MPSD	0.360784	0.355871	0.370638	0.311817	0.218065	
RMSE	0.048496	0.013104	0.0311	0.018268	0.025935	
ARE	0.325293	0.089701	0.251654	0.153837	0.280131	
SSE	0.009407	0.000687	0.003869	0.001335	0.002691	
X2	1.687982	1.609393	1.555606	0.943907	0.310613	
EABS	3.308304	3.197825	2.967801	2.140497	1.007205	
Sre	1.544593	1.498193	1.384903	1.264202	0.990176	

Table 4.27: Nonlinear Redlich Peterson isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
Α	0.1	0.078	0.07	0.056	0.055	
В	0.14	0.18	0.2	0.245	0.247	
У	0.3	0.29	0.288	0.26	0.26	
\mathbf{R}^2	0.99956	0.998624	0.999687	0.971978	0.985504	
Mean	9.516	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.048104	0.090699	0.017089	0.91619	0.634915	
MPSD	0.063488	0.150934	0.128232	0.040666	0.127381	
RMSE	0.060663	0.075561	0.03105	0.204397	0.173936	
ARE	1.795717	0.240068	0.110074	-0.89648	0.730056	
SSE	0.01472	0.022838	0.003856	0.167113	0.121015	
X2	0.081099	0.413615	0.265856	0.020533	0.218854	
EABS	0.903245	1.93773	1.466009	0.357027	1.214887	
Sre	2.534089	2.499542	2.080089	2.153629	1.786047	

Table 4.28: Nonlinear Redlich Peterson isotherm parameters using RHAC

4.5.2.2. Radke-Prausniiz Isotherm model

The Radke-Prausnitz isotherm parameters were obtained by nonlinear statistical fit of experimental data. The regression coefficient (R2) obtained at different temperatures were all greater than 0.99 suggesting good fit.

The Radke-Prausnitz maximum adsorption capacity q_{RP} values were between 0.4 and 0.14mg/g and 0.071 and 0.05mg/g for the removal of phenol using RHAC and CCAC respectively as tabulated in Tables 4.29 and 4.30. These values were found to decrease as the temperature increased, becoming almost constant at temperatures above 50 oC.

The Radke-Prausnitz equilibrium constant K_{RP} and Radke-Prausnitz model exponent m, equally decreased as the temperature decreased. The values of Radke-Prausnitz equilibrium constant K_{RP} and Radke-Prausnitz model exponent m, obtained in this work

were relatively close to that reported in the removal of picric acid by carboxylated multiwalled carbon nano tubes (Soheila and Hasan, 2017).

Nimibofa et al, (2017) reported that at low adsorbate concentration, the Radke-Prausnitz isotherm model reduces to a linear isotherm, while at high adsorbate concentration it becomes the Freundlich isotherm. When Radke-Prausnitz model exponent m = 0, it becomes the Langmuir isotherm. Important characteristic of this isotherm model includes the fact that it gives a good fit over a wide range of adsorbate concentration and it is used in the adsorption of organic solutes from dilute aqueous solutions (Soheila and Hasan, 2017; Vijayaraghavan et al, 2006). These important properties of Radke-Prausnitz isotherm model make it more preferred in most adsorption systems at low adsorbate concentration (Subramanyam and Ashutosh, 2012).

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q	0.071	0.067	0.064	0.063	0.063	
К	0.21	0.22	0.19	0.18	0.18	
Α	0.005	0.008	0.01	0.0092	0.0092	
\mathbf{R}^2	0.998921	0.999439	0.998857	0.981598	0.981351	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.004329	0.00306	0.001412	0.065854	0.027166	
MPSD	0.383615	0.002288	0.00169	0.011775	0.008565	
RMSE	0.011361	0.009455	0.005908	0.039548	0.022428	
ARE	0.076206	0.064725	0.047807	-0.33303	-0.24225	
SSE	0.000516	0.000358	0.00014	0.006256	0.002012	
X2	8.65778E-05	6.11996E-05	2.82453E-05	0.001317082	0.000543311	
EABS	3.51766	3.427897	3.142612	0.079096	0.044856	
Sre	0.049464	-10.7897	0.029812	0.206065	0.143551	

Table 4.29: Nonlinear Radke-Prausnizz isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q	0.4	0.21	0.2	0.15	0.14	
K	0.15	0.19	0.18	0.17	0.19	
Α	0.006	0.003	0.006	0.01	0.006	
\mathbf{R}^2	0.992433	0.993567	0.990953	0.990825	0.991229	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.843326	0.424002	0.494646	0.299988	0.38413	
MPSD	0.023452	0.018351	0.020938	0.018137	0.020077	
RMSE	0.254273	0.163374	0.167052	0.116959	0.135291	
ARE	0.663322	-0.51906	0.592207	-0.51298	-0.56785	
SSE	0.25862	0.106764	0.111625	0.054718	0.073215	
X2	0.016866519	0.008480049	0.009892914	0.005999759	0.007682592	
EABS	-0.50855	0.326747	1.783144	0.233918	0.270583	
Sre	0.585934	0.422903	0.463155	0.373449	0.419219	

Table 4.30: Nonlinear Radke-Prausnizz isotherm parameters using RHAC

4.5.2.3 Sips Isotherm model

Tables 4.31 and 4.32 show the values of the different Sips isotherm parameters obtained at varying temperatures. The add-in solver in Excel was employed in analyzing the Sips isotherm. The Sips constant model (K_s) values obtained using CCAC were lower (3.7 to 2.2 l/g) than that obtained using RHAC (7.5 to 5.6 l/g) though both of them decreased with increase in temperature. The Sips isotherm exponent βs , values obtained were all less than unity suggesting that the experimental data fitted the Sips isotherm. In the removal of Cu (II), Kara et al (208) obtained significantly different values of the isotherm exponent. The correlation coefficients of the model were good (>0.9) at the experimental temperatures used. According to Foo and Hamed (2010), at low adsorbate concentration, the Sips model reduces to the Freundlich model, but at high concentration of adsorbate, it predicts a monolayer adsorption capacity characteristics of the Langmuir model. The parameters of the Sips isotherm model are pH, temperature, and concentration-dependent and the isotherm constants differ by linearization and nonlinear regression (Elmorsi, 2011; Chen, 2012; Perez-Marin et al, 2007).

According to Travis and Etnier (1981), the Sips isotherm model is suitable for predicting adsorption on heterogeneous surfaces, thereby avoiding the limitation of increased adsorbate concentration normally associated with the Freundlich model.

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
K	3.7	3.55	3.1	2.9	2.2	
В	0.0098	0.0099	0.0094	0.0091	0.0092	
a	0.32	0.34	0.32	0.34	0.35	
\mathbf{R}^2	0.999008	0.995684	0.996982	0.996836	0.999304	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.003995	0.023326	0.003715	0.011247	0.001017	
MPSD	0.002584	0.006346	0.002747	0.004883	0.001655	
RMSE	0.010894	0.026223	0.009601	0.0164	0.004334	
ARE	-0.07307	0.179505	0.077692	0.138103	-0.04681	
SSE	0.000475	0.002751	0.000369	0.001076	7.51E-05	
X2	7.9609E-05	0.000470708	7.45955E-05	0.000226486	2.02902E-05	
EABS	0.021788	-0.05245	-0.0192	-0.0328	0.008668	
Sre	0.047432	0.115975	0.048447	0.085451	0.027741	

Table 4.31: Nonlinear Sips isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
K	7.5	6.9	6.5	5.8	5.6	
В	0.023	0.02	0.018	0.015	0.012	
a	0.38	0.35	0.32	0.29	0.34	
\mathbf{R}^2	0.997211	0.998618	0.999304	0.995999	0.999432	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.317222	0.090012	0.038393	0.128644	0.025067	
MPSD	0.014238	0.008506	0.005809	0.011977	0.00511	
RMSE	0.154372	0.075726	0.046349	0.077237	0.034436	
ARE	-0.40271	0.240591	-0.16431	0.338759	-0.14454	
SSE	0.095323	0.022938	0.008593	0.023862	0.004743	
X2	0.006216696	0.001821902	0.000761551	0.002616469	0.000497725	
EABS	0.308744	-0.15145	0.092698	-0.15447	0.068872	
Sre	0.355726	0.196022	0.128503	0.246616	0.106704	

Table 4.32: Nonlinear Sips isotherm parameters using RHAC

4.5.2.4 Toth isotherm model

The Toth isotherm was investigated using the Add-in solver of Excel spreadsheet and the parametric constants evaluated and summarized in Tables 4.33 and 4.34.

The Toth isotherm model showed a good fit to the adsorption data for the adsorption of phenol using both CCAC and RHAC adsorbents. The coefficients of correlation of the Toth isotherm model were good varying from 0.992 to 0.9999 for the adsorbents. The Toth's maximum adsorption capacity q_m , were close to the experimental adsorption capacity.

Its correlation presupposes an asymmetrical quasi-Gaussian energy distribution, with most of its sites having adsorption energy lower than the peak (maximum) or mean value (Ho et al, 2002). The Toth exponent n, was almost constant (between 0.63 to 0.64mg/g)
for adsorption using CCAC adsorbent but gradually decreased using RHAC adsorbent, with increase in the solution temperature.

This model is most useful in describing heterogeneous adsorption systems which satisfy both low and high end boundary of adsorbate concentration (Padder and Majunder, 2012). Jefari and Jefari, (2014) reported that the parameter n characterizes the heterogeneity of the adsorption system; and that if n = 1, this equation reduces to Langmuir isotherm equation but if it deviates further away from unity (1), then the system is said to be heterogeneous. Hence, this adsorption process cannot be said to be heterogeneous though it has been reported that the Toth isotherm model has been applied for the modeling of several multilayers and heterogeneous adsorption systems (Benzaoui et al, 2017). The Toth isotherm is another empirical modification of the Langmuir equation with the aim of reducing the error between experimental data and the predicted value of equilibrium data (Jefari and Jefari, 2014).

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _m	7.9	7.7	6.6	6.3	4.8	
K	0.03	0.03	0.027	0.028	0.034	
n	0.638	0.642	0.645	0.643	0.63	
\mathbf{R}^2	0.996889	0.997629	0.998637	0.998886	0.997632	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.012484	0.012927	0.001684	0.003987	0.00345	
MPSD	0.004575	0.004703	0.001846	0.002897	0.003052	
RMSE	0.019293	0.019434	0.006452	0.009731	0.007993	
ARE	0.129414	0.133033	0.052207	0.081946	0.086329	
SSE	0.001489	0.001511	0.000167	0.000379	0.000256	
X2	0.000249685	0.000258534	3.3684E-05	7.9743E-05	6.89988E-05	
EABS	0.038587	0.038868	0.012904	0.686284	0.015985	
Sre	0.045414	0.047083	0.019652	0.031242	0.035172	

Table 4.33: Nonlinear Toth isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _m	17.9	16.3	15.6	14.3	14.5	
K	0.04	0.028	0.025	0.018	0.019	
n	0.82	0.75	0.69	0.61	0.638	
\mathbf{R}^2	0.99964	0.996749	0.995513	0.999874	0.997592	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.040148	0.21431	0.245329	0.004122	0.105468	
MPSD	0.005117	0.013047	0.014745	0.002126	0.01052	
RMSE	0.05548	0.11615	0.117646	0.013711	0.070891	
ARE	0.14473	-0.36902	-4.82396	0.060135	-0.29755	
SSE	0.012312	0.053963	0.055362	0.000752	0.020102	
X2	0.000802961	0.004286208	0.004906572	8.24491E-05	0.002109353	
EABS	-3.82928	-0.2323	-0.23529	0.027421	-0.14178	
Sre	0.016885	0.068362	0.090885	0.016357	0.077883	

Table 4.34: Nonlinear Toth isotherm parameters using RHAC

4.5.2.5 Khan isotherm model

The Khan isotherm model constants were evaluated by the nonlinear regression of the isotherm model and presented in Tables 4.35 and 4.36. The high values of the correlation coefficient (above 0.99) signify that the experimental data is in close agreement with the predicted data. The Khan isotherm maximum adsorption capacity q_m obtained using CCAC was much closer to the experimental value than that obtained using RHAC. Hence, the Khan isotherm described the adsorption of phenol using CCAC adsorbent

better than using RHAC. Kara et al, (2018) reported that if the Kahn isotherm model exponent a is equal to unity, then the Khan isotherm reduces to Langmuir isotherm. Equally, When b value is much bigger than unity, Khan isotherm turns into the Freundlich isotherm. Adsorption data using Khan isotherm has been reported for phenol and phenol derivatives in aqueous medium for single and bisolute systems (Khan et al, 1997; Kara et al, 2018).

The Kahn isotherm model is a generalized model suggested for adsorption from pure solutions (Amrhar and Nassali, 2015).

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _m	5.5	5.3	4.5	4.2	3.1	
b	0.028	0.026	0.03	0.033	0.37	
a	0.84	0.82	0.83	0.81	0.83	
\mathbf{R}^2	0.9981	0.997485	0.998989	0.998932	0.999817	
Mean	5.271467	5.045067	4.5938	4.166933	3.374867	
HYBRID	0.007627	0.013716	0.001249	0.003822	0.000266	
MPSD	0.003576	0.004845	0.00159	0.002837	0.000848	
RMSE	0.01508	0.020018	0.005557	0.009527	0.002221	
ARE	0.101152	3.448376	-0.04497	1.656087	-0.02399	
SSE	0.00091	0.001603	0.000124	0.000363	1.97E-05	
X2	0.000152538	0.000274319	2.49885E-05	7.64405E-05	5.32649E-06	
EABS	0.03016	0.040037	-0.01111	-0.01905	-0.00444	
Sre	0.035496	0.048499	0.016926	0.030588	0.009772	

Table 4.35: Nonlinear Khan isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _m	11.2	9.6	9.5	8.2	8.3	
b	0.53	0.48	0.41	0.33	0.35	
a	0.72	0.76	0.84	0.88	0.88	
\mathbf{R}^2	0.999845	0.999715	0.999577	0.997946	0.995981	
Mean	9.487333	8.516067	7.770733	6.677933	6.640733	
HYBRID	0.017233	0.018762	0.023119	0.067142	0.176039	
MPSD	0.003352	0.00386	0.004527	0.00858	0.013591	
RMSE	0.036348	0.034367	0.036115	0.055333	0.091588	
ARE	-0.09482	0.109187	0.12803	-0.24269	0.384418	
SSE	0.005285	0.004724	0.005217	0.012247	0.033553	
X2	0.000344651	0.000375239	0.000462378	0.001342849	0.003520787	
EABS	-0.0727	0.068733	0.07223	-0.11067	0.183175	
Sre	0.011062	0.020227	0.0279	0.066011	0.100621	

Table 4.36: Nonlinear Toth isotherm parameters using RHAC

4.5.2.5 Koble-Carrigan Isotherm model

The add-in solver function in excel was employed in determining theKoble-Carrigan Isotherm parameters which are tabulated in Tables 4.37 and 4.38.

At all temperatures, the correlation coefficients were high for both CCAC and RHAC adsorbents. The Koble-Carrigan's isotherm exponent, p, was greater than unity at lower temperatures with its value decreasing as the temperature increased even becoming less than unity above 50 °C.Nimibofa et al (2017) reported that when the Koble-Carrigan's isotherm exponent, p, is less than unity, it signifies that the model is incapable of defining

the experimental data even if it has high correlation coefficient and low error value. It is only valid when it is greater than or equal to 1.Therefore, at temperatures above 50°C, Koble-Carrigan isotherm cannot describe the adsorption of phenol unto these adsorbents. According to Kara et al, (2018), when the adsorption experiments are carried out at high adsorbate concentrations, the Koble-Carrigan isotherm model approaches the Freundlich isotherm. The isotherm has an exponential dependence on concentration in the numerator and denominator. It is usually used with heterogeneous adsorption surfaces (Hossein et al, 2013).

Parameter		TEN	IPERATURE	(°C)	
	30	35	40	50	60
Α	6	5.9	5	4.8	3.7
В	0.6	0.6	0.8	2.1	2.3
р	1.2	1.1	0.8	0.8	0.8
\mathbf{R}^2	0.998199	0.997012	0.999491	0.99696	0.99776
Mean	5.271467	5.045067	4.5938	4.166933	3.374867
HYBRID	0.00723	0.016293	0.00063	0.01088	0.003263
MPSD	0.003482	0.00528	0.001129	0.004786	0.002968
RMSE	0.014682	0.021818	0.003945	0.016075	0.007773
ARE	0.098485	-0.14936	0.031919	0.135368	-0.08395
SSE	0.000862	0.001904	6.22E-05	0.001034	0.000242
X2	0.000144599	0.000325867	1.25913E-05	0.000217603	6.52524E-05
EABS	-0.02936	-0.04364	-0.00789	-0.03215	0.015545
Sre	0.03456	0.052859	0.012015	0.051609	0.034203

Table 4.37: Nonlinear Koble-Corrigan isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)						
	30	35	40	50	60		
Α	15.2	12.8	11.2	9.3	9.5		
В	1.3	1.1	0.92	0.87	0.87		
р	1.5	1.3	1.1	0.8	0.77		
\mathbf{R}^2	0.999459	0.997509	0.999125	0.99878	0.99742		
Mean	9.487333	8.516067	7.770733	6.677933	6.640733		
HYBRID	0.060285	0.164175	0.047838	0.03988	0.112978		
MPSD	0.00627	0.011419	0.006511	0.006613	0.010888		
RMSE	0.067984	0.10166	0.05195	0.042644	0.073372		
ARE	-0.17735	-0.32299	-0.18417	0.187037	-0.30796		
SSE	0.018487	0.041339	0.010795	0.007274	0.021534		
X2	0.001205699	0.003283504	0.000956755	0.000797607	0.002259567		
EABS	0.135968	-0.20332	0.103901	-0.08529	0.146744		
Sre	0.020691	0.059833	0.040133	0.050874	0.080609		

Table 4.38: Nonlinear Koble-Corrigan isotherm parameters using RHAC

4.5.3 Four terms parametric isotherm

4.5.3.1 Fritz-Schlunder Isotherm model

The nonlinear Fritz-Schlunder Isotherm was carried out using the add-in Solver in Microsoft excel and the parameters presented in Table 4.39 and 4.40.

The Fritz-Schlunder adsorption capacity q_F , increased from 5.4mg/g to 5.8mg/g as the temperature increased though it was relatively constant at high temperatures.

The correlation coefficient was very good as the values were all greater than 0.99. The values of the Fritz-Schlunder model exponent m were all less than unity at a relatively constant value of 0.6 Nimibofa et al (2017) reported that when the Fritz-Schlunder model exponent m, is unity, the isotherm model reduces to the Langmuir isotherm. The values of the equilibrium maximum adsorption capacity q_m obtained were less than the experimental values obtained. For higher liquid-phase concentrations, the Fritz-Schlunder isotherm model is converted to the Freundlich isotherm model (Soheila and Hasan, 2017).

Parameter	TEMPERATURE (° C)				
	30	35	40	50	60
$q_{\rm f}$	5.4	5.6	5.7	5.8	5.8
K_{f}	0.302	0.304	0.304	0.304	0.304
$q_{\rm m}$	1.8	1.77	1.77	1.78	1.78
m	0.68	0.69	0.693	0.693	0.695
R^2	0.9978	0.9980	0.9986	0.9998	0.9995
Mean	5.4577	5.2691	4.893	4.53728	3.8772
HYBRID	0.0149	0.0193	0.02175	0.00397	0.02344
SSE	0.0019	0.00247	0.00278	0.00051	0.00299
RMSE	0.0218	0.02484	0.02636	0.01126	0.02736
ARE	0.1367	0.1555	0.1650	-0.0705	0.1713
Sre	0.0465	0.05291	0.05615	0.02399	0.05829
EABS	0.0437	0.04967	0.05271	-0.0225	0.05473
MPSD	0.0048	0.00549	0.00583	0.00249	0.00606
X2	0.00029	0.000386	0.00044	0.000079	0.00047

Table 4.39: Nonlinear Fritz-Schlunder isotherm parameters using CCAC

Table 4.40: Nonlinear Fritz-Schlunder isotherm parameters using RHAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
$q_{\rm f}$	5.1	5.3	5.4	5.41	5.41	
\mathbf{K}_{f}	0.288	0.291	0.293	0.294	0.294	
$q_{\rm m}$	1.52	1.55	1.57	1.57	1.57	
m	0.69	0.694	0.697	0.697	0.697	
R^2	0.9998	0.9999	0.9994	0.9997	0.9995	
Mean	8.9709	8.16155	7.5404	6.6297	6.5988	
HYBRID	0.00641	0.00019	0.00659	0.000158	0.000158	
SSE	0.000819	0.000024	0.00084	0.000201	0.000020	
RMSE	0.014308	0.002463	0.01452	0.002243	0.002243	
ARE	0.089577	-0.01542	0.0909	-0.01404	-0.01404	
Sre	0.030481	0.005246	0.03093	0.004778	0.004778	
EABS	0.028615	-0.00493	0.029038	-0.00449	-0.00449	
MPSD	0.003167	0.000545	0.003214	0.000497	0.000497	
X2	0.000128	0.0000038	0.000132	0.000003	0.000005	

4.5.3.2 Baudu isotherm model

Tables 4.41 and 4.42 show the values of the different Baudu isotherm parameters obtained at different temperatures. The Baudu maximum adsorption capacity q_{m} , increased from 6.02mg/g to 6.09 mg/g as the temperature increased for adsorption of phenol using CCAC while the range of increase was from 6.03mg/g to 6.05mg/g for RHAC. Other Baudu isotherm parameters were relatively constant over the range of temperature used in this work as seen in Tables 4.41 and 4.42.

The Baudu isotherm model showed a good fit to the adsorption data as the coefficients of correlation were high, with some reaching up to 0.999. According to Nimibofa et al, (2017), at lower surface coverage, the Baudu isotherm model reduces to Freundlich model. The calculations of the Langmuir coefficients at different equilibrium concentrations were found not to constant over a wide concentration range hence, the Langmuir isotherm was modified to the Baudu isotherm (Soheila and Hasan, 2017).

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _m	6.02	6.05	6.06	6.07	6.09	
b	1.85	1.84	1.83	1.83	1.82	
Х	0.5	0.5	0.5	0.5	0.5	
у	0.01	0.01	0.01	0.01	0.01	
\mathbf{R}^2	0.9998	0.9986	0.9987	0.9988	0.9989	
Mean	5.4577	5.2691	4.893	4.5373	3.8772	
HYBRID	0.00077	0.01367	0.0215	0.03112	0.05563	
SSE	0.000098	0.001747	0.00275	0.003976	0.00711	
RMSE	0.00496	0.02089	0.02621	0.03153	0.04216	
ARE	-0.0310	-0.13085	-0.1641	-0.1974	-0.2639	
Sre	0.01056	0.044524	0.05584	0.067166	0.08981	
EABS	-0.00991	-0.0418	-0.0524	-0.06306	-0.08431	
MPSD	0.00109	0.004626	0.00580	0.00697	0.00933	
X2	0.000015	0.000273	0.00043	0.000622	0.00111	

Table 4.41: Nonlinear Baudu isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _m	6.03	6.04	6.05	6.02	6.02	
b	0.81	0.83	0.84	0.84	0.84	
Х	0.4	0.4	0.4	0.3	0.2	
у	0.01	0.01	0.01	0.01	0.01	
R^2	0.9999	0.9997	0.9987	0.9990	0.9994	
Mean	8.9709	8.16155	7.5404	6.6298	6.5987	
HYBRID	0.00294	0.00706	0.01296	0.000448	0.000219	
SSE	0.000376	0.000903	0.00165	0.000057	0.0000280	
RMSE	0.009689	0.01502	0.02034	0.003785	0.002646	
ARE	-0.06066	-0.09405	-0.1273	-0.02369	-0.01657	
Sre	0.02064	0.032002	0.04334	0.008063	0.00564	
EABS	-0.01938	-0.03004	-0.04069	-0.00757	-0.00529	
MPSD	0.002145	0.003325	0.004503	0.000838	0.000586	
X2	0.000059	0.0001413	0.000259	0.0000089	0.000044	

Table 4.42: Nonlinear Baudu isotherm parameters using RHAC

4.5.3.3 Marczewski-Jaroniec isotherm model

The Marczewski-Jaroniec isotherm parameters were obtained by a nonlinear statistical fit of experimental data. At the different temperature ranges employed in this work, the regression coefficient (R2) obtained were all greater than 0.99 suggesting a good fit for both CCAC and RHAC adsorbents. The Marczewski-Jaroniec maximum adsorption capacity (mg/g) as expressed in Tables 4.43 and 4.44 was quite close (slightly lower) to the experimental adsorption capacity.

Ramsenthil and Dhanasekaran, (2018) reported that the Marczewski-Jaroniec isotherm reduces to Langmuir isotherm when n and m are equal to unity and reduces to Langmuir-Freundlich isotherm model only whenever n is equal to m. Marczewski-Jaroniec isotherm is the resemblance of Langmuir isotherm model and was recommended on the basis of the supposition of local Langmuir isotherm and adsorption energies distribution in the active sites on adsorbent (Ramsenthil and Dhanasekaran, 2018).

Parameter	TEMPERATURE (° C)				
	30	35	40	50	60
q _m	5.9	5.95	5.97	5.99	6.0
Κ	4.5	4.6	4.6	4.7	4.8
n	1.01	1.01	1.01	1.01	1.01
m	1.0002	1.0002	1.0004	1.0004	1.0004
R^2	0.9986	0.9997	0.9995	0.9991	0.9993
Mean	5.4577	5.2691	4.893	4.53728	3.8772
HYBRID	0.00948	0.003284	0.00812	0.023776	0.03538
SSE	0.001212	0.0004197	0.001038	0.003038	0.004521
RMSE	0.017404	0.010243	0.01610	0.02756	0.03362
ARE	0.10896	-0.06413	-0.10085	-0.17254	-0.21049
Sre	0.037076	0.021821	0.034316	0.058713	0.07162
EABS	0.034807	-0.02049	-0.03222	-0.05512	-0.06724
MPSD	0.003852	0.002267	0.003566	0.0061	0.007442
X2	0.0001896	0.000657	0.000162	0.000476	0.000707

Table 4.43: Nonlinear Marczewski-Jaroniec isotherm parameters using CCAC

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q _m	6.01	6.006	6.003	5.97	5.97	
Κ	4.7	4.2	3.3	3.3	3.2	
n	1.01	1.01	1.01	1.01	1.01	
m	1.0004	1.004	1.0004	1.0004	1.0004	
\mathbf{R}^2	0.9991	0.9987	0.9984	0.9980	0.9983	
Mean	8.9709	8.1615	7.5404	6.6298	6.5988	
HYBRID	0.04596	0.03308	0.01657	0.00088	0.00058	
SSE	0.005873	0.004227	0.002119	0.000113	0.000074	
RMSE	0.038318	0.03251	0.02301	0.005323	0.004315	
ARE	-0.2399	-0.20355	-0.14406	-0.03332	-0.02701	
Sre	0.08163	0.069262	0.04902	0.011339	0.00919	
EABS	-0.07664	-0.06502	-0.04602	-0.01065	-0.00863	
MPSD	0.00848	0.007196	0.005093	0.001178	0.000955	
X2	0.000919	0.0006617	0.0003315	0.0000177	0.0000117	

Table 4.44: Nonlinear Marczewski-Jaroniec isotherm parameters using RHAC

4.5.4 Five terms parametric isotherm model

4.5.4.1 Fritz-schlunder-V isotherm model:

The fitness of the Fritz-schlunder-V isotherm to the experimental data was carried out in an iteration method using the Solver add-in function of the Microsoft excel. A minimization procedure was adopted in solving the equation by maximizing the correlation coefficient between the experimental data points and theoretical model prediction. The Fritz-Schlunder maximum adsorption capacity q_m , was within the narrow range of 6.0 mg/g to 6.09mg/g as seen in Tables 4.45and 4.46. These ranges of values were within the experimental range of values of maximum adsorption capacity. It is assumed that the Fritz-schlunder fitted closely to the experimental data because the correlation coefficient was high (>0.97).

Nimibofa et al, (2017) reported that Fritz-Schlunder-V isotherm model can be applied over a wide range of equilibrium data. This model approaches the Langmuir model as the exponents α_{FS} and β_{FS} tends to unity. For very high concentrations, this model reduces to the Freundlich isotherm (Nimibofa et al, 2017).

Parameter	TEMPERATURE (° C)					
	30	35	40	50	60	
q	6.0	6.01	6.01	6.05	6.05	
K ₁	4.3	4.32	4.33	4.33	4.35	
α	0.6	0.6	0.6	0.6	0.6	
K_2	2.1	2.1	2.1	2.1	2.1	
β	0.69	0.69	0.69	0.69	0.69	
R^2	0.9963	0.9993	0.9998	0.9999	0.9996	
Mean	5.6923	5.5306	5.2083	4.9034	4.3376	
HYBRID	0.05224	0.01228	0.00455	0.00331	0.02096	
SSE	0.00741	0.00174	0.00065	0.00047	0.00297	
RMSE	0.04306	0.02088	0.01271	0.01083	0.02728	
ARE	0.24260	0.11763	0.07160	-0.06103	-0.15369	
Sre	0.00612	0.00144	0.00053	0.000387	0.002456	
EABS	0.08612	0.04176	0.02542	-0.02167	-0.05456	
MPSD	0.00858	0.00416	0.00253	0.002158	0.005434	
X2	0.00104	0.00025	0.000091	0.000066	0.000419	

Table 4.45: Nonlinear Fritz-Schlunder V isotherm parameters using CCAC

Parameter		TEM	PERATURE (°	C)	
	30	35	40	50	60
Q	6.2	6.1	6.05	6.04	6.04
K ₁	4.35	4.31	4.31	4.32	4.32
α	0.6	0.6	0.6	0.6	0.6
K ₂	2.1	2.1	2.1	2.1	2.1
β	0.69	0.69	0.69	0.69	0.69
R^2	0.9791	0.9973	0.9991	0.9997	0.9998
Mean	8.7037	8.0099	7.4775	6.6969	6.6704
HYBRID	0.37887	0.01579	0.000088	0.0003	0.0003
SSE	0.053799	0.00224	0.000126	0.000043	0.000042
RMSE	0.11597	0.02368	0.00561	0.003262	0.003262
ARE	-0.65337	-0.1334	0.03163	0.018379	0.018379
Sre	0.0444	0.00185	0.000104	0.000035	0.000035
EABS	-0.23195	-0.04736	0.01123	0.006525	0.006525
MPSD	0.0231	0.004716	0.00112	0.00065	0.00065
X2	0.007577	0.000316	0.000018	0.000006	0.000006

Table 4.46: Nonlinear Fritz-Schlunder V isotherm parameters using CCAC

4.6 Kinetic Studies

Kinetics models (such as Pseudo-first order, Pseudo-second order, Elovich, Natarajan and kinetic, Boyd, etc) were used to investigate the mechanism of adsorption and the potential rate controlling steps such as mass transport and chemical reaction processes (Rajeshkannan et al, 2011). The applicability of these kinetic models in describing the adsorption process was adjudged mainly by the correlation coefficient values.

4.6.1 Natarajan and Khalaf kinetic model

Natarajan and Khalaf developed a model based on initial concentration and the concentration at any time t (Yilmaz et al. 2015). The model is given in equation 4.16

$$\log\left(\frac{C_{o}}{C_{t}}\right) = \left(\frac{K_{N}}{2.303}\right) t \tag{4.16}$$

where Co = initial concentration (mg/L); Ct = concentration (mg/L) at time t. The value of K_N was calculated from the slope of the plot of log (Co/Ct) against time (minutes) as given in appendix D and presented in Tables 4.47 and 4.48.

The experimental data were found to fit the Natarajan and Khalaf kinetic model due to the fact that the correlation coefficients were high. Venkatesan andRajagopalan (2016) reported the same trend in the removal of copper ions from solution using clay.

4.6.2 Elovich kinetic model

The Elovich model is given in equation 4.17:

$$q_{t} = (1/\beta) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t$$
(4.17)

Where α (mg g-1 min-1) is the initial sorption rate and the parameter β (g mg-1) is related to the extent of surface coverage and activation energy for chemisorptions (Chakrapani et al, 2010).

The Elovich model was studied by plotting q_e against ln t at different concentrations as given in appendix D. The initial adsorption rate, α and the extent of coverage, β were calculated from the slope and the intercept respectively and summarized in Tables 4.47 and 4.48 as well as the correlation coefficient R².

High values of the correlation coefficient R^2 (>0.96) obtained using both adsorbents indicate that the adsorption of phenol unto these adsorbents described the Elovich model. The Elovich equation has been shown to be useful in describing chemisorptions on highly heterogeneous adsorbents. The small values of β obtained in most cases are in reasonable agreement with that obtained by Atef and Waleed, (2009), Ozer et al, (2007) and Sivakumar and Palanisang, (2009).

As the concentration increased from 100 to 500 mg/l, the initial sorption rate α (mg g-1 min-1) increased from 1.159 to 3.572 mg/g and from 1.55 to 9.546 mg/g for the

adsorption of phenol using adsorbents produced from corn cob and rice husk respectively.

4.6.3 Pseudo first-order kinetic model

The pseudo first-order kinetics was analyzed using plots of log $(q_e - q_l)$ against t at different concentrations (see appendix D). The pseudo first-order rate constant K_1 and amount of adsorbate adsorbed at equilibrium q_e were calculated from the slope and intercept respectively and tabulated in Tables 4.47 and 4.48. The amount of adsorbate adsorbed (mg/g) increased as the concentration increased. This is expected because, at higher concentration, there are more adsorbate particles to be removed. The amount adsorbed (q_e) ranged from 1.55mg/g to 2.93mg/g for adsorption using CCAC and from 2.09 to 3.31mg/g for adsorption using RH. These values do not agree with the experimentally determined amount adsorbed. This suggests that the applicability of the pseudo first-order kinetic model to the adsorption processes of phenol onto CCAC and RHAC is not feasible. In the removal of phenol from water using sewage based adsorbent, Salim and Abdeslam (2014) obtained a similar result.

The correlation coefficient obtained was between 0.84 and 0.99 which suggests that the adsorption of phenol unto these adsorbents followed pseudo first-order kinetic model especially using RHAC adsorbent.Muhammed and Muhammed(2010) reported that even though an adsorption process will have a high correlation coefficient R^2 value but so far as the values of q_e calculated were not close to the experimental value of q_e , the adsorption is assumed not to have followed the kinetic model. Hence, this adsorption did not follow the Pseudo first-order. Xiangliang and Daoyong, (2009) and Ozer et al, (2007) reported similar trend.

4.6.4 Pseudo second-order kinetic model

At different concentrations, the plot of t/q_e versus t was used to study the pseudo-second order kinetic model as shown in appendix D. The values of the pseudo second-order rate constant K₂, and amount adsorbed q_e were obtained from the intercept and slope of the plot respectively and expressed in Tables 4.47 and 4.48.

The correlation coefficient R^2 has extremely high values ranging from 0.995 to 0.996 for adsorption using CCAC while for adsorption using RHAC, it was between 0.94 and 0.99. These high values of the correlation coefficient show excellent linearity and suggest that the adsorption process fitted the pseudo second-order kinetic model (Salim and Abdeslam, 2014).

The pseudo second-order rate constants K_2 were all less than 1.0 mg/min for the adsorbents except for the adsorption using corn cob with initial concentration of 500 mg/l which was 1.121 mg/min. The calculated amount of adsorbate adsorbed q_o progressively increased as the initial concentration increased even reaching up to 14.29 mg/g for adsorption using CCAC and 20.01 mg/g for adsorption using RHAC. This is quite high and close to the experimental amount of adsorbate adsorbed. Uddin et al (2007) reported that if the theoretical values q_e values were closer to the experimental q_e values and the correlation coefficient values high then, the adsorption process definitely followed the kinetic model.

Hence, it is seen that the pseudo second-order kinetic model is satisfactorily applicable to the adsorption of phenol onto this adsorbents. Similar results were also obtained by Salim and Abdeslam, (2014), Xiangliang and Daoyong, (2009), Muhammed and Muhammed, (2010) and Atef and Waleed, (2009).

4.6.5 Bhattacharya-Venkobachor model

Bhattacharya and Venkobachar presented a simple first-order reversible kinetic model, based on solution concentration to study the mechanism of sorption and characteristic constants of sorption. The Bhattacharya-Venkobachor model equation is given Venkatesan and Rajagopalan (2016) in equation 4.18

$$\ln (1 - U_t) = K_B t$$

$$\text{where} U_t = \frac{C_t - C_e}{C_o - C_e}$$
(4.18)

where B = B-V constant (min-1); Co = initial concentration(mg/L); Ct and Ce = concentration (mg/L) at time t and at equilibrium.

The plot of $\ln[1 - U_t]$ against t was used to investigate the Bhattacharya-Venkobachor model (see appendix D). The value of the rate constant K_B which was obtained from the slope of the linear plot was used to calculate the effective diffusion coefficient D₂ and presented in Tables 4.47 and 4.48. The effective diffusion coefficients D₂, determined were of the order 1.0 x 10⁻¹⁰ to 9.0 x 10⁻¹² m²/s. The correlation coefficient R² was high (>0.97) which shows that the adsorption process conformed to the Bhattacharya-Venkobachor model. Vikrant and Deshmuckh (2012) obtained similar result.

4.6.6 Power function kinetic model

The power function model given by equation 4.19

$$\log q_t = \log a + b \log t \tag{4.19}$$

Where a and b are power function constants with b indicating the specific sorption rate at unit time ie t = 1 (Venckatesh et al, 2010).

The power function model was investigated by plotting log q_t against log t (see appendix D) and the constants 'a' and 'b' were determined from the slope and the intercept and summarized in Tables 4.47 and 4.48. The low values of the correlation coefficient R^2 show that the adsorption of phenol unto these adsorbents did not fit the power function model. In the adsorption of Cr(VI) using stannic oxide, Goswami and Uday (2005) reported that the experimental data fitted the power function model.

4.6.7 Lagergren second-order kinetic model

Lagergren second-order kinetic model was investigated using the plots of $1/(q_e - q_t)$ against t as shown in appendix D. The rate constant K and equilibrium adsorption capacity q_e calculated from the slope and the intercept respectively and tabulated in Tables 4.47 and 4.48.

The correlation coefficient ranged from 0.886 to 0.912 for adsorption of phenol using RHAC and 0.937 to 0.983 when using CCAC. This suggested that the adsorption process using RHAC did not fit Lagergren second-order kinetic model. Furthermore, the equilibrium adsorption capacity q_e calculated did not agree with that from the experimental data. Goswani and Ghosh, (2005) got similar results.

Kinetic		Con	centration (mg	g/l)				
Model	100	150	200	300	500			
Natarajan Khalaf								
R^2	0.964	0.956	0.923	0.905	0.939			
K _n	0.117	0.108	0.103	0.097	0.071			
Elovich								
R^2	0.898	0.921	0.928	0.937	0.965			
β	1.093	0.814	0.694	0.520	0.334			
α	1.159	1.408	1.606	2.102	3.572			
Pseudo-first or	der							
R^2	0.849	0.848	0.954	0.952	0.996			
Κ	0.0529	0.0438	0.0507	0.0461	0.0576			
q _o	1.554	1.751	1.956	2.223	2.929			
Pseudo-Second	l order							
R^2	0.995	0.996	0.996	0.996	0.996			
q_{o}	4.464	5.988	6.993	9.434	14.286			
Κ	0.515	0.616	0.705	0.900	1.121			
Battacharya-V	enkobachor							
\mathbf{R}^2	0.801	0.801	0.778	0.759	0.793			
K _B	0.050	0.050	0.049	0.049	0.051			
Power Functio	n							
R^2	0.807	0.824	0.825	0.827	0.865			
b	0.402	0.412	0.417	0.418	0.451			
a	1.105	1.001	1.060	1.196	1.326			
Lagergren seco	ond-order							
R^2	0.957	0.937	0.961	0.983	0.944			
Κ	0.096	0.068	0.076	0.035	0.046			
q_e	5.01	2.994	1.770	8.475	2.358			

 Table 4.47 Kinetic parameters for phenol adsorption using CCAC

Kinetic	Concentration (mg/l)					
model	100	150	200	300	500	
Natarajan						
Khalaf						
\mathbf{R}^2	0.974	0.988	0.977	0.899	0.969	
K _n	0.0345	0.0069	0.0115	0.0392	0.0092	
Elovich						
R^2	0.938	0.944	0.945	0.879	0.941	
β	0.744	0.518	0.436	0.329	0.258	
А	1.555	3.402	5.461	9.171	9.546	
Pseudo-first						
order						
\mathbf{R}^2	0.964	0.986	0.970	0.941	0.981	
\mathbf{K}_1	0.0612	0.0530	0.0484	0.0507	0.0461	
q _o	2.098	2.416	2.593	3.177	3.313	
Pseudo-						
Second order						
R^2	0.999	0.976	0.961	0.944	0.946	
q _o	6.623	9.259	11.628	14.706	20.01	
K ₂	0.503	0.472	0.384	0.464	0.627	
Battacharya-						
Venkobachor						
R^2	0.927	0.925	0.961	0.954	0.954	
K _B	0.048	0.059	0.065	0.065	0.061	
Power						
Function						
R^2	0.902	0.901	0.929	0.761	0.935	
b	0.419	0.513	0.583	0.668	0.577	
а	1.011	1.070	1.174	1.274	1.074	
Lagergren						
second-order						
\mathbf{R}^2	0.886	0.895	0.912	0.894	0.894	
Κ	0.113	0.051	0.030	0.026	0.016	
q _e	1.026	2.674	5.952	5.952	11.236	

 Table 4.48 Kinetic parameters for phenol adsorption using RHAC

4.7 Non Linear Adsorption Kinetics

The non linear kinetic analysis was carried out by fitting five different non linear kinetic models to the experimental data. The non linear kinetic models used were pseudo first-order, pseudo second-order, Elovich, and Avrami models. The values of the non linear kinetic models parameters, their correlation coefficients and the different error terms were summarized in Tables 4.49 to 4.56. It was seen that the correlation coefficients were high in most cases especially in pseudo second-order model and Avriam model where the correlation coefficients were all greater than 0.99 in all cases.

Benmaamar et al, (2017) reported that the non linear kinetics is appropriate because the linear transformed regression methods distort the experimental error and create an inherent error estimation problem which limits the studied tools validity. Among the different error terms employed, the HYBRID errors were smallest in pseudo second-order and Avriam models for both CCAC and RHAC as seen in Tables 4.53 to 4.60. Equally, the SSE, RMSE and X2 all indicate that the experimental data were better described by the pseudo second-order and Avriam models.

Furthermore, the equilibrium maximum adsorption capacity q_e determined through the non linear analysis closely approximates the experimental equilibrium maximum adsorption capacity, especially in pseudo second-order analysis. This confirms the possibility of the violation of the normality assumptions behind the linear regression method. In most cases, the values q_e increased with increase in initial concentration of phenol for Avriam and pseudo second-order models. From the above discussions, it can be concluded that pseudo second-order model best describes the non linear kinetic analysis.

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
К	1.5	1.3	1.5	1.2	1.2		
q_e	5.2	3.955	6.34	6.09	8.7		
R^2	0.9617	0.9829	0.9989	0.9904	0.9823		
Mean	3.0295	3.9417	4.5852	6.0778	8.6643		
HYBRID	0.03499	0.05413	0.0000642	0.0927	0.1555		
MPSD	0.0921	0.09922	0.003169	0.1037	0.1108		
RMSE	0.3580	0.5141	0.0191	0.8422	1.3227		
ARE	2.605	2.8065	-0.08962	-2.9334	-3.1334		
SSE	1.1549	2.3809	0.003287	6.3908	15.7609		
X2	0.2799	0.43304	0.000514	0.7416	1.2440		
EABS	1.0747	-1.543	-0.05733	-2.528	-3.97		
Sre	1.2265	1.4498	0.04899	1.8205	2.3678		

Table 4.49: Nonlinear Pseudo first-order kinetic parameters using CCAC

 Table 4.50: Nonlinear Elovich kinetic parameters using CCAC

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
α	1.53	0.95	0.58	0.83	1.38		
β	1.00	1.26	0.906	0.700	0.51		
R^2	0.9945	0.9921	0.9932	0.9952	0.9716		
Mean	3.029	3.9417	4.5852	6.0778	8.6643		
HYBRID	0.03619	0.0546	0.06373	0.09314	0.1538		
SSE	1.1943	2.4031	3.2615	6.4217	15.5901		
RMSE	0.3641	0.5164	0.6017	0.84427	1.3155		
ARE	2.6491	-2.8195	-2.8229	-2.9405	-3.1164		
Sre	1.2473	1.4566	1.5429	1.8249	2.3549		
EABS	1.0928	-1.5502	-1.8059	-2.5341	-3.9484		
MPSD	0.0937	0.09969	0.09981	0.10396	0.1102		
X2	0.2895	0.43708	0.5098	0.74515	1.2305		

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
q _e	4.27	5.8	6.8	8.95	13.3		
Κ	2.0	2.5	2.8	3.5	4.5		
n	0.2	0.2	0.2	0.2	0.2		
\mathbf{R}^2	0.9959	0.9990	0.9952	0.9999	0.9965		
Mean	3.0295	3.9417	4.5852	6.0778	8.664		
HYBRID	0.000146	0.0000529	0.000309	0.0000042	0.00055		
SSE	0.00483	0.002325	0.01581	0.00029	0.05575		
RMSE	0.02316	0.01606	0.04188	0.005676	0.07867		
ARE	-0.1685	0.0877	0.19653	0.01977	0.18636		
Sre	0.07934	0.045306	0.10742	0.012269	0.1408		
EABS	-0.0695	0.04822	0.12572	0.01703	0.23612		
MPSD	0.00596	0.003101	0.006948	0.000699	0.006589		
X2	0.00117	0.000423	0.00247	0.0000337	0.0044		

Table 4.51: Nonlinear Avraim kinetic parameters using CCAC

Table 4.52: Nonlinear Pseudo second-order kinetic parameters using CCAC

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
K ₂	1.8	2.1	2.4	2.7	3.3		
q _e	8.2	5.4	6.3	8.4	12.3		
R^2	0.9952	0.9957	0.9969	0.9924	0.9914		
Mean	5.0513	3.9417	4.5852	6.0778	8.664		
HYBRID	0.000803	0.000236	0.000199	0.000709	0.001369		
SSE	0.054115	0.010397	0.01016	0.04888	0.13877		
RMSE	0.0775	0.03397	0.03358	0.07366	0.12411		
ARE	-0.2760	-0.1855	-0.1575	-0.2565	-0.2940		
Sre	0.16955	0.09581	0.08613	0.1592	0.22218		
EABS	-0.2326	-0.1097	-0.1008	-0.22109	-0.3725		
MPSD	0.009759	0.006557	0.00557	0.00907	0.01039		
X2	0.006421	0.00189	0.00158	0.00567	0.01095		

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
K ₁	1.2	1.3	1.3	1.5	1.5		
q_e	3.95	4.85	5.07	5.99	8.5		
R^2	0.9803	0.9943	0.9889	0.9986	0.9772		
Mean	3.9323	4.8423	5.0513	5.9868	8.4307		
HYBRID	0.06881	0.1198	0.1672	0.2572	0.3089		
SSE	3.1518	7.2253	11.276	21.9773	35.8003		
RMSE	0.5915	0.8955	1.1188	1.5619	1.9934		
ARE	-3.1008	-3.5659	-3.9843	-4.3903	-4.1312		
Sre	1.6254	2.0846	2.4474	3.0261	3.3715		
EABS	-1.7753	-2.688	-3.358	-4.688	-5.9833		
MPSD	0.1096	0.1261	0.1408	0.1552	0.1461		
X2	0.5505	0.9585	1.3379	2.0582	2.4718		

Table 4.53: Nonlinear Pseudo first-order kinetic parameters using RHAC

Table 4.54: Nonlinear Elovich kinetic parameters using RHAC

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
α	2.25	1.8	1.68	1.15	1.15		
β	0.699	1.13	1.055	0.78	0.502		
\mathbf{R}^2	0.9845	0.9805	0.9802	0.9900	0.9867		
Mean	3.932	4.8423	5.0513	5.9868	8.4307		
HYBRID	0.0691	0.1182	0.1657	0.2551	0.31198		
SSE	3.1652	7.1254	11.177	21.7874	36.1484		
RMSE	0.5927	0.8893	1.1138	1.555	2.0031		
ARE	3.1074	-3.5412	-3.9667	-4.3713	-4.1512		
Sre	1.6288	2.0701	2.4366	3.0130	3.3878		
EABS	1.7791	-2.6693	-3.3431	-4.6677	-6.0124		
MPSD	0.1099	0.1252	0.1402	0.1545	0.1467		
X2	0.5528	0.9453	1.3261	2.0404	2.4958		

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
q _e	6.03	7.79	8.96	11.4	14.4		
Κ	2.5	2.9	3.2	3.2	4.5		
n	0.2	0.2	0.2	0.2	0.2		
R^2	0.9995	0.9995	0.9966	0.9960	0.9929		
Mean	3.9322	4.8423	5.0513	5.9868	8.4307		
HYBRID	0.000036	0.000056	0.00057	0.00103	0.00224		
SSE	0.00167	0.00339	0.0389	0.08776	0.2599		
RMSE	0.0136	0.01939	0.06576	0.09870	0.1698		
ARE	0.0713	-0.0772	0.2342	0.27743	-0.3519		
Sre	0.03737	0.04513	0.1439	0.19122	0.2873		
EABS	0.04082	-0.05819	0.1974	0.29624	-0.5098		
MPSD	0.002521	0.002729	0.0083	0.00980	0.01244		
X2	0.000291	0.000449	0.0046	0.00822	0.01794		

Table 4.55: Nonlinear Avraim kinetic parameters using RHAC

Table 4.56: Nonlinear Pseudo second-order kinetic parameters using RHAC

Parameter	Initial Concentration (mg/l)						
	100	150	200	300	500		
K ₂	1.6	1.9	2.23	3.29	3.65		
q_e	5.62	7.38	8.28	10.4	14.32		
\mathbf{R}^2	0.9962	0.9964	0.9979	0.9964	0.99925		
Mean	3.9323	4.8423	5.0513	5.9868	8.43066		
HYBRID	0.00027	0.000437	0.00034	0.00092	0.00024		
SSE	0.01221	0.02636	0.02302	0.07869	0.02743		
RMSE	0.03683	0.05410	0.05055	0.09346	0.05518		
ARE	-0.1931	-0.2154	-0.1800	-0.2627	-0.1144		
Sre	0.1012	0.12593	0.11059	0.18108	0.09332		
EABS	-0.1105	-0.1624	-0.1517	-0.2805	-0.1656		
MPSD	0.00683	0.00762	0.00637	0.00928	0.0040		
X2	0.00213	0.00350	0.00273	0.00737	0.00189		

4.8 Mechanistic Modeling

The adsorption mechanism of a sorbate onto the adsorbent follows three steps viz. film diffusion, pore diffusion (external mass transfer) and intraparticle transport diffusion. The slowest of three steps controls the overall rate of the process (Goswami and Uday, 2005). There is a high possibility for pore diffusion to be the rate-limiting step in a batch process, though the adsorption rate parameter which controls the batch process for most of the contact time is the intraparticle diffusion. For a continuous flow system, film diffusion is more likely the rate-limiting step (Okewale et al, 2013). The adsorption mechanism was investigated using the intra-particle diffusion model, Bangham model and Boyd kinetics model.

4.8.1 Intra-particle diffusion model

One of the most commonly used technique in identifying the mechanism involved in the adsorption process is the intra-particle diffusion plot. It expresses the relationship between the adsorption capacity (q_t) at time $t^{1/2}$ (Okewale et al, 2013; Guibal et al, 1998). The Intra-particle diffusion is given by equation 4.20

$$q_t = K_d t^{1/2} + \delta$$
 (4.20)

The plot of q_t against $t^{1/2}$ was given in appendix D, from which the intra-particle diffusion constant, K_d was determined and presented in Tables 4.57 and 4.58 together with the intercept δ and the correlation coefficient R^2 values. Ozer et al, (2007) reported that if the linear plot of q_t versus $t^{1/2}$ passes through the origin, then intra-particle diffusion will be the sole rate-limiting process. The values of the correlation coefficient R^2 were quite high for both adsorbents indicating that the adsorption of phenol followed the intra-particle diffusion but, since the linear plot did not pass through the origin, then the intra-particle diffusion though involved in the adsorption process, is not the rate-controlling step. This may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption (Chakrapani et al, 2010; Okewale et al, 2013). Similar results were obtained by Atef and Waleed, (2009) and Ozer et al, (2007).

4.8.2 Boyd Model

Boyd's model is often used to obtain insight into the mechanism of the adsorption kinetics. It also determines if the adsorption mechanism was governed by external mass transport. When applied to external mass transfer, it supposes a linear dependence through the origin between the fractional approach to equilibrium and time. The Boyd model is given as expressed by Tsibranska and Hristova (2011) in equation 4.21

$$\ln (1 - F) = -kt$$
 (4.21)

where F represents the fraction of solute adsorbed at any time given by q_t/q_e and t is the time in minutes and k denotes the external mass transfer coefficient.

The linear plot of ln(1-F) against t was used to investigate the Boyd model (see appendix D). The correlation coefficient and the external mass transfer coefficient at different conditions were tabulated in Tables 4.57 and 4.58.

Okewale (2003) reported that if the adsorption process followed the Boyd kinetic model then the adsorption mechanism was governed by external mass transport where particle diffusion is the rate limiting step and the three sequential steps involved in the adsorption are:

1. Film diffusion, where adsorbate ions travel towards the external surface of the adsorbent.

2. Particle diffusion where adsorbate ions travel within the pores of the adsorbent excluding a small amount of adsorption that occurs on the exterior surface of the adsorbent

3. Adsorption of the adsorbate ions on the interior surface of the adsorbent (Tan and Hameed, 2010).

The correlation coefficient of the adsorption of phenol using rice husk and corn cob adsorbents were very high (above 0.97) in most cases suggesting that the adsorption mechanism was governed by external mass transport where particle diffusion is the rate limiting step.

4.8.3 Bangham's model

Bangham's model is also called Pore diffusion model. It was used to evaluate whether the adsorption is pore-diffusion controlled. The kinetic model is given Rajendran and Namasivayam (2008) in equation 4.22

$$\log\left\{\frac{C_{o}}{C_{o}-qm}\right\} = \log\left(\frac{K_{o}M}{2.30V}\right) + \alpha\log t$$
(4.22)

where C_o is initial concentration (mg/l), V is volume of the solution (mL), M is weight of the adsorbent (gL⁻¹), q_m is amount of adsorbate retained at time 't' (mmol g-1) while α and K_o are Bangham constants.

The Bangham model was investigated by plotting log {log [$C_o/(C_o-q_m)$]} against log t in appendix D from where α and K_o were calculated from the slope and intercept respectively and summarized in Tables 4.57 and 4.58. (Chakrapani et al 2010).

The correlation coefficients obtained were up to 0.901 for adsorption of phenol using corn cob and 0.945 for adsorption of phenol using rice husk. This showed that the

adsorption of phenol unto RHAC fitted the Bangham model more than that of CCAC. Rajendran and Namasivayam (2008) reported that if the correlation coefficient is close to unity the adsorption is said to be pore-diffusion controlled. Therefore, the adsorption of phenol unto these adsorbents is probably not controlled by pore diffusion. A similar trend was reported in the removal of fluorides from aqueous solutions using peels of citrus fruits (Chakrapani et al 2010).

In conclusion, the adsorption of phenol unto CCAC and RHAC can be said to be governed by external mass transport mechanism where particle diffusion is the rate limiting step.

Mechanistic		Concentration (mg/l)			
model					
	100	150	200	300	500
Bangham					
R^2	0.719	0.777	0.839	0.846	0.901
α	0.017	0.016	0.014	0.013	0.014
K _o	118.79	117.99	117.42	117.19	116.04
Intra-particle					
diffusion model					
\mathbf{R}^2	0.975	0.975	0.959	0.948	0.974
K _d	0.803	1.033	1.173	1.518	1.092
δ	0.375	0.483	0.482	0.529	1.092
Boyd model					
R	0.814	0.887	0.941	0.913	0.956
Κ	0.038	0.036	0.040	0.035	0.044

Table 4.57 Mechanistic model parameters for adsorption of phenol unto CCAC

Mechanistic		Concentration (mg/l)			
model					
	100	150	200	300	500
Bangham					
R^2	0.938	0.945	0.944	0.880	0.940
α	0.029	0.027	0.024	0.021	0.016
Ko	115.53	116.86	117.40	117.68	116.60
Intra-particle					
diffusion model					
R^2	0.985	0.979	0.958	0.828	0.936
K _d	1.02	1.41	1.514	1.913	2.400
δ	0.581	1.463	1.928	3.058	2.863
Boyd model					
R	0.910	0.943	0.978	0.961	0.984
Κ	0.045	0.041	0.057	0.044	0.041

Table 4.58 Mechanistic model parameters for adsorption of phenol unto RHAC

4.9 Point of zero charge

The point of zero charge (pzc) obtained for adsorption of phenol using RHAC was 4.67 while that of CCAC was 5.83 as shown in figures 4.33 and 4.34. The point zero charge determines the surface charge of the sorbent at a given pH and gives information about the possible electrostatic interactions between adsorbent and the adsorbate in terms of the possible attraction and repulsion between them. The knowledge of the point of zero charge also gives information on the ionization of functional groups and their interaction with adsorbate species in solution. At solution pHs higher than the point of zero charge, the adsorbent surface interacts with the positive species because it is negatively charged

while at pHs lower than point of zero charge, it interacts with negative species since the surface is positively charged (Nuria and Isabel, 2009).

Batch studies showed that maximum phenol uptake was obtained at pH of 6 for both RHAC and CCAC adsorbents which were slightly greater than pH of the point of zero charge for both adsorbents. Therefore, electrostatic attractions between negatively charged surface of these adsorbents and phenol ions could take place and contribute to the adsorption (Nuria and Isabel, 2009). Maximum sorption of phenol was obtained at a pH around 6.7 which is quite higher than the pH_{pzc} obtained using RHAC.

Therefore, it is clear that the sorbent surface is not negatively charged at this pH.In the absence of sorbed ions other than protons, the pzc is equal to the point of zero proton charge (pzpc). Arlette et al (2012) reported that due to non homogeneities that can develop in certain suspensions, the pzc values measured for the same adsorbent may vary widely.



Fig 4.33 Point of zero charge for adsorption of phenol using CCAC



Fig 4.34 Point of zero charge for adsorption of phenol using RHAC

4.10 Thermodynamics Properties

In order to estimate the feasibility and the nature of the adsorption process, relevant thermodynamic properties such as free energy (ΔG), enthalpy change (ΔH) and entropy change were determined using the Van't Hoff equations in equations 4.23 and 4.24.

$$\Delta G^{o} = -RT \ln K_{L} \tag{4.23}$$

$$\ln K_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$
(4.24)

By plotting ln K against 1/T as shown in Figure 4.35, the quantities Δ H and Δ S were calculated from the slope and intercept respectively and presented in Tables 4.59.



Figure 4.35 Thermodynamic plot for phenol adsorption using CCAC and RHAC

The values of the enthalpy change (Δ H) obtained were 14.83KJ/mol for adsorption of phenol using CCAC and 13.959KJ/molfor RHAC. The positive values of Δ H indicate the endothermic nature of the adsorption process and a good concordance between the used methods (Vicente et al, 2011). This is also supported by the decrease in the value of adsorbed capacity of the sorbent with the increase in temperature.

The change in entropy (Δ S) obtained were 73.79 J/mol K using CCAC and 75.47 J/mol K using RHAC. The values of Δ S were positive suggesting favorable randomness (Pregneshet al, 2010). The positive of Δ S reflects an affinity of the phenol for the adsorbent and increasing randomness of the solid-solution interface during the adsorption (Vicente et al, 2011). This is because the number of water molecules surrounding the phenol ions decreased during the adsorption process and thus, the degree of freedom of the water molecules increases (Muhammad and Muhammad, 2006). Atef and Waleed (2009) got Δ S value of 9.2 (J/mol K).

The Van Hoff plot is given in figure 4.36. The Gibbs free energy ΔG ranged from -7.7 to -9.8 KJ/mol K for the phenol removal using CCAC and from -9.04 to -11.16 KJ/mol K using RHAC. The negative values of ΔG indicated that the adsorption process was non-spontaneous. The values of ΔG increased slightly with temperature and were relatively

close meaning that there is no much effect of temperature on the free energy of adsorption (Muhammad and Muhammad, 2010).



Fig 4.36: Van't Hoff plot for the adsorption of phenol

Adsorbents	T (K)	∆G (KJ/mol)	$\Delta \mathbf{S} (\mathbf{J}/\mathbf{mol} \ \mathbf{K})$	$\Delta \mathbf{H} (\mathbf{KJ/mol})$
CCAC				
	303	-7.753	73.79	14.832
	308	-9.182		
	313	-7.895		
	323	-9.991		
	333	-9.876		
RHAC				
	303	-9.039	75.47	13.959
	308	-9.245		
	313	-9.599		
	323	-9.701		
	333	-11.156		

 Table 4.59
 Thermodynamics parameters for the adsorption of phenol

4.10.1. Activation Energy

The linear form of the Arrhenius equation was used to determine the activation energy of the adsorption process. The equation is given in equation 4.25

$$\ln K = \ln A - \frac{E_a}{RT} \tag{4.25}$$

where K is the second-order rate constant (g/mol min), A is the frequency factor (g/mol min), T is the temperature (K), R is the gas constant (J/mol K) and E_a is the activation energy (KJ/gmol).

From the linear plot of ln K against 1/T (Figures 4.37), E_a was evaluated from slope and shown in Table 4.60.



Fig 4.37: Activation energy plot for the adsorption of phenol

Table 4.60 Activation energy for the adsorption of phenol

Adsorbent	Ea (KJ/mol)	Α	(g/mol
		min)	
Corn Cob	6.43 x 10 ⁻⁶	7.65 x	10-6
Rice Husk	1.32 x 10 ⁻⁷	3.61 x	10-6

4.11 Regeneration studies

Regeneration studies were conducted to analyze the possibility of reuse of the adsorbent for further adsorption and to make the process more economical. Among other substances used, NaOH solution has been found to be effective in regeneration studies. Infact, Zhu et al. (2009), Zhang et al. (2009) and Hu et al. (2005) reported NaOH solution as the most effective regenerating/desorbing agent. Therefore, the study was done using batch equilibrium method with different concentrations of sodium hydroxide (NaOH) solution as shown in figures 4.38 and 4.39 for the spent RHAC and CCAC.

The figures indicated that after about 300 minutes, the regeneration adsorption efficiency using RHAC was 71.30%, 78.03% and 86.17% using NaOH solutions of concentrations 0.05M, 0.1M and 0.2M respectively. Using CCAC, the regeneration adsorption efficiency was 56.48%, 66.05% and 74.99% using 0.05M, 0.1M and 0.2M of NaOH solution respectively. In the regeneration-adsorption studies on chromium VI removal, Hu et al (2005) obtained an efficiency of about 87.7% using NaOH solution. In another study of Selenium IV removal, Zhang et al (2009) reported regeneration-adsorption efficiency of 95% using NaOH solution as the regenerating agent. The efficiency was found to be relatively within these ranges for about 3 cycles of regeneration before it showed much significant decrease which will no longer be economically viable. These results reveal that these carbon based adsorbents could be recovered and repeatedly used in adsorption of phenol from an aqueous solution.

The resultant desorption phenomenon observed by using NaOH might be attributed to ion exchange type interaction rather than chemical sorption (Ayodele and Godswil, 2014). This is because the phenol is soluble in the alkaline solution due to the presence of phenolic hydroxyl group and carboxyl functional group (Qiu and Chen, 2006). This releases the adsorbed phenolic ions when it dissolves in the NaOH solution freeing up the vacant sites again for reuse. A good adsorbent for any adsorbate removal must be able to

be regenerated otherwise the waste has to be disposed of and fresh sorbent used always (Parimalam et al, 2011).



Figure 4.38 Regeneration plot using different concentrations of NaOH for RHAC



Figure 4.39 Regeneration plot using different concentrations of NaOH for CCAC
4.12 Optimization of phenol adsorption using CCAC

The adsorption of the phenol removal was optimized using central composite design (CCD) as shown in Table 4.61.

Std Run	Temperature	Concentration	Contact time	Dosage	Percentage
	(°C)	(mg/l)	(mins)	(gram)	Adsorbed (%)
1	40	100	30	1.0	58.2
2	50	100	30	1.0	62.8
3	40	200	30	1.0	41.9
4	50	200	30	1.0	44.3
5	40	100	90	1.0	60.1
6	50	100	90	1.0	66.1
7	40	200	90	1.0	48.9
8	50	200	90	1.0	53.1
9	40	100	30	1.5	65.5
10	50	100	30	1.5	67.8
11	40	200	30	1.5	62.0
12	50	200	30	1.5	64.8
13	40	100	90	1.5	79.3
14	50	100	90	1.5	93.5
15	40	200	90	1.5	74.8
16	50	200	90	1.5	77.3
17	37.93	150	60	1.25	54.9
18	52.07	150	60	1.25	57.6
19	45	79.29	60	1.25	75.4
20	45	220.71	60	1.25	59.7
21	45	150	17.57	1.25	45.3
22	45	150	102.43	1.25	72.1
23	45	150	60	0.896	61.2
24	45	150	60	1.603	76.9
25	45	150	60	1.25	68.5
26	45	150	60	1.25	68.9
27	45	150	60	1.25	68.4
28	45	150	60	1.25	67.8
29	45	150	60	1.25	68.6
30	45	150	60	1.25	68.6

Table 4.61 Experimental result of phenol adsorption using CCAC

The result was obtained using 30 experiments which consist of 16 core points, 8 star like points and 6 centre points or null points as shown in Table 4.63. The distance of the starlike point, α , used was 1.412. The experiments were performed in random to avoid systematic error. The highest percentage of phenol adsorbed was 93.5%. This was obtained at a temperature of 50°C, contact time of 90 minutes, initial concentration of 100mg/l and adsorbent dosage of 1.5g. The responses obtained from various runs were significantly exceptional which implies that each of the factors has a substantial effect on the response.

4.12.1 Model fitting

The Model summary is presented in Table 4.62 while the Fit summary and Sequential fit summary are given in the appendix. They were used to evaluate the adequacy of the experimental results on different models such as linear, two factor interaction (2FI), quadratic or cubic models. Design-Expert version 11 was used to analyze the results. The Fit summary, Sequential fit summary and Model summary all indicated that a quadratic model best fitted the optimization analysis and hence it was suggested. The linear and 2FI models were not suggested. The Cubic model is always aliased because the CCD does not contain enough runs to support a full cubic model.

The coefficient of regression, R^2 , was used to validate the fitness of the model equation. The R^2 of the quadratic model has a high value of 0.9464 indicating that 94.64% of the variability in the response can be explained by the model. This implies that the prediction of experimental data is quite satisfactory. However, if the regression coefficient (R^2) of the modeling process is low (< 70%), then the mathematical model is not good (Daniel and Gast, 2014). The adjusted R^2 for the quadratic model was 0.8964 while the predicted R^2 was 0.7431. These values were within 0.2 of each other showing that there is no problem with either the data or the model (Taran and Aghaie, 2015). Also, a PRESS value of 819.10 indicates an adequate signal implying that the quadratic model can be used to navigate the design space.

Source	Std. Dev.	\mathbf{R}^2	Adjusted	Predicted	PRESS	Remark
			\mathbf{R}^2	\mathbf{R}^2		
Linear	5.27	0.7819	0.7417	0.6910	985.27	Not
						suggested
2FI	5.17	0.8409	0.7572	0.7122	917.82	Not
						suggested
Quadratic	3.37	0.9464	0.8964	0.7431	819.10	Suggested
Cubic	2.62	0.9850	0.9378	-0.6765	5345.92	Aliased

Table 4.62 Model summary statistics of phenol adsorption using CCAC

4.12.2 ANOVA of phenol adsorption using CCAC

The analysis of variance (ANOVA) was used to test the significance of the quadratic model suggested including the significance of the individual terms in Table 4.63. The degree of freedom of the quadratic model was 14 as expected.

The F-value tests were performed using the ANOVA to calculate the significance of each type of model. Based on the results of F-value, the highest order model with significant terms which shows the most accurate relationship between parameters would be chosen.

The model F-value of 18.93 implies that the model is significant which is in agreement with the P-value being less than 0.0001. There is only a 0.01% chance that an F-value this large could occur due to noise.

A confidence level of 95% was used hence the significance level was 5%. This means that P-values greater than 0.05 are considered insignificant while those at 0.05 or less are significant. The ANOVA showed that there were not many insignificant model terms hence model reduction was not needed to improve the model.

The adequate precision ratios of 17.09 indicate adequate signal. Kumar et al, (2007) reported that adequate precision ratio above 4 indicates adequate model efficacy since it measures the signal to noise ratio and compares the range of the predicted value at the design points to the average prediction error.

The Statistical analysis was given in at the foot of Table 6.63. The coefficient of variation (C.V) is a measure of reproducibility and repeatability of the models. Chen et al., (2010) reported that if the C.V is not greater than 10, the suggested model is considered reasonably reproducible. Hence, the C.V of 5.31% shows that the model is reasonably reproducible.

Source	Sum of	df	Mean	F - value	P-value	Remark
	squares		square			
Model	3017.90	14	215.56	18.93	< 0.0001	Significant
A –	53.85	1	53.85	4.73	0.0461	
Temperature						
B –	484.16	1	484.16	42.51	< 0.0001	
Concentration						
C – Contact	646.39	1	646.39	56.75	< 0.0001	
time						
D – Dosage	1309.01	1	1309.01	114.93	< 0.0001	
AB	1.69	1	1.69	0.1484	0.7055	
AC	1.44	1	1.44	0.1264	0.7271	
AD	1.82	1	1.82	0.1600	0.6948	
BC	2.56	1	2.56	0.2248	0.2248	
BD	109.20	1	109.20	9.59	0.0074	
CD	71.40	1	71.40	6.27	0.0243	
A^2	183.93	1	183.93	16.15	0.0011	
B^2	13.68	1	13.68	1.20	0.2904	
C^2	96.43	1	96.43	8.47	0.0108	
D^2	35.88	1	35.88	3.15	0.0962	
Residual	170.85	15	11.39			
Lack of Fit	170.18	10	17.02	126.37	< 0.0001	
Pure Error	0.6733	5	0.1347			
Cor Total	3188.75	29				
Std. Dev.	3.37		Mea	an	64.14	
C.V(%)	5.26		R2		0.9464	
Adjusted R2	0.8964		Prec	licted R2	0.7431	
Adeq Precision 17.094						

Table 4.63 ANOVA analysis of phenol adsorption using CCAC

4.12.3 Modeling of the optimization process

4.26

Model equations obtained for the adsorption of phenol using CCAC are given in equation

Percent Adsorbed =
$$-253.07 + 16.72*A - 0.462*B + 0.136*C - 82.167*D - 0.0013*A*B + 0.002*A*C - 0.270*A*D + 0.000267*B*C + 0.209*B*D + 0.282*C*D - 0.178*A2 + 0.000484*B2 - 0.00357*C2 + 31.37*D2$$
 (4.26)

Since a confidence level of 5% was used, P-values less than 0.05 indicate the model terms are significant otherwise, it is insignificant. Therefore, eliminating the insignificant terms, the final model equations is expressed in equations (4.27)

Percent Adsorbed = -253.07 + 16.72*A - 0.462*B + 0.136*C - 82.167*D + 0.209*B*D+ $0.282*C*D - 0.178*A^2 - 0.00357*C^2$ (4.27)

4.12.4 Comparison of predicted and experimental values

Table 4.64 is a comparison of the actual experimental response and the predicted response obtained from the mathematical equations. It is seen that there is a very close correlation between the actual experimental response and the predicted response. This close relationship is desirable for optimisation process because the predicted optimal result will produce an insignificant deviation from the experimental value indicating the suitability of the quadratic model selected in predicted the adsorption of phenol using CCAC.

Std	Temperature	Concentration	Contact	Dosage	Experimental	Predicted
Run	(°C)	(mg/l)	time	(gram)	Percentage	Percentage
			(mins)		Adsorbed (%)	Adsorbed (%)
1	40	100	30	1.0	58.2	56.92
2	50	100	30	1.0	62.8	60.92
3	40	200	30	1.0	41.9	41.70
4	50	200	30	1.0	44.3	44.41
5	40	100	90	1.0	60.1	62.66
6	50	100	90	1.0	66.1	67.87
7	40	200	90	1.0	48.9	49.05
8	50	200	90	1.0	53.1	52.95
9	40	100	30	1.5	65.5	64.32
10	50	100	30	1.5	67.8	66.98
11	40	200	30	1.5	62.0	59.56
12	50	200	30	1.5	64.8	60.91
13	40	100	90	1.5	79.3	78.52
14	50	100	90	1.5	93.5	92.37
15	40	200	90	1.5	74.8	75.35
16	50	200	90	1.5	77.3	77.91
17	37.93	150	60	1.25	54.9	55.93
18	52.07	150	60	1.25	57.6	60.57
19	45	79.29	60	1.25	75.4	76.51
20	45	220.71	60	1.25	59.7	62.59
21	45	150	17.57	1.25	45.3	52.66
22	45	150	102.43	1.25	72.1	68.74
23	45	150	60	0.896	61.2	59.61
24	45	150	60	1.603	76.9	82.49
25	45	150	60	1.25	68.5	67.13
26	45	150	60	1.25	68.9	67.13
27	45	150	60	1.25	68.4	67.13
28	45	150	60	1.25	67.8	67.13
29	45	150	60	1.25	68.6	67.13
30	45	150	60	1.25	68.6	67.13

Table 4.64 Experimental and Predicted responses using CCAC

4.12.5 Error analysis using CCAC

The Normal plot of Residuals in figure 4.40 was used to check whether the points will follow a straight line in which we conclude that the residuals follow a normal distribution in the adsorption of phenol using CCAC. The points of the normal distributions are seen to be mostly interlocked with the straight line with a few points lying outside the diagonal line in a moderately scattered manner. Therefore, since the data points on the normal plot of residuals showed a close distributed to the straight line of the plot, it is concluded that there is a good relationship between the experimental values and the predicted values of the response. This confirms that the selected quadratic model was adequate in predicting the response variables in the experimental values.



Figure 4.40 Normal probability plots of Residuals obtained using CCAC

The predicted versus actual plot was used to ascertain if the theoretical normal distribution forms an approximate straight line. Departures from this straight line indicate departures from normality (Chambers, et al., 1983). The farther the points vary from this line, the greater the indication of departures from normality. If the resulting plot is approximately linear, we proceed to assume that the process data are normally distributed (Ryan, 1997). Figure 4.41 shows that the experimental values were distributed confidently near the predicted values, implying a good correlation between the actual and predicted values.



Figure 4.41 Linear correlation between Predicted vs. Actual values using CCAC

The Perturbation graph shows the deviation from the reference point in terms of coded terms. The reference point of a deviation is the mean. The reference point is at 70% adsorption as seen in figure 4.42. The contact time (C) has the least deviation from the mean ranging from 60 to 70% while adsorbent dosage (D) showed the greatest deviation from 60 to 75% as the coded values ranged from -1 to +1.



Fig 4.42 Perturbation plot showing deviation from the Reference point using CCAC

4.12.6 Three Dimensional (3D) surface plots using CCAC

In order to visualize the relationship between the experimental variables and the responses, three dimensional (3-D) surface plots generated from the quadratic model were used for estimating the removal of phenol using CCAC in figures 4.43 to 4.48. The 3-D response surface plots are graphical representation of the interactive effects of any two variables factors. The surface plots were plotted as a function of two factors at a time maintaining all other factors at fixed levels. They are helpful in understanding the single and interaction effects of all the factors.

The nature of the response surface curves shows the interaction between the variables. The elliptical nature of the 3-D response surface plots illustrates the interaction between the two independent variables plotted together and also indicates good interaction of the two variables while a circular shape of the 3D – plots indicates no interaction between the variables (Li, et al., 2011). Therefore the elliptical nature of the contour graphs in figures 4.85 to 4.90 depicted mutual interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted yield as indicated by the surface confined in the smallest ellipse in the contour diagrams. Temperature was found to have a small negative effect on the percentage of phenol adsorbed. This is because as the temperature decreased, the percentage of phenol adsorbed increased.



Percent Adsorbed (%) C: Contact Time (mins) A: Temp (oC)

Figure 4.43 3-D plot showing combined effects of temperature and concentration using CCAC

Figure 4.44 3-D plot showing combined effects of temperature and contact timeusing CCAC





Figure 4.45 3-D plot showing combined effects of temperature and dosageusing CCAC

Figure 4.46 3-D plot showing combined effects of contact time and concentrationusing CCAC



Figure 4.47 3-D plot showing combined effects of dosage and concentrationusing CCAC

Figure 4.48 3-D plot showing combined effects of contact time and dosageusing CCAC

4.12.7 Validation of the results using CCAC

Ninety-three (93) different solutions of optimization desirabilities were proposed by the central composite design as given in Appendix A. These show the combination of factors at different conditions and their predicted responses. The desirability is a measure of the accuracy in predicting the response at the chosen conditions. The desirability values range from 0 to unity based on how close the response is towards the objective (Sunil, 2015). The closer the desirability is to one, the better the accuracy. The percentage of phenol adsorbed was set at the maximum level because the purpose is to maximize the adsorption of phenol. The contact time, phenol concentration and adsorbent dosage were set at minimum level while the operating temperature was set in range.

Condition number 1 with desirability of 0.819 and process conditions of temperature 40.843°C, phenol concentration of 100 mg/l, contact time of 31.979 minutes and

adsorbent dosage of 1.0 gram was selected. The percentage adsorbed was 59.23.19%. The adsorption process was validated by using the test-retest method and the mean percentage of phenol adsorbed unto CCAC was 60.56% at those selected process conditions as seen in Table 4.65. This validates the proposed optimum conditions.

Table 4.65: The validation result using CCAC

Pr	edicted condi	Predicted	Experimental			
Temperat	erat Phenol Contact time Adsorben		Adsorbent	Percentage	Percentage	
ure °C	ure °C concentrati d		dosage	adsorption	adsorption	
	on					
46.04°C	100 mg/l	30.0 minutes	1.0g	59.23%	60.56%	

4.12.8 ANN analysis using CCAC

The artificial neural network was used to map a set of data of numeric inputs of the process parameters (that is, the contact time, adsorbent dosage, initial concentration and temperature) and a set of numeric targets. ANN helps to create a neural network model to train, validate and test the data set (Devika et al, 2014). Multi-Layer Perceptron networks were used for error minimization.

Multi-Layer Perceptron (MLP) are normally trained with error back-propagation (BP) algorithm. The case scaled conjugate gradient back propagation can be used when there is not enough memory. A two-layer feed-forward network with sigmoid hidden neurons and liner output neurons were used to fit the multi-dimensional mapping problems arbitrarily well. The network architecture was given as shown in figure 4.49



Figure 4.49: The Neural Network Architecture of adsorption phenol using CCAC

4.12.9 ANN Training, Testing and Validation

The analysis ANN involves training, testing and validation of the model. A total of 30 experimental runs were involved in the ANN analysis. About 70% comprising 20 experimental runs were used for training. During the training process, the weights are adjusted in order to make the actual outputs (predicated) close to the target (measured) outputs of the network and minimize its errors. Equally, 15% (that is 5 experimental runs) were used for testing. At this stage, unseen data are exposed to the model. The testing provides an independent measure of network performance during and after training. It has no effect on the training. The remaining 15% (5 experimental runs) was used to validate the model. In the validation, the network generalization was measured by network validation and halted when generalization stops improving to stop over fitting. A large percentage was mapped out for training the model because Kiran and Pragnesh et al,

(2016) reported that more data sets in training reduces processing time in ANN learning and improves the generalization capability of models.

Repeated testing of different number of hidden neurons in the hidden layer was used to determine the best appropriate number of hidden neurons. Mansour and Mostafa (2011) used and equally recommended this method. This was done to determine the best network performance and to define a fitting neural network model architecture.

Decision on the optimum number of hidden neurons was based on the minimum error of testing. Hence the objective was to obtain

- (i) The number of neurons that will give the regression a value closet to unity. Regression values (R) measures the correlation between outputs and inputs. A regression value very close to 1 means a close relationship while 0 a random relationship. The plot is given in figure 4.50
- (ii) The number of neurons that will give the lowest number of mean square error. Mean Square Error (MSE) is the average squared difference between outputs and targets. Lower values are better. Zero means no error. Figure 4.51 gave the relationship between the number of neurons and the MSE



Figure 4.50 Relationship between number of neurons and regression values



Figure 4.51 Relationship between number of neurons and MSE values

Neuron numbers between 2 to 20 were used based on the different formulae suggested by different authors as reported by Antonio et al (2017). Based on the two factors above, 6 number of hidden neurons was chosen and modeled appropriately. The regression values and the mean square errors for the selected 6 number of neurons were given in Table 4.66.

Table 4.66 Regression values and the mean square errors for 6 neurons in the hidden layer

Objective	Number of samples	Regression value	Mean square error
Training	20	0.962	17.55
Validation	5	0.996	9.99
Testing	5	0.711	45.76

The network has four inputs (solution temperature, adsorbent dosage, initial phenol concentration and contact time) and one output is the percentage of phenol adsorbed. The flow diagram is shown in Figure 4.52.



Fig 4.52 Flow diagram of the ANN network with 6 hidden neurons

4.12.10 Post-Training Analysis

Network testing and network validation was performed in the post training analysis of the ANN.

4.12.10.1 Network Validation

The neural network was validated to check the network performance and also determine whether some changes needed to be made to the training process, the network architecture or the data sets. The plot of the training errors, validation errors, and testing errors was shown in figure 4.53. The performance was 0.0282 suggesting a good network performance.

The validation stabilized at Epoch 6 while it took 12 epochs to obtain repetition. The performance at the epoch was about 10. The type of plot generated indicated that there was no major problem with the validation. This is because if the test curve had increased significantly before the validation curve increased, then it could be possible that some over fitting might have occurred.



Figure 4.53: Plot of the network validation performance

The plot of the validation output and the best fit line is given in figure 4.54. The regression value was 0.9959 suggesting a good correlation of the neural network process between the validation data and the line of best fit. The mean square error was 9.997.



Figure 4.54: Plot of the network validation data and the best fit line

4.12.10.2 Network Testing

The regression value and the mean square error were used to test the network. If the values obtained were not appropriate, it may mean over fitting showing poor performance. The result can be improved by increasing or decreasing the number of neurons. The mean square error was 4.5 while the regression value was 0.941 indicating that the performance on the training set is good as shown in figure 4.55.



Figure 4.55 Network testing of the test data points

The Network test/evaluation shows the output tracks the target very well for training, testing, and validation and the R-value is over 0.9000 for the responses. The output tracks the target very well since the R values and the MSE values show good network performance. Based on these performance values, a satisfactory network response can be concluded. The model generated sets of output equation that relates the target to the output for training, testing, validation and the overall model output equation.

4.12.11. ANN response prediction

Figure 4.56 is the overall plot that expresses the relationship between the output and the target. The regression value of 0.9318 indicates a good correlation between the output and the target.



Figure 4.56 Plot of the overall output against the target

The model equation generated is given in equation (4.28). It was used to predict the ANN model values.

 $Y = 0.83T + 13 \tag{4.28}$

Where Y = the ANN model value,

T = the experimental value used to generate the corresponding ANN value.

The ANN predicted values were compared with the experimental values. This was done to ascertain the degree of correlation between the experimental values and the ANN predicted values as shown in Table 4.67. The percentage error in all the experimental runs was all below $\pm 1.0\%$ signifying good correlation between them.

Std	Temperature	Concentrat	Contact	Dosage	Experimental	ANN	Percentag
Run	(°C)	ion (mg/l)	time	(gram)	Percentage	percentage	e error
			(mins)		Adsorbed (%)	adsorbed	
						(%)	
1	40	100	30	1.0	58.2	61.306	-0.0566
2	50	100	30	1.0	62.8	65.124	-0.15385
3	40	200	30	1.0	41.9	47.777	-0.63107
4	50	200	30	1.0	44.3	49.769	-0.90045
5	40	100	90	1.0	60.1	62.883	-0.03576
6	50	100	90	1.0	66.1	67.863	-0.11111
7	40	200	90	1.0	48.9	53.587	-0.33545
8	50	200	90	1.0	53.1	57.073	-0.57895
9	40	100	30	1.5	65.5	67.365	-0.01818
10	50	100	30	1.5	67.8	69.274	-0.1245
11	40	200	30	1.5	62.0	64.46	-0.01083
12	50	200	30	1.5	64.8	66.784	-0.09948
13	40	100	90	1.5	79.3	78.819	0.101604
14	50	100	90	1.5	93.5	92.305	0.054054
15	40	200	90	1.5	74.8	75.084	0.008264
16	50	200	90	1.5	77.3	77.159	-0.02564
17	37.93	150	60	1.25	54.9	58.567	-0.09091
18	52.07	150	60	1.25	57.6	60.808	-0.53846
19	45	79.29	60	1.25	75.4	75.582	0.071823
20	45	220.71	60	1.25	59.7	62.551	-0.42615
21	45	150	17.57	1.25	45.3	50.599	-0.17155
22	45	150	102.43	1.25	72.1	72.843	0.092873
23	45	150	60	0.896	61.2	63.796	-0.43836
24	45	150	60	1.603	76.9	76.827	0.050847
25	45	150	60	1.25	68.5	69.855	0.030023
26	45	150	60	1.25	68.9	70.187	0.026651
27	45	150	60	1.25	68.4	69.772	0.023256
28	45	150	60	1.25	67.8	69.274	0.028902
29	45	150	60	1.25	68.6	69.938	0.028902
30	45	150	60	1.25	68.6	69.938	0.041096

Table 4.67 ANN predicted result of phenol adsorption using CCAC

4.12.12 Comparison of RSM and ANN results

The models generated by the RSM and the ANN were compared with the experimental result simultaneously to determine the best correlated model. The experimental and predicted values for each experiment were plotted against the run numbers of each experiment as shown in Figure 4.57. It was observed that the prediction of the percentage of phenol adsorbed in both models was in full agreement with that of experimental values.



Figure 4.57 Comparison plot of Experimental, RSM and ANN values

The ANN model predictions fitted the line of perfect prediction more than RSM model. This can be attributed to its approximation ability through nonlinearity of the system (Maranet al.2013) whereas the RSM belongs only to a second-order polynomial (Shanmugaprakash and Sivakumar 2013). However, the drawback is in the application of some studied variables and factors through the training process (Rajkovic et al. 2013) The error in each standard run was determined by subtracting the particular model prediction from the experimental result. The percentage error obtained showed that there was no significant difference between the experimental result and the ANN and RSM model predictions as given in Table 4.68.

		ANN			RSM		
Std	Exp	ANN (%)	Error	Percentage	RSM	Error	% Error
Run	(%)			error	(%)		
1	58.2	61.306	-3.106	-0.0566	56.92	1.28	2.199313
2	62.8	65.124	-2.324	-0.15385	60.92	1.88	2.993631
3	41.9	47.777	-5.877	-0.63107	41.7	0.2	0.477327
4	44.3	49.769	-5.469	-0.90045	44.41	-0.11	-0.24831
5	60.1	62.883	-2.783	-0.03576	62.66	-2.56	-4.25957
6	66.1	67.863	-1.763	-0.11111	67.87	-1.77	-2.67776
7	48.9	53.587	-4.687	-0.33545	49.05	-0.15	-0.30675
8	53.1	57.073	-3.973	-0.57895	52.95	0.15	0.282486
9	65.5	67.365	-1.865	-0.01818	64.32	1.18	1.801527
10	67.8	69.274	-1.474	-0.1245	66.98	0.82	1.20944
11	62.0	64.46	-2.46	-0.01083	59.56	2.44	3.935484
12	64.8	66.784	-1.984	-0.09948	60.91	3.89	6.003086
13	79.3	78.819	0.481	0.101604	78.52	0.78	0.983607
14	83.5	82.305	1.195	0.054054	82.37	1.13	1.353293
15	74.8	75.084	-0.284	0.008264	75.35	-0.55	-0.73529
16	77.3	77.159	0.141	-0.02564	77.91	-0.61	-0.78913
17	54.9	58.567	-3.667	-0.09091	55.93	-1.03	-1.87614
18	57.6	60.808	-3.208	-0.53846	60.57	-2.97	-5.15625
19	75.4	75.582	-0.182	0.071823	76.51	-1.11	-1.47215
20	59.7	62.551	-2.851	-0.42615	62.59	-2.89	-4.84087
21	45.3	50.599	-5.299	-0.17155	52.66	-7.36	-16.2472
22	72.1	72.843	-0.743	0.092873	68.74	3.36	4.660194
23	61.2	63.796	-2.596	-0.43836	59.61	1.59	2.598039
24	76.9	76.827	0.073	0.050847	82.49	-5.59	-7.26918
25	68.5	69.855	-1.355	0.030023	67.13	1.37	2
26	68.9	70.187	-1.287	0.026651	67.13	1.77	2.56894
27	68.4	69.772	-1.372	0.023256	67.13	1.27	1.856725
28	67.8	69.274	-1.474	0.028902	67.13	0.67	0.988201
29	68.6	69.938	-1.338	0.028902	67.13	1.47	2.142857
30	68.6	69.938	-1.338	0.041096	67.13	1.47	2.142857

Table 4.68 Comparison of ANN and RSM optimization result using CCAC

Furthermore, the Absolute Average Deviation (AAD) and the Coefficient of determination were evaluated for both models. According to Josh et al (2014), the AAD gives an indication of how accurate the model predictions can be. The equation is as given in equation 4.29

AAD (%) =
$$\left(\frac{1}{n}\sum_{i=1}^{n}\left\{\frac{(R_{art.pred} - R_{art.exp})}{R_{art.exp}}\right\}\right) \times 100$$
 (4.29)

where n is the number of sample points, $R_{art,pred}$ is the predicted percentage of phenol adsorbed and $P_{art,exp}$ is the experimentally determined percentage of phenol adsorbed. The coefficient of determination was obtained from the interactive plots of the RSM and ANN models in figure 4.58. It was used to validate the fitness of the model equation.



Figure 4.58 Interactive plots for RSM and ANN models

The AAD computation showed a value of 0.03868 for ANN and value of 0.00189 for RSM in Table 4.73. The lower the AAD value, the smaller the errors involved in

predicting the percentage of phenol adsorbed. The correlation coefficient of the ANN was 0.987 while that of the RSM was 0.946. These values measure how close the predicted value of the responses of ANN and RSM are to the actual experimental values.

These values confirm that both ANN and RSM are adequate in predicting the optimization of the adsorption of phenol unto CCAC.

Table 4.69 AAD and R^2 values for the optimization models

Model	AAD	\mathbf{R}^2
ANN	0.0.03868	0.987
RSM	0.001893	0.946

4.13 Optimization of phenol adsorption using RHAC

The experimental runs that were developed using the central composite design of response surface methodology in Design-Expert Software were used to optimize the adsorption of phenol using RHAC. Response surface methodology uses a minimum number of experiments to optimize a process while analyzing the interaction between the parameters. The result of the experimental runs consists of 16 core points, 8 star like points and 6 null points as shown in Table 4.70.

The result of the experimental runs indicated that the maximum phenol adsorption of 92.6% was obtained at a dosage of 0.8g, contact time of 70.8 minutes, phenol concentration of 150 mg/l and solution temperature of 50 °C. The result equally showed that the contact time has the greatest effect on the percentage removal of phenol while solution temperature has the least effect though all the responses obtained from various runs are significant implying that each of the independent variables has a substantial effect on the response.

Std Run	Temperature	Concentration	Contact time	Dosage	Percentage
	(°C)	(mg/l)	(mins)	(gram)	Adsorbed (%)
1	40	100	30	0.6	79.5
2	60	100	30	0.6	72.8
3	40	200	30	0.6	51.5
4	60	200	30	0.6	44.2
5	40	100	60	0.6	81.1
6	60	100	60	0.6	75.6
7	40	200	60	0.6	62.9
8	60	200	60	0.6	53.2
9	40	100	30	1.0	82.5
10	60	100	30	1.0	74.7
11	40	200	30	1.0	83.1
12	60	200	30	1.0	76.4
13	40	100	60	1.0	93.5
14	60	100	60	1.0	88.8
15	40	200	60	1.0	84.7
16	60	200	60	1.0	81.9
17	32.81	150	45	0.8	77.0
18	67.19	150	45	0.8	54.6
19	50	60.06	45	0.8	90.5
20	50	235.94	45	0.8	58.9
21	50	150	19.22	0.8	71.7
22	50	150	70.78	0.8	92.6
23	50	150	45	0.46	58.4
24	50	150	45	1.14	88.5
25	50	150	45	0.8	86.6
26	50	150	45	0.8	86.3
27	50	150	45	0.8	86.0
28	50	150	45	0.8	86.5
29	50	150	45	0.8	86.5
30	50	150	45	0.8	87.6

Table 4.70 Experimental result of phenol adsorption using RHAC

4.13.1 Model fitting

The adequacy of the experimental results on different models such as linear, two factor interaction (2FI), quadratic or cubic models was evaluated using Fit summary as given in Table 4.71. Sequential fit summary and Model summary was given in the Appendix. The fit summary compares the variation around the model with pure variation within the replicated observation. The lack-of-fit test measured the adequacy of the different models based on the response analysis (Lee et al, 2006). The model summary compares the correlation coefficient (\mathbb{R}^2), the adjusted \mathbb{R}^2 and the predicted \mathbb{R}^2 of the different models in predicting the response.

The R-square measures how efficient the variability in the actual response values can be explained by the experimental variables and their interactions. The R^2 has a high value of 0.9542 showing that 95.42% of the variability in the response can be explained by the model. This implies that the prediction of experimental data is quite satisfactory. The closer the R^2 value is to unity, the better the model predicts the response.

Adjusted- R^2 is a measure of the amount of variation around the mean explained by the model, adjusted for the number of terms in the model. The adjusted- R^2 decreases as the number of terms in the model increases, if those additional terms don't add value to the model. Predicted- R^2 is a measure of the amount of variation in new data explained by the model. The predicted- R^2 and the adjusted- R^2 should be within 0.20 of each other. Otherwise, there may be a problem with either the data or the model (Taran and Aghaie, 2015). The result showed that the quadratic model has the highest R-squared value of 0.9542 with Adjusted- R^2 and Predicted- R^2 values of 0.9115 and 0.7460 which were within 0.2 of each other. The aim is to select the highest order polynomial where the additional terms are significant and the model is not aliased.

The Cubic model was aliased because the central composite design does not contain enough runs to support a full cubic model. Aliases are false signals of any sort present.Hence the quadratic model was suggested as the best model that describes the experimental runs. Based on these results, the effect of each parameter was evaluated using the quadratic model as shown on ANOVA for response surface quadratic model.

Source	Sequential	Lack of Fit	Adjusted R ²	Predicted	
	p-value	p-value		\mathbf{R}^2	
Linear	<0.0001	< 0.0001	0.6473	0.5803	
2FI	0.3553	< 0.0001	0.6624	0.5505	
Quadratic	<0.0001	< 0.0001	0.9115	0.7460	Suggested
Cubic	0.1515	< 0.0001	0.9468	-0.5581	Aliased

Table 4.71Fit summary analysis using RHAC

4.13.2 ANOVA of phenol adsorption using RHAC

The ANOVA was used to analysis the result and validate the adsorption model. It tests the significance of the model suggested including the significance of the individual terms. The ANOVA analysis table was given in Table 4.72 while the statistical analysis was given in Table 4.80. A confidence level of 95% was used hence the significance level was 5%. This means that P-values greater than 0.05 are considered insignificant while those at 0.05 or less are significant. The model F-value of 22.32 implies that the model is significant which is in agreement with the P-value being less than 0.0001. There is only a 0.01% chance that an F-value this large could occur due to noise. The P values check the significance of the factors and equally help to understand the pattern of the mutual interactions between the test variables (Shrivastava et al, 2008). Since P-values less than 0.050 is significant, this means that only A, B, C, D, BD, A2, B, and D are significant model terms. If there are many insignificant terms model terms (not counting those required to support hierarchy), model reduction may improve the model.

Source	Sum of	df	Mean	F - value	P-value
	squares		square		
Model	5163.15	14	368.80	22.32	< 0.0001
A – Temperature	367.27	1	367.27	22.23	0.0003
B – Concentration	1241.38	1	1241.38	75.14	< 0.0001
C – Contact time	394.13	1	394.13	23.86	0.0002
D – Dosage	1763.07	1	1763.07	106.71	< 0.0001
AB	0.2025	1	0.2025	0.0123	0.9133
AC	2.10	1	2.10	0.1273	0.7263
AD	3.24	1	3.24	0.1961	0.6642
BC	0.250	1	0.250	0.0151	0.9037
BD	438.90	1	438.90	26.57	0.0001
CD	3.42	1	3.42	0.2072	0.6555
A^2	608.75	1	608.75	36.85	< 0.0001
B^2	146.08	1	146.08	8.84	0.0095
C ²	2.40	1	2.40	0.1455	0.7082
D^2	191.94	1	191.94	11.62	0.0039
Residual	247.82	15	16.52		
Lack of Fit	246.36	10	24.64	83.89	< 0.0001
Pure Error	1.47	5	0.2937		
Cor Total	5410.97	29			

Table 4.72	ANOVA of	phenol	adsorption	using RHAC
				<u> </u>

Std. Dev.	4.06	Mean	76.60
C.V (%)	5.31	R2	0.9542
Adjusted R2	0.9115	predicted R2	0.7460
Adeq. Precision	17.2807		

The P-values were used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the test variables (Shrivastava et al, 2008). The larger the magnitude of F-test value and the smaller the magnitude of P-values, the higher the significance of the corresponding coefficient (Alam et al, 2008).

The adequate precision measures the signal to noise ratio and compares the range of the predicted value at the design points to the average prediction error. The adequate precision ratio above 4 indicates adequate model efficacy (Kumar et al, 2007). Hence, the adequate precision ratios of 17.28 indicate adequate signal. This indicates that an adequate relationship of signal to noise ratio exists. Equally, a PRESS value of 1374.49 indicates an adequate signal implying that the models can be used to navigate the design space.

The C.V called coefficient of variation which is defined as the ratio of the standard deviation of estimate to the mean value of the observed response is independent of the unit. It is also a measure of reproducibility and repeatability of the models (Chen et al., 2010; Chen et al., 2011). The result indicated a C.V value of 5.31% which showed that the model can be considered reasonably reproducible (because its CV was not greater than 10%) (Chen et al., 2011).

4.13.3 Modeling of the optimization process using RHAC

The generated model for the adsorption process was given in equation 4.30

Percent Adsorbed (%) = +85.72 - 4.09A - 7.53B + 4.24C + 8.97D - 0.11125AB + 0.3625AC + 0.4500AD - 0.1250BC + 5.24BD + 0.4625CD - 5.91A² - 2.89B - 0.3711C² - 3.32D² (4.30)

The model can be used to make predictions about the response for given factor levels of each factor. It is useful for identifying the relative impact of the factors by comparing the factor coefficients. Be default, the high levels of the factors are coded as +1 and the low levels are coded as -1.

The positive sign of a factor indicates that there will be increase in the response when there is an increase in the factor while negative sign will lead to decrease in the response (Kumur et al, 2008). Increase in contact time and adsorbent dosage will show the most significant increase in the response on the account that their coefficients were positive.

Model reduction eliminates insignificant terms while improving the model prediction accuracy and the model reproducibility. Since a significant level of 5% was used, all independent factors with P-values greater than 0.05 were eliminated giving the final model equation as equation 4.31.

Percent Adsorbed (%) = $+85.72 - 4.09A - 7.53B + 4.24C + 8.97D + 5.24BD - 5.91A^{2} - 2.89B - 3.32D^{2}$ (4.31)

4.13.4 Comparison of predicted and experimental values

A comparison of the actual experimental response and the predicted response were given in Table 4.73. The response values obtained by inserting the independent values are the predicted values of the model. These values are compared to the actual experimental values. The close correlation between the actual experimental response and the predicted response confirms the suitability of the quadratic model used the analysis.

Std	Temperature	Concentrat	Contact	Dosage	Actual	Predicted
Run	(°C)	ion (mg/l)	time	(gram)	Percentage	Percentage
			(mins)		Adsorbed (%)	Adsorbed (%)
1	40	100	30	0.6	79.5	77.92
2	60	100	30	0.6	72.8	68.33
3	40	200	30	0.6	51.5	52.87
4	60	200	30	0.6	44.2	42.83
5	40	100	60	0.6	81.1	85.0
6	60	100	60	0.6	75.6	76.9
7	40	200	60	0.6	62.9	59.5
8	60	200	60	0.6	53.2	50.9
9	40	100	30	1.0	82.5	83.6
10	60	100	30	1.0	74.7	75.8
11	40	200	30	1.0	83.1	79.5
12	60	200	30	1.0	76.4	71.2
13	40	100	60	1.0	93.5	92.5
14	60	100	60	1.0	88.8	86.2
15	40	200	60	1.0	84.7	87.9
16	60	200	60	1.0	81.9	81.1
17	32.81	150	45	0.8	77.0	75.3
18	67.19	150	45	0.8	54.6	61.2
19	50	60.06	45	0.8	90.5	90.1
20	50	235.94	45	0.8	58.9	64.2
21	50	150	19.22	0.8	71.7	77.3
22	50	150	70.78	0.8	92.6	91.9
23	50	150	45	0.46	58.4	60.5
24	50	150	45	1.14	88.5	91.3
25	50	150	45	0.8	86.6	85.7
26	50	150	45	0.8	86.3	85.7
27	50	150	45	0.8	86.0	85.7
28	50	150	45	0.8	86.5	85.7
29	50	150	45	0.8	86.5	85.7
30	50	150	45	0.8	87.6	85.7

Table 4.73 :Comparism of experimental and predicted result using RHAC

4.13.5 Error analysis of the optimization process using RHAC

The error analysis was done by investigating the Perturbation graph, the Predicted vs Actual plot and the Normal plot of Residuals in figures 4.59 to 4.61. The Perturbation graph shows the deviation from the reference point in terms of coded terms. The reference point of a deviation is the mean. The reference point is at 85% adsorption. It was also seen that concentration (B) and dosage (D) has the greatest deviation from the reference point from 90% to 85% and from 73% to 90% respectively as the coded points ranged from -1 to +1. Contact time (C) has the least deviation from the mean.



Fig 4.59 Perturbation plot showing deviation from the Reference point for RHAC

The Predicted vs Actual plot and the Normal plot of Residuals were used to determine if the residuals follow a normal distribution. It is assumed to have followed a normal distribution if the points closely aligned to the straight line of the plot (Onu and Nwabanne, 2014). It was seen that the points were closely distributed to the straight line of the plot in both graphs. This relationship is desirable for optimisation step because the predicted optimal result will produce an insignificant deviation from the experimental value.



Figure 4.60 Linear correlation between Predicted vs. Actual values for RHAC

The points of the normal distributions are seen to be mostly interlocked with the straight line with a few points lying outside the diagonal line in a moderately scattered manner. This confirms the good relationship between the experimental values and the predicted values of the response though some small scatter like an "S" shape is always expected. This observation shows that the central composite design is well fitted into the model and that the selected model was adequate in predicting the response variables in the experimental values.



Figure 4.61 Normal probability plots of Residuals obtained from RHAC

4.13.6 Three Dimensional (3D) surface plots using RHAC

The three Dimensional (3D) surface plots were used to visualize the relationship between the experimental variables and the responses. It was also used to study the single and interaction effects of all the factors. The response surface and interaction plots were generated from the quadratic model. They illustrate the response of different experimental variables and can be used to identify the major interactions between the variables.

Response surface estimation for maximum phenol adsorption represents surface plots as a function of two factors at a time while maintaining all other factors at fixed levels. This is more helpful in understanding both the main and interaction effects of these two factors. These plots can be easily obtained by calculating from the model, the values taken by one factor where the second varies with constraint of a given response value. The response surface curves were plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum response.

From figures 4.62 to 4.67, it was observed that the elliptical nature of the contour depicted the mutual interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted response as indicated by the surface-confined in the smallest ellipse in the contour diagrams. It can be seen from the graphs that there is good interaction between the variables especially contact time and adsorbent dosage. Equally, as the contact time increased, the percent of phenol adsorbed increased significantly till time of about 90 minutes in which the significance reduces.



Fig 4.62 3D surface plot showing the interactive effects of initial phenol concentration and temperature effects of contact time and temperature

Fig 4.63 3D surface plot showing the interactive





Fig 4.64 3D surface plot showing the interactive effects of contact time and initial phenol concentration

Fig 4.65 3D surface plot showing the interactive effects of adsorbent dosage and temperature




Fig 4.66 3D surface plot showing the interactive effects of adsorbent dosage and initial phenol concentration

Fig 4.67 3D surface plot showing the interactive effects of adsorbent dosage and contact time

4.13.7 Validation of results using RHAC

In the desirabilities report, about eighty-four (84) different solutions were suggested by the central composite design (Appendix A4). Using the numerical optimization technique, a combination of factors that concurrently satisfy the requirements placed on each of the responses and factors could be determined by the software. The desirability values range from 0 to unity based on how close the response is towards the objective. Different considerations were made in choosing the goal for each factor of the numerical optimization (Sunil, 2015).

The desirability values closet to unity were selected as the most effective parameters value with respect to the percentage of phenol adsorbed. The operating temperature was set in range while the contact time, phenol concentration and adsorbent dosage were set

at minimum level. The percentage of phenol adsorbed was set at maximum level.Optimum percent adsorption of 77.92% was suggested at a temperature of 40oC, phenol concentration of 100 mg/l, contact time of 30 minutes and adsorbent dosage of 0.6 gram as given in Table 4.74. This has desirability of 0.909.

The test-retest was employed in validating the optimum result. An average percentage phenol adsorption of 76.89% was obtained at the optimum conditions of temperature 40 °C, phenol concentration 100 mg/l, contact time of 30 minutes and adsorbent dosage of 0.6 gram. This validates the optimum conditions proposed by the model.

Table 4.74: The predicted and validation result using RHAC

Predicted conditions				Predicted	Experimental
Temperat ure °C	Phenol concentrati	Contact time	Adsorbent dosage	Percentage adsorption	Percentage adsorption
	on				
40°C	100 mg/l	30 minutes	0.6g	77.92%	76.89%

4.13.8 Artificial Neural Network Analysis using RHAC

The artificial neural network (ANN) was used to optimize the adsorption of phenol process. The ANN analysis using RHAC is outlined in this section. The network was trained with Levenberg-Marquardt (LM) back propagation algorithm which is one of the Multi-Layer Perceptron (MLP) networks that is used for error minimization. A two-layer feed-forward network with sigmoid hidden neurons was used to fit the multi-dimensional mapping problems with consistent data and enough neurons in its hidden layer. If there

was not enough memory, the case scaled conjugate gradient back propagation was used. MLPs are normally trained with error back-propagation (BP) algorithm. It is a general method for iteratively solving for weights and biases (Nourbakhsh*et al.*, 2014). The network architecture of the ANN is given in Figure 4.68



Figure 4.68: The Neural Network Architecture for adsorption of phenol using RHAC

4.13.9 ANN Training, Validation and Testing

For the adsorption of phenol using RHAC, thirty (30) experimental runs were generated from which 24 samples were set aside for training, 3 samples for validation and 3 samples for testing representing 80% training, 10% validation and 10% testing. It is clear that more data sets in training reduces processing time in ANN learning and improves the generalization capability of models (Kiran and Pragnesh et al, 2016). Hence, a large number of data sets (80%) are used to train the models.

For the training, the network was trained and adjusted according to its error. In the validation, the network generalization was measured by network validation and halted when generalization stops improving to stop over fitting. The testing has no effect on training and so provide an independent measure of network performance during and after training.

The best number of hidden neurons was obtained by testing different numbers of hidden neurons ranging from 5 to 20. This was done to determine the best network performance and to define fitting neural network model architecture. The objective was to obtain the number of neurons that will give the regression value very close to unity and the lowest mean square error. Regression values (R) measures the correlation between outputs and inputs. A regression value very close to 1 means a close relationship while 0, a random relationship. Mean Square Error (MSE) is the average squared difference between outputs and targets. Lower values are better. Zero means no error.

Most of the results showed a regression value of above 0.9999, hence the values of the mean square error were used in determining the best performance. Figure 4.69 illustrates the mean square error performance of the network for testing data *versus* the number of neurons in the hidden layer.



Figure 4.69. The performance of the network at different hidden neurons using quick propagation (QP) algorithm

A close observation of the values revealed that the best performance was given by the network architecture using between 10 to 15 number of hidden neurons. After repeated trials, it was found that a network with 13 neurons in the hidden layer produced the best performance. The mean square error of the best-trained network was 0.0075 while the regression value was 0.9999 as shown in Table 4.75. This shows good performance of the process.

Table 4.75 The regression value and the mean square error for 13 neurons in the hidden layer

Objective	Number of samples	Regression value	Mean square error
Training	24	0.9999	0.0075
Validation	3	1.0000	14.27
Testing	3	0.9970	1.379

The flow diagram with the 13 hidden neurons is given in figure 4.70. The network has four inputs (solution temperature, adsorbent dosage, initial phenol concentration and

contact time) and one output is the percentage of phenol adsorbed. The Artificial neural network is a Feed-Forward network with tan-sigmoid transmission function in the hidden and output layers (Seyyed et al, 2013).



Fig 4.70 Flow diagram of the ANN network with 13 hidden neurons

4.13.10 Post-Training Analysis

The Post-training analysis was carried out using the network validation and network testing

4.13.10.1 Network Validation

To validate the artificial neural network, the network was analyzed to check the network performance and to ascertain if some changes needed to be made to the training process, the network architecture or the data sets. The plot of the training errors, validation errors, and testing errors was shown in figure 4.71. The performance was 0.057 suggesting a good network performance. The best validation performance shows a training error of about only 9.3 at Epoch 3 when the training and testing error is at epoch 3 and 1 respectively. The figure does not indicate any major problems with the validation. If the test curve had increased significantly before the validation curve increased, then it could

be possible that some over fitting might have occurred. Figure 4.72 gave the curve of the validation data and the best fit line. The regression value was 0.974 showing a very good correlation between the validation data and the line of best fit.



Figure 4.71: Plot of the network validation performance



Figure 4.72: Plot of the network validation data and the best fit line

4.13.10.2 Network Testing

The network was tested using the mean square error and the regression value. The mean square error was 1.371 while the regression value was 0.9884 indicating that the performance on the training set is good as shown in figure 4.73. But if the test performance was significantly worse, which could indicate over fitting, reducing the number of neurons can improve the result. If training performance is poor, then the number of neurons will be increased.

The Network test/evaluation shows the output tracks the target very well for training, testing, and validation and the R-value is over 0.9000 for the responses. The output tracks the target very well since the R values and the MSE values show good network performance. Based on these performance values a satisfactory network response can be concluded. The model generated sets of output equation that relates the target to the output for training, testing, validation and the overall model output equation.



Figure 4.73: Plot of the network testing data and the best fit line

4.13.11. ANN response prediction

The plot of the relationship between the overall output and the target is given in Figure 4.74. The correlation coefficient value was 0.9851 showing a good relation between the output and the target.



Figure 4.74 Plot of the overall output against the target

The model equation generated is given in equation (4.32). It was used to predict the ANN model values.

$$Y = 0.99T + 0.84 \tag{4.32}$$

Where Y = the ANN model value,

T (Target) = the experimental value used to generate the corresponding ANN value.

In order to determine the suitability of the model, the experimental (actual) values were compared to those predicted by the ANN model as given in Table 4.76. The table reveals a close correlation between the experimental percentage adsorbed and the predicted percentage adsorbed.

Std	Temperature	Concentration	Contact	Dosage	ExpPercentage	ANN
Run	(°C)	(mg/l)	time	(gram)	Adsorbed (%)	predicted
			(mins)			Percent
1	40	100	30	0.6	79.5	79.545
2	60	100	30	0.6	72.8	72.912
3	40	200	30	0.6	51.5	51.825
4	60	200	30	0.6	44.2	44.598
5	40	100	60	0.6	81.1	81.129
6	60	100	60	0.6	75.6	75.684
7	40	200	60	0.6	62.9	63.111
8	60	200	60	0.6	53.2	53.508
9	40	100	30	1.0	82.5	82.515
10	60	100	30	1.0	74.7	74.793
11	40	200	30	1.0	83.1	83.109
12	60	200	30	1.0	76.4	76.476
13	40	100	60	1.0	93.5	93.405
14	60	100	60	1.0	88.8	88.752
15	40	200	60	1.0	84.7	84.693
16	60	200	60	1.0	81.9	81.921
17	32.81	150	45	0.8	77.0	77.07
18	67.19	150	45	0.8	54.6	54.894
19	50	60.06	45	0.8	90.5	90.435
20	50	235.94	45	0.8	58.9	59.151
21	50	150	19.22	0.8	71.7	71.823
22	50	150	70.78	0.8	92.6	92.514
23	50	150	45	0.46	58.4	58.656
24	50	150	45	1.14	88.5	88.455
25	50	150	45	0.8	86.6	86.574
26	50	150	45	0.8	86.3	86.277
27	50	150	45	0.8	86.0	85.98
28	50	150	45	0.8	86.5	86.475
29	50	150	45	0.8	86.5	86.475
30	50	150	45	0.8	87.6	87.564

Table 4.76 ANN predicted result using RHAC

4.13.12 Comparison of ANN and RSM models

The percentage error of each standard run in the ANN and RSM models were respectively evaluated. These values were tabulated on Table 4.77 where it was observed that the errors in RSM were more pronounced than the errors in ANN.

Std	Exp (%)		ANN (%)		RSM (%)	
Run		ANN	Error	% Error	RSM	Error	% Error
1	79.5	79.545	-0.045	-0.0566	77.92	1.58	1.987421
2	72.8	72.912	-0.112	-0.15385	68.33	4.47	6.14011
3	51.5	51.825	-0.325	-0.63107	52.87	-1.37	-2.66019
4	44.2	44.598	-0.398	-0.90045	42.83	1.37	3.099548
5	81.1	81.129	-0.029	-0.03576	85	-3.9	-4.80888
6	75.6	75.684	-0.084	-0.11111	76.9	-1.3	-1.71958
7	62.9	63.111	-0.211	-0.33545	59.5	3.4	5.405405
8	53.2	53.508	-0.308	-0.57895	50.9	2.3	4.323308
9	82.5	82.515	-0.015	-0.01818	83.6	-1.1	-1.33333
10	74.7	74.793	-0.093	-0.1245	75.8	-1.1	-1.47256
11	83.1	83.109	-0.009	-0.01083	79.5	3.6	4.33213
12	76.4	76.476	-0.076	-0.09948	71.2	5.2	6.806283
13	93.5	93.405	0.095	0.101604	92.5	1	1.069519
14	88.8	88.752	0.048	0.054054	86.2	2.6	2.927928
15	84.7	84.693	0.007	0.008264	87.9	-3.2	-3.77804
16	81.9	81.921	-0.021	-0.02564	81.1	0.8	0.976801
17	77	77.07	-0.07	-0.09091	75.3	1.7	2.207792
18	54.6	54.894	-0.294	-0.53846	61.2	-6.6	-12.0879
19	90.5	90.435	0.065	0.071823	90.1	0.4	0.441989
20	58.9	59.151	-0.251	-0.42615	64.2	-5.3	-8.9983
21	71.7	71.823	-0.123	-0.17155	77.3	-5.6	-7.81032

Table 4.77 ANN and RSM comparison result using RHAC

22	92.6	92.514	0.086	0.092873	91.9	0.7	0.75594
23	58.4	58.656	-0.256	-0.43836	60.5	-2.1	-3.59589
24	88.5	88.455	0.045	0.050847	91.3	-2.8	-3.16384
25	86.6	86.574	0.026	0.030023	85.7	0.9	1.039261
26	86.3	86.277	0.023	0.026651	85.7	0.6	0.695249
27	86	85.98	0.02	0.023256	85.7	0.3	0.348837
28	86.5	86.475	0.025	0.028902	85.7	0.8	0.924855
29	86.5	86.475	0.025	0.028902	85.7	0.8	0.924855
30	87.6	87.564	0.036	0.041096	85.7	1.9	2.16895

In order to establish the superiority of either of the models generated by the RSM and ANN, a couple of techniques were applied. These were;

- 1) Absolute Average Deviation (AAD) observed for both models;
- 2) Coefficient of determination for both models.

The AAD observed for both models give an indication of how accurate the model predictions can be (Josh *et al.*, 2014). It is given by equation 4.33

AAD (%) =
$$\left(\frac{1}{n}\sum_{i=1}^{n}\left\{\frac{(R_{pred} - R_{exp})}{R_{exp}}\right\}\right) \times 100$$
 (4.33)

where n is the number of sample points, R_{pred} is the predicted percentage of phenol adsorbed and R_{exp} is the experimentally determined percentage of phenol adsorbed (Josh *et al.*, 2014).

The correlation coefficients were obtained from the interactive plots of the RSM and ANN models as 0.994 and 0.954 for ANN and RSM respectively as shown in figure 4.75. It was observed that the correlation coefficient for the ANN model is closer to unity with a value of 0.994 than that of RSM with a value of 0.954. These values measure how close

the predicted value of the responses of ANN and RSM are to the actual experimental values.



Figure 4.75 Interactive plot for RSM and ANN models

The AAD analysis revealed a value of 0.1617 and 0.1396 for RSM and ANN analysis respectively in Table 4.84. The lower the AAD value, the smaller the errors involved in predicting the percentage of phenol adsorbed.

From these analyses, ANN model was superior to the RSM model for the optimization of the adsorption of phenol using RHAC.

Table 4.78 AAD and R^2 values for the optimization models

Model	AAD	\mathbf{R}^2
RSM	0.1617	0.954
ANN	0.1396	0.994

4.14 Column adsorptive studies

The plot of the breakthrough curves was used to analyze the effects of flow rate, influent phenol concentration, particle size and bed height in the packed bed studies.

4.14.1 Effect of Flowrate

The effect of different flowrates was determined by operating the column adsorption process at flowrates of 9ml/min, 13ml/min and 18ml/min. This was done at a bed height of 10cm and inlet phenol concentration of 100mg/l at pH of 7 and a maximum time of 24 hours. The breakthrough curve for the column was determined by plotting Ce/C_o against time (hours) as shown in figures 4.76 and 4.77.

It was observed that as the flow rate increases from 9ml/min to 18ml/min, the breakthrough curve becomes steeper and the break point time decreases. The velocity variation along the packed adsorbent was of little or no importance because the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at high flow rate (Abdelkreem, 2013). Hence, at such high flow rate, the phenol solution leaves the column before equilibrium occurs.

Mahsa et al (2014) reported that this can be due to a decrease in the residence time which inhibited phenol ion contact to the adsorbent and the fact that the phenol ions did not have enough time to diffuse into the pores of the adsorbent and it exited the column without being adsorbed. So at high flow rate, the adsorbate solution leaves the column before equilibrium occurs thus leading to a reduction in the removal efficiency of phenol in the adsorption column. This is in agreement with the observation of Nouh et al, (2010).

Equally, at high flowrate, the contact time between the adsorbate and the adsorbent is minimized, leading to early breakthrough (Sivakumar and Palanissamy, 2009). Increasing the flow rate gave rise to a shorter time for saturation. Across the three flowrates, rapid adsorption of phenol was noticed in the initial stages which gradually decreased thereafter before finally reached equilibrium saturation. Nwabanne and Igbokwe (2012) obtained a similar trend in the removal of lead II ions. At lower flowrates, more

favourable ions exchange conditions can be achieved. This is because there will be more contact between the adsorbent and the adsorbate in the column.



Figure 4.76 Effect of flowrate on the breakthrough curve using CCAC



Fig 4.77 Effect of flowrate on the breakthrough curve using RHAC

4.14.2 Effect of influent phenol concentration

The effect of inlet adsorbate concentration on the breakthrough curve was investigated using different inlet concentrations ranging from 100mg/l to 300mg/l as shown in Figures

4.78 and 4.79. During these simulations, other parameters such as bed height and flow rate were kept constant at 10cm and 9ml/min respectively.

It was observed that as the inlet phenol concentration increases from 100mg/l to 300mg/l, the break point time decreases from 32 hours to 21 hours. On increasing the initial phenol concentration, the breakthrough volume decreased because of the lower mass-transfer flux from the bulk solution to the particle surface due to the weaker driving force (Sivakumar and Palanisamy, 2009.,Baek et al, 2007). At higher concentration, the availability of the phenol molecules for the adsorption sites is more, which leads to higher uptake of phenol at higher concentration even though the breakthrough time is shorter than the breakthrough time of lower concentrations (Nwabanne and Igbokwe, 2012).

In addition, at high concentration, the isotherm gradient is lower, yielding a higher driving force along the pores. Thus the equilibrium is attained faster for values of higher adsorbate concentration. Increased influent concentration of phenol resulted in an early breakpoint time because the higher concentration gradient could cause quicker transport as a result of an increased diffusion or increased mass transfer coefficient. A greater concentration difference gives a larger driving force for adsorption and causes a larger adsorption capacity of the column fed. Moreover, the availability of the phenol ions for the adsorption sites was more at the higher influent concentration.

However, a further increase of the influent phenol concentration from 100 mg/L to 300 mg/L decreased the adsorption capacity. With respect to a lower influent phenol concentration, the inflow adsorbate molecules were adequate to the active sites on the surface of the adsorbent. For a higher influent phenol concentration, extreme inflow of phenol exceeded the limited available active sites on the adsorbent surface. Nevertheless, an increase in the influent phenol concentration enhances the concentration gradient which can overcome mass transfer resistance and increase the adsorption capacity (Yanhong et al, 2018). The bed can be saturated faster when a larger amount of phenol is

introduced into the column reactor (Podder, Majumder 2016; Han et al. 2007; Goelet al. 2005).



Figure 4.78 Effect of influent concentration on the breakthrough curve using CCAC



Figure 4.79 Effect of influent concentration on the breakthrough curve using RHAC

4.14.3 Effect of Bed height

In order to study the effect of bed height on the adsorption of phenol, breakthrough curves for the adsorption of phenol onto these adsorbents at various bed heights were plotted, at the inlet phenol concentration of 100 mg/L and flow rate of 9ml/min. The bed heights used were 5cm, 7.5cm and 10cm as shown in figures 4.80 and 4.81.

The results indicate that the breakthrough time of the aqueous solution increased with increase in bed height, due to the availability of more number of sorption sites (Sivakumar and Palanisamy, 2009). Larger bed height corresponds to higher amount of adsorbent. This shows that at smaller bed height the effluent adsorbate concentration ratio increases more rapidly than for higher bed height. Furthermore, the bed is saturated in less time for smaller bed heights. Consequently, a smaller capacity for the bed to adsorb adsorbate from solution and a faster increase in rate of adsorbate adsorption is expected. It is also observed that phenol removal was increased with increase in bed height. This is probably due to the availability of more number of sorption sites. At smaller bed height, phenol ions do not have enough time to be adsorbed on the adsorbent hence, there is a reduction in breakthrough time (Mahsa et al, 2014)



Fig 4.80 Effect of bed height on the breakthrough curve using CCAC



Fig 4.81 Effect of bed height on the breakthrough curve using RHAC

4.14.4 Effect of Particle size

The effect of particle size for the adsorption of phenol onto CCAC and RHAC were investigated at particle sizes of 300 μ m, 600 μ m and 800 μ m as shown in figures 4.82 and 4.83. This was carried out at a constant inlet phenol concentration of 100 mg/L and flow rate of 9ml/min, bed height of 10cm and pH of 7. The time taken to reach equilibrium concentration decreased as the particle size increased. For a particle size of 330 μ m, it took about 12 hours to reach equilibrium concentration while particle sizes of 600 μ m and 800 μ m, equilibrium concentration was achieved after about 16 hours and 23 hours respectively.

It was also observed that the maximum phenol removal occurred at the initial stage of the experiments. After some time of operation, the rate of phenol removal decreases and gradually reaches almost zero. This is because of the non-availability of sorbent site for the sorption to occur after such a time interval (Mahsa et al, 2014).



Fig 4.82 Effect of particle size on the breakthrough curve using CCAC



Fig 4.83 Effect of particle size on the breakthrough curve using RHAC

4.14.5 Column kinetics study

Severally column kinetics models were investigated by fitting the experimental data to the kinetic models. Such kinetic models used include Thomas model, Yan model, Wloborska model, Adam Bohart model etc

4.14.5.1 Adam Bohart kinetics model

The Adam Bohart kinetic model is as given by equation 4.38

$$\ln \frac{c_t}{c_o} = K_{AB} C_o t - K_{AB} N_o \frac{z}{U_o}$$
(4.38)

The Adam-Bohart kinetic model was investigated by plotting the graph of $\ln(C_t/C_o)$ against t at different adsorption conditions as given in appendix F. Respective values of K_{AB} and N_o were calculated from the slope and the intercept respectively and presented in Tables 4.79 to 4.92 together with the correlation coefficients.

As the flowrate increased from 9ml/min to 18ml/min, the Adam-Bohart kinetic constant K_{AB} decreased from 0.033 L/mg.min to 0.028 L/mg.min using CCAC and from 0.0198 to 0.0174 L/mg.min using RHAC as seen in Tables 4.85 and 4.86. Equally, as the influent phenol concentration increased from 100mg/l to 300mg/l, Adam-Bohart kinetic constant K_{AB} decreased from 0.026 L/mg.min to 0.0102 L/mg.min and from 0.0126 to 0.0084 L/mg.min for CCAC and RHAC respectively. This shows that the external mass transfer was the dominant kinetics at low flowrate and low influent concentration for the adsorption of the phenol (Yanhong et al, 2018). But as the bed height increased from 5cm to 10cm, there was a significant increase in K_{AB} from 0.0354 to 0.1398 L/mg.min.Shanmugam et al., (2016) reported that the Adams–Bohart model is based on the assumption that the rate of adsorption is proportional to both the concentration of the adsorbing species and the residual capacity of the adsorbent.

The correlation coefficients were above 0.9 in most cases getting as high as 0.99 for flowrate of 13ml/min. This shows that the experimental column data fits into the Adam-

Bohart kinetic model perfectly. Therefore, it is confirmed that Adam's – Bohart model is suitable in explaining the overall adsorption kinetics in the column.

The Adams–Bohart model sorption capacity N_o was seen to be dependent on flowrate and influent concentration, increasing with increase in flowrate and influent concentration reaching 33.8 mg/L and 41.1 mg/L for adsorption using CCAC and RHAC respectively at influent concentration of 300mg/l. The N_o value increased with high flow rates which can be attributed to the larger mass transfer driving force.

With increase in bed height, the sorption capacity decreased for both adsorbents. This is probably because of the increased amount of adsorbent as the bed height increases. The number of active sites competing for the same number of influent phenol ions will increase thereby reducing the sorption capacity N_o of the adsorbents.

4.14.5.2 Yoon Nelson kinetic model

The Yoon and Nelson kinetic model was developed based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent (Meenakshi and Mamta, 2010). The linear form of the model is as given in equation 4.39

$$\ln\left(\frac{c_{t}}{c_{o}-c_{t}}\right) = K_{YN} t - \tau K_{YN}$$
(4.39)

Yoon–Nelson model was fitted to the experimental data with respect to bed height, influent phenol concentration, flow rate and particle size. A linear regression analysis involving the plot of $\text{Ln}[C_t/(C_o - C_t)]$ against adsorption time (t) as given in appendix F was used to determine the Yoon–Nelson model parameters of K_{YN}(rate constant) and τ

(50% breakthrough time). The correlation coefficient values of each experiment together with the model parameters are presented in Tables 4.79 to 4.92.

As the flow rate increased from 9ml/min to 13ml/min, the rate constant K_{YN} increased from 0.096 L/min to 0.347 L/min and from 0.074 L/min to 0.328 L/min for the adsorption of phenol using CCAC and RHAC respectively. Shreyashi and Sudip (2006) reported a similar trend in the removal of hexavalent chromium from aqueous solution. This is likely because of the fact that more phenol ions pass through the adsorbent over a given period of time. There was also an increase in the rate constant as the influent phenol concentration increased but a decrease in the rate constant as the bed height increased from 5 cm to 10 cm.

The time required for 50% breakthrough, τ , decreased with increasing flow rate but increased with bed height as presented in Tables 4.79 to 4.92. This is because, with an increase in bed height, the phenol ions take more time to pass through the packed column. The values of τ obtained by the model are close to the experimental results.

The regression coefficients were very high (> 0.9) for the different parameters tested. This indicated that the Yoon Nelson kinetic model can be used to describe the experimental data of the adsorption of phenol unto the CCAC and RHAC adsorbents. Shreyashi and Sudip (2006) and Nouri and Ouederni (2013) reported the fitting of the Yoon Nelson kinetic model to the removal of chromium and phenol using coconut shell and olive stones respectively. The Yoon and Nelson model is not only less complicated than the other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed (Chawki and Oualid, 2014).

4.14.5.3 Thomas kinetic model

Thomas proposed a kinetic model that assumes a plug flow behavior in the packed bed. It uses Langmuir isotherm for equilibrium, and second- order reversible reaction kinetics (Nouri and Ouederni, 2013). The linear form of the Thomas kinetic model is as given in equation 4.40

$$\ln\left(\frac{C_{o}}{C_{t}}-1\right) = \frac{K_{T}q_{e}m}{Q}-K_{T}C_{o}t$$
(4.40)

The Thomas kinetic model was investigated by the linear plot of $\ln(C_o/C_t - 1)$ against the adsorption time t, (see appendix F) at varying experimental conditions. The Thomas kinetic rate constant K_{Th} and the equilibrium adsorption capacity q_e were calculated from the slope and intercept respectively (Chafi, 2015) and tabulated in Tables 4.79 and 4.92.

The correlation coefficients (\mathbb{R}^2) values of the linear regression ranged from 0.89 to 0.99 indicating a significant correlation between the experimental data and the Thomas kinetic model. From the analysis, it can be deduced that all of the factors considered (the flow rate, the influent phenol concentration, bed height and the particle size) affect the Thomas rate constant (K_{TH}) and the equilibrium of phenol adsorption (qe).As the flow rate increased from 9 ml/min to 18 ml/min, the Thomas rate constant K_{TH} increased from 0.0558 ml/mg.min to 0.1512 ml/mg.min and from 0.044 ml/mg.min to 0.1968 ml/mg.min for the uptake of phenol using CCAC and RHAC respectively. The adsorption capacity decreased from 43.5 to 11.4 mg/g. Several authors reported a similar trend (Shanmugam et al, 2016; Nouri and Ouederni, 2013).

A direct relationship was also observed between the influent concentration and the Thomas rate constant K_{TH} which increased with increased in influent concentration. The concentration difference between the phenol ions in the solution and those on the adsorbent surface was the driving force for adsorption. Hence, the higher influent phenol concentration resulted in the higher driving force and better column performance.

The linear Thomas kinetic model ignores both the intraparticle (solid) mass transfer resistance and the external (fluid-film) resistance directly. As seen in figure 4.412, at flowrates of between 9 ml/min and 13 ml/min, the rate of adsorption is controlled by the surface reaction between the adsorbate and the unused capacity of the adsorbent.

4.14.5.4 Wolborska kinetic model

The column kinetic model given by Wolborska generally describes the concentration distribution in the packed bed for the low concentration region of the breakthrough curve (Yanhong et al, 2018). The linearized model equation is represented as in equation 4.41

$$\ln \frac{C_{t}}{C_{o}} = \frac{\beta C_{o}}{N_{o}} t - \frac{\beta Z}{U_{o}}$$
(4.41)

The model parameterswere determined by plotting the line of $ln(C_t/C_o)$ against the time of adsorption t (see appendix F) from which the model parameters were determined under different conditions of the experiment. Using the slope and intercept of the plot, the kinetic coefficient of external mass transfer, β , (1/min) and the predicted adsorption capacity by Wolborska model, N_o, (mg/L) were determined and presented in Tables 4.79 to 4.92. As the influent flow rate increased from 9ml/min to 18ml/min, the kinetic coefficient of external mass transfer β , decreased from 1.224 min⁻¹ to 0.581 min⁻¹ and from 0.813 min⁻¹ to 0.404 min⁻¹ for uptake of phenol using CCAC and RHAC. The Wolborska adsorption capacity N_o also decreased for the same increase in flowrate. This same trend was observed as the influent concentration increased from 100 mg/l to 300 mg/l. These observations suggest that the external mass transfer was the dominant kinetics in the initial part of the phenol adsorption in the column system.

As the bed height increased from 5cm to 10 cm, there was a slight increase in the kinetic coefficient of external mass transfer β and the adsorptive capacity N_o. Shanmugam et al, (2016) reported a similar trend and equally affirm that β is an effective coefficient reflecting on the effects of both mass transfer in the liquid phase and axial diffusion.

The linearized equation of the Wolborska model is equivalent to the Adams–Bohart model only when the Adam-Bohart coefficient, K is equal to β/N_o . Therefore the same plots were used in the calculation of parameters for both models

The correlation coefficients for the different experimental conditions were high, about 0.90 indicating there is a good correlation between the Wolborska model and the experimental data.

4.14.5.5 Clark kinetic model

The Clark kinetic model was developed based on the use of a mass-transfer concept in combination with the Freundlich isotherm (Nouri and Ouederni, 2013). The Clark kinetic model is expressed in equation 4.42

$$\ln\left[\left(\frac{C_{t}}{C_{0}}\right)^{1-n} - 1\right] = \ln A - rt$$
(4.42)

Linear regression involving the plot of $\ln((C_t/C_o)^{-1}-n-1)$ against the time of adsorption t was used to fit the Clark model with the experimental result under conditions of different flow rate, influent concentration, bed height and particle size (see appendix F). n is the Freundlich isotherm constant.

The Clark model constant A (min) and the adsorption rate, r, (mg/L.min) were calculated from the intercept and the slope of the line respectively and summarized in Tables 4.79 to 4.92. The Clark adsorption rate increased from 0.203 min to 0.419 min as the flowrate increased. This trend is similar to that reported by Chawki and Oualid (2014) in the removal of methylene blue using melon peel in fixed bed columns. This is probably because there is an increase in the number of phenol ions per unit time passing through the adsorbent as the flow rate increases. But as the influent concentration and the bed height increased, there were no regular changes in the Clark adsorption rate.

The Clark model constant gave a more regular variation as the influent concentration and the bed height increased. It decreased regularly as the influent concentration increased but decreased as the bed height increased. The results indicated that the predicted line of the Clark kinetic model has a good correlation with the experimental data points with respect to the effects of the influent phenol concentration ($R^2 = 0.911 - 0.977$), the flow rate ($R^2 = 0.942 - 0.988$), the adsorbent bed height ($R^2 = 0.0.912 - 0.988$) and the adsorbent size ($R^2 = 0.946 - 0.989$).

4.14.5.6 Yan kinetic model

Yan proposed a kinetic model that can give a good description of the breakthrough curve of the fixed bed column study. The Yan kinetic model is as reported by Shreyashi and Sudip (2006) in equation 4.43

$$\ln\left(\frac{C_{t}}{C_{o}-C_{t}}\right) = \frac{K_{y}}{Q}C_{o}\ln\left(\frac{Q^{2}}{K_{y}q_{y}m}\right) + \frac{K_{y}C_{o}}{Q}\ln t$$
(4.43)

This kinetic model was investigated by plotting $\ln(C_t/C_o - C_t)$ against the adsorption time t in appendix F. The adsorption parameters, that is, the Yan rate constant K_y and the adsorption capacity q_y were evaluated from the slope and the intercept respectively of the plot and tabulated in Tables 4.79 to 4.92.

From the tables, it was observed that the kinetic rate constant increases with increase in flow rate and influent concentration but decreases with increase in bed height. The values of the kinetic rate constant ranged from 0.0359 ml/mg.min to 0.321 ml/mg.min. This demonstrates that the mass transfer resistance of diffusivity in the liquid layer cannot be neglected under these given conditions of flowrate and influent phenol concentration.

According to Shanmugam et al, (2016) and Mohammad et al (2014), the Yan model can be used to overcome the drawback in Thomas model, especially its serious deficiency in predicting the effluent concentration with respect to time zero. It was observed from the figures that the predicted breakthrough curves fitted the Yan model well only within the initial part of the experimental data. Generally, the correlation coefficient was not high (<0.9) being as low as 0.429 in some cases. Hence, it is concluded that the Yan kinetic model did not fit the adsorption of phenol using these adsorbents.

The Yan adsorption capacity (q_Y) decreased with increase in flow rate and influent phenol concentration but increased with increase in bed height for the adsorption process using CCAC. But with RHAC, there was no regular relationship or pattern in the process. This equally confirms that Yan kinetic model can not be used to describe these adsorption processes.

4.14.5.7 Modified dose-response kinetic model

Shanmugam et al, (2016) reported that the Modified dose-response kinetic model is based on mathematical issues instead of mechanistic fundamentals. However, its final form is similar to Thomas and Yoon–Nelson model and is shown in equation (4.44)

$$\ln\left(\frac{C_{t}}{C_{o}-C_{t}}\right) = a \ln(C_{o} Q t) - a \ln(q_{md} m)$$
(4.44)

In fitting the experimental data to the modified dose-response model, the plot of $\ln(C_t/(C_0 - C_t))$ is drawn against $\ln(q_m m)$ at different conditions of flowrate, bed height, influent concentration and particle size as shown in appendix F. The predicted adsorption capacity by modified dose response model q_{md} (mg/g) and the model constant parameter a was calculated and presented in Tables 4.79 to 4.92 together with the correlation coefficient values.

The modified dose adsorption capacity q_{md} increased as the bed height increased from 5cm to 10cm. The increase ranged from 5.34 mg/g to 36.3 mg/g and from 5.34 to 19.28 mg/g for adsorption using CCAC and RHAC respectively. However, as the flow rate and the influent concentration increased, the adsorption capacity decreased.

In most cases, the correlation coefficients were very small especially for adsorption using RHAC which was about 0.606. This suggests that the experimental data cannot be described with the modified dose-response model.

		R2	K _{ab}	No
Flowrate				
	9ml/min	0.988	0.033	5.226
	13ml/min	0.994	0.033	7.546
	18ml/min	0.884	0.0282	12.22
Influent				
concentration				
	100mg/l	0.985	0.0264	13.062
	200mg/l	0.985	0.015	22.990
	300mg/1	0.983	0.0102	33.809
Bed height				
	5cm	0.881	0.0354	9.741
	7.5cm	0.973	0.0522	6.606
	10cm	0.927	0.1398	2.466
Particle size				
	300um	0.977	0.0606	5.690
	600um	0.96	0.063	5.473
	800um	0.902	0.0378	9.123

Table 4.79 Adam-Bohart kinetic parameters using CCAC

Table 4.80 Adam-Bohart kinetic parameters using RHAC

		R2	K _{ab}	No
Flowrate				
	9ml/min	0.985	0.0198	8.710
	13ml/min	0.987	0.0174	14.31
	18ml/min	0.923	0.0192	17.96
Influent				
concentration				
	100mg/l	0.93	0.0126	27.36
	200mg/l	0.984	0.0096	35.92
	300mg/1	0.977	0.0084	41.055
Bed height				
	5cm	0.902	0.0162	21.28
	7.5cm	0.986	0.0258	13.36
	10cm	0.989	0.0384	8.980
Particle size				
	300um	0.971	0.0474	7.275
	600um	0.938	0.0294	11.72
	800um	0.967	0.0126	27.36

		R2	K	τ
Flowrate				
	9ml/min	0.985	0.096	11.885
	13ml/min	0.939	0.158	4.5506
	18ml/min	0.898	0.347	2.6340
Influent				
concentration	n			
	100mg/l	0.984	0.082	9.951
	200mg/l	0.984	0.082	2.000
	300mg/l	0.67	0.285	0.908
Bed height				
	5cm	0.965	0.273	2.842
	7.5cm	0.971	0.175	9.251
	10cm	0.97	0.239	14.86
Particle size				
	300um	0.984	0.146	13.52
	600um	0.965	0.256	6.933
	800um	0.883	0.447	3.496

Table 4.81 Yoon-Nelson kinetic parameters using CCAC

		R2	K	τ
Flowrate				
	9ml/min	0.976	0.074	6.0678
	13ml/min	0.986	0.097	0.0206
	18ml/min	0.878	0.328	1.3201
Influent				
concentration	L			
	100mg/l	0.955	0.055	2.181
	200mg/l	0.981	0.072	9.069
	300mg/l	0.682	0.419	0.274
Bed height				
	5cm	0.957	0.244	1.983
	7.5cm	0.937	0.156	5.756
	10cm	0.969	0.143	10.75
Particle size				
	300um	0.986	0.237	5.531
	600um	0.939	0.304	2.891
	800um	0.835	0.389	0.483

		R2	K _{TH}	q _e
Flowrate				
	9ml/min	0.98	0.0558	43.548
	13ml/min	0.954	0.0768	22.628
	18ml/min	0.99	0.1512	11.400
Influent				
concentration				
	100mg/1	0.972	0.0486	36.000
	200mg/l	0.977	0.0456	9.189
	300mg/1	0.894	0.0768	29.868
Bed height				
	5cm	0.965	0.1638	10.232
	7.5cm	0.971	0.105	33.305
	10cm	0.97	0.1434	53.502
Particle size				
	300um	0.988	0.0906	48.325
	600um	0.97	0.1596	25.606
	800um	0.891	0.2844	14.134

Table 4.83 Thomas kinetic model parameters using CCAC

Table 4.84 Thomas kinetic model parameters using RHAC

		R2	K _{TH}	q _e
Flowrate				
	9ml/min	0.976	0.0444	21.843
	13ml/min	0.986	0.0582	10.074
	18ml/min	0.876	0.1968	4.752
Influent				
concentration				
	100mg/1	0.955	0.033	-7.854
	200mg/l	0.981	0.0432	-32.65
	300mg/1	0.682	0.2514	-0.988
Bed height				
	5cm	0.957	0.1464	7.140
	7.5cm	0.937	0.0936	20.72
	10cm	0.969	0.0858	38.71
Particle size				
	300um	0.987	0.1446	19.956
	600um	0.869	0.2106	12.410
	800um	0.835	0.2334	1.739

		R2	β	No
Flowrate				
	9ml/min	0.988	1.224	2.225
	13ml/min	0.994	1.224	2.225
	18ml/min	0.884	0.5805	1.235
Influent				
concentration	n			
	100mg/l	0.985	1.0269	2.333
	200mg/l	0.985	0.5193	2.077
	300mg/l	0.983	0.2331	1.371
Bed height				
	5cm	0.881	1.404	2.379
	7.5cm	0.973	1.8828	2.164
	10cm	0.927	3.3273	1.428
Particle size				
	300um	0.977	1.8378	1.819
	600um	0.96	1.4265	1.358
	800um	0.902	0.7659	1.2154

Table 4.85 Wolborska kinetic model parameters using CCAC

1 able 4.80 woldorska kinetic model parameters using RH.
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		R2	β	No
Flowrate				
	9ml/min	0.985	0.8127	2.462
	13ml/min	0.987	0.5688	1.961
	18ml/min	0.923	0.4032	1.260
Influent				
concentration				
	100mg/l	0.93	0.5616	2.674
	200mg/l	0.984	0.3573	2.233
	300mg/1	0.977	0.1719	1.227
Bed height				
	5cm	0.902	0.909	3.366
	7.5cm	0.986	1.1184	2.600
	10cm	0.989	1.3302	2.078
Particle size				
	300um	0.971	1.0656	1.348
	600um	0.938	0.6156	1.256
_	800um	0.967	0.2619	1.247

		R2	r	Α
Flowrate				
	9ml/min	0.988	0.203	120.18
	13ml/min	0.974	0.244	31.343
	18ml/min	0.942	0.419	23.057
Influent				
concentratio	n			
	100mg/1	0.977	0.17	56.260
	200mg/1	0.977	0.118	6.8688
	300mg/l	0.911	0.15	1.7023
Bed height	-			
_	5cm	0.977	0.331	20.267
	7.5cm	0.988	0.307	33.450
	10cm	0.912	0.606	112.42
Particle size				
	300um	0.981	0.364	132.74
	600um	0.989	0.462	38.683
	800um	0.946	0.575	8.5712

Table 4.87 Clark kinetic model parameters using CCAC

Table 4.88 Clark kinetic model p	parameters using RHAC
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		R2	r	Α
Flowrate				
	9ml/min	0.985	0.182	143.88
	13ml/min	0.987	0.162	32.330
	18ml/min	0.923	0.176	11.763
Influent				
concentration				
	100mg/l	0.937	0.124	30.325
	200mg/l	0.985	0.12	8.3144
	300mg/l	0.718	0.455	7.7990
Bed height				
	5cm	0.989	0.32	35.837
	7.5cm	0.99	0.295	237.93
	10cm	0.994	0.376	393.63
Particle size				
	300um	0.985	0.443	63.587
	600um	0.946	0.458	10.416
	800um	0.883	0.445	1.3887

		R2	K	a	b	q
Flowrate						
	9ml/min	0.78	0.03591	1.002	0.230	4.343
	13ml/min	0.804	0.06929	0.750	0.702	1.067
	18ml/min	0.65	0.30726	0.234	0.585	0.400
Influent						
concentration						
	100mg/l	0.941	0.05346	1.346	1.003	1.342
	200mg/l	0.815	0.0639	1.126	4.774	0.235
	300mg/1	0.429	0.32382	0.222	1.014	0.219
Bed height						
	5cm	0.721	0.30114	0.239	0.441	0.540
	7.5cm	0.702	0.19224	0.374	0.256	1.462
	10cm	0.756	0.17946	0.401	0.122	3.264
Particle size						
	300um	0.83	0.15516	0.464	0.236	1.962
	600um	0.856	0.17442	0.412	0.561	0.734
	800um	0.734	0.17838	0.403	1.589	0.254

Table 4.89 Yan kinetic model parameters using CCAC

Table 4.90 Yan kinetic model parameters using RHAC

		R2	K	a	b	q
Flowrate						
	9ml/min	0.815	0.04743	0.7590	0.079	9.558
	13ml/min	0.705	0.10764	0.4830	0.313	1.540
	18ml/min	0.682	0.32886	0.2189	0.448	0.487
Influent						
concentration						
	100mg/1	0.789	0.06318	1.1396	0.085	13.35
	200mg/1	0.337	0.02322	3.1007	0.652	0.004
	300mg/1	0.675	0.09594	0.7504	0.6639	0.113
Bed height						
	5cm	0.789	0.3375	0.2133	0.378	0.563
	7.5cm	0.784	0.21474	0.3352	0.148	2.253
	10cm	0.942	0.32166	0.2238	0.068	3.258
Particle size						
	300um	0.857	0.15300	0.4705	0.061	7.657
	600um	0.787	0.26082	0.2760	0.190	1.450
	800um	0.648	0.43902	0.1640	0.357	0.458

		R2	a	qe (mg/g)
Flowrate				
	9ml/min	0.811	0.432	38.202
	13ml/min	0.751	0.578	7.0958
	18ml/min	0.863	1.198	4.0622
Influent				
concentration				
	100mg/l	0.789	0.351	26.251
	200mg/l	0.836	0.337	1.5388
	300mg/l	0.675	0.533	0.3400
Bed height	-			
C	5cm	0.857	1.523	5.3380
	7.5cm	0.846	0.96	17.009
	10cm	0.957	1.647	36.309
Particle size				
	300um	0.857	0.85	36.587
	600um	0.787	1.449	11.744
	800um	0.648	2.439	6.2589

Table 4.91 Modified dose-response kinetic model parameters using CCAC

Table 4.92 Modified dose-response kinetic model parameters using RHAC

	<u>+</u>		-	0
		R2	a	qe (mg/g)
Flowrate				
	9ml/min	0.78	0.399	10.233
	13ml/min	0.804	0.533	3.3859
	18ml/min	0.65	1.707	4.0434
Influent				
concentration				
	100mg/l	0.941	0.297	2.360
	200mg/l	0.815	0.355	0.497
	300mg/1	0.429	1.799	2.323
Bed height				
	5cm	0.721	1.673	5.339
	7.5cm	0.702	1.068	9.216
	10cm	0.756	0.997	19.27
Particle size				
	300um	0.834	0.787	10.408
	600um	0.859	0.895	4.0429
	800um	0.803	0.826	1.1007
CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This research work investigated the suitability of adsorbents prepared from agro-waste (CCAC and RHAC) in adsorbing phenol from stimulated refinery effluent in batch and column processes. From the study, the following conclusions were drawn:

- 1) Both CCAC and RHAC can effectively be used as alternative adsorbents to the commercial activated carbon in the treatment of refinery effluent
- 2) The adsorptive efficiency increased with adsorbent dosage and contact time but decreased with temperature and initial phenol concentration.
- 3) The BET surface area of CCAC was 903.7 m²/s while that of RHAC was 417.7 m^2/s .
- 4) The equilibrium study showed that Langmuir and Flower-Guggenheim isotherms best described the adsorption process
- 5) Kinetic study showed that the experimental data best fitted the pseudo secondorder model
- 6) The mechanistic modeling showed that the adsorption processes were governed by external mass transport mechanism where particle diffusion was the rate limiting step
- 7) The values of the thermodynamic parameters ΔG and ΔH revealed that adsorption process was spontaneous and endothermic.
- 8) The point of zero charge was 4.67 for RHAC and 5.83 for CCAC (slightly acidic) while the regeneration studies showed more than 75% of the adsorbent can be regenerated using 0.2M of sodium hydroxide
- 9) Response surface methodology (RSM) and artificial neural network (ANN) were adequately employed in optimizing the adsorption process
- 10)Influent phenol concentration, flowrate and bed height were the major factors that affect the column adsorption process

11)Wolborska and Clark column kinetic models best described the continuous adsorption process

5.2 Recommendations

- 1. The efficiency of CCAC and RHAC in treating other industrial effluents should be studied.
- 2. The potentials of other unexplored agricultural wastes should be investigated in the treatment of phenolic wastewater.
- 3. Physical method of activation should be employed in preparing the activated carbon so that comparison can be made with the acid activation method used in this work.

5.3 Contributions to Knowledge

- 1. Corn cobs and rice husks were successfully converted into activated carbon for treatment of phenol wastewater.
- 2. Regeneration of spent activated carbons was successfully carried out.
- 3. Model equations were developed for the optimum phenol uptake from aqueous solution using these agricultural wastes.
- 4. This work has provided column adsorption data for phenol uptake from aqueous solution.

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APPENDIX A

BATCH TABLES FOR BOTH ADSORBENTS

	100mg/l	150mg/l	200mg/l	300mg/1	500mg/l
3	12.5	10.8	9.2	7.9	6.8
5	20.2	17.3	14.8	13.7	10.9
10	37.8	32.4	28.1	25.9	20.5
15	42.2	36.2	31.1	27.9	22.9
20	47.9	41.2	37.3	33.3	26
25	54.4	46.6	40	34.3	29.5
30	58.2	49.9	41.9	36.8	31.6
60	59.8	51.3	45.8	40.8	36.9
90	60.1	53.4	48.9	41.4	37.2
120	61.9	54.9	49.3	43.1	38

Table A1: Effects of initial phenol concentration using CCAC

Table A2: Effects of Temperature using CCAC

	100mg/l	150mg/l	200mg/l	300mg/l	500mg/l
30	63.8	41.3	38.5	32.4	17.9
35	57.9	40.4	37.7	31.8	17.5
40	54.9	39.5	36.9	31.1	17.1
50	52.7	38.3	35.7	30.1	16.6
60	49.7	37.4	34.9	29.4	16.2

 Table A3:
 Effects of particle size using CCAC

	75µm	150µm	300µm	600µm	850µm	
100	59.2	52.4	48.9	42.7	23.1	
150	55.5	47.9	43.4	35.6	14.9	
200	50.5	42.3	36.4	27.5	8.1	
300	46.9	38.9	30.8	20.9	5.57	
500	38.5	32.5	22.6	8.2	2.7	

	0.4g	0.6g	0.8g	1.0g	1.5g	2.0g
100	36.3	40.6	45.9	50.9	55.6	55.9
150	34.1	38.9	43.4	46.2	50.9	51.2
200	30	36.4	40.8	43.4	46.5	46.8
300	23.3	30.1	36.4	39.1	40.8	41.1
500	16.9	23.2	28.6	33.9	35.6	35.7

Table A4: Effects of adsorbent dosage using CCAC

Table A5: Effects of initial phenol concentration using RHAC

	100mg/l	150mg/l	200mg/l	300mg/l	500mg/l
3	18.8	11.8	8.28	6.9	5.6
5	28.2	18.9	12.5	10.1	9.4
10	37.8	24.3	18.2	14.3	11.7
15	46.2	38.3	24.8	18.6	15.7
20	59.9	48.7	34.8	26.4	21.4
25	67.4	58.4	43.1	32.8	29.8
30	78.2	63	51.9	44.6	33.2
60	83.6	72.2	59.2	50.2	40.5
90	84.1	73.2	62.9	52.1	40.2
120	85.9	75.4	63.4	59.4	43.5

 Table A6:
 Effects of Temperature using RHAC

	100mg/l	150mg/l	200mg/l	300mg/l	500mg/l	
30 oC	85.5	72.1	68.5	50.3	46	
35 oC	84	70.8	67.2	49.1	40.3	
40 oC	83.1	69.9	66.4	48.4	39.8	
50 oC	82.1	68.9	65.4	47.6	38.2	
60 oC	80.6	67.5	64.1	46.4	37.4	

	75µm	150µm	300µm	600µm	850µm	
100	86.3	77.8	60.8	49.3	29.1	
150	81.7	59.6	55.6	36.7	13.2	
200	72.2	46.2	42.4	22.9	12.7	
300	40.8	30.4	26.7	20.4	9.8	
500	31.9	22.6	18.6	15.5	3.6	

 Table A7:
 Effects of particle size using RHAC

Table A8: Effects of adsorbent dosage using RHAC

	0.4g	0.6g	0.8g	1.0g	1.5g	2.0g
100	55.6	66.2	72.6	78.3	83.6	83.8
150	49.5	56.5	63.1	67	76.8	77.1
200	40.7	48.5	53.5	61.6	67.6	67.8
300	28	40.7	46.9	56.7	62.2	62.6
500	18.7	38.7	41.6	49.3	57.5	57.7

APPENDIX B

BET SURFACE AREA AND SEM MORPHOLOGY



Figure B1: BET plot for the determination of CCAC surface area



Figure B2: BET plot for the determination of RHAC surface area



Figure C3: FTIR spectrum of CCAC



Figure C4: FTIR spectrum of RHAC

APPENDIX C

ISOTHERM STUDY

Со	Co1	% Ads	Ce	qe	Ce/qe	log Ce	ln Ce	log qe	ln qe
100	0.1	63.8	36.2	4.253333	8.510972	1.558709	3.589059	0.628729	1.447703
150	0.15	45.22	82.17	4.522	18.17116	1.914713	4.40879	0.655331	1.508954
200	0.2	38.51	122.98	5.134667	23.95092	2.089834	4.812022	0.710512	1.636015
300	0.3	32.42	202.74	6.484	31.26774	2.306939	5.311924	0.811843	1.869338
500	0.5	17.89	410.55	5.963333	68.84572	2.613366	6.017498	0.775489	1.78563

Table C1: Isotherm data for adsorption of phenol using CCAC at 30 °C

Table C2: Isotherm data for adsorption of phenol using CCAC at 30 °C Contd

				In(Ce(1-	In		1/Ce(1-	
1/q2	E	E2	θ	0/0)	(ፀ/Co)	ln(1-Ө)	θ)	1/ 0
					-	-		
0.055277	68.64185	4711.703	0.638	3.022365	5.05459	1.01611	0.07631	1.567398
					-	-		
0.048903	30.47092	928.4768	0.4522	4.600576	5.80427	0.60185	0.022216	2.211411
					-			
0.037929	20.40018	416.1672	0.3851	5.279978	6.25257	-0.4863	0.013224	2.596728
					-	-		
0.023786	12.39424	153.6172	0.3242	6.046461	6.83018	0.39186	0.007299	3.084516
					-	-		
0.02812	6.128211	37.55497	0.1789	7.541316	7.93554	0.19711	0.002966	5.589715

Table C3: Isotherm data for adsorption of phenol using CCAC at 35 $^{\circ}\mathrm{C}$

Со		Co1	% Ads	Ce	qe	Ce/qe	log Ce	ln Ce	log qe	ln qe
	100	0.1	57.93	42.07	3.862	10.89332	1.623973	3.739335	0.586812	1.351185
	150	0.15	41.34	87.99	4.134	21.28447	1.944433	4.477223	0.61637	1.419245
	200	0.2	37.74	124.52	5.032	24.74563	2.095239	4.824466	0.701741	1.615818
	300	0.3	31.77	204.69	6.354	32.21435	2.311097	5.321497	0.803047	1.849085
	500	0.5	17.53	412.35	5.843333	70.5676	2.615266	6.021873	0.766661	1.765301

				In(Ce(1-	In		1/Ce(1-	
1/q2	Е	E2	θ	0/0)	(⊖/Co)	ln(1- 0)	θ)	1/ 0
						-		
0.067046	60.1625	3619.527	0.5793	3.419434	-5.1511	0.86584	0.056501	1.726221
					-	-		
0.058514	28.94143	837.6064	0.4134	4.827151	5.89397	0.53341	0.019374	2.418965
					-	-		
0.039493	20.48483	419.6283	0.3774	5.325065	6.27277	0.47385	0.012899	2.649709
					-	-		
0.024769	12.48114	155.7788	0.3177	6.085859	6.85043	0.38229	0.00716	3.147624
					-	-		
0.029287	6.203225	38.47999	0.1753	7.570393	7.95586	0.19274	0.002941	5.704507

Table C4: Isotherm data for adsorption of phenol using CCAC at 35 $^{\circ}\mathrm{C}$ Contd

Table C5: Isotherm data for adsorption of phenol using CCAC at 40 $^{\circ}\mathrm{C}$

Со	Co1	% Ads	Ce	qe	Ce/qe	log Ce	ln Ce	log qe	ln qe
100	0.1	59.96	40.04	3.997333	10.01668	1.602494	3.689879	0.60177	1.385627
150	0.15	38.41	92.385	3.841	24.05233	1.965601	4.525965	0.584444	1.345733
200	0.2	33.94	132.12	4.525333	29.19564	2.120969	4.883711	0.655651	1.509691
300	0.3	28.31	215.07	5.662	37.98481	2.33258	5.370964	0.75297	1.733777
500	0.5	14.83	425.85	4.943333	86.14633	2.629257	6.054087	0.69402	1.59804

Table C6: Isotherm data for adsorption of phenol using CCAC at 40 °C cont	Table C6: Isotherm	data for adsorption	n of phenol using	CCAC at 40 °C conto
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				In(Ce(1-	In		1/Ce(1-	
1/q2	E	E2	θ	0/0)	(Ə/Co)	ln(1-Ө)	θ)	1/ 0
					-	-		
0.062583	64.21145	4123.11	0.5996	3.28608	5.11666	0.91529	0.062375	1.667779
					-	-		
0.067782	28.02417	785.3542	0.3841	4.998146	5.96749	0.48467	0.017575	2.603489
					-	-		
0.048831	19.6276	385.2427	0.3394	5.54968	6.37889	0.41461	0.011458	2.946376
					-	-		
0.031193	12.07499	145.8053	0.2831	6.3001	6.96574	0.33282	0.006486	3.532321
					-	-		
0.040922	6.105315	37.27488	0.1483	7.802084	8.12313	0.16052	0.002757	6.743088

Со	Co1	% Ads	Ce	qe	Ce/qe	log Ce	In Ce	log qe	ln qe
100	0.1	52.65	47.35	3.51	13.49003	1.67532	3.857567	0.545307	1.255616
150	0.15	34.62	98.07	3.462	28.32756	1.991536	4.585682	0.539327	1.241846
200	0.2	31.94	136.12	4.258667	31.96306	2.133922	4.913537	0.629274	1.448956
300	0.3	24.27	227.19	4.854	46.8047	2.356389	5.425787	0.6861	1.579803
500	0.5	14.25	428.75	4.75	90.26316	2.632204	6.060874	0.676694	1.558145

Table C7: Isotherm data for adsorption of phenol using CCAC at 50 $^{\circ}\mathrm{C}$

Table C8: Isotherm data for adsorption of phenol using CCAC at 50 $^{\circ}\mathrm{C}$ contd

				In(Ce(1-	In		1/Ce(1-	
1/q2	E	E2	θ	0/0)	(0 /Co)	ln(1-Ө)	θ)	1/ 0
					-			
0.081168	56.1149	3148.881	0.5265	3.751467	5.24667	-0.7476	0.044603	1.899335
					-	-		
0.083435	27.23976	742.0045	0.3462	5.221466	6.07137	0.42495	0.015596	2.888504
					-	-		
0.055138	19.65314	386.2459	0.3194	5.670067	6.43963	0.38478	0.010794	3.13087
					-			
0.042442	11.79237	139.0599	0.2427	6.56372	7.11971	-0.278	0.005812	4.120313
					-	-		
0.044321	6.255099	39.12626	0.1425	7.855553	8.16302	0.15373	0.00272	7.017544

Table C9: Isotherm data for adsorption of phenol using CCAC at 60 $^{\circ}\mathrm{C}$

Со		Co1	% Ads	Ce	qe	Ce/qe	log Ce	In Ce	log qe	ln qe
	100	0.1	49.73	50.27	3.315333	15.16288	1.701309	3.917408	0.520527	1.198558
	150	0.15	31.63	102.555	3.163	32.42333	2.010957	4.630399	0.500099	1.151521
	200	0.2	25.7	148.6	3.426667	43.36576	2.172019	5.001258	0.534872	1.231588
	300	0.3	16.33	251.01	3.266	76.85548	2.399691	5.525493	0.514016	1.183566
	500	0.5	11.11	444.45	3.703333	120.0135	2.647823	6.096838	0.568593	1.309233

				In(Ce(1-	In		1/Ce(1-	
1/q2	Е	E2	θ	0/0)	(0 /Co)	ln(1- 0)	θ)	1/ 0
					-	-		
0.09098	54.54185	2974.813	0.4973	3.928209	5.30373	0.68776	0.039571	2.010859
						-		
0.099954	26.86936	721.9624	0.3163	5.401227	-6.1617	0.38024	0.014262	3.161555
						-		
0.085164	18.5715	344.9005	0.257	6.062878	-6.657	0.29706	0.009057	3.891051
					-	-		
0.093749	11.00952	121.2095	0.1633	7.159369	7.51595	0.17829	0.004761	6.123699
					-	-		
0.072915	6.223174	38.72789	0.1111	8.176392	8.41193	0.11777	0.002531	9.0009

Table C10: Isotherm data for adsorption of phenol using CCAC at 60 $^\circ$ C contd

Table C11: Isotherm data for adsorption of phenol using RHAC at 30 $^{\circ}\text{C}$

Со	Co1	% Ads	Ce	qe	Ce/qe	log Ce	ln Ce	log qe	ln qe
100	0.1	85.5	14.5	5.7	2.54386	1.161368	2.674149	0.755875	1.740466
150	0.15	72.1	41.85	7.21	5.804438	1.621695	3.734092	0.857935	1.975469
200	0.2	68.5	63	9.133333	6.89781	1.799341	4.143135	0.960629	2.211931
300	0.3	50.3	149.1	10.06	14.82107	2.173478	5.004617	1.002598	2.308567
500	0.5	46	270	15.33333	17.6087	2.431364	5.598422	1.185637	2.730029

Table C12: Isotherm data for adsorption of phenol using RHAC at 30 $^{\circ}\mathrm{C}$ contd

				ln(Ce(1-			1/(Ce(1-	
1/q2	E	E2	θ	Ө)Ө)	ln(θ/Co)	ln(1-Ө)	θ)	1/ 0
					-	-		
0.030779	167.9956	28222.51	0.855	0.899781	4.76182	1.93102	0.475624	1.169591
					-	-		
0.019237	59.48328	3538.261	0.721	2.784664	5.33775	1.27654	0.085645	1.386963
					-	-		
0.011988	39.67011	1573.718	0.685	3.366289	5.67665	1.15518	0.050391	1.459854
					-	-		
0.009881	16.8383	283.5283	0.503	4.992617	6.39095	0.69917	0.013495	1.988072
					-	-		
0.004253	9.312395	86.7207	0.46	5.758765	6.99114	0.61619	0.006859	2.173913

Со	Co1	% Ads	Ce	qe	Ce/qe	log Ce	In Ce	log qe	ln qe
100	0.1	84	16	5.6	2.857143	1.20412	2.772589	0.748188	1.722767
150	0.15	68.23	47.655	6.823	6.984464	1.678108	3.863988	0.833975	1.920299
200	0.2	63.67	72.66	8.489333	8.558976	1.861295	4.285791	0.928874	2.13881
300	0.3	45.39	163.83	9.078	18.04693	2.214393	5.098829	0.95799	2.205854
500	0.5	37.77	311.15	12.59	24.71406	2.49297	5.740275	1.100026	2.532903

Table C13: Isotherm data for adsorption of phenol using RHAC at 35 $^\circ\text{C}$

Table C14: Isotherm data for adsorption of phenol using RHAC at 35 $^\circ$ C contd

				In(Ce(1-			1/(Ce(1-	
1/q2	E	E2	θ	0)0)	ln(θ/Co)	ln(1-Ə)	θ)	1/ 0
					-	-		
0.031888	155.2597	24105.56	0.84	1.114361	4.77952	1.83258	0.390625	1.190476
					-	-		
0.021481	53.18434	2828.574	0.6823	3.099626	5.39292	1.14665	0.06605	1.465631
					-	-		
0.013876	35.00601	1225.421	0.6367	3.724721	5.74977	1.01253	0.037883	1.570598
					-	-		
0.012134	15.58454	242.878	0.4539	5.283755	6.49366	0.60495	0.011177	2.203128
					-	-		
0.006309	8.217559	67.52827	0.3777	6.239597	7.18826	0.47433	0.005165	2.647604

Table C15: Isotherm data for adsorption of phenol using RHAC at 40 $^{\circ}\mathrm{C}$

Со		Co1	% Ads	Ce	qe	Ce/qe	log Ce	ln Ce	log qe	ln qe
1	100	0.1	81.42	18.58	5.428	3.422992	1.269046	2.922086	0.73464	1.691571
1	150	0.15	64.21	53.685	6.421	8.360847	1.729853	3.983134	0.807603	1.859574
2	200	0.2	57.28	85.44	7.637333	11.18715	1.931661	4.447814	0.882942	2.033049
3	300	0.3	40.42	178.74	8.084	22.11034	2.252222	5.185932	0.907626	2.089887
Ę.	500	0.5	33.85	330.75	11.28333	29.31315	2.5195	5.801363	1.052437	2.423327

				In(Ce(1-			1/(Ce(1-	
1/q2	E	E2	θ	0)0)	ln(⊖/Co)	ln(1-Θ)	θ)	1/ 0
					-	-		
0.033941	136.4568	18620.46	0.8142	1.444551	4.81072	1.68308	0.289673	1.228199
					-			
0.024255	48.04049	2307.889	0.6421	3.398643	5.45365	-1.0275	0.052046	1.55739
					-			
0.017144	30.28892	917.4184	0.5728	4.15453	5.85554	-0.8505	0.027397	1.74581
					-	-		
0.015302	14.52247	210.902	0.4042	5.573927	6.60963	0.51785	0.00939	2.474023
					-	-		
0.007855	7.858119	61.75004	0.3385	6.471349	7.29784	0.41325	0.004571	2.95421

Table C16: Isotherm data for adsorption of phenol using RHAC at 40 °C contd

Table C17: Isotherm data for adsorption of phenol using RHAC at 50 $^\circ\text{C}$

Со	Co1	% Ads	Ce	qe	Ce/qe	log Ce	ln Ce	log qe	ln qe
10	0.1	74.36	25.64	4.957333	5.172136	1.408918	3.244154	0.695248	1.600868
15	0.15	59.19	61.215	5.919	10.34212	1.786858	4.114392	0.772248	1.778168
20	0.2	53.89	92.22	7.185333	12.83448	1.964825	4.524177	0.856447	1.972042
30	0.3	31.04	206.88	6.208	33.32474	2.315719	5.332139	0.792952	1.825839
50	0.5	27.36	363.2	9.12	39.82456	2.560146	5.894954	0.959995	2.21047

Table C18: Isotherm data for adsorption of phenol using RHAC at 50 $^{\circ}\mathrm{C}$ contd

				In(Ce(1-			1/(Ce(1-	
1/q2	E	E2	θ	Ө)Ө)	ln(0/Co)	ln(1-Ə)	θ)	1/ 0
					-	-		
0.040692	102.7287	10553.18	0.7436	2.179389	4.90142	1.36102	0.152112	1.344809
					-	-		
0.028543	43.50739	1892.893	0.5919	3.742567	5.53505	0.89624	0.040029	1.689475
					-	-		
0.019369	28.95843	838.5909	0.5389	4.368262	5.91654	0.77414	0.023517	1.855632
					-	-		
0.025948	12.94727	167.6318	0.3104	6.130389	6.87368	0.37164	0.007009	3.221649
						-		
0.012023	7.382463	54.50076	0.2736	6.871387	-7.5107	0.31965	0.00379	3.654971

Со	Co1	% Ads	Ce	qe	Ce/qe	log Ce	In Ce	log qe	ln qe
100	0.1	71.36	28.64	4.757333	6.020179	1.456973	3.354804	0.677364	1.559687
150	0.15	55.55	66.675	5.555	12.0027	1.823963	4.19983	0.744684	1.714698
200	0.2	49.63	100.74	6.617333	15.22366	2.003202	4.612543	0.820683	1.889692
300	0.3	33.72	198.84	6.744	29.48399	2.298504	5.2925	0.828918	1.908653
500	0.5	28.59	357.05	9.53	37.4659	2.552729	5.877876	0.979093	2.254445

Table C19: Isotherm data for adsorption of phenol using RHAC at 60 $^\circ\text{C}$

Table C20: Isotherm data for adsorption of phenol using RHAC at 60 $^{\circ}\text{C}$ contd

				In(Ce(1-			1/(Ce(1-	
1/q2	E	E2	θ	0)0)	ln(⊖/Co)	ln(1-Ə)	θ)	1/ 0
						-		
0.044185	95.03335	9031.337	0.7136	2.441871	-4.9426	1.25037	0.121914	1.401345
					-	-		
0.032406	41.22145	1699.208	0.5555	3.976912	5.59852	0.81081	0.033742	1.80018
					-	-		
0.022837	27.35107	748.0811	0.4963	4.627343	5.99889	0.68577	0.019707	2.01491
					-	-		
0.021987	13.89087	192.9562	0.3372	5.968298	6.79086	0.41128	0.007588	2.965599
					-	-		
0.011011	7.744376	59.97537	0.2859	6.793257	7.46672	0.33673	0.003922	3.497726

ISOTHERM PLOTS



Figure C1. Henry's isotherm plot for adsorption of phenol using CCAC



Figure C2: Henry's isotherm plot for adsorption of phenol using RHAC


Figure C.3: Freundlich isotherm plot for adsorption of phenol using CCAC



Figure C.4: Freundlich isotherm plot for adsorption of phenol using RHAC



Figure C.5: Langmuir isotherm plot for adsorption of phenol using CCAC



Figure C.6: Langmuir isotherm plot for adsorption of phenol using RHAC



Figure C.7: Halsay isotherm plot for adsorption of phenol using CCAC



Figure C.8: Halsay isotherm plot for adsorption of phenol using RHAC



Figure C.9: Harkins-Jura isotherm plot for adsorption of phenol using CCAC



Figure C.10: Harkins-Jura isotherm plot for adsorption of phenol using RHAC



Figure C.11: Temkin isotherm plot for adsorption of phenol using CCAC



Figure C.12: Temkin isotherm plot for adsorption of phenol using RHAC



Figure C.13: Fowler-Guggenheim isotherm plot for adsorption of phenol using CCAC



Figure C.14: Fowler-Guggenheim isotherm plot for adsorption of phenol using RHAC



Figure C.15: Flory-Huggins isotherm plot for adsorption of phenol using CCAC



Figure C.16: Flory-Huggins isotherm plot for adsorption of phenol using RHAC



Figure C.17: Dubinin-Radushevich isotherm plot for adsorption of phenol using CCAC



Figure C.18: Dubinin-Radushevich isotherm plot for adsorption of phenol using RHAC



Figure C.19: Jovanovic isotherm plot for adsorption of phenol using CCAC



Figure C.20: Jovanovic isotherm plot for adsorption of phenol using RHAC



Figure C.21: Kiselev isotherm plot for adsorption of phenol using CCAC



Figure C.22: Kiselev isotherm plot for adsorption of phenol using RHAC

APPENDIX D KINETIC DATA TABLES

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
				-					
3	12.53	87.47	0.835333	0.13387	1.732051	1.098612	0.477121	-0.07814	3.591381
				-					
5	20.16	79.84	1.344	0.22515	2.236068	1.609438	0.69897	0.128399	3.720238
				-					
10	37.78	62.22	2.518667	0.47449	3.162278	2.302585	1	0.401171	3.970355
				-					
15	42.22	57.78	2.814667	0.54853	3.872983	2.70805	1.176091	0.449427	5.329228
				-					
20	47.99	52.01	3.199333	0.65373	4.472136	2.995732	1.30103	0.505059	6.251302
				-					
25	54.36	45.64	3.624	0.78439	5	3.218876	1.39794	0.559188	6.898455
				-					
30	58.21	41.79	3.880667	0.87251	5.477226	3.401197	1.477121	0.588906	7.73063
				-					
60	59.21	40.79	3.947333	0.89673	7.745967	4.094345	1.778151	0.596304	15.20014
				-					
90	60.08	39.92	4.005333	0.91829	9.486833	4.49981	1.954243	0.602639	22.47004
				-					
120	61.88	38.12	4.125333	0.96443	10.95445	4.787492	2.079181	0.615459	29.08856

Table D1: Kinetic data for adsorption of phenol using CCAC at initial concentration of 100 mg/l

Table D2: Kinetic data for adsorption of phenol using CCAC at initial concentration of 100 mg/l contd

					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F = qt/qe	ln(1-F))
	0.30395	0.51719	0.79751	-		0.20250	-	
3.29	1	6	1	1.59707	0.007317	5	0.22628	0.058141
2.78133		0.44425	0.67420			0.32581	-	
3	0.35954	3	8	-1.1215	0.011834	8	0.39426	0.097779
1.60666	0.62240	0.20592	0.38946	-		0.61058	-	
6	7	6	3	0.49342	0.022447	6	0.94311	0.20607
1.31066	0.76297	0.11749	0.31771			0.68234	-	
6	1	2	2	-0.3823	0.025163	3	1.14678	0.238222
	1.07991		0.22446			0.77559	-	
0.926	4	-0.03339	7	-0.2542	0.028718	6	1.49431	0.283913
0.50133	1.99468		0.12152	-		0.87854	-	
3	2	-0.29987	6	0.12957	0.032677	5	2.10822	0.340654
0.24466	4.08719		0.05930	-		0.94076	-	
6	9	-0.61143	8	0.06114	0.035087	8	2.82629	0.378928
	5.61798		0.04314	-		0.95692	-	
0.178	8	-0.74958	8	0.04411	0.035715	9	3.14491	0.389446
	8.33335		0.02908	-			-	
0.12	6	-0.92082	9	0.02952	0.036263	0.97099	3.54011	0.398809

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
				-					
3	10.75	133.875	1.075	0.11373	1.732051	1.098612	0.477121	0.031408	2.790698
				-					
5	17.3	124.05	1.73	0.18995	2.236068	1.609438	0.69897	0.238046	2.890173
				-					
10	32.42	101.37	3.242	0.39186	3.162278	2.302585	1	0.510813	3.084516
				-					
15	36.22	95.67	3.622	0.44973	3.872983	2.70805	1.176091	0.558948	4.141358
				-					
20	41.18	88.23	4.118	0.53069	4.472136	2.995732	1.30103	0.614686	4.856727
				-					
25	46.64	80.04	4.664	0.62811	5	3.218876	1.39794	0.668759	5.360206
				-					
30	49.94	75.09	4.994	0.69195	5.477226	3.401197	1.477121	0.698449	6.007209
				-					
60	51.29	73.065	5.129	0.71929	7.745967	4.094345	1.778151	0.710033	11.69819
				-					
90	53.45	69.825	5.345	0.76464	9.486833	4.49981	1.954243	0.727948	16.83817
				-					
120	54.98	67.53	5.498	0.79806	10.95445	4.787492	2.079181	0.740205	21.82612

Table D3: Kinetic data for adsorption of phenol using CCAC at initial concentration of 150 mg/l

Table D4: Kinetic data for adsorption of pher	nol using CCAC at initial concentration c	f 150 mg/l contd
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					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	U	ln(1-Ut)	-qm))	F = qt/qe	ln(1-F))
	0.22609	0.64571	0.80447	-		0.19552	-	
4.423	1	7	4	1.63206	0.00627	6	0.21757	0.049392
	0.26539	0.57611		-			-	
3.768	3	1	0.68534	1.15626	0.010135	0.31466	0.37784	0.082494
	0.44326	0.35333	0.41033	-		0.58966	-	
2.256	2	9	1	0.52819	0.019191	9	0.89079	0.170182
	0.53304	0.27323	0.34121	-		0.65878	-	
1.876	9	3	5	0.41736	0.021497	5	1.07524	0.195315
	0.72463	0.13987		-				
1.38	8	9	0.251	0.28902	0.024525	0.749	-1.3823	0.230475
	1.19904		0.15169	-		0.84830	-	
0.834	1	-0.07883	2	0.16451	0.027884	8	1.88591	0.272784
	1.98412			-			-	
0.504	7	-0.29757	0.09167	0.09615	0.029926	0.90833	2.38956	0.300509
	2.71002		0.06711	-		0.93288	-	
0.369	7	-0.43297	5	0.06947	0.030764	5	2.70134	0.312382
	6.53594		0.02782	-		0.97217		
0.153	8	-0.81531	8	0.02822	0.032109	2	-3.5817	0.33208
0	#DIV/0!	#NUM!	0	0	0.033064	1	#NUM!	0.346595

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
3	9.22	181.56	1.229333	0.096731	1.732051	1.098612	0.477121	0.08967	2.440347
5	14.84	170.32	1.978667	0.160638	2.236068	1.609438	0.69897	0.296373	2.526954
10	28.81	142.38	3.841333	0.339818	3.162278	2.302585	1	0.584482	2.603263
15	31.08	137.84	4.144	0.372224	3.872983	2.70805	1.176091	0.61742	3.619691
20	37.33	125.34	4.977333	0.467287	4.472136	2.995732	1.30103	0.696997	4.018216
25	40.02	119.96	5.336	0.511159	5	3.218876	1.39794	0.727216	4.685157
30	41.85	116.3	5.58	0.542144	5.477226	3.401197	1.477121	0.746634	5.376344
60	45.87	108.26	6.116	0.613782	7.745967	4.094345	1.778151	0.786467	9.810334
90	46.89	106.22	6.252	0.632805	9.486833	4.49981	1.954243	0.796019	14.39539
120	47.98	104.04	6.397333	0.653542	10.95445	4.787492	2.079181	0.805999	18.75782

Table D5: Kinetic data for adsorption of phenol using CCAC at initial concentration of 200 mg/l

Table D6: Kinetic data for adsorption of phenol using CCAC at initial concentration of 20 mg/l contd

					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F = qt/qe	ln(1-F))
	0.19349	0.71332	0.80783	-		0.19217	-	
5.168	8	2	7	1.64941	0.005372	3	0.21341	0.04201
4.41866	0.22631	0.64529	0.69070	-		0.30931	-	
6	3	1	4	1.17346	0.008679	2	0.37007	0.069764
	0.39123	0.40756	0.39954	-			-	
2.556	6	1	1	0.51006	0.017012	0.60049	0.91752	0.147581
2.25333	0.44378	0.35282		-		0.64780	-	
3	7	5	0.35223	0.43422	0.018381	4	1.04357	0.161655
	0.70422	0.15228	0.22196	-		0.77807	-	
1.42	6	8	7	0.25099	0.022173	3	1.50541	0.20294
1.06133	0.94221	0.02585	0.16590			0.83414	-	
3	1	2	2	-0.1814	0.023815	1	1.79662	0.221994
0.81733	1.22349		0.12776	-		0.87228	-	
3	2	-0.0876	2	0.13669	0.024936	4	2.05795	0.23545
0.28133	3.55450		0.04397	-		0.95607	-	
3	7	-0.55078	7	0.04497	0.027408	3	3.12523	0.266562
0.14533			0.02271	-		0.97733	-	
3	6.88075	-0.83764	8	0.02298	0.028038	3	3.78685	0.274824
						1.00005		
0	#DIV/0!	#NUM!	0	0	0.028712	2	#NUM!	0.28383

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
3	7.91	276.27	1.582	-0.0824	1.732051	1.098612	0.477121	0.199206	1.896334
				-					
5	13.73	258.81	2.746	0.14769	2.236068	1.609438	0.69897	0.438701	1.82083
				-					
10	25.86	222.42	5.172	0.29921	3.162278	2.302585	1	0.713659	1.933488
15	26.67	219.99	5.334	-0.3102	3.872983	2.70805	1.176091	0.727053	2.812148
				-					
20	33.31	200.07	6.662	0.40512	4.472136	2.995732	1.30103	0.823605	3.002101
				-					
25	34.34	196.98	6.868	0.42068	5	3.218876	1.39794	0.83683	3.64007
				-					
30	36.77	189.69	7.354	0.45839	5.477226	3.401197	1.477121	0.866524	4.079413
				-					
60	40.77	177.69	8.154	0.52374	7.745967	4.094345	1.778151	0.911371	7.358352
				-					
90	41.44	175.68	8.288	0.53512	9.486833	4.49981	1.954243	0.91845	10.85907
120	43.09	170.73	8.618	-0.5637	10.95445	4.787492	2.079181	0.935406	13.92434

Table D7: Kinetic data for adsorption of phenol using CCAC at initial concentration of 300 mg/l

Table D8: Kinetic data for adsorption of phenol using CCAC at initial concentration of 300 mg/l contd

					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F = qt/qe	ln(1-F))
	0.14212	0.84732	0.81643	-		0.18356	-	
7.036	6	6	1	1.69516	0.004605	9	0.20281	0.035788
		0.76878	0.68136	-		0.31863	-	
5.872	0.1703	6	5	1.14371	0.008024	5	0.38366	0.06414
	0.29019	0.53731	0.39986	-		0.60013	-	
3.446	2	5	1	0.51059	0.015239	9	0.91664	0.129947
	0.30450	0.51640	0.38106	-		0.61893	-	
3.284	7	3	3	0.47975	0.015725	7	0.96479	0.134718
	0.51124	0.29136	0.22696	-		0.77303	-	
1.956	7	9	7	0.25743	0.01973	3	1.48295	0.175939
	0.57142	0.24303	0.20306	-		0.79693	-	
1.75	9	8	3	0.22698	0.020355	7	1.59424	0.182699
	0.79113	0.10174		-			-	
1.264	9	7	0.14667	0.15861	0.021832	0.85333	1.91957	0.199077
	2.15517		0.05384	-		0.94615	-	
0.464	2	-0.33348	1	0.05534	0.024274	9	2.92172	0.227458
	3.03030		0.03829	-		0.96170	-	
0.33	3	-0.48149	2	0.03904	0.024685	8	3.26252	0.232399
0	#DIV/0!	#NUM!	0	0	0.025697	1	#NUM!	0.244811

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
				-					
3	6.79	467.5	2.166667	0.06721	1.732051	1.098612	0.477121	0.335792	1.384615
				-					
5	10.93	445.35	3.643333	0.11575	2.236068	1.609438	0.69897	0.561499	1.37237
				-					
10	20.47	397.65	6.823333	0.22904	3.162278	2.302585	1	0.833997	1.465559
				-					
15	22.88	385.6	7.626667	0.25981	3.872983	2.70805	1.176091	0.882335	1.966783
				-					
20	26.01	369.95	8.67	0.30124	4.472136	2.995732	1.30103	0.938019	2.306805
				-					
25	29.46	352.7	9.82	0.34899	5	3.218876	1.39794	0.992111	2.545825
				-					
30	31.55	342.25	10.51667	0.37907	5.477226	3.401197	1.477121	1.021878	2.852615
				-					
60	36.89	315.55	12.29667	0.46029	7.745967	4.094345	1.778151	1.089787	4.879371
				-					
90	37.23	313.85	12.41	0.46569	9.486833	4.49981	1.954243	1.093772	7.252216
120	38.01	309.95	12.67	-0.4782	10.95445	4.787492	2.079181	1.102777	9.471192

Table D9: Kinetic data for adsorption of phenol using CCAC at initial concentration of 500 mg/l

Table D10: Kinetic data for adsorption of phenol using CCAC at initial concentration of 500 mg/l contd

					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F = qt/qe	ln(1-F))
10.5033	0.09520	1.02132	0.82899	-		0.17100	-	
3	8	7	2	1.76605	0.00378	8	0.18754	0.029188
9.02666	0.11078	0.95552	0.71244	-		0.28755	-	
7	3	7	4	1.24634	0.006376	6	0.33905	0.050269
5.84666	0.17103	0.76690	0.46145	-		0.53854	-	
7	8	8	8	0.61889	0.012018	2	0.77337	0.099469
5.04333	0.19828	0.70271	0.39805	-		0.60194	-	
3	2	8	3	0.50759	0.013455	7	0.92117	0.112833
			0.31570	-		0.68429	-	
4	0.25	0.60206	6	0.37937	0.015329	4	1.15294	0.130827
	0.35087	0.45484	0.22494	-		0.77505	-	
2.85	7	5	1	0.25482	0.017403	9	1.49192	0.151565
2.15333	0.46439	0.33311	0.16995	-		0.83004	-	
3	6	1	5	0.18628	0.018665	5	1.77222	0.164627
0.37333	2.67857		0.02946	-		0.97053	-	
3	1	-0.4279	6	0.02991	0.021905	4	3.52452	0.199902
	3.84615		0.02052	-		0.97947	-	
0.26	4	-0.58503	1	0.02073	0.022112	9	3.88631	0.202248
0	#DIV/0!	#NUM!	0	0	0.022587	1	#NUM!	0.207678

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
				-					
3	18.53	81.47	1.235333	0.20494	1.732051	1.098612	0.477121	0.091784	2.428494
				-					
5	28.16	71.84	1.877333	0.33073	2.236068	1.609438	0.69897	0.273541	2.663352
				-					
10	37.78	62.22	2.518667	0.47449	3.162278	2.302585	1	0.401171	3.970355
				-					
15	46.22	53.78	3.081333	0.62027	3.872983	2.70805	1.176091	0.488739	4.868023
				-					
20	59.99	40.01	3.999333	0.91604	4.472136	2.995732	1.30103	0.601988	5.000833
				-					
25	67.36	32.64	4.490667	1.11963	5	3.218876	1.39794	0.652311	5.567102
				-					
30	78.21	21.79	5.214	1.52372	5.477226	3.401197	1.477121	0.717171	5.75374
				-					
60	83.63	16.37	5.575333	1.80972	7.745967	4.094345	1.778151	0.746271	10.76169
				-					
90	84.08	15.92	5.605333	1.83759	9.486833	4.49981	1.954243	0.748601	16.05614
				-					
120	85.88	14.12	5.725333	1.95758	10.95445	4.787492	2.079181	0.757801	20.95948

Table D11: Kinetic data for adsorption of phenol using RHAC at initial concentration of 100 mg/l

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					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F=qt/qe	ln(1-F))
	0.22271	0.65224	0.78423	-		0.21577	-	
4.49	7	6	4	1.53356	0.010865	9	0.24306	0.089002
	0.25987	0.58523	0.67210	-		0.32791	-	
3.848	5	5	1	1.11505	0.01662	8	0.39738	0.143634
3.20666		0.50605	0.56008	-		0.43994	-	
6	0.31185	4	4	0.82117	0.022447	2	0.57971	0.20607
	0.37821	0.42226	0.46180	-		0.53822	-	
2.644	5	1	7	0.61954	0.027624	4	0.77268	0.269379
	0.57937	0.23704	0.30146	-		0.69857	-	
1.726	4	1	7	0.35877	0.036206	4	1.19923	0.397831
1.23466	0.80993					0.78439	-	
6	5	0.09155	0.21565	-0.2429	0.04087	6	1.53431	0.48625
0.51133	1.95567		0.08931	-		0.91074	-	
3	3	-0.2913	1	0.09355	0.047828	2	2.41623	0.661743
	6.66668		0.02619	-		0.97385	-	
0.15	1	-0.82391	9	0.02655	0.051346	7	3.64419	0.785951
	8.33335		0.02095	-		0.97909	-	
0.12	6	-0.92082	9	0.02118	0.051639	8	3.86789	0.798057
						1.00005		
0	#DIV/0!	#NUM!	6.21E-17	-1.1E-16	0.052815	8	#NUM!	0.850165

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
3	11.83	132.255	1.183	-0.1259	1.732051	1.098612	0.477121	0.072985	2.535926
				-					
5	18.94	121.59	1.894	0.20998	2.236068	1.609438	0.69897	0.27738	2.639916
				-					
10	24.3	113.55	2.43	0.27839	3.162278	2.302585	1	0.385606	4.115226
				-					
15	38.34	92.49	3.834	0.48353	3.872983	2.70805	1.176091	0.583652	3.912363
				-					
20	48.65	77.025	4.865	0.66651	4.472136	2.995732	1.30103	0.687083	4.110997
				-					
25	58.44	62.34	5.844	0.87803	5	3.218876	1.39794	0.76671	4.277892
				-					
30	63.01	55.485	6.301	0.99452	5.477226	3.401197	1.477121	0.799409	4.761149
				-					
60	72.19	41.715	7.219	1.27977	7.745967	4.094345	1.778151	0.858477	8.3114
90	73.15	40.275	7.315	-1.3149	9.486833	4.49981	1.954243	0.864214	12.30349
				-					
120	75.38	36.93	7.538	1.40161	10.95445	4.787492	2.079181	0.877256	15.91934

Table D13: Kinetic data for adsorption of phenol using RHAC at initial concentration of 150 mg/l

Table D14: Kinetic data for adsorptio	n of phenol using RHAC at initial	concentration of 1500 mg/l conto
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					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F=qt/qe	ln(1-F))
	0.15735	0.80311	0.84306			0.15693	-	
6.355	6	6	2	-1.8519	0.006905	8	0.17071	0.054679
	0.17717	0.75158		-			-	
5.644	9	7	0.74874	1.38127	0.011108	0.25126	0.28936	0.091193
	0.19577	0.70825	0.67763	-		0.32236	-	
5.108	1	1	3	1.13207	0.014304	7	0.38915	0.120904
	0.26997	0.56867	0.49137	-		0.50862	-	
3.704	8	1	7	0.67605	0.022789	3	0.71054	0.209996
	0.37411	0.42699	0.35460	-		0.64539	-	
2.673	1	9	3	0.43789	0.029126	7	1.03676	0.28946
	0.59031	0.22891	0.22472	-		0.77527	-	
1.694	9	3	8	0.25454	0.035231	2	1.49286	0.381324
	0.80840		0.16410	-		0.83589	-	
1.237	7	0.09237	2	0.17925	0.038111	8	1.80727	0.431916
	3.13479		0.04231	-		0.95768	-	
0.319	6	-0.49621	9	0.04324	0.043953	1	3.16252	0.555799
	4.48430		0.02958	-		0.97041	-	
0.223	5	-0.6517	3	0.03003	0.044569	7	3.52054	0.571056
0	#DIV/0!	#NUM!	6.28E-17	-1.1E-16	0.046002	1	#NUM!	0.608712

				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
				-					
3	8.28	183.44	1.104	0.08643	1.732051	1.098612	0.477121	0.042969	2.717391
				-					
5	12.45	175.1	1.66	0.13296	2.236068	1.609438	0.69897	0.220108	3.012048
				-					
10	18.15	163.7	2.42	0.20028	3.162278	2.302585	1	0.383815	4.132231
				-					
15	24.81	150.38	3.308	0.28515	3.872983	2.70805	1.176091	0.519566	4.534462
				-					
20	34.81	130.38	4.641333	0.42786	4.472136	2.995732	1.30103	0.666643	4.309107
				-					
25	43.06	113.88	5.741333	0.56317	5	3.218876	1.39794	0.759013	4.354389
				-					
30	51.98	96.04	6.930667	0.73355	5.477226	3.401197	1.477121	0.840775	4.328588
				-					
60	59.21	81.58	7.894667	0.89673	7.745967	4.094345	1.778151	0.897334	7.600068
				-					
90	62.89	74.22	8.385333	0.99128	9.486833	4.49981	1.954243	0.92352	10.73303
				-					
120	63.21	73.58	8.428	0.99994	10.95445	4.787492	2.079181	0.925725	14.23825

Table D15: Kinetic data for adsorption of phenol using RHAC at initial concentration of 200 mg/l

Table D16: Kinetic data for	adsorption of phenol	using RHAC at initial of	concentration of 200 mg/l cor	ntd
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					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F=qt/qe	ln(1-F))
	0.13653	0.86474	0.86900	-		0.13099		
7.324	7	8	8	2.03262	0.004821	2	-0.1404	0.037536
	0.14775		0.80303	-		0.19696	-	
6.768	4	0.83046	7	1.62474	0.00727	3	0.21935	0.057744
	0.16644		0.71286	-		0.28713	-	
6.008	5	0.77873	2	1.24779	0.010639	8	0.33847	0.086981
	0.19531		0.60749	-		0.39250	-	
5.12	3	0.70927	9	0.93522	0.014609	1	0.49841	0.12384
3.78666	0.26408	0.57825	0.44929	-		0.55070	-	
7	5	7	6	0.59656	0.02064	4	0.80007	0.185819
2.68666	0.37220	0.42921	0.31877	-		0.68122	-	
7	8	4	9	0.38387	0.025679	1	1.14326	0.244583
1.49733	0.66785	0.17531	0.17766			0.82233	-	
3	4	8	2	-0.1956	0.031193	8	1.72787	0.318578
0.53333			0.06328	-		0.93671	-	
3	1.875	-0.273	1	0.06537	0.035715	9	2.76017	0.389446
0.04266			0.00506	-		0.99493		
7	23.4375	-1.36991	2	0.00508	0.038035	8	-5.2859	0.430509
0	#DIV/0!	#NUM!	0	0	0.038237	1	#NUM!	0.43427

				U	-	-		0.	-
				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
				-					
3	6.87	279.39	1.374	0.07117	1.732051	1.098612	0.477121	0.137987	2.183406
				-					
5	10.09	269.73	2.018	0.10636	2.236068	1.609438	0.69897	0.304921	2.477701
				-					
10	4.28	287.16	0.856	0.04374	3.162278	2.302585	1	-0.06753	11.68224
				-					
15	18.61	244.17	3.722	0.20592	3.872983	2.70805	1.176091	0.570776	4.030091
				-					
20	26.41	220.77	5.282	0.30666	4.472136	2.995732	1.30103	0.722798	3.786445
				-					
25	32.82	201.54	6.564	0.39779	5	3.218876	1.39794	0.817169	3.808653
				-					
30	44.55	166.35	8.91	0.58969	5.477226	3.401197	1.477121	0.949878	3.367003
				-					
60	50.21	149.37	10.042	0.69736	7.745967	4.094345	1.778151	1.00182	5.974905
				-					
90	52.11	143.67	10.422	0.73626	9.486833	4.49981	1.954243	1.017951	8.635579
				-					
120	53.39	139.83	10.678	0.76336	10.95445	4.787492	2.079181	1.02849	11.23806

Table D17: Kinetic data for adsorption of phenol using RHAC at initial concentration of 300 mg/l contd

Table D18: Kinetic data for	adsorption of phen	ol using RHAC at initial co	oncentration of 300 mg/l contd
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					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F=qt/qe	ln(1-F))
	0.10748		0.87132	-		0.12867	-	
9.304	1	0.96867	4	2.05046	0.003996	6	0.13774	0.03091
	0.11547	0.93751	0.81101	-		0.18898	-	
8.66	3	8	3	1.66608	0.005882	7	0.20947	0.046192
	0.10181		0.91983	-		0.08016	-	
9.822	2	0.9922	5	2.52367	0.002485	5	0.08356	0.018997
	0.14376		0.65143	-		0.34856	-	
6.956	1	0.84236	3	1.05392	0.010912	7	0.42858	0.089429
	0.18532	0.73207	0.50533	-		0.49466	-	
5.396	2	2	8	0.70388	0.015569	2	0.68253	0.133181
	0.24307	0.61426	0.38527	-		0.61472	-	
4.114	2	4	8	0.48659	0.019433	2	0.95379	0.17276
	0.56561	0.24748	0.16557	-		0.83442	-	
1.768	1	2	4	0.18101	0.026595	6	1.79834	0.256098
	1.57232		0.05956	-		0.94043	-	
0.636	7	-0.19654	2	0.06141	0.030094	8	2.82074	0.302858
			0.02397	-		0.97602	-	
0.256	3.90625	-0.59176	5	0.02427	0.031274	5	3.73076	0.319755
							-	
0	#DIV/0!	#NUM!	0	0	0.032072	1	36.7368	0.331521

	Riffe du		ption of phe	chief doing i		al concentre	01 200	11.91	
				In					
t	% Ads	Ct	qt	(Ct/Co)	t^1/2	ln t	log t	log qt	t/qt
				-					
3	5.6	472	1.866667	0.05763	1.732051	1.098612	0.477121	0.271067	1.607143
				-					
5	9.42	452.9	3.14	0.09894	2.236068	1.609438	0.69897	0.49693	1.592357
10	11.68	441.6	3.893333	-0.1242	3.162278	2.302585	1	0.590322	2.568493
				-					
15	15.7	421.5	5.233333	0.17079	3.872983	2.70805	1.176091	0.718778	2.866242
				-					
20	21.42	392.9	7.14	0.24105	4.472136	2.995732	1.30103	0.853698	2.80112
				-					
25	29.75	351.25	9.916667	0.35311	5	3.218876	1.39794	0.996366	2.521008
				-					
30	33.16	334.2	11.05333	0.40287	5.477226	3.401197	1.477121	1.043493	2.714113
				-					
60	40.51	297.45	13.50333	0.51936	7.745967	4.094345	1.778151	1.130441	4.443347
90	42.23	288.85	14.07667	-0.5487	9.486833	4.49981	1.954243	1.1485	6.393559
				-					
120	43.45	282.75	14.48333	0.57004	10.95445	4.787492	2.079181	1.160869	8.285386

Table D19: Kinetic data for adsorption of phenol using RHAC at initial concentration of 500 mg/l

Table D20: Kinetic data for a	dsorption of phenol	using RHAC at initial	concentration of 500 mg/l contd
	· · · · · · · · ·	0 0	

					log(Co/(Co			log(Co/Ct
qe - qt	1/qe - qt	log qe-qt	Ut	ln(1-Ut)	-qm))	F=qt/qe	ln(1-F))
12.6166		1.10094	0.87111	-		0.12891	-	
6	0.07926	5	6	2.04884	0.003255	3	0.13801	0.025028
11.3433	0.08815	1.05474	0.78319	-		0.21685	-	
3	8	1	9	1.52878	0.005489	1	0.24443	0.042968
	0.09442	1.02489	0.73118	-		0.26887	-	
10.59	9	6	5	1.31373	0.006817	7	0.31317	0.053941
9.24999	0.10810	0.96614	0.63866	-		0.36141	-	
7	8	2	5	1.01795	0.009188	8	0.44851	0.074172
	0.13617	0.86589		-		0.49309	-	
7.34333	8	3	0.50702	0.70729	0.012584	4	0.67943	0.104688
4.56666	0.21897	0.65959	0.31530	-		0.68485	-	
3	8	9	5	0.37878	0.017578	3	1.15472	0.153354
3.42999	0.29154	0.53529	0.23682	-		0.76335	-	
7	5	4	4	0.27027	0.019639	2	1.44118	0.174964
0.97999	1.02041		0.06766	-		0.93255	-	
7	2	-0.00878	4	0.07006	0.024115	1	2.69638	0.225556
0.40666	2.45903		0.02807	-		0.97214	-	
3	7	-0.39076	8	0.02848	0.025169	5	3.58076	0.238298
-3.3E-06	-300000	#NUM!	0	0	0.025918	1.00023	#NUM!	0.247567

KINETICS PLOTS



Figure D.1: Natarajan and Khalaf plot of adsorption of phenol using CCAC



Figure D.2: Natarajan and Khalaf plot of adsorption of phenol using RHAC



Figure D.3: Elovich kinetic plot for adsorption of phenol using CCAC



Figure D.4: Elovich kinetic plot for adsorption of phenol using RHAC



Figure D.5: Pseudo first-order kinetics plot for adsorption of phenol using CCAC



Figure D.6: Pseudo first-order kinetics plot for adsorption of phenol using RHAC



Figure D.7: Pseudo second-order kinetics plot for adsorption of phenol using CCAC



Figure D.8: Pseudo second-order kinetics plot for adsorption of phenol using RHAC



Figure D.9: Bhattacharya-Venkobachor model plot of adsorption of phenol using CCAC



Figure D.10: Bhattacharya-Venkobachor model plot of adsorption of phenol using RHAC



Figure D.11: Power function plot of the adsorption of phenol using CCAC



Figure D.12: Power function plot of the adsorption of phenol using RHAC







Figure D.14: Lagergren second-order kinetic plot for the adsorption of phenol using RHAC



Figure D.15: Intra-particle diffusion model plot of adsorption of phenol using CCAC



Figure D.16: Intra-particle diffusion model plot of adsorption of phenol using RHAC



Figure D.17: Boyd kinetic model of the adsorption of phenol using CCAC



Figure D.18: Boyd kinetic model of the adsorption of phenol using RHAC



Figure D.19: Bangham kinetic plot for adsorption of phenol unto CCAC



Figure D.20: Bangham kinetic plot for adsorption of phenol unto RHAC

APPENDIX E

OPTIMIZATION RESULTS

Source	Sequential	Lack of Fit	Adjusted R ²	Predicted	Remark
	p-value	p-value		\mathbf{R}^2	
Linear	< 0.0001	< 0.0001	0.7471	0.6910	Not
					suggested
2FI	0.3606	< 0.0001	0.7572	0.7122	Not
					suggested
Quadratic	0.0017	< 0.0001	0.8964	0.7431	Suggested
Cubic	0.1514	< 0.0001	0.9378	-0.6765	Aliased

Table E1: Fit summary analysis of phenol adsorption using CCAC

Table E2: Sequential fit summary of phenol adsorption using CCAC

Source	Sum of	df	Mean	F - value	P - value	Remark
	squares		squares			
Mean vs	1.23 x 10 ⁻⁵	1	1.23 x 10 ⁻⁵			Not
Total						suggested
Linear vs	2493.42	4	6.23.35	22.41	< 0.0001	Not
Mean						suggested
2FI vs	188.12	6	31.35	1.17	0.3606	
Linear						
Quadratic	336.37	4	84.09	7.38	0.0017	Suggested
vs 2FI						
Cubic vs	122.96	8	15.37	2.25	0.1514	Aliased
Quadratic						
Residual	47.90	7	6.84			
Total	1.27 x 10 ⁻⁵	30	4220.66			

Source	Sum of Squares	df	Mean Square	F-value	p-value	<u> </u>
Linear	694.66	20	34.73	257.92	< 0.0001	<u> </u>
2FI	506.54	14	36.18	268.68	< 0.0001	
Quadratic	170.18	10	17.02	126.37	< 0.0001	Suggested
Cubic	47.22	2	23.61	175.33	< 0.0001	Aliased
Pure Error	0.6733	5	0.1347			

Table E3: Lack of fit of phenol adsorption using CCAC

Table E4: Desirability values for optimization using CCAC

Number Temp	Conc	Contact Time	Dosage Po	ercent Adsorbed D	esirability
1 40.843	100.000	31.979	1.000	59.228	0.819 Selected
2 40.822	100.000	31.788	1.000	59.130	0.819
3 40.884	100.000	32.039	1.000	59.321	0.819
4 40.834	100.000	31.470	1.000	59.057	0.819
5 40.928	100.000	31.492	1.000	59.241	0.819
6 40.924	100.000	32.106	1.000	59.416	0.819
7 40.768	100.000	31.450	1.000	58.927	0.819
8 40.919	100.000	32.335	1.000	59.475	0.819
9 40.704	100.000	32.361	1.000	59.076	0.819
10 40.705	100.000	32.896	1.000	59.233	0.819
11 40.954	100.000	30.894	1.000	59.107	0.819
12 40.649	100.000	31.912	1.000	58.836	0.819
13 40.880	100.000	30.435	1.000	58.829	0.819
14 41.018	100.000	30.732	1.000	59.174	0.819
15 40.977	100.000	32.110	1.000	59.514	0.819
16 40.917	100.000	33.364	1.000	59.771	0.819
17 40.674	100.000	30.864	1.000	58.568	0.819
18 40.775	100.000	32.169	1.001	59.154	0.819

19 40.744 100.000	33.849	1.000	59.583	0.819
20 40.608 100.000	30.933	1.000	58.460	0.819
21 40.516 100.000	32.347	1.000	58.703	0.819
22 41.066 100.000	30.112	1.000	59.068	0.819
23 40.518 100.000	33.382	1.000	59.008	0.819
24 41.042 100.001	33.441	1.000	60.022	0.819
25 40.564 100.000	33.932	1.000	59.256	0.819
26 40.474 100.000	31.622	1.000	58.403	0.819
27 41.009 100.057	33.354	1.000	59.926	0.819
28 40.893 100.001	34.473	1.000	60.041	0.819
29 41.206 100.000	30.003	1.000	59.283	0.819
30 40.516 100.000	34.647	1.000	59.361	0.818
31 40.580 100.000	34.898	1.000	59.556	0.818
32 40.829 100.000	34.962	1.000	60.057	0.818
33 40.344 100.000	32.695	1.000	58.454	0.818
34 40.342 100.000	32.110	1.000	58.279	0.818
35 40.914 100.000	35.133	1.000	60.264	0.818
36 40.690 100.000	35.912	1.000	60.050	0.818
37 40.248 100.001	32.462	1.001	58.187	0.818
38 41.107 100.000	35.333	1.000	60.670	0.818
39 40.762 100.000	32.916	1.005	59.349	0.818
40 41.511 100.000	30.003	1.000	59.800	0.818
41 41.443 100.000	32.948	1.000	60.578	0.818
42 40.340 100.000	36.038	1.000	59.380	0.817
43 40.125 100.000	32.914	1.000	58.058	0.817
44 40.776 100.482	31.428	1.000	58.839	0.817
45 40.756 100.000	36.803	1.000	60.413	0.817
46 40.585 100.000	36.894	1.000	60.104	0.817
47 40.881 100.565	30.002	1.000	58.583	0.817

48 40.182 100.000	30.000	1.000	57.305	0.817
49 41.713 100.000	31.234	1.000	60.505	0.817
50 40.000 100.000	31.092	1.000	57.250	0.816
51 41.118 100.000	37.393	1.000	61.240	0.816
52 40.435 100.005	38.359	1.000	60.177	0.816
53 41.102 100.000	30.061	1.009	59.110	0.816
54 40.892 100.989	32.966	1.000	59.410	0.816
55 40.650 100.000	38.955	1.000	60.757	0.815
56 40.000 100.000	37.893	1.000	59.141	0.815
57 42.060 100.000	30.001	1.000	60.646	0.814
58 40.272 100.000	39.896	1.000	60.219	0.814
59 40.556 100.000	40.039	1.001	60.838	0.814
60 41.062 101.134	36.905	1.000	60.786	0.813
61 40.602 100.514	40.147	1.000	60.851	0.812
62 41.535 100.000	39.611	1.000	62.518	0.812
63 40.000 100.000	41.419	1.000	59.991	0.812
64 40.000 100.001	30.000	1.012	56.910	0.811
65 41.986 100.000	37.146	1.002	62.600	0.810
66 41.221 100.000	41.618	1.000	62.457	0.810
67 40.894 100.000	30.002	1.029	58.713	0.809
68 41.979 100.000	41.085	1.000	63.570	0.806
69 40.030 102.535	30.000	1.000	56.475	0.806
70 42.913 100.000	30.000	1.000	61.749	0.805
71 41.245 103.687	34.599	1.003	59.980	0.804
72 41.863 100.001	43.019	1.000	63.833	0.804
73 41.795 100.000	30.000	1.038	60.243	0.803
74 40.004 100.000	30.571	1.040	57.123	0.803
75 43.043 100.000	32.658	1.000	62.710	0.802
76 40.832 100.000	40.258	1.040	61.549	0.801

77 42.350 103.244	30.000	1.000	60.394	0.801
78 41.071 100.000	33.187	1.057	60.087	0.800
79 40.003 100.000	30.126	1.061	57.026	0.795
80 40.356 104.761	44.478	1.000	60.491	0.792
81 40.000 100.001	51.619	1.000	61.950	0.790
82 40.470 107.579	30.001	1.000	56.403	0.790
83 42.751 100.000	45.311	1.000	65.553	0.790
84 40.000 100.000	51.538	1.005	61.964	0.789
85 40.000 100.000	52.282	1.000	62.051	0.788
86 42.742 106.250	36.122	1.000	62.100	0.784
87 40.328 110.122	30.000	1.000	55.626	0.779
88 40.000 100.001	56.376	1.000	62.609	0.775
89 40.000 111.101	30.000	1.000	54.749	0.772
90 40.000 100.000	48.672	1.092	62.133	0.771
91 42.600 100.000	58.077	1.000	67.409	0.753
92 43.622 100.000	54.350	1.000	68.078	0.751
93 41.519 124.452	45.379	1.000	59.220	0.724

 Table E5:
 Report of Internal and External Studentized Residuals

					Intornally	Fytomolly		Influence	
Run	Actual	Predicted	Decidual	I avana ca	Studentized	Externally	Cook's	on Fitted	Standard
Order	Value	Value	Kesiuuai	Leverage	Studentized	Studentized	Distance	Value	Order
					Residuals	Residuals		DFFITS	
1	67.80	66.98	0.8220	0.632	0.402	0.390	0.018	0.511	10
2	68.60	67.13	1.47	0.129	0.466	0.454	0.002	0.174	29
3	67.80	67.13	0.6686	0.129	0.212	0.205	0.000	0.079	28
4	79.30	78.52	0.7838	0.632	0.383	0.372	0.017	0.487	13
5	61.20	59.61	1.59	0.514	0.675	0.663	0.032	0.682	23
6	44.30	44.41	-0.1073	0.632	-0.052	-0.051	0.000	-0.066	4

7	41.90	41.70	0.1995	0.632	0.097	0.094	0.001	0.123	3
8	77.30	77.91	-0.6078	0.632	-0.297	-0.288	0.010	-0.377	16
9	74.80	75.35	-0.5509	0.632	-0.269	-0.261	0.008	-0.342	15
10	60.10	62.66	-2.56	0.632	-1.251	-1.277	0.179	-1.674	5
11	53.10	52.95	0.1476	0.632	0.072	0.070	0.001	0.091	8
12	66.10	67.87	-1.77	0.632	-0.864	-0.856	0.085	-1.122	6
13	76.90	82.49	-5.59	0.514	-2.378	-2.911	0.399	-2.996 ⁽¹⁾	24
14	59.70	62.59	-2.89	0.514	-1.231	-1.254	0.107	-1.290	20
15	68.50	67.13	1.37	0.129	0.434	0.422	0.002	0.162	25
16	57.60	60.57	-2.97	0.514	-1.264	-1.292	0.113	-1.330	18
17	83.50	82.37	1.13	0.632	0.551	0.537	0.035	0.704	14
18	65.50	64.32	1.18	0.632	0.576	0.563	0.038	0.738	9
19	68.90	67.13	1.77	0.129	0.561	0.548	0.003	0.211	26
20	68.60	67.13	1.47	0.129	0.466	0.454	0.002	0.174	30
21	62.80	60.92	1.88	0.632	0.917	0.912	0.096	1.196	2
22	58.20	56.92	1.28	0.632	0.627	0.614	0.045	0.805	1
23	68.40	67.13	1.27	0.129	0.403	0.391	0.002	0.150	27
24	72.10	68.74	3.36	0.514	1.427	1.483	0.144	1.526	22
25	64.80	60.91	3.89	0.632	1.899	2.105	0.413	2.760 ⁽¹⁾	12
26	54.90	55.93	-1.03	0.514	-0.439	-0.427	0.014	-0.439	17
27	62.00	59.56	2.44	0.632	1.194	1.213	0.163	1.590	11
28	48.90	49.05	-0.1456	0.632	-0.071	-0.069	0.001	-0.090	7
29	75.40	76.51	-1.11	0.514	-0.472	-0.460	0.016	-0.473	19
30	45.30	52.66	-7.36	0.514	-3.130	-5.136 ⁽²⁾	0.692	-5.285 ⁽¹⁾	21
Source	Sum of	df	Mean	F - value	P - value				
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	squares		squares						
Mean vs	$1.76 \ge 10^5$	1	$1.76 \ge 10^5$						
Total									
Linear vs	3765.84	4	941.46	14.31	< 0.0001				
Mean									
2FI vs	448.12	6	74.69	1.19	0.3553				
Linear									
Quadratic	949.18	4	237.30	14.36	< 0.0001	Suggested			
vs 2FI									
Cubic vs	178.34	8	22.29	2.25	0.1515	Aliased			
Quadratic									
Residual	69.49	7	9.93						
Total	1.815 x	30	6048.44						
	10 ⁵								

Table E6 : Sequential fit summary using RHAC

Table E7: Model summary analysis using RHAC

Source	Std. Dev.	\mathbf{R}^2	Adjusted	Predicted	PRESS	
			\mathbf{R}^2	\mathbf{R}^2		
Linear	8.11	0.6960	0.6473	0.5803	2271.24	
2FI	7.94	0.7788	0.6624	0.5505	2432.00	
Quadratic	4.06	0.9542	0.9115	0.7460	1374.49	Suggested
Cubic	3.15	0.9872	0.9468	-0.5581	8430.60	Aliased

Source	Sum of	df	Mean	F-value	p-value	
	squares		square			
Linear	1643.66	20	82.18	279.85	< 0.0001	
2FI	1195.54	14	85.40	290.79	< 0.0001	
Quadratic	246.36	10	24.64	83.89	< 0.0001	Suggested
Cubic	68.02	2	34.01	115.81	< 0.0001	Aliased
Pure Error	1.47	5	0.2937			

Table E8: Lack of Fit test using RHAC

Table E 9: Desirability values for optimization using RHAC

Number Temp	Conc	Contact time	Dosage 1	Percent Adsorbed I	Desirability
1 40.000	100.000	30.000	0.600	77.921	0.909 Selected
2 40.000	100.055	30.000	0.602	78.009	0.909
3 40.000	100.591	30.000	0.600	77.846	0.909
4 40.076	100.000	30.000	0.601	78.005	0.909
5 40.000	100.159	30.162	0.600	77.946	0.908
6 40.000	101.192	30.000	0.600	77.759	0.908
7 40.000	100.000	30.000	0.605	78.151	0.908
8 40.213	100.008	30.000	0.600	78.066	0.908
9 40.000	101.599	30.000	0.600	77.724	0.908
10 40.000	100.001	30.380	0.600	78.031	0.907
11 40.355	100.158	30.001	0.600	78.141	0.907
12 40.000	100.007	30.000	0.611	78.431	0.906
13 40.002	103.356	30.000	0.600	77.457	0.906
14 40.462	100.025	30.001	0.600	78.229	0.906
15 40.005	104.071	30.000	0.600	77.357	0.906
16 40.637	100.001	30.019	0.600	78.349	0.905
17 40.000	100.001	30.839	0.600	78.159	0.905
18 40.588	100.029	30.155	0.600	78.354	0.904
19 40.000	105.221	30.000	0.600	77.203	0.904
20 40.000	106.203	30.000	0.600	77.040	0.903
21 40.497	104.891	30.000	0.600	77.567	0.901
22 40.000	100.001	31.202	0.605	78.499	0.901

23 40.108 100.001	31.378	0.600	78.387	0.901
24 40.000 108.041	30.000	0.604	76.978	0.901
25 40.026 100.000	31.514	0.600	78.368	0.900
26 40.000 101.003	30.001	0.629	79.089	0.900
27 40.000 100.000	31.655	0.600	78.389	0.900
28 40.001 110.079	30.000	0.600	76.445	0.899
29 40.000 100.001	30.002	0.634	79.427	0.899
30 40.001 100.060	32.147	0.600	78.519	0.897
31 41.783 100.000	30.000	0.600	78.985	0.895
32 41.329 100.001	30.799	0.600	78.979	0.895
33 41.961 100.001	30.000	0.602	79.156	0.893
34 42.047 100.003	30.004	0.600	79.110	0.893
35 40.000 100.000	30.054	0.657	80.376	0.890
36 40.001 100.045	32.882	0.611	79.226	0.889
37 40.000 100.001	33.367	0.600	78.863	0.889
38 40.000 100.000	30.000	0.662	80.537	0.888
39 40.000 100.049	33.485	0.600	78.890	0.888
40 40.000 118.945	30.000	0.607	75.353	0.888
41 40.001 106.312	30.000	0.654	79.497	0.887
42 41.112 100.001	30.000	0.644	80.570	0.887
43 40.037 121.131	30.000	0.600	74.581	0.886
44 42.785 100.005	30.001	0.600	79.416	0.885
45 42.965 100.000	30.001	0.600	79.483	0.884
46 40.000 100.000	30.001	0.674	80.963	0.883
47 43.095 100.001	30.000	0.601	79.566	0.882
48 40.271 100.000	33.699	0.624	80.224	0.878
49 40.000 109.580	30.000	0.671	79.809	0.878
50 40.000 127.063	30.002	0.600	73.427	0.877
51 40.000 129.114	30.000	0.600	73.023	0.874
52 40.001 100.001	30.000	0.693	81.589	0.874
53 43.795 101.435	30.000	0.600	79.536	0.873
54 40.000 115.900	30.000	0.676	79.223	0.871
55 40.000 132.090	30.000	0.600	72.403	0.870
56 40.000 100.000	30.000	0.703	81.913	0.868
57 44.182 100.001	30.013	0.611	80.337	0.867
58 43.316 100.000	30.000	0.643	81.493	0.867
59 40.000 134.319	30.000	0.667	75.920	0.856
60 40.000 100.008	35.904	0.651	81.801	0.855

61 40.006 136.400	30.000	0.665	75.460	0.853
62 40.005 100.000	38.693	0.600	80.283	0.849
63 40.000 100.000	38.967	0.600	80.349	0.847
64 40.000 147.125	30.000	0.600	68.997	0.842
65 40.049 100.001	30.000	0.746	83.083	0.841
66 40.000 124.794	30.000	0.727	80.169	0.840
67 40.000 105.987	39.605	0.600	79.653	0.836
68 40.000 146.645	30.000	0.698	75.353	0.831
69 40.000 135.666	30.000	0.729	78.764	0.830
70 44.895 134.369	30.000	0.600	73.901	0.821
71 40.000 154.351	30.001	0.710	74.480	0.817
72 43.180 148.707	30.000	0.600	70.207	0.816
73 43.437 147.901	30.000	0.600	70.484	0.815
74 40.000 159.562	30.001	0.686	71.942	0.815
75 40.000 150.765	30.411	0.726	76.204	0.814
76 40.000 165.608	30.000	0.669	69.352	0.806
77 40.000 164.536	30.005	0.600	64.420	0.800
78 40.000 169.339	30.000	0.779	75.292	0.769
79 40.000 178.668	30.000	0.771	72.840	0.760
80 40.000 188.891	30.000	0.753	69.178	0.748
81 40.000 184.748	30.000	0.784	72.216	0.745
82 40.000 161.722	40.081	0.723	76.523	0.741
83 46.552 170.690	30.000	0.717	73.489	0.729
84 41.821 100.001	30.000	0.871	85.833	0.706

APPENDIX F

COLUMN KINETIC PLOTS





Figure F.1: Adam-Bohart kinetic model for adsorption of phenol using CCAC at different flow rates

Figure F.2: Adam-Bohart kinetic model for adsorption of phenol using CCAC at different influent concentrations



Figure F.3: Adam-Bohart kinetic model for adsorption of phenol using CCAC at different bed heights





Figure F.4: Adam-Bohart kinetic model for adsorption of phenol using CCAC at different particle sizes



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Figure F.9: Yoon-Nelson kinetic model for adsorption of phenol using CCAC at different flow rates



Figure F.10: Yoon-Nelson kinetic model for adsorption of phenol using CCAC at different influent concentrations



Figure F.11: Yoon-Nelson kinetic model for adsorption of phenol using CCAC at different bed heights



Figure F.12: Yoon-Nelson kinetic model for adsorption of phenol using CCAC at different particle sizes



Figure F.13: Yoon-Nelson kinetic model for adsorption of phenol using RHAC at different flow rates



Figure F.14: Yoon-Nelson kinetic model for adsorption of phenol using RHAC at different influent concentrations



Figure F.15: Yoon-Nelson kinetic model for adsorption of phenol using RHAC at different bed heights



Figure F.16: Yoon-Nelson kinetic model for adsorption of phenol using RHAC at different particle sizes





Figure F.17: Thomas kinetic model for adsorption of phenol using CCAC at different flow rates





Figure F.18: Thomas kinetic model for adsorption of phenol using CCAC at different influent concentrations



Figure F.20: Thomas kinetic model for adsorption of phenol using CCAC at different particle sizes









Figure F.24: Thomas kinetic model for adsorption of phenol using RHAC at different influent concentration



Figure F. 25: Wolborska kinetic model for adsorption of phenol using CCAC at different flow rates



Figure F.26: Wolborska kinetic model for adsorption of phenol using CCAC at different influent concentrations

0.5





Figure F.27: Wolborska kinetic model for adsorption of phenol using CCAC at different bed heights



Figure F.28: Wolborska kinetic model for adsorption of phenol using CCAC at different particle sizes





Figure F.31: Wolborska kinetic model for adsorption of phenol using RHAC at different bed heights



Figure F.32: Wolborska kinetic model for adsorption of phenol using RHAC at different particle size





Figure F.33: Clark kinetic model for adsorption of phenol using CCAC at different flow rates



Figure F.35: Clark kinetic model for adsorption of phenol using CCAC at different bed height

Figure F.34: Clark kinetic model for adsorption of phenol using CCAC at different influent concentrations



Figure F.36: Clark kinetic model for adsorption of phenol using CCAC at different particle sizes





Figure F.37: Clark kinetic model for adsorption of phenol using RHAC at different flow rate

Figure F.38: Clark kinetic model for adsorption of phenol using RHAC at different influent concentration

y = -0.443x + 6.455





Figure F.39: Clark kinetic model for adsorption of phenol using RHAC at different bed heights

Figure F.40: Clark kinetic model for adsorption of phenol using RHAC at different particle sizes



Figure F.41: Yan kinetic model for adsorption of phenol using CCAC at different bed heights



Figure F.42: Yan kinetic model for adsorption of phenol using CCAC at different influent concentrations



Figure F.43: Yan kinetic model for adsorption of phenol using CCAC at different bed heights



Figure F.44: Yan kinetic model for adsorption of phenol using CCAC at different particle sizes



Figure F.45: Yan kinetic model for adsorption of phenol using RHAC at different flow rates



Figure F.46: Yan kinetic model for adsorption of phenol using RHAC at different influent concentrations



Figure F.47: Yan kinetic model for adsorption of phenol using RHAC at different bed heights





Figure F.49: Modified dose-response kinetic model for adsorption of phenol using CCAC at different flow rates



Figure F.50: Modified dose-response kinetic model for adsorption of phenol using CCAC at different influent concentrations



Figure F.51: Modified dose-response kinetic model for adsorption of phenol using CCAC at different bed heights



Figure F.52: Modified dose-response kinetic model for adsorption of phenol using CCAC at different particle sizes



Figure F.53: Modified dose-response kinetic model for adsorption of phenol using CCAC at different flow rates



Figure F.54: Modified dose-response kinetic model for adsorption of phenol using CCAC at different influent concentrations



Figure F.55: Modified dose-response kinetic model for adsorption of phenol using RHAC at different bed heights



Figure F.56: Modified dose-response kinetic model for adsorption of phenol using RHAC at different particle sizes