THE ADSORPTION OF 4-CHLOROPHENOL AND HYDROQUINONE FROM AQUEOUS SOLUTION ONTO ACTIVATED SHELLS OF OIL BEAN SEED.

BY

EZEIHEUKWU, CHIKA MARY (BSc. Pure and Ind. Chemistry, 2012)

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A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI,

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (M.Sc.) IN ANALYTICAL CHEMISTRY

APRIL, 2024

CERTIFICATION

This is to certify that this work "**The Adsorption of 4-Chlorophenol and Hydroquinone From Aqueous Solution Onto Activated Shells Of Oil Bean Seed.**" was carried out by **EZEIHEUKWU CHIKA MARY** (with Registration no. **20134870988**) in partial fulfillment of the requirements for the award of the Degree of Master of Science (MSc.) in Analytical Chemistry in the Department of Chemistry, Federal University of Technology, Owerri, Imo State.

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DEDICATION

I dedicate this project work to the Almighty God for granting me the grace and the undying perseverance through the obstacles and setbacks I met in this course of study. May His name be praised forever! Amen.

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I am highly indebted to God Almighty for life, good health, traveling mercies, favour, wisdom, strength, finance and general provision which He out of his abundant mercy, granted unto me in the course of this study. I am bewildered by his infinite magnanimity. May His name be praised and honour forever and ever in Jesus name. Amen.

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May God keep and bless them all in Jesus name. Amen!

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ABSTRACT

Oil bean seed shell (OBSS) activated carbon was investigated for adsorption of 4-Chlorophenol and Hydroquinone in aqueous solution. The effects of pH, contact time, initial concentration and temperature were evaluated. Adsorption increased as the contact time increased with the optimum Adsorption at 50 minutes (for $ZnCl_2$ activated carbon) and 40 minutes (for H_3PO_4 activated carbon) for 4-Chlorophenol and Hydroquinone respectively. The influence of pH on 4-Chlorophenol and Hydroquinone uptake by OBSS activated carbons were carried out between pH 4 and pH 10. The level of uptake of 4-Chlorophenol and Hydroquinone by OBSS activated carbon increased at lower pH values studied. The effect of temperature on the uptake of 4-chlorophenol and Hydroquinone were carried out between 29 °C and 60 °C. The result indicated that adsorption increased at low temperature. The adsorption capacity and adsorption intensity for 4-Chlorophenol were calculated to be 0.75 and 1.0 (for $ZnCl_2$ activated carbon), 0.82 and 0.96 (for H_3PO_4 activated oil bean seed shells) respectively and 0.878 and 1.12 (for $ZnCl_2$ activated oil bean seed shells) and 0.827 and 0.90 (for H_3PO_4 activated oil bean seed shells). The thermodynamic parameters ΔG^o, was calculated to be from -135.70 to -3426.3 $jmol^{-1}$ k^{-1} (for $ZnCl_2$ activated carbon shells of oil bean seed, -26.6 to -3073.4 $jmol^{-1}$ $k^{-1}$for H_3PO_4 activated carbon of oil bean seed shells for 4-chlorophenol removal, from -360.0 to 4156.5 $jmol^{-1}$ k^{-1} (for $ZnCl_2$ activated carbon shells of oil bean seed) and from -276.8 to -3526.8 $jmol^{-1}$ k^{-1} (for H_3PO_4 activated carbon shells of oil bean seed) for hydroquinone removal. The enthalpy change (ΔH) were calculated to be -3733.7 and -3379.3 for $ZnCl_2$ activated carbon shells of oil bean seed respectively for 4-chlorophenol, and -4700 and -3654 for $ZnCl_2$and H_3PO_4 activated carbon shells of oil bean seed for hydroquinone removal respectively. The negative ΔG^o values of 4-chlorphenol and Hydroquinone at various temperatures were due to adsorption process being spontaneous with respect to 4-chlorophenol and hydroquinone adsorption onto OBSS.

Keywords: Absorption 4-Chlorophenol, Concentration Hydroquinone Activated Carbon.

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF STUDY

Phenolic compounds in wastewaters are hazardous pollutants which appear in almost all chemical and petrochemical effluents from industries. These compounds are mostly by-products of industrial processes including pharmaceutical, pesticide, paint and solvent production, and wood, paper and pulp processing. Additionally, as a result of the widespread agricultural use of these compounds as herbicides, insecticides, and fungicides.

4-Chlorophenol and Hydroquinone have also been detected in many sources of waste water and drinking water (Anku and Govender, 2017). When these chemicals, enter water water bodies, they have tendency of transforming into other moieties that can be more harmful than the original compounds. This transformation is normally due to their interaction with physical, chemical, biological or microbial factors in the water (Kulkarni S. and Kaware D., 2013). Polychlorophenols are easily absorbed when injested.

1.2 ADSORPTION

Adsorption is a phenomenon that occurs on the surface of substances when a gas or liquid solute accumulates on it forming a molecular or atomic film. It is a separation process in which molecules tend to concentrate on the surface of an adsorbent as a result of Vander Waal forces which exist between the molecules (Ujile A., 2014). It arises due to the presence of unbalanced forces at the surface of liquids or solid phase. These residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface. Adsorption is a term which is quite different from absorption. While absorption means uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. But, when adsorption and absorption processes take place simultaneously, the process is called sorption. Adsorption process involves two components:

a) Adsorbent; the surface onto which the adsorption takes place.
b) Adsorbate; the substance which is adsorbed on the surface of the adsorbent.

Adsorption = Adsorbate + Adsorbent

Adsorption is an exothermic process. Heat energy is usually released due to the force of attraction which exists between the adsorbate and adsorbent. If the adsorbent and adsorbate are contacted long enough, an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by adsorption isotherms.

Adsorption can be understood by considering a simple example. In case of liquid state, water molecules present on the surface is attracted inwards by the molecules of water present in the bulk. This gives rise to surface tension. While, the molecules of water present within the bulk is equally attracted from all the side and the net force experienced by the water molecules in the bulk is insignificant. This clearly shows that particles on the bulk are in different environment. Water molecules on the surface experience unbalanced forces as compared to molecules inside which experiences forces from all direction.

Adsorption has been described as an effective separation process for treating domestic and industrial effluents. It is widely used as effective physical method of separation in order to eliminate or reduce the concentration of a wide range of dissolved pollutants (organics or inorganics) in the effluent (Ansari and

Mohammad-Khan, 2009). It has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants, and does not involve the formation of harmful substances (Wang and Li, 2007).

1.2.1 Types of Adsorption

Depending on the nature of attractive forces existing between the adsorbent and adsorbate, adsorption can be classified into: physical adsorption and chemical adsorption.

a. Physical Adsorption

Physical adsorption is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. It is also known as physisorption. This comes into play when there is weak Vander Waal forces between the adsorbent and adsorbate.

b. Chemical adsorption

Chemical adsorption: This is a type of adsorption in which there is a strong attraction between the adsorbate and adsorbent. Chemical adsorption is accompanied by release of energy because the adsorbates lose their translational freedom when they get to the surface of the adsorbent.

1.2.2 Factors Affecting Adsorption

The adsorption capacity of activated carbon depends on various factors such as: temperature, surface area of adsorbent, activation of the solid adsorbent, solubility of adsorbates, pH of solution and nature of adsorbent.

a. Effect of Temperature

If the assumption of instantaneous equilibrium is not valid, then for physical adsorption, temperature increase will reduce adsorption due to increased solubility of adsorbate. The adsorption reaction is written below:

$A + X \longrightarrow A.X \qquad \Delta H = \text{negative}$

X = active site, A = reactant.

Since, adsorption (forward reactionary) is exothermic i.e. followed by heat liberation the Le Chatelier's principle states that an increase in temperature will favour the backward reaction (desorption). Hence in this case increase in temperature reduces the rate of adsorption.

b. Effect of surface area of the adsorbent

The rate of adsorption increases with increase in surface area of the adsorbents. The extent of adsorption is directly proportional to the specific area. Specific area can be defined as that portion of the total surface area that is available for adsorption.

c. Activation of the solid adsorbent

This involves increasing the adsorbing power of an adsorbent. This is usually done by increasing the surface area of the adsorbent which can be achieved by any of the following;

i. By making the surface rough: either by mechanical rubbing, chemical action or by depositing finely dispersed metals on the surface of the adsorbent by electroplating.
ii. By finely dividing the adsorbent into smaller pieces or grains.
iii. By the removal of adsorbates already adsorbed.

d. Solubility of Adsorbate

The rate of adsorption of solutes is inversely proportional to its solubility in the solvent. The greater the solubility, the stronger the solute-solvent bond and therefore the smaller the extent of the rate of adsorption. This theorem is referred to as the Landeliu’s rule.

e. pH of the solution

The higher the pH of a solution, the more the hydroxyl ion becomes present in the solution, while more of the hydrogen ion become present as the solution pH decreases. For a neutral specie, adsorption decreases with corresponding decrease in pH and vice versa. For a positively charged ion, the adsorption reduces as the pH is decreased due to the repulsive force between the adsorbed H^+ and the adsorbing specie, but gets higher as the pH increases due to electrostatic attraction between the adsorbed OH^- and the adsorbing specie. For a negatively charged specie, the adsorption increases as pH is reduced due to electrostatic attraction between H^+ and the adsorbing specie but decreases as the pH increases.

f. Nature of Adsorbent:

The physical and chemical nature of the adsorbent can have profound effects on both the rate and also the capacity for adsorption. Each type of activated carbon definitely has some unique properties. Also other adsorbents like zeolite, silica gel etc. also have properties in relation to adsorption rates. For instance, the temperature sensitivity of various adsorbent are not usually the same, carbon rapidly loses working capacity above 120^oF when compared to zeolite, which can withstand a higher temperature.

1.2.3 Adsorption Equilibrium

Work carried out earlier on the nature of adsorbents sought to explain the equilibrium capacity and the molecular forces involved. Adsorption equilibrium is a dynamic proces achieved when the rate at which molecules adsorb on to a surface is equal to the rate at which they desorb (Coulsine and Richardson, 2002).

Adsorption isotherm

An adsorption isotherm is a curve which relatesthe relationship between the equilibrium concentration of a solute on the surface of an adsorbent, q_e, to the concentration of the solute in the liquid, c_e, with which it is in contact. It is also an equation relating the amount of solute adsorbed onto the solid and equilibrium concentration of the solute in solution at a given temperature.

$q_e = K_f C_e^{1/n}$

Where,

q_e = amount of solute adsorbed per unit weight of solid at equilibrium. Unit is either g/g or mg/g.

K_f = adsorption capacity

c_e = equilibrium concentration of solute remaining in solution when amount adsorbed equals q_e.

q_e/c_e relationships depend on the type of adsorption that occurs, multi-layer, chemical, physical adsorption, etc. It is assumed that the rate of adsorption or condensation of a gas on to the sites is proportional to the product of the number of unoccupied sites and the gas pressure.

1.3.1 Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm relates the amount of adsorbate adsorbed per unit mass of the adsorbent q_e to the concentration of the adsorbate in solution at equilibrium. The empirical Freundlich adsorption isotherm is used to describe multi-side adsorption isotherm for heterogeneous surface and expressed by the following equation: $q_e= K_fC_e^{1/n}$ the equation can be linearized by taking logarithms to find the parameters K_f and n, (Ozer and Dursun, 2007).

$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log Ce}$

Where;

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

C_e = The equilibrium concentration of the adsorbate.

K_f is the adsorption capacity of the adsorbent and n is Freundlich constant that gives an indication of how favourable the adsorption process is. These constants, K_f and n are determined from the linear plot of log q_e against log C_e .

1.3.2. Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm describes the quantitative build up of the layer of molecules on an adsorbent surface as a function of the concentration of the adsorbed material in the liquid in which it is in contact. Ozer and Dursun (2007), stated that Langmuir adsorption isotherm is most widely used model for the adsorption process and based on monolayer coverage of adsorbate on the surface of the adsorbents. According to Langmuir theory, adsorption occurs at a specific homogeneous site within the adsorbent, each site is occupied only by adsorbate molecule, all sites are equivalent and there are no interactions between adsorbate molecules. The non-linear form of Langmuir isotherm model is presented by:

$q_e = q_e K\, C_e/1+KC_e$

q_e is the amount of 4-chlorophenol or hydroquinone at saturation, K.

The linear form of Langmuir is given by the following equation:

$C_e/q_e = 1/q_e K + C_e/q_e$

When C_e/q_e is plotted against C_e, straight line with slope $1/q_o$ which indicates that the adsorption follows the model is obtained. Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of the adsorbent surface. The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless separation parameter RL, which indicates the isotherm shape that predicts whether an adsorption system is favorable or not. RL is defined as:

$RL = 1(1 + bC_o)$

Where, b is Langmuir isotherm constant,

C_o is the initial concentration of the adsorbate (mg/l).

The value of RL indicates the type of the isotherm to be either unfavorable ($RL > 1$), linear ($RL = 1$), favorable ($0 < RL < 1$) or irreversible ($RL = 0$) (Nwabanne and Igbokwe, 2008).

1.4 PHENOLIC COMPOUNDS

Phenolic compounds are a class of organic compounds with a hydroxyl group(s) directly bonded to one or more aromatic rings. The first member of chemicals belonging to this category of organic compounds is called phenol, also known as carbolic acid, benzophenol or hydroxybenzene with the chemical formula of C_6H_5OH. All other members of the group are derivatives of phenol (Muna G.W, Quaiserova-Mocko V, and Swain G.M. 2005).

Phenolic compounds exist in water bodies due to the discharge of polluted wastewater from industrial, agricultural and domestic activities into water bodies. They also occur as a result of natural phenomena. These compounds are known to be toxic and inflict both severe and long-lasting effects on both humans and animals. They act as carcinogens and cause damage to the red blood cells and the liver, even at low concentrations. Interaction of these compounds with microorganisms, inorganic and other organic compounds in water can produce substituted compounds or other moieties, which may be as toxic as the original phenolic compounds.

1.4.2. 4-Chlorophenols

4-Chlorophenols are synthetic organic compounds, obtained on large, industrial and commercial scales by chlorinating phenols, or hydrolyzing chlorobenzene. It consists of benzene ring, -OH and chlorine atoms. It is used or formed as a result of the activity of some industries mainly chemical, textile, pharmaceutical and metallurgical.

1.4.3. Hydroquinone

Hydroquinone is a well-known benzene metabolite, which is a well-known haematotoxic and carcinogenic solution associated with malignancy in occupational environments.

Exposure to hydroquinone can be through dietary, occupational and environmental means.

Chemical formular; $C_6H_6O_2$

1.5. DESCRIPTION OF OIL BEAN PLANT *(Pentaclethramacrophylla benth)*

African oil bean, also known as ‘ugba’or ‘ukpaka’ scientifically called *Pentaclethramacrophylla benth* is a multipurpose tree from Africa. It is the sole member of the genus occurring naturally in the humid lowlands of West Africa. It is a leguminous plant that belongs to the family of leguminosae; sub-family of mimosoideae and is recognized by peasant farmers in the South East of Nigeria for its soil improvement properties. It has been cultivated in Nigeria since 1937. The tree is usually about 21m in height and 6 m in girth. The bark is greyish to reddish brown. The compound leaves has a short angular petiole. The flowering season is around March and April with smaller flushes in June and November is a native plant in the tropical regions in Africa. It is usually grown in farm lands and forest areas. Its branches spread like a canopy. The oil bean tree is normally found in rainforests, Southern West Africa where it grows wildly. Oil bean trees are usually planted at roadsides as shadews and by few farmers as cash crops. When mature its pod splits explosively to release about eight flat, glossy brown seeds measuring about 5-7 cm in diameter and weighing between 15-20g

The numbers of the seeds depend on the length and size of the pod. The raw seed is a potential source of edible protein, energy and fatty acids (Enujiugha and Agbede, 2000). The oil bean seed is a family food. It has received most attention as fortifiers or ingredients for cheap nutritious and high nutrient quality formulated foods. Oil bean seed is among the oil seeds that store energy in form of oil. The quality of oil seed protein is not as high as that of animal (Enujiugha, 2003). However, it is highly proteinous than that of cereals.

1.6 PROBLEM STATEMENT

The contamination of most waters by toxic chemicals through the discharge of industrial effluents is becoming a serious environmental problem in Nigeria. The presence of these toxic solvents in these waters has been responsible for several health problems with plants, animals and human beings. Some of these toxic solvents are 4-Chlorophenol and Hydroquinone. The problems encountered in the industry is how to remove these toxic solvents from aqueous solutions using cheap materials, since the imported materials are very expensive. This research work is designed to use effective and cheap adsorbent to remove toxic solvents such as 4-Chlorophenol and Hydroquinone. The activated oil bean seed shells was used as cheap and effective adsorbent for the removal of 4-Chlorophenol and Hydroquinone from aqueous solution.

1.7. OBJECTIVES OF THE RESEARCH

The aim of this research is to produce activated carbon from the local agricultural waste which is *Pentaclethramacrophylla benth* (African oil bean) shells impregnated with two activating agents for a particular application. To achieve these, a study was carried out with the following objectives:

- To study the effect of contact time (10, 20, 30, 40, 50, 60, 70 and 80 mins) on adsorption of 4-Chlorophenol and hydroquinone onto activated carbon produced from African oil bean seed shells.
- To study the effect of temperature (30 ^{0}C, 35 ^{0}C, 40 ^{0}C, 45 ^{0}C, 50^{0}C, 55^{0}C and 60^{0}C) on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells.
- To study the effect of pH (4, 6, 9.2 and 10) on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells.
- To study the effect of concentration (5 mg/l, 10 mg/l, 15 mg/l, 20 mg/l, 25 mg/l, 30 mg/l, 35 mg/l, 40 mg/l, 45 mg/l and 50 mg/l) on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells.
- To evaluate the potential application of locally produced activated carbon in the removal of organic pollutants such as 4-chlorophenol and hydroquinone from aqueous solution.

1.8 JUSTIFICATION OF THE STUDY

Phenolic compounds in wastewaters are hazardous pollutants which appear in almost all chemical and petrochemical effluents from industries. Phenolic compounds are very harmful even at very low concentrations due to their toxic and carcinogenic properties. They cause damage to the eyes and the tissues under the skin. Inhalation, or ingestion, can damage the respiratory and gastrointestinal tracts, and can lead to genetic damage (Damjanović L, Rakić C.,Rac V., Stošić D. and Auroux A., 2010). It is an indispensable requirement to treat the phenol from industrial effluents before discharging into the environment specifically water stream.

1.9. SCOPE OF THE RESEARCH

This study will cover the production of two different activated carbon using oil bean seed shell as the precursor and, zinc chloride and phosphoric acid as the activating agents respectively. The activated carbon produced will be used for the removal of 4-Chlorophenol and Hydroquinone at pH 4, pH 6, pH 9.2 and pH 10. Optimum adsorption of 4-Chlorophenol and Hydroquinone will be determined. The effect of temperature on the adsorption mechanism of 4-chlorophenol and hydroquinone adsorption onto oil bean seed shell activated carbon will be determined, and the rate mechanism will be determined. The kinetics of adsorption of 4- Chlorophenol and hydroquinone will be established. The adsorption capacity and adsorption intensity for 4-Chlorphenol and hydroquinone will be calculated using Freundlich isotherm. The thermodynamic parameters ΔG^o, ΔH^o and ΔS^o will be calculated at various adsorption of 4-Chlorophenol and hydroquinone onto the activated carbon.

CHAPTER TWO

2.0 LITERATURE REVIEW

There are two basic manufacturing processes for activated carbons which include physical (thermal) and chemical activation methods (Giraldo and Moreno-Pirajan, 2008).

Ajayi and Olewale (2009), working on the thermal and chemical activation of Carnarium Schweinfurt nutshell reported that chemical method of activation using KOH leads to higher porosity formation, and higher adsorptive capacity at relatively higher temperature than thermal formation of the tars, as well as lesser gasification.

Khadija A, Mabroka D, Al-Tohami F., Mohamed E, and Mohamed Z, (2015) investigating the effect of physical and chemical preparation with the characterization of activated carbon from Agricultural solid waste, and their potential applications reported that the carbon yield of the activated carbon from chemical process was higher than those from physical process, due to its highly porous structure, enabling a higher adsorption capacity.

Abugu H.O., Okoye P.A.C, Ajiwe V.I.E, Omuku P.E and Umeobika U.C., (2015) investigated the adsorptive capacity of H_3PO_4, H_2SO_4 and HCl activated shells of oil bean seed and snail for the adsorption of Ni and Cd and observed that those activated with H_3PO_4 were better adsorbents irrespective of the heavy metal, followed by those activated with HCl, while those activated with H_2SO_4 were the least. The experimental adsorption data fitted well on the Freundlich isotherm model much better than the Langmuir isotherm model indicating heterogenous surface energies which gives an exponential distribution.

Giovanny N., Silva R., Juan C. Morenopirajan J.C., and Giraldo L. (2015) studied the adsorption of phenol, 4-chlorophenol, and 4-nitrophenol using activated carbon obtained from eucalyptus seed husk. They characterized the activated carbon in physical and chemical properties. They also studied the adsorption of these adsorbates, and observed that the adsorption of phenolic compounds was produced in greater quantity on NaOH activated carbon samples, and not on solids with more surface area. The adsorption capacities (at 20 ^oC), on the activated carbon were 2.12, 2.57, and 3.89mmolg^{-1} respectively. They also reported that the adsorption of phenolic compounds decreases with increasing temperature, so it checks the exothermic nature of the adsorption process.

Okey-Onyesolu, C.F, Okoye. C.C, and Chime, D.C. (2018) studied the removal of eosin yellow dye from aqueous solution using oil bean seed shells based activated carbon (H_2SO_4 and KCl activated carbons), and reported that the percentage adsorption of eosin yellow dye onto the produced oil bean seed acid activated carbon had the highest value than the carbon produced from salt activation. This was as a result of higher availability of microscopic pores and area created by the strong acid, which enhanced adsorption rate process. From the experimental results, it was discovered that the percentage of eosin yellow dye adsorbed varies with initial solution pH, the initial concentration of the adsorbate, temperature and particle size, contact time and adsorbent dosage onto the activated carbons. The adsorption equilibrium data was studied but found to fit the Langmuir isotherm ($R^2 > 0.90$) at 30 ^oC. The pseudo-second order kinetic model was found to be more favorable ($R^2>0.90$) at 30 ^oC. The thermodynamic study gave a negative value of change in ΔH^o at 30 ^oC, which indicated that the reaction process was exothermic. The negative values of the change in entropy confirmed the decreased randomness at the solid-liquid interphase during adsorption.

Sivaraj R., Rajedran V., and Gunalan S., (2010) working on the preparation and characterization of activated carbons from *parthenium* biomass by physical and chemical activation techniques reported that among the carbons prepared (H_2SO_4

, HCl, HNO_3, $ZnCl_2$ and H_3PO_4 activation), $ZnCl_2$ impregnated carbon was found to possess the characteristic features of an efficient adsorbent.

Batch experiments for phenol adsorption were performed using microporous activated carbons obtained from both kenaf and rapeseed precursors, (Nabais, J.M.V., Gomes, J.A., Suhas Carrott, P.J.M., Laginhas, C., Roman, S., 2009). In particular, the phenol adsorption capacities of both adsorbents were higher than 70 mg/g.

In other study, .Alam M.Z, Mamun A.A, Isam Y., Qudsieh and Muyibi M., (2009) studied the effect of different synthetic conditions of activated carbon obtained from oil palm empty fruit bunches on phenol removal. These parameters include temperature, activation time and CO_2 flow rate. In general, these carbons showed phenol adsorption capacities from 1.03 to 4.83 mg/g.

Recently, Bello-huitle V. Atenco-Fernandez and Mazzoco .R., (2010) studied the removal of phenol using activated carbons obtained by chemical activation and pyrolysis of pecan and castile nutshells. These authors synthesized different samples of activated carbons using these crops and adsorption isotherms were performed at 20 °C and pH 7. This study indicated that the activated carbon from pecan nutshells showed better phenol uptakes.

On the other hand, Timur, S., Kantarli, I. C., Onenc, S., and Yanik, J. (2010). reported that activated carbons obtained from oak cups pulp using $ZnCl_2$ have higher phenol adsorption capacities than those obtained for activated carbons produced with H_3PO_4. They suggested that this best performance was related to the lower amount of acidic surface groups on activated carbon.

Aningo J.N, Chime T.O and Nevo C.O (2017) investigated the use of activated carbon produced from oil bean seed shell to remove Cd (II) from aqueous solution under batch mode. The FTIR and SEM analyses were also carried out. The effect of time, pH, and adsorbent dosage were investigated. The isotherm followed both Langmuir and Freundlich models satisfactorily.

Nuhu .D.,Nabeel J., MukarrahZ., and Omar A. (2017) investigated the removal of phenolic compounds such as 4-Chlorophenol, phenol, 2-Chlorophenol, 2,4-dichlorophenol, 4-nitrophenol and P-chlorophenol from water. They concluded that the chemically activated carbons produced better textural properties and superior phenolic compound adsorptive performance compared to physical activation. The isotherm models carried out fits into the freudlich and Langmuir models.

Bassim H.H, Chin L.H., Rengaraj S. (2008) investigated the adsorption of 4-Chlorophenol onto activated carbon prepared from rattan sawdust. Different experimental parameters such as initial pH, contact time and initial concentration on the adsorption 4-Chlorophenol were evaluated.

Allaboun H., Fahmi A, and Al-Rub A. (2016) used phosphoric acid and air activated carbon from dried date pits for the removal of 4-Chlorophenol from contaminated water. He observed that 4-Chlorophenol adsorption was pH and contact time dependent, and its isotherm fitted well with the Langmuir model.

Timurah K., Hussein M., Zainal Z. and Rusli R. (2015) used pit soil to prepare activated carbon using H_3PO_4 and $ZnCl_2$ activation at 500°C for 3hr. They characterized these activated carbons and observed that the activated carbon produced using H_3PO_4 posseses more crystalline structure than the activated carbon prepared using $ZnCl_2$ activation.

Das D., Samal D.P.S., and Meikap B.C. (2015), working on the preparation and characterization of activated carbon produced from green coconut shell reported that the adsorption capacity of coconut shell increased with increase in adsorbent dosage, and the percentage removal of methylene blue increased with time.

Bassim H., Chin L. and Rengaraj S. (2008) working on the adsorption of 4-Chlorophenol onto activated carbon prepared from rattan saw dust, investigated the effects of different parameters such as initial pH, contact time and initial concentrations. The rates of the adsorption were found to obey the rules of the pseudo second order model with good correlation.

Haimour N. and Emeish. S. (2006) used date stones for the production of H_3PO_4 and $ZnCl_2$ activated carbons by chemical activation and compared both the temperature, impregnation and particle size on the yield, and adsorptive capacity were carried out. The maximum number of the iodine number at the activated carbon produced using H_3PO_4 was more compared to that of $ZnCl_2$ activated. The yield obtained when H_3PO_4 was used was also smaller than when $ZnCl_2$ was used.

Allwar A., Halima Z., Febriyantri and Risky Y. (2018) preparing activated carbon from banana empty fruit using $ZnCl_2$ hydrothermal activation at 200^oC. The activated carbon was characterized and used for the removal of phenol in solution. The effects of pH, contact time, concentration and adsorbent dosage were carried out. The equilibrium adsorption was also calculated by the langmuir and freudlich isothermal models. The freudlich isothermal showed a good fit with a correlation coefficient R2 value of 0.9958 which was a more favorable adsorption than those in a Langmuir adsorption.

Okwunodulu F. and Mgbemena N., (2015), utilized the unmodified and mercaptoacetic acid modified oil bean seed shells in the uptake of Cd^{2+}, Ni^2+ and Pb^{2+} from their aqueous solutions. They studied the adsorption in batch process at various contact time with initial metal ions concentration of 100 mg/L using 1g of 25 ^oC and pH of 7.5. The kinetic study showed that the adsorption of some of the heavy metal ions by the oil bean seed shells fitted the Elovich adsorption model excellently except in the adsorption of Cd^{2+} by the unmodified shell that showed lower R^2 value.

Muthanna and Samar (2013), studied the adsorption of P-chlorophenol using *Albizia Lebbeck* seed pods. They produced microporous activated carbon from this precursor using one-step microwave assisted K_2CO_3 activation. The effects of the radiation time, radiation power, and impregnation ratio on sorption performance were studied to determine the best preparation conditions. The experimental kinetic data were well represented by the pseudo-second order model.

Namane A. and Hella J. (2005) evaluated the adsorptive capacities of granular activated carbon produced from coffee grounds by chemical activation (using H_3PO_4 $ZnCl_2$ activation). The adsorption of different phenols, acid and basic dyes onto produced and commercial granular activated carbon were experimentally determined by batch tests. Both Freundlich and Langmuir models are well suited to fit the adsorption isotherm data.

Xiaoli, Chai and Zhao V., (2006), working on the adsorption of phenolic compounds by aged-refuse, determined the adsorption isotherms of phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, and the data fitted well with the freundlich equation. The chlorinated phenols were adsorbed more than the phenol. The adsorption capacities have an oblivious relationship with the number and the position of chlorine substituents. The result obtained also showed that it fits into the pseudo-second order model.

Castro C. Abreu A, Silva C. and GuerreiroM. (2011) produced activated carbons using spent coffee grounds, an agricultural residue, as carbon precursor, and two different activating agents; water vapor and K_2CO_3. These activated carbons presented microporous nature and high surface area. The carbons as well as commercial activated carbon used as reference, were evaluated as phenol adsorbent showing high adsorption capacity. The activated carbon produced from spent coffee showed good adsorption property for phenol.

Girish and Ramachandramurty V., (2013) studying the removal of phenol from waste water using different agricultural wastes like rice-mill residue, wheat-meal-residue, Dall-mill residue and banana-mill residue, reported that the possibility of employing dall-mill residue waste as an adsorbent for removing phenol from waste water. The performance of the activated carbon from the dall-mill residue with commercial available activated carbon were compared. A batch mode experiment was conducted to study the effects of initial concentration of phenol, pH, and temperature of the aqueous solution on adsorption. The equilibrium adsorption isotherms and kinetics, with the Temkin and freundlich models was represented well with monolayer adsorption capacities.

Muhammad (2018) investigated the adsorptive removal of 2,4-dinitrophenol from aqueous solution onto *Cucumissativus* peels and kidney bean shells. He worked on the effects of pH, adsorbent dosage, contact time and initial concentration. Kidney bean shells was found to be more efficient in the adsorption of 2,4-dinitrophenol from aqueous solution in comparison to *cucumissativus* peels. Kinetic studies showed that the rate of the adsorption of 2,4-dinitrophenol was best followed by pseudo second order kinetic model, while the increased adsorption of both adsorbents were obtained by Langmuir equation.

Yusef A, Nourmoradi H., Ali J. and Taheri F. (2015) synthesized activated carbon from Aloe vera green waste. They utilized this activated carbon as sorbent to remove 4-Chlorophenol from aqueous solutions. They studied the influence of contact time, pH, adsorbent dosage, and initial 4-chlorophenol concentration in batch system. The experimental data as well fitted the pseudo-second order kinetic and freundlich isotherm.

Evwerhoma E.T, Madubiko O.D. and Jaiyelo A. (2018) produced activated carbon from bean husk, using four different activating agents; potassium hydroxide (KOH), sulphuric acid (H_2SO_4), orthophosphoric acid (H_3PO_4) and zinc chloride ($ZnCl_2$). They investigated the influence of these activating agent on the surface area of the activated carbon. The one prepared using orthophosphoric acid produced the best activated carbon. The results of the characterizations showed that the results of the apparent density, ash content, moisture content and pH of the activated carbons fall within the recommended by ASTM.

Molina-sabio, and Rodriguez-Reinoso F. (2004) utilized olive and peach stones as precursors for granular activated carbon using phosphoric acid, zinc chloride and potassium hydroxide as activating agents. The three chemicals produced an increased microporosity, while KOH only resulted to the widening of micropore width, $ZnCl_2$ additionally developed little mesoporosity and H_3PO_4 to a more heterogeneous pore size distribution and with $ZnCl_2$ and H_3PO_4 leading to increased micropores of homogeneous breath, and have been selected to produce bindless carbon monolithic disc.

Nuhu D., Nabeel J., Mukarrah Z., and Omar A. (2017) investigated the adsorption of phenolic compounds such as 4-Chlorophenol, phenol, 2-chlorophenol, 2,4-dichlorophenol, using impregnated granular activated carbon (Fe-GAC) developed from sewage sludge, and characterized for various properties. They carried out a comparative study for its use as an adsorbent as well as a catalyst during catalytic oxidation of hydroquinone. Pseudo second order model best-fitted the hydroquinone adsorption kinetics, whereas Langmuir model fitted the isothermal equilibrium behavior.

Hassan Q., Rachid A.A, Douch J, Amane J and Hamdani M.(2015) studied the removal of hydroquinone from water using natural quartz sand. They investigated the physicochemical properties controlling its adsorption from water on natural quartz sand. They studied the influence of some parameters such as ionic strength, pH, the flow rate and the nature of the electrolyte cation. They observed that when the ionic strength of the effluent increased, the adsorbed hydroquinone amount decreased.

Jacob A., Tijani A., Oluwole .O. and Hamisu S., (2015), working on the treatment of waste water by activated carbon produced from *Borassus aethopium*, using H_3PO_4 and $ZnCl_2$ as the activating agents, and by changing the concentration of the solutions, reported that $ZnCl_2$ activated carbon exhibited better adsorption than H_3PO_4 activated carbons.

Okey-Onyesolu C.,Onukwuli O. and Okoye C. (2016), studied the optimization and characterization of the adsorptive behaviour of pentaclethramacrophylla benth activated carbon on aqueous solution for the uptake of lead(II). Parameters such as; the particle size, adsorbent dosage, initial pH of the solution, initial Concentration, temperatures and contact time were investigated. The experimental result suggested the optimal condition as follows; solution temperature; 30 ^{0}C, contact time; 120 mins, adsorbent dosage; 1.50 g, and pH 7. The functional group of the *Pentaclethramacrophylla benth* activated carbon were also investigated using fourier transform infrared spectroscopy.

Iyaomolere (2013), worked on the influence of salt treatment on the pore development of pyrolysed periwinkle shell. The effects of impregnation on the physiochemical characteristics of periwinkle under study Showed that the optimum impregnation of zinc chloride was gotten at IR 1.0.

Arneli, Safitri Z F, Pangestika A, Fauziah F., Wahyuningrum V. N and Astuti Y, (2017), studied the influence of activating agents on the production of rice-based activated carbon with high adsorption capacity and efficiency for either hazardous organic molecules or heavy metals, which are unfriendly for the environment. The precursor was activated with H_3PO_4 and KOH. The results showed that activation of carbon using phosphoric acid (H_3PO_4) was more effective than potassium hydroxide (KOH).

CHAPTER THREE

3.0. MATERIALS AND METHODS

3.1. MATERIALS

Reagents; 0.5M sodium hydroxide solution and Hydroquinone for adjustment of pH.

Activating Agents: Phosphoric acid, zinc chloride.

Adsorbent; Oil bean seed shells.

Adsorbates; 4-Chorophenol and Hydroquinone.

Instruments; Air drying oven, digital weighing balance, Jenway 3510 pH meter, mechanical shaker, thermostated water bath, ultra violet spectrophotometer, muffle furnace.

All chemicals were obtained from chemical stores at Head Bridge Onitsha except the 4-Chlorophenol which was obtained from a reliable chemical store at Port Harcourt.

3.2 SAMPLE COLLECTION

The oil bean seed shells used in this work was bought from oil bean sellers in Eke, Ekwulobia, Aguata Local Government Area, Anambra State and Oye Akokwa, Ideato Local Government Area, Imo State.

3.3. SAMPLE PREPARATION AND ACTIVATION.

The oil bean seed shells was thoroughly washed using clean water, dried, and ground to smaller sized particles. The ground particles was divided into two equal parts 1000 g each and treated with 20 % zinc chloride and 20 % phosphoric acid respectively. This was to activate before carbonizing (chemical activation). The raw materials was drained after 24 hours, dried and carbonized in a muffle furnace at a temperature of 450 ^{o}C for 30 mins to give an activated carbon (Akpan .U., Chubu .J.M. and Olutoye .M.A, (2015).

The activated carbon produced was washed with 0.5 M sodium hydroxide solution, rinsed thoroughly with distilled water, and dried in an oven at a temperature of 110 ^{o}C. It was sieved with a sieve of 250 um mesh size and stored in an air tight container until use.

3.4. SAMPLE ANALYSIS

The samples were analysed biz:

3.4.1 The preparation of calibration curves for 4-Chlorophenol

The wave length of 4^{-}chlorophenol is 280 nm, while its molecular weight is 128.55 g/mol. 0.01 M solution of 4^{-}chlorophenol will be prepared by dissolving 1.28g of 4^{-}chlorophenol in I L of distilled water. Sub-solutions of the following concentrations; 2 mg/l, 4 mg/l, 6 mg/l, 8 mg/l, 10 mg/l, 15 mg/l, 20 mg/l, 25 mg/l, 30 mg/l, and 35mg/l will be prepared and adsorptions will be read using the UV-vis Spectrophotometer.

3.4.2. Preparation of calibration curve for 4-Chlorophenol and Hydroquinone.

The wave length of 4-Chlorophenol is 280 nm, while its molecular weight is 128.55 g/mol. 0.01 M solution of 4-Chlorophenol was prepared by dissolving 1.28g of 4^{-}chlorophenol in I L of distilled water. Sub-solutions of the following concentrations; 2 mg/l, 4 mg/l, 6 mg/l, 8 mg/l, 10 mg/l, 15 mg/l, 20 mg/l, 25 mg/l, 30 mg/l, and 35mg/l were prepared and adsorptions were read using the UV spectrophotometer.

The wavelength of hydroquinone is 302 nm and its molecular weight, 110.11 g/mol 0.01 M solution of 4^{-}chlorophenol was prepared by dissolving 1.10 g of hydroquinone in I L of distilled water. Sub-solutions of the following concentrations; 2 mg/l, 4 mg/l, 6 mg/l, 8 mg/l, 10 mg/l, 15 mg/l, 20 mg/l, 25 mg/l, 30 mg/l, and 35 mg/l were prepared and adsorptions were read using the UV spectrophotometer.

3.4.3 Effect of contact time on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells.

0.3 g of Oil bean seed shell was added into a conical flask containing 30 mg/l of 4-Chlorophenol solution diluted with 50 ml of distilled water in six different conical flasks at pH 6.5 and temperature 30 ^{o}C. The flask containing the sample as suspended in a mechanical shaker and agitated for various time 10, 20, 30, 40, 50, 60, 70 and 80 minutes.

After agitation, the sample was allowed to settle for 30mins, and then filtered through Whatman filter paper No.110. The absorbance of the filtrates was read using UV spectrophotometer. A plot of amount of 4-Chlorophenol adsorbed against contact time for oil bean seed shell samples were obtained. The same method was used for effect of contact time on adsorption of Hydroquinone onto oil bean seed shell (Zhang J., Li Y., Zhang C. and Jing Y., 2008).

3.4.4. Effect of pH on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells

Distilled water was used to prepare a solution of different pH (4, 6, 9.2 and 10) by adjustment using 0.1 M HCl and 0.1 M NaOH. The pH solutions were used to prepare solution of different concentration such as 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L 25 mg/l, 30 mg/l, 40 mg/l, 45 mg/l and 50 mg/L. 0.3 g of oil bean seed shells was added to 50 ml of each solutions of different concentrations and agitated for 40mins (optimum time for H_3PO_4 of activated Carbon) and 50 minutes (for $ZnCl_2$ activated carbon). After agitation, the samples were allowed to settle for about 30mins. It wwas filtered using whatman filter paper NO.110. The absorbance of the filtrates was read using UV spectrophotometer.

A plot of amount of 4-Chlorophenol adsorbed against concentrations of different pH solutions of oil bean seed shell samples was obtained. The same method was used for effect of pH at different concentrations on adsorption of Hydroquinone unto oil bean seed shell concentration on adsorption of hydroquinone onto oil bean seed shells.

3.4.5. Effect of temperature on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shells.

0.3g of oil bean seed shells was added to 50ml of 30 mg/l 4-chlorophenol solution and maintained at pH 6.5. The sample was immersed in a thermostated water bath and agitated for 40 minutes at different temperature 30 ^{o}C, 35 ^{o}C, 40 ^{o}C, 50 ^{o}C, 55 ^{o}C, and 60 ^{o}C. The same was withdrawn and allowed to settle for 30mins and filtered severally until clear solutions were obtained. The absorbance reading of the filtrate was read with UV spectrophotometer (model). The amount of 4^{-}chlorophenol was calculated. A plot of amount of 4-chlorophenol adsorbed at different temperatures was obtained. The same method was used for effect of temperature on the adsorption of Hydroquinone onto oil bean seed shell.

The equilibrium amount of 4-Chlorophenol or Hydroquinone per unit mass of adsorbent, q_e (mg/g), was calculated using equation below;

$$q_e = \frac{(C_o - C_e)v}{W} \quad \ldots\ldots\ldots (1)$$

Where, v (L) is the volume of the solution, and w (g) is the mass of the dry adsorbent.

C_o = initial concentration (mg/l) of 4-Chlorophenol or hydroquinone.

C_e = Concentration (mg/l) of 4-Chlorophenol or hydroquinone at equilibrium.

In order to study the kinetics of the adsorption process, the concentration of each of the 4-Chlorophenol and Hydroquinone solution was determined at intervals of time, and the amount of the two adsorbates adsorbed at time t.

$q_t =$ (mg/g) was also calculated using equation (2).

$$q_t = \frac{(C_o - C_t)v}{W} \quad \ldots\ldots\ldots (2)$$

Where, V (L) is the volume of the solution, and w(g) is the mass of the dry aww qaa.

Where, C_t (mg/l) is the 4-Chlorophenol or Hydroquinone concentration at time t.

CHAPTER FOUR

4.0. RESULTS AND DISCUSSION

4.01. THE CALIBRATION CURVES FOR 4-CHLOROPHENOL AND HYDROQUINONE

The calibration curve for 4-Chlorophenol and hydroquinone are presented in tables 4.1 and 4.2 respectively. Figures 4.0.1 and 4.0.2 are graphs of absorbance of 4-Chlorophenol and Hydroquinone as a function of concentration of 4-Chlorophenol at 280 nm and Hydroquinone at 302 nm respectively. The relation is linear in the range of concentration considered and may therefore, serve as a calibration for 4-Chlorophenol and Hydroquinone, respectively.

Table 4.01: Calibration table for Hydroquinone

Concentration (mg/l)	Absorbance at 302 nm
2	0.038
4	0.05
6	0.076
8	0.103
10	0.15
15	0.225
20	0.284
25	0.293
30	0.297
35	0.368

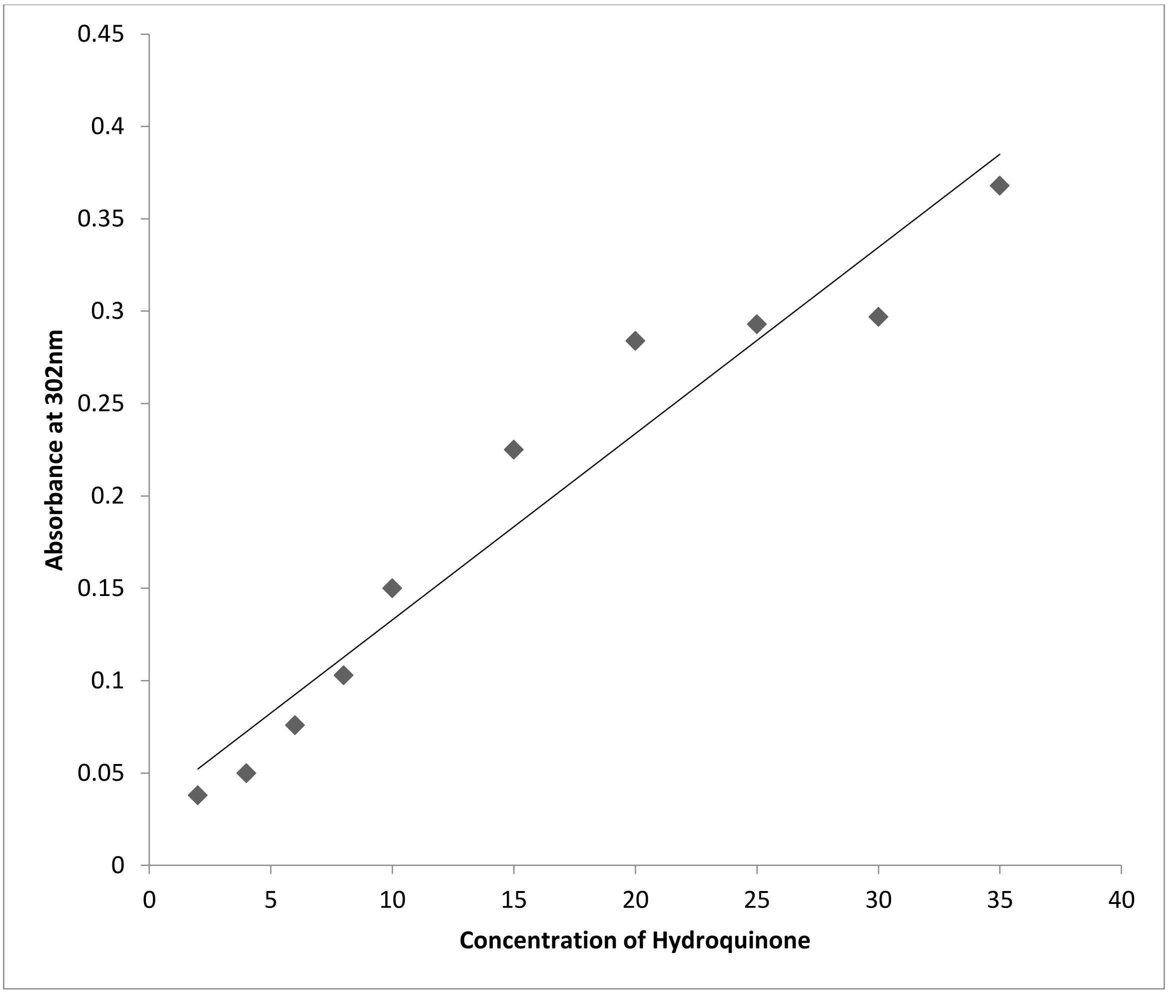


Figure 4.01: Calibration plot for Hydroquinone

Table 4.02: Calibration table for 4-Chlorophenol

Concentration (mg/l)	**Absorbance at 280 nm**
2	0.031
4	0.075
6	0.104
9	0.148
10	0.157
15	0.189
20	0.262
25	0.292
30	0.314
35	0.431

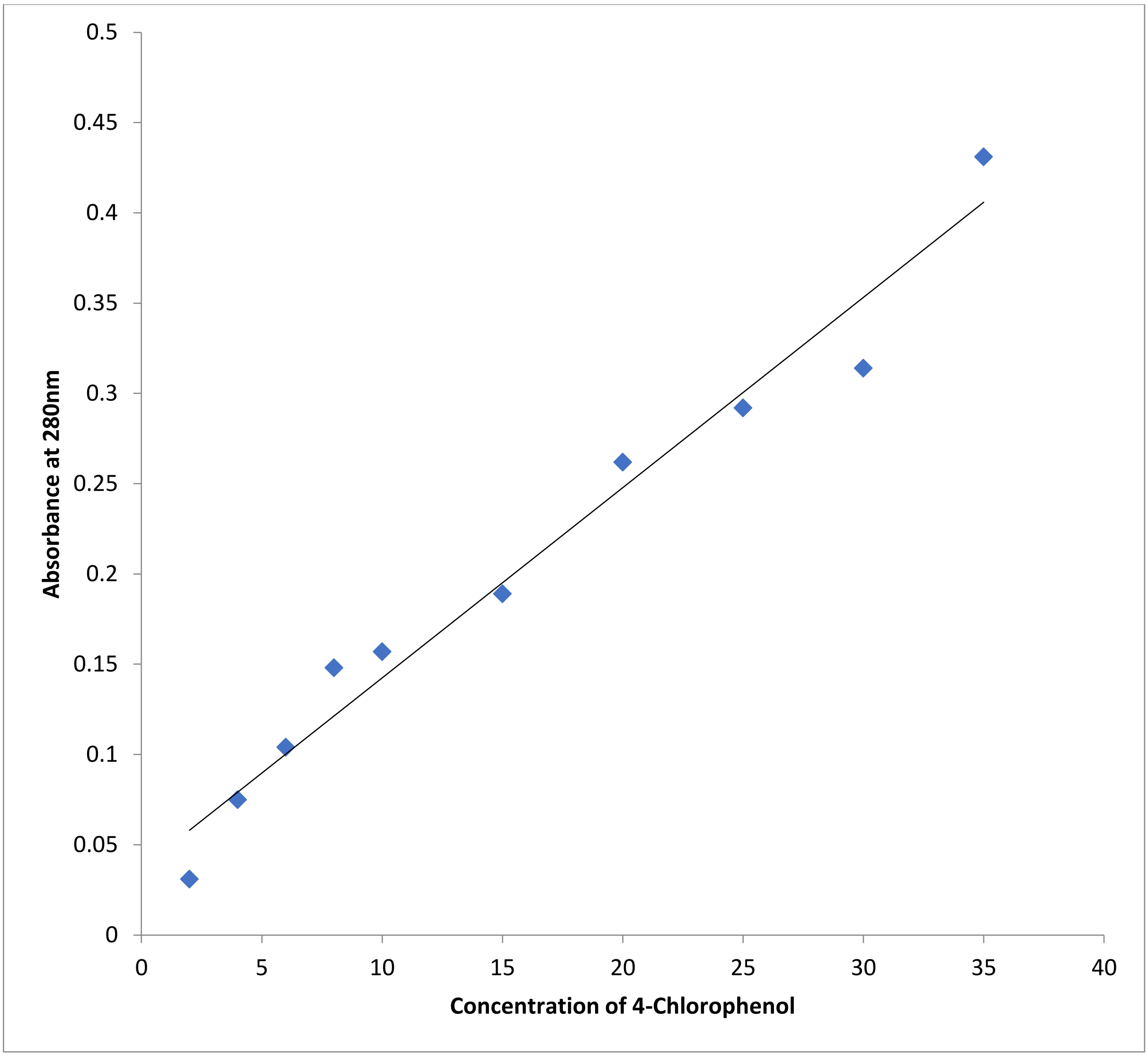
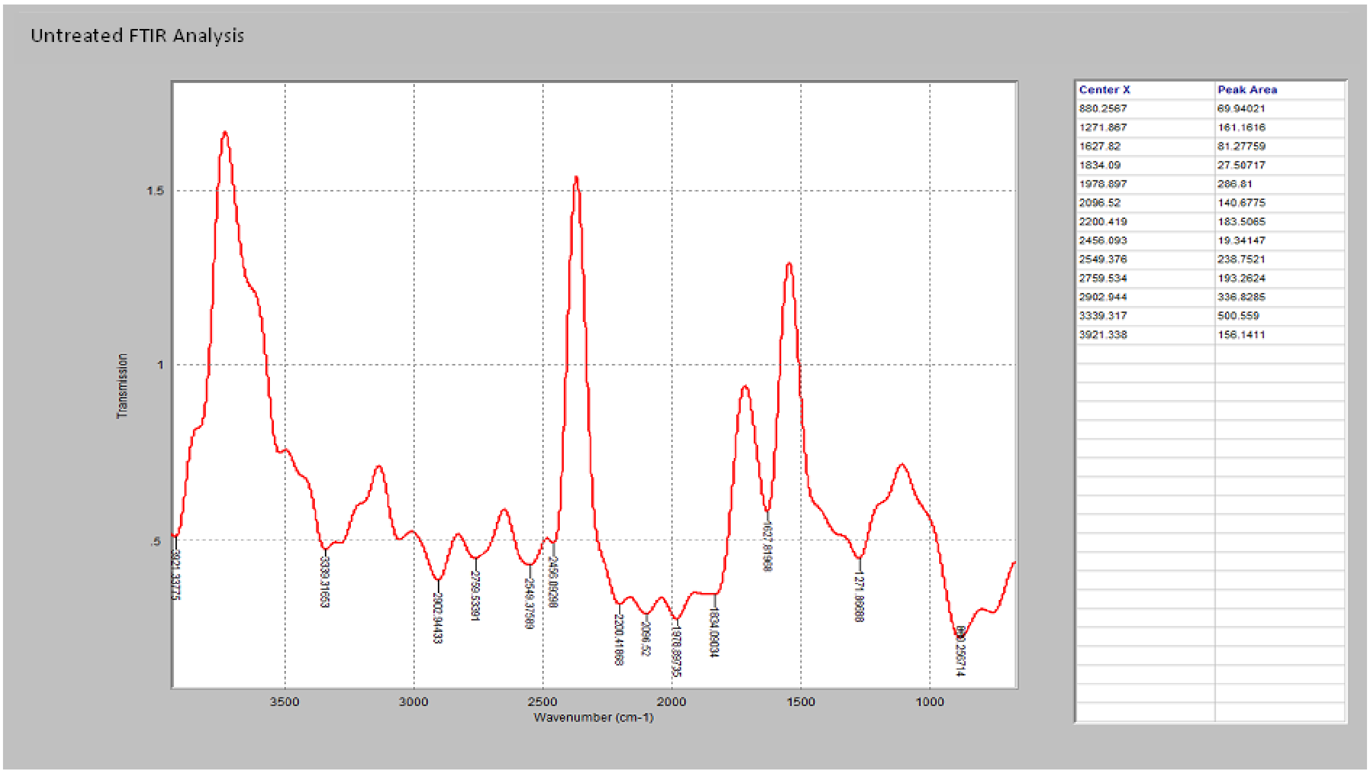


Figure 4.02: The calibration curve of 4-Chlorophenol

4.2. FTIR AND SEM ANALYSIS OF PENTACLETHRAMACROPHYLLA BENTH SEED SHELLS

Figures 4.3 to 4.5 show the spectral of FTIR of unactivated and activated *pentaclethramacrophylla benth* seed shell samples, respectively. The analysis was carried out before the commencement of adsorption process. Figures 4.6 to 4.8 show the SEM image of unactivated and activated *pentaclethramacrophylla* benthseed samples, respectively. The analyses was were also carried out before the commencement of all the adsorption process.



Center X	Peak Area
880.2567	69.94021
1271.867	161.1616
1627.82	81.27759
1834.09	27.50717
1978.897	286.81
2096.52	140.6775
2200.419	183.5065
2456.093	19.34147
2549.376	238.7521
2759.534	193.2624
2902.944	336.8285
3339.317	500.559
3921.338	156.1411

Fig. 4.03: Spectrum of FTIR of unactivated *pentaclethramacrophylla benth* seed shells.

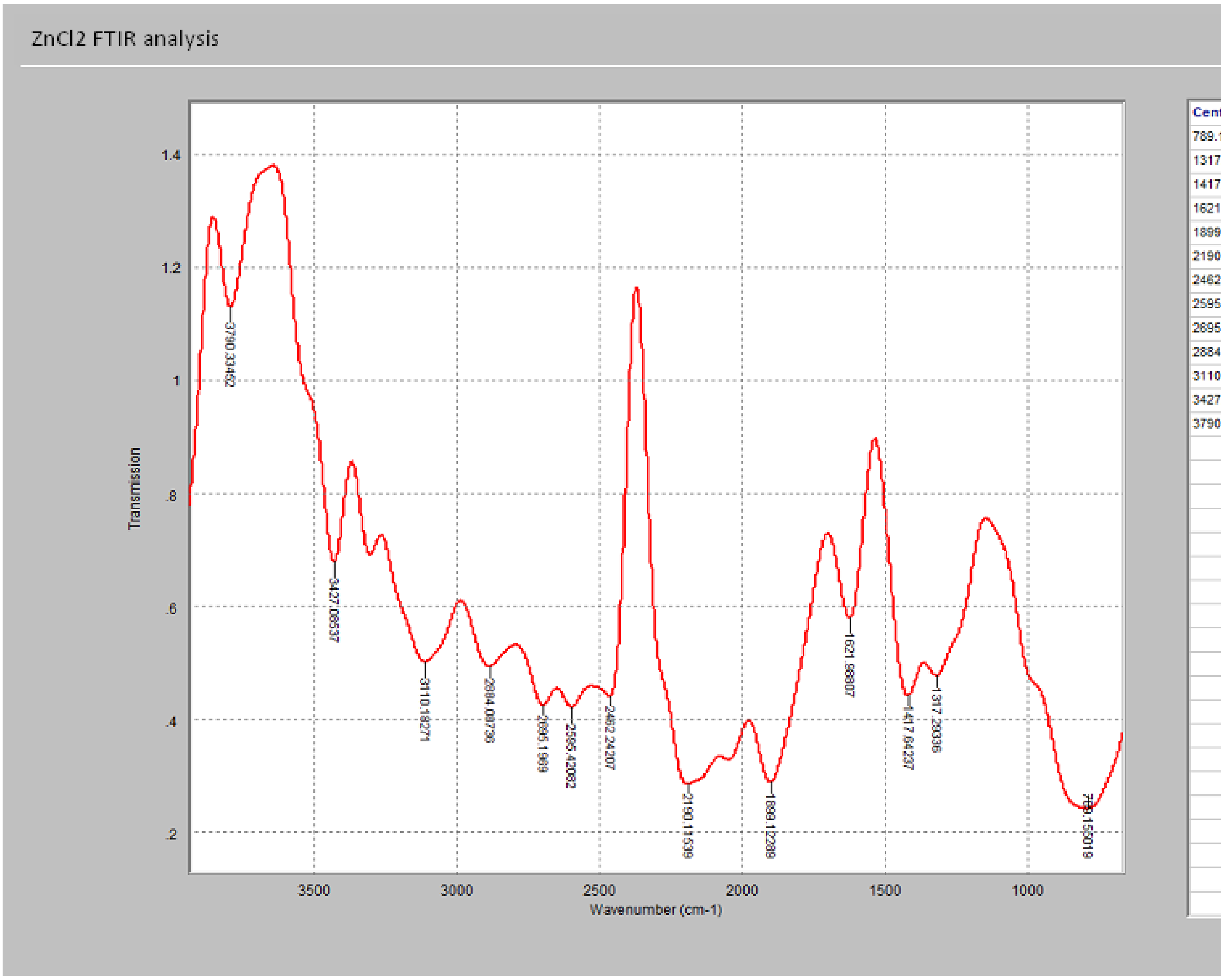
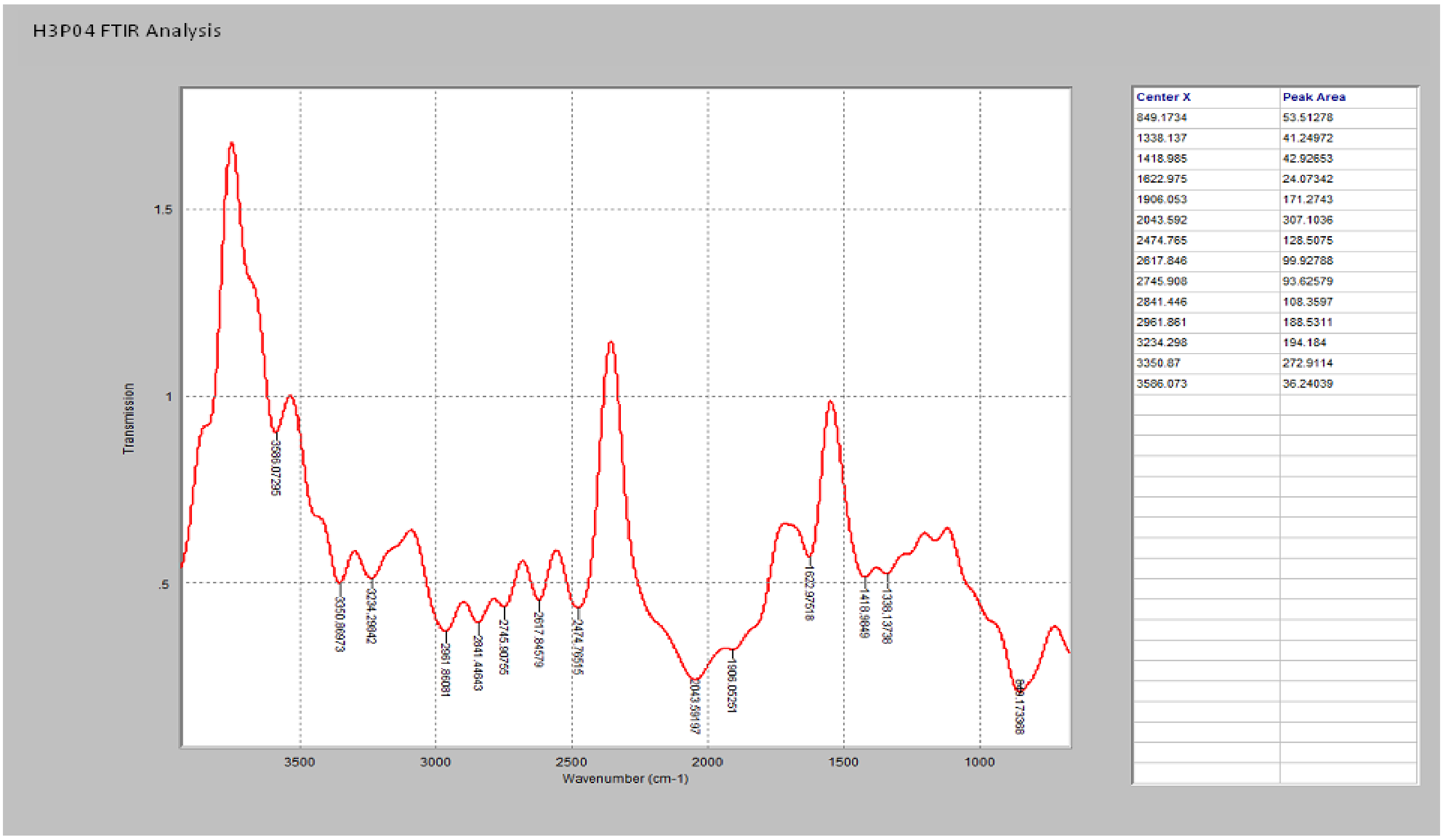


Fig 4.04: Spectrum of FTIR of ZnCl$_2$ activated *pentaclethramacrophylla benth* seed shells.



Center X	Peak Area
849.1734	53.51278
1338.137	41.24972
1418.985	42.92653
1622.975	24.07342
1906.053	171.2743
2043.592	307.1036
2474.765	128.5075
2617.846	99.92788
2745.908	93.62579
2841.446	108.3597
2961.861	188.5311
3234.298	194.184
3350.87	272.9114
3586.073	36.24039

Fig. 4.05: Spectrum of FTIR of H_3PO_4 activated *pentaclethramacrophylla benth* seed shells.

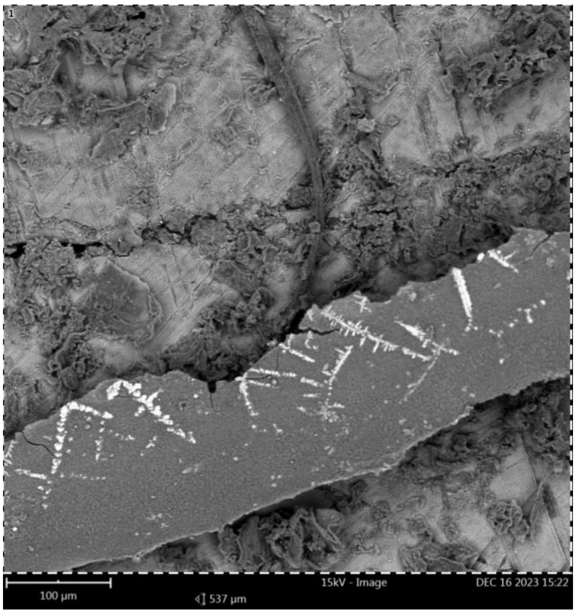


Fig. 4.06: SEM image of unactivated *pentaclethramacrophylla benth* seed shells.

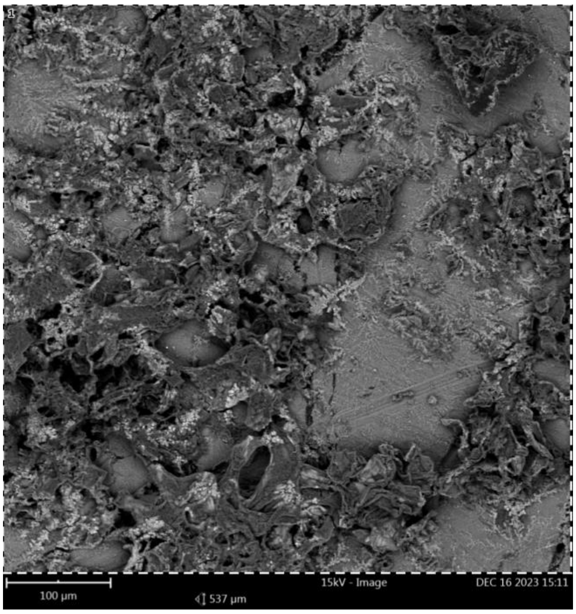


Fig. 4.07: SEM image of $ZnCl_2$ activated *pentaclethramacrophylla benth* seed shells.

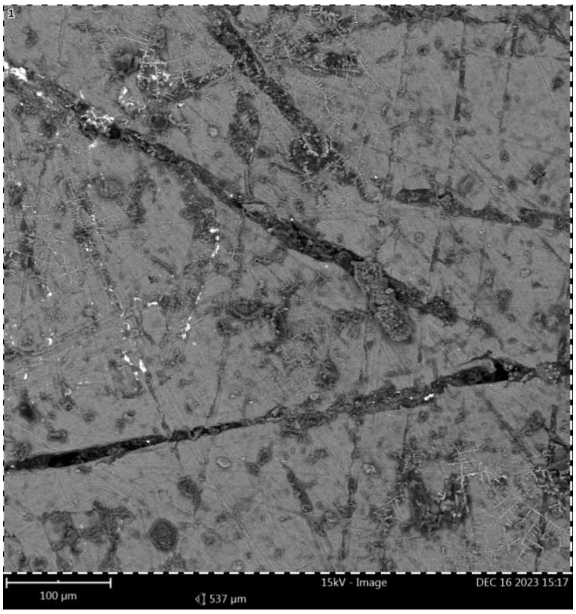


Fig 4.08: SEM image of H_3PO_4 activated *pentaclethramacrophylla benth* seed shells.

4.3 EFFECT OF CONTACT TIME ON THE ADSORPTION OF 4-CHLOROPHENOL AND HYDROQUINONE ONTO ACTIVATED OIL BEAN SEED SHELLS.

The effect of contact time on the adsorption of 30 mg/l of 4-chlorophenol and hydroquinone adsorption onto oil bean seed shells activated with $ZnCl_2$ were presented in tables 4.3 and 4.4 respectively. Fig 4.0.3 and 4.0.4 showed rapid adsorption of 4-chlorophenol and Hydroquinone onto oil bean seed from 2.73 mg/g to 3.15 mg/g for 4-chlorophenol and 2.96 mg/g to 3.42 mg/g for hydroquinone at 10 minutes and 20 minutes respectively. Beyond 20 minutes, the amount of 4-chlorophenol and hydroquinone adsorbed onto oil bean seed shells increases gradually and reaches a maximum adsorption of 3.92 mg/g and 4.47 mg/g at 50 minutes (for the salt activated carbon) and 40 minutes (for the acid activated carbon) respectively. The fast uptake of 4-chlorophenol and hydroquinone molecules at the beginning of the adsorption time may be attributed to the availability of large numbers of vacant sites on the adsorbent surface. With the increase of contact time, these vacant sites were saturated with 4-chlorophenol and hydroquinone. Tyaji .A, Das .S and Syrivastava V.C, (2018) reported removal of Hydroquinone from aqueous solution using iron-impregnated activated carbon. Yusef .O., Abadi, Nourmoradi H., and Taheri A., (2015) also reported that the optimum contact time of 40mins was established for the removal of 4-chlorophenol from aqueous solution using activated carbon synthesized from Aloe Vera green wastes.

Table 4.03. Effect of contact time on the adsorption of 30 mg/l of 4-Chlorophenol and Hydroquinone onto $ZnCl_2$ activated carbon shells of oil bean seed.

Contact Time (mins)	Absorbance (A) at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol Adsorbed at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed at equilibrium (mg/g)
10	0.140	13.65	16.35	2.73
20	0.120	11.10	18.90	3.15
30	0.150	10.70	19.30	3.25
40	0.095	9.00	21.00	3.50
50	0.07	6.50	23.50	3.9
60	0.07	6.50	23.50	3.92
70	0.07	6.50	23.50	3.92
80	0.07	6.50	23.50	3.92

Table 4.04: Effect of contact time on the adsorption of 30 mg/l Hydroquinone onto $ZnCl_2$ activated shells of oil bean seed.

Contact time (mins)	Absorbance (A) at equilibrium (nm)	Hydroquinone concentration at equilibrium supernatant solution (mg/l)	Hydroquinone adsorbed at equilibrium (mg/l)	Amount of hydroquinone adsorbed (mg/g)
10	0.150	12.20	17.80	2.96
20	0.115	9.50	20.50	3.42
30	0.085	7.00	23.00	3.83
40	0.055	4.40	25.60	4.27
50	0.040	3.20	26.80	4.47
60	0.040	3.20	26.80	4.47
70	0.040	3.20	26.80	4.47
80	0.040	3.20	26.80	4.47

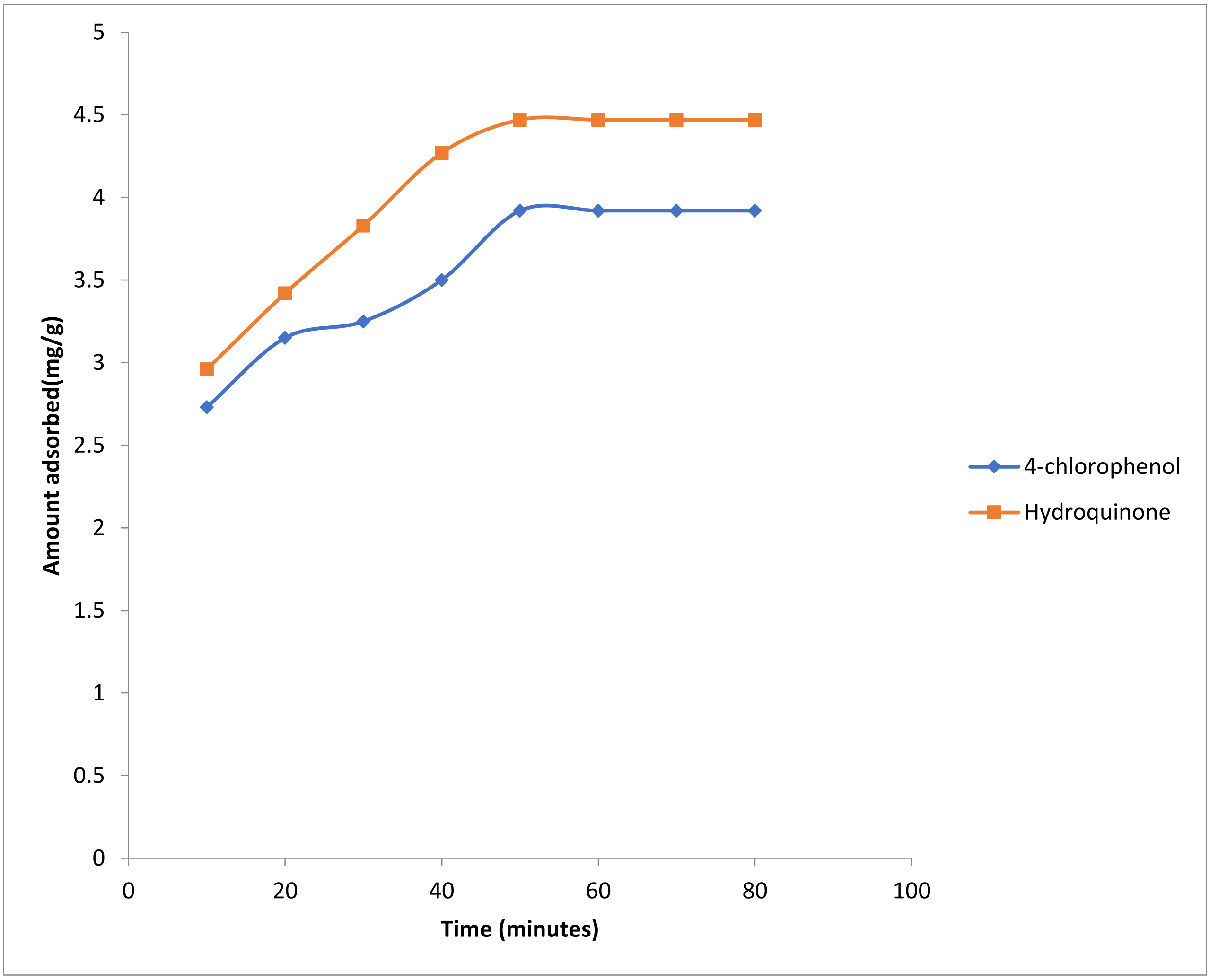


Figure 4.9: Plots of the effect of contact time on the adsorption of 30 mg/l of 4-Chlorophenol and Hydroquinone onto $ZnCl_2$ activated oil bean seed shells.

Table 4.05: Effects of contact time on the adsorption of 4-chlorophenol onto H_3PO_4 activated shells of oil bean seed.

Contact time (mins)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed at equilibrium (mg/g)
10	0.155	14.9	15.10	2.51
20	0.130	12.6	17.40	2.90
30	0.115	11.0	19.00	3.17
40	0.105	9.90	20.10	3.35
50	0.105	9.90	20.10	3.35
60	0. 105	9.90	20.10	3.35
70	0.105	9.90	20.10	3.35
80	0.105	9.90	20.10	3.35

Table 4.06: Effect of contact time on the adsorption of Hydroquinone onto H_3PO_4 activated oil bean seed shell.

Contact time (mins)	Absorbance(A) at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed (mg/g)
10	0.170	14.00	16.00	2.60
20	0.130	10.50	19.50	3.25
30	0.100	8.00	22.00	3.60
40	0.090	7.20	22.80	3.80
50	0.090	7.20	22.80	3.80
60	0.090	7.20	22.80	3.80
70	0.090	7.20	22.80	3.80
80	0.090	7.20	22.80	3.80

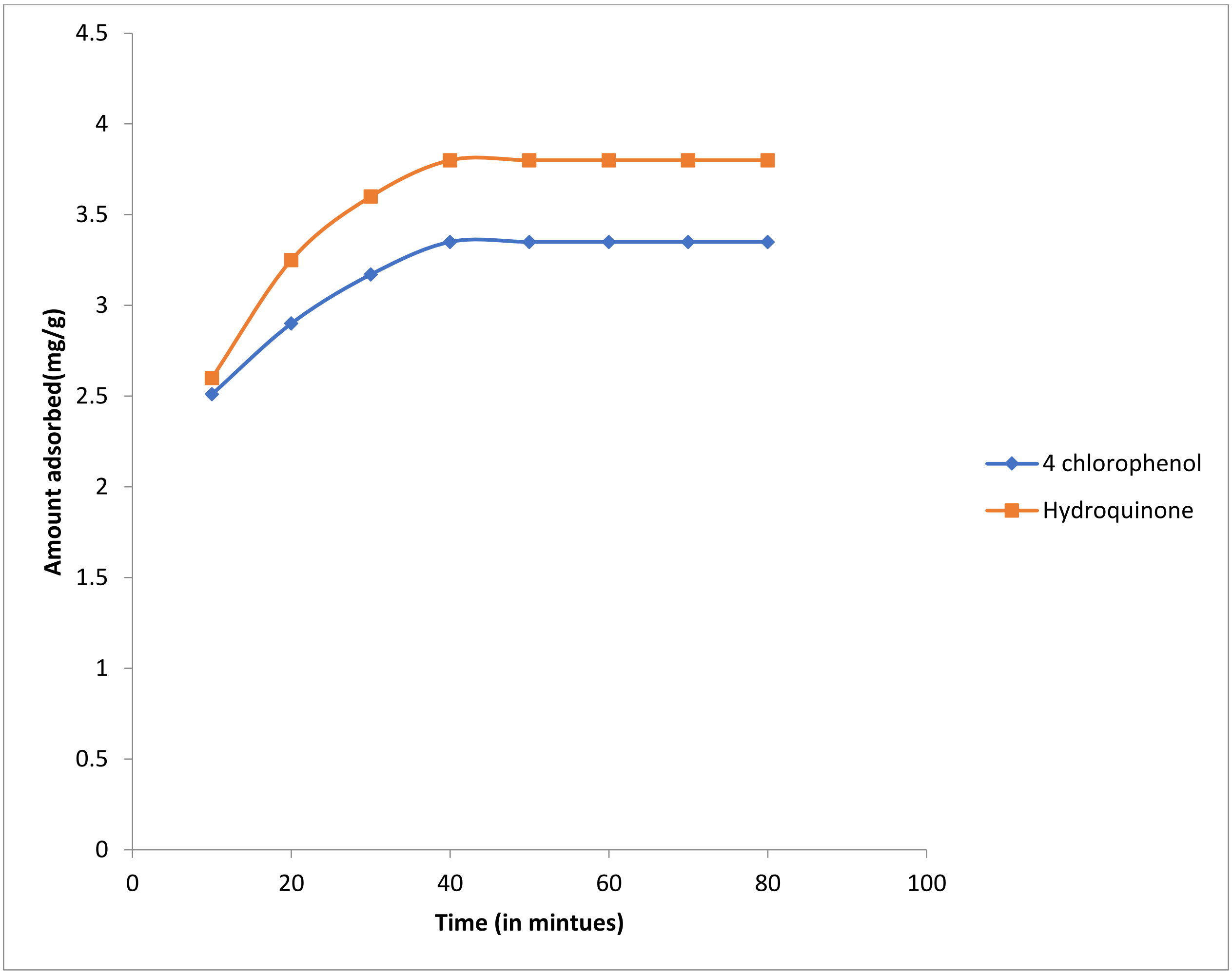


Figure 4.10: Plots of the effect of contact time on the adsorption of 4-Chlorophenol using H_3PO_4 activated shells of Oil bean seed.

4.2 Adsorption kinetics for a plot of 4-Chlorophenol and Hydroquinone

The rate constant for adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shell were determined using first order kinetics

In $(C_0/C_t) = K_t$

Where C_0 is the initial 4-chlorophenol and hydroquinone solution concentration

C_t is the concentration at time t

K_t is the rate constant

A plot of In (C_0/C_t) versus t yielded a straight line from the slope of which the rate constant k, was calculated to be -0.005 per min, and-0.004 per min for 4-Chlorophenol and Hydroquinone concentration at 30 mg/l respectively using $ZnCl_2$ activated carbon, and -0.0094 per min for 4-Chlorophenol, and -0.012 per minute for Hydroquinone using H_3PO_4 activated shells of oil bean seeds.

Table 4.07. First order kinetic table for the adsorption of 4-Chlorophenol and Hydroquinone onto $ZnCl_2$ activated oil bean seed shells

Time(mins)	$\ln C_o/C_t$. 4-Chlorophenol	$\ln C_o/C_t$ Hydroquinone
10	0.604	0.525
20	0.460	0.378
30	0.430	0.262
40	0.360	0.157
50	0.246	0.120
60	0.246	0.120
70	0.246	0.120
80	0.246	0.120

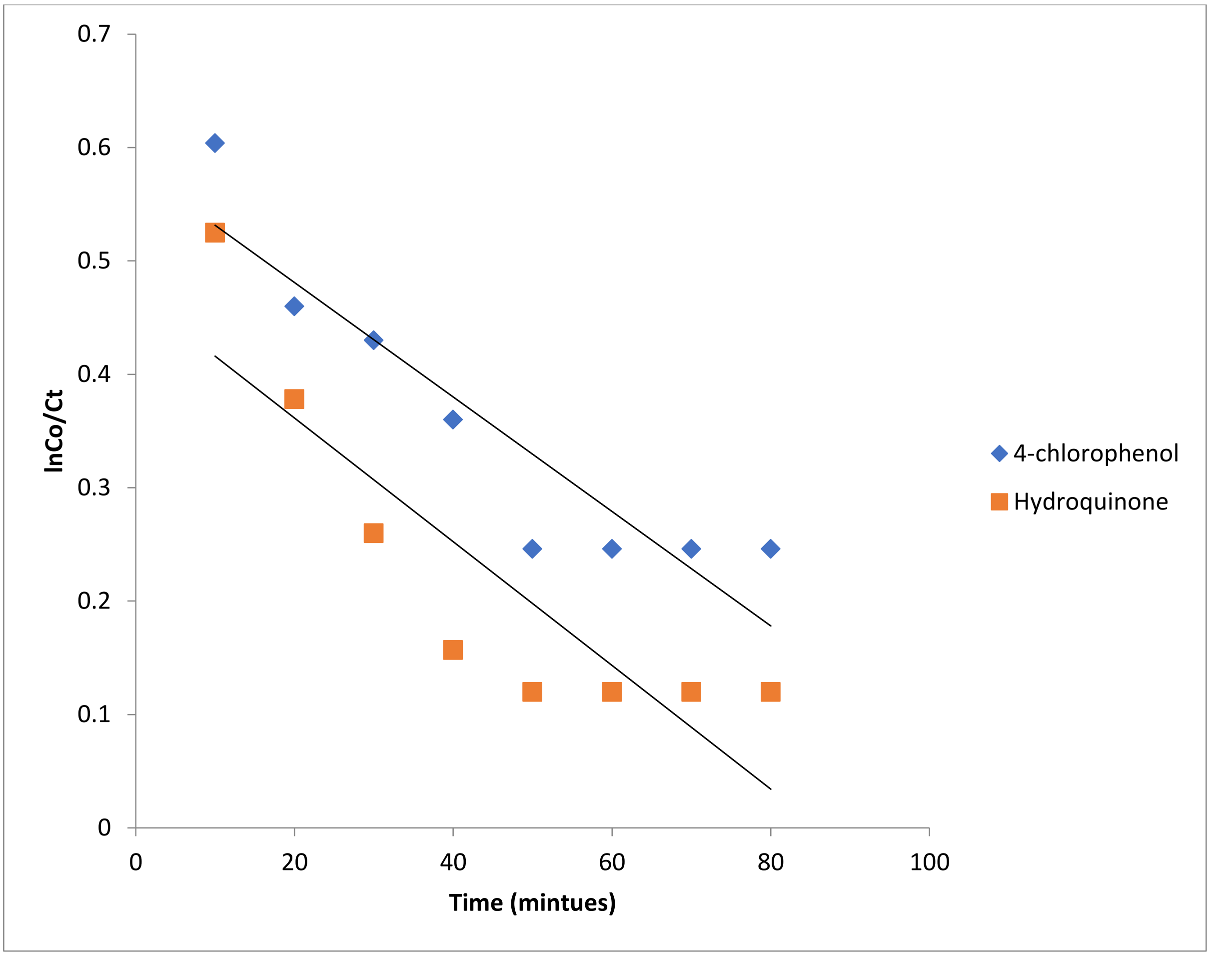


Figure 4.11. First order kinetic plots of the adsorption of 4-Chlorophenol and Hydroquinone onto $ZnCl_2$ activated oil bean seed shell.

Table 4.08: First order kinetic table for the adsorption of 4-Chlorophenol and Hydroquinone onto H_3PO_4 activated oil bean seed shell

Time (mins)	$\ln C_o/C_t$ 4-Chlorophenol	$\ln C_o/C_t$ Hydroquinone
10	0.683	0.628
20	0.542	0.430
30	0.451	0.262
40	0.399	0.270
50	0.399	0.270
60	0.399	0.270
70	0.399	0.270
80	0.399	0.270

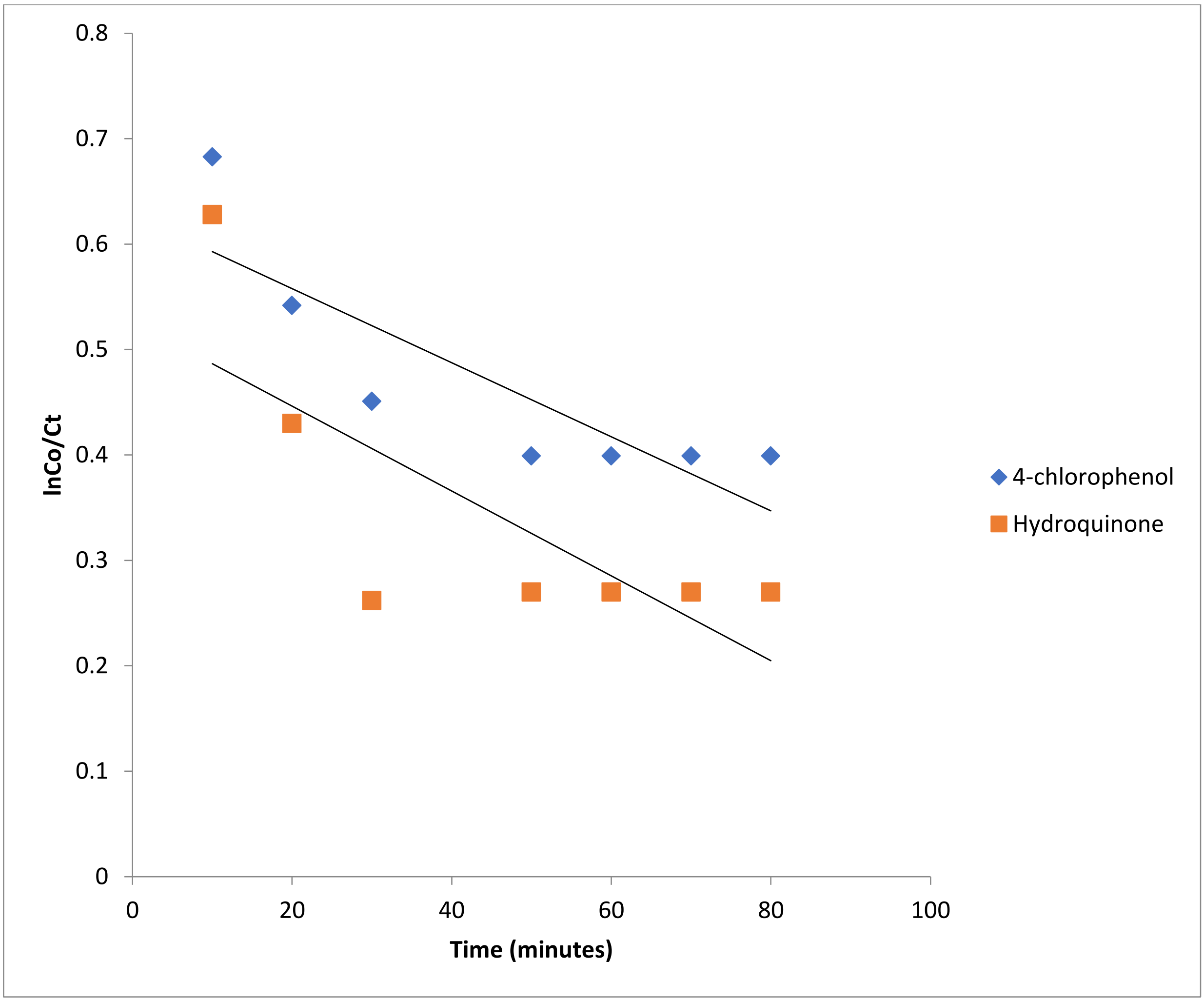


Figure 4.12: First order kinetic plots of the adsorption of 4-Chlorophenol and Hydroquinone onto H_3PO_4 activated oil bean seed shell.

4.9. THE EFFECTS OF pH ON THE ADSORPTION OF 4-CHLOROPHENOL AND HYDROQUINONE ONTO ACTIVATED OIL BEAN SEED SHELL AT DIFFERENT CONCENTRATIONS

Tables 4.10, 4.11, 4.12, and 4.13 showed the effect of pH on the adsorption process of 4-Chlorophenol onto activated oil bean seed shell. The effect of adsorption of 4 -Chlorophenol onto activated oil bean seed shell was studied between pH 4 and pH 10 at various concentration range; 5 mg/l to 50 mg/l.

The Adsorption isotherm of 4- Chlorophenol at various pH ranges were depicted in figs 4.0.7 and 4.0.8. The result showed that uptake of 4- Chlorophenol onto activated carbon. ($ZnCl_2$ and H_3PO_4) of oil bean seed shell is significantly high at pH4, when compared to values obtained at pH 6, pH 9.2 and pH 10 respectively.

At low pH 4, the uptake of 4- Chlorophenol onto activated oil been seed shell (OBSS) increases rapidly as concentration of 4-Chlorophenol increases. At pH 4 the surface of oil seed shell was positively charged. The increase in adsorption of 4- Chlorophenol onto OBSS at pH 4 when compared to pH 6, pH 9.2 and pH 10 might be attributed to dissociation of 4- Chlorophenol into 4- Chlorophenol ate anions. These 4- Chlorophenolate anions will rapidly adsorbed onto the positively charged surface of OBSS.

The decrease of the uptake of 4-Chlorophenol onto OBSS at pH 6 when compared to pH 4 may be attributed to 4-Chlorophenol being partially converted to positively charged Chlorophenol ions. In view of the presence of 4-Chlorophenol ions in aqueous solution, repulsion occurs between the positively charged OBSS and positively charged 4- Chlorophenol ions. This resulted in the decrease of adsorption of 4-Chlorophenol onto oil bean seed at pH 6.

At pH 10 OBSS surface acquires negative charge due to the adsorption of OH^-. At high pH levels, 4-Chlorophrnol is dissociated into 4-Chlorophenolate anions. The negatively charged surface would have repulsed the resultant 4-Chlorophenolate ion with each other, which would have resulted in a lower adsorption of 4-Chlorophenol at pH 10 and pH 9.2 respectively.

The same reason could be associated on the effect of pH on the adsorption of Hydroquinone onto activated oil been shell, also reported that at pH4, the carbon surface and the chlorophenolic compound is in a protonated form. Majlesi and Hashempour, 2017 also reported that acidic conditions were more suitable for the removal of 4-Chlorophenol but, when the pH was greater than 6, the removal efficiency decreased. That at acidic pH, the concentration of H^+ ions increases and the surface of the adsorbent has a positive charge by absorption of the protons.

Table 4.09: Effect of pH 4 on adsorption of 4-Chlorophenol onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-Chlorophenol adsorbed (mg/g)
5	0.028	2.20	2.80	0.47
10	0.030	2.50	7.50	1.25
15	0.550	5.00	10.00	1.70
20	0.085	8.00	12.00	2.00
25	0.090	8.50	16.50	2.75
30	0.105	9.75	20.25	3.36
35	0.135	12.74	22.26	3.67
40	0.095	9.34	30.66	5.11
45	0.165	15.90	29.10	4.85
50	0.230	22.40	27.60	4.60

Table 4.10: Effect of pH 6 on adsorption of 4-Chlorophenol onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-chlorophenolconcentration in equilibrium supernatant liquid (mg/l)	4-chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed (mg/g)
5	0.032	2.90	2.10	0.35
10	0.049	4.20	5.80	0.97
15	0.065	6.00	9.00	1.50
20	0.105	9.80	10.22	1.70
25	0.125	11.85	13.15	2.19
30	0.130	12.50	17.50	2.91
35	0.167	16.00	19.00	3.27
40	0.150	14,22	25.78	4.29
45	0.210	20.10	24.90	4.15
50	0.280	27.00	23.00	3.87

Table 4.11. Effect of pH 9.2 on adsorption of 4-Chlorophenol onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed (mg/g)
5	0.040	3.20	1.80	0.30
10	0.065	6.00	4.00	0.67
15	0.075	7.35	7.65	1.28
20	0.115	10.90	9.10	1.52
25	0.140	13.20	11.80	1.97
30	0.150	14.25	15.75	2.65
35	0.195	18.90	16.10	2.68
40	0.180	18.52	21.48	3.58
45	0.27	25.88	19.12	3.19
50	0.325	31.40	18.60	3.10

Table 4.12: Effect of pH 10 on adsorption of 4-Chlorophenol onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed (mg//g)
5	0.042	3.90	1.10	0.18
10	0.07	6.75	3.25	0.54
15	0.09	8.65	6.35	1.06
20	1.00	13.0	7.00	1.17
25	0.14	15.3	9.75	1.63
30	0.16	16.7	13.3	2.22
35	0.24	22.2	12.8	2.13
40	0.30	22.1	17.9	2.99
45	0.28	28.8	16.2	2.79
50	0.36	34.7	15.4	2.58

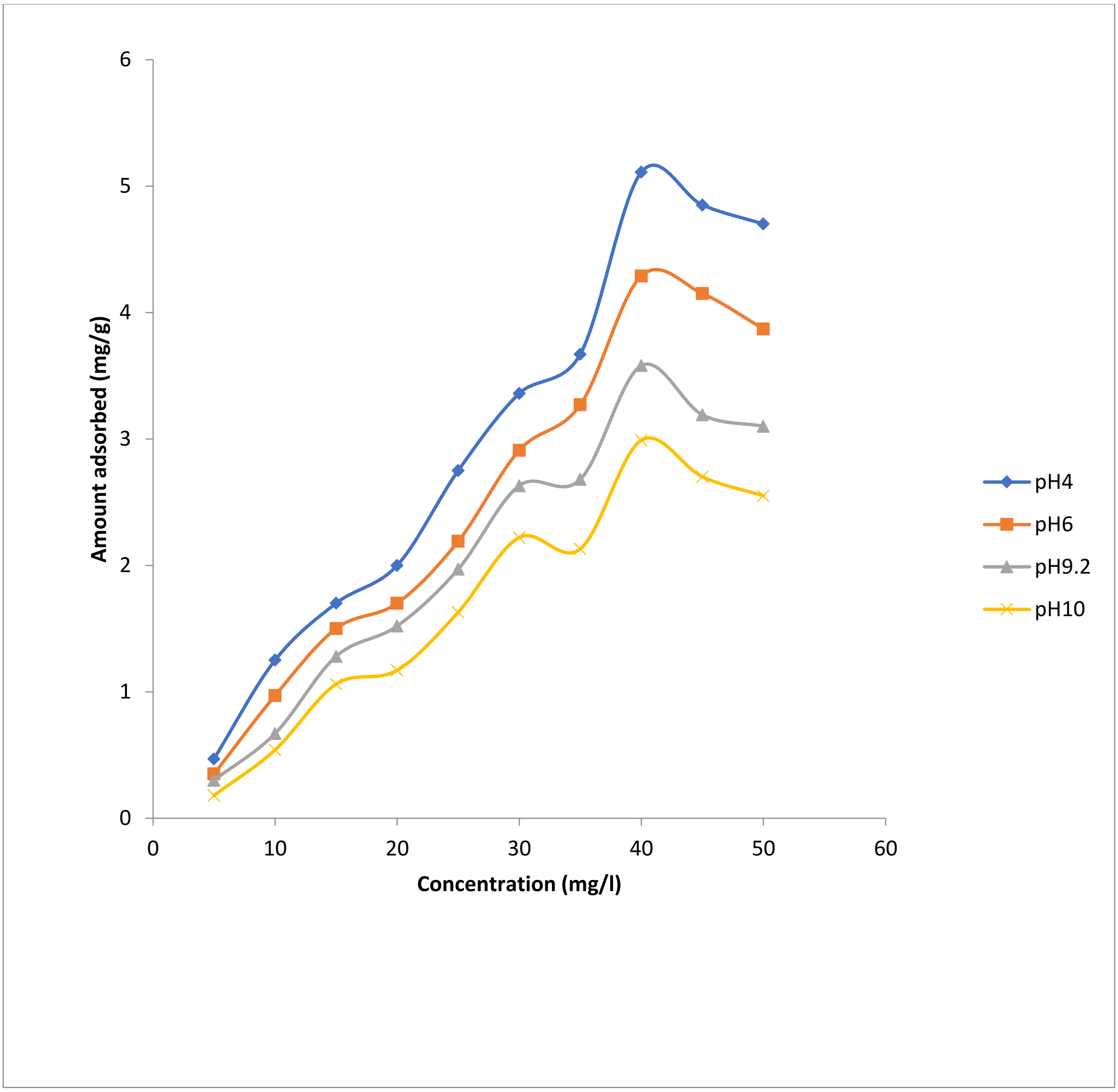


Figure 4.13: Effect of pH on the adsorption of 4-Chlorophenol onto $ZnCl_2$ activated oil bean seed shells at different concentrations

Table 4.13: Effect of pH 4 on adsorption of 4-Chlorophenol onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-Chlorophenol adsorbed (mg/g)
5	0.032	2.80	2.20	0.37
10	0.035	3.00	7.00	1.20
15	0.067	6.25	8.75	1.46
20	0.095	8.75	11.25	1.88
25	0.098	9.20	14.80	2.47
30	1.125	11.80	18.20	3.13
35	0.155	1455	20.45	3.40
40	0.120	11.25	28.75	4.82
45	0.185	17.25	27.75	4.63
50	0.255	24.80	25.20	4.20

Table 4.14: Effect of pH 6 on adsorption of 4-Chlorophenol onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-Chlorophenol adsorbed (mg/g)
5	0.040	3.05	1.95	0.33
10	0.055	5.00	5.00	0.83
15	0.078	7.40	7.60	1.27
20	0.113	10.50	9.50	1.58
25	0.120	11.30	13.20	2.28
30	0.150	14.50	15.50	2.58
35	0.170	16.70	18.30	3.05
40	0.145	13.75	26.25	4.38
45	0.200	19.30	25.70	4.28
50	0.280	26.85	23.15	3.85

Table 4.15: Effect pH 9.2 on adsorption of 4-Chlorophenol onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-chlorophenol adsorbed (mg/g)
5	0.040	3.55	1.45	0.24
10	0.068	6.75	3.25	0.54
15	0.100	9.45	5.55	0.96
20	0.125	11.85	8.45	1.38
25	0.145	13.75	11.25	1.88
30	0.175	16.80	13.20	2.20
35	0.195	18.55	16.45	2.74
40	0.165	15.94	24.00	4.00
45	0.235	22.20	22.80	3.80
50	0.30	28.90	21.10	3.52

Table 4.16: Effect of pH 10 on adsorption of 4-Chlorophenol onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-Chlorophenol adsorbed (mg/g)
5	0.043	3.95	1.05	0.18
10	0.075	7.20	2.80	0.47
15	0.110	10.30	4.70	0.78
20	0.130	11.35	7.35	1.23
25	0.155	14.90	10.10	1.67
30	0.198	18.65	11.35	1.89
35	0.215	20.85	14.15	2.36
40	0.185	18.80	21.20	3.80
45	0.255	24.15	20.85	3.53
50	0.320	30.90	19.10	3.18

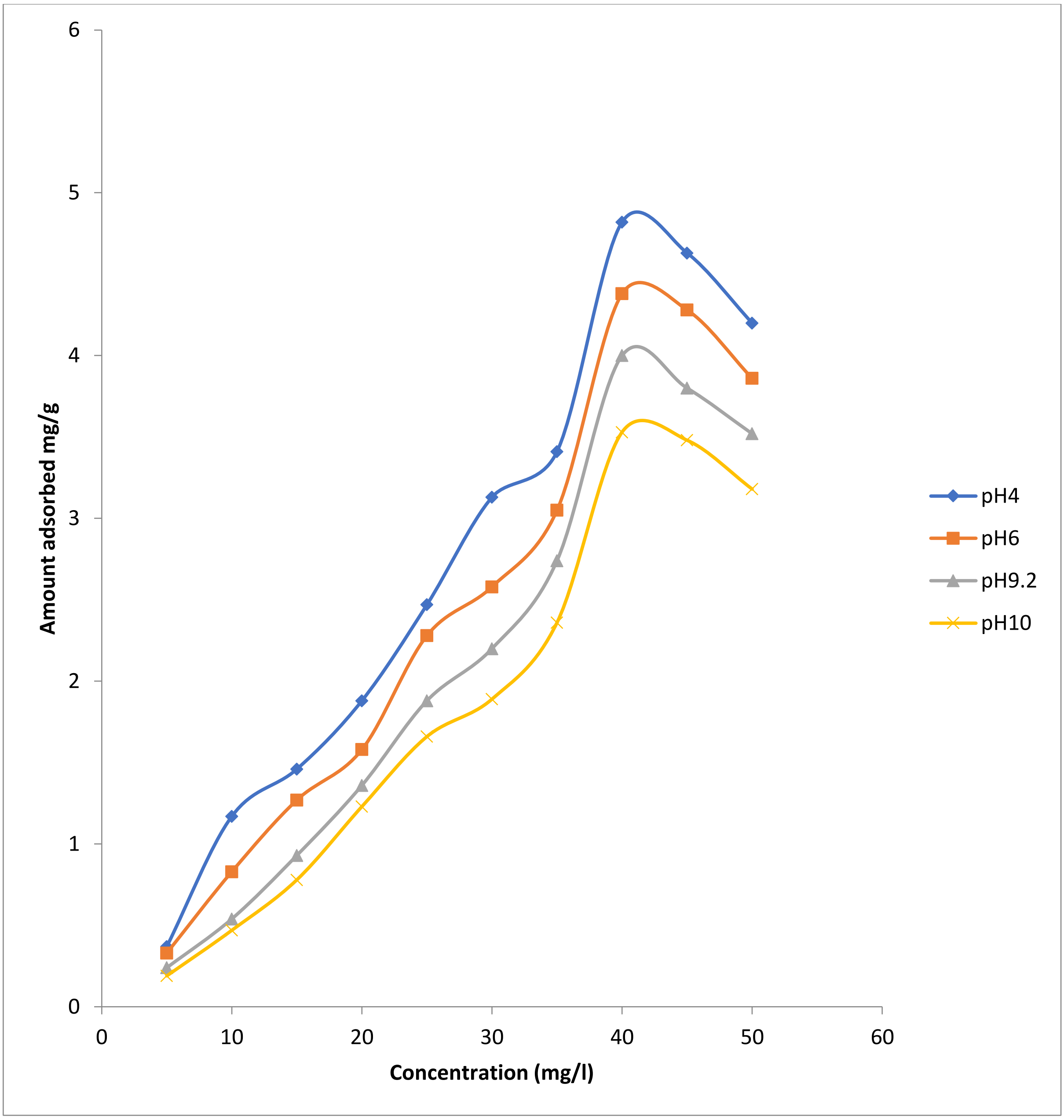


Figure 4.14: Effect of pH on the adsorption of 4-Chlorophenol onto H_3PO_4 activated oil bean seed shells at different concentrations.

Table 4.17: Effect of pH 4 on adsorption of Hydroquinone onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.030	2.00	3.00	0.5
10	0.038	2.20	7.80	1.23
15	0.550	4.20	11.80	1.97
20	0.085	6.60	13.40	2.23
25	0.090	7.35	19.65	2.94
30	0.100	8.00	22.00	3.66
35	0.125	10.3	24.70	4.00
40	0.095	7.70	32.30	5.38
45	0.16	13.1	31.90	5.32
50	0.23	19.0	31.00	5.16

Table 4.18: Effect of pH 6 on adsorption of Hydroquinone onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.040	3.00	2.00	0.34
10	0.050	3.90	6.10	1.02
15	0.060	4.90	10.10	1.68
20	0.110	1.65	11.35	1.90
25	0.120	10.50	14.50	2.42
30	0.145	10.60	19.40	2.23
35	0.180	14.60	20.40	3.40
40	0.175	13.90	26.10	4.35
45	0.24	19.80	25.20	4.20
50	0.290	24.10	24.50	4.00

Table 4.19: Effect of pH 9.2 on adsorption of Hydroquinone onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.042	3.02	1.90	0.32
10	0.060	4.70	5.30	0.88
15	0.085	7.00	8.00	1.33
20	0.115	9.50	10.5	1.75
25	0.150	12.2	12.80	2.13
30	0.195	15.8	14.20	2.37
35	0.210	17.8	17.20	2.87
40	0.200	16.7	23.35	3.74
45	0.280	23.3	21.75	3.63
50	0.350	29.0	22.00	3.50

Table 4.20: Effect of pH 10 on adsorption of Hydroquinone onto activated $ZnCl_2$ oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.050	3.60	1.40	0.23
10	0.065	5.15	4.85	0.81
15	0.090	7.70	7.30	1.22
20	0.149	11.9	8.15	1.36
25	0.180	14.9	10.1	1.75
30	0.225	18.7	11.4	1.89
35	0.260	21.7	13.4	2.23
40	0.255	20.9	19.0	3.20
45	0.375	27.6	17.4	2.90
50	0.400	33.1	16.9	3.00

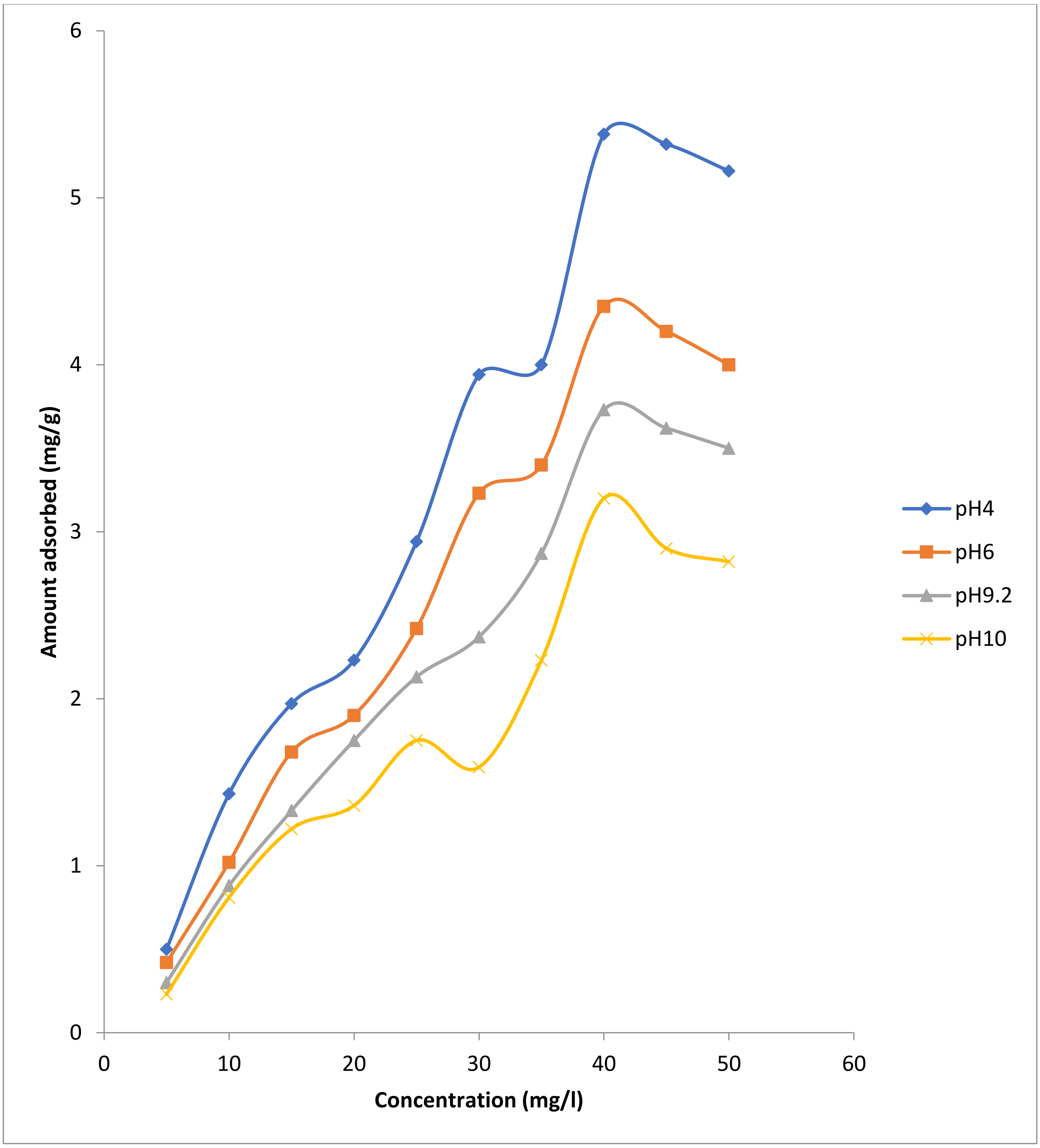


Figure 4.15: Effect of pH on the adsorption of Hydroquinone onto $ZnCl_2$ activated oil bean seed shells at different concentrations.

Table 4.21: Effect of pH 4 on adsorption of Hydroquinone onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.03	2.30	2.70	0.45
10	0.04	2.80	7.20	1.20
15	0.05	3.75	11.35	1.89
20	0.049	7.40	12.60	2.1
25	0.115	9.50	15.50	2.58
30	0.125	10.45	19.55	3.25
35	0.15	12.35	22.65	3.73
40	0.115	9.2	30.30	5.13
45	0.19	15.75	29.25	4.95
50	0.25	20.5	29.05	4.84

Table 4.22: Effect of pH 6 on adsorption of Hydroquinone onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.039	2.90	2.10	0.35
10	0.045	4.80	5.20	0.87
15	0.07	5.75	9.25	1.54
20	0.12	9.30	10.70	1.78
25	0.15	12.00	13.00	2.7
30	0.17	13.75	16.25	3.042
35	0.20	15.55	19.45	3.24
40	0.17	14.70	25.30	4.22
45	0.25	20.55	24.45	4.67
50	0.26	26.10	23.90	3.98

Table 4.23: Effect pH 9.2 on adsorption of Hydroquinone onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.0495	3.15	1.35	0.31
10	0.065	5.25	4.75	0.79
15	0.95	7.75	7.25	1.25
20	0.125	10.10	9.90	1.85
25	0.136	12.90	12.10	2.02
30	0.18	14.35	15.15	2.79
35	0.235	18.65	16.35	2.70
40	0.21	17.05	22.95	3.83
45	0.28	23.15	21.85	3.64
50	0.36	29.40	20.60	3.5

Table 4.24: Effect of pH 10 on adsorption of Hydroquinone onto activated H_3PO_4 oil been seed shell at different concentrations.

Initial Concentration (mg/l)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
5	0.060	3.85	1.13	0.192
10	0.075	6.00	4.00	0.67
15	0.10	8.20	6.80	1.13
20	0.155	12.85	7.15	1.19
25	0.195	15.80	9.20	1.53
30	0.24	20.00	10.00	1.67
35	0.272	22.75	12.25	2.04
40	0.24	20.3	19.70	3.28
45	0.31	25.95	19.05	3.175
50	0.38	31.45	18.55	3.09

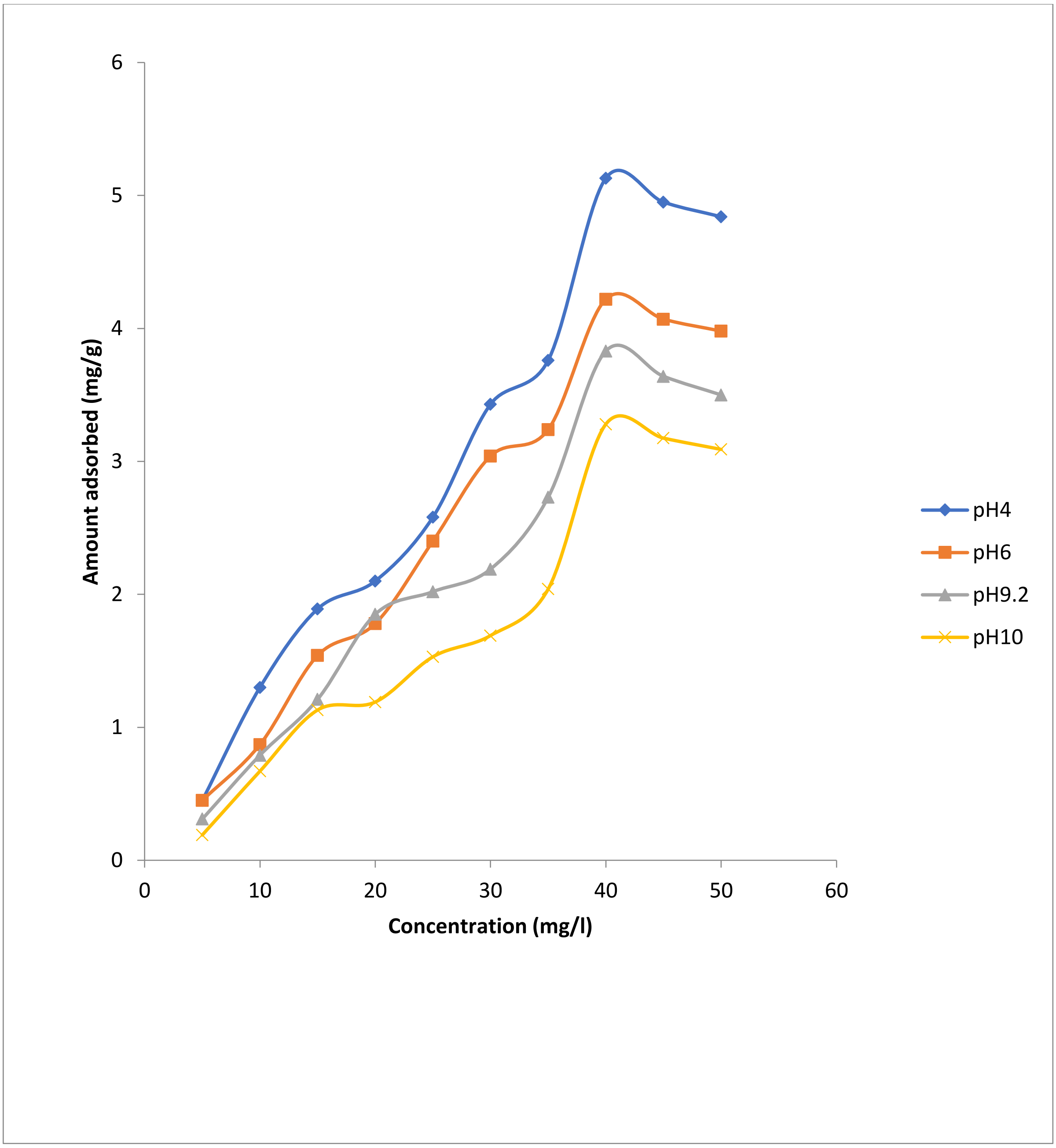


Figure 4.16: Effect of pH on the adsorption of Hydroquinone onto H_3PO_4 activated oil bean seed shells at different concentrations.

4.5 EFFECTS OF TEMPERATURE ON THE ADSORPTION OF 4-CHLOROPHENOL AND HYDROQUINONE.

Tables 4.26, 4.27, 4.28, and 4.29 shows the effect of temperature on the adsorption of 4-Chlorophenol and Hydroquinone onto activated oil bean seed shell. The removal of 4-Chlorophenol and Hydroquinone from aqueous solution is temperature dependent. The kinetic plots shows the amount of 4-Chlorophenol and Hydroquinone removed from aqueous solution as a function of temperature at 4-Chlorophenol and Hydroquinone concentration of 40 mg/l, respectively. There was a progressive decrease on the Adsorption of 4-Chlorophenol and Hydroquinone from aqueous solution onto OBSS as temperature increases from 30 ^{o}C to 60 ^{o}C as shown in fig 4.12 and 4.13.

As temperature increases, the amount of 4-Chlorophenol and Hydroquinone removed from aqueous solution decreases rapidly from 5.30 to 3.42 mg/g, (for $ZnCl_2$ activated oil bean seed shells), 5.15 to 2.70 mg/g, (for H_3PO_4 activated oil bean seed shells) and from 5.6 to 3.5 mg/g, (for $ZnCl_2$ activated oil bean seed shells), from 5.35 to 2.90 mg/g, (for H_3PO_4 activated oil bean seed shells) respectively.

This study indicates that uptake of 4-Chlorophenol and Hydroquinone from aqueous solution increases at low temperature. The decrease on the uptake of 4-Chlorophenol and Hydroquinone as temperature increases may be explained in terms of the increase in the average kinetic energy of 4-Chlorophenol and hydroquinone ions. The increase in kinetic energy will thus, increase the repulsive force between 4-Chlorophenolate anions and negatively charged oil been seed shell surface, as well as Hydroquinone anions negatively charged oil bean seed shell.

Therefore, the increase in temperature may be associated with the decrease in the stability of 4-Chlophenonate-anion-adsorbent complex and Hydroquinone anion-adsorbent complex, respectively. Ekpete O.A., Horsfall M. and Tarawou T., 2011 also reported that as the temperature increases, the percentage of Chlorophenol removed from H_3PO_4 activated fluted and commercial activated carbon becomes lesser.

Table 4.25: Effect of Temperature on the adsorption of 4-Chlorophenol onto activated $ZnCl_2$ oil bean seed shells.

Temperature (ºC)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	4-Chlorophenol concentration adsorbed at equilibrium (mg/l)	Amount of 4-Chlorophenol adsorbed (mg/g)
30	0.085	8.20	31.80	5.30
35	0.115	10.0	30.0	5.00
40	0.135	13.0	27.0	4.50
45	0.150	14.80	25.20	4.20
50	0.175	17.02	22.98	3.83
55	0.185	18.22	21.78	3.63
60	0.200	19.48	20.52	3.42

Table 4.26: Effect of Temperature on the adsorption of Hydroquinone onto activated $ZnCl_2$ oil bean seed shells

Temperature (ºC)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed (mg/g)
30	0.080	6.4	33.60	5.6
35	0.115	9.4	30.60	5.1
40	0.140	11.2	28.80	4.8
45	0.155	12.4	27.60	4.6
50	0.195	16.0	24.00	4.0
55	0.215	17.8	22.20	3.7
60	0.230	19.0	21.00	3.5

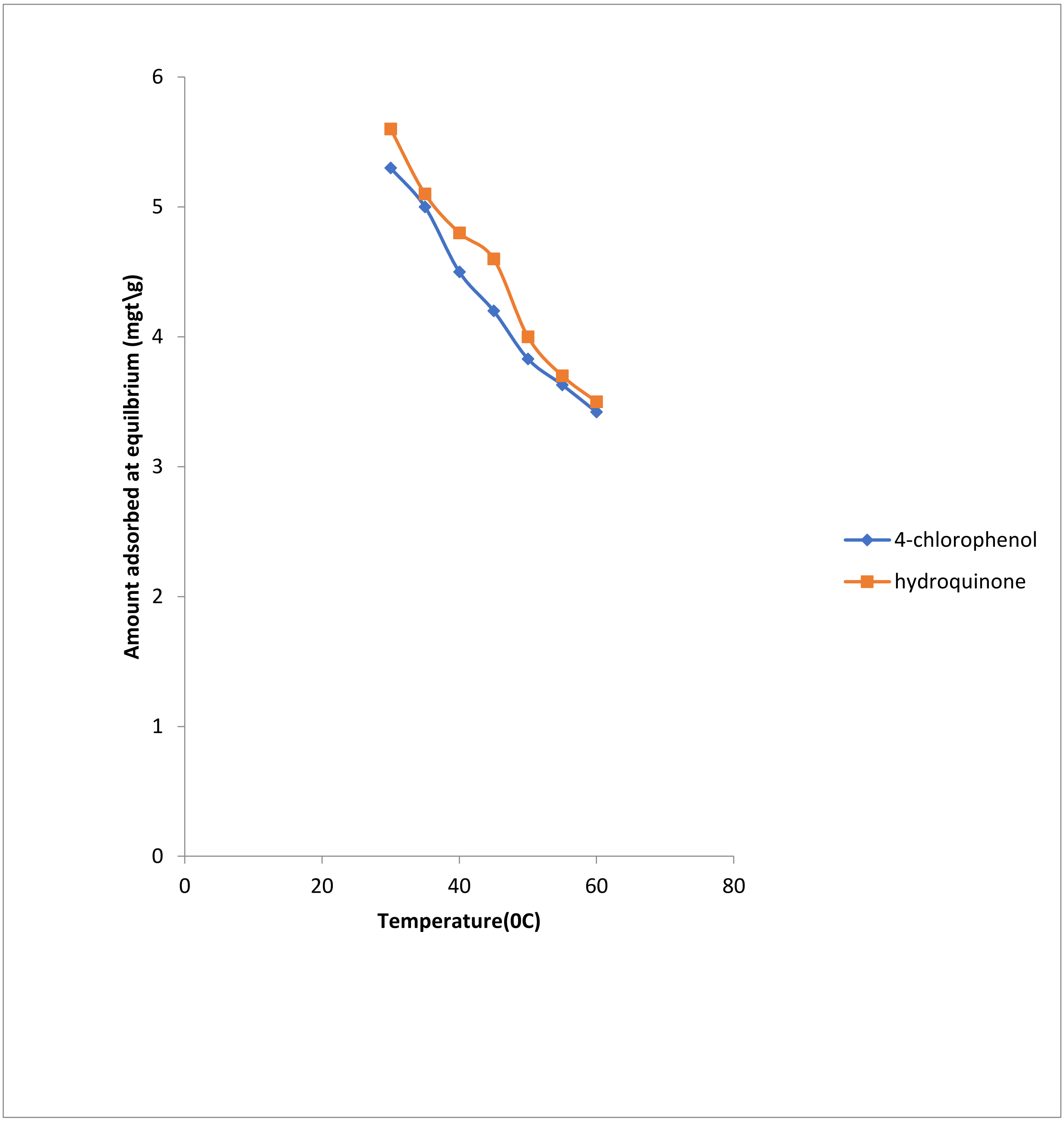


Figure 4.17: Effects of Temperature on the adsorption of 4-Chlorophenol and Hydroquinone using $ZnCl_2$ activated oil bean seed shell.

Table 4.27: Effect of Temperature on the adsorption of 4-Chlorophenol onto activated $ZnCl_2$ oil bean seed shells

Temperature (ºC)	Absorbance at equilibrium (nm)	4-Chlorophenol concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinoneadsorbed at equilibrium (mg/g)
30	0.095	9.10	30.9	5.15
35	0.120	11.50	28.5	4.75
40	0.145	14.20	25.8	4.30
45	0.165	15.70	24.3	4.05
50	0.221	20.44	19.6	3.26
55	0.22_	21.40	18.6	3.10
60	0.235	23.80	16.2	2.70

Table 4.28: Effect of Temperature on the adsorption of Hydroquinone onto activated H_3PO_4 oil bean seed shells

Temperature (ºC)	Absorbance at equilibrium (nm)	Hydroquinone concentration in equilibrium supernatant liquid (mg/l)	Hydroquinone concentration adsorbed at equilibrium (mg/l)	Amount of Hydroquinone adsorbed at equilibrium (mg/g)
30	0.085	7.90	32.10	5.35
35	0.130	10.60	29.40	4.90
40	0.150	12.10	27.90	4.65
45	0.170	14.80	25.20	4.20
50	0.210	17.25	22.75	3.75
55	0.245	20.20	19.80	3.30
60	0.265	22.60	17.40	2.90

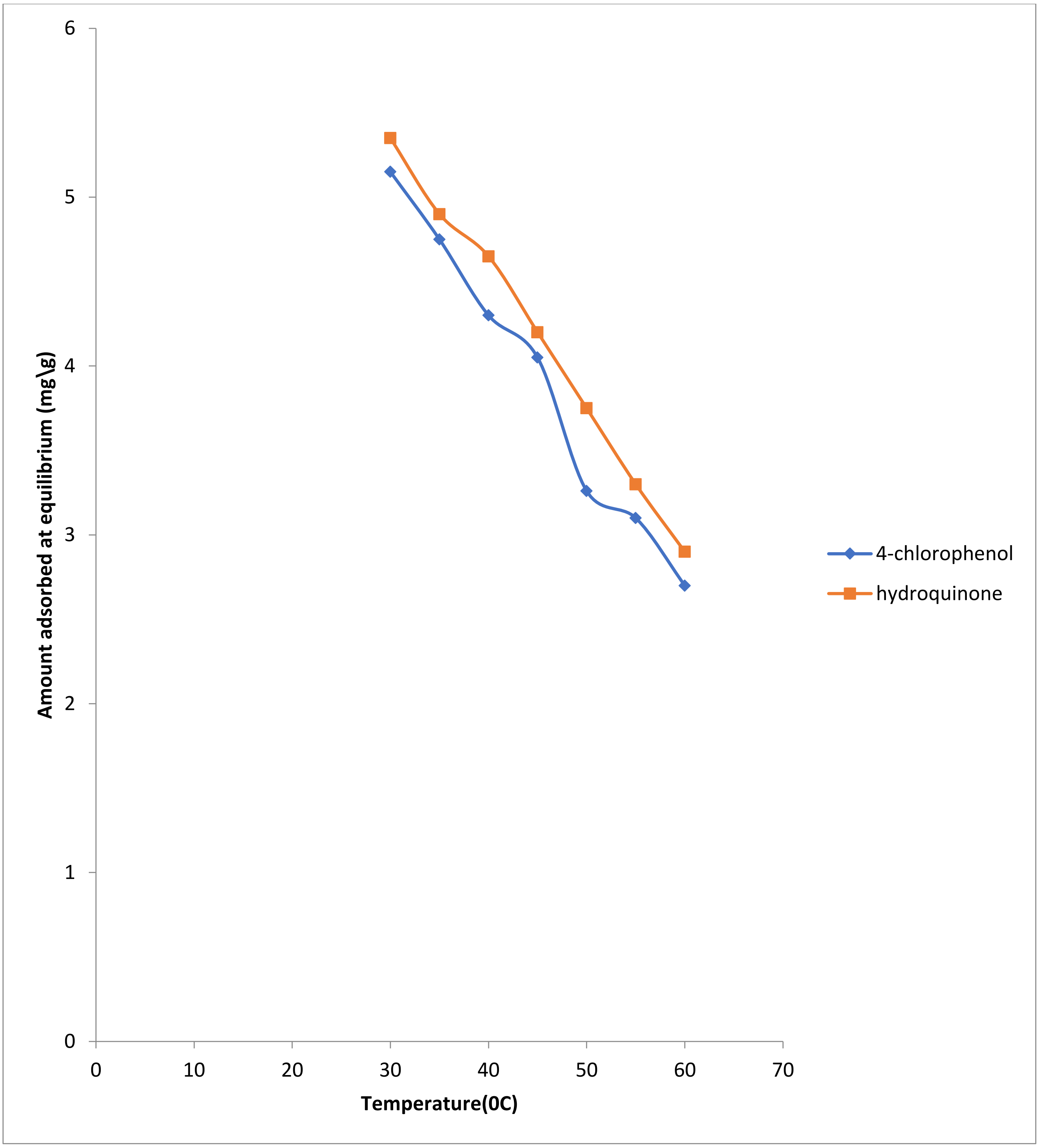


Figure 4.18: Effects of temperature on the adsorption of 4-chlorophenol and hydroquinone using H_3PO_4 Activated oil bean seed shell

4.6. DETERMINATION OF THERMODYNAMIC PARAMETERS OF 4-CHLOROPHENOL AND HYDROQUINONE

The standard free energy (ΔG^o) for the interaction of 4-Chlorophenol and hydroquinone with oil bean seed shell were calculated from the relationship;

$\Delta G^o = -RT\ln K_o$

Where,

ΔG^o = Standard Gibbs free energy change.

R = Universal gas constant ($8.314 Jmol^{-1}K^{-1}$)

T = Absolute Temperature (K)

$K_o = C_{adc}/C_e$

C_{adc}= Concentration of 4-Chlorophenol or Hydroquinone adsorbed at equilibrium

C_e = equilibrium 4-Chlorophenol or Hydroquinone concentration.

The enthalpy (ΔH) and entropy (ΔS^o) can be obtained from the slope and intercept of Van't Hoff equation of ΔG^o versus temperature (K).

$\Delta G^o = \Delta H^o - T\Delta S^o$

The thermodynamic study indicated that the adsorption process was exothermic and spontaneous. The thermodynamic parameters ΔG^o, was calculated to be from -135.70 to -3426.3 $jmol^{-1}\ k^{-1}$ (for $ZnCl_2$ activated carbon shells of oil bean seed, -26.6 to -3073.4 $jmol^{-1}\ k^{-1}$for H_3PO_4 activated carbon of oil bean seed shells for 4-Chlorophenol removal, from -360.0 to -4156.5 $jmol^{-1}\ k^{-1}$ (for $ZnCl_2$ activated shells of oil bean seed) and from -276.8 to -3526.8 $jmol^{-1}\ k^{-1}$ (for H_3PO_4 activated carbon shells of oil bean seed) for Hydroquinone removal. The enthalpy change (ΔH) were calculated to be -3733.7 and -3379.3 for $ZnCl_2$ activated carbon shells of oil bean seed respectively for 4-chlorophenol, and -4700 and -3654 for $ZnCl_2$and H_3PO_4 activated shells of oil bean seed for Hydroquinone removal respectively.The negative ΔG^o values of 4-Chlorphenol and Hydroquinone at various temperatures were due to adsorption process being spontaneous with respect to 4-Chlorophenol and Hydroquinone adsorption onto activated oil bean seed shells.

Table 4.29: The thermodynamics of 4-Chlorophenol adsorption onto $ZnCl_2$ activated oil bean seed shells.

Temperature (K)	**C_e (mg/l)**	**C_{adc} (mg/l)**	**K_o $=C_{adc}/C_e$**	**$\ln K_o$**	**$\Delta G = -RT\ln K_o$**
303	8.20	31.80	3.88	1.36	-3426.3
308	9.70	30.30	3.14	1.14	-2916.7
313	13.0	27.00	2.07	0.73	-1891.9
318	14.8	25.20	1.07	0.53	-1406.5
323	16.8	23.20	1.38	0.33	-878.13
328	18.2	21.80	1.97	0.18	-490.90
333	19.50	20.50	1.051	0.05	-135.70

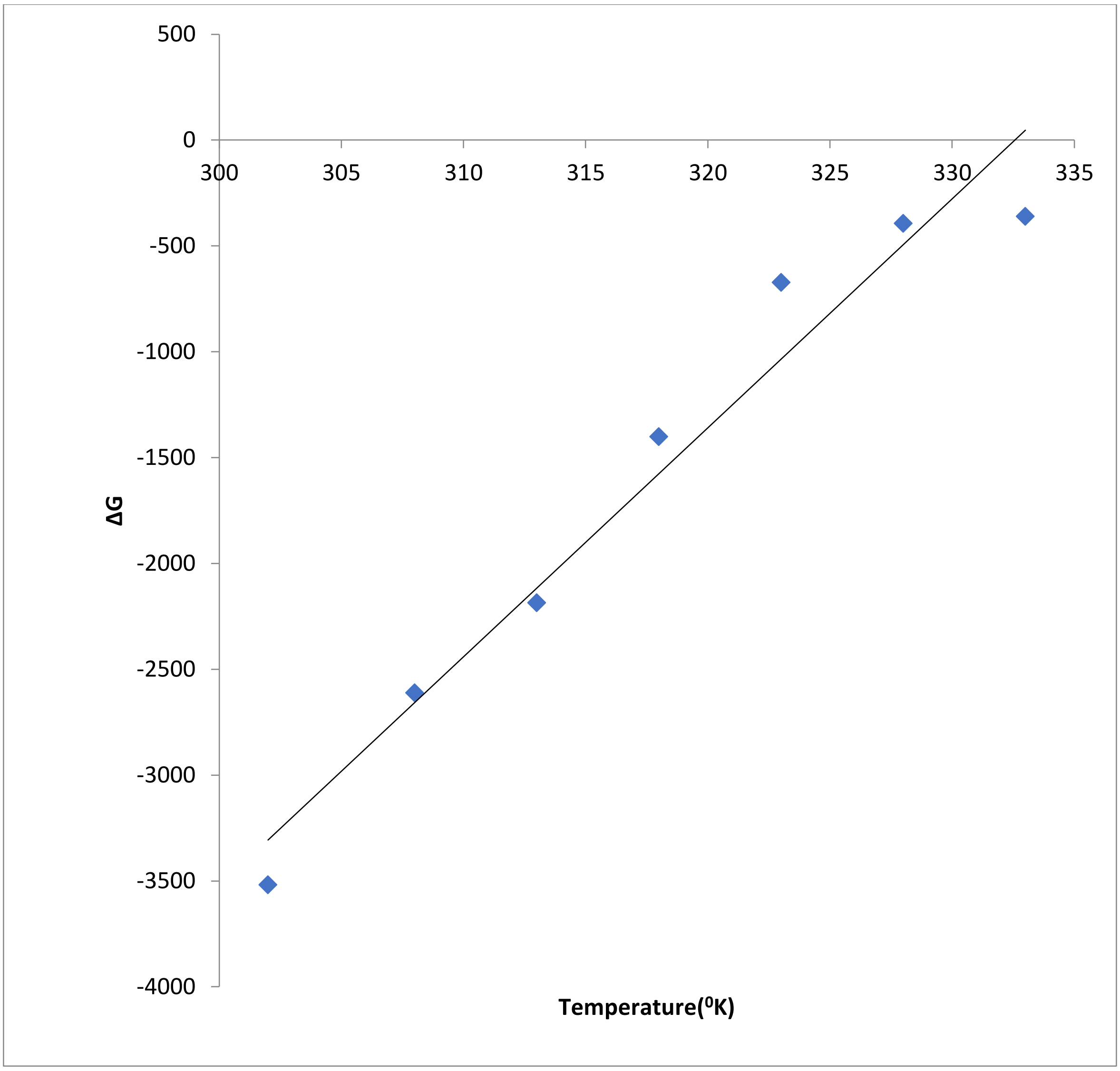


Figure 4.19: Thermodynamics of 4-Chlorophenol adsorption onto $ZnCl_2$ activated oil bean seed shells.

ΔS^0 = 112.41 kjmolk^{-1}

ΔH^0 = -3733.7

Table 4.30: The thermodynamics of hydroquinone onto $ZnCl_2$ activated oil bean seed shells.

Temperature (K)	**C_e (mg/l/)**	**C_{adc} (mg/)**	**K_o= C_{adc}/C_e**	**lnK_o**	**$\Delta G = -RTlnK_o$**
303	6.4	33.6	5.25	1.65	-4156.5
308	9.4	30.6	3.25	1.19	-3047.2
313	11.2	28.8	2.57	0.97	-2524.2
318	12.4	27.6	2.25	0.79	-2088.6
323	16.0	24.0	1.50	0.41	-1101.0
325	18.4	21.6	1.12	0.16	-428.1
333	19.0	21.0	1.11	0.10	-276.8

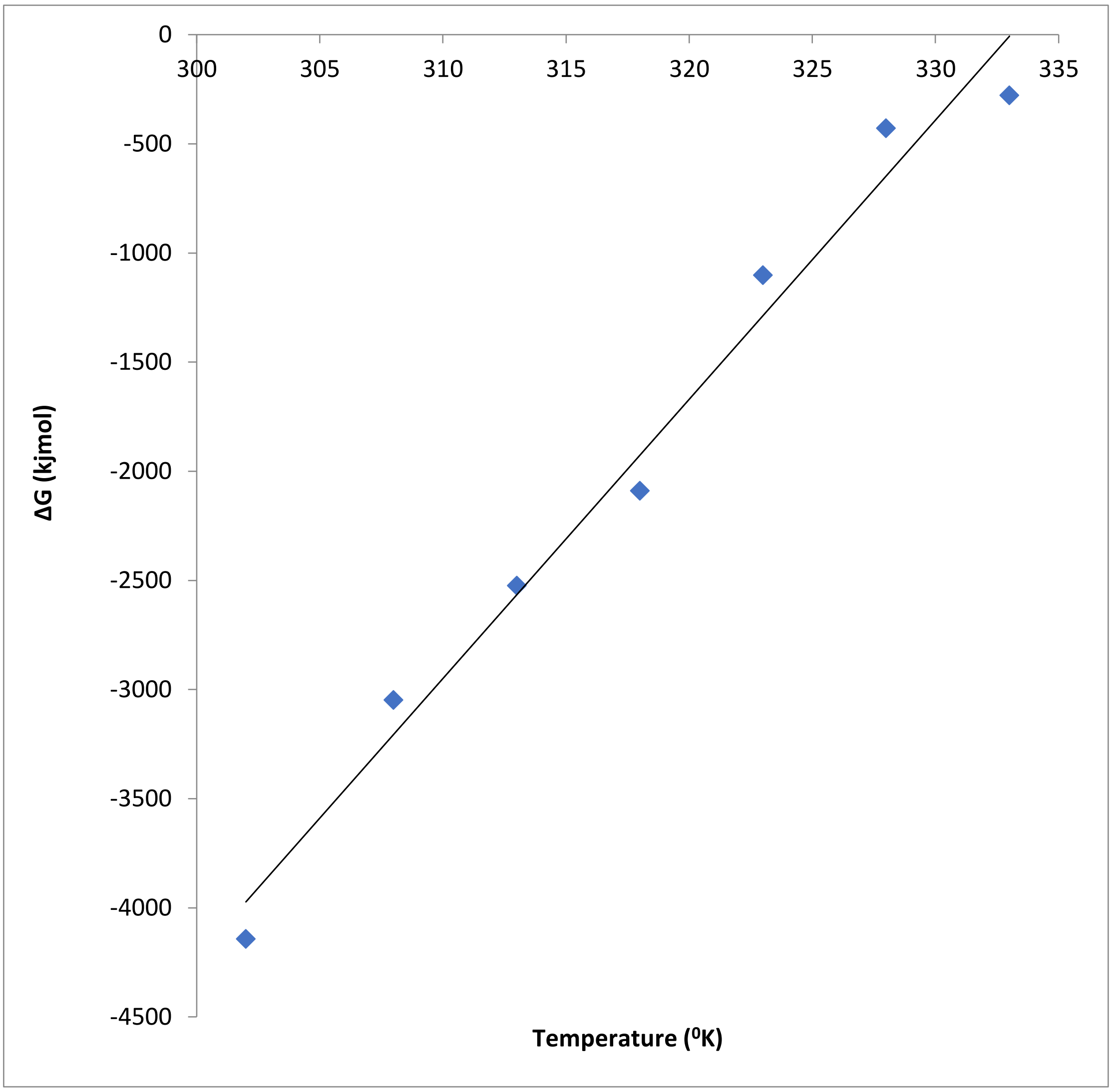


Figure 4.20: The thermodynamics of the adsorption of Hydroquinone onto $ZnCl_2$ activated oil bean seed shells.

$\Delta S^0 = 142.12kjmolk^{-1}$

$\Delta H^0 = -4700$

Table 4.31: The thermodynamics of the adsorption of 4-Chlorophenol onto H_3PO_4 activated oil bean seed shells.

Temperature (K)	**C_e (mg/l)**	**C_{adc} (mg/l)**	**$K_o = C_{adc}/C_e$**	**$\ln K_o$**	**$\Delta G = -RT\ln K_o$**
303	9.10	30.90	3.40	1.22	-3073.4
308	11.50	28.50	2.47	0.90	-2314.8
313	14.20	25.80	1.82	0.60	-1561.3
318	15.46	24.54	1.58	0.46	-1216.2
323	18.28	21.72	1.18	0.17	-443.1
328	21.00	19.00	1.11	0.104	-283.6
333	19.90	20.10	1.01	0.01	-26.6

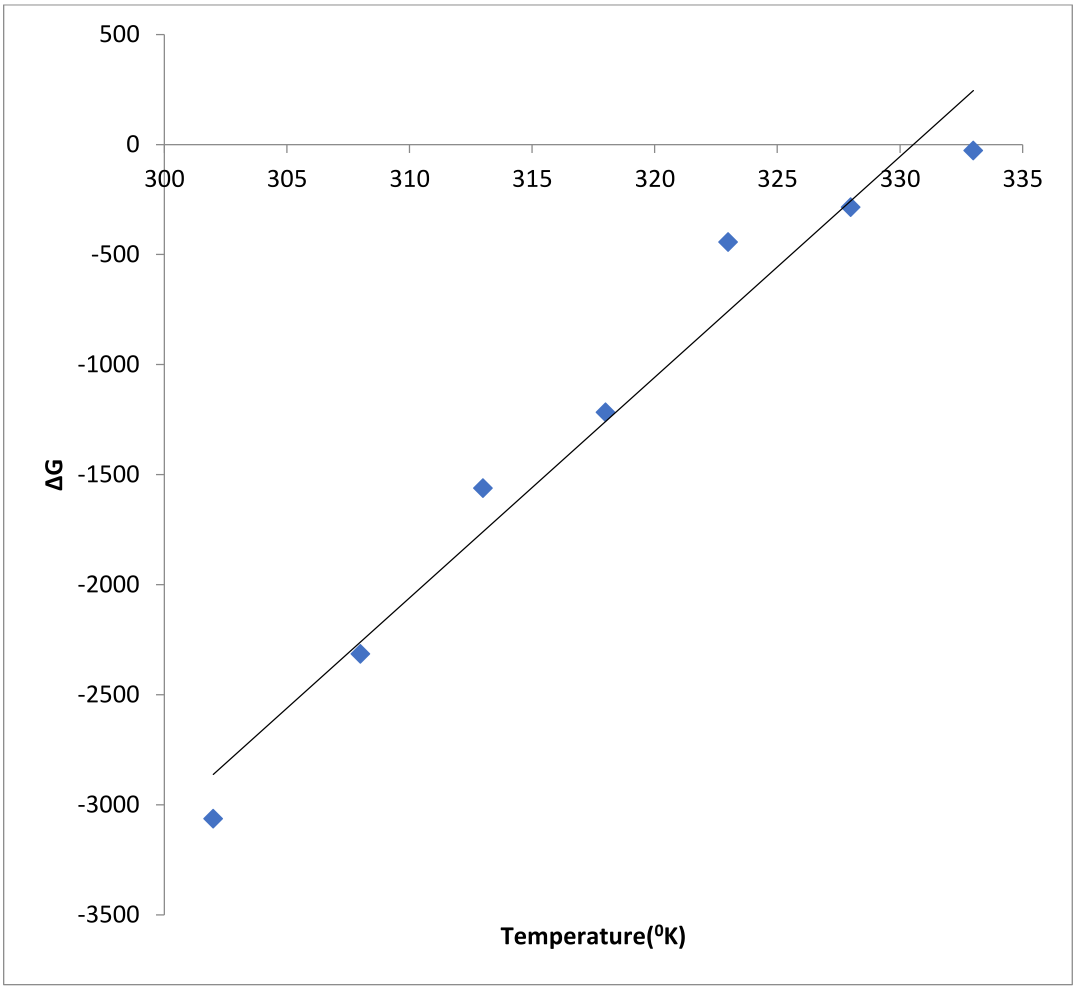


Table 4.21: The thermodynamics of the adsorption of 4-Chlorophenol onto H_3PO_4 activated oil bean seed shells.

ΔS^o = 102.26 kjmolk^{-1}

ΔH^o = -3379.3

Table 4.32: The thermodynamics of the adsorption of Hydroquinone onto H_3PO_4 activated oil bean seed shells.

Temperature (K)	**C_e (mg/l)**	**C_{adc} (mg/l)**	**K_o= C_{adc}/C_e**	**InK_o**	**ΔG = -RTlnK_o**
303	7.90	32.10	4.06	1.40	-3526.8
308	10.60	29.40	2.77	1.02	-2611
313	12.10	27.90	2.31	0.84	-2185.9
318	14.80	25.20	1.70	0.53	-401.2
323	17.50	22.50	1.28	0.25	-671.35
328	18.08	21.92	1.15	0.14	-392.7
333	18.70	21.30	1.14	0.130	-360.0

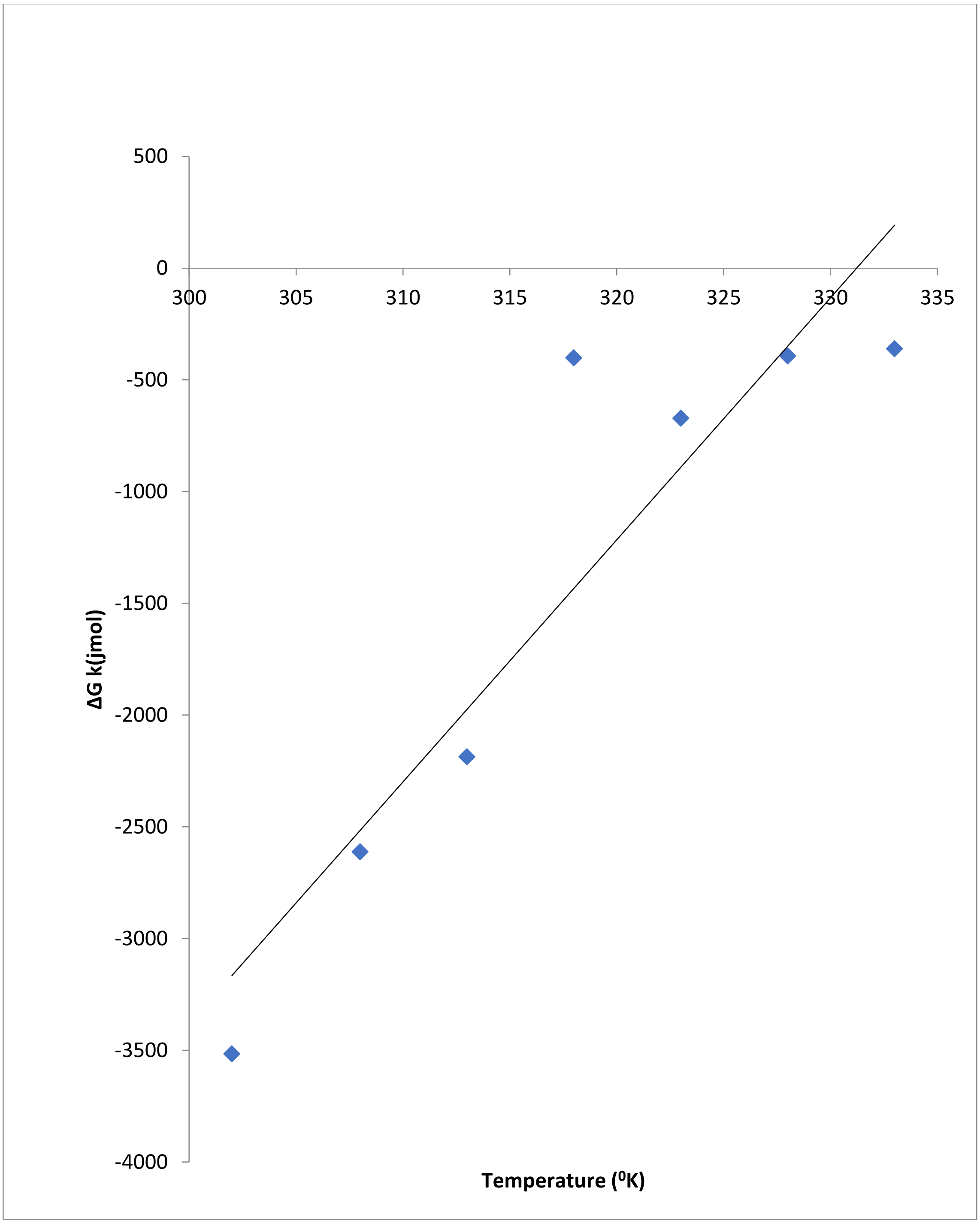


Figure 4.22: The thermodynamics of the adsorption of Hydroquinone onto H_3PO_4 activated oil bean seed shells.

$\Delta S^o = 110.75$ kjmolk^{-1}

$\Delta H^o = -3654$

4.7. ADSORPTION ISOTHERM

The adsorption behavior of this study can be satisfactorily described by using equation state between the two phases composing the adsorption system. The best fit was achieved using Freundlich isotherm.

Freundlch isotherm is given by the equation;

$q_e = k_f . C_e^{1/n}$

where, q_e(mg/g) is the amount of 4-Chlorophenol or Hydroquinone adsorbed at equilibrium.

C_e (mg/l) is the concentration of 4-Chlorophenol or Hydroquinone in solution at equilibrium.

k_f (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. The linearization of Freundlich isotherm yield

$\log q_e = \log k_f + 1/n \log C_e$

The plot of log q_e against log C_e yields a straight line in which k_f and n can be obtained from intercept and slope respectively.

The adsorption capacity, k_f and adsorption intensity, n for 4-Chlorophenol were calculated to be 0.75 and 1.0 (for $ZnCl_2$ activated carbon), 0.82 and 0.96 (for H_3PO_4 activated oil bean seed shells) respectively and 0.878 and 1.12 (for $ZnCl_2$ activated oil bean seed shellsf) and 0.827 and 0.90 (for H_3PO_4 activated oil bean seed shells). This shows that the adsorption study fitted Freudlich adsorption isotherm

Table 4.33: Freundlich isotherm of contact time at 30 mg/l of 4-Chlorophenol adsorption onto $ZnCl_2$ activated oil bean seed shell.

C_e	**Log C_e**	**q_e**	**Log q_e**
16.35	1.214	2.73	0.436
18.90	1.276	3.15	0.498
19.30	1.286	3.25	0.519
21.00	1.322	3.50	0.544
23.50	1.371	3.92	0.593
23.50	1.371	3.92	0.593
23.50	1.371	3.92	0.593
23.50	1.371	3.92	0.593

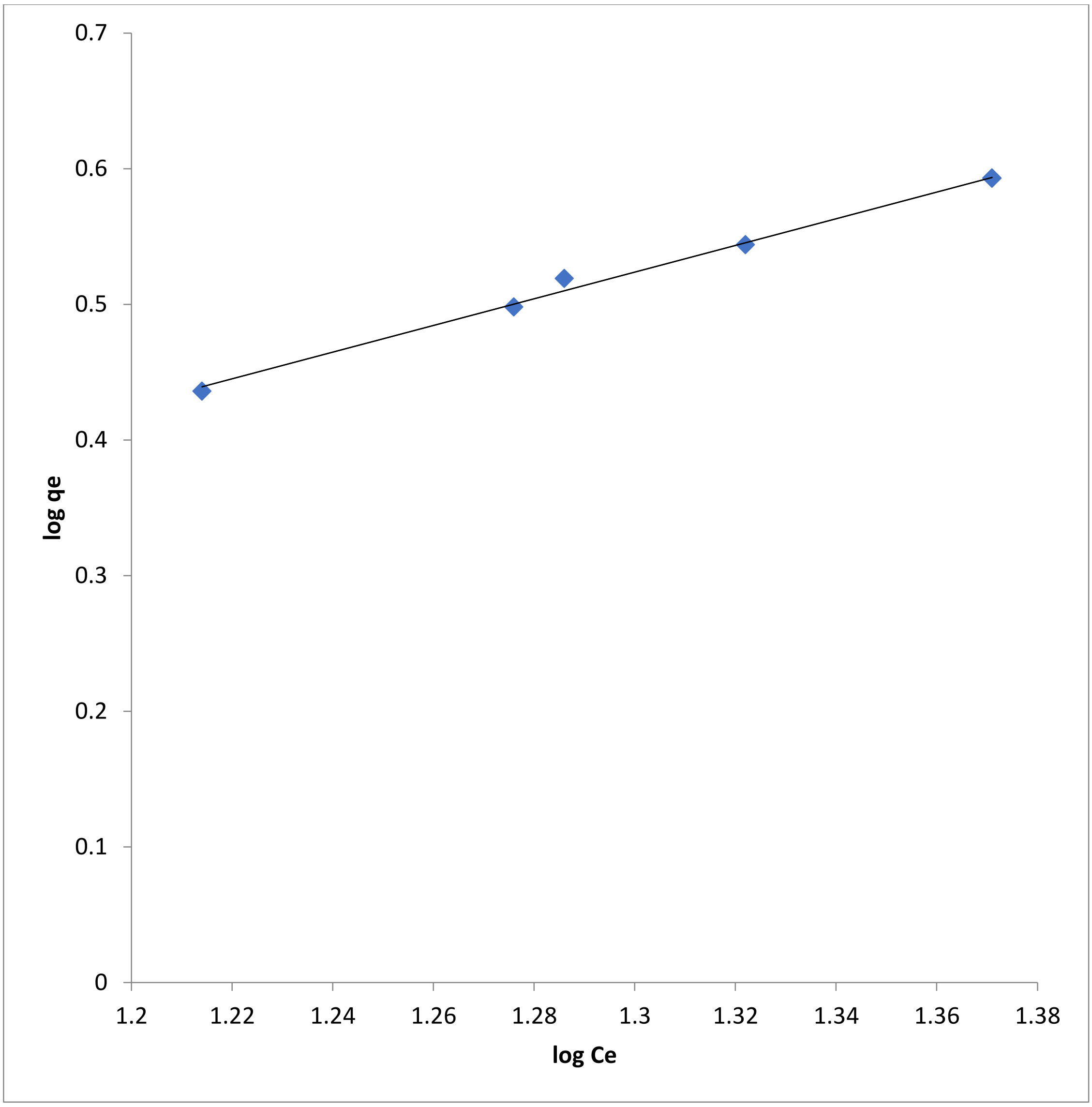


Figure 4.23: Freundlich isotherm of contact time at 30 mg/l of 4-Chlorophenol adsorption onto activated oil bean seed shell.

n=1.006

k_f= 0.754

Table 4.34: Freundlich isotherm of contact time at 30 mg/l of Hydroquinone adsorption onto $ZnCl_2$ activated oil bean seed shells.

C_e	Log Ce	q_e	Log q_e
17.80	1.250	2.96	0.500
20.50	1.311	3.42	0.539
23.00	1.360	3.83	0.583
25.60	1.408	4.27	0.630
26.80	1.428	4.47	0.650
26.80	1.428	4.47	0.650
26.80	1.428	4.47	0.650
26.80	1.428	4.47	0.650

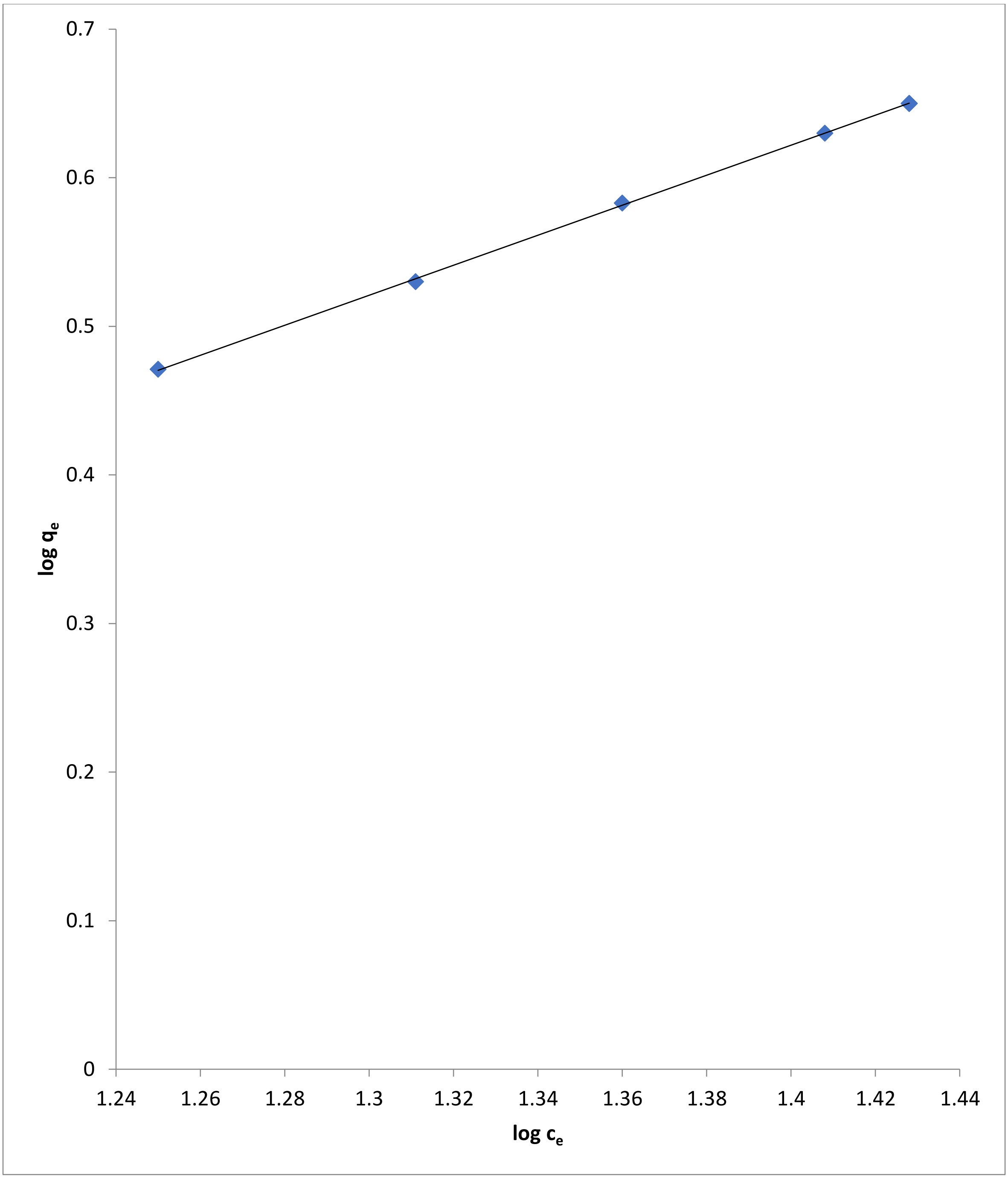


Figure 4.24: A plot of the Freundlich isotherm of contact time at 30 mg/l of Hydroquinone adsorption onto $ZnCl_2$ activated oil bean seed shell.

n=1.12

k_f = 0.626

Table 4.35: Freundlich isotherm of contact time at 30mg/l of 4-Chlorophenol adsorption onto H_3PO_4 activated oil bean seed shells.

C_e	Log C_e	q_e	Log q_e
15.10	1.179	2.51	0.400
17.40	1.241	2.90	0.462
19.00	1.279	3.17	0.501
20.10	1.303	3.35	0.525
20.10	1.303	3.35	0.525
20.10	1.303	3.35	0.525
20.10	1.303	3.35	0.525
20.10	1.303	3.35	0.525

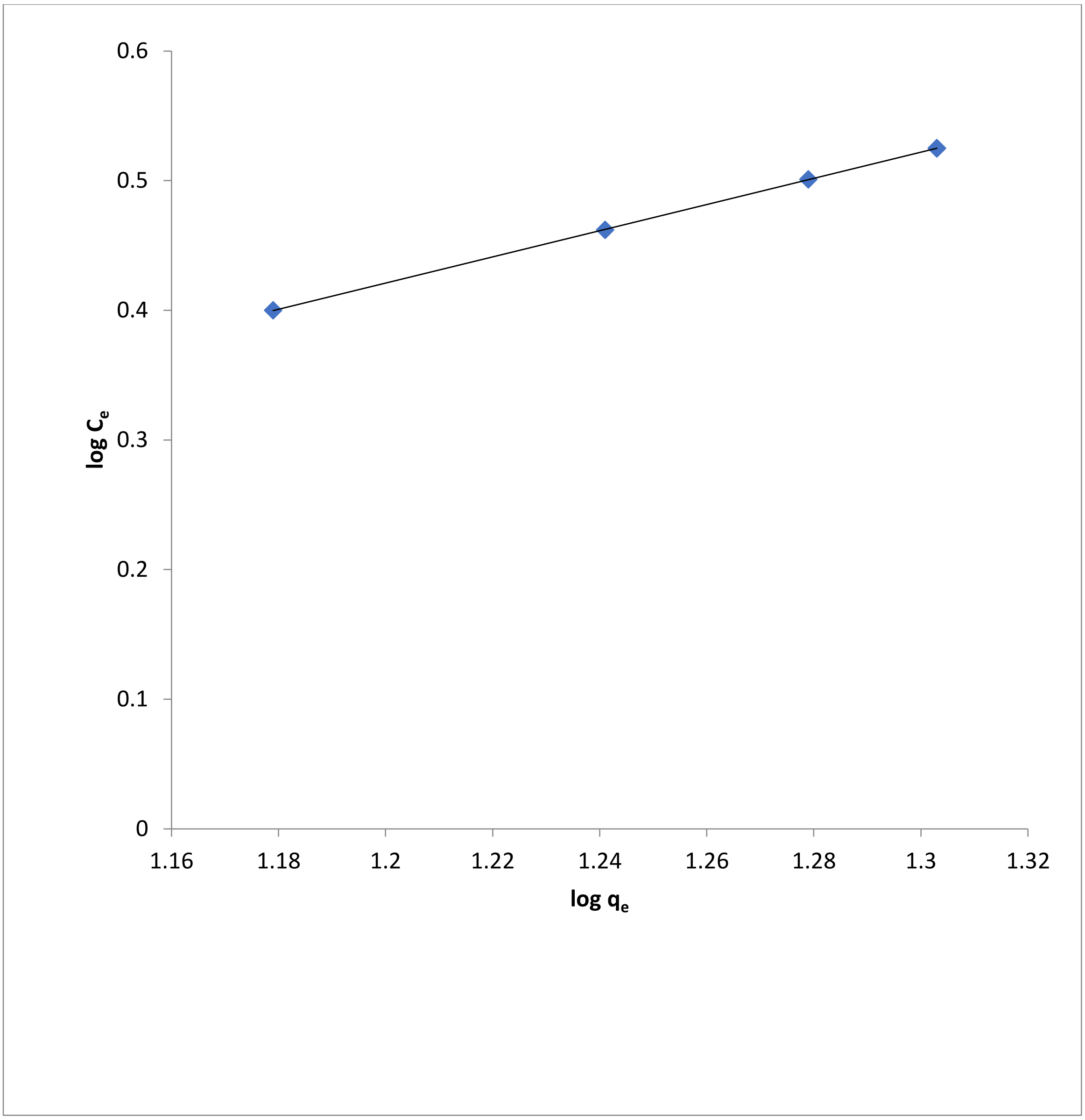


Figure 4.25: A plot of Freundlich isotherm of contact time at 30 mg/l of Hydroquinone adsorption onto $ZnCl_2$ activated oil bean seed shells.

n = 0.96

k_f = 0.821

Table 4.36: Freundlich isotherm of contact time at 30mg/l of hydroquinone adsorption onto H_3PO_4 activated oil bean seed shells.

C_e	Log C_e	q_e	Log q_e
16.00	1.200	2.60	0.415
19.50	1.290	3.25	0.512
22.00	1.340	3.60	0.550
22.80	1.350	3.80	0.580
22.80	1.350	3.80	0.580
22.80	1.350	3.80	0.580
22.80	1.350	3.80	0.580
22.80	1.350	3.80	0.580

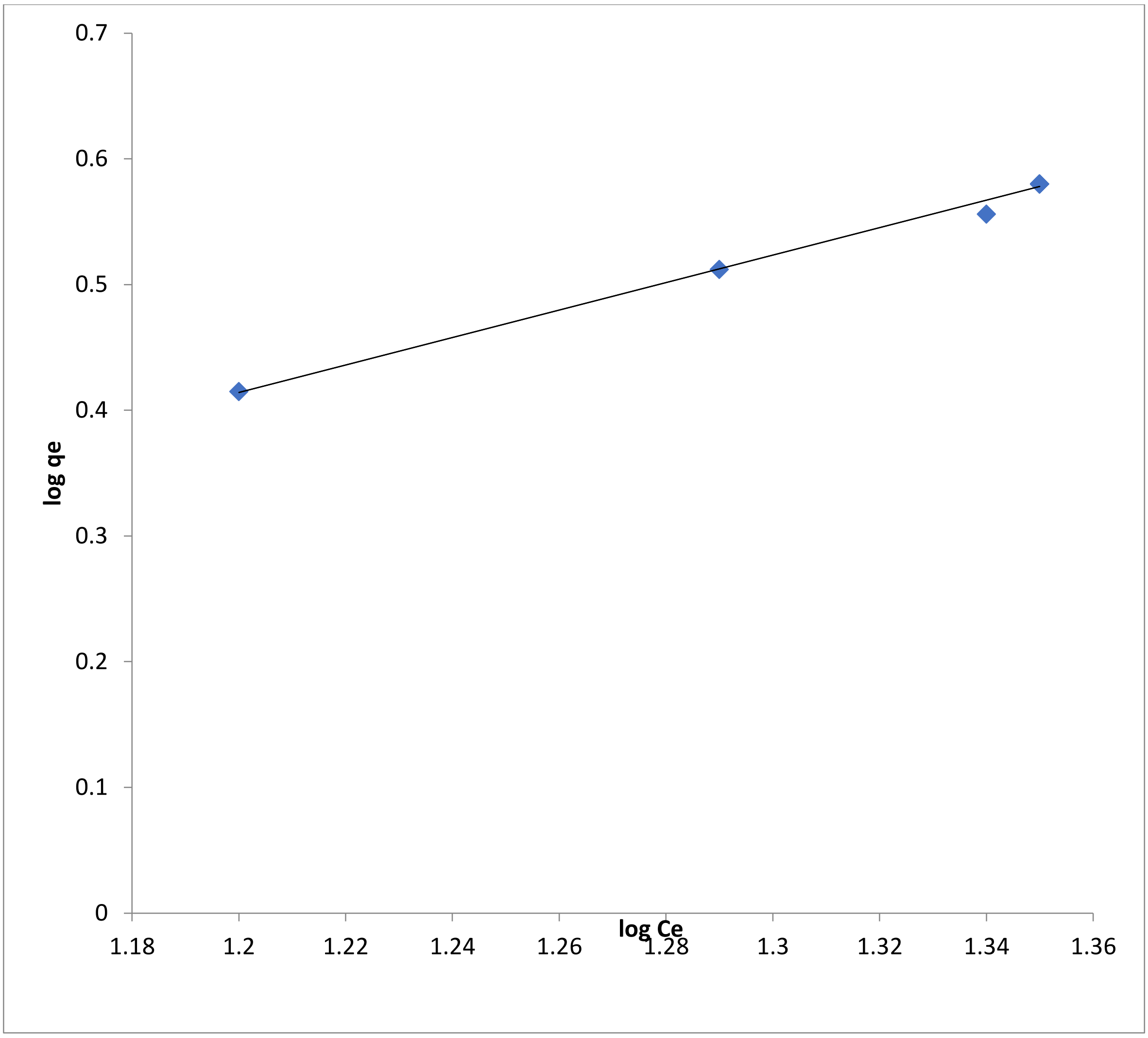


Figure 4.26: A plot of Freundlich isotherm of contact time at 30 mg/l of hydroquinone adsorption onto H_3PO_4 activated oil bean seed shell.

n=0.90

k_f= 0.896

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This study indicates that oil bean seed shell is a good adsorbent for the removal of toxic solvent from waste water. The kinetic study indicates that hydroquinone and 4-Chlorophenol was adsorbed onto oil bean seed shells rapidly within the first 20 minutes, while equilibrium was established within 50 minutes (for $ZnCl_2$ activated oil bean seed shells), and within 40 minutes (for H_3PO_4 activated oil bean seed shells) for both concentrations of hydroquinone and 4-Chlorophenol studied for both concentrations respectively. The investigation revealed that Hydroquinone and 4-Chlorophenol uptake was high at pH4. The Gibbs free energy change ΔG^o, ΔS^o, and ΔH^o were negative for 4-Chlorophenol and Hydroquinone adsorption onto oil bean seed shells which indicates that the adsorption processes was spontaneous. This study also revealed that adsorption process was high at low temperature for Hydroquinone and 4-Chlorophenol onto oil bean seed shells.

5.2 RECOMMENDATION

Oil bean seed shell is a cheap Agricultural waste that can be recommended for an effective adsorption of Hydroquinone and 4-chlorophenol, toxic metallic ions and also in oil pollution remediation in oil communities than using imported chemical adsorbent for such purposes. It can also be recommended as a good source of revenue earner because using oil bean seed shell adsorbent will save a huge amount of money for the company and manufacturers since it is less expensive, and also can be sourced locally than when compared to other chemical adsorbents. It is therefore recommended for industries. I also recommend a study on the toxicity of 4-Chlorophenol and hydroquinone.

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