ADSORPTION STUDIES OF PHENOL USING ACTIVATED CARBON
PREPARED FROM GROUNDNUT SHELL

A Thesis submitted in partial fulfillment of the requirements for the degree of

Bachelor of Technology in Chemical Engineering

BY

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CERTIFICATE

This is to certify that the thesis entitled "**Adsorption Studies of Phenol using Activated Carbon Prepared from Groundnut Shell"** submitted by **Bibhuti Kumar Swain** (110CH00089) in partial fulfillment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To best of knowledge, the matter embodied in this thesis has not been submitted to any other university or institute for the award of any degree.

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Nomenclatures

ACs	Activated Carbons
IR	Impregnated Ratio
m	Mass of adsorbent in grams
V	Volume of the phenol solution
C_o	Initial concentration of phenol
C_t	Final concentration of phenol after adsorption
q_e	Amount of phenol adsorbed per unit mass of the adsorbent
K_L	Free energy of adsorption (Langmuir parameter)
q_o	Maximum adsorption capacity (Langmuir parameter)
K_F	Adsorption capacity (Freundlich parameter)
n	Adsorption intensity (Freundlich parameter)
PPM	Parts per million
PAC	Powered Activated Carbon
GAC	Granular Activated Carbon

Abstract

Due to the rapid urbanization and increasing world population, the need for fresh, clean and uncontaminated water has become a problem of great importance since many sources have been exhausted and others are likely to be contaminated. Phenol is very toxic substance even at low concentration. The major industries that discharge phenolic wastewater include petroleum refineries, petrochemicals, textile, dye manufacturing, phenolic resin manufacturing, glass fiber units, varnish industries and smelting related to metallurgical operations. Activated carbons are the most widely used adsorbents due to their excellent adsorption abilities for organic pollutants.

In the present study, Activated carbons were prepared from biomass by chemical activation, using Na_2CO_3 as a chemical agent for our research work preparation of activated carbon from biomass i.e. peanut shell. The effects of different parameters, such as chemical/biomass ratio, activation time and activation temperature, weight loss, proximate analysis, TGA, FTIR and iodine number of the produced activated carbons will be studied. The adsorption capacity of the activated carbons was evaluated through phenol adsorption and adsorption isotherms were plotted. . It was found that yield % decreased with increase in both temperature and concentration of acid. It was found that the ACs prepared at 700 °C temperature and 100 % impregnation ratio had highest no of microporosity, which was determined by iodine number. The iodine number of the sample was 543.4 mg/g. In the phenol adsorption experiment the increase in dosage showed increased phenol removal efficiency and with increase in phenol concentration the decrease in removal efficiency, but with increase in phenol concentration decreased the phenol removal efficiency. Langmuir and Freundlich isotherms plot were drawn from equilibrium isotherm data. The Freundlich isotherm was much better fit than the Langmuir isotherm.

Key words: Phenol, Adsorption, Activated carbon, Na_2CO_3

CHAPTER 1

INTRODUCTION &

LITERATURE REVIEW

1. Introduction & Literature Review

Due to the rapid urbanization and increasing world population, the need for fresh, clean and uncontaminated water has become a problem of great importance since many sources have been exhausted and others are likely to be contaminated. Toxic wastes are being released into the environment, causing extensive environmental contamination such that many of our natural water reserves are damaged beyond repair. Many organic compounds are present in industrial wastewater, affecting water quality, human health and biodiversity in the ecosystems. Humans, who are acutely exposed to phenol by the oral route, suffer damage in blood, liver, kidney and cardiac toxicity including weak pulse, cardiac depression and reduced blood pressure. Due to these adverse health effects of phenolic, the World Health Organization (WHO) has set a permissible upper limit of 1 mg/L to regulate the phenol concentration in drinking waters.

1.1. Phenol

Phenol is an organic compound having formula C_6H_5OH. The molecule consists of a phenyl group ($-C_6H_5$) bonded to a hydroxyl group (-OH). It is a white crystalline solid .It is volatile and mildly acidic in nature. Phenol is used to make pharmaceuticals, synthetic resin, dyes, pesticides, synthetic tanning agents, lubricating oils and solvents. Phenol is very toxic substance even at low concentration. Acute exposure of phenol can result in myocardial depression and central nervous system disorders. Exposure to phenol may result in irritation of the eye, conjunctional swelling, corneal whitening and finally blindness. It leads to collapse and coma. A reduction in body temperature is resulted and this is known as hypothermia. Mucus membrane is highly sensitive to the action of phenol. Muscle weakness and tremors are also observed. Phenol has an anesthetic effect and causes gangrene. Renal damage and salivation may be induced by continuous exposure to phenol. Chronic exposure may result in anorexia, dermal rash, dysphasia, vomiting, weakness, weightlessness, muscle pain and hepatic tenderness .Other effects include frothing from nose and mouth followed by headache. Phenol can cause hepatic damage also. It is also suspected that exposure to phenol may cause paralysis, cancer. Hence phenol and its derivatives are classified as hazardous materials by EPA.

Several treatment methods are available for treating the phenolic waste water like granular activated carbon based adsorption, reverse osmosis, stripping-oxidation and distillation processes etc (Teng et al ., 1998). All of these are used for treating organic and inorganic waste. Most of these methods suffer from some drawbacks, such as high capital and operational cost, regeneration

cost, and problem of residual disposal. Liquid phase adsorption has been shown to be a highly efficient, well-established technique for the removal of organic compounds due to its simplicity, adsorbent cost effectiveness and the availability of a wide range of adsorbents (Ma et al., 2013). Generally, the conventional water treatment processes (coagulation–sedimentation–filtration) were difficult to remove these phenolic compounds effectively in polluted source water. PAC adsorption pretreatment processes may be employed to increase the conventional treatment performance on removing phenolic compounds, because powdered activated carbon is an inexpensive treatment option (capital cost) that can readily be added to an existing water treatment system. Among various technologies, the adsorption technology which is simple and effective has been used extensively for the removal of phenol. There are various adsorbents in use and activated carbons are the most widely used adsorbents due to their excellent adsorption abilities for organic pollutants.

1.2. Activated Carbon

Activated carbon is an amorphous carbon-based material which has a highly developed porosity and an extended interparticulate surface area and used for the removal of liquids and gaseous pollutants as well for the gas storage application (Bagheri et al., (2009). Activated carbons contain mainly micropores, but they also contain meso and macropores, which is very significant in helping contact of the adsorbate molecules to the interior of carbon particles (Ahmadpour et al., 1995). These pores can be classified into three categories (IUPAC Manual., 1972) i.e. Micropores <2 nm, Mesopores 2-50 nm, Macropores >50 nm. Adsorption by activated carbons (ACs) is one of the most commonly used because ACs possesses perfect adsorption ability for that class of compounds.

1.2.1. Classification of Activated Carbon

The general classification of activated carbons based on particle size divides them into Powered Activated Carbon (PAC) and Granular Activated Carbon (GAC).

1.2.1.1. Powered Activated Carbon

Powered Activated Carbon (PAC), has a typical particle size of less than 0.1 mm and the common size of the particle ranges from 0.015 to 0.025 mm. Typical applications of PAC are industrial and municipal waste water treatments, sugar decolorization, in food industry, pharmaceutical, and mercury and dioxin removal from a flue gas stream (Satyawali and Balakrishanan, 2009).

1.2.1.2. Granular Activated Carbon

Granular Activated Carbon (GAC) has mean particle size between 0.6 to 4 mm. It is usually used in continuous processes of both liquid and gas phase applications. GAC has an advantage over PAC, of offering a lower pressure drop along with the fact that it can be regenerated and therefore reused more than once. In addition to the proper micropore size distribution, its high apparent density, high hardness, and a low abrasion index made GAC more suitable over PAC for various applications (Scharf et al., 2010;).

1.3. Adsorption by activated carbons

In an adsorption process, molecules atoms or ions, in a gas or liquid diffuse to the surface of a solid, where they bond with the solid surface or are held there by weak intermolecular forces. The adsorbed solutes are referred to as adsorbate, whereas the solid material is the adsorbent. To achieve a very large surface area for adsorption per unit volume, highly porous solid particles with small-diameter interconnected pores are used, with the bulk of the adsorption occurring within the pores. The process of adsorption is broadly divided into two categories depending on the type of forces involved between adsorbent and adsorbate-physiorption and chemisorption. Physiorption involves intermolecular forces of attraction between the adsorbent and the adsorbate. It is based on the simple fact that all molecules exhibit attractive forces. Due to the difference in concentration of the adsorbate between the solution and the adsorbent, the adsorbate migrates through the pore structure to reach the point of maximum attractive forces and gets deposited on the surface. Chemisorption involves chemical bonding or interaction between the adsorbent and the adsorbate (Seader Smith., Separation Process Principles). The adsorption performance of an activated carbon cannot be understood on the basis of surface area and pore size distribution alone as carbon surface has an exclusive character. It consists of porous structure which controls its capacity for adsorption; it has a chemical arrangement which impacts its interaction with polar and nonpolar adsorbate. It consists of active sites in the form of edges, discontinuities and dislocations which regulates its chemical reactions with other atoms.

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.

PAC (Powered Activated Carbon) adsorption pretreatment processes may be employed to increase the conventional treatment performance on removing phenolic compounds, because powdered

activated carbon is an inexpensive treatment option (capital cost) that can readily be added to an existing water treatment system. Among various technologies, the adsorption technology which is simple and effective has been used extensively for the removal of phenol. There are various adsorbents in use and activated carbons are the most widely used adsorbents due to their excellent adsorption abilities for organic pollutants (Tancredia et al., 2004).

As activated carbons are excellent adsorbents, their application find way for the removal of color, odor, taste, food processing, purification of many chemicals, pharmaceutical products, in respirators for work under hostile environments and undesirable organic and inorganic pollutants from drinking water. It is used in medicine and health applications to combat certain types of bacterial ailments and for the adsorptive removal of certain toxins and poisons, and for the purifications of blood.

Ania et al., (2002) had investigated the effect of texture and surface chemistry on adsorptive capacities of activated carbons for phenolic compounds removal. They used three microporous commercial activated carbons (AC) were used for the adsorption of phenol and salicylic acid from aqueous solution and they found that long periods of time were needed for reaching equilibrium. Carbons with high oxygen content were found to present lower adsorptive capacities for both phenol and salicylic acid.

Bandosz et al., (2003) had studied adsorption of aromatic compounds from solution, particularly phenols, has been studied extensively. The adsorption process depends on several factors, which include the nature of the adsorbent, adsorbate, and adsorption conditions. It is found that the uptake of phenol is a combined effect of physiorption and surface polymerization. Phenol adsorption from solution (at trace concentrations) was studied at temperatures close to ambient without maintaining a specific pH of the solution. The results showed, as expected, that the phenol uptake is dependent on both the porosity and surface chemistry of the carbons. Furthermore, phenol adsorption showed a strong dependence on the number of carboxylic groups due to two factors: (1) phenol reacts with carboxylic groups on the carbon surface, forming an ester bond, and (2) carboxylic groups on the carbon surface remove the π-electron from the activated carbon aromatic ring matrix, causing a decrease in the strength of interactions between the benzene ring of phenol and the carbon's basal planes, which decreases the uptake of phenol.

Lambert et al., (2009) had reported that phenol adsorption on carbons depends on porosity, but more importantly on the surface chemistry of the carbons. Phenol adsorption is governed by non-

electrostatic interactions, such as dispersion, hydrophobic or donor–acceptor interactions between the surface carbonyl groups (electron donors) and the aromatic rings of phenol acting as acceptor.

1.4. Preparation of activated carbons from biomass

The most commonly used raw materials for the preparation of activated carbons in commercial practice are peat, coal, lignite, wood and agricultural by-products. Production of activated carbon from agricultural by-products serves a double purpose by converting unwanted, surplus agricultural waste to useful, valuable material and provides an efficient adsorbent material for the removal of organic pollutants from water/waste water. There are a large number of studies regarding the preparation of activated carbon from a variety of raw materials, such as coal, wood char, petroleum and biomass, which includes by-products, bagasse fly ash, tamarind nut, soya bean hulls and coconut husk (Singh et al., (2008). Basically, there are two different processes for the preparation of activated carbon physical and chemical activation. Physical activation involves the carbonization of a carbonaceous precursor followed by activation of the resulting char in the presence of some mildly oxidizing gases such as carbon dioxide or steam. The other method chemical activation consists of carbonization at a relatively low temperature (e.g. 400–700°C) in the presence of a dehydrating agent (e.g. $ZnCl_2$, KOH and H_3PO_4). These chemical reagents may promote the formation of cross-links, leading to the formation of a rigid matrix, less prone to volatile loss and volume contraction upon heating to high temperatures (Barret et al., (1951).

Teng et al., (1998) had prepared activated carbon from bituminous coal with phosphoric acid activation shows maximum values of surface area and pore coal was compared with that of the untreated coal. The surface area and pore volume of the resulting carbons increase with the chemical ratio, H_3PO_4 /coal. The development of porosity is also accompanied by a widening of the porosity as the amount of H_3PO_4 is increased.

Kennedy et al., (2007) had prepared mesoporous activated carbons from rice husk using phosphoric acid as a chemical activating agent through physico-chemical activation method. The surface area, pore volume and pore size distribution of carbon samples activated at three different temperatures 700, 800 and 900 °C have been carried out using nitrogen adsorption isotherms at 77 K. The production yield was observed to decrease with increase in activation temperature. Those mesoporous carbons had registered a maximum uptake of phenol of 2.35×10^{-4} mol/g at 20 °C and final pH of 2.7.

Hannafi et al., (2008) had prepared activated carbons from the date cores for the purpose of aqueous phase phenol adsorption. For that they have used chemical mode of activation, several activating agents were tested for the preparation of the activated carbon but best results was obtained with the phosphoric acid with 54% of yield elimination. It was also found that temperature was practically not influencing phenol elimination while using this activated carbon for the purpose; consequently, tests of adsorption were carried out at the ambient temperature.

Altenor et al., (2009) had prepared activated carbons (ACs) by chemical activation method from Vetiver roots maintaining different impregnation ratios of phosphoric acid, XP (g H_3PO_4/g precursor) = 0.5:1; 1:1 and 1.5:1. Textural characterization was determined by nitrogen adsorption at 77K shows that mixed micropores and mesoporous structures activated carbons (ACs) with high surface area (>1000 m^2/g) and high pore volume (up to 1.19 cm^3/g) can be obtained. Their textural and chemical characteristics were compared to those of an AC sample obtained by steam activation of vetiver roots.

Bagheri et al., (2009) had Activated carbons through chemical activation of biomass, i.e. corn cobs, using potassium hydroxide as the chemical agent. The effects of different parameters, such as particle size, method of mixing, chemical/biomass ratio, activation time and activation temperature, on pore size distribution, weight loss and BET surface area of the produced activated carbons were investigated. It was found that the chemical/biomass ratio and the method of mixing were the most important parameters in the chemical activation of biomass. The porosity and storage capacity of the activated carbons were evaluated through nitrogen adsorption and methane adsorption, respectively. Under the experimental conditions investigated, the optimal conditions for production of high surface area carbons by chemical activation were identified.

Din et al., (2009) had prepared coconut shell-based activated carbon, (CS850A) for liquid phase adsorption of phenol. Coconut shell was converted into high quality activated carbon through physiochemical activation at 850 °C under the influence of CO_2 flow. Beforehand, the coconut shell was carbonized at 700 °C and the resulted char was impregnated with KOH maintaining an impregnation ratio of 1:1 w/w. They found an impressive adsorption capacity for CS850A of 205.8 mg/g carbons.

Dash and Murthy (2010) had studied the activated carbon preparation from *Shorea robusta* leaf litter, a non-convectional material, as a novel material for preparation of carbonaceous adsorbent

impregnated with phosphoric acid, used for the reduction of Zinc and Copper metal ions from aqueous phase. Basically they have followed chemical activation method.

1.5. Characterization of activated carbon

Various methods are used for characterization of activated carbon. Ultimate and proximate analysis are used to find out the elemental analysis of the activated carbon and the moisture content, volatile matter, ash content and fixed carbon are known. Scanning electron Microscope (SEM) is used to visualize the porous structure of the activated carbon. The X-ray photoelectron spectroscopy (XPS) and Boehm titration are used to study surface chemical properties of these ACs. FTIR is used to find out the functional groups present in ACs. In FTIR, infrared radiation is passed through the sample. A part of this radiation is absorbed by the sample and the other part is transmitted. This produces a spectrum in the form of transmittance/absorbance plotted against the wave number. This spectrum represents a fingerprint of the sample with absorption peaks corresponding to the frequencies of vibrations between the bonds of the atoms which make up the material. Thus, it gives an idea about the organic functional groups present in the sample. Thermo-gravimetric analysis measures the loss in weight of a material with respect to temperature and time. The analysis can be done in an atmosphere of air or nitrogen as per requirement. The analyzer is fitted with sensors which gives the weight of the sample at various times. It helps to determine an approximate working range of temperature for activation process. The parameters required for analysis are heating rate, maximum temperature, and holding time. The surface areas of activated carbons are usually measured using the Brunauer-Emmett-Teller (BET) method, which employs the nitrogen adsorption at different pressures at the temperature of liquid nitrogen. Adsorption test with Iodine and methylene blue provides Additional information about the porous structure of activated carbons. Phenol and methylene blue are commonly used as model compound in order to assess the adsorption ability of ACs. According to the dimensions of the methylene blue molecule, it is mainly adsorbed in mesopores. In relation to methylene blue, the iodine molecule possesses inferior dimensions which make its penetration in micropores possible.

Figueiredo et al., (2011) had investigated the Effect of texture and surface chemistry for adsorption of phenol onto supercritically activated carbon fibres. ACFs were prepared by carbonization of a phenolic textile fiber under nitrogen flow, followed by activation with H_2O and CO_2 (under atmospheric pressure and supercritical state). The materials were 18 characterized by N_2 and CO_2 adsorption, and by temperature programmed desorption studies. The relationship

between surface oxygen concentration and amount of physiosorbed and chemisorbed phenol was assessed, and it was found that higher amounts of surface oxygen groups decreased the phenol chemisorption capacity of ACFs.

Activated carbons were prepared from biomass by chemical activation, using Na_2CO_3 as a chemical agent for our research work preparation of activated carbon from biomass i.e. peanut shell. The effects of different parameters, such as chemical/biomass ratio, activation time and activation temperature, weight loss, proximate analysis, TGA, FTIR and iodine number of the produced activated carbons will be studied. The adsorption capacity of the activated carbons was evaluated through phenol adsorption and adsorption isotherms were plotted.

1.6 Scope of the Study:

This study shall provide a detailed analysis of activated carbon prepared from chemical activation using Na_2CO_3 as chemical agent and peanut shell as a precursor and an effective solution to remove phenol from waste water with the development of a better adsorbent. Also this will provide an ideal method for better utilisation of peanut shell in to activated carbon which can be commercialized.

CHAPTER 2

<u>OBJECTIVES</u>

2.1.   Objectives

1. Preparation of Activated Carbon from peanut shell by chemical activation method using Na_2CO_3 as activating agent
2. Characterization of all the Activated Carbon for their various absorbable properties such as proximate analysis, TGA, Iodine number and FTIR.
3. Study of phenol adsorption

CHAPTER 3

<u>MATERIALS AND METHODS</u>

3.1   Preparation of Activated Carbon:

Raw Material	⇒	Cleaning/ Washing	⇒	Drying in oven at 110°C	⇒	Grind/ Sieve

⇓

Washing with 5% HCl Water	⇐	Carbonization at 500-700°C	⇐	Drying in oven at 110°C	⇐	Chemical activation

⇓

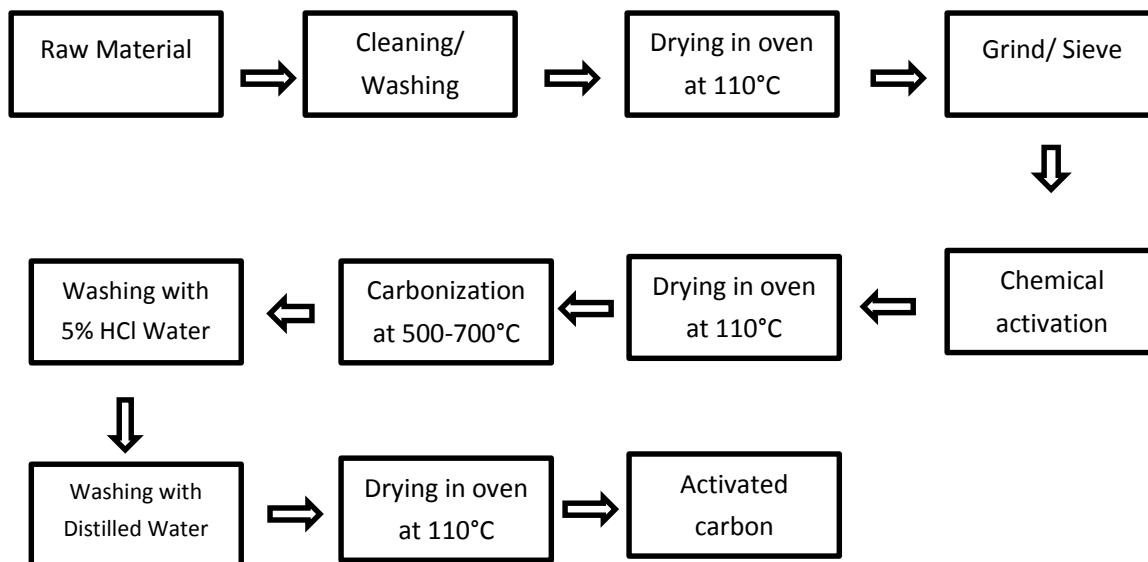| Washing with Distilled Water	⇒	Drying in oven at 110°C	⇒	Activated carbon

Fig 1 General flow sheet for the production of chemically activated Carbon

3.1.1   Adsorbent preparation

After collection of peanut shell, they were thoroughly cleaned and washed for 3-4 times under running tap water for removing impurities if any adhered to the Shells. Then the shells were air dried followed by drying at 100°C in hot air oven before crushing them down to powdered form using hand blender. These materials were impregnated with Na_2CO_3 with an impregnation ratio (w/w) chemical/biomass ratio of 0.5:1, 1:1, 1.5:1, 2:1 after soaking for 6 hours. It was dried before carbonization at 500 °C, 600 °C and 700 °C for 1 hour in an inert atmosphere using a Tubular furnace. The resulting material was again washed with 5% HCl. Then it was washed with warm and cold distilled water till it reached to normal pH level and dried for 12 hours. The samples of 500 °C burning temperature with impregnation ratio 50%, 100%, 150%, 200% were named as 5S1, 5S2, 5S3, 5S4 respectively. Similarly for 600 °C and 700 °C of burning temperature the samples were named from 6S1 to 6S4 and 7S1 to 7S4. Then the sample was stored in an air tight container till further use.

3.2. Characterization of Activated Carbon:

3.2.1. Thermo-gravimetric analysis (TGA)

A small amount (5mg approximately) of powdered sample was taken in a vial and placed in the TGA analyzer in N_2 atmosphere at a flow rate of 30ml/sec. The heating rate and maximum temperature were set as 10 $^{\circ}$C/ min. and 900 $^{\circ}$C respectively.

3.2.2. Proximate analysis

ASTM defines proximate analysis as the determination by prescribed methods of moisture, volatile matter, fixed carbon, and ash. It is defined by ASTM D 121. The proximate analysis of the raw sample and the activated carbon were done according to the procedure.

3.2.2.1 Moisture content

A small amount of the sample was put in a crucible, covered with a lid and weighed using a weighing balance. The crucible was placed in the hot air oven at 150 $^{\circ}$C with its lid removed and dried for 3 hours. The crucible was taken out, immediately covered with the lid, cooled in a desiccator and weighed.

The moisture content M = 100(B-F)/ (B-G)

B= Mass of crucible + original sample

F= Mass of crucible + dried sample

G= Mass of crucible

3.2.2.2 Ash content

The crucible was ignited in the muffle furnace at 650 ± 25 $^{\circ}$C for 1 hour. The crucible was placed in the dessicator, cooled to room temperature and weighed. A known amount of the sample which was dried in the hot air oven at 150 $^{\circ}$C for 3 hours was put in the crucible and the crucible was placed back in the muffle furnace at 650 ± 25 °C for 3 hours. The crucible was taken out of the furnace, placed in the dessicator, cooled to room temperature and weighed.

The ash content A= 100(F-G)/ (B-G)

G= Mass of empty crucible

B= Mass of crucible + dried sample

F= Mass of crucible + ashed sample

3.2.2.3 Volatile matter content

A known amount of sample was put in a crucible. The crucible was placed in a muffle furnace at 900 $^{\circ}$C $\pm$ 10 $^{\circ}$C, covered with lid, and placed for exactly 7 minutes. The crucible was taken out, allowed to cool and weighed.

Volatile matter on dry basis VM=100[100(B-F)-M (B-G)]/ [(B-G) (100-M)]

B= Mass of crucible, lid and sample before heating

F= Mass of crucible, lid and contents after heating

G= Mass of empty crucible and lid

M= % of moisture as determined above

3.2.2.4 Fixed carbon content

Fixed carbon FC=100-(volatile matter + ash content)

3.2.3. Fourier Transform Infra-Red spectroscopy (FTIR)

The raw sample of peanut shell and the activated carbon prepared from peanut shell were undergone the infrared spectroscopic study.

3.2.4. Iodine number of Activated Carbon

Iodine number is the milligrams of iodine adsorbed by 1 gram of activated carbon from a standard 0.1 N iodine solution when the equilibrium iodine concentration is exactly 0.02 N. iodine number is a measure of the micropore content of the activated carbon. A higher iodine number indicates higher microporosity of the sample. ASTM D4607 – 94(2006) gives the standard procedure for the determination of the iodine number of the activated carbon. 1g of dried activated carbon was mixed with 10 ml of 5% by weight HCl and swirled in a conical flask until the activated carbon was wetted. The flask was boiled for 30 sec. by placing it on a hot plate. The contents of the flask were cooled to room temperature and 100 ml 0.1N iodine solution was added to it. The flask was shaken vigorously for 30 sec. The contents were filtered through a filter paper. Initial 20-30 ml of the filtrate was discarded and the remaining filtrate was collected in a clean beaker. 50 ml of this filtrate was titrated against 0.1N sodium thiosulphate solution until yellow color just disappeared. 2 ml starch solution was added and titration was continued till blue color just disappeared.

3.2.5. Preparation of stock phenol solution

The phenol solutions for the test were prepared from a stock phenol solution of (1g/L), which was prepared initially. The stock phenol was prepared by dissolving 1g of phenol (mention concentration) in distilled water and then diluted to 1000ml.The required intermediate solutions of various concentration of 20mg/l, 40 mg/l, 60 mg/l, 80 mg/l, 100mg/l were prepared by adding 2ml, 4ml, 6 ml, 8ml, 10ml of stock solution and diluting it to 100ml in a 250 ml flask.

3.2.5.1. Adsorption Studies

As the adsorption studies were carried out in batch process, in the experiment for the determination of phenol uptake capacity of various Activated carbons prepared from specific temp and IR were taken in a 250ml flask. 0.1g of each adsorbent were added to a known concentration of phenol solution i.e. 100 mg/l in each flask with a volume of 100ml. It was then kept in a shaker at 200 rpm, at $25 \pm 1^{\circ}C$ for 24 hours to attain equilibrium. The pH of the solution was not changed. After that the samples were filtered in a filter paper and the concentration of the solutions were determined by UV spectroscopic analysis. For studying the effect of adsorbent dose, amount of sample was varied from 0.05 g to 0.2 g with keeping the phenol solution concentration at 100 mg/l. For studying the effect of concentration, the concentration of the solution was varied from 20 mg/l to 80 mg/l keeping the adsorbent weight constant at 0.05g. In all the experiments the phenol solution volume was kept at 100ml.

Phenol removal by AC was calculated by following equation

$$q_e = (C_0 - C_e)V/m$$

q_e = The amount of adsorbed phenol at equilibrium ($\mu g/mg$);

C_0 and C_e are initial and equilibrium concentrations of phenol ($\mu g/L$) respectively;

V = the solution volume (liter);

m = the mass of the adsorbent (mg).

The % removal of phenol was calculated by the following equation

$$\%R = [(C_0 - C_e)/C_0]*100$$

3.2.5.2. Analytical measurement of phenol

The standard calibration curve of known concentrations of phenol was plotted by finding out the absorbance at the characteristic wavelength of λ_{max} = 270nm. For the calibration plot, a spectrophotometer was used.

3.2.6. Adsorption isotherms study

3.2.6.1 Langmuir isotherm model

The Langmuir isotherm equation is expressed as

$q_e = (q_0 K_L C_e)/(1 + K_L C_e)$

Where q_0 and K_L are Langmuir constants. q_0 related to maximum adsorption capacity and K_L represents free energy of adsorption.

Langmuir equation can be written in linear form as

$1/q_e = (1/q_0) + (1/q_0 K_L)(1/C_e)$

The value of Langmuir constants q_0 and K_L were calculated by plotting graph between $1/q_e$ vs $1/C_e$.

3.2.6.2 Freundlich isotherm model

The Freundlich isotherm model is an empirical equation and the model is valid for adsorption that occurs on the heterogeneous surfaces. Freundlich isotherm equation is expressed as

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

Where K_F and n are the Freundlich constants. K_F indicates of the relative capacity of the adsorbent and n is indicates the adsorption intensity.

The equation can be represented in linear form as

$\ln q_e = \ln K_F + (1/n) \ln C_e$

The value of Freundlich constants K_F and n were calculated by plotting graph between $\ln q_e$ vs. $\ln C_e$

Figure 1: Shaker used for adsorption experiment

Figure 3: Tubular furnace used for ACs carbonization

CHAPTER 4

RESULTS AND

DISCUSSIONS

4.1 Production yield and burn-off

The production yield of all the samples was calculated and represented in the table below. The yield of activated carbons is the ratio of the weight of the activated carbon (w) (after washing, drying and activation) to that of the dry peanut shell (w_0) : yield% = $(w/w_0) \times 100$. The burn off is the weight loss percentage due to the activation step.

Table 1: Production yield and burn-off after chemical activation of peanut shell

Sample Name	Burning Temp	IR (W/W %)	Yield%	Burn off %	Chemical Removal %
5S1	500	50	26.3	73.7	87.3
5S2	500	100	20.53	79.47	85.14
5S3	500	150	11.888	88.112	92.653
5S4	500	200	14.36	85.64	94.596
6S1	600	50	31.893	68.106	97.98
6S2	600	100	25.3	74.7	77.133
6S3	600	150	14.576	85.424	90.5
6S4	600	200	12.708	87.292	89.732
7S1	700	50	25.652	74.347	95.791
7S2	700	100	17.060	82.939	98.878
7S3	700	150	14.452	85.547	85.962
7S4	700	200	11.263	88.737	87.885

It was observed that the yield percentage of the activated carbon from the raw material decreased with increase in temperature. In case of 500ºC and 50% IR the yield was between 600ºC and 700ºC but in 200% IR the yield percentage was less with increasing temperature. It also can be observed that with increase in IR the yield percentage decreased. The burn off percentage increased with increase in temperature and impregnation ratio. The graph of yield percentage vs impregnation ratio and the graph of burn off % vs impregnation ratio for samples of temperature profile of 500ºC, 600ºC, 700ºC has been plotted.
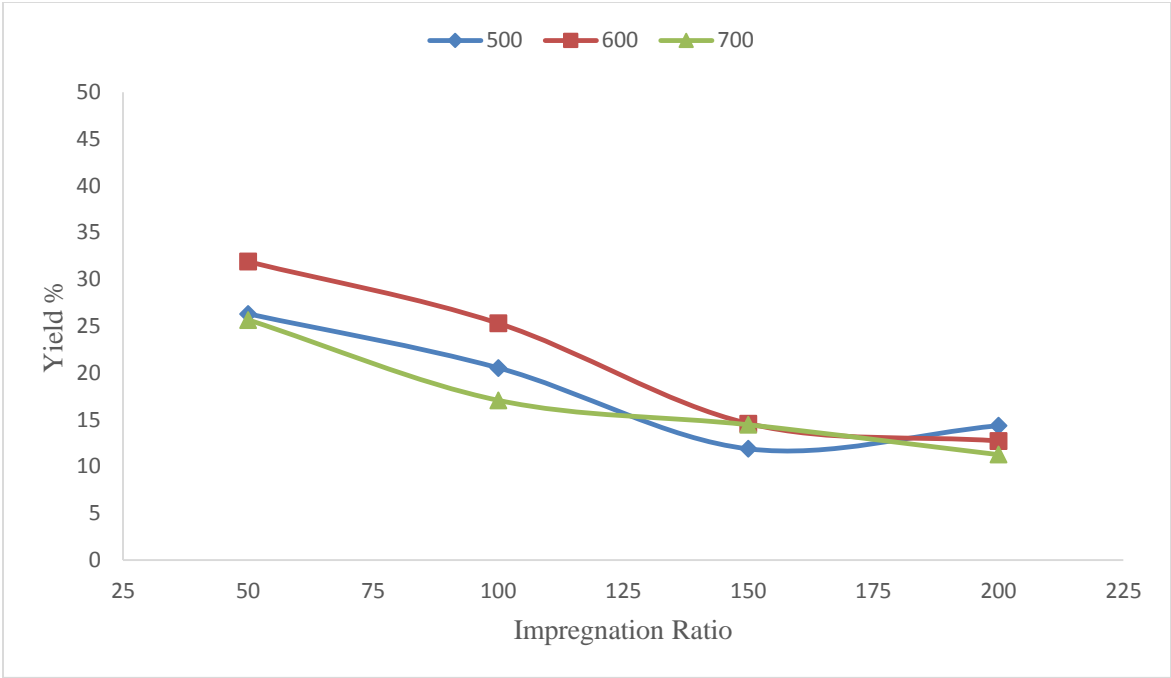
Figure 4: Yield % vs Impregnation ratio of activated carbons
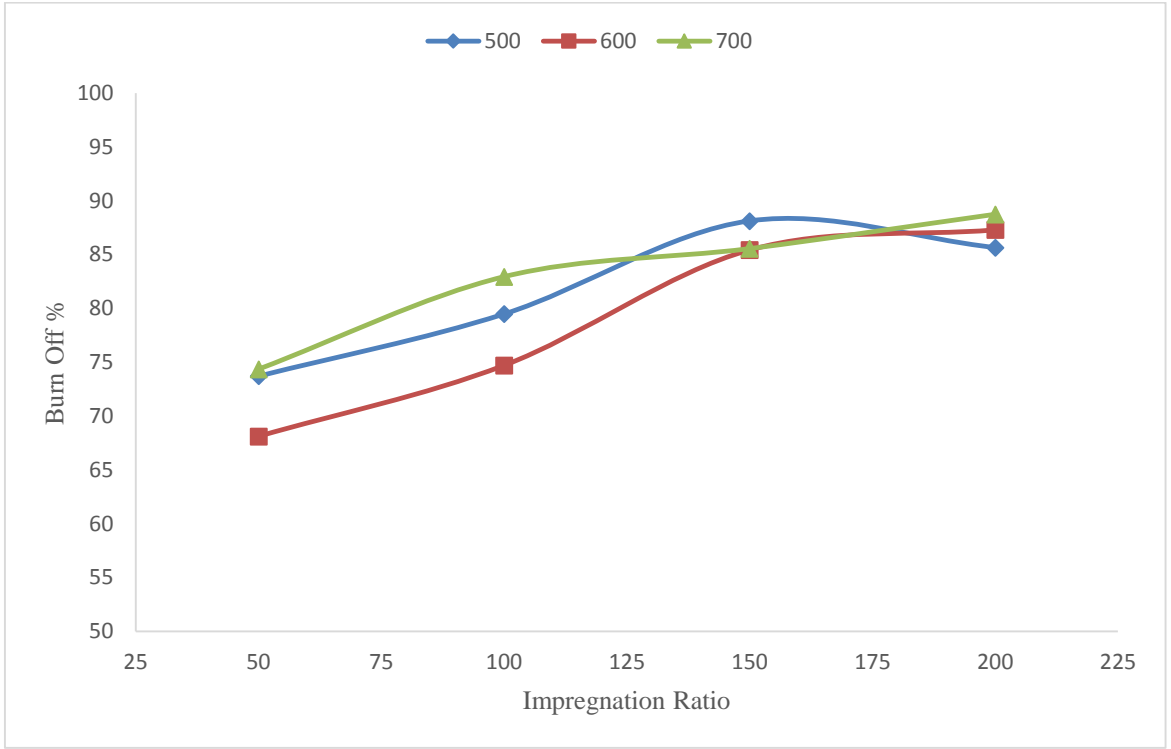

Figure 5: Burn off % vs Impregnation ratio of activated carbon

4.2 Thermo gravimetric analysis

The weight loss thermographs of peanut shells are shown in the figure no 8. The TGA graphs are shown below.
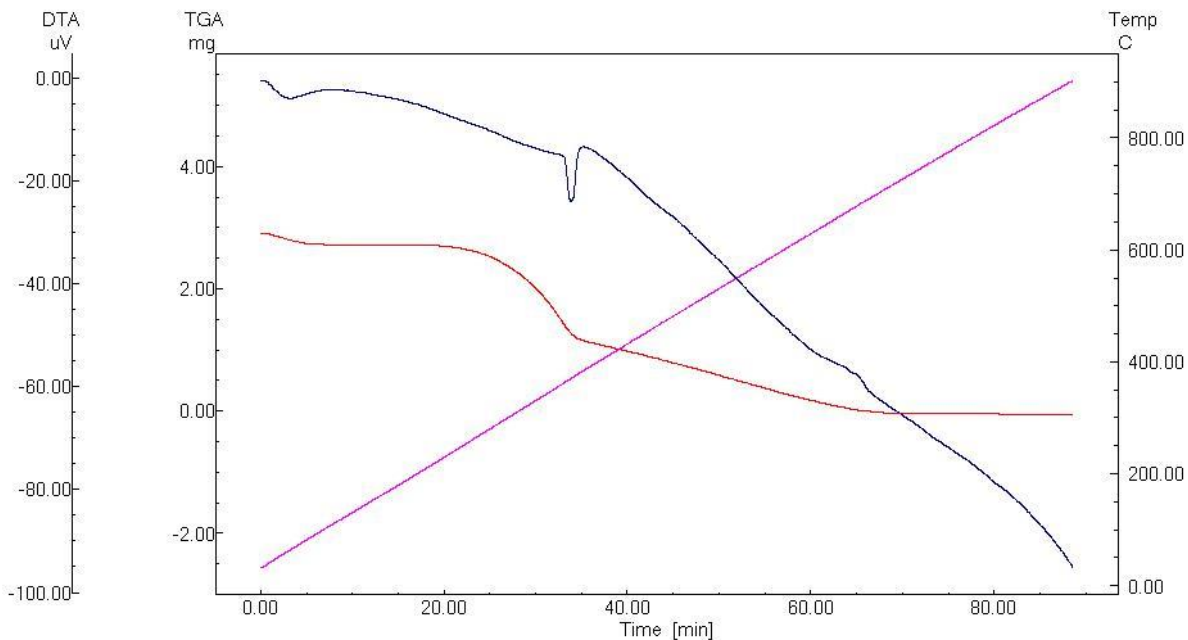
Figure 4: weight loss % vs temperature (ºC)

Table 6: TGA plot

The weight loss can be explained in 4 steps: 1) below 150ºC a slight weight loss is due to the moisture evaporation and dehydration. 2) In the second step i.e. the temperature range between 200ºC to 375ºC, the sudden sharp weight loss is due to the elimination of main volatile matters and tars. 3) In the third step i.e. the temperature range between 375ºC to 680ºC, the constant decrease in weight loss is due to the carbonization of peanut shell. 4) at temperature > 680ºC the material is almost fully carbonized.

4.3 Proximate Analysis:

The detailed analysis of proximate values of the samples containing moisture content, volatile matter, ash content, and fixed carbon are given in the table.

Sample Code	IR (W/W %)	Moisture Content	Ash content	Volatile Matter	Fixed Carbon
5S1	50	9	8.911	41.3	40.789
5S2	100	6	8.000	38.9	47.100
5S3	150	2	10.000	35.3	52.700
5S4	200	7	10.891	33.7	48.409
6S1	50	4	10.000	27.4	58.600
6S2	100	2	9.000	25.7	63.300
6S3	150	3	10.000	24.3	62.700
6S4	200	2	10.784	21.8	65.416
7S1	50	2	10.000	6.8	81.200
7S2	100	2	11.000	5.9	81.100
7S3	150	3	11.000	5.3	80.700
7S4	200	2	10.000	5.1	82.900
Raw Material	0	5	9.2	76.4	9.4

Table 2: Proximate Analysis of ACs of various impregnation ratio and temperature profile

4.4 FTIR

The FTIR analysis of both raw peanut shell and ACs prepared from were made in the range of 550-4000 cm^{-1} region.
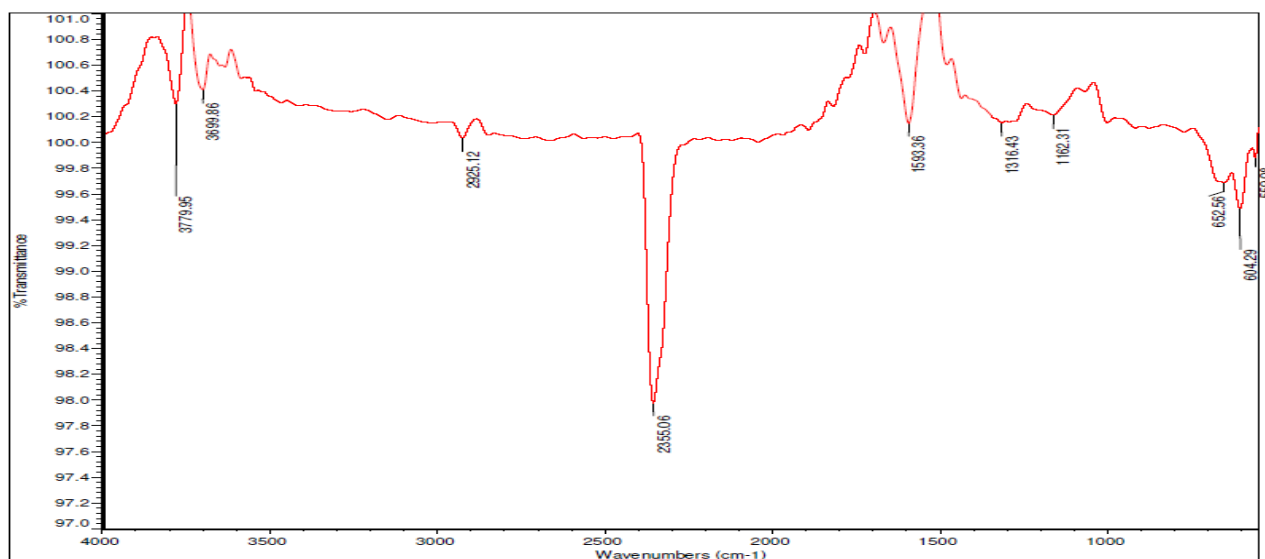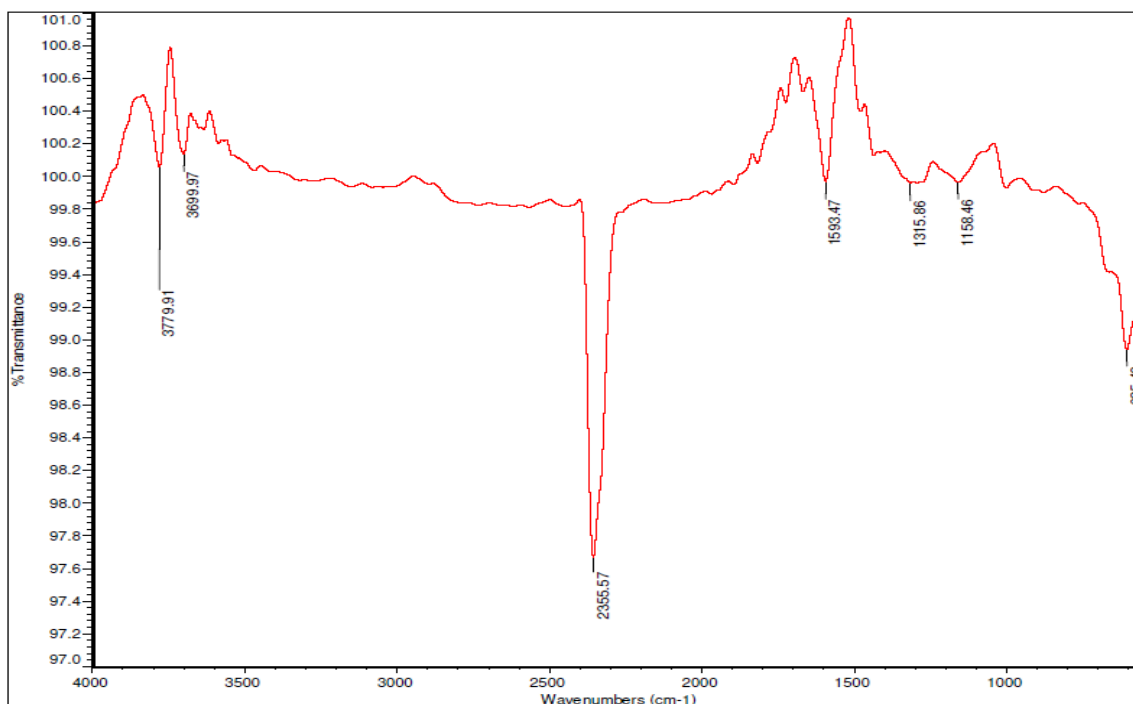

Figure 7: FTIR of Raw peanut shell

Figure 8: FTIR of ACs prepared from peanut shell

The functional groups which represent surface functionality of both the raw peanut shell and the ACs prepared from it are listed in table below.

Wave length (cm^{-1})	Type of Vibration	Functional Group	Intensity	Raw	ACs
3779.95	(stretch, free)	O-H	strong, sharp	✔	✔
3699.86	(stretch, free)	O-H	strong, sharp	✔	✔
2925.12	stretch	Alkane C-H	strong	✔	
2355.06		water		✔	✔
1593.36	Stretch	Aromatic C=C	medium-weak, multiple bands	✔	✔
1316.43	Stretch	Amine C-N	medium-weak	✔	✔
1162.31	stretch	Ether C-O	strong	✔	✔
652.56	stretch	Alkyl Halide C-Cl	strong	✔	
604.29	stretch	Alkyl Halide C-Cl	strong	✔	✔
559.08	stretch	Alkyl Halide C-Br	strong	✔	

Table 3: Surface functionality of raw Peanut shell and the ACs prepared from it

4.4 Iodine number

The iodine number of all the samples were calculated from the experiment and shown below.

Sample Code	5S1	5S2	5S3	5S4	6S1	6S2	6S3	6S4	7S1	7S2	7S3	7S4
Iodine number (mg/g)	387.3	428.5	347.4	315.1	467.6	497.4	448.1	419.5	517.7	543.4	478.1	454.3

Table 4: Iodine number of ACs of various impregnation ratio and temperature profile

From the iodine number data it was concluded that the sample 7S3 was finalized for adsorption studies of phenol.

4.5 Calibration curve

A **calibration curve** is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration.
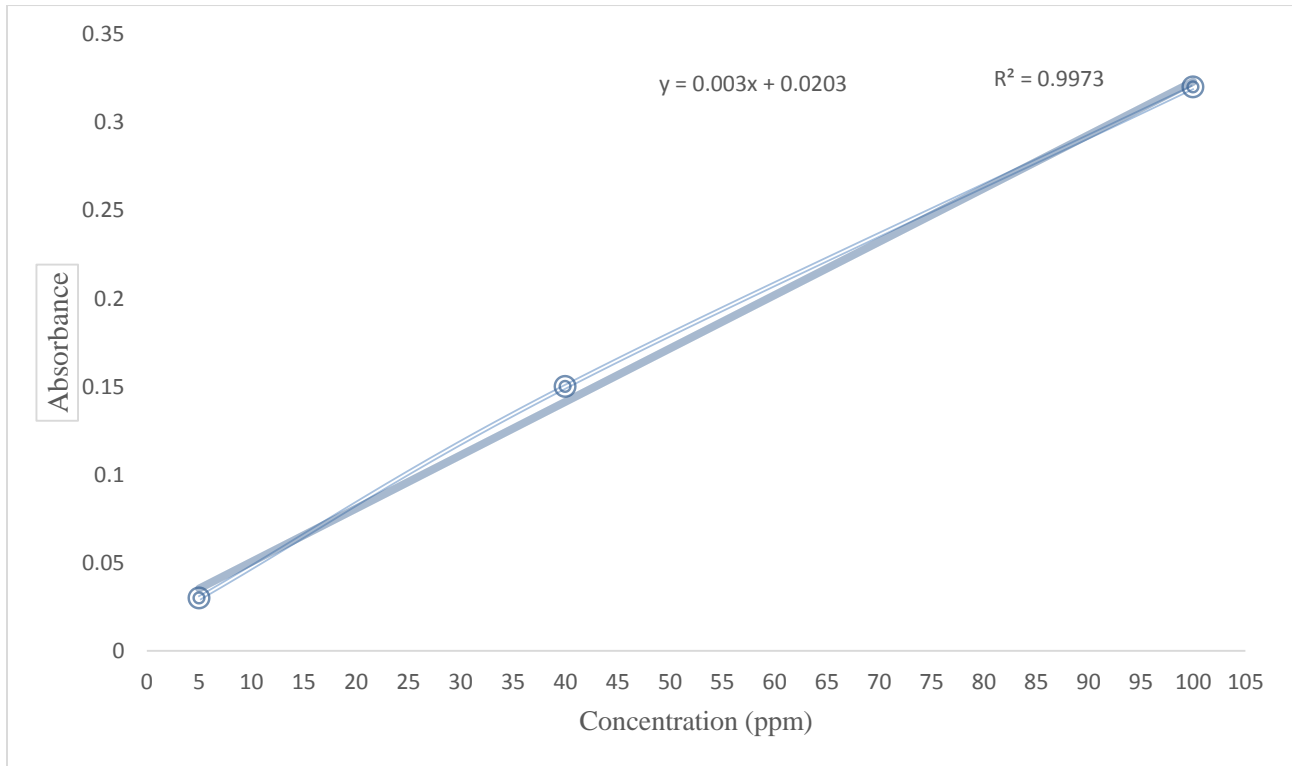

$y = 0.003x + 0.0203$ $R^2 = 0.9973$

Figure 9: Calibration curve plot

4.6 Study of various parametric effects on adsorption of phenol

4.6.1 *Effect of initial phenol concentration on the removal of phenol*

For this study the sample weight of 7S2 was kept constant at 50 mg per 100 ml of phenol solution in each flask with the concentration of phenol varying with 20 mg/L to 80 mg/L in a 250 ml flask. Appropriate method was followed (see adsorption studies in methods for detailed procedure). The results of the experiment is plotted in the graphs below i.e. removal efficiency vs initial phenol concentration and phenol uptake capacity vs initial phenol concentration. From the graphs it can be observed that with the increase in concentration of phenol in the solution the effective removal of phenol by the activated carbon decreased. Also with the increase in the concentration of phenol in the solution the phenol uptake capacity of the activated carbon increased, but it increased in faster rate for lower concentration of phenol and its rate slowed down with increase in concentration. The decreased in the phenol removal efficiency can be explained on the basis of the availability of the porous surface area, because the porous surface area of the activated carbon is fixed in fixed quantity of sample. As the concentration of the phenol increases the adsorption of phenol to the activated carbon decreases because the free surface is covered with phenol. But in case of phenol uptake capacity the increase in phenol concentration increases the mass transfer driving force of the adsorption of phenol to the surface of activated carbon.
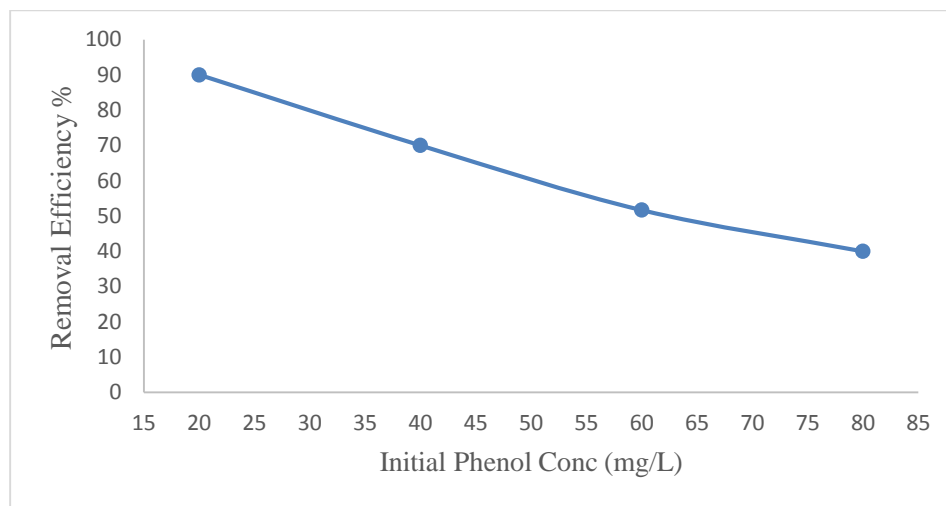

Figure 10: Effect of initial phenol concentration on the removal of phenol by ACs prepared from peanut shell
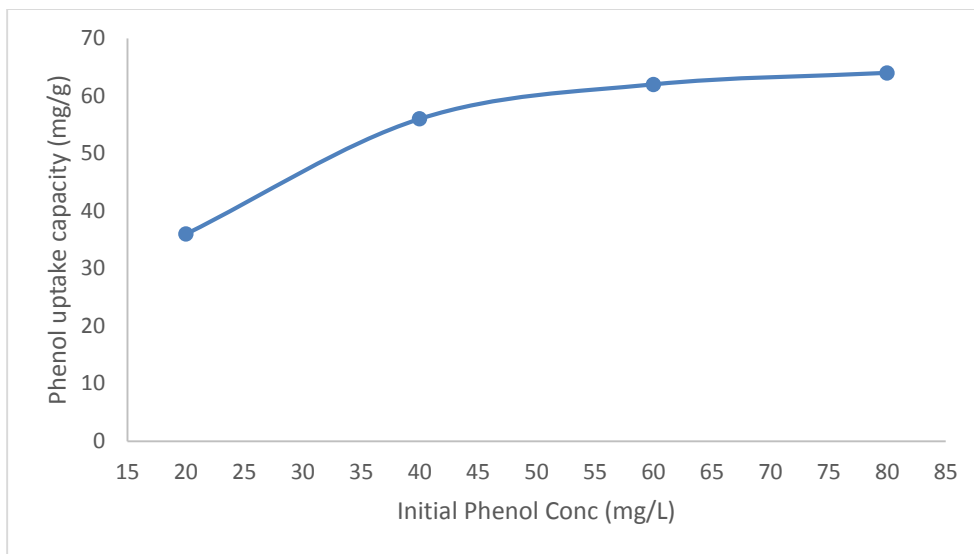
Figure 11: Effect of initial phenol concentration on the uptake capacity of phenol adsorption by ACS prepared from peanut shell

4.6.2 *Effect of adsorbent dose on the removal of phenol*

For this study the concentration of the phenol solution was kept constant at 100 mg/L with the increase in adsorbent concentration from 50 mg to 200 mg. Required procedures were followed with calculation and the graph of removal efficiency vs the adsorbent dose was plotted.
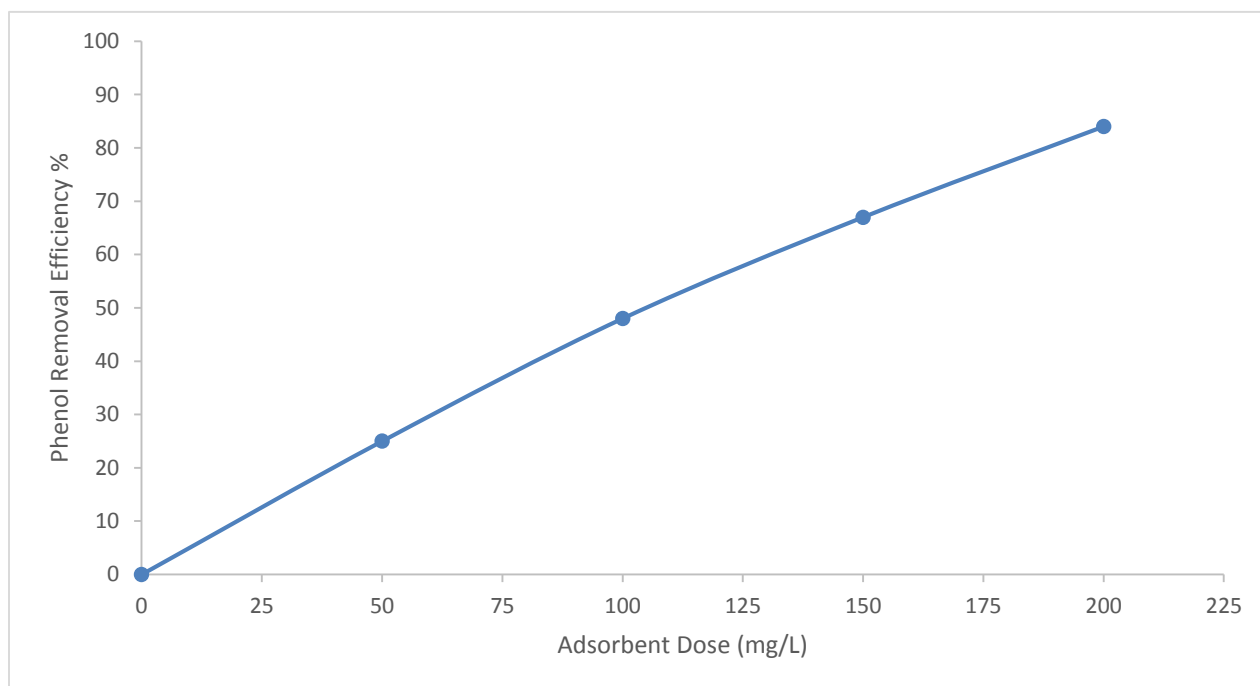

Figure 12: Effect of adsorbent dose on the removal of phenol by ACs prepared from peanut shell

From the graph it is observed that with increase in the adsorbent dose i.e. the carbon mass the phenol removal efficiency increased. This can be explained on the increase in the carbon dosage the available free porous surface increases which in turn results in higher adsorption of phenol and an increased phenol removal.

4.7 Adsorption isotherm

4.7.1 *Langmuir isotherm*

The value of Langmuir constants q_0 and K_L from the linearized form of the Langmuir isotherm equation were calculated by plotting graph between $1/q_e$ vs $1/C_e$.

Temperature ($^{\circ}$C)	q_0	K_L	R^2
25	51.282	0.2653	0.9128

Table 5: Langmuir isotherm parameters for the adsorption of phenol by ACs prepared from peanut shell
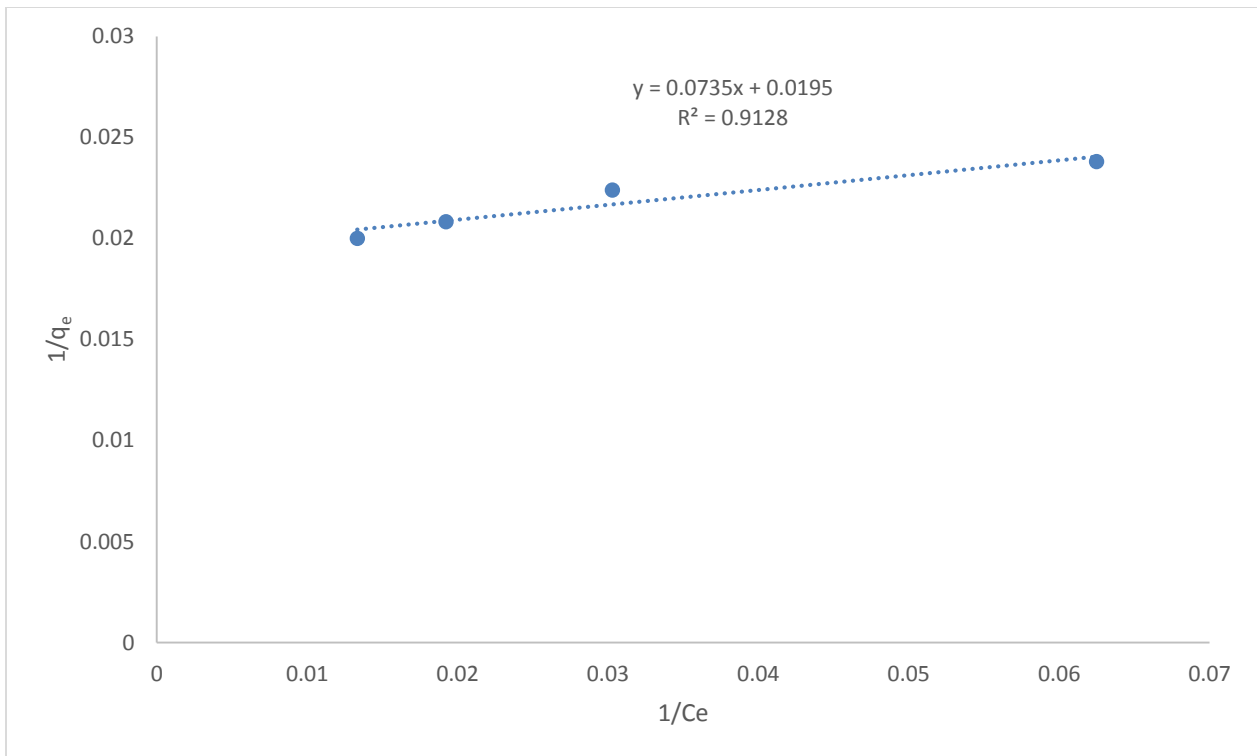

Figure 13: Langmuir isotherm plot for the adsorption of phenol by ACs prepared from peanut shell

The monolayer capacity (q_0), Langmuir constant (K_L) and correlation coefficients (R^2) are not satisfactory, so the adsorption does not follow the Langmuir model.

4.7.2 *Freundlich isotherm*

The value of Freundlich constants K_F and n from the linearized form of the Freundlich isotherm equation were calculated by plotting graph between ln q_e vs. ln C_e.

Temperature (°C)	n	K_F	R^2
25	8.688	30.3197	0.9831

Table 6: Freundlich isotherm plot for the adsorption of phenol by ACs prepared from peanut shell

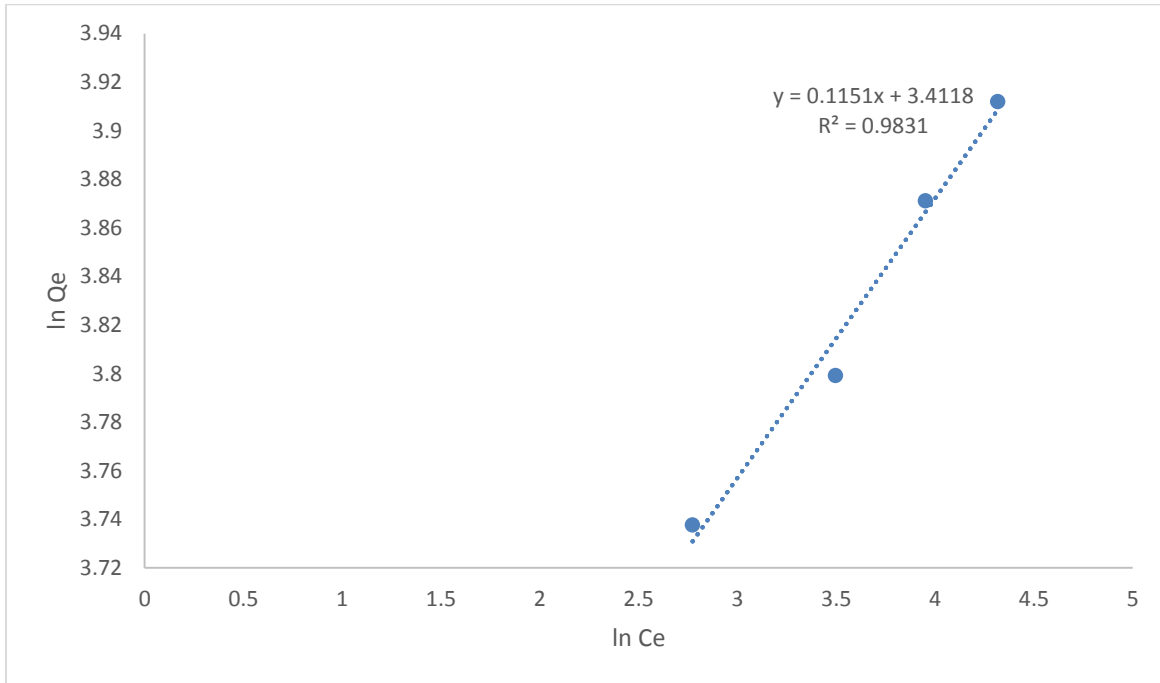The Freundlich constants and R^2 values indicate that Freundlich model is more suitable.

Figure 14: Freundlich isotherm plot for the adsorption of phenol by ACs prepared from peanut shell

CHAPTER 5

<u>CONCLUSION</u>

Conclusion:

Proximate analysis of the precursor gives an idea about the physical properties of the sample. According to proximate analysis the raw material has a carbon content of about 8 % and combined moisture and volatile matter content of about 78 %. So there are more amount of easily escapable components present in peanut shell. It can be observed that the FC content of the ACs were high.

Temperature range of activation was determined by thermo gravimetric analysis. With the help of this result proper carbonization time and optimum temperature was determined.

Iodine number is the measure of micro porosity of the activated sample. Maximum iodine number of mg/gm. of activated carbon was obtained at a temperature of 700°C with 100% phosphoric acid impregnation. It helped in choosing the appropriate activated carbon for adsorption studies.

The effect of temperature and concentration of activated carbon on the yield of the activated carbon was determined. It was found that yield decreased with increase in both temperature and concentration of acid.

The iodine number for the sample of 700 °C burning temperature and 100% impregnation ratio was highest i.e. 543.4 mg/g.

In adsorption studies the increase in dosage showed increased phenol removal efficiency and with increase in phenol concentration the decrease in removal efficiency.

The Freundlich isotherm was more suitable than the Langmuir isotherm.

CHAPTER 6

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