

REMOVAL OF p-NITROPHENOL FROM SYNTHETIC WASTE WATER BY ADSORPTION

A DISSERTATION

*Submitted in partial fulfillment of the
requirements for the award of the degree*

of

INTEGRATED DUAL DEGREE

(Bachelor of Technology & Master of Technology)

in

CHEMICAL ENGINEERING

(With specialization in Hydrocarbon Engineering)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work being presented in the dissertation titled "Removal Of p-nitrophenol Form Sytnhetic Waste Water By Adsorption" in partial fulfillment of the requirements for the award of Integrated Dual Degree (With M.Tech Specialization in Hydrocarbon Engineering) and submitted in the department of Chemical Engineering of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work under the supervision of Dr. Shri Chand, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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I would also take a moment to thank all the friends that I made here in Roorkee. I had the best times of my life and thanks to all of you.

Nitin Aggarwal

ABSTRACT

Batch adsorption experiments were performed for the removal of hazardous and toxic organic compound 4-nitrophenol. Adsorption was carried out with the help of activated carbon. Apricot stones were used as a raw material for the preparation of low cost activated carbon. Two types of activating agents were used, sulfuric acid and phosphoric acid. Characterization of carbon samples prepared was done. Their potential for adsorption of 4-nitrophenol from aqueous solutions was studied. Optimum conditions were found out by varying process parameters. From the different isothermal models examined for the experimental data Redlich-Peterson isothermal model resembled data the best. Almost 99% removal was observed for high doses of activated carbon. From the study it was clear that apricot stones can be a promising raw material for preparation of low cost activated carbon for removal of 4-nitrophenol from industrial waste water using adsorption.

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

It is a well known fact that clean water is necessary for healthy living. Fresh and clean water is the basic building block of life on earth, yet millions are not able to get adequate supply of it. Fresh water resources all around the globe are threatened by over exploitation and ecological degradation. The main sources of water pollution are municipal sewage discharged into the water bodies, run off from the agricultural fields and untreated industrial wastes. Over exploitation of water resources has led to water table going way below in many places. It is established that contaminated water is a major source of a lot of diseases and deaths worldwide.

Water is called contaminated when it becomes unfit for human use that is drinking etc. or is unable to support the biological life. Waste water pollution has become a serious problem to the present world. It has posed a great threat to not only aquatic life but to the whole world. Water pollution is the contamination of water bodies by direct or indirect discharge of pollutants into the water bodies without adequate treatment. Rapid urbanization, industrialization and use of chemical fertilizers have left no scope for this problem to unnoticed. Almost all the countries in the world face the problem of industrial discharge of harmful chemicals in water bodies. So it has become the utmost priority to limit the water pollution to minimum and design techniques to tackle the industrial pollution.

When large quantities of organics are discharged into the surface water organic pollution occurs. Many organic pollutants discharged from the industries into the surface water are refractory in nature which can't be treated by conventional biological processes. When organics discharged into the water bodies are decomposed they use oxygen dissolved in the water at a greater rate than it can

be replenished and thereby results in its deficiency for aquatic life. Organic matter also contains a lot of suspended solids which after settling on the water surface blocks the light leading to problems in photosynthesis. Most of the synthetic organic compounds do not decompose in the water bodies and are accumulated in the food chain. Organic material is also rich in disease causing pathogens.

Structure of nitrophenols is similar to insecticides or fungicides and are resistant to biological degradation. They also have a high mobility and a long persistence in the environment. World Health Organization has suggested a limit for use of aromatic substances in drinking water and the European Environment Agency (EEA) has included these compounds in its list of priority pollutants to be monitored in industrial discharges.

Great efforts have been made in the past few years for hunt of new and improvement of the existing technologies to get rid of the organic pollutants in waste water and make them fit for human use. Methods conventionally used for removal of organic pollutants are adsorption, reverse osmosis, catalytic oxidation, ozonation, photo-catalytic oxidation nano-filtration. Each of the following processes poses some limitations. In the past few years great priority has been give to the preparation of activated carbon at low cost for the removal of organic pollutants by adsorption. Great attention has been given to the development of low cost activated carbons from agricultural and other organic wastes. Agricultural wastes and by-products are proving to be a very useful raw material in the production of activated carbon due to their high carbon content and low cost.

Primary raw materials used for the production of activated carbon can be anything with very high carbon content. The use of special thermo-chemical processes have resulted in the manufacture of activated carbons with very high surface areas. The resultant activated carbon has a very high surface area per unit volume. The adsorption capacity of an activated carbon depends upon many parameters like chemical properties of the surface, pH of the solution and its porous structure.

1.2 ADSORPTION

Adsorption is the removal of a material from a solution by adhesion on solid surfaces. It enables the separation of different compounds from dilute solutions. As compared to other processes for separation it is preferred because of its low cost, relatively simpler design for the process to work out, ease of regeneration, high capacity and favorable rate. In adsorption process gas or solid molecules of the solutes are accumulated at the surface of the adsorbent. The exact nature of adhesion is a function of the physical and chemical properties of adsorbent and adsorbate. On the basis of nature of adsorption, it can be classified into two types-

Physiorption is done when the adsorbate adheres to the surface of the adsorbent via weak vander vaals forces.

Chemisorptions take place when there is a formation of chemical bond between the adsorbent and adsorbate molecules at the active sites of the surface.

1.3 ADSORBENTS

A typical adsorbent is generally in the form of spherical granules or cylindrical in structure. It generally has a high surface area which increases the contact area with the solute. It is thermally and chemically stable and has a high pore area.

For adsorption of different compounds from a solution the requirements for adsorbents are different. The adsorption depends a lot on the porous structure and chemical nature of the activated carbon which is a function of the raw material and activation method used for the production. Moreover every adsorption process will have a set of requirements which will vary from carbon to carbon.

1.4 ACTIVATED CARBON

A monocrystalline and nongraphitic form of carbon is called the activated carbon. It is because of its chemical structure that it is able to absorb organics and other non-polar compounds. Raw materials with high carbon content are treated specifically to enhance their surface area by opening up billions of small pores. Now a days activated carbon has found widespread use in removal of harmful chemicals and pollutants from industrial waste water. Emphasis has been laid on development of activated carbon at low cost. For this there is a greater tendency to use carbonaceous waste materials from agricultural and municipal waste. Techniques are being continuously developed to prepare activated carbon at low cost .

1.5 PRINCIPLES OF ACTIVATION PROCESS

The basic principle involved in the production of activated carbon is the selective removal of groups of carbon containing materials and formation of a highly porous structure. It can be done by carbonization and chemical treatment.

Manufacturing of activated carbon is carried out in two phases, first is carbonization which is then followed by activation. Carbonization is generally carried out at a high temperature of 400-700 °C in the absence of oxygen. Substances are added to restrict the formation of tar and other impurities are also removed. The carbonized material is then activated by use of a suitable activating agent. Activating agent oxidizes the material and remove the pore blocking materials to increase the porous structure thereby forming a three dimensional structure same as the graphite lattice. The pores developed during this phase are directly proportional to the contact time. Longer the time more is the porous structure formation. Activated carbon is a promising material for the removal of impurities from water and in the last two decades a lot of research has taken place to develop activated carbons for adsorption.

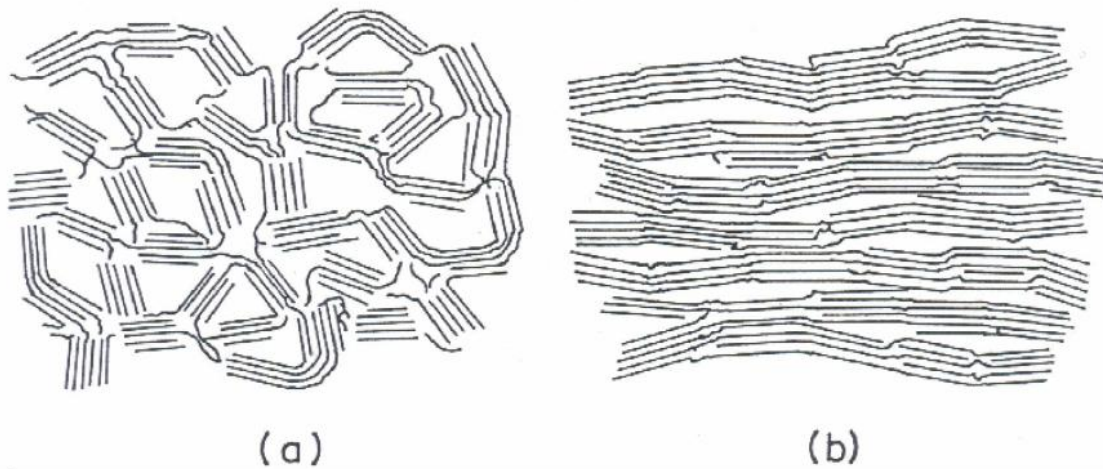


Fig1. (a) nongraphitizing and (b) graphitizing structure of activated carbon

Basically there are two processes for the formation of activated carbon-

Chemical activation is generally used when the carbonaceous raw material is of recent origin. The activation agent plays an important role in determining the quality of the activated carbon produced. In this process raw material is first crushed to very fine particles and moisture is removed from it. Then it is sieved and treated with a chemical agent. The raw material immersed in the chemical agent is then carbonized and washed. After removing the impurities the material is then treated with an activating agent. Common activating agents used are sulfuric acid, phosphoric acid, zinc chloride, potassium sulfide etc. all these chemicals dehydrate the carbonaceous raw material. Due to this aromatization of carbon skeleton occurs and surface area is increased. Dehydration inhibits the formation of tar by the action of heat. Processing of carbons prepared using this process is relatively difficult and complex. The activated carbon produced has to be washed many times before use to make it free from the activating agent. Activated carbon produced from this process is generally in powdered form.

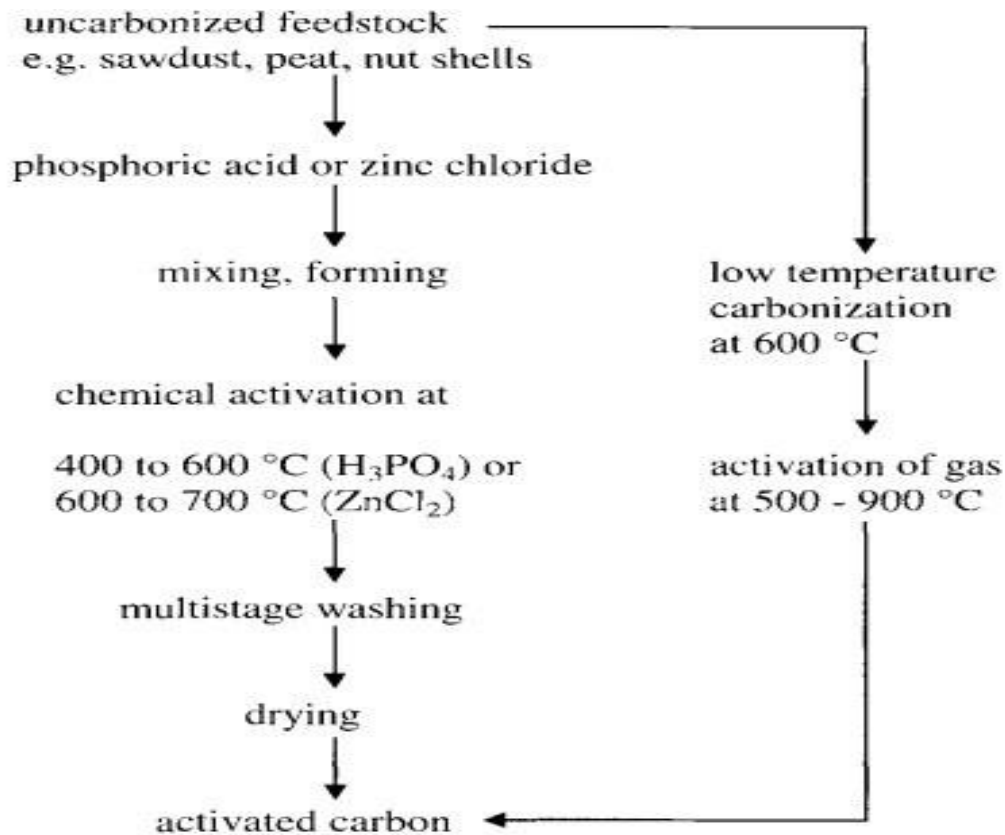
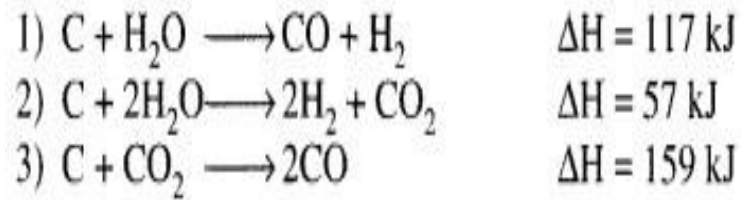


Fig 2. Process flow diagram for chemical activation

Gas activation follows the same principle as chemical activation, the only difference being that the activating agent in this process is a gas. In this type of activation the main aim of carbonization is to remove volatile material so that there is no further hindrance to the activation. Carbonization starts at approx. 150 °C and is completed around 600 °C. The carbonized materials thus formed are partially activated by heating them with steam or an inert gas. The activating agents used in this process are steam, carbon dioxide, oxygen etc. The activation step is generally carried out at approx 900 °C. In the activation step oxidation takes place and carbon is removed from the pores. This step is highly endothermic, so oxygen has to be constantly supplied to ensure exothermic combustion of hydrogen and carbon mono-oxide to maintain the activation temperature. Following are the reactions taking place-



Generally carbonization and activation steps are performed separately, but nowadays technologies are being developed to carry out both the processes simultaneously for relative ease of the production.

The main drawback of this process is that high temperatures have to be maintained throughout the process and there can also be overheating if high quantity of oxygen is supplied. The activated carbon thus produced has a relatively larger surface area as compared to that produced by the process of chemical activation.

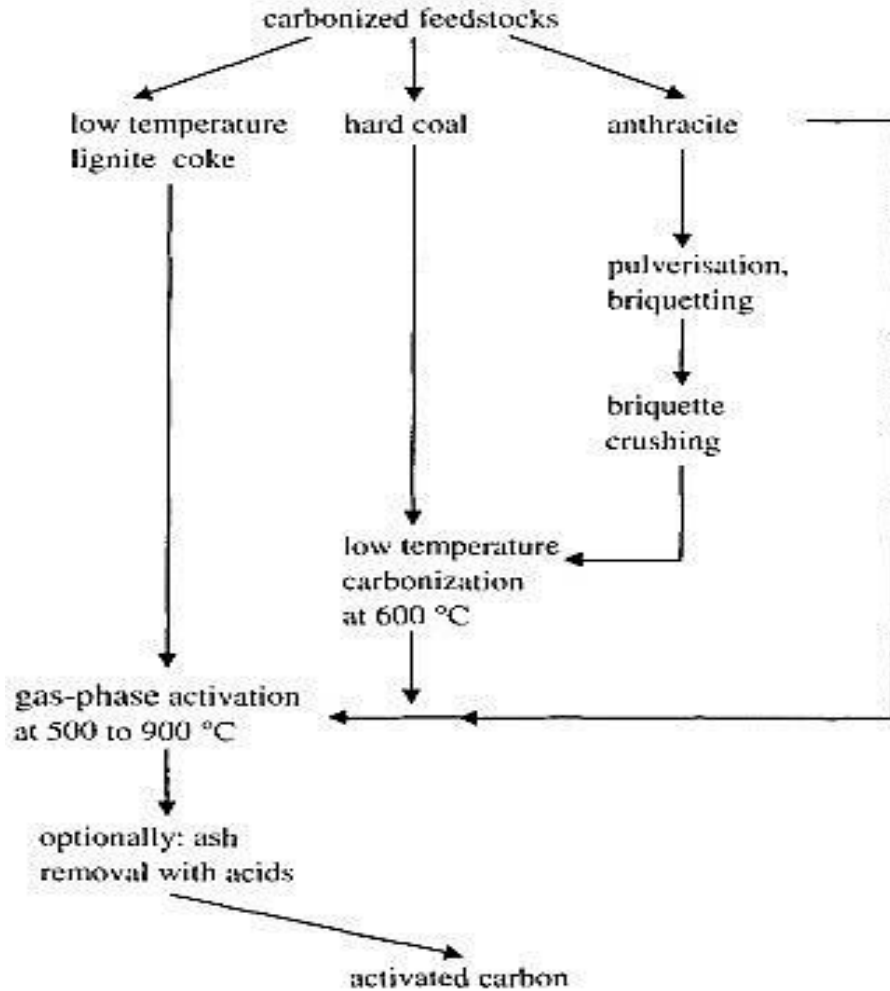


Fig 3. Process flow diagram for gas activation

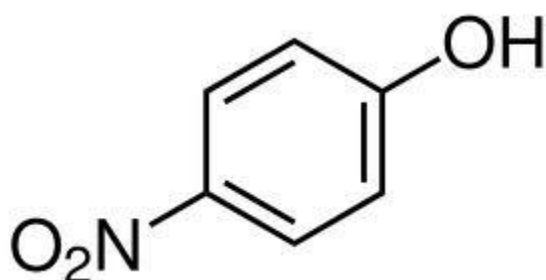
1.6 RAW MATERIALS FOR ACTIVATED CARBON

Raw materials used for the production of activated carbon plays an important role in deciding the quality of activated carbon. Agricultural wastes and municipal wastes can be promising raw materials due to their high carbon content. A wide variety of agricultural wastes like rice husk, coconut shell, wheat barn etc can be used as a raw material for the production of activated carbon. Price, availability and chemical properties of the material plays a dominant role in deciding the raw material for carbon production. Due to the increasing use of biomass , activated carbons with large surface areas and high removal efficiencies are being

continuously developed at cheaper prices. Technological advancements has led to better removal efficiencies, almost comparable to commercially available activated carbon.

1.7 4-NITROPHENOL

Usually 4-nitrophenol exists as a mixture of two polymorphs in the crystalline state. It is an aromatic compound and has a nitro group attached at its opposite portion on the hydroxy group in the benzene ring.



4-nitrophenol is mainly used as an intermediate in the manufacture of rubber chemicals, dyes, leather industry, pigments, paracetamol, fungicides etc.

Constant touch with 4-nitrophenol can cause allergic response. It causes irritation of eyes and skin. Inhaling can cause nausea, vomiting and unconsciousness. Consumption can cause abdominal pain and vomiting. Bureau of Indian Standards have set a discharge standard of 1.0 mg/l concentration of phenolic compounds in the industrial effluents.

Table 1 : Physical and chemical properties of 4-nitrophenol

S.NO.	PROPERTY	VALUE
1	Molecular formula	C ₆ H ₅ NO ₃
2	Molecular weight	139
3	Color	Greenish or yellow
4	Solubility in water	16.1 g/L(25 ⁰ C)
5	Boiling point	278 ⁰ C

6	Melting point	113 °C
7	Density	1.235 g/cm ³ (160 °C)
8	pKa value	7.16
9	pH	5.6
10	Heat of vaporization	56.1 kJ/mol
11	Vapor pressure	.6 mm Hg at 120°C
12	Odor threshold	58.1 mg/L
13	Air and water reactions	Soluble in water

1.6 OBJECTIVE OF THESIS

- Preparation of activated carbon from a low cost agricultural waste, apricot stones.
- Characterization of the activated carbon to be used as adsorbent in waste water treatment like BET, FTIR, SEM etc.
- To determine the adsorptive capacity of the activated carbon formed for the removal of 4-nitrophenol from synthetic waste water.
- To study the effects of various parameters on the adsorption of 4-nitrophenol using prepared activated carbon.
- To determine the optimum operating conditions for the adsorption to take place.

CHAPTER 2

LITERATURE REVIEW

Bevla et al. (1984) produced activated carbon from an agricultural waste (almond shell). Several activating agents like H_3PO_4 , $ZnCl_2$ and Na_2CO_3 were used. Zinc chloride gave the best results. It was also observed that as the particle size decreased adsorption capacities and BET surface area values also decreased.

Reinoso et al. (1985) used plum and peach stones to prepare activated carbon. Gas activation method with carbon dioxide was used in this process. The adsorption of N_2 , CO_2 , i-butane, paranitrophenol and methylene blue was studied to investigate the microporosity. Activated carbon prepared from plum stones had a well developed structure of macro and meso pores.

Laine et al. (1989) used both untreated and phosphoric acid treated coconut shells to prepare different samples of activated carbon. First of all carbonization was done and the resultant product is activated with the use of nitrogen and oxygen in muffle furnace. The highest surface area activated carbon was produced when treatment was done at $450\text{ }^\circ\text{C}$. The products obtained under the forced flow showed a decrease in surface area and yield.

Blasco et al. (1990) used holm oak wood for the preparation of activated carbon using thermogravimetry technique and activation energy distribution was measured. Three different activating agents were used in the process: sulfuric acid, phosphoric acid and zinc chloride. Paralysis energy distribution of treated and untreated sulfuric acid samples was same but for other agents it differed considerably. For wood treated with zinc chloride, major weight losses occurred at low temperature due to dehydration reactions.

Gergova and Eser(1996) prepared activated carbon using different process using apricot stones and studied there effects on pore structure. Carbonization followed by steam activation and one step activation were the methods used. The

process was cheaper but higher surface areas were obtained in the two step process.

Daifullah and Girgis(1997) studied the removal of several phenolic compounds by using activated carbon prepared from apricot stones. Phosphoric acid was used as an activating agent. Adsorption of mono-substituted phenols was less than the di-substituted ones.

Chern et al.(2002) used activated carbon to determine the adsorption isotherms of nitrophenol in synthetic waste water solution. Volumetric mass transfer rate in the liquid phase was predicted. The effects of various process variables on the adsorption isotherms were also studied.

Riaz et al.(2002) studied removal of various phenolic compounds from industrial waste water using commercially available activated carbon. Optimum conditions for the maximum removal to take place were determined by changing process variables. Data was fitted onto the adsorption isotherms.

Kobyia et al.(2004) prepared activated carbon from apricot stones by activating it with H_2SO_4 . Batch experiments were carried out to study the effects of pH on removal of certain heavy metal ions using this activated carbon. Highest removal was at pH(1-2) for Cr^{4+} and at pH(3-6) for other metals.

Youssef et al.(2004) used H_3PO_4 , $ZnCl_2$ and steam as activating agents to prepare activated carbon from apricot stones. Textural properties were analyzed and considerable differences were found in different activated carbons. Adsorption models were also studied for adsorption results.

Shalaby et al.(2005) used one step activation/pyrolysis process to prepare activated carbon from apricot stones. The effects of process variables were studied by varying them. The carbon produced was characterized and studied for adsorption properties.

Ioannidou and Zabaniotou(2006) presented a review for activated carbon preparation from biomass. Effects of process of activation were found out by

characterization of activated carbons prepared. Prepared carbon was compared with the commercially available carbon for adsorption use.

Tang et al.(2007) studied adsorption of 4-nitrophenol from an aqueous solution and determined the effects of various process variables. Isotherm models and kinetic models were determined for the batch adsorption experiments using activated carbon. Removal was found out to be 92 % and second order model was followed.

Kazemipour et al.(2007) prepared activated carbons from agricultural wastes and studied them for the removal of heavy metal ions in industrial waste water. Optimum conditions for the removal were found out. Removal capacity was found out to be considerable in case of cations.

Demirbas et al.(2007) used sulfuric acid to prepare activated carbon from apricot stones to remove astrazon yellow(dye) from industrial waste water. The effects of process variables on adsorption were studied and optimum conditions were determined. Different models were studied for adsorption kinetics. Highest adsorption was found out to be 222.2 mg/g. various thermodynamic parameters were also evaluated and data fitted the Langmuir and Freundlich isotherms.

Singh et al.(2007) obtained activated carbon from coconut shells. Characterization of carbon was done and it was used for the removal of various phenol derivatives. Langmuir and Freundlich isotherm best resembled the experimental data. Kinetic models were established and thermodynamic properties were found out. Efforts were made to determine the rate limiting step in the batch adsorption process.

Hameed and Rehman(2008) prepared activated carbon from saw dust and used it for the adsorption of 4-nitrophenol from waste water. Optimum conditions were determined by varying process parameters. Isotherm models were established. Experimental data fitted well with the pseudo second order kinetic model.

Lin and Juang (2009) removed phenol and its derivatives from waste water by using activated carbon made from various low cost synthetic resins. Cheap materials which are available easily were used like sludge, rice husk, fly ash etc.

the removal capacity of carbon from these is compared with the commercially available activated carbon in the study.

Loannou and Simitzis(2009) used activated carbon produced from olive stones and used it for the adsorption of phenol and its derivatives. They also compared the results with the commercially available activated carbon. Characterization of activated carbon was also done. Kinetic models and isotherm models were prepared.

Bhatnagar and Sillanpaa (2010) studied various materials in municipal agricultural waste to prepare activated carbon at low cost. Adsorption studies were carried out by various activated carbons. It was proven in the study that removal was good for certain carbons.

Rafatullah et al.(2010) carried out adsorption of methylene blue on low cost adsorbents. Various agricultural wastes, municipal wastes etc were used for the formation of activated carbon to carry out the removal. Activated carbons produced were characterized and their performance was studied here.

Mouni et al.(2011) separated lead from an aqueous solution using activated carbon prepared from apricot stones. Sulfuric acid was used as an activating agent. Adsorption measurements were done by varying various parameters and their effect on adsorption was studied. Removal was max at pH 6 and second order model resembled the kinetics. Highest adsorption capacity was found to be 21.35 mg/g.

Sato et al.(2011) performed recovery, concentration and purification of phenolic compounds by adsorption. This study reviews the various processes for the removal of phenols from aqueous solutions.

Fu et al.(2012) removed organics from industrial waste water using activated carbon made from bamboo charcoal. Various adsorption parameters were varied and there effects noted. Adsorption was spontaneous on the carbon surface and was an endothermic process. Electrostatic interactions were also measured and studied.

Cotoruelo et al.(2012) studied removal of 4-nitrophenol from aqueous solution using different activated carbons made from eucalyptus lignin. Two step process was followed for carbon preparation and adsorption measurements were done by changing process variables to know there effect. The process followed second order model and isotherm models were also established.

CHAPTER 3

MATERIALS AND METHODS

3.1 APRICOT STONES FOR PREPARATION OF ACTIVATED CARBON

In this research activated carbon was prepared using apricot stones. The ultimate analysis of apricot stones was carried out. Following were the results:

Elements	%wt
C	49.4
H	6.66
N	Trace
O	42.661
Ash	0.31

Table 2: Composition of apricot stones

3.2 PREPARATION OF ACTIVATED CARBON

In this process chemical activation method was used for the preparation of activated carbon from the apricot stones. Two samples of activated carbon were prepared: one was activated with phosphoric acid and the other used sulfuric acid as an activating agent.

First the apricot stones obtained were dried to remove any moisture in them. The dried stones were then crushed. The resulting particles were sieved and the particles having size less than 2 mm were taken for the experiment.

For preparation of sample treated with phosphoric acid a 50% by vol solution of phosphoric acid was taken. The apricot stones were immersed in the solution at 25 °C for 24 hours in a ratio of 2.6:1(wt). After impregnating apricot stones with phosphoric acid the solution was filtered. The impregnated material was taken out and washed many times to remove the remaining acid. After washing properly the impregnated sample was dried for three days at room temperature (25 °C). The impregnated samples were then carbonized by a supply of constant amount of heat in a muffle furnace. The final temperature reached in the carbonization process was 450 °C. After reaching the final temperature sample heated for one hour. The carbonized sample was then taken out and cooled. After cooling it was washed several times with distilled water and then dried in an oven. Thus activated carbon is produced which is then crushed and used for adsorption.

For preparing activated carbon using sulfuric acid, almost similar procedure was followed and a solution of 50% sulfuric acid in distilled water is taken. The crushed apricot stones are then immersed in this solution. This solution is then heated in a muffle furnace at 210 °C for 2 hours. Constant heat is supplied to the furnace until the temperature reaches 210 °C and after reaching the final temperature it is kept constant for two hours. The resulted solution is then filtered to remove the acid and the sulfuric acid impregnated apricot stones are then washed many times with distilled water until the pH of solution reaches 4. The resulting chemical loaded material is then carbonized in a muffle furnace. A constant heat at a rate of 10 °C per minute is applied until the final carbonization temperature of 650 °C is reached. The sample was heated at this temperature for 30 minutes. After the carbonization was over, the sample was taken out, cooled and washed many times to get it acid free. Deacidification with water was followed by the use of liquid aqueous ammonia solution without affecting its surface properties. The activated carbon thus produced is dried at 60 °C.

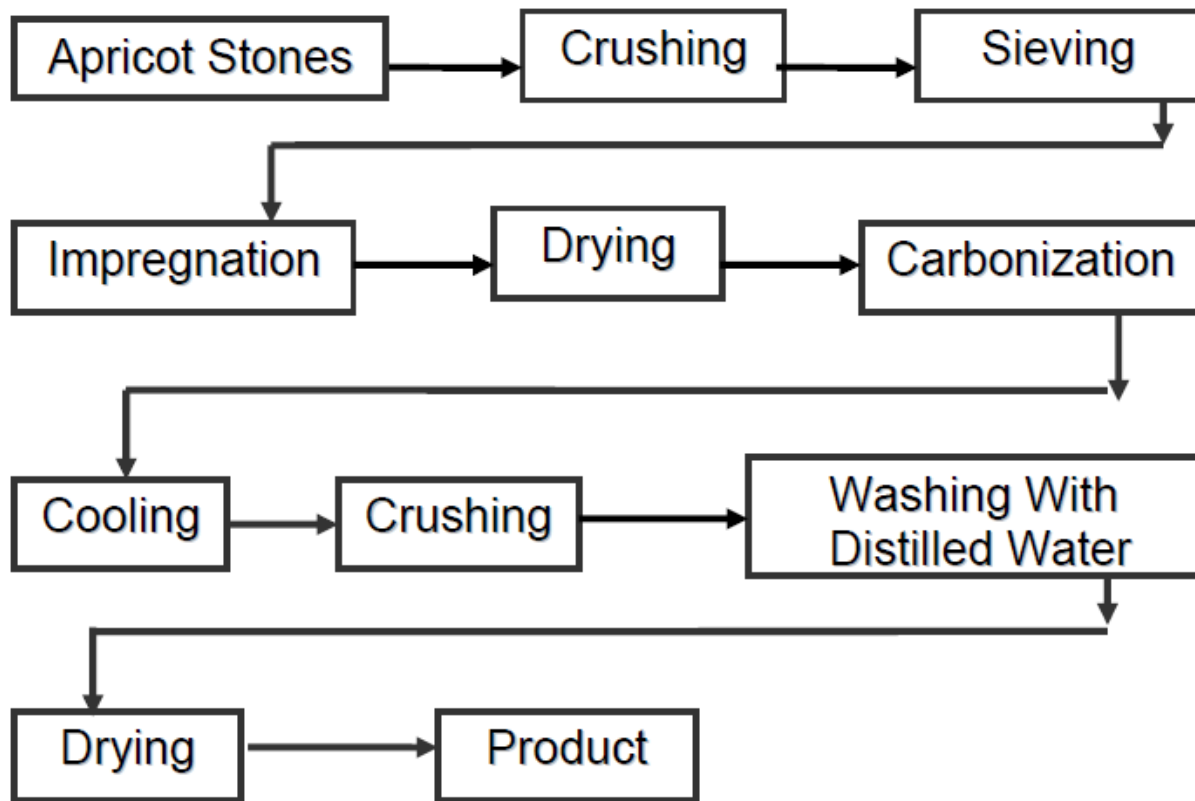


Fig 4: Procedure followed in experiments

3.3 CHARACTERIZATION OF ACTIVATED CARBON

3.3.1 CHEMICAL COMPOSITION OF ACTIVATED CARBON

Chemical composition of the activated carbon formed from the phosphoric acid activation was analyzed and following were the results:

Elements	%wt
C	72.3
H	2.2
O	20.6
N	Trace
Ash	3.5

Table 3: chemical composition of activated carbon

3.3.2 FOURIER TRANSFORM INFRARED ANALYSIS

It was done using NICOLET AVTAR 370, USA model. FTIR analysis is used for the determination of functional groups in activated carbon at room temperature. Pellet technique was used in this process by using KBr. Pellets were prepared by mixing adsorbent in KBr. The spectral range chosen was from 4000 to 400 cm^{-1} .

3.3.3 BET SURFACE AREA ANALYZER

Brunauer–Emmett–Teller (BET) aims to measure the adsorption of gas molecules on solid surface. Chemisorb – 2720 model (Micromeritics, USA) was used with the help of software Chemisoft TPx. It gives us the surface area, pore volume, monolayer volume etc. of the sample.

3.3.4 SCANNING ELECTRON MICROSCOPE

It is a type of electron microscope which uses a focused beam of electrons in a raster scan pattern to produce images of a sample. It provides us with the information regarding surface topography and morphology, chemistry, crystallography and composition. It was conducted using LEO 435VP(England) and EDX analysis was conducted by using QUANTA 200 FEG.

3.4 PREPARATION OF ADSORBATE SOLUTION

The adsorbate 4-nitrophenol was of laboratory reagent and analytical reagent grades (purity>99%). It was supplied by Loba Chemicals Private Ltd, Mumbai (India). This procured 4 – nitrophenol was used to prepare synthetic solutions of different concentrations in distilled water. The concentration range was from 100mg/L to 400mg/L. Fresh solutions were prepared all the time so that organic matter could not degenerate.

3.5 CALIBRATION CURVE FOR 4 – NITROPHENOL

Synthetic solutions of 4-nitrophenol in distilled water with different concentrations were prepared in the laboratory. The calibration of the adsorbate solutions was done in a UV (UV – 1800) Visible Spectrophotometer (Shimadzu Corporation, USA) at a maximum wavelength of 317 nm. The concentration was taken from 0 to 6 mg/L. the software used was UV Probe. All the absorbance values were found out for different concentrations respectively and a curve was plotted between the absorbance and concentration. The temperature was kept constant at 298 K.

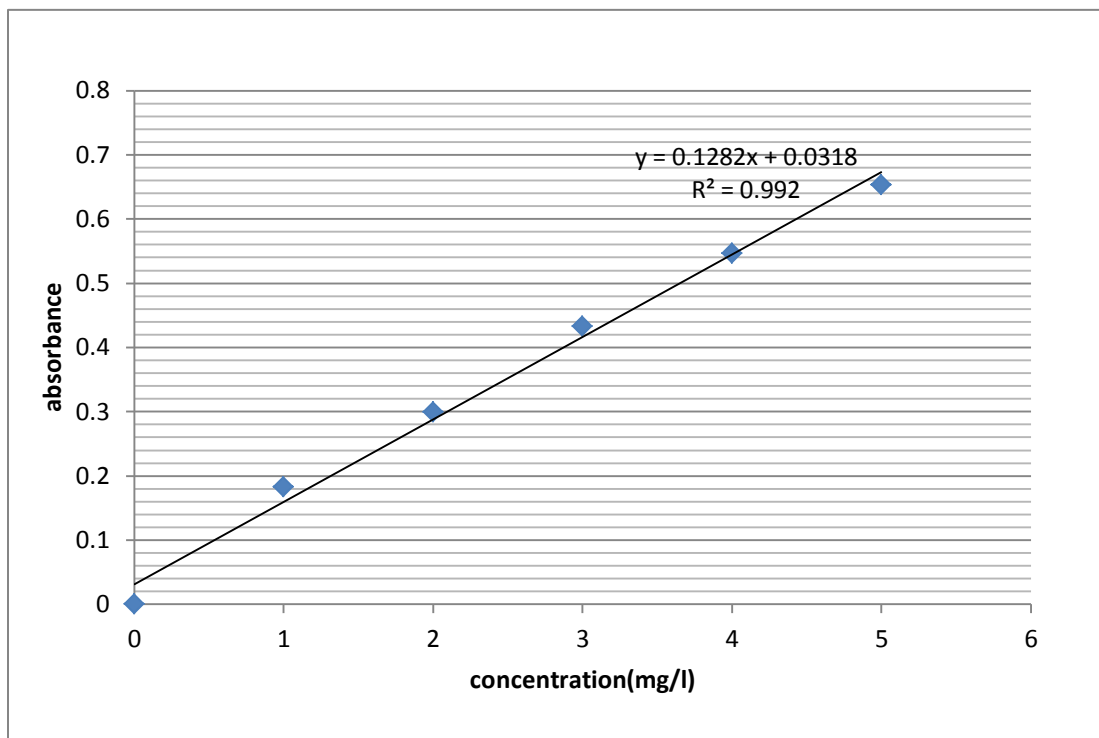


Fig 5: Calibration curve for 4-nitrophenol

3.6 EXPERIMENTAL PROCEDURE

A solution of 4-nitrophenol in distilled water with known concentration was prepared initially at room temperature. Batch isothermal experiments were conducted to determine the removal of 4-nitrophenol by activated carbon. The stock solutions were prepared with concentrations ranging from 100 mg/L to 400mg/L. A 50 ml solution of each concentration was taken in stoppered conical flask to carry on the experiments. A known quantity of activated carbon was put in the solution and it was shaken at a set rpm on a reciprocating type horizontal shaker (Metrex Scientific Instruments Ltd., New Delhi) throughout the experiment. pH of the solutions were changed using 0.1 N NaOH and HCl respectively. Adsorbent dosage was measured using an electronic weighing machine with the help of an aluminium foil. After the shaking was carried out for a prescribed time interval the solution was taken out and was filtered using a filter paper. The filtered solution was diluted 10 times and its absorbance was

found out using a UV spectrophotometer at a wavelength of 317 nm. Thus the concentration could be found out using the calibration curve. Readings were taken by changing different process variables to find out the optimum conditions for maximum adsorption to take place.

Initially solutions of different concentrations of p nitrophenol were taken. 50 ml of each was put in a conical flask and .1 g of activated carbon was also put in. the flasks were put in orbital shaker at 150 rpm for sufficiently long time and readings taken. Then the amount of activated carbon was also varied and readings taken at 25 °C.

Then for different concentration solutions of 4-nitrophenol in distilled water, 0.1 g of activated carbon was put in the flasks and adsorptions measurements were done using batch experiments at different temperatures. For same concentrations and at 25 °C readings were taken to determine the effect of contact time on the batch adsorption.

After reaching the equilibrium the samples were taken and the concentrations measured for each run were found out using the calibration curve prepared. These concentrations were then used for measuring the amount of the 4-nitrophenol adsorbed in each run per gram of adsorbent. The formula used was:

$$q_e = \frac{V(C_0 - C_e)}{M}$$

Where,

q_e = 4-nitrophenol adsorbed per gram of activated carbon

V= volume of solution

C_0 = initial concentration of adsorbate

C_e = concentration of solute at equilibrium

M= mass of adsorbent

Average of three values was taken for each adsorption measurement. Process parameters were varied accordingly and their effect on the adsorption process was elaborately studied.

3.7 EQUILIBRIUM MODELLING

Adsorption measurements were carried out for aqueous solutions of 4-nitrophenol in water using activated carbon. The amounts absorbed were measured when equilibrium was attained as there is no change in concentrations after the attainment of the equilibrium. Different isotherm models were tested to fit and correlate the data obtained in the study: Freundlich isotherm(2-parameter), Langmuir isotherm and Temkin isotherm.

The Langmuir adsorption model is the most widely used model to measure the amount of adsorbate, adsorbed on an adsorbent with respect to partial pressure or concentration at a given temperature. It assumes a monolayer adsorption on a homogeneous surface. It is considered that the binding sites are evenly distributed over the surface of activated carbon and have the same affinity. Interaction between the adsorbed molecules is neglected. Mathematical expression is:

$$q_e = \frac{QbC}{1+bC}$$

Where,

q = metal uptake

C= concentration of solution at equilibrium

b= affinity

Q= maximum metal uptake

Freundlich adsorption isotherm is a purely empirical formula. It can be applied to adsorption on a heterogeneous surface. Freundlich Adsorption Isotherm does not fit well to the experimental data at higher pressures.

$$q_e = kC_e^{1/n}$$

Where,

k= constant related to amount adsorbed

n= constant related to adsorption intensity

Temkin isotherm contains a factor that takes into account the effects of adsorbing species-adsorbent interactions. By ignoring the extreme values of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease proportionally with coverage. The mathematical equation for this model is:

$$q_e = \frac{RT}{b} \ln(A_T C_e)$$

Where,

A_t = equilibrium binding constant

b= constant related to heat of adsorption

Sips isotherm model is a combination of Langmuir and Freundlich isothermal models. It is used on a large scale for interpretation of experimental data:

$$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$$

Where,

a_s = median association constant

β_s = heterogeneity factor

Redlich-Peterson isotherm model is also used widely in study of adsorption results. The equation is :

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CHARACTERIZATION OF ACTIVATED CARBON

Activated carbon production from apricot stones has been achieved by the chemical activation technique using phosphoric acid and sulfuric acid as activating agent.

Chemical composition of activated carbon from phosphoric acid activation is given below:

C= 72.3%, H=2.2%, O=20.6%, N=trace, ash=3.5%

BET surface area for both types of activated carbon was analyzed:

Property	Sulfuric acid activated	Phosphoric acid activated
Initial treatment temperature	473 K	298 K
Initial treatment time	2 h	24 h
Carbonization temperature	923 K	723 K
BET surface area	84.25 m ² /g	223.1 m ² /g
Total pore volume	.0314 m ² /g	.0992 m ² /g
Monolayer volume	11.962 cm ³ /g	40.718 cm ³ /g

Table 4: BET surface area comparisons of activated carbon samples

FTIR analysis of both the samples was performed.

For the sample of activated carbon which was treated with sulfuric acid FTIR curve was found to be:

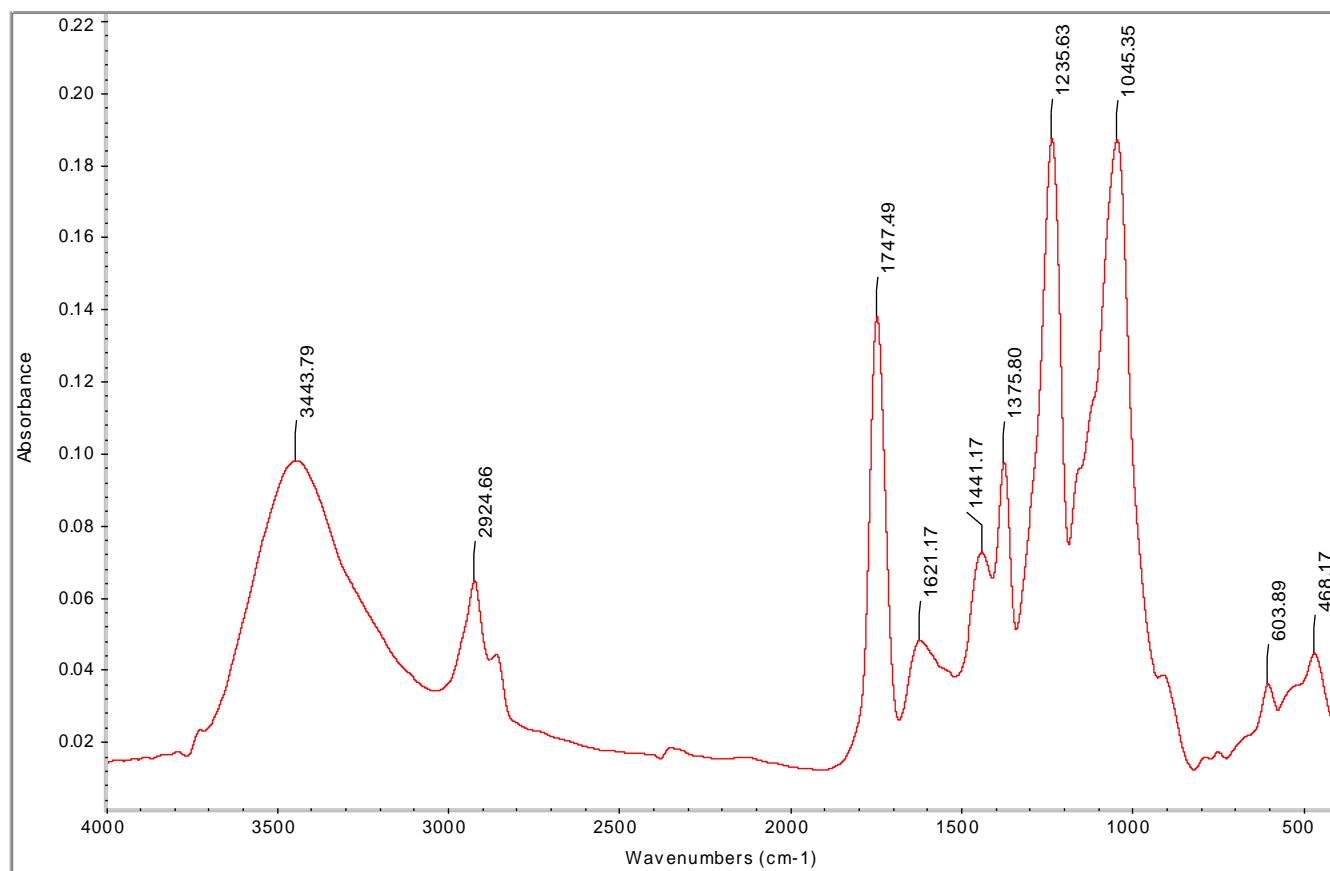


Fig 6: FTIR analysis for sulfuric acid activated sample

In the analysis of sulfuric acid activated sample presence of aliphatic groups was found ($-CH_3$ and $-CH_2$). No traces of inorganic compounds were found. There were compounds of alcohol functional group like 1-pentanol, 2-butanol, 3-methyl-3-hexanol. There were also some derivatives of phenol.

For the analysis of activated carbon prepared by activating apricot stones with phosphoric acid FTIR analysis showed presence of some inorganic phosphate compounds and carboxylic acids. Phosphate compounds present were potassium phosphate and silver phosphate. Carboxylic acids present were pentanoic acid

and butyric acid. A considerable amount of olefins (3-propenal, isotopes of hexene and octene), were also present in the sample. There was also presence of some alcohol functional group compounds and phenol derivatives.

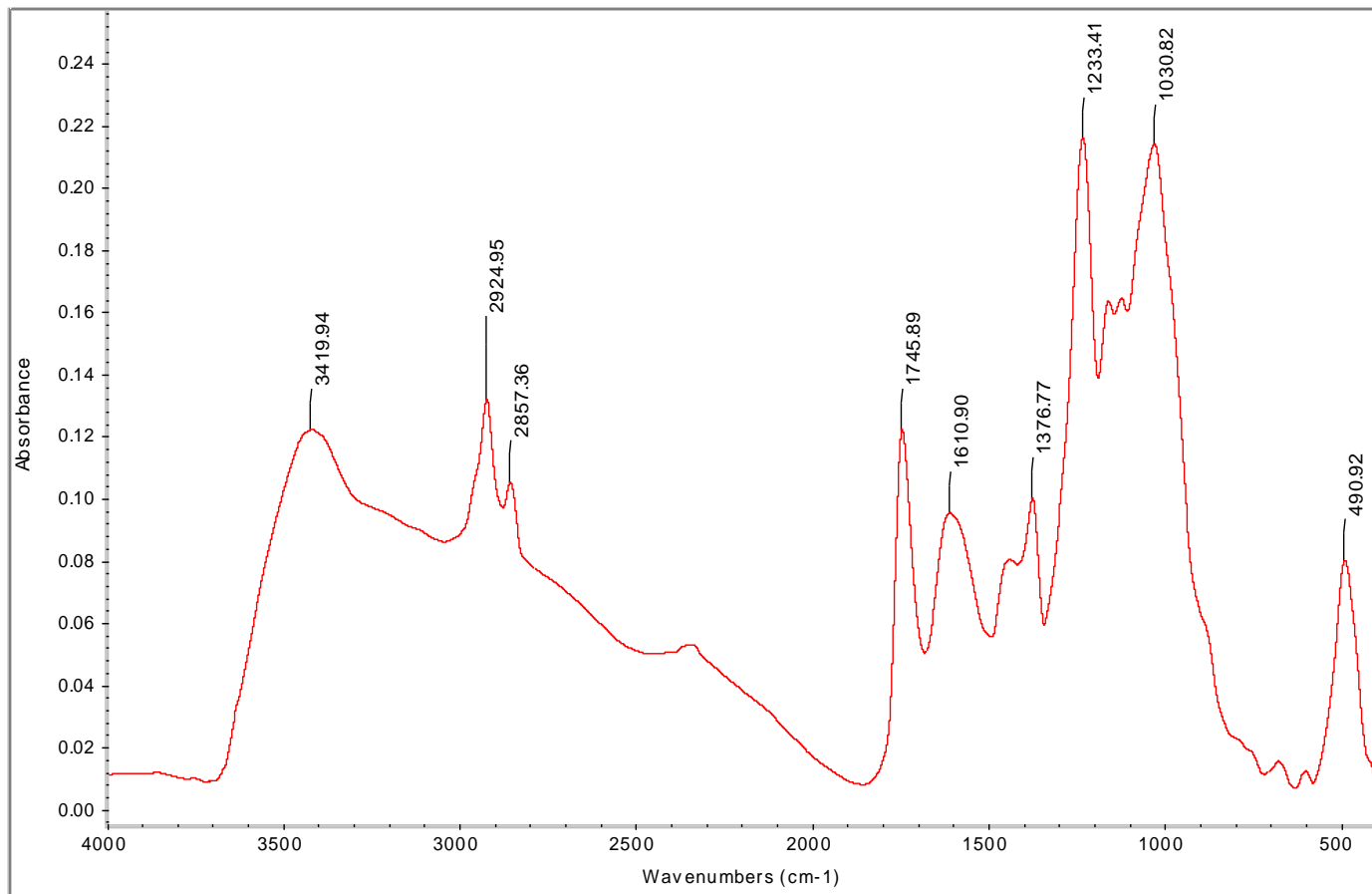


Fig 7: FTIR analysis of phosphoric acid activated sample

4.2 UV ABSORBANCE WITH pH

To find the effects changes in pH have on absorbance a sample solution of 50 mg/L of 4-nitrophenol in water is taken. The samples were analyzed with the help of a UV-1800 Visible Spectrophotometer at wavelength of 317 nm. The increase in absorbance with pH was very less, so it can be assumed that pH changes have no major effect on the removal process.

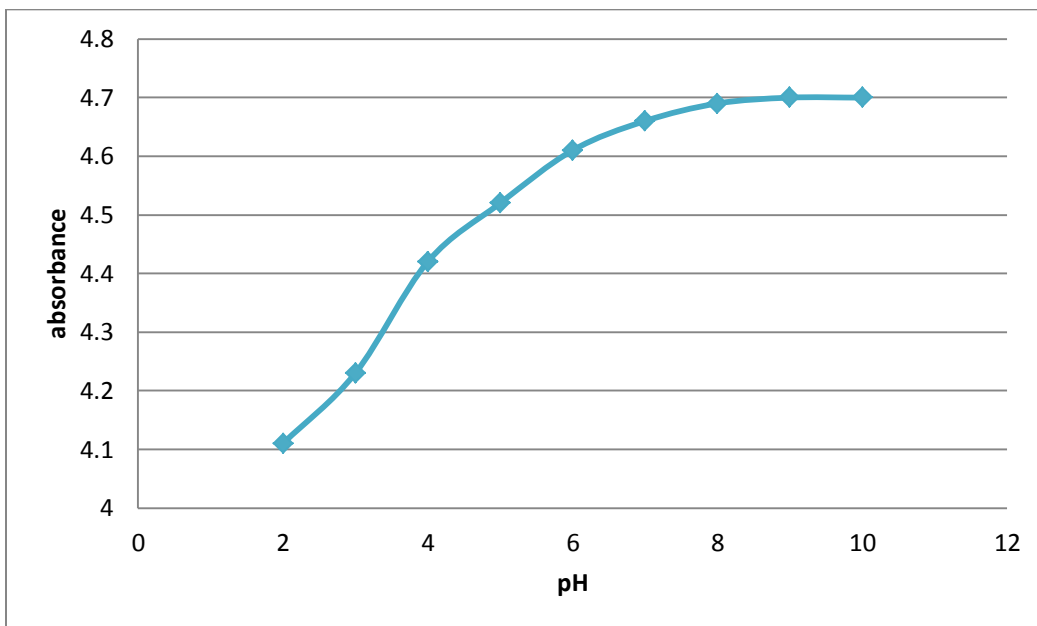


Fig 8: pH versus absorbance of 4-nitrophenol

4.3 EFFECT OF CONTACT TIME

To find the time required to attain the equilibrium in this batch adsorption experiment, measurements were done at different time intervals. Three solutions were prepared of concentration 100mg/L, 200mg/L, 400mg/L. 50 ml of each was taken in flasks and .1 g of activated carbon was added in each. Readings were taken every hour and at 298 K. Equilibrium time was found out to be 6 hours.

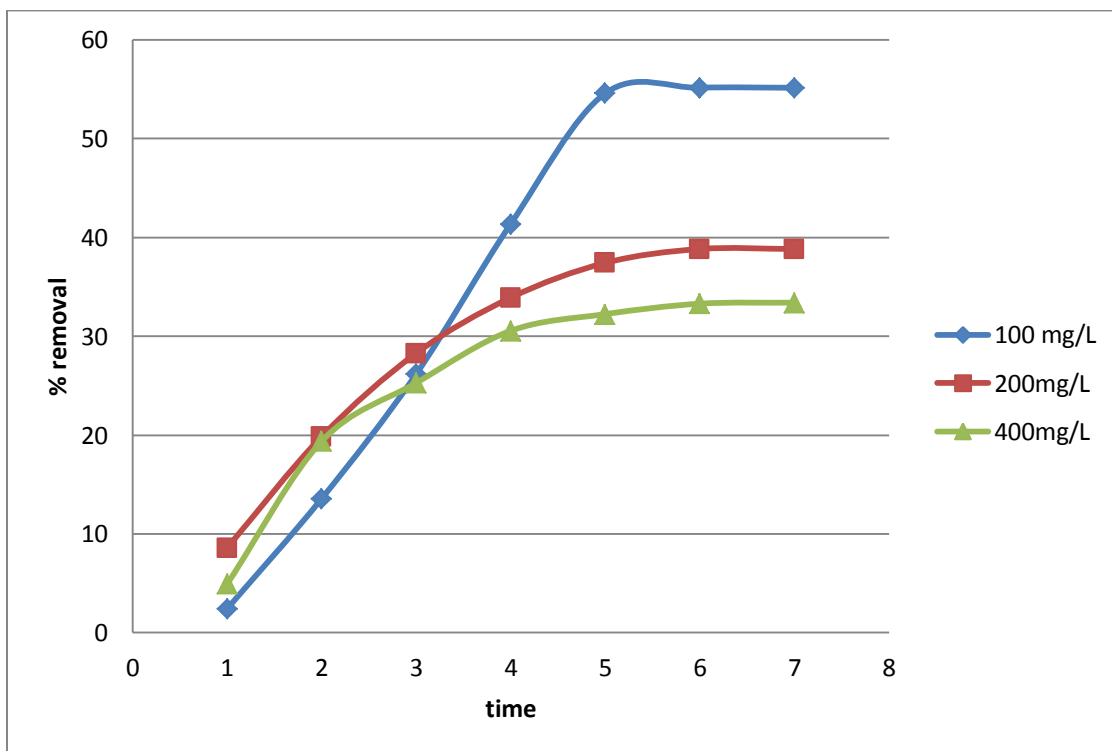


Fig 9: %removal of 4-NP versus time at different initial concentrations

4.4 EFFECT OF ADSORBENT DOSE

As the adsorbent dosage was increased, removal of 4-nitrophenol also increased. At high adsorbent concentration there was almost complete removal of 4-nitrophenol from the aqueous solution. Experiment was carried out for 6 hours till the equilibrium was reached. Adsorbent dose was varied from 2g/l to 9g/l. measurements were done at 298 K.

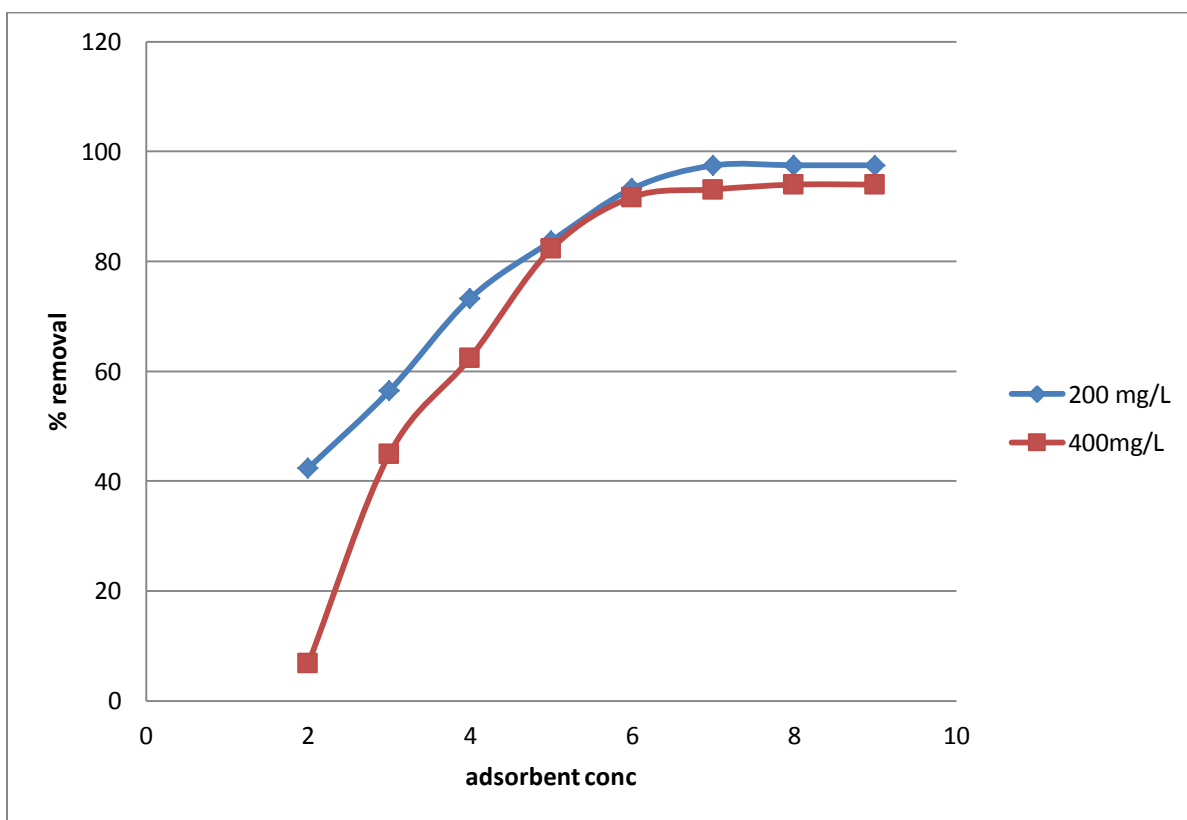


Fig 10: %removal of 4-NP versus adsorbent concentration

4.5 EFFECT OF INITIAL CONCENTRATION

As the concentration of 4-nitrophenol in the initial solution was increased, percentage removal showed a decline. Experiments were carried out by taking 50ml of each sample and by adding .1 g of activated carbon in each flask. Temperature was maintained at 298 K and they were shaken at 150 rpm for 6 hours.

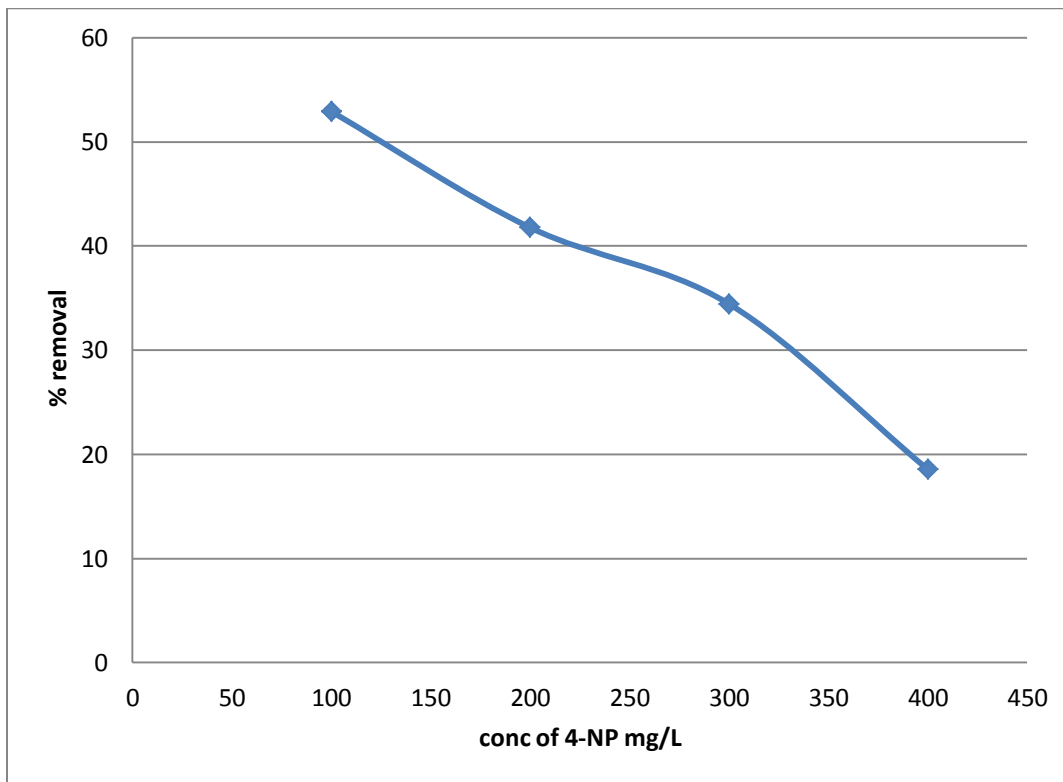


Fig 11: %removal versus initial concentration of 4-NP

4.6 EFFECT OF pH

The effect of pH on removal of 4-nitrophenol was studied by varying the pH between 2 to 8. For experiments 50 ml solutions with 200mg/l 4-nitrophenol concentration were taken in a stoppered flask and .1 g activated carbon was added in each of them. Temperature was set at 298K and flasks were rotated at 150 rpm in a orbital shaker. The pH was varied by using NaOH and HCl solutions. Agitation was made for a period of 7 hours till the equilibrium conditions were achieved. The samples were then analyzed with the help of a UV Visible Spectrophotometer.

The initial pH has a major effect in deciding the rate of adsorption. pH effects the charge on the surface of the activated carbon which in turn has a role in the rate of adsorption. From these experiments it was found that removal of 4-nitrophenol decreased with the increase in pH.

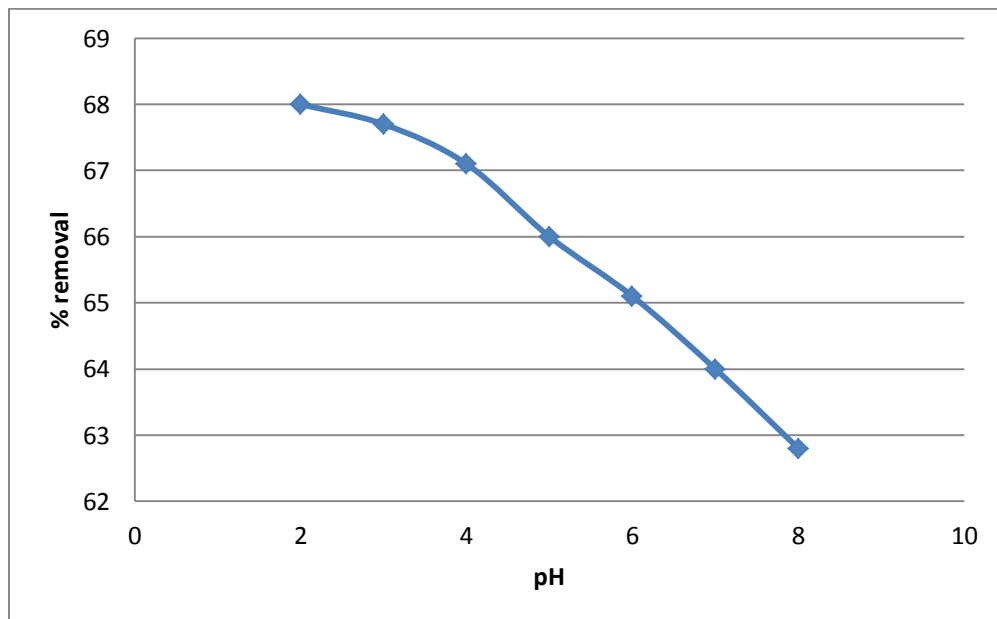


Fig 12: %removal versus pH for 4-NP conc=100mg/L

4.7 EFFECT OF TEMPERATURE

The effect of temperature was studied by taking 100mg/L, 200mg/L and 400mg/L concentrations of 4-nitrophenol in distilled water. The temperature was varied within a range of 15 °C to 45 °C. 50 ml of solution was taken in a conical flask and .1 g of activated carbon added to it. The flasks were then put in a orbital shaker at 150 rpm. Readings were taken with the help of a UV spectrophotometer (UV 1800). From the measurements it was found that with the increase in the temperature of the batch adsorption experiment, removal of 4-nitrophenol increased. It may be because of the endothermic form of the process that with the increase in the temperature of the process adsorption of 4-nitrophenol on activated carbon increased.

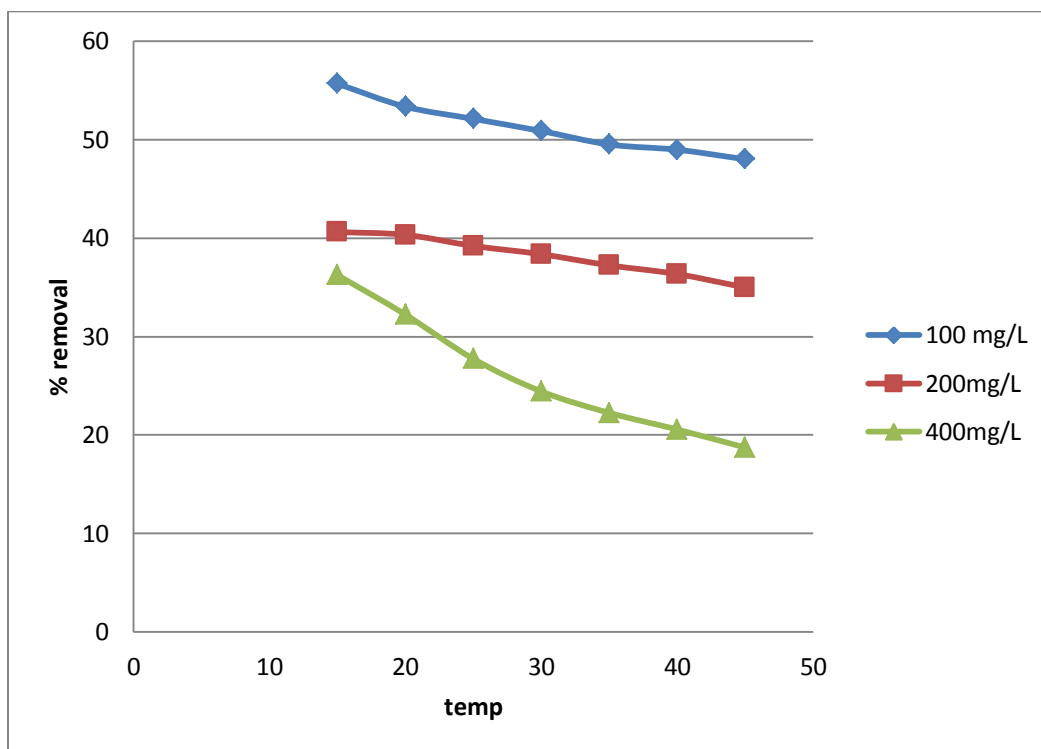


Fig 13: Effect of temperature on removal of 4-NP at different concentrations

4.8 REMOVAL PER GRAM OF ACTIVATED CARBON

Following experiment were performed at three different temperatures. The concentrations of 4-nitrophenol used were 100mg/L, 200mg/L, 300mg/L and 400mg/L. The solutions were taken in conical flasks and were agitated in an orbital shaker at 150 rpm. It was found that the removal capacity of activated carbon was highest at 15 °C. As the temperature of the adsorption process was increased, removal of 4-nitrophenol per gram of activated carbon declined. Also as the concentration of 4-nitrophenol in the solution was increased, removal capacity of activated carbon increased for some time, after which it became constant.

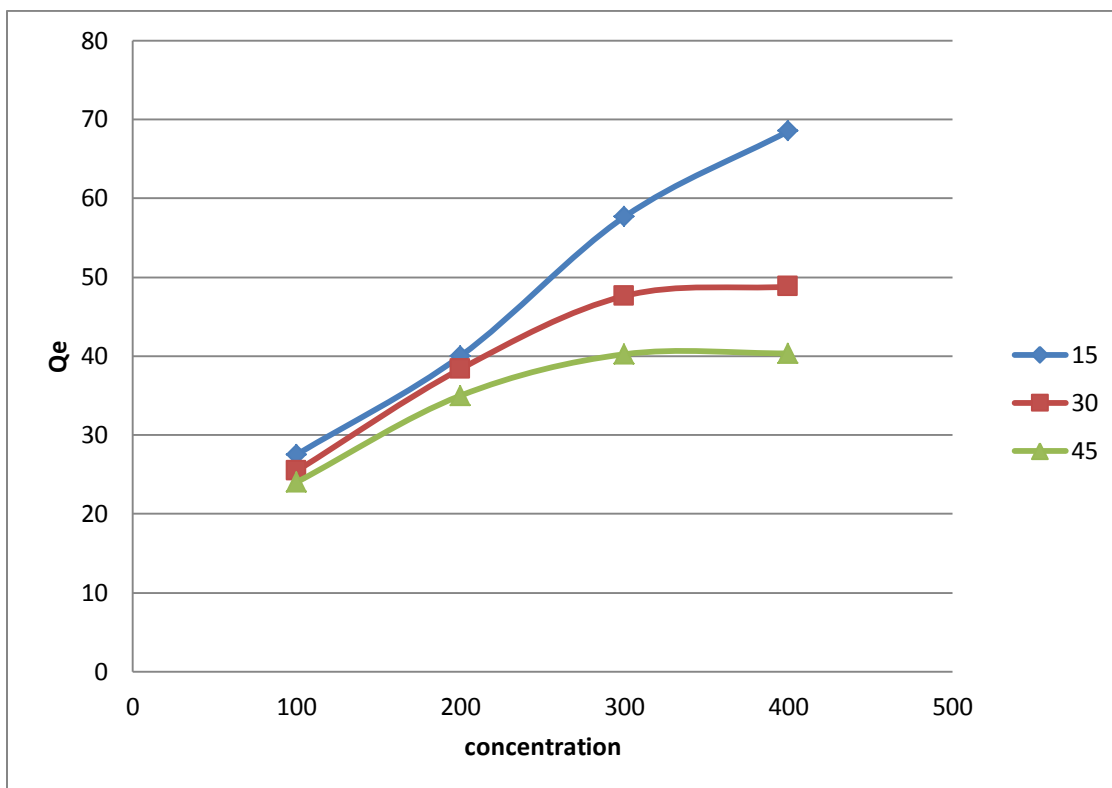


Fig 14: Effect of temperature and initial concentration on removal per gram of AC

4.9 ISOTHERM MODEL VALIDATION

Adsorption isotherm model	Parameters	Temperature (°C)		
		15	30	45
Langmuir $q_e = \frac{Q_o b C_e}{1 + b C_e}$	Q_o	162.637	72.743	53.962
	b (mg/g)	.002	.006	.009
	R^2	.984	.981	.969
Freundlich $q_e = K_F C_e^{1/n}$	K_F (L/mg)	1.073	3.312	4.933
	N	.694	.457	.359
	R^2	.99	.951	.915
Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	a_R (L/mg)	.708	.303	.290
	K_R (L/mg)	.241	$2.7 \cdot 10^{-4}$	$1.77 \cdot 10^{-4}$
	G	.428	1.434	1.545
	R^2	.989	.991	.997
Sips $q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	K_s	525.1	58.601	43.447
	a_s (mg/g)	.002	.001	$2.38 \cdot 10^{-4}$
	β_s	.765	1.435	1.856
	R^2	.989	.988	.992

Table 5: Isotherm models tested for experimental data

From regression studies and curve fitting it was found that Redlich-Peterson isothermal model best suited the experimental data.

CHAPTER 5

CONCLUSION

The following conclusions were made from the present study:

- Activated carbon samples were prepared from apricot stones using sulfuric acid and phosphoric acid respectively. Characterization of both the samples was done.
- A comparison was done between the two samples prepared and was found that phosphoric acid prepared sample had higher surface area with a well defined pore structure which best suited the requirement for removal of 4-nitrophenol from water.
- Batch adsorption studies were carried out for the adsorption of 4-nitrophenol from waste water using this carbon. It was found that this activated carbon can be used efficiently for the removal of 4-nitrophenol from water.
- The adsorption was found to be dependent on various process parameters and optimum conditions for the maximum removal were determined.
- The optimum pH was found to be 2. Batch adsorption reached its equilibrium in six hours. 2g/L was determined as the optimum adsorbent dosage.
- Under optimum operating conditions maximum removal efficiency was found out to be 98% for 4-nitrophenol solution.
- The removal efficiency for the activated carbon prepared from apricot stones by phosphoric acid was found out to be considerable for 4-nitrophenol aqueous solution. This shows that it can be used efficiently for the removal of 4-nitrophenol from industrial waste water.
- The batch adsorption experimental data were found to be fitting to the Redlich-Peterson isothermal model.

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