ADSORPTIVE MODE OF PHENOL ABATEMENT FROM AQUEOUS SOLUTION USING ACTIVATED CARBONS

A Thesis Submitted in Partial Fulfillment for the Award of the Degree

Of

MASTER OF TECHNOLOGY

In

CHEMICAL ENGINEERING

By

Manoj Kumar Mahapatra

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY,

ROURKELA-769008, INDIA

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CERTIFICATE

This is to certify that the thesis entitled **Adsorptive mode of Phenol abatement from aqueous solution using activated carbons**, submitted by **Manoj Kumar Mahapatra** to National Institute of Technology, Rourkela is a record of bonafide project work under my supervision and is worthy for the partial fulfillment of the degree of Master of Technology (Chemical Engineering) of the Institute. The candidate has fulfilled all prescribed requirements and the thesis, which is based on candidate's own work, has not been submitted elsewhere.

Supervisor

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Place: Rourkela

Date: /5/2012   **(Manoj Kumar Mahapatra)**

Abstract

Fresh water crisis has been emerged as one of the most acute issues in the current global scenario, forcing the waste water reutilization concept a must. The reutilization of waste water again demands proper yet effective treatment. Among organic contaminants of waste water phenolic compounds are the principal components, which due to its toxic and carcinogenic nature forces people for its removal from waste water. Adsorption being the highly efficient, simple, cost effectiveness and the availability of a wide range of adsorbents is used as one of the most indispensable method for treatment of phenolic waste water.

In the present study, two different types of activated carbons were used as adsorbents namely, commercial granular activated carbon and laboratory prepared water hyacinth activated carbon prepared from roots of water hyacinth by chemical activation method with phosphoric acid impregnation. For batch adsorption process, operating variables studied were adsorbent dose, contact time, pH, initial phenol concentration, and temperature respectively. Sorption experiments indicated that the sorption capacity was dependent on operating variables and the process was strongly pH dependent. Adsorption of phenol onto GAC witnessed following optimal values of different operating variables as, w=3g/L, t=360mins, pH=9 and highest uptake capacity of 39.0056 mg/g and those for phenol-WHAC system are 5g/L, 360 mins, 6 and 28.0049mg/g respectively. In both the cases adsorption capacity was shown to be decreasing with increase in temperature. Kinetic measurements showed that the process was uniform and rapid. In order to investigate the mechanism of sorption, kinetic data were modelled using the pseudo-first-order and pseudo-second-order kinetic equations. Among the kinetic models studied, the pseudo-second-order equation was the best applicable model to describe the adsorption process of phenol onto both the adsorbents. Equilibrium isotherm data were analyzed using the Langmuir, Freundlich isotherms. The Langmuir model yields a much better fit than the Freundlich model for phenol adsorption onto GAC, in contrast Freundlich model was better fitted for WHAC. Isotherm parameters have also been used to obtain the thermodynamic parameters such as free energy, enthalpy, and entropy of sorption. The value of $\Delta H°$ was found negative, supporting that the phenol adsorption by the GAC and WHAC are exothermic in nature.

Key words: Phenol, GAC, WHAC, Adsorption, Isotherm, Exothermic

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Nomenclature

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
q	The amount of Phenol is adsorbed at time t (min)
%R	Percentage of removal
K_1	Rate constant of pseudo-first-order kinetics
K_2	Rate constant of pseudo-second-order kinetics
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)
ΔH^o	Change of Enthalpy of adsorption at standard state, J/mol
ΔG^o	Change in Gibb's free energy of adsorption at standard state, J/mol
ΔS^o	Change in the entropy for adsorption at standard state, J/mol
PPM	Parts per million
PPB	Parts per billion

nm	Nano metre
AC	Activated carbon
RPM	Revolutions per minute
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray spectroscopy
BET	Brunauer-Emmett-Teller
FTIR	fourier transform infrared spectroscopy
GAC	Granular activated carbon
WHAC	Water hyacinth activated carbon
PACT	Powdered activated carbon treated
CCM	Carbon cryogel modified
CNTs	Carbon nanotubes
APET	Activated polyethylene terephthalate

CHAPTER-1

INTRODUCTION

1. Introduction

In the current scenario several acute global issues came up like, global warming, fresh water crisis, environmental pollution, dreadful diseases etc. However the fresh water crisis among all these are crucial since in day to day life we need water the most for our survival. The industrial and domestic activities have polluted the surface water as well as ground water up to a greater extent [3]. In order to deal with the problem we need to treat the waste water and reuse it instead of leaving that as such. Among the various organic and inorganic pollutants there is a common organic pollutant exists named as, 'Phenol' [7].

Phenol is widely used for the commercial production of a wide variety of resins, including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications. Phenolic pollutants occur in wastewater of a number of industries, such as high temperature coal conversion, petroleum refining, resin and plastics etc. Such aromatic hydroxyl compounds are considered as priority pollutants since they are harmful to organisms especially human and also to aquatic life, at low concentrations and can be toxic when present elevated levels and are known or suspected to be carcinogens [35]. Phenol decomposition is difficult due to, principally, its stability and its solubility in water. Phenol and substituted phenols have a half-life time between 2 and 72 days. They have a strong and unpleasant smell which makes the contaminated water totally unusable [46]. Phenol finds its way in to the environment through industrial effluents and is present in very high amounts in several industrial effluents, which makes its removal a must. Before looking in to permissible levels of phenol let us have a look in to the amount of phenol present in various effluents which is given as,

Table-1.1 Amount of phenol present in various industrial effluents [7]

Industry	Amount of phenol in ppm
Refineries	6-500
Coal processing	9-6800
Coking	28-3900
Petrochemicals manufacturing	2.8-1220

Due to the toxic nature of phenol several regulatory bodies all over the globe like the Ministry of Environment and Forests (MOEF), Government of India and EPA, USEPA have listed phenol and phenolic compounds on the priority-pollutants list as well as also have

proposed maximum permissible limits of phenol in different categories of water. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances. Phenol being highly toxic and difficult to degrade biologically, it has led to setting up of rigid limits on the acceptable level of phenol in the environment.

Table-1.2 Maximum permissible limits of phenol in water

Agency	Type of water	Maximum permissible limit	References
USEPA	Wastewater	0.1 PPM	[38]
BIS	Drinking water	1.0 PPB	[5][38]
WHO	Drinking water	1.0 PPB	[27][38]
MoEF	Industrial effluent	1.0 PPM	[27][30]

1.1 Treatment methods

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, has been tabulated in table-3 below [7]. 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 [38].

Table-1.3 Different technologies for removal of phenol [7]

Techniques	Temp range(^{o}c)	Pressure in atm and pH	Reactor	Additional chemicals or materials	Performance	Comments
Distillation	95-180	1 atm, as such	Distillation column	no	Complete separation possible	Commercial; recovery of phenol; costly process
Adsorption (AC)	20–50	1 atm, Neutral	Fixed bed column	AC	Adsorption capacity 200–400 mg phenol /g AC	Commercial
Pre-evaporation	20–50	1 atm, as such	Membrane module	Membrane	enrichment factor 4–60 (m^2h) permeate flux/ 0–0.3 kg phenol	Commercial, recovery of phenol
Membrane Extraction	20–50	1 atm, as such	Membrane module	Membrane Solvent	Depletion 50- 100 %	Commercial, recovery of Phenol
Oxidation	180–315	20–160Atm Slightly acidic	Bubble column, stirred reactor	Air, an acid	COD 10–100 g/l, 15–120 min, COD Conv. 75–90%	Commercial, further treatment needed

1.2 Adsorption by activated carbons

Adsorption by activated carbons (ACs) is one of the most frequently used methods to remove phenolic compounds from water, because ACs possesses perfect adsorption ability for that class of compounds. Heterogeneous surface of activated carbon is consequence of both geometrical heterogeneity (porosity) as well as chemical one. Geometrical heterogeneity is the result of differences in shape and size of pores, as well as vacancies, pits, etc. Chemical heterogeneity is connected with different functional groups at a surface, and with various surface contaminants. Functional groups and delocalized electrons of the graphitic structure determine the apparent chemical character of an activated carbon surface. Some of the groups, e.g., carbonyl, carboxyl, phenolic hydroxyl and lactonic ones, are acidic. The existence of pyrone, chromene and quinone structures was postulated to account for the basic nature of the carbon surface. Owing to the amphoteric character of the carbon surface, i.e. to the acidic and/or basic functional groups, the surface properties may be influenced by the pH value of the coexisting liquid bulk phase. It is usually assumed that basic surface groups play a dominant role in phenol adsorption. The micropore volume of carbons limits phenol adsorption, and the actual position below this limit is determined by their acid–basic characteristics [36].

1.3 Objectives of the research work

- Study of the effects of various parameters on adsorption of phenol.
- Preparation of low cost adsorbent from biomass i.e. water hyacinth roots.
- Comparison of adsorption results of phenol with those available in literature.
- Characterization of all the adsorbents for their various adsorbable properties such as surface area, CHNS, FTIR and SEM.
- Kinetics and equilibrium study of the phenol adsorption.

1.4 Organization of thesis:

The thesis is organized into six chapters as follows,

Chapter 1 represents complete introduction of project work including reason of phenol abatement, details of its concentration in industrial effluents and its permissible levels. Apart from that it also provides information regarding technologies of phenol abatement and last but not the least objectives of the work.

Chapter 2 is devoted on the extensive literature survey on topics namely Phenol adsorption by different adsorbents with the emphasis on activated carbons, activated carbon preparation and surface characteristics of activated carbons.

Chapter 3 deals with the detail idea of each and every material and methods of this project work starting from making of standard phenol solutions to characterization studies as well.

Chapter 4 is devoted towards the detailed discussions of various results obtained during the course of this project work. This includes study of parametric effects, characterization and optimization of process parameters.

Chapter 5 represents the various conclusions those were drawn from the work, and future scopes.

Chapter 6 deals with the complete references of literatures from journals, books and internet; those were referred during the course of work and also the publications list from thesis.

CHAPTER-2

LITERATURE REVIEW

2. Literature review

This chapter reviews adsorptive mode of phenol removal from wastewater using activated carbons, their characterization and preparation as well. In the later part of this chapter a brief review of work by the different researcher is presented. The literature survey is arranged in a similar way to the work done in this thesis. In this literature review emphasis is given on:

2.1 Phenol adsorption by different adsorbents with the emphasis on activated carbons
2.2 Activated carbon preparation
2.3 Surface characteristics of activated carbons.

2.1 Phenol adsorption by different adsorbents with the emphasis on activated carbons

Liquid phase adsorption has been shown to be a highly efficient, well-established technique for the removal of organic compounds due to its simplicity, low adsorbent cost, effectiveness and the availability of a wide range of adsorbents. Adsorption by activated carbons (ACs) is one of the most frequently used methods to remove phenolic compounds from water, because ACs possesses perfect adsorption ability for that class of compounds because of their heterogeneous surface. Heterogeneous surface of activated carbon is consequence of both geometrical heterogeneity (porosity) as well as chemical one i.e. due to presence of several functional groups which act as the potential adsorption sites [48].

Fernandez et al., (2003) had investigated the process of micropore filling by phenol from its dilute and concentrated solutions. Combined calorimetric and adsorption techniques showed that in the case of phenol adsorption from either dilute or concentrated aqueous solutions, water is always adsorbed preferentially by the oxygen-containing surface groups of the carbon which reduces the surface and/or the micropore volume accessible to the phenol molecule and quantitatively explains the decrease in the limiting adsorption of phenol on a given carbon after oxidation. In the case of dilute solutions, as established earlier, the mechanism corresponds to the coating of the total surface (external surface and micropore walls) by a monolayer of phenol. On the other hand, for concentrated solutions (15-25% of water), they had observed a process of micropore filling by phenol. Both mechanisms were described in the framework of Dubinin's theory.

Khalid et al., (2004) had investigated the phenol removal from aqueous solutions using zeolites as adsorbent. They worked with phenol concentration ranging from 0.1 to 1.6 g/L and

compared their results with that by activated carbons. The high Si/Al ratio of zeolites was proved to be advantageous because that imparts high grade of hydrophobicity which is desired for an adsorbent. Thus, purely siliceous BEA zeolite (Si/Al=∞) was used with success. The adsorption capacity was slightly higher at low phenol concentration (≤ 1.6 g/L) than the one of activated carbon (surface area close to 1150 m^2/g). Furthermore, siliceous BEA zeolite appeared as an efficient adsorbent which was able to be easily regenerated keeping initial properties intact.

Roostaei et al., (2004) had investigated the liquid-phase adsorption of phenol from water using several different types of adsorbents such as activated carbons, activated alumina, filtrasorb-400, silica gel and zeolites like HiSiv 1000, HiSiv 3000 etc. Results of kinetic experiments indicated that HiSiv 1000 had the highest rate of adsorption among the adsorbents studied and therefore more detailed studies were carried out with this adsorbent. The influence of particle size, temperature, and thermal regeneration on adsorption of phenol by HiSiv 1000 was evaluated. The particle size experiments have confirmed that adsorption capacity was not affected by increase in particle size but the adsorption rate was decreased considerably, temperature studies supported the exothermic nature of adsorption. Although the adsorption capacities of activated carbon and Filtrasorb-400 were several times higher than that of HiSiv 1000 but the reusability of HiSiv 1000 plays a crucial role in making it a robust adsorbent as compared to the earlier one, their studies have showed that after thermal regeneration of HiSiv 1000 at 360 ^{o}C adsorption capacity of HiSiv 1000 did not change even after 14 regeneration cycles.

Cardenas et al., (2005) had studied the adsorption of phenol and dichlorophenols (2,5 DCP and 3,4 DCP) from water by porous clay heterostructure (PCH). Experiments were carried out for the analysis of analysis of adsorption equilibrium capacities using batch equilibrium technique. The Freundlich adsorption model was found to be the best to describe adsorption equilibrium data for dichlorophenols. The adsorption capacities showed by the PCH for both phenol and DCPs from water (48.7 mg/g for 3,4-DCP, 45.5 mg/g for 2,5-DCP and 14.5 mg/g for phenol), suggests that the PCH have both hydrophobic and hydrophilic characteristics due to the presence silanol and siloxane groups formed during the pillaring and preparation of the PCH.

Dursun et al., (2005) had investigated the adsorption of phenol onto carbonized beet pulp prepared by them in presence of N$_2$. They made the studies for effects of various parameters

and found that the maximum phenol adsorption capacity was obtained as 89.5 mg.g^{-1} at the temperature of 60 ^{o}C at pH= 6.0. Freundlich isotherm and pseudo second order models fitted very well to the adsorption datas. The thermodynamic parameters such as, equilibrium constant (K), Gibbs free energy changes (ΔG$^{\circ}$), standard enthalpy change (ΔH$^{\circ}$) and standard entropy change (ΔS$^{\circ}$) had been determined. The result showed that adsorption of phenol on BPC was endothermic and spontaneous in nature.

Vasu (2007) had made an experimental study on adsorptive removal of phenol and o-cresol from dilute aqueous solutions using commercial granular activated carbon. Batch mode adsorption studies were performed by varying parameters such as concentration of phenol solution, time, pH and temperature. For the adsorption equilibrium study he applied the well-known Freundlich, Langmuir and Redlich-Peterson isotherm equations to the adsorption data and evaluated various isotherm parameters. The Langmuir monolayer adsorption capacities were found to be 0.7877 and 0.5936 mmole/g, respectively, for phenol and o-cresol. Kinetic studies performed by him indicate that the sorption processes can be better represented by the pseudo-second order kinetics. The processes were found to be endothermic and the thermodynamic parameters were evaluated. Apart from adsorption studies he also made desorption studies and which indicate that the sorbed phenol molecules can be desorbed with dil. HCl.

Ozkaya (2006) had studied the potential of activated carbon for phenol adsorption from aqueous solution was studied. Batch kinetics and isotherm studies were carried out to evaluate the effect of contact time, initial concentration, and desorption characteristics of activated carbon. The equilibrium data in aqueous solutions was represented by the isotherm models. Desorption studies to recover the adsorbed phenol from activated carbon performed with NaOH solution. It is necessary to propose a suitable model to gain a better understanding on the mechanism of phenol desorption. For this purpose, pore diffusion and first-order kinetic models were compared. The diffusivity rate (D/r^2) and first-order desorption rate (k$_D$) constants were determined as 6.77×10^{-4} and 3.924×10^{-4} s^{-1}, respectively. It was determined that best-fitted adsorption isotherm models were determined to be in the order: Langmuir > Toth > Redlich–Peterson > Freundlich isotherms.

Huang et al., (2007) had investigated adsorption of phenol in cyclohexane onto polymeric adsorbents with amide group like macroporous cross-linked poly(N-methyl-N-p-vinylbenzylacetamide) (PMVBA), poly(N-methyl-N-p-vinylbenzylcaprolactam) (PMVBC),

and poly(N-methyl-N-p-vinylbenzylurea) (PMVBU) prepared by them. The results indicated that the adsorption capacities of phenol on the three adsorbents followed the order PMVBU > PMVBA > PMVBC. Adsorption isotherms of phenol on the three polymeric adsorbents were measured and correlated to a Freundlich isotherm. Adsorption enthalpy, adsorption Gibbs free energy, and adsorption entropy were calculated using thermodynamic function relationships. It was found that the adsorption enthalpy of phenol on PMVBU was almost twice that on PMVBA and PMVBC. Analysis of the adsorption mechanism suggested that hydrogen bonding was the primary driving force for phenol adsorbed on the adsorbents in cyclohexane, and multiple hydrogen bonding was involved for PMVBU with phenol.

Shawabkeh and Abu-Nameh, (2007) had prepared the activated carbon by pretreating the pecan shell with phosphoric acid followed by surface treatment with sodium dodecyl sulphate (an anionic surfactant) for the removal of phenol and methylene blue. For the phenol surfactant suppress the phenol removal efficiency. While on the other hand the maximum uptake of activated carbon for dye was 98 %. The sorption capacity of 410 mg/g was obtained at pH 9 and for phenol 18 mg/g at pH 11 for initial concentration 35 mg/l. They also have observed that moderate adsorption was obtained for phenol with a capacity of 18 mg/g at pH 11 and the same solution concentration. The increase or decrease in solution pH has a favourable effect on the sorption of both adsorbates. Langmuir and Freundlich models were used to fit the experimental data.

Kamble et al., (2008) had done the comparative study of phenol and o-chlorophenol on commercial zeolite-Y, fly ash based zeolite (FAZ-Y) and surface modified fly ash based zeolite (SMZ-Y) was studied. It was observed that the adsorption of phenol on SMZ-Y was 4.05 and 3.24 times higher than the FAZ-Y and commercial zeolite-Y, respectively. For O-chlorophenol efficiency was higher than phenol which may be due to the hydrophobicity imparted by surfactant molecules on the surface of fly ash zeolite, consequently leading to organic partitioning. Again during the study of effect of pH they found that adsorption rates of phenol and o-chlorophenol were maximum at neutral pH.

Lin and Juang (2009) had reviewed the technical feasibility of the use of activated carbon, synthetic resins, and various low-cost natural adsorbents for the removal of phenol and its derivatives from contaminated water. They basically involved those research works in their study in which researchers have worked on inexpensive materials such as coal fly ash, sludge, biomass, zeolites, and other adsorbents, which have high adsorption capacity and are locally

available. Apart from that they have also made a comparison of their removal performance with that of activated carbon and synthetic resins and found that adsorbents that stand out for high adsorption capacities are coal-reject, residual coal treated with H_3PO_4, dried activated sludge, red mud, and cetyl-trimethyl ammonium bromide-modified montmorillonite among those of synthetic resins, HiSiv 1000 and IRA-420 displayed high adsorption capacity of phenol and XAD-4 had shown good adsorption capability for 2-nitrophenol. These polymeric adsorbents were found suitable for treating industrial effluents containing phenol and its derivatives.

Lin et al., (2009) had studied the adsorption of phenol from aqueous solution on hydroxyapatite nano powders prepared by chemical precipitation method. It was found that phenol uptake showed an increment with the excess of all the parameters. One interesting fact that was observed is the adsorption process was fast, and it reached equilibrium in 2 hours of contact time. The maximum phenol adsorption capacity was obtained as 10.33 mg/g for 400 mg/L initial phenol concentrations at pH 6.4 and 60 $^\circ$C. The adsorption kinetic and the isotherm studies showed that the pseudo-second-order model and the Freundlich isotherm were the best choices to describe the adsorption behaviours. The thermodynamic parameters suggested that the adsorption of phenol onto HAp was physiosorption, spontaneous and endothermic in nature.

Song Liu et al., (2010) had investigated adsorption of phenolic compounds like phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (DNP) onto Activated carbon fibers (ACFs) from aqueous solutions. The adsorption capacities followed the order of TCP >DNP≈DCP > 4-NP > 4-CP > 2-CP > phenol. Adsorption isotherms at different temperatures were determined and modelled with Langmuir, Freundlich and Redlich–Peterson equations. Thermodynamic parameters were calculated and correlated with the adsorption behaviours. The effects of solution pH on the adsorption were also studied. The adsorption mechanism was discussed based on the experimental results, and the π-π interactions, solvent effects, hydrophobic interactions and molecular dimensions were considered to be important in the adsorption. Kinetic studies showed rapid adsorption kinetics of the phenols, due to the open pore structure of the ACFs. The kinetics was fitted with the pseudo-first order, pseudo-second-order and intraparticle diffusion models. Steric effects on adsorption kinetics were observed for TCP, 4-NP and DNP, but serious impact on the

ultimate uptake was only found for DNP. The relationship between the steric effects and the molecular dimension was also proposed.

2.2 Activated carbon preparation

Activated carbon preparation is also synonymous as activation. However activated carbons are not cost effective which made the scientists to rethink about the raw materials which will lead to cut down the cost of activated carbons considerably. Among the raw materials animal waste products, plants and agricultural wastes, industrial wastes etc are the potential candidates for the preparation of very low-cost activated carbons. Again there are two standard activation methods exist namely, physical activation and chemical activation.

The physical activation process involves carbonization in two steps, in the first step carbonization is done at 400-500 ^{o}C, to eliminate the bulk of the volatile matter and then further heating at 800-1000 ^{o}C to develop the porosity and surface area. In the chemical activation process no pre-carbonization step is needed and is usually used for the lingo-cellulosic raw materials. In this method raw materials are blended with activators and then carbonized at 500-900 ^{o}C, the remaining chemicals are removed from the carbon by acid or water wash. Product which is produced is usually in powdered form and is used for aqueous and gas phase adsorption purposes. This method needs a stream of mild oxidizing gases for ensuring uniform pore development during oxidation. Activated carbons produced by this mode are primarily used for gas and vapour adsorption [48].

This part of the chapter will review upon the preparation of low-cost activated carbons.

```
                          RAW MATERIALS

        PHYSICAL ACTIVATION          CHEMICAL ACTIVATION

        PRE CARBONIZATION            CHEMICAL BLENDING

        PARTIAL GASIFICATION         CARBONIZATION
```
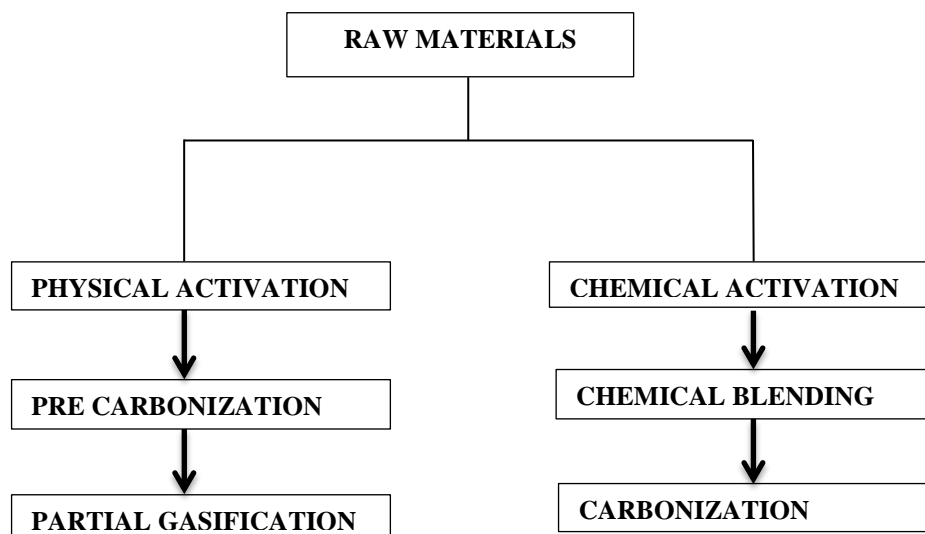
Fig.2.1 Flow-sheet representation of methods of carbonization

Kennedy et al., (2007) had prepared mesoporous activated carbons from rice husk using phosphoric acid activation 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 ^{o}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 ^{o}C and final pH of 2.7.

Vazquez et al., (2007) had investigated the batch adsorption kinetics of Phenol adsorption by Pinus pinaster bark pre-treated with formaldehyde in acid medium. The results showed with increasing the solid/liquid ratio, the percentage of phenol removal increased and with decreasing the initial phenol concentration and the pH. Phenol adsorption has been described using a kinetic model based on the control of mass transfer within the pores of the bark, which has allowed determining the diffusion coefficients for the higher concentrations. Adsorption equilibrium data have been fitted satisfactorily by BET and Freundlich isotherms primarily for lower concentration of phenol.

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, X_P(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 microporous 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. The surface chemical properties of these ACs were investigated by X-ray photoelectron spectroscopy (XPS) and Boehm titration. Their textural and chemical characteristics were compared to those of an AC sample obtained by steam activation of vetiver roots.

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 ^{o}C under the influence of CO_2 flow. Beforehand, the coconut shell was carbonized at 700 ^{o}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.

Girodsa et al., (2009) had prepared activated carbons from particle board for aqueous phase phenol adsorption. The reason for choosing this raw material was to prevent problems of valorisation of particleboard. They followed physical activation mode of activation with activation by steam at 800 ^{o}C. Depending on the preparation conditions, surface areas within the range 800–1300 m^2/g were obtained, close to that of a commercial activated carbon (CAC) specially designed for water treatment and used as a reference material. The resulted material had shown an uptake capacity of 500 mg/g. Although it is of very low cost but large scale production leads to increment of cost even more than that of commercial activated 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.

2.3 Surface characteristics of activated carbons

The surface characteristics of activated carbon play a crucial role in adsorption from aqueous solutions and catalytic properties of carbon. The surface characteristics of the activated carbons are mainly due to the presence of different functional groups which can either acidic or basic. The acidic functional groups can be created by oxidation with oxygen at elevated temperatures or with liquid oxidants, typically nitric acid. The acidic surface shows cation exchange properties in aqueous solutions. However if the carbon is de-gassed at a high temperature e.g. 950 ^{o}C in vacuo or under an inert atmosphere and subsequently oxidized at room temperature after cooling, it exhibits basic character and hence acquires an anion exchange capacity [4].

In this part of the chapter review will be done on the surface chemistry and texture of the activated carbons and their effect on aqueous phase phenol adsorption.

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.

Salame and Bandosz et al., (2003) had investigated the role of surface chemistry on adsorption of phenol on to activated carbon. Two samples of activated carbon of wood origin were oxidized using ammonium persulfate. The structural properties and surface chemistry of the samples and their oxidized counterparts were characterized using sorption of nitrogen and Boehm titration, respectively. 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.

Terzyk (2003) had investigated the temperature as well as pH dependence of phenol adsorption (and adsorption kinetics) on four carbons with different chemical compositions of the surface layer but almost identical porosity. They noticed irreversiable kind of phenol adsorption onto activated carbons due to the reasons like the creation of strong complexes between phenol and surface carbonyl and lactones as well as by the polymerization and due to the ability of carbon to adsorb the oxygen from solution and form superoxo ions. As a final point, they concluded that the mechanism of phenol adsorption is not only determined by so called "π–π interactions" and "donor–acceptor complex formation" but also by (strongly depending on temperature) the "solvent effect" balancing the influence of the two mentioned factors on this mechanism.

Fierro et al., (2008) had a made a comparative study for phenol adsorption by six different activated carbons having different textural and surface properties. Six types of ACs were used: three were commercial, and three were obtained from Kraft lignin chemically activated

with sodium hydroxide, potassium hydroxide or ortho-phosphoric acid. The apparent surface areas of the commercial ACs varied from 620 to 1320 m^2/g, while those made from lignin presented surface areas as high as 1300 m^2/g and 2900 m^2/g when prepared with H_3PO_4 and alkaline hydroxides, respectively; moreover, the highest proportion of microporosity was found for ACs derived from lignin. High phenol adsorption capacities were found for the ACs prepared by activation of Kraft lignin with NaOH and KOH: 238 and 213 mg/g of AC, respectively. Finally it was concluded that the adsorption of phenol was found to depend not only on the micropore volume, but also on the total amount of carbonyl and basic groups and on the ratio of acid to basic groups.

Stavropoulos et al., (2008) had investigated the effect of activated carbons modification on porosity, surface structure and phenol adsorption. Production of activated carbons with desired properties was accomplished by modification of surface functional groups and introduction of acidic/basic properties. Modification of an activated carbon was performed using partial oxygen gasification, nitric acid treatment, urea impregnation followed by pyrolysis and pyrolysis in a urea saturated stream. The surface properties of the produced samples were estimated by Boehm titration and by the CO/CO_2 gas evolution profiles, while pore structure development was measured by the N_2 and CO_2 gas adsorption isotherms. The introduction of surface functional groups depended upon the severity of the treatment: carbonylic and phenolic type groups were introduced in all partially gasified samples, while low temperatures and short reaction times enhanced the basic character of the carbon. However, nitric acid treatment resulted in the introduction of high nitrogen amounts in the samples, the reduction of surface area and the development of a surface containing carboxylic, lactonic, phenolic and carbonylic groups with negligible HCl neutralization capacity. Treatment of activated carbon by urea supported the formation of basic groups and carbonyls. The presence of surface functional groups affected the adsorption capacity of the produced samples for the removal of specific pollutants such as phenols. Urea treated samples with a basic character and high nitrogen content presented the highest phenol uptake capacity; nitric acid treated carbons and oxygen gasified samples presented an acidic surface functionality and a low phenol adsorption capacity.

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 fibre under nitrogen flow, followed by activation with H_2O and CO_2 (under atmospheric pressure and supercritical state). The materials were

characterised 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.

CHAPTER-3

MATERIALS AND METHODS

3.1 Phenol

Phenol was discovered in 1834, when it was extracted from coal tar, which remained the primary source until the development of the petrochemical industry. Phenol, also known as carbolic acid, is an organic compound with the chemical formula C_6H_5OH. It is a white crystalline solid. The molecule consists of a phenyl ($-C_6H_5$), bonded to a hydroxyl (-OH) group. The antiseptic properties of phenol were used by Sir Joseph Lister (1827–1912) in his pioneering technique of antiseptic surgery, although the skin irritation caused by continual exposure to phenol eventually led to the substitution of aseptic (germ-free) techniques in surgery. It is produced on a large scale (about 7 billion kg/year) as a precursor to many materials and useful compounds. It is only mildly acidic but requires careful handling due to its propensity to cause burns. Phenol was first extracted from coal tar, and its major uses involve its conversion to plastics or related materials. Phenols are the key for building polycarbonates, epoxies, Bakelite, nylon, detergents and a large collection of drugs, herbicides and pharmaceuticals [7].

The various physical properties phenol are as, it has a molecular weight of 94.11 g/mol, appears as transparent crystalline solid, it has density of 1.07 g/cm^3, the melting point, boiling point, flash point, auto ignition temperatures are 40.9, 181.5, 79, 715 ^{o}C respectively. Chemically it is slightly acidic: the phenol molecules have weak tendencies to lose the H^+ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion $C_6H_5O^-$ (also called phenoxide). Compared to aliphatic alcohols, phenol is about 1 million times more acidic, although it is still considered a weak acid. It reacts completely with aqueous NaOH to loose H^+, whereas most alcohols react only partially. Phenols are less acidic than carboxylic acid, and even carbonic acid [7] [23].

Although various methods for phenol production are available, still about 95% of phenol is produced by the partial oxidation of cumene (isopropyl benzene) via the Hock rearrangement as,

$$C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5OH + (CH_3)_2CO \tag{3.1}$$

The major uses of phenol, are consuming two thirds of its production, involve its conversion to plastics or related materials. Condensation with acetone gives bisphenol-A, a key precursor to polycarbonates and epoxide resins. Condensation with formaldehyde gives phenolic resins,

a famous example of which is Bakelite. Hydrogenation of phenol gives cyclohexanone, a precursor to nylon. Non-ionic detergents are produced by alkylation of phenol to give the alkyl phenols, e.g., nonylphenol, which are then subjected to ethoxylation. Phenol is also a versatile precursor to a large collection of drugs, most notably aspirin but also many herbicides and pharmaceuticals. Phenol is also used as an oral anaesthetic/analgesic, commonly used to temporarily treat pharyngitis. Phenol injections were used as a means of individual execution by the Nazis during the Second World War [14]. The health hazards caused by phenol are given in tabular form as,

Table-3.1 Health hazards caused by phenol [14]

Exposure mode	Effects due to exposure
Inhalation	• Can irritate the nose, throat, and lungs.
	• Higher exposures may cause a build-up of fluid in the lungs.
Oral	• Ingestion of as little as 1 gram can be fatal to humans.
Eyes	• Can also cause severe eye damage, including blindness.
Skin	• Irritating and corrosive to the skin.
	• Little or no pain may be felt on initial contact due to its local anaesthetic effect.
	• Skin contact will cause the skin to turn white; later severe burns may develop.
	• Rapidly absorbed through the skin; toxic or fatal amounts can be absorbed through relatively small areas.
Chronic exposure	• Repeated or prolonged exposure to phenol or its vapours may cause headache, nausea, dizziness, difficulty swallowing, diarrhoea or vomiting.
	• Can affect the central nervous system, liver and kidneys.

3.2 Adsorption

By definition adsorption is the "phenomenon of concentration or assimilation of gas (or liquid) at the surface of a solid (or liquid) with which it is in close proximity or contact called adsorption. Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or the gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atoms, or ions of the gas or liquid, adsorption is associated with decrease in residual surface energy. The molecules which are adsorbed are

called adsorbates and the surface is called as adsorbent. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. The process of adsorption of gases into the solid surface is called 'occlusion'. The adsorption involves two types of forces: physical forces that may be dipole moments, polarization forces, dispersive forces, or short range repulsive interactions and chemical forces are valency forces arising out of the redistribution of electrons between the solid surface and the adsorbed atoms. Depending upon the nature of the forces involved, the adsorption is of two types: physical adsorption and chemisorption. In the case of physical adsorption, the adsorbate is bound to the surface by relatively weak van der Walls forces, which are similar to the molecular forces of cohesion and are involved in the condensation of vapours into liquids. Chemisorption, on the other hand, involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. The bond formed between the adsorbate and the adsorbent is essentially a chemical bond and is thus much stronger than in the physiosorption. Physiosorption and chemisorption again differ from each other due to following two differences namely, 'magnitude of the enthalpy of adsorption', in physical adsorption the enthalpy of adsorption is of the same order as the heat of liquefaction and does not usually exceed 10 to 20 KJ per mol., whereas in chemisorption the enthalpy change is generally of the order of 40 to 400 KJ per mol. Taking into account 'specificity' physical adsorption is nonspecific and occurs between any adsorbate-adsorbent systems, but chemisorption is specific. Another important point of difference between physiosorption and chemisorption is the 'thickness of the adsorbed phase' although it is multimolecular in physiosorption and is unimolecular in chemisorption [4].

Some of the potent adsorbents are charcoal, silica gel, clay, fuller's earth, alumina gel, zeolites etc. the reverse process of adsorption is called desorption in which the adsorbed substances are removed from the surface. By nature adsorption is exothermic, the amount of heat evolved when one mole of any molecule is adsorbed on a solid adsorbent surface is called 'enthalpy (or heat) of adsorption'. Again depending upon the linkage between adsorbates and adsorbents the process of adsorption is of two types namely physical and chemical. In the former one the linage is van-der-waals type and is of course reversible in nature, but in the latter case the linkage is valence type and is therefore irreversible in nature [6].
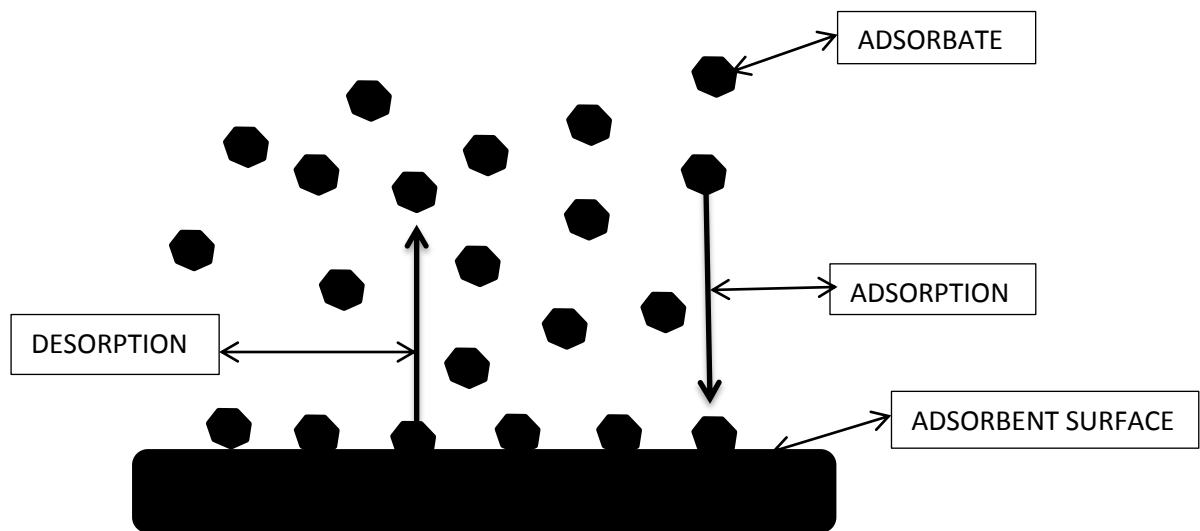
Fig.3.1. Adsorption and desorption process [26]

However adsorption acts as the basic mechanism in various fields such as,

- Activated charcoal is used in gas masks adsorbs poisonous gases.
- By employing adsorption technique we are able to remove colouring matters from sugar solution and vinegar.
- Adsorption is also used for humidity control and moisture removal.
- Modern water purifiers employ adsorption technique to remove organic matters from water by using activated carbon.
- Arsenic poisoning can be treated by adsorption technique using colloidal ferric hydroxide.
- Oil refining employs adsorption technique.

3.3 Activated carbon

Activated carbon is a porous material which is commercially used for the removal of liquids and gaseous pollutants as well for the gas storage application because of its large surface area. It is carbonaceous adsorbent and has highly amorphous structure [7]. There are several factors on which the effectiveness of adsorption process depends upon these adsorption conditions which may either be the nature of the adsorbent (acidic/ basic) or the characteristics of adsorbent which includes the high surface area, pore size distribution, ash content and hydrophobicity. These characteristics defined the concentration of carbon atoms in the matrix, and the density and type of functional groups present on the surface [28]. The acidity or basicity of the activated carbon depend upon the presence of heteroatom's such as

oxygen, which can form phenols, ethers, lactones ketone, carboxyl and nitrogen in the form of amines and nitro groups; and phosphorus as a phosphate can determine. On the other hand, adsorption also depends on the nature of the adsorbate depends on its hydrophobicity, polarity, and size of the molecule [27].

There are several agricultural and biomass waste materials such as waste apple pulp, ,straw, coconut shell, coir pith, saw dust, apricot stone shell, olive stones, sugarcane bagasse peanut hull, water hyacinth roots and many others have been employed to produce activated carbons with high surface area [40].

Table-3.2 Alternative raw materials for preparing low-cost adsorbents [40]

Alternative feedstocks			
Animal waste products	**Plants and agricultural wastes**	**Industrial wastes**	**Miscellaneous wastes**
Bones	Sunflower seeds	Bagasse	News paper
Blood	Jute stick	Petroleum acid sludge	Municipal waste
Fish scales	Wheat straw	Petroleum coke	Reffination earth
	Carbohydrates	Refinery waste	Spent Fuller's earth
Corncobs	Nut shells	Tea leaves	Lignite
Kelp and seaweed	Palm tree cobs	Leather waste	Graphite
	Fruit pits	Fertilizer waste slurry	Blue dust
	Bark	Coal	Fuller's earth
	Cereals	Scrap tires	Oil shale
	Cottonseed hulls	Rubber waste	Olive stones
	Coconut shell	Molasses	Potassium ferrocynide residue
	Coconut coir	Lampblack	
	Wood	Pulp-mill waste	
	Rice hulls	Distillery waste	
	Beat-sugar sludge		
	Coffee beans		

Two main processes are involved in the production of activated carbons

a) Carbonization of precursor material (< 800 ^{o}C)

b) Activation (using activating agent) of resulting carbonized substances

The porosity of raw material can be increased by activation process, which can be done by physical activation and chemical activation. The physical activation involves oxidation and gasification of the char at high temperatures greater than (800°C). While the chemical activation process is carried out in a single step by the thermal decomposition of the raw material impregnated with certain chemicals such as HCl, H_2SO_4, $MgCL_2$, NaOH, KOH, $ZnCL_2$, NH_4CL, $BaCL_2$ and H_3PO_4. The temperatures used in chemical activation are lower than that used in the physical activation process. Although physical activation permits better control over the creation of a desired micro porous structure, chemical activation is an adequate procedure to develop large pores in activated carbons [40].

In the present work, we have used commercially procured granular activated carbon (GAC), and water hyacinth activated carbon (WHAC) to be prepared from a biomass i.e. root part of water hyacinth (*Eichornia crassipes*), an aquatic weed.

Fig.3.2 Granular activated carbon (GAC)

Fig.3.3 Water hyacinth activated carbon (WHAC)

3.4 Raw material for adsorbent preparation

The root part of *Eichornia crassipes* (water hyacinth) commonly known as borajhanji dala in odia. It is a free-floating perennial notorious aquatic weed. Its taxonomic classification is given as,

Table-3.3 Taxonomic classification of water hyacinth [21]

Kingdom	Plantae
Division	Magnoliophyta
Class	Liliopsida
Order	Liliales
Family	Pontederiaceae
Genus	*Eichhornia*
Species	*crassipes*

Fig.3.3 (A) Water hyacinth plant (B) Roots of water hyacinth [21]

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The roots of water hyacinth are slender in shape with secondary root growth on them and are quite soft in nature. The entire root portions after proper separation from the stem part were used as the raw material for adsorbent preparation. The raw materials were collected from the ponds of Baripada town, Odisha.

3.5 Adsorbent preparation

After collection of raw materials they were thoroughly cleaned and washed for 5-6 times under running tap water for removing impurities if any adhered to the roots. Then the roots were air dried followed by drying at 50 ^{o}C in hot air oven before crushing them down to powdered form using hand blender. Then the sample were washed with diluted acids, followed by distilled water to remove the foreign materials adhering to these particles and dried at 100 ^{o}C for 4 hours. The resulting material was washed with dilute HCl and dried again at 100 ^{o}C for 6 hours. These materials were impregnated with H_3PO_4 solution (2N) with an impregnation ratio (w/w) of 4:1, after soaking of 6 hours. It was dried before carbonization at 500 ^{o}C for 1 hour in an inert atmosphere using a pyrolysis reactor shown in figure-3.4 below. The resulting material was again washed with distilled water and dried for 6 hours. Then the sample was stored in an air tight container till further use [11].

However it was also found that, with an increase in carbonization temperature the percentage of volatile matter decreased along with yield. Decrease in yield of adsorbent is due to rapid carbonization occurring in (400-800 ^{o}C) this region. It was also recommended not to prepare activated carbons when carbonization temperature is more than 800 ^{o}C as uncontrolled and sudden evaporation of volatile matter occurs in that temperature resulting in improper development of pores. Since, the successive decreased in volatile matter is minimal. Hence 500 ^{o}C is the optimum condition for developing mesopores [9].
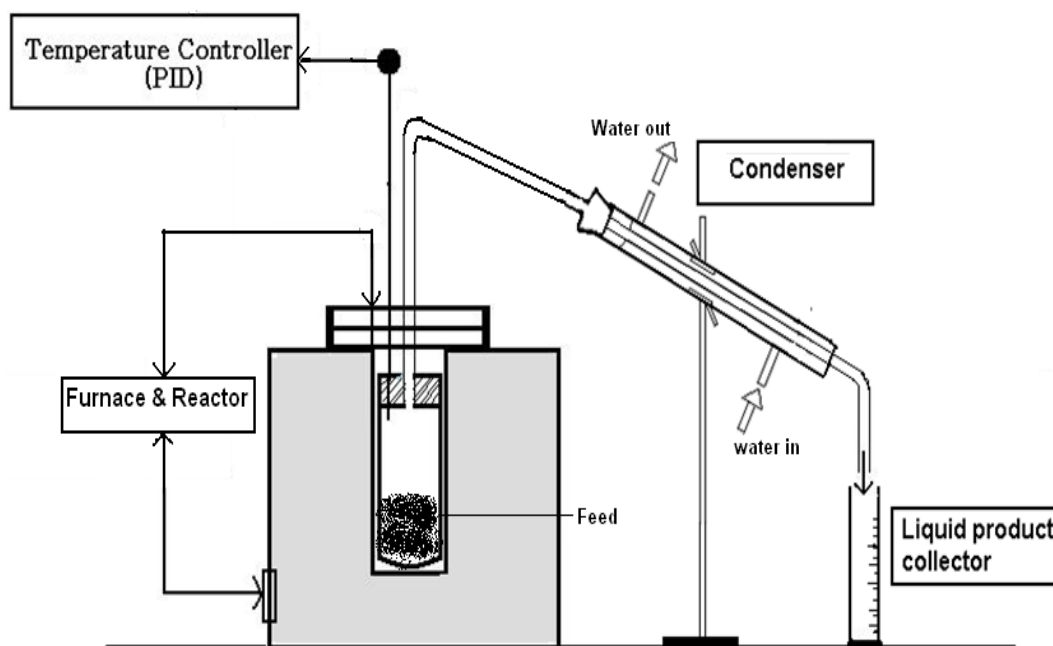
Fig.3.4. Experimental setup for pyrolysis reactor

3.6 Reagents and equipments

All the necessary chemicals used in the study were of analytical grade and obtained from Rankem chemicals, New Delhi, India. UV visible Spectrophotometer (JASCO UV/Vis-530) was used for determination of phenol content respectively in standard and treated solution. The pH of the solution was measured with a Cyberscan 510 (EUTECH Instruments) pH meter. The various characterizations of the adsorbent was carried out like surface area analysis (BET), surface texture and porosity analysis (SEM), types of functional groups on adsorbent surface responsible for adsorption of phenol (FTIR), elemental and component analysis (proximate, ultimate analysis and EDX) etc. The Langmuir and BET surface area were measured by nitrogen adsorption technique. Scanning electron microscopic (SEM; Model JSM5410, JELO) study was also conducted to observe the surface texture and porosity of the adsorbent. FTIR (FTIR RX-1, PerkinElmer, USA) spectrometer was employed to determine the type of functional groups on GAC and WHAC responsible for Phenol adsorption. The EDX analysis was made by using the energy dispersive X-ray spectrometer of the same scanning electron microscope used for SEM analysis i.e. Model JSM5410, JELO. For ultimate analysis the equipment used was CHNS Thermo Finnigan Flash EATM 1112 analyzer.

3.7 Preparation of standard phenol solution

The stock solution containing 1000 mg/l of standard Phenol was prepared by dissolving 0.5 g of AR grade Phenol in 200 ml milli-q water. After dissolution both the solutions were diluted

to 500 ml with milli-q water in 500 ml volumetric flask. Batch adsorption experiments were performed after proper dilution of stock solution.

3.8 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 $\lambda_{max} = 270 nm$. A spectrophotometer (JASCO UV/Vis-530) was used for the calibration plot, which showed a linear variation of absorbance up to 80 mg/l concentration. Therefore, the samples with higher concentration of phenol were diluted with milli-q water.

3.9 Batch adsorption procedure

All the batch adsorption experiments were performed in a mechanical shaker equipped with a thermostatic water bath at constant speed of 120 rpm using 100 ml conical flasks containing 50 ml each of phenol solutions of 100 ppm concentration. Experiments were performed at room temperature (30^oC). The pH of the solution was maintained natural as well as desired one when needed likewise the other parameters such as adsorbent doses, temperature, contact time were also either varied or kept at desired level as per the need. All solution samples post adsorption were filtered through syringe driven Millipore Whatman (0.45μm) filter paper. The concentrations of phenol in treated samples were determined by UV spectrophotometer.

The amount of phenol adsorbed per unit mass of the adsorbent was evaluated by using the following equation,

$$q_e = (C_o - C_t)\frac{V}{m}$$

(3.2)

The percentage removal of phenol was calculated by the following equation,

$$\%R = \left(\frac{C_o - C_t}{C_o}\right) \times 100$$

(3.3)

3.10 Surface characterization of GAC and WHAC

The surface area and the porous texture of activated carbon were characterized using adsorption BET surface area and SEM. The textural characterization (surface area) of GAC and WHAC were determined at -196 ^oC in presence of nitrogen atmosphere. The N_2

adsorption–desorption isotherm was used to determine surface area using the Brunauer–Emmett–Teller (BET) equation. The surface characteristics of samples were analysed using scanning electron microscopy (SEM) JSM 5410, JELO. Surface morphology analysis was performed using SEM in situ on GAC and WHAC at different magnifications. Energy dispersive X-ray spectrometer (EDX) of GAC and WHAC was investigated by semi-quantitative elemental analysis using the energy dispersive X-ray spectrometer of a scanning electron microscope. The ultimate elemental analysis of GAC and laboratory prepared WHAC sample was performed by a CHNS Thermo Finnigan Flash EATM 1112 analyzer. Fourier transform infrared spectroscopy (FTIR) spectrometer (FTIR RX-1, PerkinElmer, USA) was used in the characterization of the presence of surface functional groups. The absorbance data were processed for the wave number range 4000-400 cm^{-1} using the essential software. Proximate and ultimate analyses of the adsorbents were made by following the standard laboratory protocols using ASTM D 3173-75 and Elementor CHNS analyzer respectively.

3.11 Kinetics models

Kinetics models are used to examine the rate of the adsorption process and potential rate-controlling step. In the present work, the kinetic data obtained from batch studies have been analysed by using pseudo-first-order and pseudo-second-order models. The first order equation of Lagergren is generally expressed as follows,

$$\frac{dq}{dt} = k_1(q_e - q) \tag{3.4}$$

Where q_e and q are the amounts of phenol adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). The linearized form of above equation is given as,

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{3.5}$$

A plot of $\ln(q_e - q)$ against t should give a linear relationship with the slop k_1 and intercept of $\ln q_e$.

The pseudo-second-order kinetic rate equation is expressed as follows,

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{3.6}$$

Where k_2 is the rate constant of pseudo-second-order sorption (g $mg^{-1}min^{-1}$). The linearized form of above equation becomes,

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(3.7)

If the second order kinetic equation is applicable, the plot of t/q against t should give a linear relationship. The q_e and k_2 can be determined from the slope and intercept of the plot [44].

3.12 Adsorption isotherms study

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. Equilibrium data can be analysed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems [11] [44].

3.12.1 Langmuir isotherm model

The most widely used isotherm equation for modelling of the adsorption data is the Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number identical site and is given by following equation,

$$q_e = \frac{q_o K_L C_e}{1 + K_L C_e}$$

(3.8)

Where q_o and K_L are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively. C_e is the equilibrium concentration in the aqueous solution and q_e is the equilibrium adsorption capacity of adsorbent. The linearized form of Langmuir equation can be written as,

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L} \cdot \frac{1}{C_e}$$

(3.9)

The Langmuir constant q_0 and K_L can be calculated by plotting $1/q_e$ versus $1/C_e$.

3.12.2 Freundlich isotherm model

The Freundlich model is an empirical equation based on sorption on heterogeneous surface. It is given as,

$$q_e = k_f C_e^{\frac{1}{n}} \tag{3.10}$$

Where K_f and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively. The linearized form of Freundlich isotherm can be written as,

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{3.11}$$

The value of K_f and n can be calculated by plotting ln q_e versus ln C_e.

3.13 Thermodynamic parameters of adsorption

The Langmuir constant K changing with temperature can be used to calculate the enthalpy (ΔH^o), free energy change (ΔG^o) and entropy change (ΔS^o). The free energy change of the adsorption is given as,

$$\Delta G^o = -RT\ln K \tag{3.12}$$

The temperature dependence of the free energy change is given by the following equation,

$$d\left(\frac{\Delta G^o}{T}\right) = -\frac{\Delta H}{T^2}dT \tag{3.13}$$

Substituting Eq. (3.12) into Eq. (3.13) yields Eq. (3.14) and the equilibrium constant can be expressed in terms of enthalpy change of adsorption as a function of temperature.

$$\frac{d(\ln K)}{T} = \frac{\Delta H^o}{RT^2}dT \tag{3.14}$$

If the process is endothermic ($\Delta H^o > 0$), the equilibrium constant increases with temperature, if the process is exothermic ($\Delta H^o < 0$), the equilibrium constant decreases as temperature is raised. Eq. (3.14) can also be written as,

$$\frac{d\ln K}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H^o}{R} \qquad (3.15)$$

Assuming that, ΔH^o is approximately independent of temperature, the slope of ln K versus 1/T plot is equal to $-\Delta H^o/R$. The change of adsorption entropy can be determined from the standard equation for Gibbs free energy which is $\Delta G^o = \Delta H^o - T\Delta S^o$. Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favourable adsorption [11].

CHAPTER-4

RESULTS AND DISCUSSIONS

4.1 The calibration curve

In analytical chemistry, 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. The calibration curve is a plot of how the instrumental response, the so-called analytical signal, changes with the concentration of the analyte (the substance to be measured). The operator prepares a series of standards across a range of concentrations near the expected concentration of analyte in the unknown. The concentrations of the standards must lie within the working range of the instrumentation. For most analyses a plot of instrument response vs. analyte concentration will show a linear relationship. The operator can measure the response of the unknown and, using the calibration curve, can interpolate to find the concentration of analyte [22].
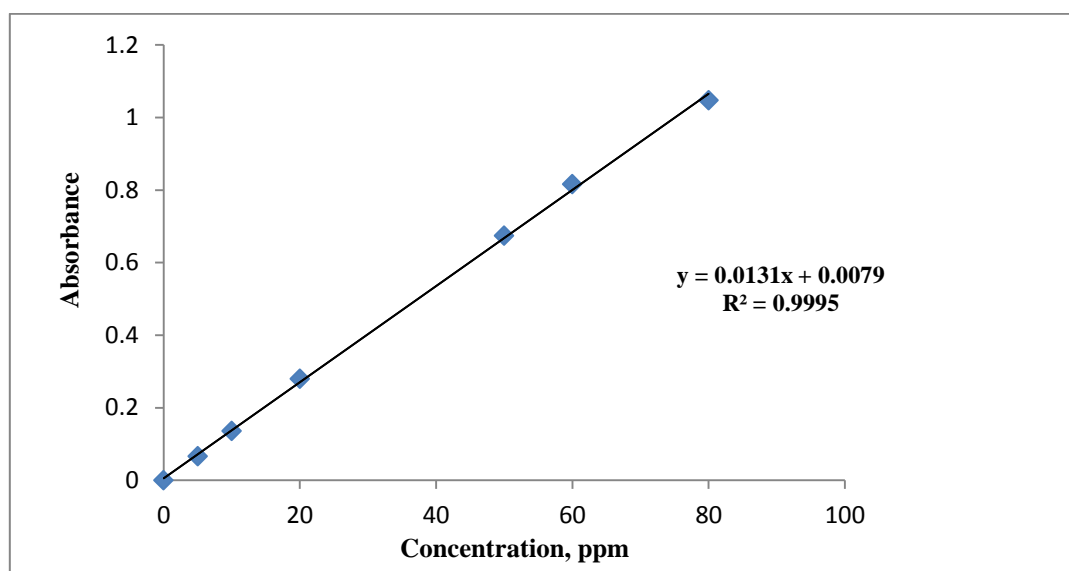

The graph shows a plot of Absorbance (y-axis, 0 to 1.2) versus Concentration, ppm (x-axis, 0 to 100). The fitted line equation is:

$$y = 0.0131x + 0.0079$$
$$R^2 = 0.9995$$

Fig.4.1 Calibration curve

4.2 Study of various parametric effects on adsorption of phenol onto GAC

4.2.1 Effect of adsorbent (GAC) dose on adsorption

The adsorbent dose is also an important parameter in adsorption studies because it involves effective removal of adsorbate and cost as well with it, i.e. if the amount of adsorbent is less then we will not find an effective removal of the adsorbate, secondly if we will be using more amount of adsorbent then though our goal will be achieved but the process will not be a cost effective one. For these reasons the study of effect of adsorbent dose on adsorption is a must for all adsorption works. Here the adsorbent is the granular activated carbon (GAC). In order

to study the effect of adsorbent dosage, the GAC dosages were varied from 2 to 40 g/L and placed into series of the 100 mL conical flasks containing 50 ml of 100 mg/L phenol solutions. These samples were agitated for 6 h at 120 rpm at the natural pH. A plot of q_e and % removal was plotted on same axis against adsorbent dose.
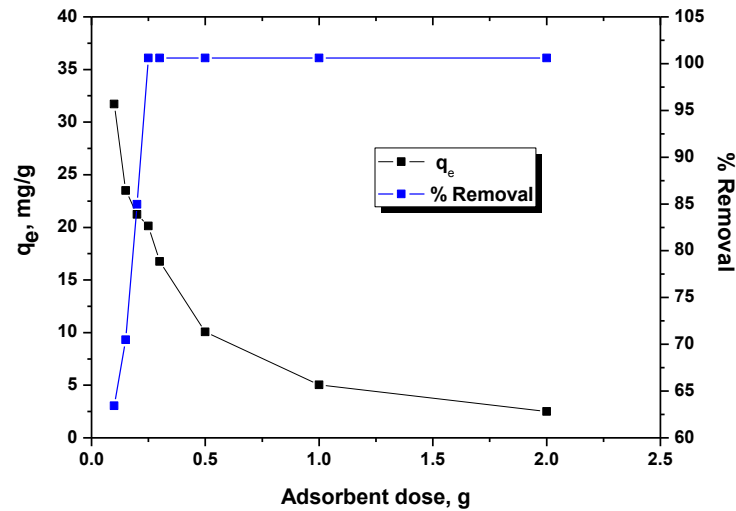

Fig.4.2 Effect of adsorbent (GAC) dose on adsorption

Referring to fig.4.2 above we obtain, It was found that with increase in adsorbent dose percentage removal is increased because large amount of adsorption sites were found, in contrast the uptake of phenol is gradually decreased because of two reasons, firstly for the same amount of phenol large number of adsorption sites are found and secondly large amount of adsorbents in the small available space clump together thereby limiting the path of diffusion and thus adsorption [40]. The corresponding point on x-axis of the intersection point of these two curves give the optimal dose of adsorbent and here we found the optimal dose for GAC as 3 gm/l of phenol solution.

4.2.2 Effect of Contact time for adsorption of Phenol onto GAC

To elucidate the effect of contact time on adsorption of phenol (C_o =100 mg/L), the batch experiments were carried out in a series of conical flasks with a constant GAC dosage of 3g/L in all the samples. These flasks were agitated in water bath shaker for 15, 30, 45, 60, 120,180, 240, 300, 360 and 420 minutes keeping natural pH in all the samples. The samples were withdrawn from the water bath shaker at predetermined time intervals. The supernatant was collected and filtered using syringe driven 0.45µm Millipore Whatman filter. The concentration of phenol in supernatant was measured for all the samples. The q_e was

evaluated for all the samples and a graph was plotted between q_e versus time as shown in Fig.4.3 below,
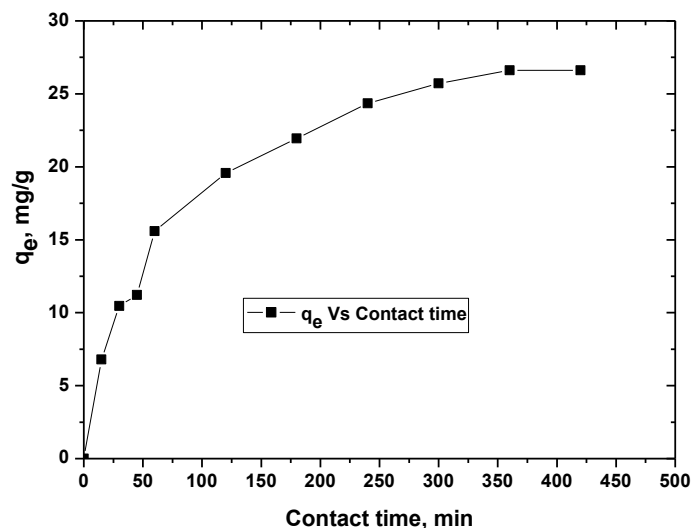

Fig.4.3 Effect of Contact time for adsorption of Phenol onto GAC

The results showed that equilibrium time required for the adsorption of phenol onto GAC was 360 min (6 h). However, the results also indicated that up to 50% of the total amount of phenol uptake was found to occur in the first 90 min. The higher sorption rate at the initial period (first 90 min) may be due to an availability of large number of vacant sites on the adsorbent at the initial stage, as a result there was an increased in concentration gradients between adsorbate in solution and adsorbate on adsorbent surface [44]. Thus tends to increase in phenol sorption at the initial stages. As time precedes this concentration gradient is reduced due to the accumulation of phenol particles in the vacant sites leading to a decrease in the sorption rate at the larger stages from 90 to 360 minutes.

4.2.3 Effect of pH on adsorption of phenol onto GAC

It is well known that phenol adsorption onto activated carbon can occur via a complex interplay of electrostatic and dispersion interactions with three possible mechanisms namely, (1) π-π dispersion interaction between the phenol aromatic ring and the delocalized electrons present in the aromatic structure of the graphite layers. (2) Hydrogen bond formation (3) Electron donor–acceptor complex formation at the carbon surface. Although in adsorption process electrostatic attraction exists between phenolate ions ($C_6H_5O^-$) and adsorbent surface plays a very significant role, the oxygen of the surface carbonyl group acts as the electron

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donor and the phenol aromatic ring as the acceptor. Both aspects are determined by the solution pH. Due to the amphoteric character of a carbon surface, its adsorption properties may be influenced by the pH value of the solution [38]. The effect of initial pH on the adsorption of phenol was also evaluated at 30 $^{\circ}$C at different initial pH values in the range of 2–12 for initial concentrations of 100 mg/l for phenol solution adjusted by adding either 0.1M HCl or 0.1M NaOH. The variation of adsorption with different values of pH is shown in Fig.4.4 below,
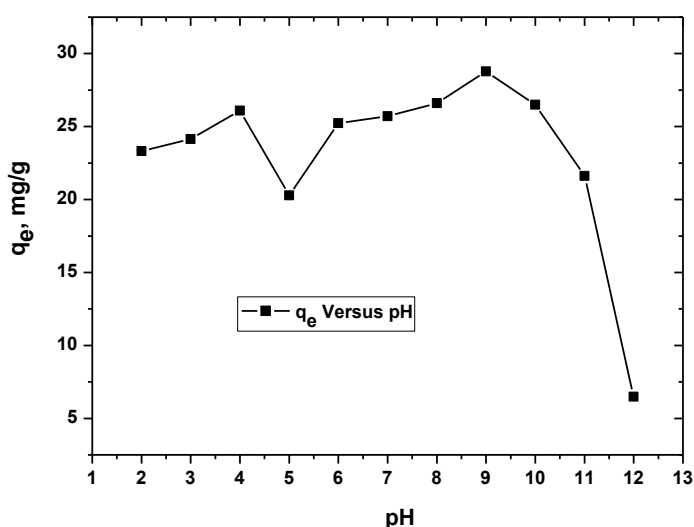

Fig.4.4 Effect of pH on adsorption of phenol onto GAC

It is evident from Fig.4.4 that the uptake of phenol increases with the increase in pH, and attain to the maximum value at pH = 4 thereafter, the uptake of phenol decreases with increase in pH up to 5. Further, increase in pH causes again increase in phenol uptake. In this study the amount of phenol adsorbed is highest at pH= 9 followed by 8, next to that the uptake of phenol gradually decreases. pH also affects the degree of ionisation of phenol in adsorption medium. In this study, the amount adsorbed decreases at both high and low pH values. The pKa value for phenol is 9.89. Phenol could be expected to become negatively charged phenolate ion above this pH and repulsion between the surface layer and the anionic phenolate results in reduced adsorption. The low pH value was obtained by using an acid solution. It introduced additional protons in the solution, which competed for the carbonyl sites, so the adsorption was reduced at low pH [36].

4.2.4 Effect of initial concentration and contact time on adsorption of phenol onto GAC

To elucidate the effect of initial phenol concentration, the experiments were carried out in different conical flasks with a fixed adsorbent dose of 3 g/l at varying phenol concentrations of 50, 100, 150 mg.L^{-1}. These flasks were agitated in shaker for 15, 30, 45, 60, 120, 180, 240, 300, 360 minutes keeping pH=9 fixed in all the samples. The samples were withdrawn from the shaker at above noted time intervals. Post adsorption the supernatant was collected and filtered using 0.45 μm Millipore whatman filter. Filtered supernatant was analysed using spectrophotometer and a graph was plotted with q_e versus time. The adsorption data for the uptake of phenol versus contact time at different initial concentrations is represented in Fig.4.5 below,
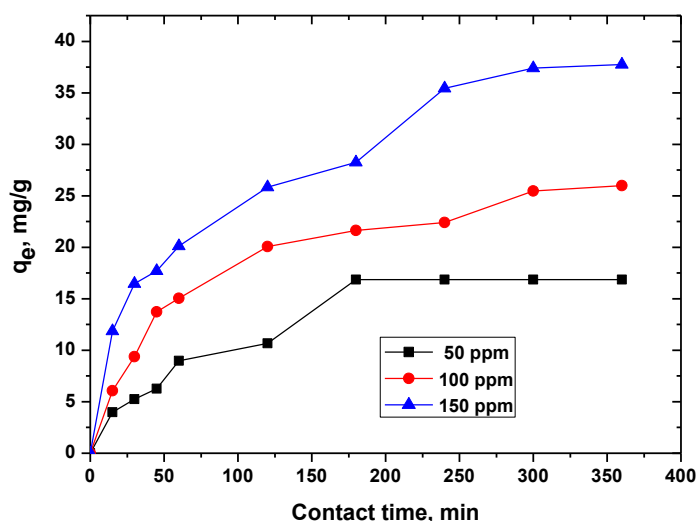

Fig.4.5 Effect of initial concentration and contact time on adsorption of phenol onto GAC

From the Fig.4.5 it is evident that, 100% removal is possible with an initial phenol concentration of 50 ppm and the equilibrium is reached 180 mins. However with initial concentration of 100 ppm about 80% removal is becoming possible and equilibrium is reached in 360 mins and the results with the initial concentration of 150 ppm have shown at the end of 360 mins about 79% removal of phenol is possible, however equilibrium was not reached even at the end of 360 mins duration. The higher sorption rate at the initial period (first 60 minutes) may be due to an increased in concentration gradients between adsorbate in solution and adsorbate on adsorbent surface, as time precedes this concentration gradient is

reduced due to the accumulation of phenol particles in the vacant sites leading to a decrease in the sorption rate at the larger stages from 60 to 360 minutes [44].

4.2.5 Effect of temperature on adsorption of Phenol onto GAC

For analysing the effect of temperature on adsorption, phenol solutions of different concentrations namely, 50, 100, 150, 200, 250 ppm were prepared. All sample solutions were maintained at pH of 9 for and 3 g/L GAC was added to each solution, then the samples were agitated for 6 hours at different temperatures 25, 35, 45 and 55 ^{o}C respectively. A plot of uptake capacity of GAC against initial concentrations at different temperatures was plotted shown in Fig.4.6 below,
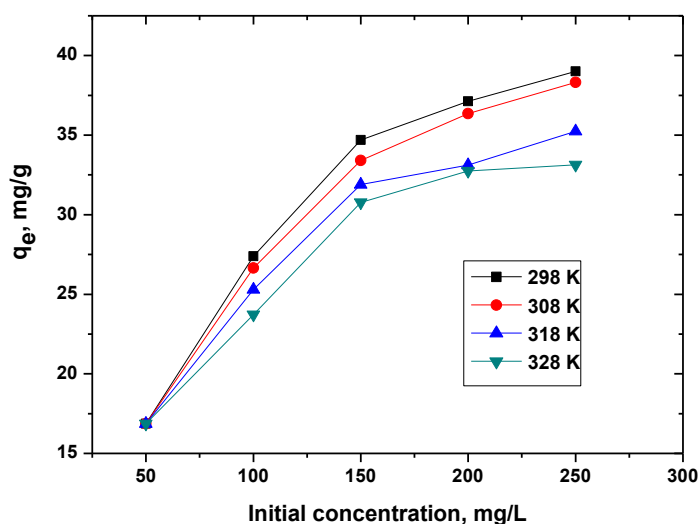

Fig.4.6 Effect of temperature on adsorption of phenol onto GAC

It is evident from Fig.4.6 that the value of maximum adsorption capacity q_e decreases with temperature thus suggesting that adsorption of phenol on GAC is exothermic in nature. The increased uptake of phenol with increase in initial concentration suggests that both physiosorption as well as chemisorption is taking place [40].

4.3 Adsorbent (WHAC) preparation

The desired adsorbent i.e. WHAC was prepared by following standard methodologies given in literatures. The percentage of yield was calculated as per the Eq. 4.1 below,

Percentage of yield (%R) $= \dfrac{W_{CHAR}}{W_{RAW}} \times 100$ (4.1)

Where W_{CHAR} = Weight of char produced after carbonization and

W_{RAW} = Weight of raw material before carbonization

$\%R = \left(\dfrac{17.779}{33.286}\right) \times 100$

$= 53.41\%$

Therefore the yield of WHAC obtained was 53.41%.

4.4 Study of various parametric effects on adsorption of phenol onto WHAC

4.4.1 Effect of adsorbent (WHAC) dose on adsorption

In order to find out the appropriate adsorbent dose of WHAC, this study was done. The effect of WHAC on the amount of removal of phenol solution was obtained by contacting 50ml of phenol solution of initial concentration of 100 mg/l with different weighed amounts (0.1, 0.15, 0.2, 0.25, 0.3, 0.5 and 1.0 g) of WHAC in stopper conical flasks. Each sample was then agitated for 6h at a constant 120 rpm at the natural pH of solution. The supernatants were then filtered using whatman filter paper 42 grade and subsequently with syringe driven whatman Millipore filter having pore size 0.45µm. The phenol concentration in the filtered supernatant was then analyzed as before. A plot of q_e and % removal was plotted on same axis against adsorbent dose.
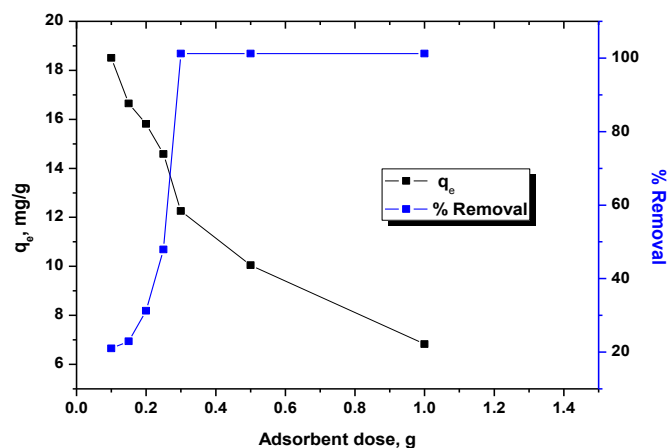

Fig.4.7 Effect of adsorbent (WHAC) dose on adsorption

Fig-4.7 shows the effect of adsorbent (WHAC) dosage on the removal of phenol. The percentage removal of phenol increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage. But amount of phenol adsorbed per unit mass of WHAC decreased with increase in adsorbent dosage, because for the same phenol concentration we got large number of adsorption sites with the increment of WHAC dose [44].

4.4.2 Effect of Contact time for adsorption of Phenol onto WHAC

To investigate the effect of contact time on adsorption of phenol (C_o =100 mg/L), the batch experiments were carried out in a series of conical flasks with a constant WHAC dose of 5g/L in all the samples. These flasks were agitated in water bath shaker for 20, 40, 60, 120,180, 240, 300 and 360 minutes at a constant 120 rpm at the natural pH in all the samples. The samples were withdrawn from the water bath shaker at predetermined time intervals. The supernatants were then filtered using whatman filter paper 42 grade and subsequently with syringe driven whatman Millipore filter having pore size 0.45μm.The concentration of phenol in supernatant was measured for all the samples. The q_e was evaluated for all the samples and a graph was plotted between q_e versus time as shown in Fig.4.8 below,
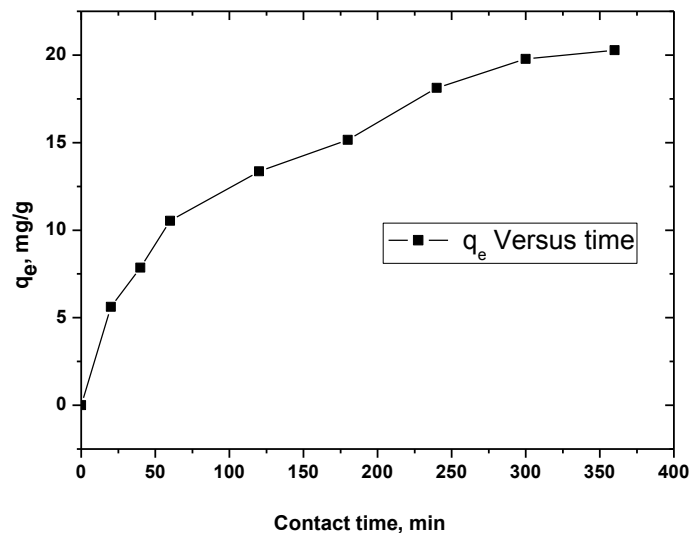

Fig.4.8 Effect of Contact time for adsorption of Phenol onto WHAC

Fig.4.8 depicts that 50% of the total amount of phenol uptake was found to occur in the first 60 minutes and the adsorption process was almost tending towards equilibrium at the end of

360 minutes. The higher sorption rate at the initial period (first 60 minutes) may be due to availability of large number of vacant sites on the adsorbent at the initial stage, as a result there was an increased in concentration gradients between adsorbate in solution and adsorbate on adsorbent surface, thus tends to increase in phenol sorption at the initial stages. As time precedes this concentration gradient is reduced due to the accumulation of phenol particles in the vacant sites leading to a decrease in the sorption rate at the larger stages from 60 to 360 minutes [1] [11].

4.4.3 Effect of pH on adsorption of phenol onto WHAC

The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. The effect of initial pH on the adsorption of phenol was also evaluated at 30 ^{o}C at different initial pH values in the range of 2–12 for initial concentrations of 100 mg/l for phenol solution adjusted by adding either 0.1M HCl or 0.1M NaOH. The variation of adsorption with different values of pH is shown in Fig.4.9 below,
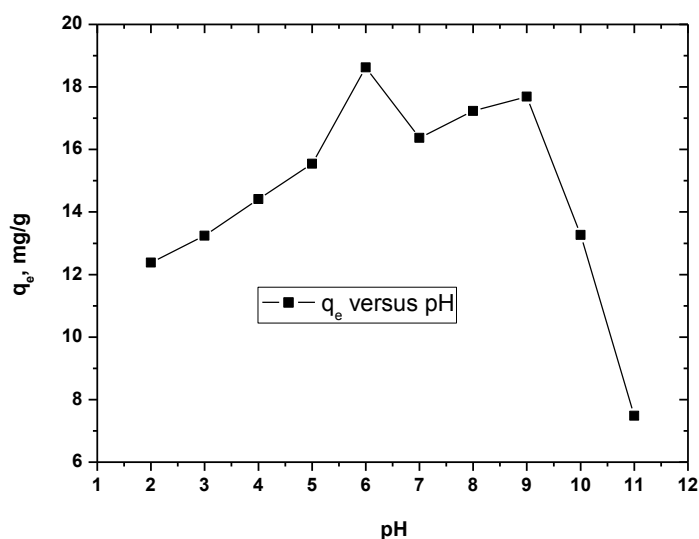
Fig.4.9 Effect of pH on adsorption of phenol onto WHAC

The Fig. 4.9 reveals that, pH primarily affects the degree of ionization of phenol and the surface properties of WHAC. Here we have observed highest uptake of phenol by WHAC at pH=6, at low pH values, the surface of the WHAC would be protonated and resulted in a stronger attraction for negatively charge phenolate ions. Phenol, being weakly acidic (pKa = 10), partially ionizes in solution. These ions are negatively charged and are directly attracted to the protonated surface of WHAC by electro-static force. Unionized phenol molecules

would also be attracted, possibly, by physical force. After that the uptake capacity goes down at pH of 7 but then increases however the uptake is not that much significant what was observed at pH=6, next to 6 we have obtained highest uptake of phenol at pH=9 and beyond that phenol adsorption capacity showed a drastic reduction. The reasons of lower adsorption of phenol at higher pH values can be attributed to the fact that at high pH, OH^- ions would compete with the phenol molecules for sorption sites. Sorption of excess of OH^- ions could convert an initial positively charged surface of WHAC into a negatively charged surface resulting repulsion of negatively charged phenoxide ions and adsorption decreased [36] [44].

4.4.4 Effect of initial concentration and contact time on adsorption of phenol onto WHAC

To study the effect of initial phenol concentration, experiments were carried out in different conical flasks with a fixed adsorbent dose of 5 g/l at varying phenol concentrations of 50, 100, 150 mg.L^{-1}. These flasks were agitated in shaker for 20, 40, 60, 120, 180, 240, 300, 360 minutes keeping pH=6 fixed in all the samples. The samples were withdrawn from the shaker at above noted time intervals. Post adsorption the supernatant was collected and double filtered, first using 42 grade whatman filter papers and then by syringe driven 0.45 µm Millipore whatman filter. Filtered supernatant was analysed using spectrophotometer and a graph was plotted with q_e versus time. The adsorption data for the uptake of phenol versus contact time at different initial concentrations is represented in Fig.4.10 below,
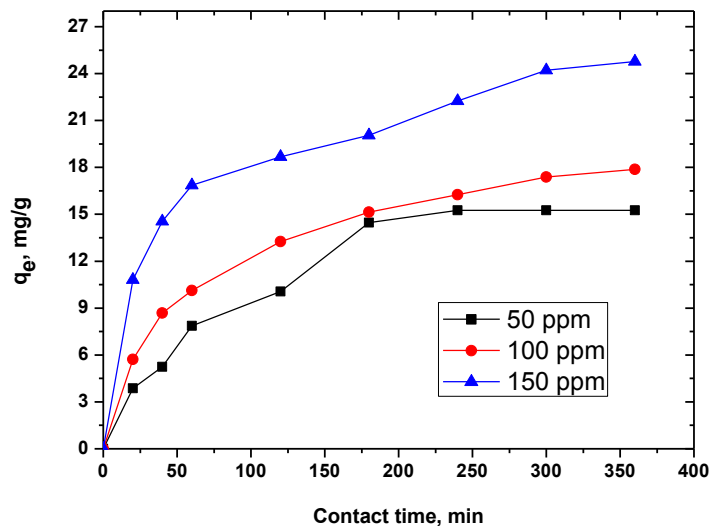

Fig.4.10 Effect of initial concentration and contact time on adsorption of phenol onto WHAC

From the Fig.4.10, it is evident that, 100% removal is possible with an initial phenol concentration of 50 ppm and the equilibrium is reached 250 mins. However with initial concentration of 100 ppm about 90% removal is becoming possible and equilibrium was in the approaching state at the end of 360 mins and the results with the initial concentration of 150 ppm have shown at the end of 360 mins equilibrium was not even reached. 50% of the total amount of phenol uptake was found to occur in the first 60 minutes and the adsorption process was almost tending towards equilibrium at the end of 360 minutes. The higher sorption rate at the initial period (first 60 minutes) may be due to an increased in concentration gradients between adsorbate in solution and adsorbate on adsorbent surface, as time precedes this concentration gradient is reduced due to the accumulation of phenol particles in the vacant sites leading to a decrease in the sorption rate at the larger stages from 60 to 360 minutes [44] [46].

4.4.5 Effect of temperature on adsorption of Phenol onto WHAC

To elucidate the effect of temperature on adsorption, phenol solutions of different concentrations namely, 50, 100, 150, 200, 250 ppm were prepared. All sample solutions were maintained at pH of 6 for and 5 g/L WHAC was added to each solution, then the samples were agitated for 6 hours at different temperatures 30, 40, 50 and 60 ^{o}C respectively. A plot of uptake capacity of WHAC against initial concentrations at different temperatures was plotted shown in Fig.4.11 below,
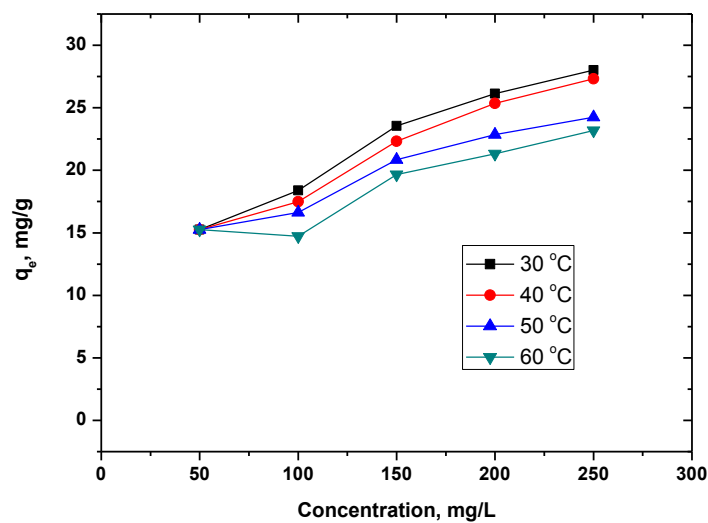

Fig.4.11 Effect of temperature on adsorption of phenol onto WHAC

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It is evident from Fig. 4.11 that the value of maximum adsorption capacity q_e decreases with temperature thus suggesting that adsorption is favoured at lower temperatures. At high temperature kinetic energy of adsorbate phenol is so high that they do not bind with the active sites available on the WHAC surface. However if the process was endothermic in nature than only the sorption capacity would increase because of inter molecular pore diffusion [47].

4.5 Adsorption kinetics study

4.5.1 Adsorption kinetics study for Phenol-GAC system

For the kinetics study pseudo-first-order and pseudo-second order models were considered. The various results obtained from this study are represented below,

4.5.1.1 Pseudo-first-order kinetics of Phenol-GAC system

The linearized form of pseudo-first-order kinetics is given by equation of chapter-3. From that equation it is clear that, a plot of $\ln(q_e - q)$ against t should give a linear relationship with the slop k_1 and intercept of ln q_e. The Pseudo-first-order kinetics of Phenol-GAC system is given below,
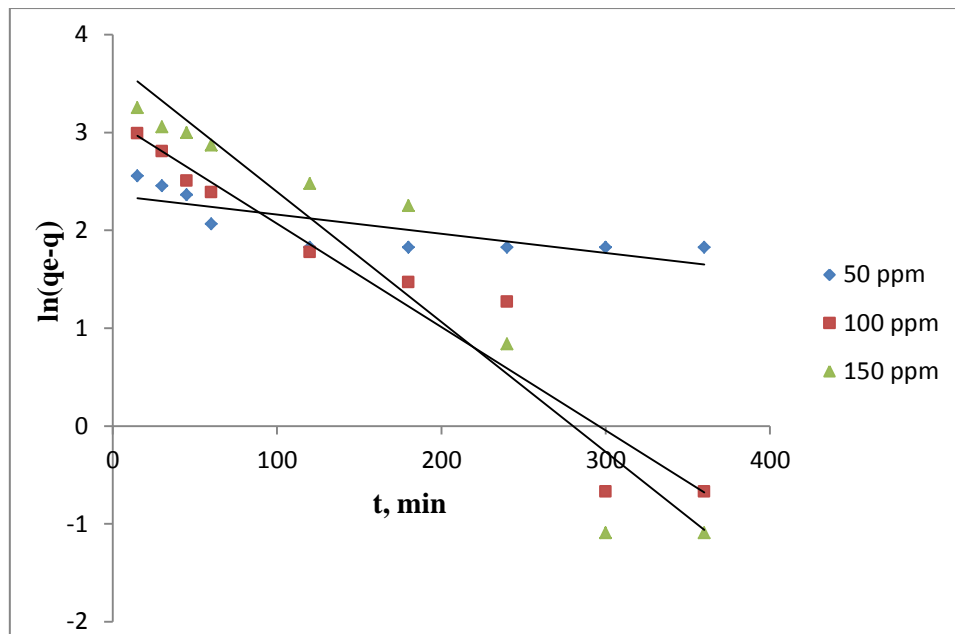

Fig. 4.12.1 Pseudo- first-order kinetics of Phenol-GAC system

Table 4.1 Pseudo-first-order kinetic constants for the adsorption of phenol onto GAC

C_o (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1	r_1^2
50	16.868	10.565	0.002	0.6453
100	25.9792	22.8031	0.0106	0.9376
150	37.7425	41.322	0.0133	0.9221

4.5.1.2 Pseudo-second-order kinetics of Phenol-GAC system

The linearized form of pseudo-second-order kinetics is given by equation 3.7 of chapter-3. From that equation, the plot of t/q against t should give a linear relationship. The q_e and k_2 can be determined from the slope and intercept of the plot The Pseudo-second-order kinetics of Phenol-GAC system is given below,

Fig. 4.12.2 Pseudo- second-order kinetics of Phenol-GAC system

Table 4.2 Pseudo-second-order kinetic constants for the adsorption of phenol onto GAC

C_o (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2	r_2^2
50	16.868	20.1207	0.00078	0.9534
100	25.9792	28.3286	0.000783	0.979
150	37.7425	41.1522	0.00052	0.9667

From the above kinetics study for adsorption of phenol onto GAC we found that r_2^2 values for all initial concentrations are higher than that of r_1^2, again the $q_{e,exp}$ values are quite closer to

those of $q_{e,cal}$ values for pseudo- second-order kinetics, hence it can be concluded that the adsorption of Phenol-GAC system is described by pseudo- second-order kinetics model.

4.5.2 Adsorption kinetics study for Phenol-WHAC system

4.5.2.1 Pseudo-first-order kinetics of Phenol-WHAC system

The linearized form of pseudo-first-order kinetics is given by equation 3.5 of chapter-3. From that equation it is clear that, a plot of $\ln(q_e - q)$ against t should give a linear relationship with the slop k_1 and intercept of ln q_e. The Pseudo-first-order kinetics of Phenol-WHAC system is given below,

Fig. 4.12.3 Pseudo- first-order kinetics of Phenol-WHAC system

Table 4.3 Pseudo-first-order kinetic constants for the adsorption of phenol onto WHAC

C_o (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1	r_1^2
50	15.247	9.1586	0.0021	0.6304
100	17.8792	17.0866	0.0095	0.936
150	27.7725	17.2239	0.0104	0.9689

4.5.2.2 Pseudo-second-order kinetics of Phenol-WHAC system

The linearized form of pseudo-second-order kinetics is given by equation 3.7 of chapter-3. From that equation, the plot of t/q against t should give a linear relationship. The q_e and k_2

can be determined from the slope and intercept of the plot The Pseudo-second-order kinetics of Phenol-WHAC system is given below,
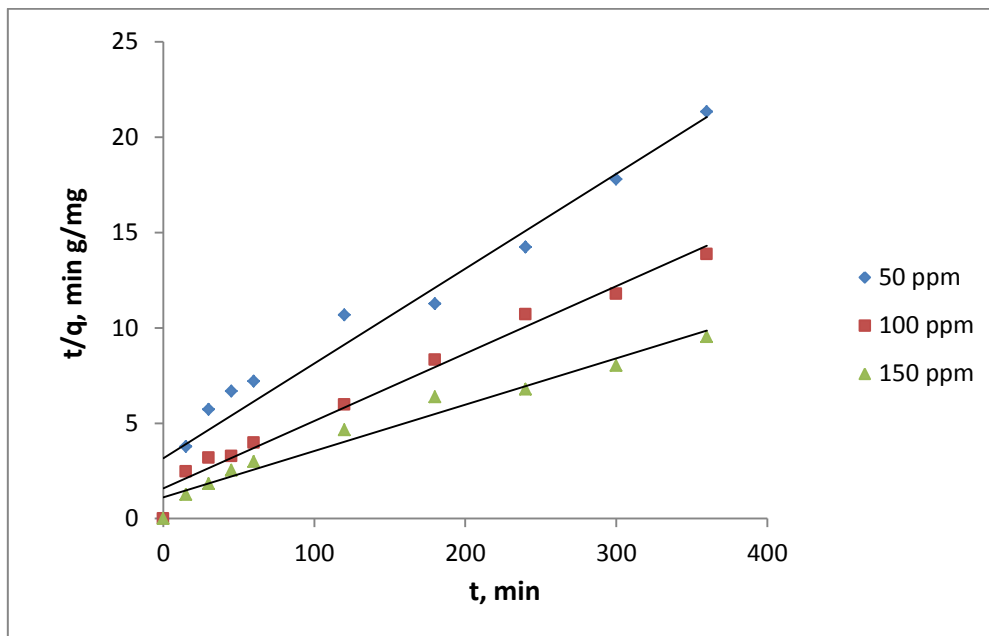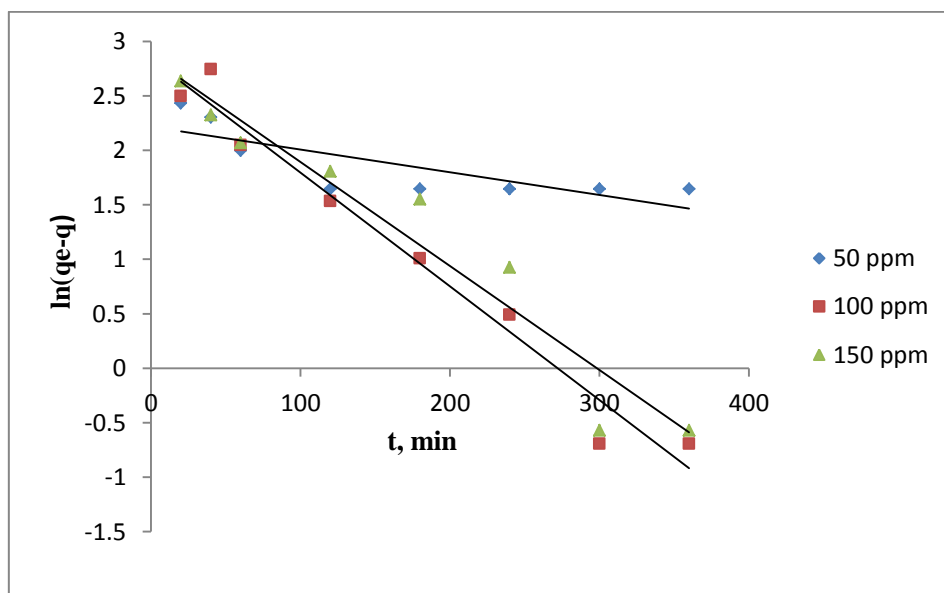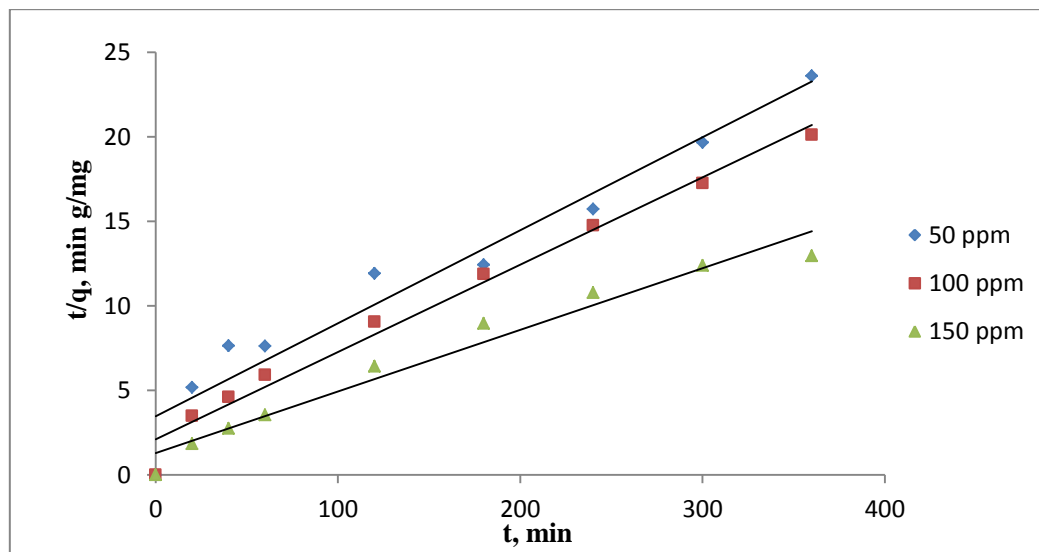

Fig. 4.12.4 Pseudo- second-order kinetics of Phenol-WHAC system

Table 4.4 Pseudo-second-order kinetic constants for the adsorption of phenol onto WHAC

C_o (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2	r_2^2
50	15.247	18.1488	0.000876	0.9485
100	17.8792	19.3423	0.00127	0.9822
150	27.7725	27.3972	0.00104	0.9667

From the above kinetics study for adsorption of phenol onto WHAC we found that r_2^2 values for all initial concentrations are higher than that of r_1^2, again the $q_{e,exp}$ values are quite closer to those of $q_{e,cal}$ values for pseudo- second-order kinetics, hence it can be concluded that the adsorption of Phenol-WHAC system is described by pseudo- second-order kinetics model.

4.6 Adsorption equilibrium study

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 [11] [44].

For this equilibrium study of our work, we have considered two basic isotherm models namely Langmuir and Freundlich isotherm models.

4.6.1 Adsorption equilibrium study for Phenol-GAC system

4.6.1.1 Langmuir isotherm

The linearized form of Langmuir isotherm is given by equation 3.9 of chapter-3. The Langmuir constant q_0 and K_L can be calculated by plotting $1/q_e$ versus $1/C_e$.

Fig. 4.13.1 Langmuir isotherm plot of Phenol-GAC adsorption system at 298K

In the similar way Langmuir isotherm plots for Phenol-GAC adsorption system at other temperatures were also made and the various parameters calculated from those plots are tabulated below.

Table 4.5 Langmuir isotherm parameters of Phenol-GAC adsorption system

Temperatures (^{o}C)	q_o (mg/g)	K_L	r^2
25	41.4937	0.1093	0.9982
35	41.1522	0.0908	0.9952
45	38.0228	0.08378	0.9846
55	37.1747	0.05884	0.9382

4.6.1.2 Freundlich isotherm

The linearized form of Freundlich isotherm is given by equation 3.11 of chapter-3. The value of K_f and n can be calculated by plotting ln q_e versus ln C_e.

Fig. 4.13.2 Freundlich isotherm plot of Phenol-GAC adsorption system at 308K

In the similar way Freundlich isotherm plots for Phenol-GAC adsorption system at other temperatures were also made and the various parameters calculated from those plots are tabulated below.

Table 4.6 Freundlich isotherm parameters of Phenol-GAC adsorption system

Temperatures (^{o}C)	K_f	n	r^2
25	16.9844	5.7306	0.9557
35	15.0864	5.1203	0.9811
45	14.8129	5.6369	0.9256
55	10.7177	4.2698	0.9731

From the above tables it is clear that the equilibrium data were very well fitted to Langmuir isotherm as compared to Freundlich isotherm. Moreover the correlation coefficient values for Langmuir isotherm are also higher. The best fit of equilibrium data in the Langmuir isotherm expression predicted the monolayer coverage of phenol onto GAC, with the maximum sorption capacity as 41.4937 mg/g.

4.6.2 Adsorption equilibrium study for Phenol-WHAC system

4.6.2.1 Langmuir isotherm

The linearized form of Langmuir isotherm is given by equation 3.9 of chapter-3. The Langmuir constant q_0 and K_L can be calculated by plotting $1/q_e$ versus $1/C_e$.
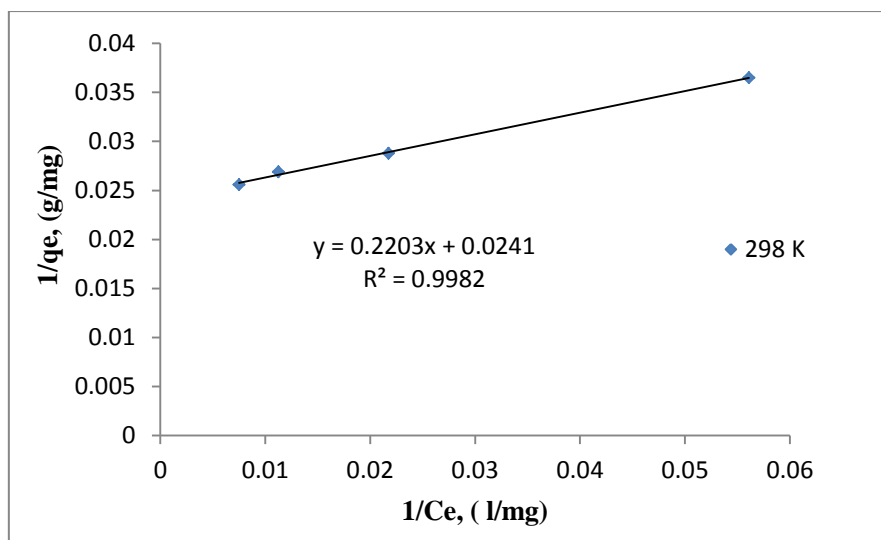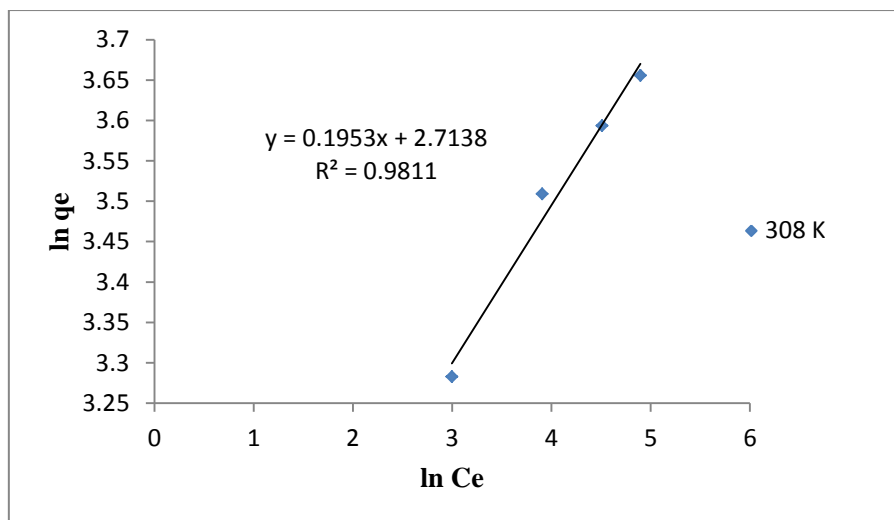

Fig. 4.13.3 Langmuir isotherm plot of Phenol-WHAC adsorption system at 303K

In the similar way Langmuir isotherm plots for Phenol-WHAC adsorption system at other temperatures were also made and the various parameters calculated from those plots are tabulated below.

Table 4.7 Langmuir isotherm parameters of Phenol-WHAC adsorption system

Temperatures (^{o}C)	q_o (mg/g)	K_L	r^2
30	31.4465	0.17415	0.9961
40	28.0339	0.0241	0.9645
50	26.0156	0.0197	0.8837
60	24.3527	0.0102	0.8629

4.6.2.2 Freundlich isotherm

The linearized form of Freundlich isotherm is given by equation 3.11 of chapter-3. The value of K_f and n can be calculated by plotting $\ln q_e$ versus $\ln C_e$.
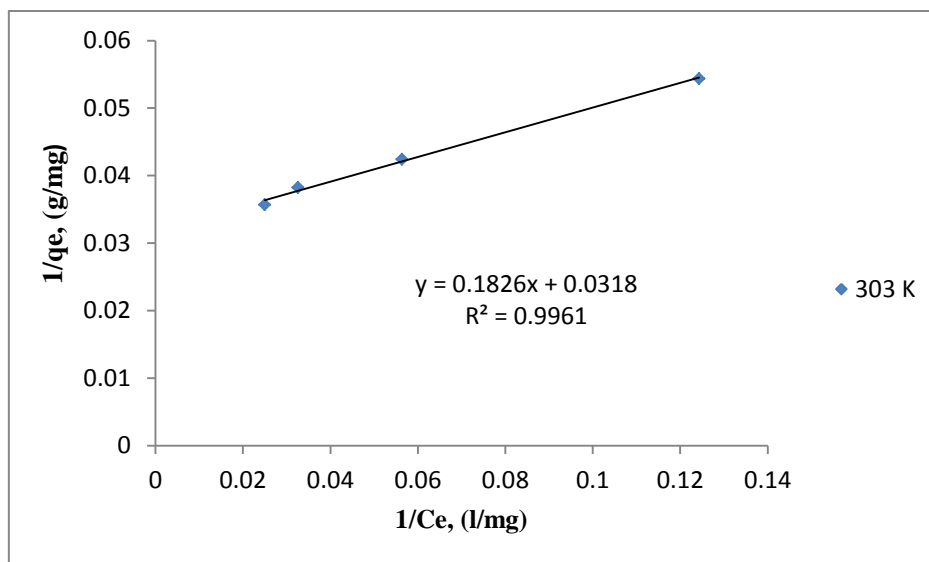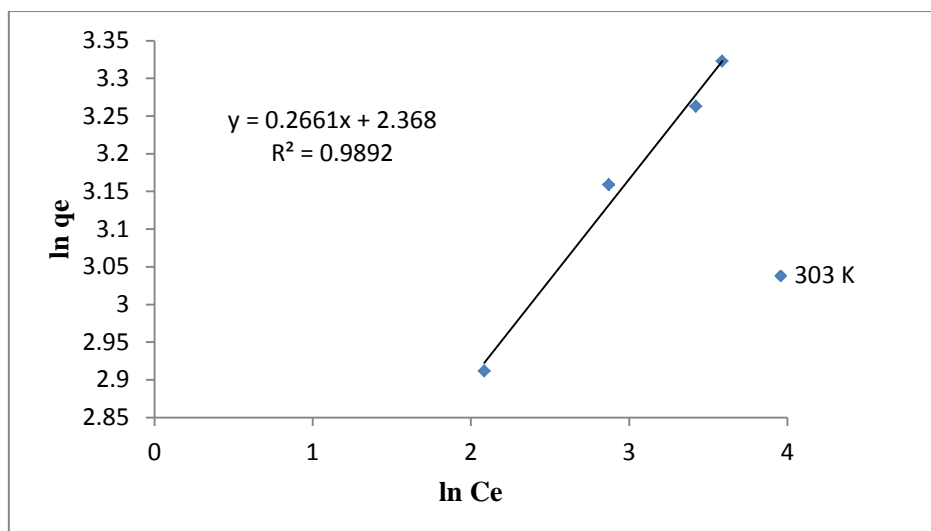
Fig. 4.13.4 Freundlich isotherm plot of Phenol-WHAC adsorption system at 303K

In the similar way Freundlich isotherm plots for Phenol-GAC adsorption system at other temperatures were also made and the various parameters calculated from those plots are tabulated below.

Table 4.8 Freundlich isotherm parameters of Phenol-WHAC adsorption system

Temperatures (^{o}C)	K_f	n	r^2
30	10.6760	3.7579	0.9892
40	8.608	3.472	0.9489
50	6.4089	1.1704	0.9234
60	3.4435	0.7072	0.9674

From the above tables it is clear that the equilibrium data were very well fitted to Freundlich isotherm as compared to Langmuir isotherm. Moreover the correlation coefficient values for Freundlich isotherm are also higher. The best fit of equilibrium data in the Freundlich isotherm expression predicted the multilayer coverage of phenol onto WHAC, with the maximum sorption capacity as 10.676 mg/g and adsorption intensity of 3.7579.

4.7 Thermodynamic parameters study

The Langmuir constant *K* changing with temperature can be used to calculate the enthalpy (ΔH^o), free energy change (ΔG^o) and entropy change (ΔS^o). The free energy change of the adsorption is given as,

The value of ΔG^o can be determined using equation 3.12 which is, ΔG^o=-RTln K. Assuming that, ΔH^o is approximately independent of temperature, the slope of ln K versus 1/T plot is equal to $-\Delta H^o/R$, where R is the universal gas constant and from thereof we can determine the value of ΔH^o. The change of adsorption entropy can be determined from the equation as ΔG^o=ΔH^o-TΔS^o. The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favourable adsorption [11].

The following table shows free energy change values of Phenol adsorption onto both GAC and WHAC.

Table 4.9.1 Gibbs free energy change parameters of Phenol-GAC/WHAC adsorption system

GAC		WHAC	
Temperature (^{o}C)	ΔG^o (j/mol)	Temperature (^{o}C)	ΔG^o (j/mol)
25	-5482.866	30	-4402.956
35	-6143.148	40	-9694.801
45	-6555.431	50	-10545.9207
55	-7018.7964	60	-12694.6873

From the table we got the ΔG^o values. Since all of the above values are in negative they suggest that the adsorption process of phenol onto both of the adsorbents were spontaneous in nature. The ΔH^o and ΔS^o values were also calculated and are tabulated below.

Table 4.9.2 Gibbs free energy change parameters of Phenol-GAC/WHAC adsorption system

GAC		WHAC	
ΔH^o	-8725.543 (j/mol)	ΔH^o	-27809.4986 (j/mol)
Temperature (^{o}C)	ΔS^o	Temperature (^{o}C)	ΔS^o
25	-47.6792	30	-106.311
35	-48.2749	40	-119.822
45	-48.0533	50	-118.7474
55	-48.001	60	-121.6341

From the values tabulated above we can conclude that the adsorption of phenol onto GAC and WHAC is exothermic in nature and is favoured at low temperatures only.

4.8 Characterization of the adsorbents

4.8.1 Proximate analysis

For the physico-chemical characterization of adsorbents there are various standard methods exists, proximate analysis is one of those methods. Proximate analysis was developed as a simple means of determining the distribution of products in coal obtained when the coal sample is heated under specified conditions strictly according to the ASTM standards. As per the definition by ASTM D 121, proximate analysis separates the products into four groups: (1) moisture, (2) volatile matter, (3) fixed carbon, and (4) ash [24]. From the proximate analysis of GAC and WHAC the following results were obtained,

Table.4.10 Datas of proximate analysis

% of Component	GAC	WHAC
Moisture	6.82	5.85
Ash	7.155	8.026
Volatile matter	15.312	17.422
Fixed carbon	70.713	68.702

4.8.2 Ultimate analysis

It is another physico-chemical characterization methodology of adsorbents. The difference from proximate analysis is that it determines individual elements occurrence in the sample. Ultimate analysis of sample is defined in ASTM D 3176, as the determination of the carbon, hydrogen, sulphur, nitrogen, and the estimation of oxygen by difference. The carbon determination includes that present in the organic substance and any originally present as mineral carbonate. The hydrogen determination includes that in the organic materials and in all water associated with the sample. All nitrogen determined is assumed to be part of the organic materials. Sulphur is assumed to occur in both organic as well as inorganic form [24]. From the ultimate analysis of GAC and WHAC the following results were obtained,

Table.4.11 Datas of ultimate analysis

% composition of elements	GAC	WHAC
C	85.05149	70.22764
H	0.678622	5.40999
N	1.327892	4.952775
S	0.580994	0
O	12.361	19.409595

4.8.3 FT-IR analysis

FT-IR stands for, fourier transform infrared. Basically it is a spectroscopic analysis technique which is used for identification of chemical bonds in a molecule by producing an infrared absorption spectrum and from thereof the functional groups present on the surface of sample. During analysis the sample is irradiated by infrared radiations, some of the infrared radiations are absorbed by the sample and rest are passed (transmitted) through. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for analysis. 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. The samples were usually prepared with KBr, in the form of pellets.

The FT-IR analysis of GAC and WHAC both in loaded and unloaded with phenol were made in the range of 400-4000 cm^{-1} region with 8cm^{-1} resolution and the %T versus cm^{-1} plot for spectrums are given below,
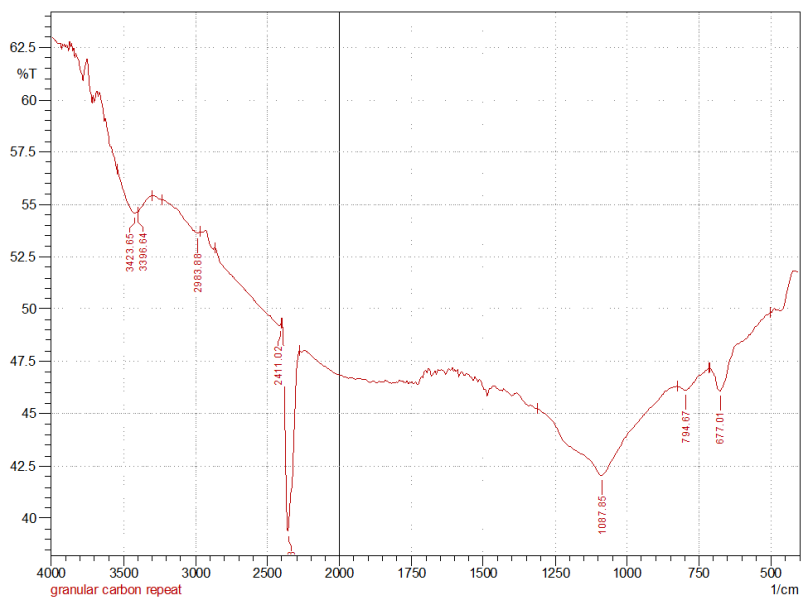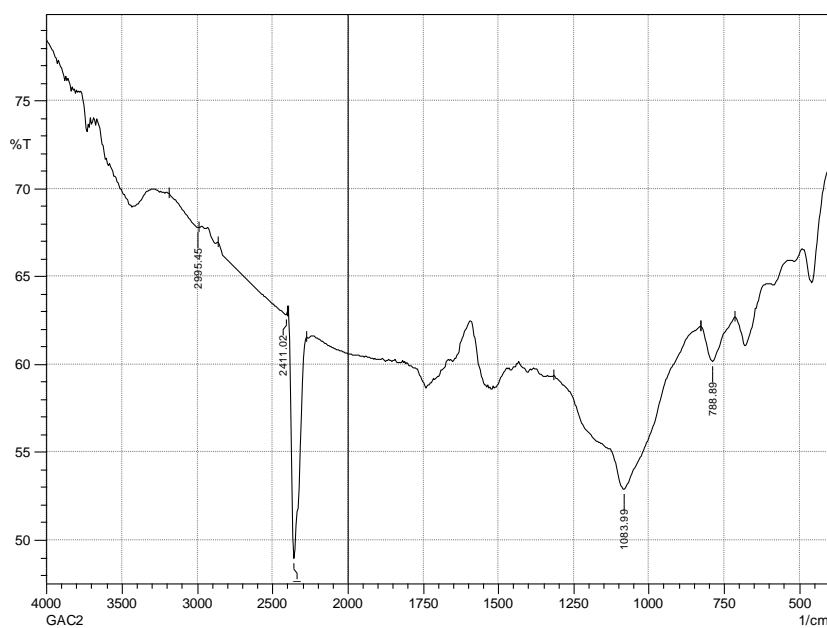
Fig.4.16. (a) FT-IR spectra of GAC (unloaded)

Fig.4.16. (B) FT-IR spectra of GAC (loaded)

The surface functionality of GAC can be characterized by FTIR spectra (Fig. 4.16) where fig. (a) represents the FT-IR spectrum of GAC before adsorption and that of (b) represents FT-IR spectrum of GAC after adsorption. The difference in peaks of both spectrums is attributed to the reason of phenol adsorption onto GAC. Several peaks were obtained in the spectrum. The characteristic absorptions up to 1000 cm^{-1} represents strong, alkene (=C-H-) bonds with bending vibrations. Absorptions at 3500-3700 and 1050-1150 cm^{-1} regions represents

alcoholic C-O bonds with stretched vibrations and strong in nature. The absorption near 4000 cm^{-1} depicts that of N-H bonds of amide groups with stretched vibrations and strong nature.
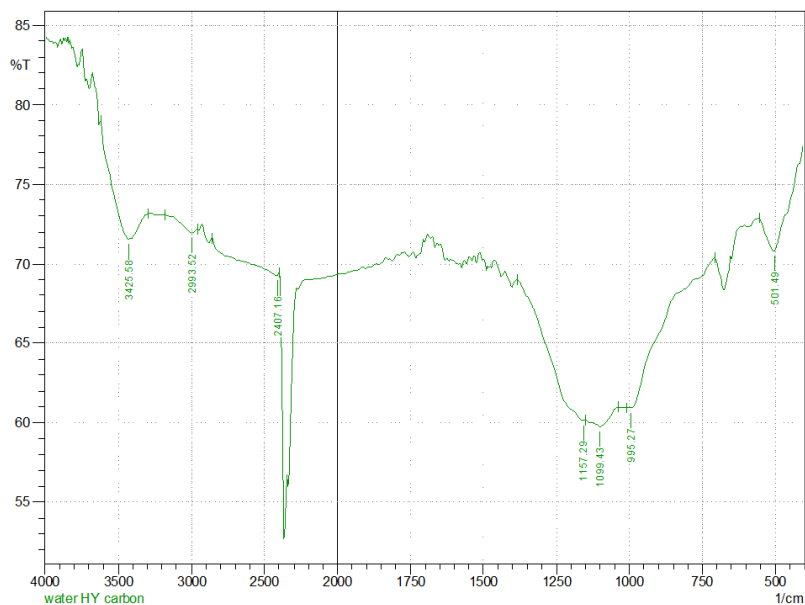

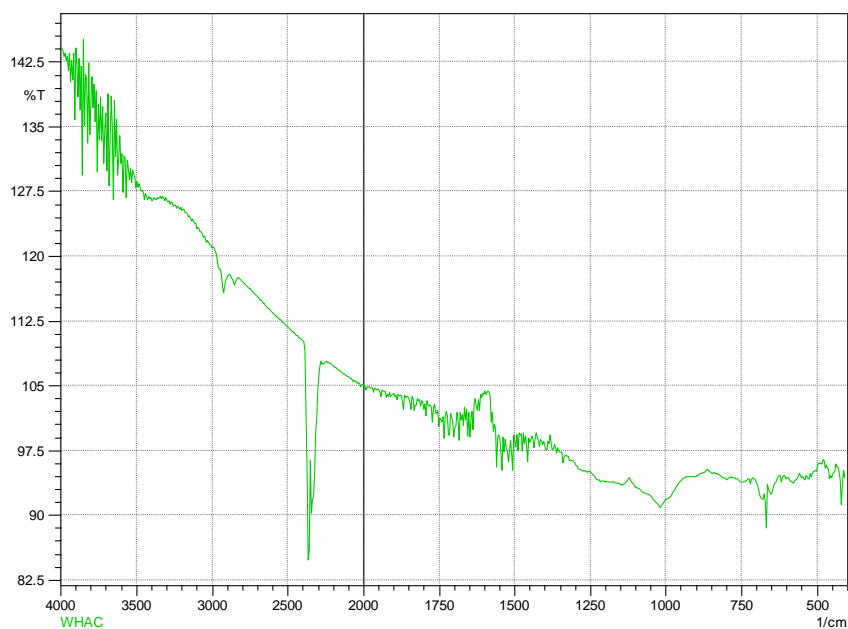Fig.4.17. (a) FT-IR spectra of WHAC (unloaded)

Fig.4.17. (b) FT-IR spectra of WHAC (loaded)

The surface functionality of WHAC can be characterized by FTIR spectra (Fig. 4.17) where fig. (a) represents the FT-IR spectrum of WHAC before adsorption and that of (b) represents

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FT-IR spectrum of WHAC after adsorption. The difference in peaks of both spectrums is attributed to the reason of phenol adsorption onto WHAC. Several peaks were obtained in the spectrum represents following types of compounds, The characteristic absorptions up to 1000 cm^{-1} represents strong, alkene (=C-H-) bonds with bending vibrations. Absorption at 1099.43, 1157.29 cm^{-1} depicts aliphatic amine and esters (C-O) groups respectively, similarly absorptions at 2993.52, 3425.58 cm^{-1} represents aromatic groups with C-H bonds with medium strength and alcohol groups with strong O-H respectively with all those bonds representing stretched vibrations.

4.8.4 SEM analysis

SEM stands for scanning electron microscopy, which is used for studying the surface morphology of substances due to its high magnification imaging capability. Scanning electron microscopy images were taken by using JEOL (JSM-6480 LV) microscope having an acceleration voltage of 15 kV.

The scanning electron micrographs are given in figure below,
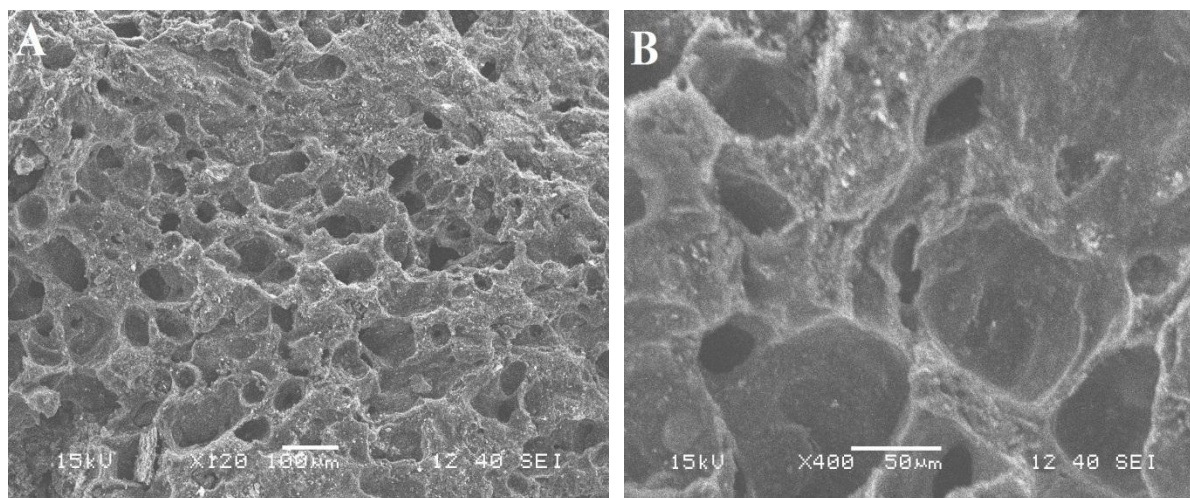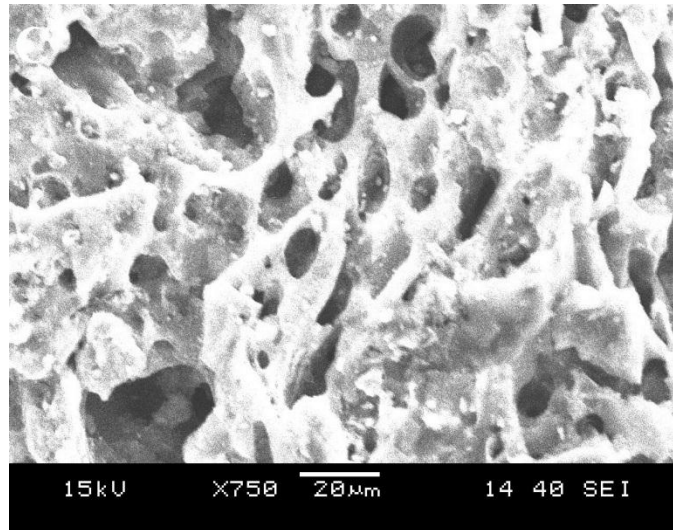
Fig. 4.18. Scanning electron micrographs of GAC (A) 120X (B) 400X (C) 750X

For studying the surface morphology of GAC, SEM analysis was done at three different magnifications namely 120, 400 and 750X respectively. The images of fig. 4.14 show heterogeneous distribution of pores and rough texture on the surface of GAC. The pore openings at 400X magnification shows that pore of the surface bubbled out, describing a sudden burst due to rapid thermal expansion. Further at higher magnification. At a higher magnification i.e. 750X it was seen that the pores build-up was found to be very clear opening that provide accessibility into internal pores. This porous structure of GAC imparts high surface area essential for the adsorption purposes [42].
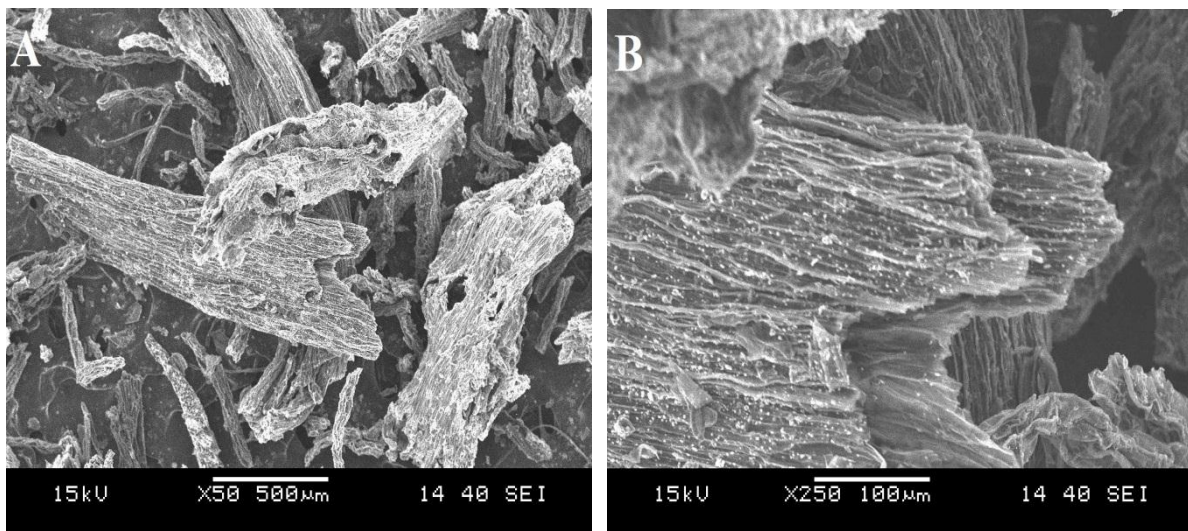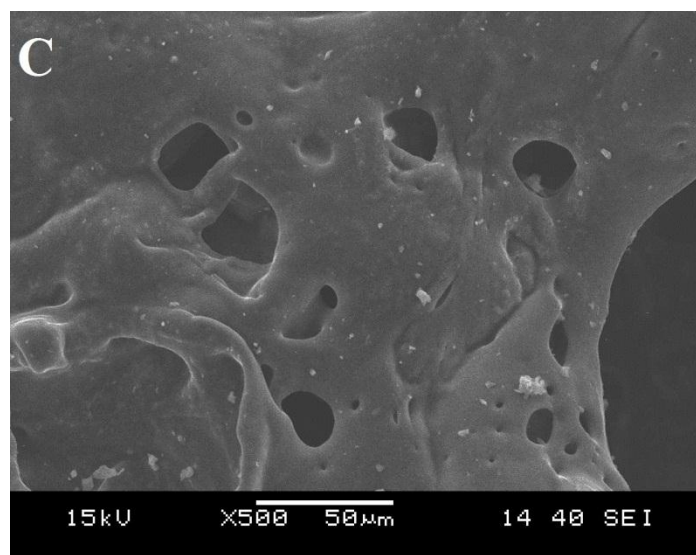
Fig. 4.19. Scanning electron micrographs of WHAC (A) 50X (B) 250X (C) 500X

In a similar fashion for studying the surface morphology of WHAC, SEM analysis was done at different magnifications namely 50, 250 and 500X respectively. At lower magnification the image showed detailed external morphology with macropores on their surfaces, and it is also revealed from the figure that the shapes of the adsorbents are somewhat cylindrical and stick like. At a five times higher magnification i.e. at 250X, one can easily visualize the fibrillar arrangement of WHAC which were of course producing a lamellar structural appearance. On further doubling the magnification, we can visualize several mesopores and a few micropores as well. These pores and fibrillar lamellae like structures leads to a high surface area of WHAC imparting high adsorption capabilities to it [41].

4.8.5 EDX analysis

EDX stands for Energy-dispersive X-ray spectroscopy, also abbreviated as EDS, is an analytical technique used for the elemental analysis or chemical characterization of a sample [16]. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. The EDX analysis was made in combination with SEM with the help of a 6587 EDX scanning spectrometry detector. The EDX analysis results of both GAC and WHAC are represented in tabular form below,

Table 4.12 EDX analysis datas of GAC and WHAC

Elements in weight %	GAC	WHAC
C	70.02	35.92
N	29.77	32.21
O	0.21	26.34
P	-	0.81
Na	-	4.76
Al	-	0.01
Mn	-	0.01
Fe	-	0.01
Total	100	100

From the data enlisted in the table we can say that, GAC is more carbonaceous than WHAC. The high nitrogen content implies organic constituents of the adsorbents. High oxygen content of WHAC is attributed to compound forms of oxygen. Apart from these WHAC also contains phosphorous, sodium, traces of aluminium, manganese and iron.

4.8.6 BET analysis

BET stands for Brunauer-Emmett-Teller, it provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size in many applications. In the field of adsorption BET analysis is used for measuring the external surface area of the adsorbents. The more is the external surface area more better is the adsorbent, as with increase in surface area, adsorbate uptake capacity of the adsorbents increases [26]. The following table gives the surface area values of both the adsorbents used by us during the course of work.

Table 4.13 BET analysis datas of GAC and WHAC

Adsorbent	External surface area m^2/g
GAC	912
WHAC	607

From the above table it is clear that the surface area of GAC is quite high as compared to WHAC because of its well-defined mesoporous texture. However WHAC represented a lamellar structure but not so distinct mesoporous structures, as shown in scanning electron micrographs (fig. 4.19), which resulted in a lesser surface area as compared to GAC.

4.9 Comparison of adsorption results of phenol with those available in literature

The comparative results of phenol adsorption onto GAC and WHAC of our work with those of available in literatures for other adsorbents as well is represented in following table,

Table 4.14 Comparative results of phenol adsorption onto various adsorbents

Adsorbents	pH	Isotherm model	Capacity, (mg/g)
GAC	9	Langmuir	39.0056
WHAC	6	Freundlich	28.0049
APET	5	Langmuir	262
APET	11	Langmuir	184.2
CCM200(carbon cryogel)	-	Langmuir	140
PACT	6.6	Langmuir	135.7
Steam-PAC (from coal)	6.3	-	226
Chemical-PAC (from coal)	6.5	Langmuir	98
GAC (F400) F-DI	-	Freundlich	75.2
GAC(F400) F-HCl	-	Freundlich	75.5
CNTs	-	-	15.9
F400-N_2	-	Freundlich	96
F400-Air	-	Freundlich	54

CHAPTER-5

CONCLUSIONS AND FUTURE SCOPES

Conclusions

The following conclusions can be drawn from the present work,

- The maximum uptake of Phenol onto GAC was found to be 39.006 mg/g.
- t=6 h, pH=9, Co=100 mg/l, T= 25 $^{\circ}$C and m= 3 g/l were the optimum condition for Phenol-GAC system.
- The kinetics studies confirmed that Phenol-GAC adsorption system can be described by pseudo- second-order kinetics model.
- Over all analysis of equilibrium model analysis indicates the fitness of Langmuir isotherm model to Phenol-GAC adsorption system, suggesting a monolayer adsorption of phenol on the surface of GAC.
- Phenol adsorption capacity of GAC was found to be decreasing with increase in temperature suggesting that the adsorption process was exothermic in nature, which was further supported by the negative values of change in enthalpy.
- The negative values of Gibb's free energy suggested that adsorption of phenol onto GAC was a spontaneous process.
- Characterization of GAC confirmed the mesoporous texture, highly carbonaceous nature and a higher effective surface area of 912 m^2/g.
- The highest phenol uptake capacity of WHAC was found to be 28.0049 mg/g.
- The optimal conditions for various process parameters are t=6 h, pH=6, Co=100 mg/l, T= 30 $^{\circ}$C and m= 5 g/l were the optimum condition for Phenol-WHAC system.
- Like Phenol-GAC system, the kinetics studies confirmed that Phenol-WHAC adsorption system can be described by pseudo- second-order kinetics model.
- Equilibrium model analysis indicates the fitness of Freundlich isotherm model to Phenol-WHAC adsorption system, suggesting a multilayer adsorption of phenol on the surface of WHAC.
- Phenol adsorption capacity of WHAC was found to be decreasing with increase in temperature suggesting that the adsorption process was exothermic in nature, which was further supported by the negative values of change in enthalpy.
- The negative values of Gibb's free energy suggested that adsorption of phenol onto WHAC was a spontaneous process.

- Characterization of WHAC confirmed the fibrous with lesser mesoporous texture, somewhat lesser carbonaceous in nature as compared to GAC and an effective surface area of 607 m^2/g.

Future scopes

In future the following works can be done,

- Desorption studies of phenol from GAC and WHAC, and reusability efficiency studies of GAC and WHAC.
- The phenol removal process can be investigated using Bioaccumulation concept.
- Modelling and simulation of the phenol adsorption process onto activated carbons.

CHAPTER-6

REFERENCES AND PUBLICATIONS

References

1. Altenora S., Carenea B., Emmanuel E., Lambert J., Ehrhardt J., Gasparda S., Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, Journal of Hazardous Materials, 165 (2009): pp.1029–1039.

2. Ania C.O., Parra J.B., Pis J.J., Effect of texture and surface chemistry on adsorptive capacities of activated carbons for phenolic compounds removal, journal of Fuel Processing Technology, 77–78 (2002): pp. 337– 343.

3. Armour, M.A., Hazardous Laboratory Chemicals Disposal Guide. CRC Press, Boca Raton, 1991.

4. Bansal R. C., Goyal M., Activated Carbon Adsorption, London, Taylor & Francis Group, LLC, 2005.

5. BIS, Tolerance Limit for Industrial Effluents Discharged into Inland Surface Waters: Coke Oven. IS 2490 (Part 1), New Delhi, Bureau of Indian Standards, 1974.

6. Brandt R. K.; Hughes M. R.; Bourget L. P.; Truszkowska K., Greenler R. G., The interpretation of CO adsorbed on Pt/SiO^{-2} of two different particle-size distributions, journal of Surface Science 286 (1–2) (1993): pp.15–25.

7. Buscaa Guido, Berardinelli Silvia, Resini Carlo, Arrighi Laura., Technologies for the removal of phenol from fluid streams: a short review of recent developments, Journal of Hazardous Materials, 160 (2008), 265–288.

8. Boehm H.P., Advances in Catalysis, New York, Academic Press, 1966.

9. Bouchelta C., Medjram Md. S., Bertrand O. and Bellat J.P., Preparation and characterization of activated carbon from date stones by physical activation with steam, Journal of Analytical and Applied Pyrolysis, 82(1) (2008): pp.70-77.

10. Cardenas S. A., Velazquez T. G., Revilla G. O., Cortez M., Perera B. G., adsorption of phenol and dichlorophenol from aqueous solutions by porous clay heterostructure, journal of the Mexican chemical society, 49(3) (2005): pp.287-291.

11. Dash S. N., Murthy V. R. C., Preparation of Carbonaceous Heavy Metal Adsorbent from Shorea Robusta Leaf Litter Using Phosphoric Acid Impregnation, international journal of environmental sciences, 1(3) (2010): pp.296-313.

12. Din A. T. M., Hameed B.H., Ahmad A. L., Batch adsorption of phenol onto physiochemical-activated coconut shell, Journal of Hazardous Materials, 161 (2009): pp.1522–1529.

13. Dursun Gulbeyi, Ciceka Handan, Dursun Arzu Y, Adsorption of phenol from aqueous solution by using carbonised beet pulp, Journal of Hazardous Materials, B125 (2005): pp.175–182.

14. Eh and s facts on phenol, courtesy: ucla environment, health and safety, (www.ehs.ucla.edu)

15. Fernandez E., Hugi-Cleary D., Lopez-Ramon M. V., Stoeckli F., Adsorption of Phenol from Dilute and Concentrated Aqueous Solutions by Activated Carbons, Langmuir, 19 (2003): pp.9719-9723.

16. Fierro V., Torne-Fernandez V., Montane D., Celzard A., Adsorption of phenol onto activated carbons having different textural and surface properties, journal of Microporous and Mesoporous Materials, 111 (2008): pp.276–284.

17. Figueiredo J.L., Mahata N., Pereira M.F.R., Sanchez Montero M.J., Montero J., Salvador F., Adsorption of phenol on supercritically activated carbon fibres: Effect of texture and surface chemistry, Journal of Colloid and Interface Science, 357 (2011): pp. 210–214.

18. Girodsa P., Dufoura A., Fierrob V., Rogaumea Y., Rogaumea C., Zoulaliana A., Celzardc A., Activated carbons prepared from wood particleboard wastes: Characterisation and phenol adsorption capacities, Journal of Hazardous Materials, 166 (2009): pp.491–501.

19. Hannafi N., Boumakhla M.A., Berrama T., Bendjama Z., Elimination of phenol by adsorption on activated carbon prepared from the peach cores: modelling and optimisation, journal of Desalination, 223 (2008): pp.264–268.

20. Huang J., Zhou Y., Huang K., Liu S., Luo Q., Xu M., Adsorption behaviour, thermodynamics, and mechanism of phenol on polymeric adsorbents with amide group in cyclohexane, Journal of Colloid and Interface Science, 316 (2007): pp.10–18.

21. http://plants.usda.gov/java/profile?symbol=eicr.

22. http://terpconnect.umd.edu/~toh/models/CalibrationCurve.html.

23. http://www.activatedcarbon.com.

24. http://www.astm.org/DIGITAL_LIBRARY/MNL/PAGES/MNL11272M.htm.

25. http://www.britannica.com/EBchecked/topic/455507/phenol.

26. http://www.ceram.com/testing-analysis/techniques/brunauer-emmett-teller-surface-area-analysis-barrett-joyner-halenda-pore-size-and-volume-analysis.

27. Kamble S.P., Mangrulkar P.A., Bansiwal A.K., Rayalu S.S., Adsorption of phenol and o-chlorophenol on surface altered fly ash based molecular sieves, Chemical Engineering journal, 138 (2008): pp.73-83.

28. Kennedy L. J., Vijaya J. J., Kayalvizhi K., Sekaran G., Adsorption of phenol from aqueous solutions using mesoporous carbon prepared by two-stage process, Chemical Engineering Journal, 132 (2007): pp.279–287.

29. Khalid M., Joly G., Renaud A., Magnoux P., Removal of Phenol from Water by Adsorption Using Zeolites, journal of Industrial and Engineering Chemistry Research, 43(2004): pp.5275-5280.

30. Kumar S., Zafar M., Prajapati J. K., Kumar S., Kannepalli S., Modelling studies on simultaneous adsorption of phenol and resorcinol onto granular activated carbon from simulated aqueous solution, Journal of Hazardous Matter, 185 (2011), 287-294.

31. Langmuir, I., The adsorption of gases on plane surfaces of glass, mica and platinum, Journal of the American Chemical Society, 40 (1918):pp.1361–1403.

32. Lin S., Juang R., Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review, Journal of Environmental Management, 90 (2009): pp.1336–1349.

33. Lin k., Pana J., Chena Y., Chenga R., Xua X., Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders, Journal of Hazardous Materials, 161 (2009): pp.231–240.

34. Liu Q., Zheng T., Wang P., Jiang J., Li N., Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, Chemical Engineering Journal, 157 (2010): pp.348–356.

35. Ozkaya B., Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models, Journal of Hazardous Materials, B129 (2006): pp.158-163.

36. Podkoscielny P., Nieszporek K., Heterogeneity of activated carbons in adsorption of phenols from aqueous solutions-Comparison of experimental isotherm data and simulation predictions, journal of Applied Surface Science 253 (2007) 3563–3570.

37. Roostaei N., Tezel F. H., Removal of phenol from aqueous solutions by adsorption, Journal of Environmental Management, 70 (2004): pp.157–164.

38. Salame I. I., Bandosz T. J., Role of surface chemistry in adsorption of phenol on activated carbons, Journal of Colloid and Interface Science, 264 (2003): pp.307–312.

39. Shawabkeh R. A., Abu-Nameh E. S. M., Absorption of Phenol and Methylene Blue by Activated Carbon from Pecan Shells, Colloid Journal, 69(3) (2007): pp.355–359.

40. Singh K. P., Malik A., Sinha S. and Ojha P., Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material, Journal of Hazardous Materials, (2008), vol. 150, 626–641.

41. Song Liu Q., Zheng T., Wang P., Jiang J., Li n., Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, Chemical Engineering Journal, 157 (2010): pp.348–356.

42. Stavropoulos G.G., Samaras P., Sakellaropoulos G.P., Effect of activated carbons modification on porosity, surface structure and phenol adsorption, journal of Hazardous Materials, 151 (2008): pp. 414–421.

43. Terzyk A. P., Further insights into the role of carbon surface functionalities in the mechanism of phenol adsorption, Journal of Colloid and Interface Science, 268 (2003): pp.301–329.

44. Uddin M. T., Islam M. S., and Abedin M. Z., Adsorption of phenol from aqueous solution by water hyacinth ash, Journal of Engineering and Applied Sciences, vol. 2, (2007), 11-17.

45. Vasu A.E., Removal of Phenol and o-Cresol by Adsorption onto Activated Carbon, E-Journal of Chemistry, 5(2) (2008): pp.224-232.

46. Vazquez G., Gonzalez A., lvarez J., Garcia A.I., Freire M.S., Antorrena v, Adsorption of phenol on formaldehyde-pretreated Pinus pinaster bark: Equilibrium and kinetics, journal of Bioresource Technology, 98 (2007): pp.1535–1540.

47. Weber Jr. W.J., Morris J.C., Kinetics of adsorption on carbon from solution, Journal of Sanitary Engineering Division-ASCE, 89(SA2) (1963): pp. 31–59.

48. Yang R. T., Adsorbents: fundamentals and applications, New Jersey, wiley-interscience, 2003.

Publications from thesis

Journal publications (to be communicated)

1. Manoj Kumar Mahapatra and Arvind Kumar, "**Phenol abatement from aqueous solutions using WHAC a novel adsorbent**".

2. Manoj Kumar Mahapatra and Arvind Kumar, "**comparative analysis of phenol adsorption from aqueous solutions using GAC and WHAC**".

Conference publications

1. Manoj Kumar Mahapatra and Arvind Kumar, "**Study of process parametric effects on phenol removal from aqueous solution by adsorption using granular activated carbon**" National conference on Recent advances in chemical and environmental engineering (RACEE-2012), NIT, Rourkela. January, 20-21, 2012.

2. Manoj Kumar Mahapatra and Arvind Kumar, "**Phenol removal from aqueous solution by adsorption using granular activated carbon**" National conference on Technological advancements in chemical and environmental engineering (TACEE-2012), BITS, Pilani. March, 23-24, 2012.