

**“TREATMENT OF HAZARDOUS POLLUTANT- PHENOL
FROM THE EFFLUENT USING ADSORPTION”**

A Major Project Report
*Submitted in partial fulfillment of the requirements
for the Degree of*

MASTER OF TECHNOLOGY

IN

**CHEMICAL ENGINEERING
(ENVIRONMENTAL PROCESS DESIGN)**

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CERTIFICATE

This is to certify that the Major Project Report entitled “Treatment of Hazardous Pollutants-Phenol from the Effluent using Adsorption” submitted by Ms. Domadia Shital N. (04MCH003), towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering (Environmental Process Design) of Nirma University of Science and Technology is the record of work carried out by her under my supervision and guidance. The work submitted has in my opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of my knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

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ABSTRACT

In the last few years, attention towards the water pollution has been increased, due to regulatory concerns and stringent environmental policies. Industries are compelled to treat their effluents as per the specifications given by pollution control board before discharge it into the natural resources.

Generally physical-biological treatments are provided to the effluents coming from various industries. Some specific effluents from industrial production processes may be difficult to purify by traditional waste water technology. These specific pollutants like phenols are not easily degradable are commonly toxic so their discharge can cause damage to the environment, and achieving legal purification levels is often very difficult. Adsorption processes have been shown to be very effective methods for the removal of these pollutants. There are various methods available for the treatment of phenol in waste water like, photo catalytic degradation, extraction, biosorption, wet air oxidation, biological oxidation, advanced oxidation, adsorption and membrane processes. Adsorption is found very effective and easy treatment for phenolic pollutants.

In this report, investigation of the adsorption capacity is done for various adsorbents for removing of phenolic contaminants from wastewater. The adsorbents considered are activated carbon, modified clays of bentonite, unmodified bentonite clay, treated fly ash and saw dust carbon. The representative contaminant used is phenol. The kinetic data are produced for the activated carbon. Effect of various parameters like adsorbent dose and initial concentration are studied for phenol adsorption on activated carbon. The equilibrium results are correlated by various isotherms like Freundlich isotherm, Langmuir isotherm and Tempkin isotherm.

The results of this study are applicable to the continuing development of adsorption wastewater treatment technology.

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NOMENCLATURE AND ABBREVIATIONS

1/n	Freundlich constant (adsorption intensity)
AC	Activated Carbon
ads	Adsorption
Al-B	Alluminum Bentonite
b	Langmuir constant
B₁	Tempkin constant
C_e	Equilibrium concentration of solute in the solution (mg/l)
C_o'	Initial conc. Of adsorbate in solution (mmole/l)
C_o	Initial concentration of solution (mg/l)
C_t	Aqueous phase concentration at time t (mg/l)
e	Equilibrium
FA	Fly Ash
h	Initial sorption rate (mg/g min)
K	Freundlich constant
K_{ads1}	First order adsorption rate constant
K_{ads2}	Second order adsorption rate constant
K_t	Tempkin isotherm constant
M	Concentration of adsorbent (g/L)
M'	The weight of adsorbent used per liter of solution
m, c	Rathi Puranik constants
m₁, c₁	Weber Morris constants
MTZ	Mass Transfer Zone
Na-B	Sodium Bentonite
o	Initial condition
Q'	Amt of adsorbate retained at time t (m mole/gm)
Q_e	Amt of Phenolic compound adsorbed per unit mass of carbon (mg/g) at equilibrium
Q_{e1}	Equilibrium adsorptive capacity by Lagergren equation (mg/g)
Q_{e2}	Equilibrium adsorptive capacity by pseudo second order equation (mg/g)

Q_o	Maximum adsorption capacity when complete monolayer forming on the surface
Q_t	Amt of Phenolic compound adsorbed per unit mass of carbon at time t (mg/g)
SDC	Saw Dust Carbon
t	at any time t(min)
T-B	Thermal bentonite
V	Volume of the solution (ml)
X	Co – Ce (mg/g)
α, k_o	Bangham's constant

1.1 Adsorption treatment for hazardous pollutants

Water is the most precious natural resource, and due to its realization becoming prevalent source of concern, core attention and emphasis is placed on its maintenance and purification than ever before. People concerned about the causes that have negative impact on the environment. Industries are also very prominent in today's society and its impact on water is increases significantly. Increasing regulatory concerns as well as stringent environmental policies compelled industries for adequate waste water treatment facilities to treat their effluents as per specification of the pollution control board.

Generally physical and biological treatments are provided to the effluent coming from various industries. Some specific effluents from industrial production processes may be difficult to purify by traditional waste water treatment technology, as a result of the complexity of some of their components. These specific components, which are not easily degradable, are commonly toxic and their discharge can cause serious problems to the environment, sometimes even achieving legal purification levels is often very difficult. Adsorption processes have been shown to be one of the most effective methods for the removal of these compounds.

Adsorption is used for abatement of various organic and inorganic pollutants coming out from industries such as dye stuff industry, textile industry, petrochemical industries, refineries, pharmaceutical industry, pulp and paper industry etc by using adsorbent like activated carbon, wood charcoal, clays, clay minerals, synthetic adsorbent, inorganic oxides/hydroxides, chitin and some low cost non conventional adsorbent. Adsorption can be used for removal of color, phenolic compounds, heavy metals and other organics. Adsorption can be applied widely for industrial waste water treatment as well for domestic water or natural water treatment. Adsorption can also be used as the first stage of treatment that shall increase efficiency of the subsequent biological treatment.

Generally adsorption is used a tertiary polishing treatment Rathi *et al* (2002, 2003) have demonstrated the adsorption as the first stage of treatment that shall increase efficiency of the subsequent biological treatment. For removal of phenol and phenolic compounds activated carbons (powdered activated carbon and granular activated carbon) are most commonly used adsorbents. Higher removal efficiency for phenol and phenolic compounds from waste water is attainable by using such conventional adsorbents. So these adsorbents can be used as common adsorbent for treating effluent containing mixture of such phenolic compounds. Due to the harmful effects of phenols on human and aquatic life phenol is emphasizing pollutant for the study in this project work. The work was done for batch operation and for single solute which is phenol. Synthetic solution was used for the study and then applied to real effluent sample. Adsorption is clean and easy technique for the waste water. It is efficient, but economical consideration should be done before applying it commercially.

1.2 Objective of the project

The objective of this project entitled “Treatment of hazardous compound from effluent using adsorption” is to carry out the batch study of the phenol adsorption on activated carbon and other non conventional adsorbents. The main objective of the project is to investigate the adsorption capacity of all the adsorbents used and to produce the equilibrium and kinetics data for activated carbon and fitting all the results to various isotherms and models available from the literature.

1.3 Significance of the Project

Industries are discharging various pollutants to water bodies and polluting the water. Phenol is the major pollutant from the various industries. Regulatory concerns and stringent environmental policies compelled the industries to reduce the phenol concentration upto the acceptable limit. As phenol is very toxic, hazardous, carcinogenic and corrosive it can damage the environment. Adsorption is very easy and effective technique to remove the phenol concentration to the limit. Adsorption can remove very low as well as high concentration of phenol. Activated carbon is mainly used adsorbent for the waste water treatment. The spent activated carbon can be regenerated by the various regeneration methods.

1.4 Project methodology

Batch experiments were carried out in laboratory for single solute phenol from synthetic sample. Various cheap adsorbents have been tried for the batch studies according to literature and they are compared with commercially available activated carbon.

Adsorbent dose was varied to find the optimum dose for the system. The equilibrium data has been produced for all the types of adsorbents. Kinetic has been studied for activated carbon. Various models were fitted to find the order of the process and the rate controlling step.

1.5 Organization of project report

This report of project contains mainly Introduction, literature survey, activated carbon adsorption mechanism, Experimental set up and procedure, Results and discussion and finally conclusion. Chapter-1 Introduction consists of significance, Objective and methodology of project work. While Chapter-2 literature survey splits into three parts; first one is on the importance of water and introduction to hazardous pollutants - phenolic pollutants. Second one is on the basis of type of industry discharging the phenolic compounds and alternative methods available for the treatment of phenolic compounds. Chapter-3 includes mainly adsorption principles and activated carbon manufacturing and the isotherms and models available for the correlation of the equilibrium and kinetic data. Further work includes the experimental set up, experimentation procedure. Chapter 5 –Results and discussion includes the results for synthetic effluent for all types of adsorbents, comparison with activated carbon and analysis of the results by fitting them into various models and isotherms available in the literature

At last, conclusions derived from the project work and the future scope of the project.

The literature survey is classified on the basis of introduction to hazardous pollutants, types of industries discharging phenols, activated carbon derived from various carbonaceous raw materials and alternative techniques available for the treatment of phenol from the effluent. At last critical review of literature survey is displayed based on the types of Activated carbon used, based on the solute, Type of the operation used for the treatment and the sample used for the lab scale experimentation.

Mainly the work in this area has been done for the single solute; very few people have done the work based on the multi solute. Also most of the research is based on the synthetic sample very few researchers have gone for the real effluent samples.

2.1 Hazardous pollutant

“Toxic, explosive, corrosive, and reactive, cause danger or likely will cause danger to health and the environment, whether alone or when coming into contact with other waste.” By United Nations environment programs UNEP in December 1985. A Hazardous pollutant is any waste material that if improperly managed or disposed of may substantial hazards to human health and the environment. [36]

2.1.1 Characteristics of Hazardous pollutants

A waste is considered hazardous if it exhibits one or more of the following characteristics like toxicity, corrosivity, chemical reactivity, flammability, non biodegradability, carcinogenicity, mutagenicity and radioactivity.

Most of the pollutants are showing any one property as described before. So it's necessary to remove such pollutants from the effluent before discharging to water bodies, using various treatment facilities. Table 1.1 shows some hazardous pollutants which are discharged in the effluent.

2.1.2 Introduction to Phenolic pollutants

Phenolic compounds are common contaminants in waste water, being generated from petroleum and petrochemical, petroleum refineries, wood processing, coal conversion, and phenol-producing industries and plants that are processing phenols to plastic, agro

industries etc. Phenols cause an increase in oxygen demand in water and they also impart a taste to drinking water with even minute concentrations of their chlorinated derivatives. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. CPCB call for lowering phenolic compounds concentration less than 1-5 mg/l for effluent discharged from petrochemical industries and Refineries. [53]

Water pollution occurs due to the presence of dissolved organic and inorganic, materials found in domestic and industrial waste waters. Among the most prevalent forms of pollutants in a typical chemical industry are phenolic compounds, occupying the front line position. They usually originate from natural as well as industrial sources. Phenols in the waste water generally consist of a variety of hydroxyl benzenes, substituted hydroxyl benzenes and are not readily biodegradable. They are toxic and are potential health hazards. [31]

Phenols is a class of aromatic organic compounds where one or more hydroxyl groups (-OH) are attached directly to the benzene ring. The major phenolic compounds (i.e. phenol and related compounds) are Phenol, Chlorophenols, Nitrophenols, Cresols, Phenolic Acids (Gallic Acid, P- hydroxybenzoic Acid, Syringic Acid) etc. Cresols and chlorophenols are used for preservation of wood. The mixture of cresols is called "Lysol" is very good disinfectant. Pyrogallol serves as a photographic developer.

Though phenols have been detected in decaying organic matter and animal urine in small quantities, their presence in surface waters is primarily attributed to the industrial waste discharge. [6, 32]. Table 2.1 gives the waste generating industries and the type of waste they are discharging. A wide variety of both organic and inorganic pollutants is coming in effluent from various chemical industries. It is observed that a major pollutant from various industries is phenol. Due to major pollutant from various industry and its toxic effects phenol is taken as main emphasizing pollutant for the study. Table 2.2 gives the idea of average concentration of phenol from various types of industries.

2.1.3 Effect of Phenol pollutant on human health and aquatic life

Phenols are strong skin irritants and consumption of water containing these, lead to severe pain, vomiting and capillary damage. Toxic effects are felt in the brain, lungs,

kidney, liver pancreas and spleen. [31] If Chlorophenols, present in water as low as 0.1 mg/l display a pronounced undesirable effect. Small concentration of phenol, in water causes taste and odor problems. Some Phenolic compounds have been found to accelerate tumour formation, cancer and mutation. [8] If water containing phenol is fed to plants, it reduces the photosynthesis. [57]

2.1.4 Limits of Phenolic compounds in drinking water and industrial effluent

World Health Organization (WHO) defines the maximum permissible concentration for various types of phenols like for 2, 4, 6 - trichlorophenol: 200 mg/l, Pentachlorophenol: 9mg/l, 2-chlorophenol: 10 mg/l and for 2, 4-dichlorophenol: 40 mg/l. [9]

US – EPA includes Federal Register, in which they listed eleven substituted phenols known as Hazardous for human health and assigns them a maximum admissible concentration range of 60- 400 mg/l in relation to their toxicity. The permissible limit for Phenolic concentration in industrial effluents before discharging into surface waters is 1 – 5 mg/l. [9]. IS 10500 (1991) gives the maximum limit in drinking water is 0.001 mg/l and maximum permissible in the absence of alternate source is 0.002 mg/l. An unpleasant taste is produced by 0.1 ppm of phenol in water and taste becomes much worse when water chlorinated. The odour threshold for phenol is 0.04 ppm. [1, 24, 25] While Ministry Of Works And Housing gives the highest desirable value of Phenolic compound is: 0.001 mg/l and maximum permissible is 0.002 gm/l [34]. Similarly CPCB, 1995 and MoEF, 1993 give the standards for discharge as Phenolic pollutants as phenol for Inland surface water the limit is specified 1.0 mg/l, for Public sewers the limit is 5.0 mg/l, for land irrigation not yet specified and for marine coastal area it is 5.0 mg/l. [23, 32, 64]

2.2 Phenol in effluents from various industries

2.2.1 For Petrochemical industries, petroleum refineries, coke industries

Wastewater coming out from petrochemical industries or petroleum refineries contains a wide range of organic compounds. Phenols and Phenolic compounds (phenol related compounds such as nitrophenols, chlorophenols, phenolic acid etc) are the pollutant that most of effluent coming from petrochemical industries contains. Concentration of this phenolic compound may vary widely depending upon the production process.

Phenolic compounds are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous-

Table 2.1: Waste generating industries and type of waste [26, 46, 47]

Waste Generator industries	Type of Waste
Coal refining	Phenol , cresol, cyanide and metal traces
Resin mfg	Phenol and chlorinated phenol
Organic chemical mfg	Strong acids, spent solvents, phenols and other reactive complex compounds
Printing industries	Heavy metals, toluene, benzene and spent solvent
Leather mfg	Toluene, benzene
Pulp and Paper industry	Strong acids and bases, phenol and chlorinated phenols
Metal industry	Cyanide waste, heavy metals, strong acid
Petroleum refining and p/c industries	Chlorinated H/C, phenol , acids and other organic pollutants
Agriculture industries	Pesticides, herbicides, chlorinated H/C & aromatic compounds
Pharmaceuticals industries	Chloroform, phenyl acetic acid, benzene and other chlorinated products of benzene
Tannery industries	Phenol , chlorophenol, nitrophenol
Phenol mfg plants	Amino phenol, resorcinol, phenol , dinitrophenol, p-nitrophenol, trinitrophenol

pollutants because of their potential harm to human health. The treatment processes for phenolic wastewater into two principal categories: destructive process such as destructive oxidation with ozone, hydrogen peroxide, or manganese oxides and recuperative processes such as adsorption into porous solids, membrane separation and solvent extraction. Adsorption is to be found one of the most effective treatments for abatement of phenolic pollutants. A comparative study of the sorption of phenol and p-chlorophenol from water has been performed using novel adsorbents prepared by carbonization and subsequent activation of straw and used rubber tires as well as

conventional activated carbons based on coal, coconut shell and wood by M. Streat *et al.* [25].

They found that the sorption of phenol and p-chlorophenol onto active carbons derived from straw and used rubber tyres is almost identical to that for conventional activated carbons. The sorption kinetics of the straw and rubber tire based carbons are likewise identical to conventional carbons based on coal and wood but appreciable faster than the coconut shell adsorbent selected for comparison. Straw based adsorbents are likely to be considerable cheaper than conventional materials based on coal, coconut shell and wood and this could, therefore, offer considerable potential to make water treatment processes more economic.

The sorption of phenol, m-nitrophenol, and o-cresol from water onto montmorillonite modified with cetyltrimethylammonium bromide (CTAB) in a fixed bed column was studied by R.S. Juang *et al.* (2004) [39]. The sorption isotherms were fitted by the Langmuir equation. Column experiments were performed at 25 °C to determine the breakthrough curves at different flow rates, feed sorbet concentrations, and bed lengths. They have provided a simple and easy-to-follow method for analyzing the breakthrough characteristics for the sorption of organic matter on the organ clays.

S. Dutta *et al.* (2001), [48] have used charred saw dust as an adsorbent for removal of nitrophenol. They observed that the degree of agitation has a significant effect on the rate of removal of p-nitrophenol. Higher initial concentration and lower temperature are more favorable for the adsorption of p-nitrophenol from aqueous solution. The rate of adsorption is influenced by the degree of agitation. Using high initial concentration of p-nitrophenol, the net removal by adsorption can be enhanced. Smaller adsorbent particles are much more effective in the removal of adsorbate. Lower temperature is favorable for the adsorption.

V. Manimozhi *et al.* (2002) [57] has investigated the adsorption of phenol on granulated activated carbon, based on Bed Depth and Service time principle method. The exhaustion of GAC is measured as a function of treated phenolic wastewater, from the exhaustion curve, bed depth and service time.

P. King *et al.* (2005) [31] have done studies on treatment of phenolic effluents using non conventional adsorbents. They used synthetic sample for study. They have also

varied the variable to see the effect on adsorption like adsorbent dose, adsorbent size, presence of other pollutants, contact time and initial concentration of phenolic pollutants. The data by experimental test were tested for Freundlich isotherms and Langmuir isotherms.

2.2.2 Pharmaceutical and steel industries

V.Srihari *et al.* [60] have done study on phenol sorption of two homogenized industrial waste water blend using activated carbon. Their study consists of use of steel and pharmaceutical industry waste water for adsorption of phenol using activated carbon. Subsequently the samples were homogenized (with respect to phenol concentration and pH) to get compatible and improved adsorption. Langmuir and Freundlich isotherms were also studied for the samples.

Rathi and Puranik, (2003), [3, 4] reported that some of the effluent streams from the paracetamol manufacturing process following p-nitrochlorobenzene route could be treated with cost effective adsorbent like lignite. They performed experiments to evaluate the efficiency of inexpensive adsorbent such as bentonite and lignite compare to that of activated carbon for treating various effluent streams coming out from paracetamol manufacturing process. Activated carbon is ten times more expensive than lignite. Rathi and Puranik have also studied the adsorption of pollutant from the diethylmalonate, a drug intermediate production industry using activated carbon, bentonite and lignite as adsorbents and found that the performance of AC and bentonite is comparable and better than lignite. Data are well fitted to new model introduced by authors, Rathi Puranik Model. This model has distinct advantage of predicting the equilibrium concentration value of give system. Considering the cost advantage of lignite over activated carbon, the usage of lignite as an adsorbent for the treatment of industrial wastewater would offer cost effective solution.

2.2.3 Agrochemical industries

The wastewater coming out from agro industries contains phenolic compounds such as chlorophenols, phenolic acids etc. Phenolic acids compounds are present in wastewaters coming from agro industrial activities related to the manufacturing of olive oil, wine, spirits, etc. Single solute and simultaneous experimental adsorption isotherms of three phenolic compounds: Gallic acid, p-hydroxybenzoic acid and syringic acid,

have been investigated at 20 °C, 30 °C and 40 °C, using a bituminous coal based activated carbon by J.F.Gracia *et al.* (2003) [20]

Table 2.2: The average concentration of phenol from industrial sources [8, 31]

Sr. no.	Industrial source	Phenol concentration, mg/l
1.	Metallurgical coke <ul style="list-style-type: none"> Spent liquor after phenol recovery Coke oven effluent 	900-1000 35- 250
2.	Coal carbonization <ul style="list-style-type: none"> Low temp. carbonization High temp. carbonization 	1000-8000 800-2000
3.	Phenol formaldehyde resin mfg.	800-2000
4.	Petroleum refining industry (per 1000 barrels of oil throughput) <ul style="list-style-type: none"> Desalting Fractionation Cracking Refining Rearrangement Separator Total 	0.0454 mg 0.7720 mg 6.9910 mg 2.3610 mg 0.0454 mg 7.6730 mg 10.215 mg/1000 barrels of oil
5.	Steel plant industrial effluent	50
6.	Pharmaceutical effluents	150
7.	Aircraft maintenance	200-400
8.	Fiberglass manufacturing	40-400
9.	Plastic factory	600-2000
10.	Petrochemical Benzene refinery	210
11.	Tar Distillation	300

In single component aqueous solution the adsorption trend was found to be syringic acid > p-hydroxybenzoic acid > gallic acid, regardless of temperature.

2.3 Alternative treatments for removal of phenol from effluent

S.Adish kumar *et al.* (2005) [41] have done work on the photocatalytic degradation of phenolic waste waters and investigated the effect of operational parameters. TiO_2 was used as a photocatalyst for the degradation of phenolic waste water. Solar radiation was used as an irradiation source. Several experiments were used to optimize the experimental parameters. They have observed 85% phenol degradation for 2 hr of contact time and 92% for 4 hr. The experiments were repeated for various pH and concentration of TiO_2 . Similarly the pollution concentration was varied.

M.J. Dietrich *et al.* (1985) [27] have studied wet air oxidation for hazardous organics in waste water. They have studied for bench scale and for pure compound, phenolic compounds, and specific organics, for solvent recovery and for non chlorinated pesticide waste waters. Also done pilot scale studies for coke plant waste water and pesticides and herbicides wastes. Also they have tried for full scale plant study for the effluent from herbicide producing plant.

2.4 Activated carbon (AC) from various carbonaceous materials and other cheap adsorbents

P.King *et al.* (2005) [31] have done studies on treatment of phenolic effluents using non conventional adsorbents. They used synthetic sample for study. They have also varied the variable to see the effect on adsorption like adsorbent dose, adsorbent size, and presence of other pollutants, contact time and initial concentration of phenolic pollutants. The data by experimental test were tested for Freundlich isotherms and Langmuir isotherms

Rathi and Puranik, (2003) [4] reported that some of the effluent streams from the paracetamol manufacturing process following p-nitrochlorobenzene route could be treated with cost effective adsorbent like lignite Activated carbon is ten times more expensive than lignite. Data are well fitted to new model introduced by authors, Rathi Puranik Model. This model has distinct advantage of predicting the equilibrium concentration value of give system. Considering the cost advantage of lignite over activated carbon, the usage of lignite as an adsorbent for the treatment of industrial wastewater would offer cost effective solution.

V.Murugesan *et al.* [58] have studied the removal of phenol from waste water by Activated carbon adsorption technique. They tried to make AC from ground nut shell using typical hot air oven. They tried to adsorb the phenol pollutant from waste water using the prepared activated carbon. Freundlich isotherm was fitted to the experimental data. Column study was carried out for the waste water from hot well and desalter. Column also functions as a filter unit.

T. Viraraghavan *et al.* 1998 [54] examined the effectiveness of less expensive adsorbents such as peat, Fly ash and bentonite in removing phenol from wastewater by adsorption. Freundlich and Langmuir were fitted for equilibrium data. From the analysis they observed the phenol adsorption capacity follows this order: peat > fly ash > bentonite. They have observed 50-60% reduction for all three types of adsorbents.

A critical review of the literature survey is shown in table 2.3 for the solute wise application in waste water.

Table 2.3: Possible adsorbents for phenol adsorption from literature

Solute	Adsorbent	Mode of operation	Sample type
Phenol	<ol style="list-style-type: none"> 1. Activated carbon [3, 4, 10, 12, 21, 25, 38, 49, 52, 60, 63] 2. AC made from used waste tires and Coconut Shell, husk and ash [31, 35, 59, 61] 3. Granular Activated carbon [57] 4. Electro Activated Carbon [19] 5. Treated Bentonite Clay or Montmorillonite clay [39,14, 40, 51, 54] 6. Fly ash [54, 56] 7. TiO₂ Powder [9] 8. Rice husk and rice husk ash [1] 9. Organo Minerals [43] 10. Paper Mill Sludge [29] 11. Activated carbon cloth [11] 12. Saw dust, saw dust carbon [7, 43] 13. Industrial waste [2] 14. organo minerals [43] 	<ol style="list-style-type: none"> 1. Batch Operation 2. Continuous Operation 	<ol style="list-style-type: none"> 1. Single solute 2. Multi-solute (Binary sample)

3. ACTIVATED CARBON ADSORPTION MECHANISM

3.1 Driving Forces for Adsorption

- ⇒ Lyophobic (solvent-disliking) character of the solute relative to the particular solvent, or a high affinity of the solute for the solid. (Hydrophilic and Hydrophobic character in an aqueous solution). The “solubility-amphoteric” character of the substance results in an orientation of the molecule at the interface; the hydrophobic part adsorbed at the interface, and the interface, and the hydrophilic part directed toward the solvent phase. [53]
- ⇒ Specific affinity of the solute for the solids (electric attraction, Vander Walls attraction, or chemical nature).

Adsorption of material from solution by porous adsorbents takes place by essentially three rate-limiting steps:

1. **Bulk Diffusion:** This is the transport of adsorbate through the bulk to the surface film around the adsorbent.
2. **Film Diffusion:** This is the transport of adsorbate through the surface film to the exterior of the adsorbent.
3. **Pore Diffusion:** This is the diffusion of the adsorbates within the pores of the adsorbent.

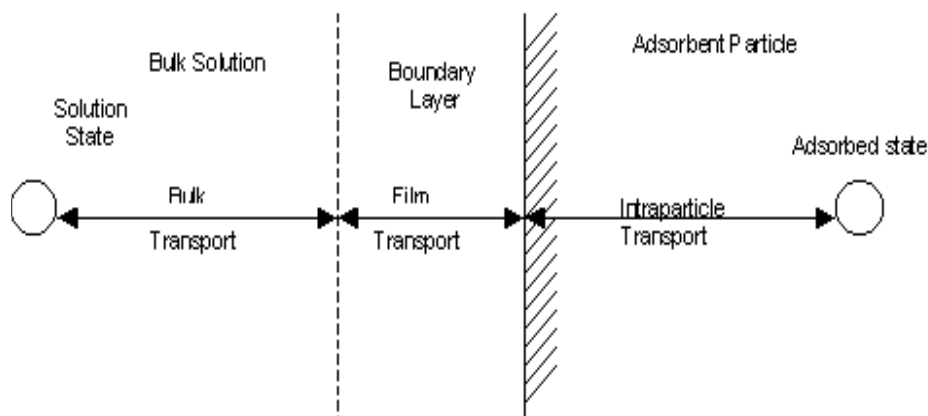


Figure 3.1: Mechanism of solute transport [72]

3.2 Types of Adsorption [32]

3.2.1 Physical adsorption

In Adsorption, the solid surface is being covered with one or more layers of molecules attracted to the surface from its liquid surrounding. If the attraction between the solid surface and adsorbed molecules is purely physical such as Vander walls forces, the adsorption is called Physical adsorption and is readily reversible

3.2.2 Chemical adsorption or chemisorption

On the other hand, if the attractive forces are chemical in nature and result in the formation of a chemical bond between the solid adsorbent and the adsorbed molecules, the adsorption is called chemical adsorption or chemisorption. In the case of chemisorption removal of the chemisorbed material to regenerate the adsorbent is more difficult.

3.3 Factors Affecting Adsorption [32, 65]

Adsorption is influenced by various factors-both chemical and physical. The factor like, initial solute concentration, adsorbent dosage, adsorbent particle size, agitation speed, pH, temperature, have influence on the adsorption. Other than these factors, influent flow rate, bed height is also influencing factor for fixed bed operation. Inlet velocity is a significant factor for fluidized bed adsorption system. Many factors influence the rate at which adsorption reactions occur and the extent to which a particular material can be adsorbed. Several of the more important factors are:

3.3.1 Surface area

Adsorption is a surface phenomenon and as such the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for the adsorption. Thus the amount of adsorption occurred per unit weight of a solid adsorbent is great, if the solid is more finely divided and more porous.

3.3.2 Nature of Adsorbent

The physicochemical nature of the adsorbent can have pronounced effects on both rate and capacity for desorption. Adsorption by activated carbon is a surface phenomenon and is affected by surface functional groups and structural details.

Significant amount of carbonyl and carboxyl groups are present on activated carbon surfaces. The adsorption capacity of activated carbon may well be accomplished by increasing the concentration of the appropriate functional groups.

3.3.3 Nature of the Adsorbate

The nature of the adsorbate (molecular structure and the solubility of the solute) is particularly important in dictating the degree of the adsorption that can actually occur. An increase in solubility acts to oppose the attraction of the adsorbate to carbon. Thus polar groups with a high affinity for water usually diminish adsorption from aqueous solutions. Adsorption increases with decreasing solubility of the solute in the solvent. The greater the solubility, the stronger the solute solvent bond and the smaller extent of adsorption. Solute molecular sizes also affect the adsorption, if the rate is controlled by intraparticle transport; the reaction generally will precede more rapidly for the smaller the adsorbate molecule.

3.3.4 Hydrogen ion concentration or pH of the solution

The pH of a solution from which adsorption occurs influences the extent of adsorption. Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of the other ions is influenced by the pH of the solution. Both the adsorbent and the adsorbate to be removed carry electrical charges, and results show that in general the adsorption efficiency of carbons is dependent largely upon the difference in electrical charges between the adsorbent and adsorbate. The adsorption increases with time upon acidification. The pH of the solution will affect the degree of dissociation of the solute from the solution.

3.3.5 Temperature

Temperature effect on adsorption Equilibria are generally not significant over the range of temperature practically encountered in water and waste water. Thus small variations in temperature do not alter the adsorption process to any significant extent. Adsorption reactions are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature.

3.3.6 Mixed solute or multi solutes

Most waste water contains a myriad compounds that may mutually enhance, interfere, or act independently in the adsorption process. For mixed solutions each solute competes in some way with the adsorption of the other. The degree of mutual inhibition of competing adsorbate should be related to the relative size of the molecules being adsorbed to the relative adsorptive affinities and to relative concentration of the solutes. Multi solute leads the rapid break through of the Activated carbon material.

3.4 Adsorption Isotherms

Adsorption is a dynamic competition among the molecules in the feed for a position on the surface of the adsorbent. The more strongly adsorbed molecules will displace the more weakly adsorbed molecules from the surface of the feed solid until equilibrium is established with the composition of the feed stream. The relationship between the amount of material adsorbed and its concentration in the feed in equilibrium with the adsorbent is called an adsorption isotherm.

The shape of isotherms may vary from concave downward through linear to concave upward. The concave downward isotherms are very desirable because they give higher solid loadings at low effluent concentration. This gives better adsorbent capacity while at the same time giving good removal of contaminant for the feed. Concave upward isotherms do not give good contaminant removal at high solids loadings. In other words, the equilibrium liquid phase must contain a lot of absorbable material to load up the adsorbent. Therefore, if suitable adsorbents having concave downward isotherms are available, they are to be preferred.

Equations often used to describe the experimental isotherm data are those developed by Freundlich, by Langmuir, and by Brunauer, Emmet and Tekker (BET isotherm). The Freundlich and Langmuir isotherms are used most commonly to describe the adsorption characteristics of activated carbons used in water and wastewater treatment.

3.4.1 Freundlich Isotherms [26, 34]

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies.

The empirically derived Freundlich equation is defined as follows:

$$X/M = K_F C_e^{1/n} \quad \dots (3.1)$$

Where K and n are empirical constants

C_o = Initial concentration of solute (mg/l)

C_e = the final concentration of solute in solution at equilibrium

$X = C_o - C_e$ (mg/l)

M = concentration of adsorbent (g/L)

For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log (X/M) = \log K_F + 1/n \log C_e \quad \dots (3.2)$$

Here the linear line obtained gives a slope, which is the value of $1/n$, and the y-intercept is $\log K_F$. The intercept is an indicator of adsorption capacity and the slope of adsorption intensity. A relatively slight slope (and hence a high value of n) indicates that adsorption is good over the entire range of concentrations studied, while a steep slope (and hence small n) means that adsorption is good at high concentrations but much less at lower concentrations. The value of $1/n$ obtained for adsorption of most organic compounds by activated carbon is < 1 . A greater value of the intercept K indicates a higher capacity for adsorption than a smaller value.

3.4.2 Langmuir Isotherms [26, 34]

Langmuir's model is characterized by the following conditions:

- ⇒ The molecules are adsorbed on definite sites on the surface of the adsorbent
- ⇒ Each site can accommodate only one molecule (monolayer)
- ⇒ The area of each site is a fixed quantity determined solely by the geometry of the surface
- ⇒ The adsorption energy is the same at all sites. In addition, the adsorbed molecules cannot migrate across the surface or interact with neighboring molecules.

The Langmuir adsorption isotherm is expressed as:

$$X/M = Q = Q_o (b C_e / 1 + b C_e) \quad \dots (3.3)$$

Where,

C_e = aqueous phase equilibrium concentration (ppm)

Q_e = adsorbed phase equilibrium concentration (mg/g)

Q₀ = is the maximum adsorption capacity when complete monolayer forming on the surface and b = Langmuir constant

By rearranging the equation to,

$$(C_e/Q_e) = (1 / b Q_0) + (1 / Q_0 C_e) \quad \dots (3.4)$$

A plot of C_e/Q_e vs. C_e would give Q₀ and b from the slope and the intercept respectively. Q₀ is the amount adsorbed per gram of adsorbent, corresponding to complete coverage and b is the Langmuir constant (l/g), which is energy constant, indicating the adsorptivity of the solute.

3.4.3 Tempkin equation [56]

$$Q_e = B_1 \ln K_T + B_1 \ln C_e \quad \dots (3.5)$$

Q_e = adsorbed phase equilibrium concentration (mg/g)

B₁ and K_T are constants

3.4.4 Redlich-peterson equation [56]

$$Q_e = K_R C_e / (1 + a_R C_e^\beta) \quad \dots (3.6)$$

Q_e = adsorbed phase equilibrium concentration (mg/g)

K_R, β and a_R are constants

3.5 Breakthrough Curve

In an adsorption unit the breakthrough curve is the variation of concentration of the exit liquid with respect to time. It is used to show the function of the adsorbent over time. An example of such a curve is given in figure. It can be seen that there is an initial rapid increase in concentration change, which slows down to produce a gradual increase. The initial rapid increase in the concentration change is due to the freshness of the adsorbent in the system. As the time increases the adsorbent has adsorbate on its surface thus reducing the activity. This results in a slower uptake of adsorbate. The curve steadily increases at a less rapid pace before the adsorbent reaches saturation.

[42, 57, 58]

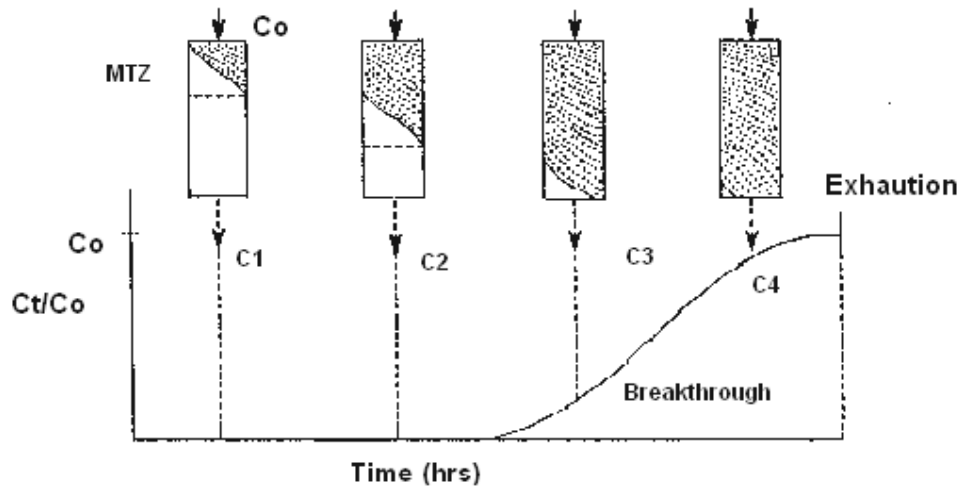


Figure 3.2: Break through curve for activated carbon column [68]

3.6 Adsorption kinetics Models

From the literature, various kinetics models found which helps to find the order of the adsorption process and also which step or mechanism is slowest and rate controlling step. Some of models predict only order of the adsorption process and some of them help to determine the rate controlling step for the adsorption.

According to literature for adsorption by activated carbon having more micro pores always controlled by the intra particular diffusion. While for some adsorbents having less micropores and for specific adsorbate solution the rate controlling step would be bulk diffusion. Here models available from literature which will help to predict the overall kinetics of adsorption.

3.6.1 Models for order of the process

These models determine the order of the adsorption for the given system. If the kinetic data is fitting to the particular model then the order of adsorption can be determined.

⇒ **Pseudo first order equation - Lagergren rate equation** [2, 56]

The Lagergren's rate equation is widely used one for the adsorption of the solute in a liquid solution. This first order equation is:

$$\text{Log}(Q_e - Q_t) = \text{log } Q_e - k_{\text{ads}1} * t / 2.303 \quad \dots(3.7)$$

Q_e = adsorbed phase equilibrium concentration (mg/g)

Q_t = adsorbed phase concentration at time t (mg/g)

k_{ads1} = first order adsorption rate constant

⇒ **Pseudo second order equation – McKay and Ho equation** [7, 56]

The pseudo second order equation can be represented in the form of:

$$Q_t = t K_{ads2} Q_e^2 / (1 + t K_{ads2} Q_e) \quad \dots(3.8)$$

The initial sorption rate, h (mg/g min), as $t \rightarrow 0$ can be defined as:

$$h = K_{ads2} Q_e^2 \quad \dots(3.9)$$

The equilibrium adsorption capacity Q_e and initial sorption rate h alongwith the K_{ads2} can be determined from the non – linear fitting of the data.

3.6.2 Models for the controlling step

There are models available in the literature by which one can find the step which is controlling the rate of adsorption. The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more step e.g. film or external diffusion, pore diffusion and combination of the two steps.

The possibility of intra particle diffusion was explored by using the intra particle diffusion model.

⇒ **Weber Morris Model** [3, 4, 40]

If the plot of $(C_0 - C_t)/C_0$ versus $t^{0.5}$ give the straight line, then the sorption process is controlled by intra – particle diffusion only. But if data exhibit multi-linear plots, then two or more steps influence the sorption process.

The model equation is:

$$(C_0 - C/C_0) = m_1 * t^{0.5} + C_1 \quad \dots(3.10)$$

Now by plotting $C_0 - C/C_0$ vs. $t^{0.5}$ we can get the coefficient slope m_1 and c_1 for the specific systems. Now based on these values of m_1 and c_1 , concentration at any time can be predicted,

$$C_{pre} = C_0 (1 - (m_1 * t^{0.5} + C_1)) \quad \dots(3.11)$$

Now from the predicted values of concentration % Deviation can be calculated.

Weber Morris model is well fitted model where the intraparticle diffusion is rate controlling for adsorption process.

⇒ **Bangham's equation** [2, 56]

Kinetic data can be further be used to check whether pore diffusion is the only rate controlling step or not in the adsorption system using this equation.

$$\log \log (C_0 / C_0 - Q_t * m) = \log (k_0 m / 2.303 V) + \alpha \log t \quad \dots(3.12)$$

Where α (< 1) and k_0 are constants. If the experimental data are represented by this equation then it is an indication that the adsorption kinetics is limited by the pore diffusion.

⇒ **Rathi Puranik Model** [3, 4]

This model is lumped model which is overall model for the entire steps.

$$\text{Log } [C_0 - C/t] = m * t + c \quad \dots(3.13)$$

By plotting $\text{Log } (C_0 - C/t)$ vs. t we can get the coefficient slope m and c for the specific systems. Now based on these values of m and c concentration at any time can be predicted.

$$C_{\text{pre}} = C_0 - 9 t * (10^{(m * t + c)}) \quad \dots(3.14)$$

Rathi Puranik model has an advantage over the existing models that it can predict the equilibrium concentration value of the given system by using equation,

$$C_{\text{eq}} = C_0 + 10^c * [1 / m \ln 10] * 10^{-1 / \ln 10} \quad \dots(3.15)$$

We can compare the C_{eq} actual by experimental and by this equation.

3.7 Usefulness of Adsorption Isotherms

Inspection of the adsorption isotherm plot can provide much valuable information.

Five important products of the adsorption isotherm are: [17]

1. The adsorbability of a component or, in other words, its relative affinity for the adsorbent.
2. The weight pickup or the concentration of the adsorbate adsorbed per weight of adsorbent or in percentages. For example, 20 percent would be equivalent to 200 mg/g capacity.
3. The degree of removal achievable as indicated by the equilibrium adsorbate concentration which remains unchanged with increasing adsorbent dosage. A constant concentration indicates a nonadsorbable component.

4. Sensitivity to adsorbate concentration change as indicated by relative steepness of the isotherm line. Based on a log-log plot of data, a steep line would mean that, for a small change in concentration, the adsorption capacity changes drastically. This has implications for adsorption process design.
5. The presence of competing adsorbates indicated by non-linear or multi-line isotherm plots.
6. The effect of pH on the adsorption isotherm test is determined by adjusting the pH of the initial solution. In this way, we can determine whether the added cost of pH adjustment will be offset by savings in the quantity of carbon

3.8 Types of absorbers

3.8.1 Fixed bed adsorber

This type of system is most often used to treat large quantities of waste water, in fixed bed adsorption system; the flow could either upflow or downflow.

Packed bed up flow carbon columns for full counter current operation are suitable only for low turbidity waters, that is, waters having a turbidity of 2.5 JU or less. Very fine carbon should not be used for upflow fixed beds because of clogging and high head loss problems. In liquid upflow operations a portions of the adsorbent is usually removed periodically from the bottom and an equal amount of regenerated solid is added to the top. The only reason for using a downflow bed is to make it possible to use the carbon for two purposes, adsorption of organics and removal by filtration of suspended and flocculated materials.

The principal advantage of this dual use of granular carbon is that of some reduction in the capital cost. The down flow bed may be fixed either in parallel or in series. Most designs consists either two or three beds in series.

In practical the liquid is fed continuously to either the top or bottom of a stationary bed of a solid bed of solid adsorbent. The solid adsorbs increasing amount of solute with time and an unsteady state condition prevails. When the adsorptive capacity of the solids is reduced, it is regenerated for reuse. In liquid down flow operation, the entire contents of the column are generated after exhaustion.

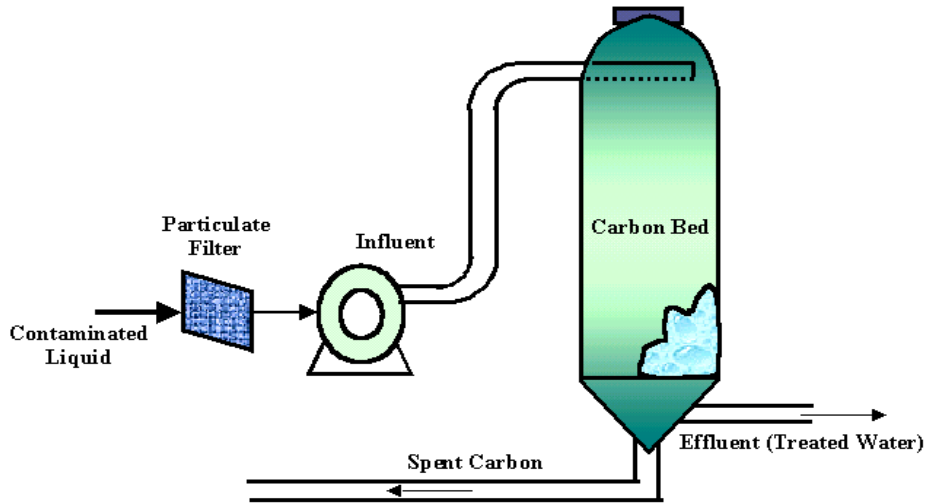


Figure 3.3: Typical fixed bed adsorption system [58]

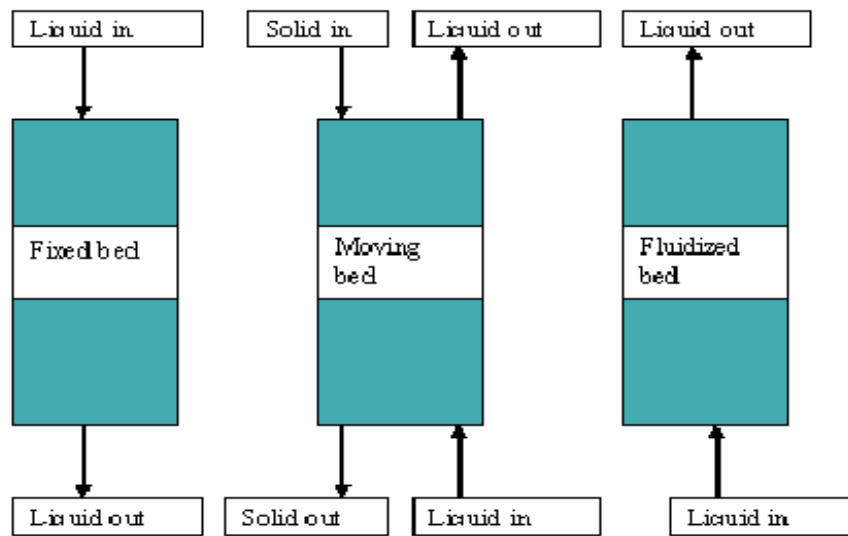


Figure 3.4: Schematic diagrams of fixed, moving and fluidized beds [32]

3.8.2 Fluidized bed adsorption

In fluidized bed adsorbers the fluid flows upward through the solid particles at a low velocity that is sufficient to suspend the particles but not high enough to carry them out the bed. As the fluid flow rate is increased in a fluidized bed, the bed expands and maintains a pressure drop that is essentially constant. For steady state operation, solids may be continuously added to the top and removed from the bottom. In comparison

with fixed beds, fluidized beds have higher capital and operating costs but can be run with higher feed rates and smaller particles without excessive pressure loss.

3.8.3 Moving bed or expanded bed adsorption system

In steady state moving bed adsorber, the fluid or solid phases are fed at constant rates to opposite's ends of the column and flow countercurrent to each other through the column. At steady state the compositions of the phases at any given point in the column do not change with time but there is a continuous gradient of concentrations in both phases along the column.

Continuous counter current adsorber has applied in the petroleum industry for separating hydrocarbon gases. They are rarely used for treating waste water because of the problems associated with moving solids continuously and uniformly through the column. Among the three, conventional fixed bed adsorption techniques are widely used for water and waste water treatment. [34]

3.9 Activated carbon

Activated carbon (AC) generally manufactured from carbonaceous material, including coal (bituminous, sub bituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The production of activated carbon consists of two phases, carbonization and activation. Carbonization is heating the material at 400 – 600°C in an oxygen-deficient atmosphere. During carbonization volatile component (H/C) and other gases, tar are released and graphite is formed. During activation the pore structure is developed in carbon. The carbonized particles are “activated” by exposing them to an activating agent, such as steam at high temperature 800 – 1000°C called “thermal activation” ,If exposed to dehydrating agents like $ZnCl_2$ and H_3PO_4 called “chemical activation” The steam burns off the decomposition products from the carbonization phase to develop a porous structure of carbon. Longer exposure times to activation agent result in larger pore sizes. [21, 48]

3.9.1 Structure of activated carbons

The pores in activated carbons are scattered over a wide range of size and shape. The pore structure may be pictured as having many small pores branching off from larger ones, which are open through the entire particle. The larger pores are called feeder and transport pore; the smaller ones, which may be dead end, are called adsorption

pores. The pores are classified by their sizes usually into three groups: (i) macropores having average diameter more than 50 nm, (ii) mesopores with diameter 2–50 nm, and (iii) micropores having average diameter less than 2 nm. These are further divided into supermicropores (0.7–2.0 nm) and ultramicropores of diameter less than 0.7 nm. [72]

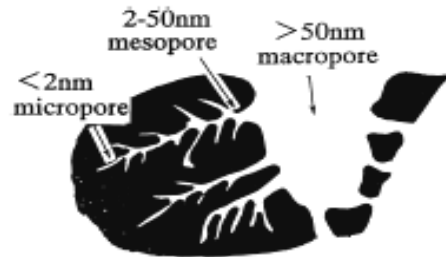


Figure 3.5: Pores inside the structure [44]

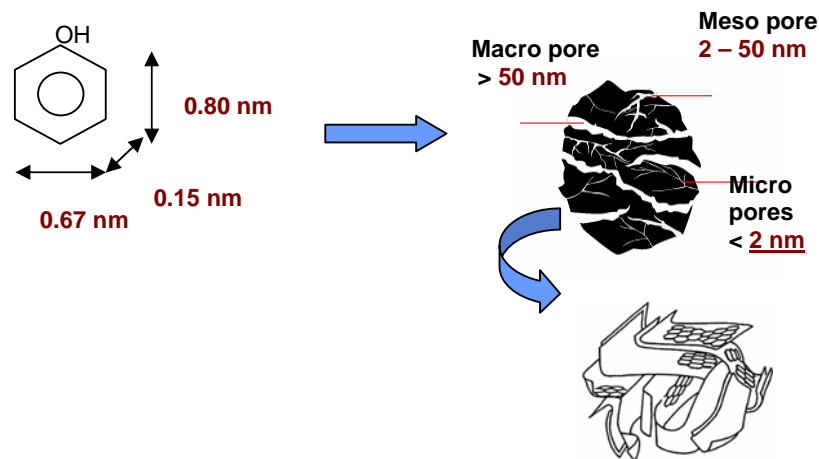


Figure 3.6: Phenol molecule adsorption in pores of activated carbon

3.9.2 Adsorption by activated carbons

Adsorption is formation of a gaseous or liquid layer by molecules in a fluid phase on the surface of a solid by molecular attraction of the van der Waals type. Atoms at the surface of solids like active carbons have imbalanced forces as compared to those within the solids and, consequently, foreign molecules in a bid to satisfy this

imbalance get attracted to the surface. These molecules (adsorbate) form a monolayer on the surface of the solid (adsorbent). [44]

Figure 3 depicts the adsorption process showing transfer of adsorbate molecules through the bulk gas phase to the surface of the solid and diffusion onto the internal surfaces of the pores in the solid adsorbent. Therefore the adsorption capacity of activated carbon depends on the type of pores and the total surface area available for adsorption. Activated carbons are characterized by their strong adsorption capacity, which can be as high as 0.6–0.8 cm³/gm which occurs mostly in cavities of molecular dimensions called micro pores.

Adsorption is a dynamic process in which some adsorbate molecules are transferred from the fluid phase on to the solid surface while some are released again to the fluid state. When the rates of two processes become equal, an adsorption equilibrium or so-called adsorption isotherm is obtained.

Table 3.1: Types of AC from different raw material and their properties [66]

Property	Coconut Activated Carbon	Coal Activated Carbon	Lignite Activated Carbon	Wood Activated Carbon (Powder)
Microspore	high	High	medium	Low
Macrospore	low	Medium	high	High
Hardness	high	High	low	n/a
Ash	5%	10%	20%	5%
Water Soluble Ash	high	Low	high	Medium
Reactivation	good	Good	poor	None
Iodine No.	1100	1000	600	1000

3.9.3 Classification of activated carbon

Activated carbons are complex products which are difficult to classify on the basis of their behavior, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics. [44]

⇒ Powdered activated carbon

Traditionally, active carbons are made in particular form as powders or fine granules less than 100mm in size with an average diameter between 15 and 25µm. Thus they present a large internal surface with a small diffusion distance.

⇒ **Granulated activated carbon**

Granulated activated carbon have a relatively larger size of particles compared to powdered activated and consequently, present a smaller external surface. Diffusion of the adsorbate is thus an important factor. Granulated carbons are used for water treatment, deodorization and separation of components of flow system.

3.9.4 Various applications of activated carbon

Activated carbons are unique and versatile because of their extended surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. Their important applications relate to their use in the removal of odour, colour, taste and other undesirable organic impurities from potable water in the treatment of domestic and industrial waste water, solvent recovery, air purification in inhabited species such as restaurants, food processing and chemical industry, for removal of colour from various types of sugar syrup, in air pollution control, in purification of many chemicals, pharmaceutical and food products and in a variety of gas phase applications. Along with other inorganics these are used as a catalyst and catalyst support. Their use in medicines to combat certain types of bacterial is well-known. These are used effectively for isolation and separation purposes. In separation of amino acids from their solutions in acetic acid, activated carbon can be used for separating aromatic acids. In order to effect chromatographic separation and to make the elution of absorbed substances easier, activated carbon is often modified, for example by treatment with nitric acid, making the surface more hydrophilic. [44]

3.9.5 Activated Carbon Properties [66]

⇒ **Iodine Number**

- Most fundamental parameter used to characterize activated carbon performance
- Measure of activity level (higher number indicates higher degree of activation)
- Measure of micropore (0 – 20 Å) content
- Equivalent to surface area of activated carbon in sq m/g between 900 – 1100
- Standard measure for liquid phase applications

⇒ **Methylene Blue value**

- Measure of mesoporous structure (20 – 500 Å)

⇒ **Molasses No.**

- Measure of macropore structure (>500 Å)
- Important for decolorizing performance

⇒ **Surface Area**

- Measure of adsorption capacity (Note: pore size distribution/pore volume is also important to determine ultimate performance)

⇒ **Apparent Density**

- Higher density provides greater volume activity and normally indicates better quality activated carbon

⇒ **Particle Size**

- Smaller size provides quicker rate of adsorption which reduces the amount of contact time required
- Smaller size results in greater pressure drop

⇒ **Hardness/Abrasion Number**

- Measure of activated carbon's resistance to attrition.
- Important indicator of activated carbon to maintain its physical integrity and withstand frictional forces imposed by backwashing etc.

⇒ **Dechlorination half-value length**

- Test to measure the dechlorination efficiency of activated carbon
- Depth of activated carbon to reduce influent chlorine level from 5 ppm to 2.5 ppm
- Lower half-value length indicates superior performance

⇒ Ash Content

- Reduces overall activity of activated carbon
- Reduces efficiency of reactivation
- Metals (Fe_2O_3) can leach out of activated carbon resulting in discoloration
- Acid/water soluble ash content is more significant than total ash content

3.10 Benefits of Activated Carbon Adsorption [66]

1. Highly effective at removing non-polar organic chemicals from water.
2. Applicable to a wide variety of organic compounds
3. Very effective at removing colors from waste streams.
4. Effective at removing low levels (ppb range) of inorganic pollutants.
5. Thermal regeneration of the carbon destroys the adsorbed waste solute.
6. Very flexible system allows rapid start-up and shut down as needed.
7. System can be designed so that it is portable, to be taken to waste sites.

3.11 Limitations of Activated Carbon Treatment [66]

1. Limited to wastes with low organic concentrations (< 5%).
2. Limited to wastes with very low inorganic concentrations (< 1%).
3. Unable to remove highly soluble organics, or those with low molecular weights.
4. Systems can not tolerate suspended solids in the influent stream (due to clogging).
5. High operating costs due to carbon costs system requirements.
6. Disposal of contaminated carbon can be problematic if it is not regenerated.

4.

EXPERIMENTAL PROCEDURE AND SET-UP

The experimental work was carried out in Chemical Process Industries laboratory, Nirma University, Ahmedabad. Prepared experimental set up is based on Batch operation and for single solute phenol. Various non conventional adsorbents were tried for the removal of phenol from synthetic waste water. Finally the results of the all the adsorbents were compared with the commercially available activated carbon.

4.1 Adsorbent preparation

4.1.1 Activated carbon (AC)

Activated carbon was washed several times before use and then it was dried in muffle furnace at 75-85 °C for 2 hr for removal of moisture. After drying keep it in desiccator for cooling. After each experiment the activated carbon was dried in furnace.

4.1.2 Activated fly ash (FA)

Fly ash was brought from Birla Copper thermal power plant, Bharuch. Fly ash was screened in 200µm sieve and then washed several times in distilled water. Fly ash was mixed with 0.1N HCl for the activation purpose. After washing it in distilled water several times and it was kept for drying, in the sun light and kept in muffle furnace for 2 hr at 50 °C for removal of moisture. Then it was cooled in desiccator and stored in plastic container.

4.1.3 Saw dust carbon (SDC)

Saw dust (SD) was collected from the Nirma University Hostel. The Saw dust was washed several times with distilled water to remove the earthy material and other impurities. Saw dust was boiled with distilled water and supernatant solution was poured off. This process was repeated several times, until clear supernatant solution is obtained. The washed adsorbent was dried in a muffle furnace at 80 °C. After the drying the saw dust was carbonized at 700 - 750 °C in muffle furnace for 1 hr in oxygen deficient atmosphere. The condition is achieved by filling SD in small steel container with small hole allowing only limited presence of air and the venting of

volatile matter and other gases. It was cooled in desiccator and stored in tight container. The carbon obtained was washed several times with distilled water to remove water soluble impurities.

4.1.4 Na-Bentonite (Na-B)

Pure bentonite was obtained from Manek minerals, Bhuj. The bentonite was then enriched with 1N NaCl solution, and then washed several times with distilled water until it is chloride free. This can be checked by the addition of AgNO₃ after washing with distilled water to make sure that no precipitate is formed, which is the evidence of chloride existence. This chemical treatment was done to offset the charge unbalance on the clay. The solid particles was separated by the filtration and dried at 70 °C.

4.1.5 Aluminum pillared bentonite (Al-B)

200 ml of 0.2N of sodium hydroxide (NaOH) was added drop wise to 100 ml of 0.2N of aluminum chloride solution (AlCl₃) with vigorous stirring. A rapid stirring is required to prevent local over concentration of OH⁻ ions. The solution was agitated slowly for one night for stability. The Al- Bentonite was prepared by slow addition of 300ml of the prepared solution to 15 gm of Na-bentonite with continuous stirring. The solid was separated by filtration and washed with distilled water and dried at 70 °C and then stored for further use in the adsorption tests.

4.1.6 Thermal bentonite (T-B)

It is a one type of physical treatment. The Na-bentonite was heated up to 850 °C for 30 min in a muffle furnace. Then it was cooled in desiccator and stored for further use for the adsorption tests.

4.2 Experimental procedure

Take known concentration of phenol solution (300 ml) in the closed 250 ml flask. Put the flask on the magnetic stirrer and add known amount of activated carbon to the solution. Take sample of the solution after each minute and analyze the water sample by spectrophotometer or by phenol standardization method. Correlate the experimental results by various models available in literature for kinetics study and

various isotherms like Langmuir, Freundlich and Tempkin, for equilibrium study. Effect of various parameters can be observed by varying the initial concentration and repeat the procedure for 200 - 400 mg/. Similarly, vary the dose of adsorbent and repeat the procedure for 0.1 - 2.5 gm.

The same procedure can be followed by varying the type of adsorbent like Na-Bentonite, Al-Bentonite, T-Bentonite, treated fly ash and Saw dust carbon. Plot X/M vs. C_e for each adsorbent. Compare the efficiency of phenol removal of all the non conventional adsorbents used for the adsorption tests and commercially available activated carbon



Figure 4.1: Batch of synthetic sample of phenol and activated carbon

4.3 Experimental Set-up

4.3.1 Instruments required at the experimental work

Hot plate magnetic stirrer with temperature variation- for stirring and for heating purpose,

UV –VIS Spectrophotometer- for analysis of phenol concentration in the solution and pH meter for pH adjustment.

4.3.2 Apparatus required at experimental work

Iodine Closed flask, Whatman filter paper 42, Beakers, pipettes

4.3.3 Chemicals and reagents for experimentation

Phenol, distilled water, phosphate buffer solution, various adsorbents like bentonites, fly ash, saw dust and commercially available activated carbon and various coloring reagents like 4 – amino anti pyrene and potassium ferricyanide for water analysis.
(Appendix: A)

5.

RESULTS AND DISCUSSION

Various adsorbents were used for the equilibrium study and then compared with the commercial activated carbon. Experimental procedure was discussed in chapter no 3. The experiments are divided as per the adsorbents used:

1. Batch results of activated carbon
2. Results of treated fly ash
3. Results of Saw dust carbon
4. Results of all three types of bentonites
5. Comparison of all the six types of adsorbents

5.1 Results of Activated carbon (AC)

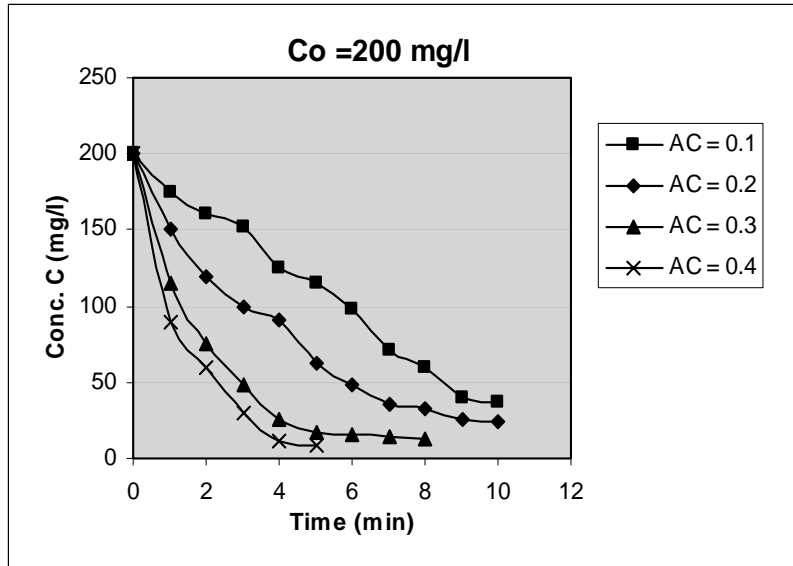
The properties of activated carbon are as follows:

Table 5.1: Properties of activated carbon

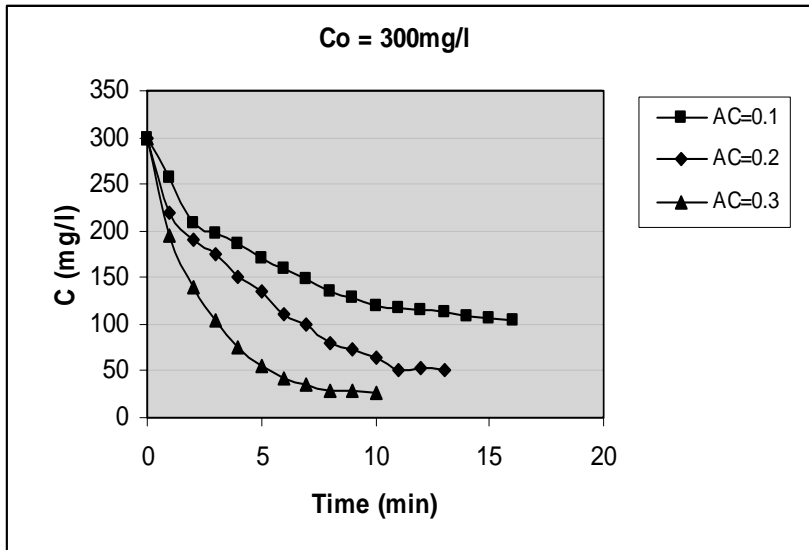
Properties	Value
Surface area	950 m ² /gm
Methylene blue value	330 mg/gm
pH	7.1
Water soluble	0.60%
Acid soluble	0.78%
Appearance	Fine black powder
Cost	35-40 Rs./kg
Particle size	0.156 mm

Table 5.2a: Kinetic data for Activated carbon (Co = 200 mg/l)

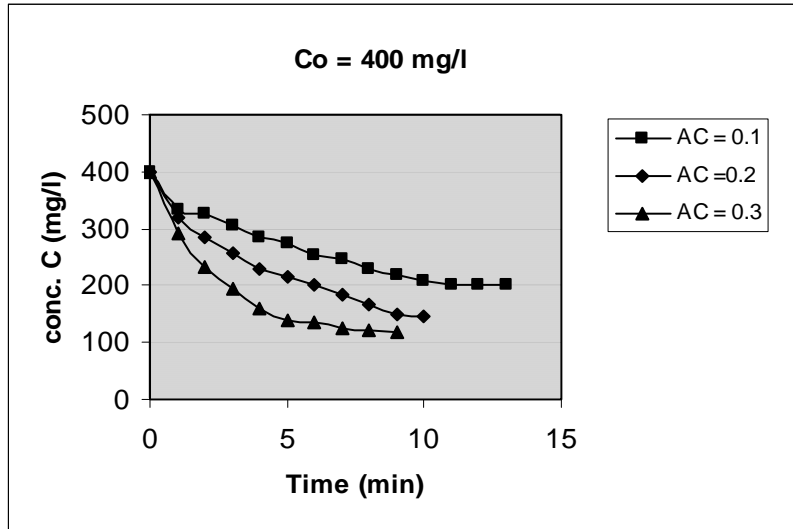
Co = 200	AC = 0.1 gm	AC = 0.2 gm	AC = 0.3 gm	AC = 0.4 gm
Time (min)	C mg/l	C mg/l	C mg/l	C mg/l
0	200	200	200	200
1	175	150	115	90
2	160	119	75	60
3	152	100	48	30
4	125	91	25	11
5	115	63	17	
6	98	49	16	
7	71	35		
8	60	33		
9	55	25		
10	48	24		
	Ce = 45	Ce = 23	Ce = 15	Ce = 11



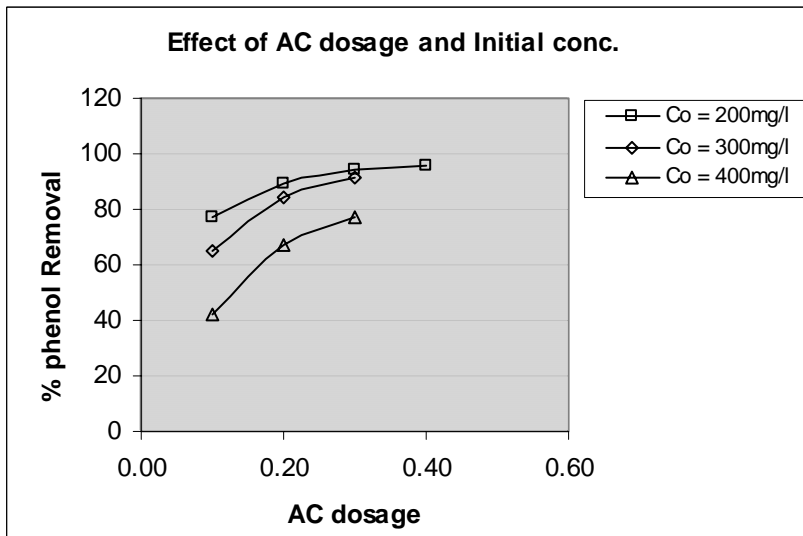
(5.1a)



(5.1b)



(5.1c)



(5.1d)

Figure 5.1: kinetic of phenol removal by activated carbon (AC) - (a) $C_o = 200$ mg/l, (b) $C_o = 300$ mg/l, (c) $C_o = 400$ mg/l and (d) Effect of AC dosage and Initial conc. of solute

5.1.1 Effect of initial conc. And AC dosage for phenol removal

Effect of variation in initial concentration on the adsorption of phenol is given in fig. 5.1 shows the effect of adsorbent dose also. It is observed that as the dose increases the phenol removal also increases and from the fig. 5.1(d) it can be observed that as C_o increases the phenol removal decreases. For dose 0.8 gm maximum removal can be achieved is 98.93% and then it starts decreases as dose increases. From Table 5.3 one can observe the % phenol removal for various doses for initial conc. 300 mg/l.

Similar things can be observed for 200 mg/l and 400 mg/l also. The concentration variation for time can be observed in fig. 5.1(d) for 200 mg/l, 300 mg/l and 400 mg/l.

Table 5.2b: Kinetic data for Activated carbon ($C_o = 300$ mg/l)

$C_o = 300$ mg/l	AC = 0.1 gm	AC = 0.2 gm	AC = 0.3 gm
Time (min)	C mg/l	C mg/l	C mg/l
0	300	300	300
1	258	220	194
2	209	190	140
3	197	175	105
4	187	150	76
5	170	135	55
6	160	110	43
7	149	100	35
8	135	80	29
9	128	72	28
10	120	65	27
11	117	50	
12	115	53	
13	113	52	
14	108		
15	107		
16	105		
	Ce = 104	Ce = 47	Ce = 25

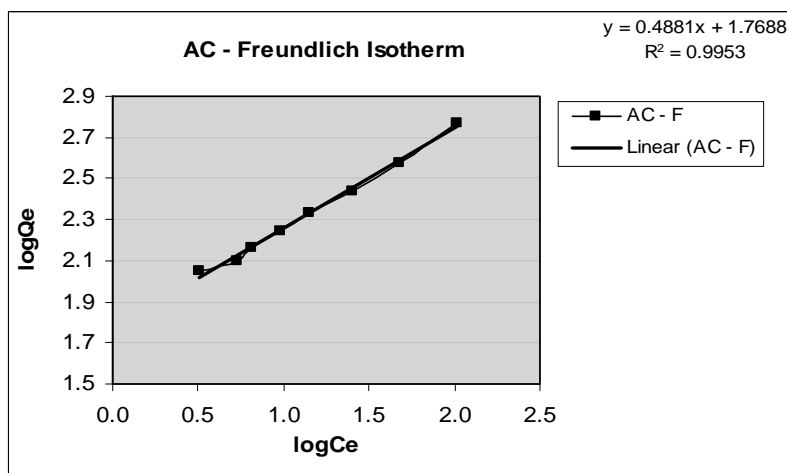
Table 5.2c: kinetic and equilibrium data for Activated carbon

(Co = 400 mg/l)

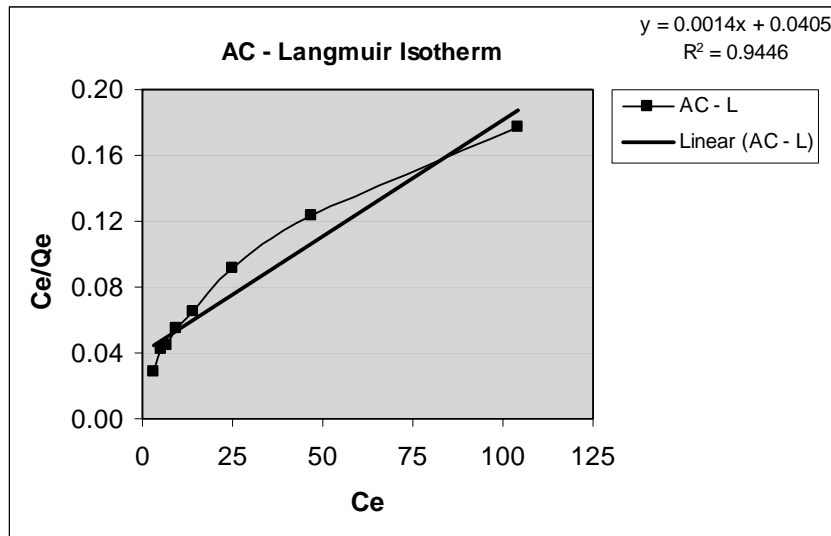
Co = 400 mg/l	AC = 0.1 gm	AC = 0.2 gm	AC = 0.3 gm
Time (min)	C mg/l	C mg/l	C mg/l
0	400	400	400
1	333	318	293
2	328	285	232
3	306	256	195
4	285	230	160
5	275	216	140
6	253	200	137
7	247	183	125
8	240	175	120
9	238	155	
10	235		
	Ce = 230	Ce = 130	Ce = 90

Table 5.3: Equilibrium data of activated carbon (Co = 300 mg/l)

AC dosages gm	M g/l	Ce mg/l	X mg/l	logCe	Qe mg/g	logQe	Ce/Qe	X/Co*100
0.10	0.33	104.00	196.00	2.01	588.00	2.76	0.17	65.33
0.20	0.66	47.00	253.00	1.67	379.50	2.57	0.12	84.33
0.30	1.00	25.00	275.00	1.39	275.00	2.43	0.09	91.66
0.40	1.33	14.00	286.00	1.14	214.50	2.33	0.06	95.33
0.50	1.66	9.58	290.42	0.98	174.25	2.24	0.05	96.80
0.60	2.00	6.54	293.46	0.81	146.73	2.16	0.04	97.82
0.70	2.33	5.40	294.60	0.73	126.25	2.10	0.04	98.20
0.80	2.66	3.21	296.79	0.50	111.29	2.04	0.02	98.93
1.00	3.33	8.23	291.77	0.91	87.53	1.94	0.09	97.25
1.20	4.00	15.24	284.76	1.18	71.19	1.85	0.21	94.92



(5.2a)



(5.2b)

Figure 5.2a and 5.2b - Freundlich and Langmuir isotherms for AC
($C_o = 300\text{mg/l}$)

Table 5.4a: Isotherm constants for activated carbon (at room temp. 26 – 27 °C)

Initial Conc. Of phenol C_o mg/l	Langmuir constants		Freundlich Constants	
	Q_o	b	K	$1/n$
200	1666.667	0.0084	19.550	0.8333
300	909.091	0.0160	49.056	0.5473
400	833.333	0.0070	30.782	0.5197

The value of $1/n$ is $0 < 1/n < 1$ show the favourability of adsorption. $K_f = 19.550$ indicates 1gm of activated carbon can remove 19.550 mg phenol for $C_o = 200$ mg/l and similar can apply for other two initial concentrations.

The efficiency of adsorption process can be predicted by dimensionless parameter R_L which can be defined by the equation:

$$R_L = 1 / (1 + bC_o)$$

b = Langmuir constant and C_o = Initial conc. (mg/l)

If $0 < R_L < 1 \rightarrow$ Favourable and if $R_L > 1 \rightarrow$ Unfavourable and if $R_L = 0$ then reversible adsorption occurs. The value of R_L is shown in Table 5.4b for various initial concentrations.

Table 5.4b: The value of R_L for various initial concentrations

Initial conc.	b	R_L
200	0.0084	0.3731
300	0.0160	0.2380
400	0.0070	0.4167

As from the Table 5.4b one can observe that for activated carbon for various initial concentrations 200 mg/l, 300mg/l and 400mg/l. The value of R_L is in between 0 and 1 and so the adsorption of phenol on activated carbon is favourable.

Table 5.5: Data for Lagergren equation and Bangham equation for AC

Time (min)	C_t mg/l	Log $(Q_e - Q_t)$	Q' (m mole/gm)	log(t)	log log $(C_o'/(C_o'-Q_t'*M'))$
1	240.00	2.61	16920	0.00	-1.01
2	209.00	2.49	25662	0.30	-0.80
3	197.00	2.44	29046	0.47	-0.73
4	187.00	2.39	31866	0.60	-0.68
5	170.00	2.29	36660	0.69	-0.60
6	160.00	2.22	39480	0.77	-0.56
7	149.00	2.13	42582	0.84	-0.51
8	135.00	1.96	46530	0.90	-0.46
9	128.00	1.85	48504	0.95	-0.43
10	120.00	1.68	50760	1.00	-0.40
11	117.00	1.59	51606	1.04	-0.38
12	115.00	1.51	52170	1.07	-0.38
13	113.00	1.43	52734	1.11	-0.37
14	108.00	1.07	54144	1.14	-0.35
15	107.00	0.95	54426	1.17	-0.34
16	105.00	0.47	54990	1.20	-0.34

5.1.2 Kinetics of adsorption

The kinetics of adsorption is important from the point of view that it controls the process efficiency. Various kinetics models have been used by different workers, where the adsorption has been treated as pseudo first order and pseudo second order process. Different systems conform to different models. The Lagergren's rate equation (eq. 2.17) is the widely used one for the adsorption of

single solute phenol in liquid solution. Also the data can be fitted in the pseudo second order equation also. Further the kinetics data were further used to learn about the slowest step occurring in the adsorption system. Bangham's equation and Weber Morries equation used for intraparticle diffusion of solute in the adsorbent. The equation is as per (eq. 2.10)

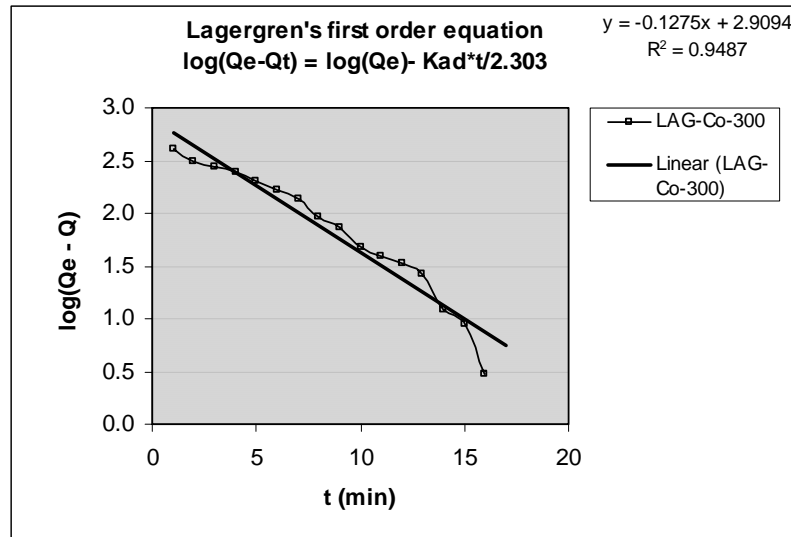


Figure 5.3: Lagergren pseudo first order equation for AC (Co = 300mg/l)

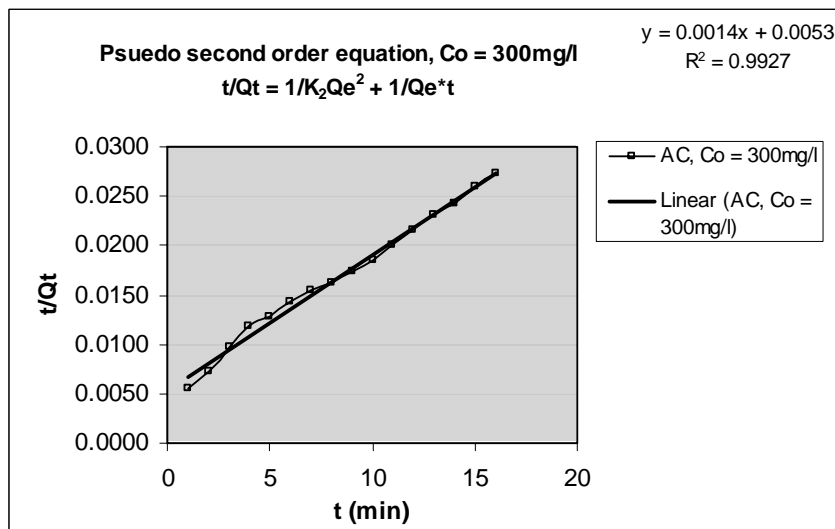


Figure 5.4: Pseudo second order equation for AC (Co=300mg/l)

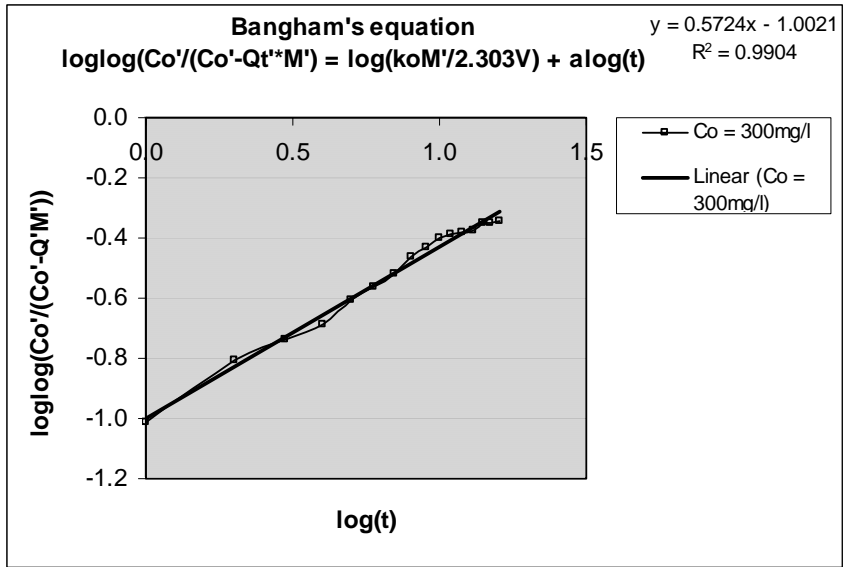


Figure 5.5a: Bangham's intraparticle diffusion equation for AC (Co = 300 mg/l)

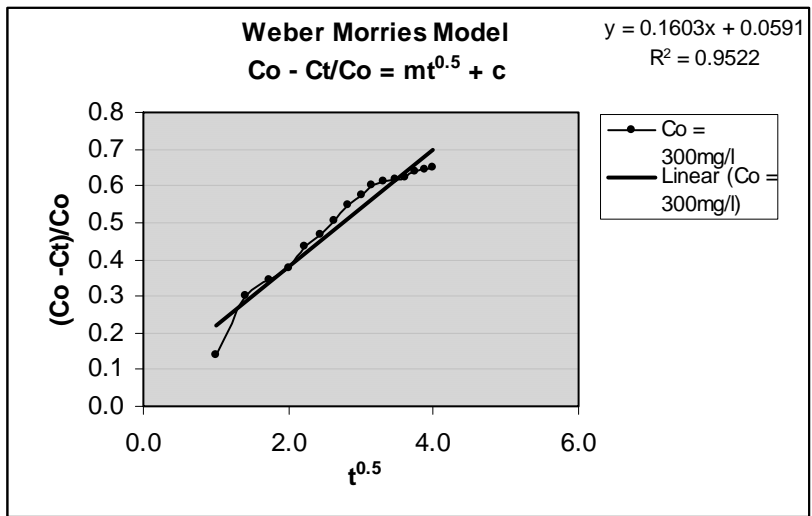


Figure 5.5b: Weber Morries Model for intraparticle diffusion (Co = 300mg/l)

From figure 5.3 and figure 5.4 one can observe that the Lagergren first order equation is having R^2 value 0.9487 and the same for Pseudo second order is 0.9927 and the second curve fitted well to the equation. So from the graph one can indicate that the phenol adsorption on activated carbon is the Pseudo second order type.

Now for the slowest step in the adsorption might be the intraparticle diffusion, bulk diffusion or might be the both. To decide the internal diffusion is rate controlling step we have to fit the kinetic data in the Bangham's Model and Weber Morries model. From the figure 5.5a and 5.5b intraparticle diffusion is controlling step for the phenol-activated carbon system. As the R^2 value for the linear fitting is 0.9904 for Bangham's equation and 0.9522 for the other one.

Table 5.6: Values of kinetic constants for AC at various concentrations

Initial Conc.	Lagergren pseudo first order constants		Pseudo second order constants		Bangham's constants	
	Kads1	Qe1	Kads2	Qe2	ko	α
200	0.390	966.496	0.0000240	1666.667	97.104	1.099
300	0.287	811.708	0.0003698	714.286	206.270	0.572
400	0.358	602.560	0.0004245	666.667	14525.679	0.727

The all the coefficients for the Lagergren equation, pseudo second order equation and for Bangham's model can determined by the plots. All the values of constants can be shown in the Table 5.6. One can observe the value of adsorption rate constant for first order as well second order equation which indicates the slower diffusion in the activated carbon. In Bangham's equation the value of constant α should less than one. For initial concentration 300 mg/l and 400 mg/l it comes 0.572 and 0.727 which is less than the one but for $C_0 = 200$ mg/l its coming 1.099.

Finally it can be concluded that the order of the adsorption of phenol on activated carbon is second order and the rate controlling step is intra particle diffusion of phenol in the pores of activated carbon. It is true because activated carbon is porous in nature and it is having more micro pores in the structure.

5.2 Results of Treated Fly ash

The fly ash produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones.

The color of fly ash can vary from tan to gray to black, depending on the amount of unburned carbon in the ash.

Table 5.7a: Normal range of chemical composition for fly ash produced from different coal types (wt. %) [70]

Component	Bituminous	Sub bituminous	Lignite
SiO ₂	20-60	40-60	15-45
Al ₂ O ₃	5-35	20-30	10-25
Fe ₂ O ₃	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO ₃	0-4	0-2	0-10
Na ₂ O	0-4	0-2	0-6
K ₂ O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

The properties of the treated fly ash used for the experiments are shown in the table 5.7b.

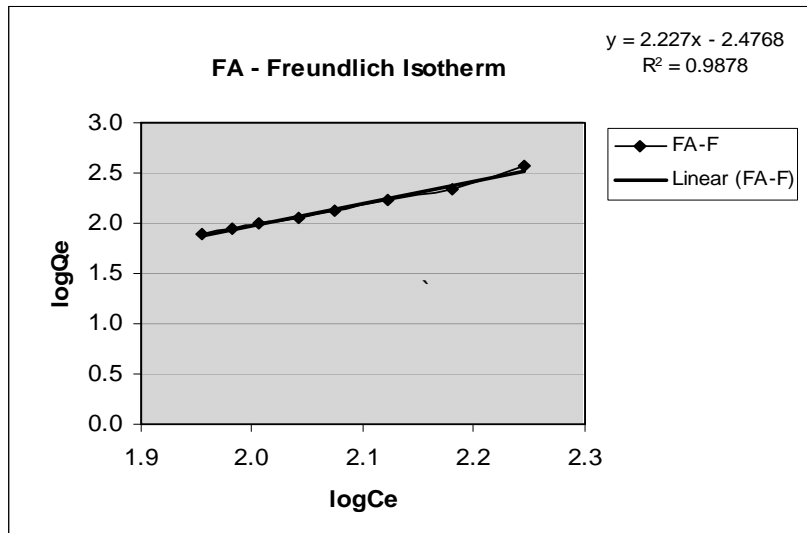
Table 5.7b: The properties of treated fly ash

Properties	Value
Particle size (mm)	0.075
Specific gravity	2.1 – 3.0
Surface area (BET) m ² /gm	38
Pore volume (cm ³ /gm)	0.079
Appearance	Dark gray
Source coal	Lignite

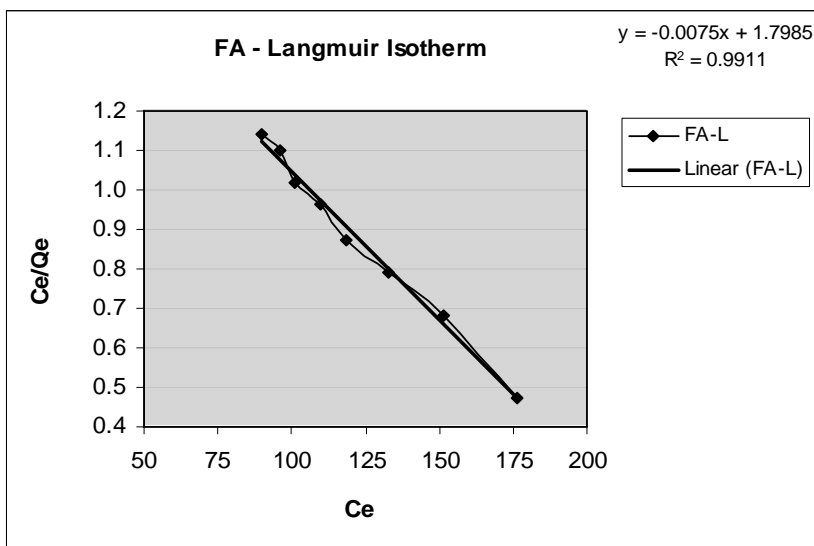
Table 5.8: Equilibrium data of treated fly ash (Co = 300 mg/l)

FA dosage gm	M g/l	Ce mg/l	X mg/l	logCe	Qe mg/g	logQe	Ce/Qe	X/Co*100
0.10	0.33	176.23	123.77	2.24	371.31	2.57	0.47	41.25
0.20	0.66	151.54	148.46	2.18	222.69	2.34	0.68	49.48
0.30	1.00	132.60	167.40	2.12	167.40	2.22	0.79	55.80
0.40	1.33	118.53	181.47	2.07	136.10	2.13	0.87	60.49
0.50	1.66	109.97	190.03	2.04	114.01	2.05	0.96	63.34
0.60	2.00	101.25	198.75	2.00	99.37	1.99	1.01	66.25
0.70	2.33	96.00	204.00	1.98	87.42	1.94	1.09	68.00
0.80	2.66	90.00	210.00	1.95	78.75	1.89	1.14	70.00
0.90	3.00	92.32	207.68	1.96	69.22	1.84	1.33	69.22
1.00	3.33	98.11	201.89	1.99	60.56	1.78	1.62	67.29

The lighter the color, the lower the carbon content. Lignite or sub bituminous fly ashes are usually light tan to buff in color, indicating relatively low amounts of carbon as well as the presence of some lime or calcium. Bituminous fly ashes are usually some shade of gray, with the lighter shades of gray generally indicating a higher quality of ash. [70]



(5.6a)



(5.6b)

**Figure 5.6a and 5.6b - Freundlich and Langmuir isotherms for FA
(Co =300mg/l)**

5.3 Saw dust carbon

The general properties of saw dust carbon are shown in Table 4.9.

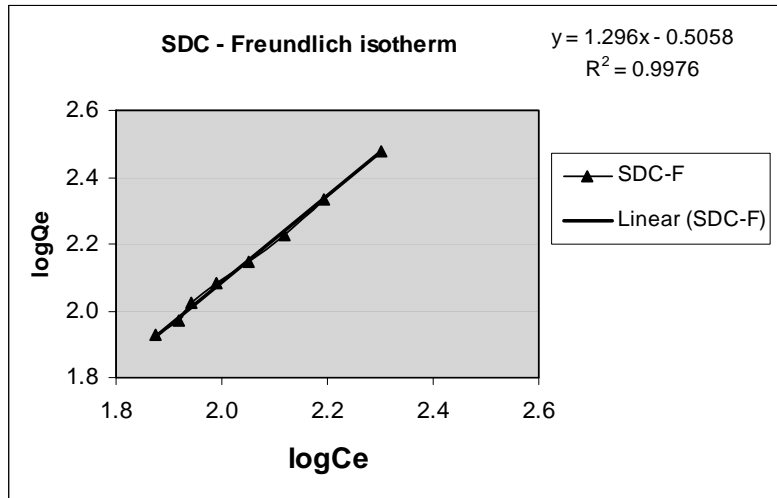
Table 5.9: General characterization of Saw dust carbon

Properties	Value
BET surface area (m ² /gm) (BET)	307
Pore volume (cm ³ /gm)	0.210
Apparent density (g/ml) *	0.370
Particle size (mm)	0.250
Ash content (%) *	5-6
Moisture content (%) *	6-7.2

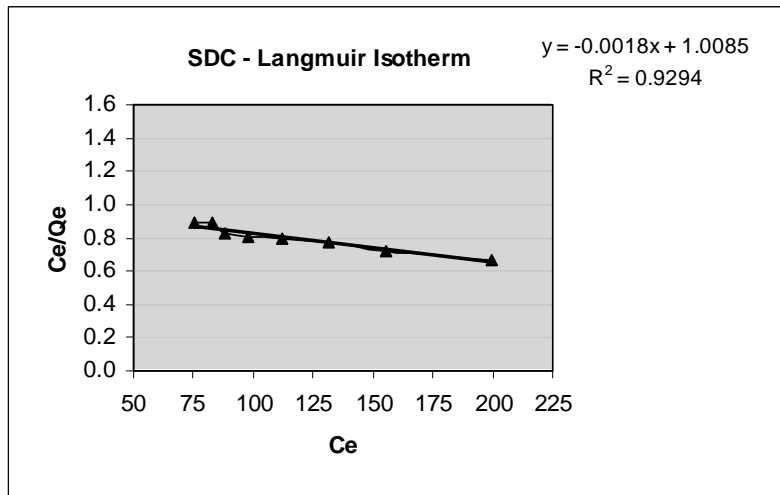
* These properties are taken from literature and others have been tested

Table 5.10: Equilibrium data of Saw dust carbon (Co = 300 mg/l)

SDC Dosage gm	M g/l	Ce mg/l	X mg/l	logCe	Qe mg/g	logQe	Ce/Qe	X/Co*100
0.10	0.33	199.54	100.46	2.30	301.38	2.47	0.66	33.48
0.20	0.66	155.62	144.38	2.19	216.57	2.33	0.71	48.12
0.30	1.00	131.23	168.77	2.11	168.77	2.22	0.77	56.25
0.40	1.33	112.16	187.84	2.05	140.88	2.14	0.79	62.61
0.50	1.66	97.88	202.12	1.99	121.27	2.08	0.80	67.37
0.60	2.00	87.80	212.20	1.94	106.10	2.02	0.82	70.73
0.70	2.33	83.11	216.88	1.92	92.95	1.96	0.89	72.29
0.80	2.66	75.11	224.88	1.87	84.33	1.92	0.89	74.96
0.90	3.00	80.85	219.15	1.90	73.05	1.86	1.10	73.05
1.00	3.33	91.00	209.00	1.95	62.70	1.79	1.45	69.66



(5.7a)



(5.7b)

**Figure 5.7a and 5.7b - Freundlich and Langmuir isotherms for SDC
 (Co =300mg/l)**

5.4 Treated bentonites

Bentonite is a relatively soft stone, formed over geological time by the natural alteration of volcanic tuffs. Bentonite is composed of plate-silicate minerals, and belongs to the group of minerals known as aluminosilicates. The sodium, calcium, and magnesium cations are interchangeable giving the montmorillonite a high ion exchange capacity. Bentonite is a clay mineral whose main constituent is "montmorillonite". Montmorillonite is a hydrous alumina silicate with exceptional behaviour due to its crystallographic structure. The basic layer is composed of two tetrahedral SiO_2 layers with an octahedral layer of mainly Al_2O_3 in the middle which can be replaced by Al, Mg or Fe. Thickness of this basic layer is about 10 Angstrom. Between each basic elementary layer the existing water makes possible the introduction of the sodium-called exchangeable cations. [71]

Table 5.11: Chemical composition of natural bentonite

Component	Percentage
SiO ₂	52
Al ₂ O ₃	16
TiO ₂	2
MnO ₂	0.2
CaO	2.0
Na ₂ O	3.0
K ₂ O	0.3
Fe ₂ O ₃	14
LOI (loss on ignition)	14

Table 5.12: Equilibrium data of Na-Bentonite (Co = 300 mg/l)

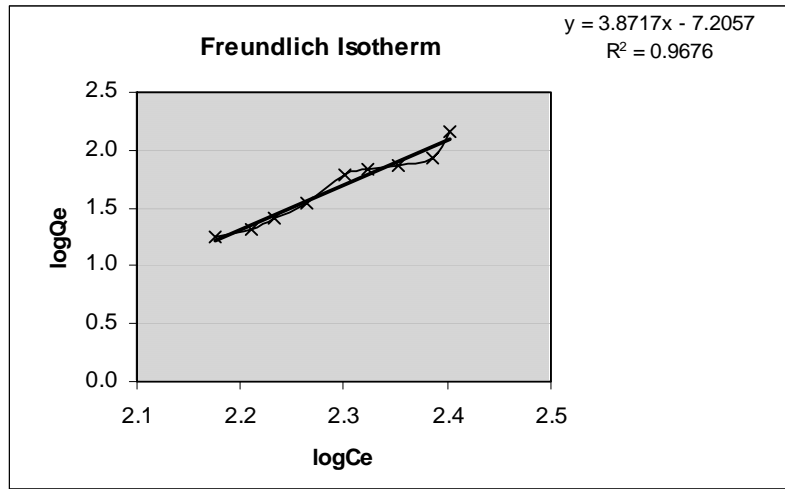
Na-B dosage gm	M g/l	Ce	X mg/l	logCe	Qe mg/g	logQe	Ce/Qe	X/Co*100
0.10	0.33	252.12	47.88	2.40	143.64	2.15	1.75	15.96
0.20	0.66	242.63	57.37	2.38	86.05	1.93	2.81	19.12
0.30	1.00	225.10	74.90	2.35	74.90	1.87	3.00	24.96
0.40	1.33	210.60	89.40	2.32	67.05	1.82	3.14	29.80
0.50	1.66	200.00	100.00	2.30	60.00	1.77	3.33	33.33
1.00	3.33	184.00	116.00	2.26	34.80	1.54	5.28	38.66
1.50	5.00	171.10	128.90	2.23	25.78	1.41	6.63	42.96
2.00	6.66	162.54	137.46	2.21	20.61	1.31	7.88	45.82
2.50	8.33	150.00	150.00	2.17	18.00	1.25	8.33	50.00

Table 5.13: Equilibrium data of Al-Bentonite (Co = 300 mg/l)

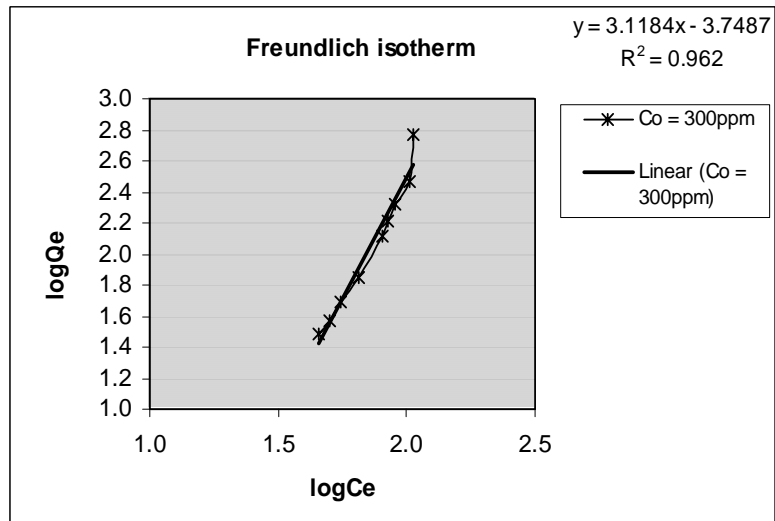
Al-B dosage gm	Ce	X mg/l	M g/l	Qe	logQe	logCe	Ce/Qe	X/Co*100
0.10	106.50	193.50	0.33	580.50	2.76	2.02	0.18	64.50
0.20	102.75	197.25	0.66	295.87	2.47	2.01	0.34	65.75
0.30	90.00	210.00	1.00	210.00	2.32	1.95	0.42	70.00
0.40	85.00	215.00	1.33	161.25	2.20	1.92	0.52	71.66
0.50	81.00	219.00	1.66	131.40	2.11	1.90	0.61	73.00
1.00	65.00	235.00	3.33	70.50	1.84	1.81	0.92	78.33
1.50	55.00	245.00	5.00	49.00	1.69	1.74	1.12	81.66
2.00	50.11	249.89	6.66	37.48	1.57	1.70	1.33	83.29
2.50	45.75	254.25	8.33	30.51	1.48	1.66	1.50	84.75
3.00	45.75	254.25	10.00	25.42	1.40	1.66	1.79	84.75

Table 5.14: Equilibrium data of T-Bentonite (Co = 300 mg/l)

T-B gm	Ce	X mg/l	M g/l	Qe	logQe	logCe	Ce/Qe	X/Co*100
0.10	114.00	186.00	0.33	558.00	2.74	2.05	0.20	62.00
0.20	106.50	193.50	0.66	290.25	2.46	2.02	0.36	64.50
0.30	97.50	202.50	1.00	202.50	2.30	1.98	0.48	67.50
0.40	91.12	208.87	1.33	156.65	2.19	1.96	0.58	69.62
0.50	82.50	217.50	1.66	130.50	2.11	1.91	0.63	72.50
1.00	67.87	232.12	3.33	69.63	1.84	1.83	0.97	77.37
1.50	60.00	240.00	5.00	48.00	1.68	1.77	1.25	80.00
2.00	55.65	244.35	6.66	36.65	1.56	1.74	1.51	81.45
2.50	53.32	246.67	8.33	29.60	1.47	1.72	1.80	82.22
3.00	53.32	246.67	10.00	24.66	1.39	1.72	2.16	82.22

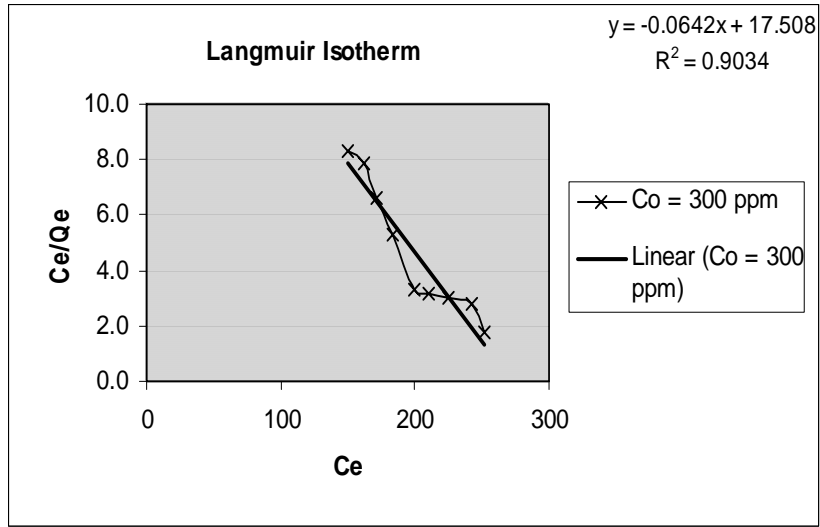


(5.8a)

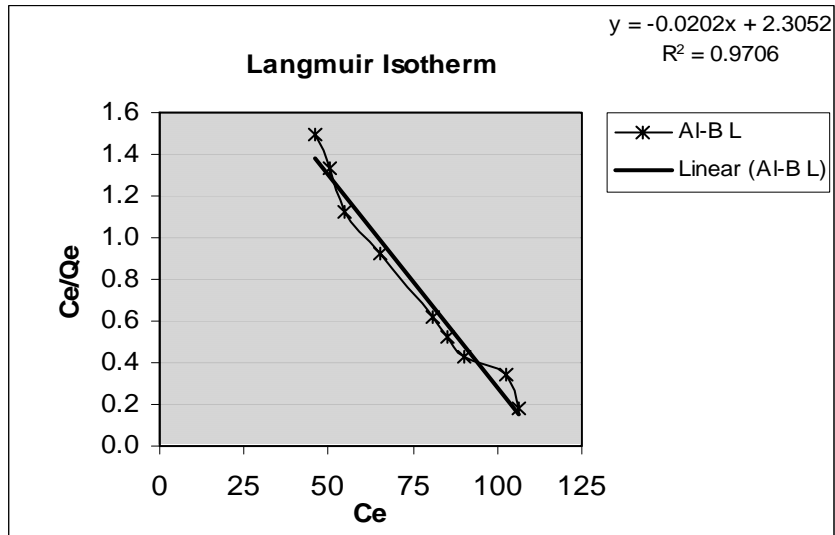


(5.8b)

Figure (5.8a)-(5.8b): Freundlich and Langmuir isotherms for Na-Bentonite

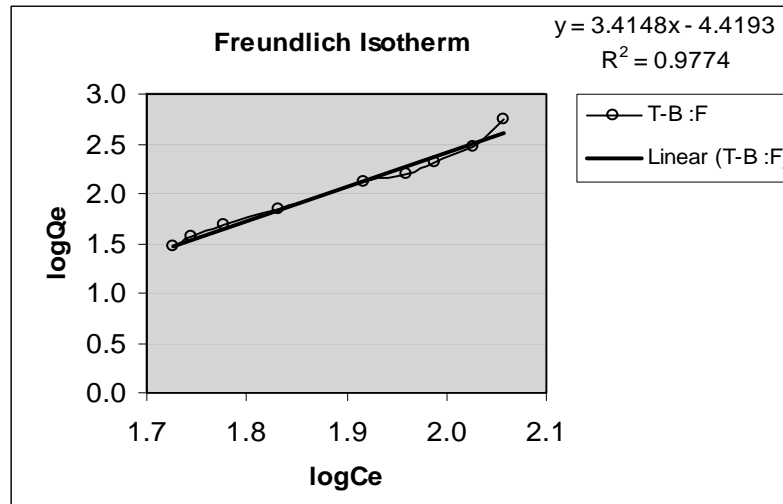


(5.8c)

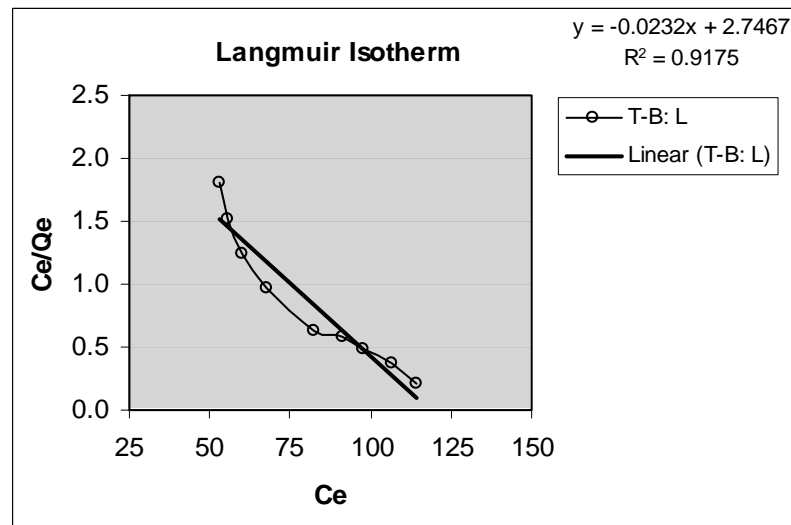


(5.8d)

Figure (5.8c) - (5.8d): Freundlich and Langmuir isotherms for Al-Bentonite



(5.8e)



(5.8f)

Figure (5.8e)-(5.8f): Freundlich and Langmuir isotherms for T-Bentonite

5.5 Comparison of all the adsorbents

The comparison of all the cheap adsorbents can be done with the performance of activated carbon. The equilibrium uptake curve is shown together for all adsorbent in figure 4.9. It can be seen that activated carbon is the best among all six adsorbents and then it is followed by Al-bentonite, T-bentonite, Saw dust carbon, fly ash and Na-bentonite. Among the activated bentonites, the natural bentonite has shown poor performance and Al-bentonite is good and also followed by T-bentonite.

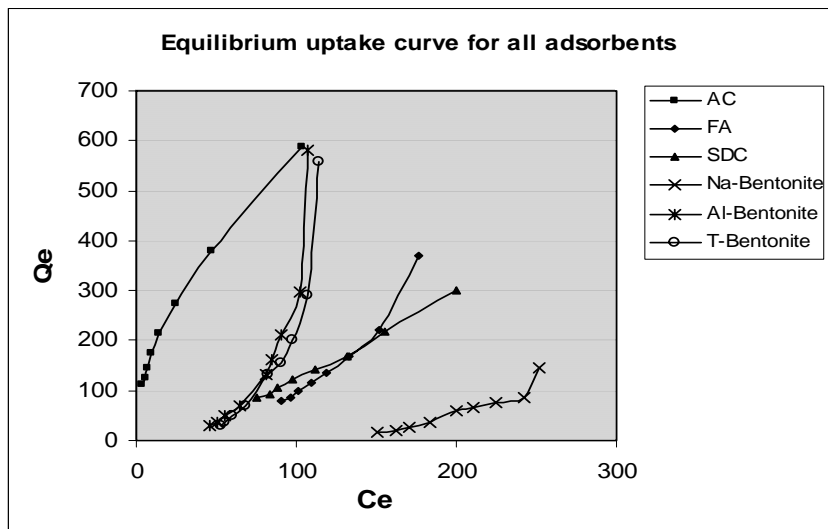


Figure 5.9: Equilibrium uptake curve

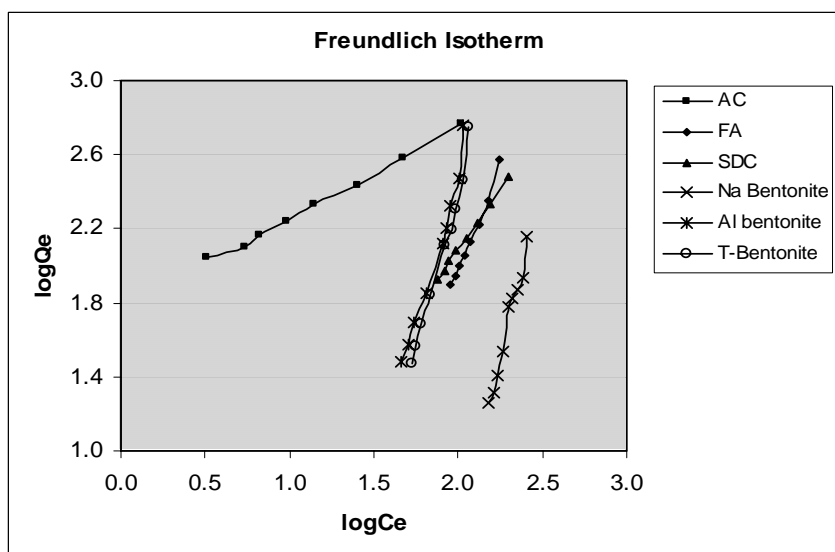


Figure 5.10: Freundlich isotherm

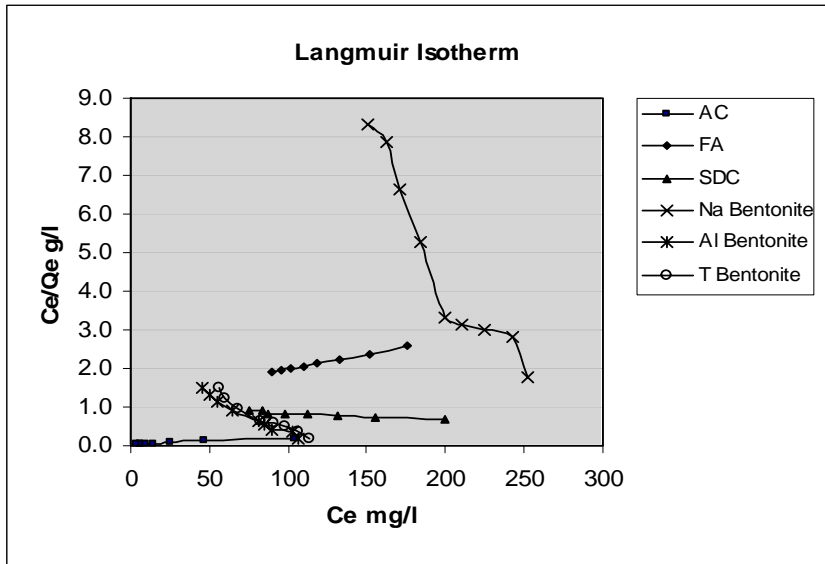


Figure 5.11: Langmuir isotherm

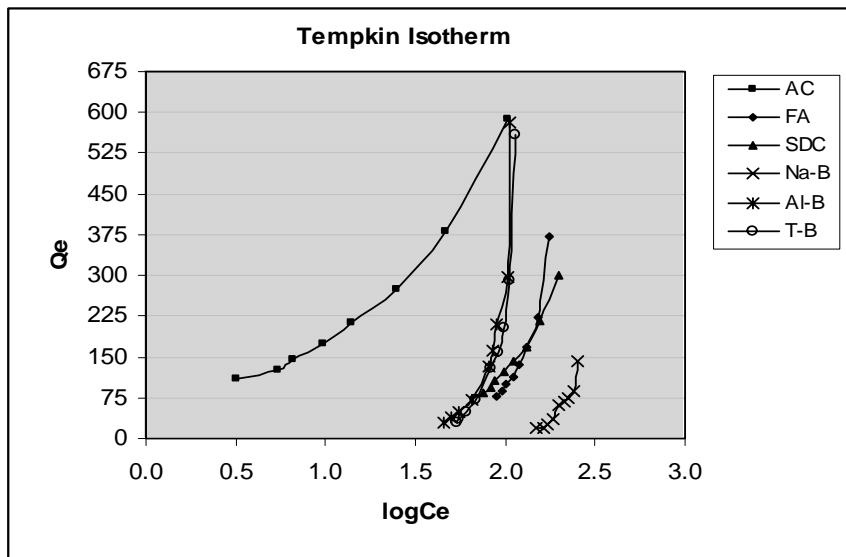


Figure 5.12: Tempkin Isotherm

The comparison was done by various isotherms like Freundlich isotherm, Langmuir isotherm and Tempkin isotherm. The isotherms plotted in figure 5.10, 5.11 and 5.12 respectively. Among the three types of isotherms Freundlich isotherm is fitting well to the experimental results. Freundlich isotherm is for heterogeneous surface and exponential distribution of energy and sites on the

surface. Phenol adsorption on activated carbon is exothermic adsorption so it is obvious that every site of the surface will be of different energy. All the constants of isotherms and the R^2 value are shown in Table 5.15. In figure 5.13, the effect of adsorbent dose is shown. From the curves it can be observed that as the dosage increases the % phenol removal also increases. But after some extent it starts to decrease for AC, FA and SDC while for Al and T bentonites it remains constant. The maximum % removal of phenol achieved by all the adsorbents is shown in Table 5.16.

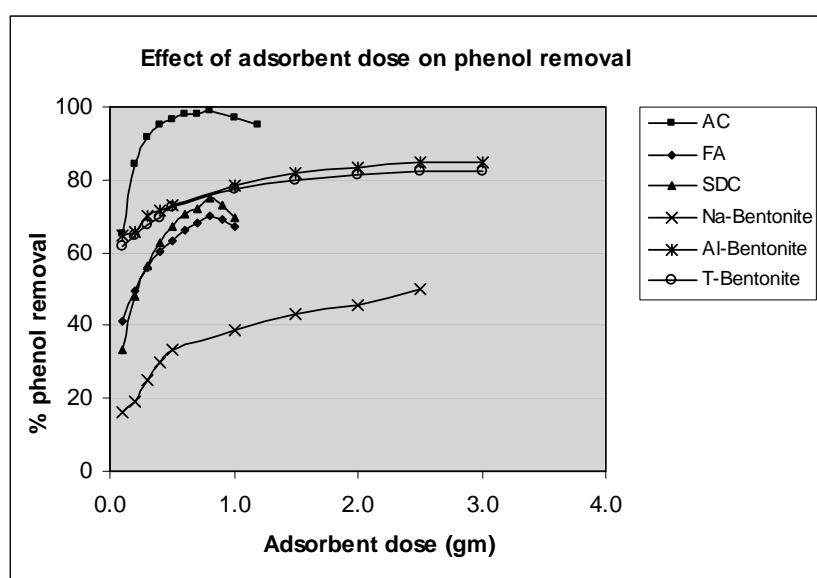


Figure 5.13: Effect of adsorbent dose on phenol removal

Table 5.15: Isotherm constants for all the adsorbents

For Co 300 mg/l	Freundlich isotherm constants			Langmuir isotherm constants			Tempkin isotherm constants		
	Kf	1/n	R ²	Q ₀	b	R ²	B1	Kt	R ²
AC	58.7219	0.488	0.995	714.286	0.035	0.945	306.02	0.462	0.924
FA	0.0033	2.227	0.988	133.333	0.004	0.991	986.90	0.012	0.901
SDC	3.120E-1	1.296	0.998	555.556	0.002	0.929	494.11	0.018	0.962
Na-B	6.227E-8	3.872	0.968	15.576	0.064	0.903	474.33	0.016	0.853
Al-B	1.784E-4	3.118	0.962	49.505	0.009	0.971	1201.40	0.019	0.665
T-B	3.808E-5	3.415	0.977	43.103	0.008	0.918	1149.80	0.018	0.720

Table 5.16: Maximum %phenol removal

Type of Adsorbent	% phenol removal
AC (950-1000 m ² /gm)	98.930
FA (38 m ² /gm)	70.000
SDC (307 m ² /gm)	74.963
Na Bentonite	50.000
Al Bentonite	84.750
T-Bentonite	82.225

From the table 5.16, it can be observed that maximum phenol removal can be achieved by activated carbon i.e. 98.93%. Al-bentonite is giving 84.75 %. Natural bentonite is not giving good performance so chemical or physical treatment is required before the use of bentonite as an adsorbent. As bentonite is very cheap raw material and can be activated physically and chemically easily. In Gujarat, Kutch area is having lots of sources of bentonite clay. Also saw dust carbon prepared by carbonization of saw dust which is the waste, showing quite good removal after carbonization. Similarly fly ash can be reused as it is the major waste from coal based power plants.

6. PRELIMINARY COST ESTIMATION OF VARIOUS ADSORBENT

Cost estimation of adsorption system can be done when break through curve and regeneration data are available. But on the basis of batch study effort was made for understanding which one would be the better adsorbent for phenol removal.

1. Powdered Activated carbon : 35 – 40 Rs/kg
2. Bentonite powder: 2.5 – 4.0 Rs/kg
3. Fly ash : waste from Thermal power plant : 0.75 Rs/kg [73]
4. Saw dust : waste from Nirma campus hostel :0.85 Rs/kg [74]

For one batch of activated carbon adsorption of single solute phenol from synthetic sample, the optimum dosage is 0.8 gm. The phenol concentration in influent: 300 mg/l
The phenol concentration in effluent: 3.21 mg/l

$X =$ the phenol conc. on the activated carbon = $C_0 - C_e = 300 - 3.21 = 296.79$ mg/l

So the AC cost for the batch will be: 0.032 Rs.

Similarly we can do for fly ash and all the types of bentonites. The results can be viewed by table 5.1. The volume of the waste water taken

Table 6.1: Cost of adsorbent and maximum phenol removal

Type of Adsorbent	Adsorbent dose (gm)	% max phenol removal	Cost of adsorbent (Rs/kg)	Cost of one batch
Activated carbon	0.8	98.930	40.000	0.03200
Fly ash	0.8	70.000	0.750	0.00060
Saw dust carbon	0.8	74.963	2.850	0.00228
Na- bentonite	2.5	50.000	8.000	0.02000
Al-bentonite	3.0	84.750	30.668	0.09200
T-bentonite	2.5	82.225	10.000	0.02500

The cost of activated carbon is high but the efficiency is also high. On the basis of efficiency the order of the adsorbent will be: AC > Al-bentonite > T-bentonite > saw dust carbon > fly ash > Na-bentonite. But according to the cost per kg the order would be AC > Al- bentonite > T- bentonite > Na – bentonite > saw dust carbon > fly ash.

The bentonite clay without treatment is not effective but once it is physically and chemically treated than it shows good removal efficiency of phenol. Saw dust and fly ash are waste from power plants and timber industries respectively but they can be used in better way as adsorbents after some treatments.

Treatment of synthetic waste water containing phenol using various cheap adsorbents was tried in Nirma University, Ahmedabad. The batch study was carried out for the evaluation of equilibrium data for all the adsorbents. Various adsorbents were tried like fly ash, saw dust and bentonite clay which are cheap and easily available. They were treated and activated physically and chemically before used in the adsorption tests. All the batch studies were carried out at constant temp. 26 ± 2 °C.

All the adsorbent were compared with commercially available activated carbon. Of course the maximum performance was shown by activated carbon and then it was followed by Al- bentonite, T- bentonite, saw dust carbon, fly ash and at last fly ash. The maximum phenol percentage removed by activated carbon found was 98.93%. Similarly for Al-bentonite-84.75%, T- bentonite - 82.225%, saw dust carbon - 74.963%, fly ash - 70.000% and Na-bentonite - 50.000% which is lesser than all other adsorbents. So it is concluded that % phenol removal using Na-B can be increased only after physical and chemical treatment.

Fly ash and saw dust are one type of waste coming for industries they can be again reused as an adsorbent for such waste water streams after some treatments. The activated carbon is best for effective removal but because of its loss during regeneration 15-20% and cost, is about high in comparison with other adsorbents.

Equilibrium, kinetics and break through data are important for the design of commercial scale adsorber. Equilibrium data has been derived for all six adsorbents and kinetic analysis was done only for activated carbon. The equilibrium data were fitted to various isotherms like Freundlich isotherm, Langmuir isotherm and Tempkin isotherm. Out of all three isotherms Freundlich found well fitted to the data. For activated carbon the adsorption is found pseudo second order process after fitting the data in Lagergren equation and pseudo second order equation. Intraparticle diffusion is found the slowest step and so rate controlling step, after fitting the kinetic

data into Weber Morris Model and Bangham's equation for intra particle diffusion rate equation.

Efforts were tried for evaluating the break through data by small column but the results were inappropriate. So the work is focused only on the equilibrium and kinetic of the phenol only.

In the present work, equilibrium data for all adsorbent have been evaluated. Kinetic study for activated carbon is also has been completed. The effect of initial concentration and the effect of adsorbent dose were also been studied for activated carbon. Effect of adsorbent dose were also been studied for other adsorbent also.

The further work can be done in the area of kinetic and break through data. The kinetic study further can be done for other adsorbents. Effect of other parameters like pH, temperature and shaking speed can be studied.

Though efforts were made for break through column but appropriate results were not obtained. So study can be elongated by installing the lab scale column and then producing break through curves for various flow rates and various bed lengths.

Also break through can be produced for saw dust carbon, all the types of bentonites and treated fly ash. After getting enough data like equilibrium data, kinetic data and break through data are useful for designing commercial adsorber for industrial waste water containing phenolic waste.

More cheap adsorbents could be found and applied to the phenolic waste water. Attapulgate clay, blends of coal and fly ash, chitin, activated carbon from rice husk, tire and ground nut shell, peat, pea nut shell and activated sludge could be the possible adsorbents.

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APPENDIX: A

PHENOL ANALYSIS

- Figure: A.1 UV-VIS Spectroscopy
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APPENDIX: A

PHENOL ANALYSIS

A.1 UV-VIS Spectroscopy

Direct photometric method used for phenol conc. > 0.1 mg/l

1. Preparation of calibration curve

⇒ Stock solution

Dissolve 100mg of phenol in 100 ml of freshly boiled water. The stock solution can be preserved for 30 days.

⇒ Phenol solution, Intermediate

Dilute 1 ml stock solution to 100 ml with fresh boiled and cooled water. Prepare this solution fresh on the day it is used.

⇒ Phenol solution, standard

Dilute 50 ml of the intermediate solution to 500 ml with freshly boiled and cooled water. Prepare this solution fresh within 2 h of use.

2. Estimation of phenol by spectrophotometer

This is a photometric test method, based on the reaction of phenol with 4-aminoantipyrine at pH 10 \pm 2 in the presence of potassium ferricyanide ($K_3Fe(CN)_6$) to form a colored antipyrine dye. The antipyrine colour formed in aqueous solution is measured at 510 nm. The concentration of phenol pollutants in the sample is expressed in terms of mg/l of phenol.

3. Apparatus: Spectrophotometer

4. Chemical and reagent

⇒ Ammonium Hydroxide

⇒ 4-aminoantipyrine

⇒ Potassium ferricyanide

5. Reagent preparation

⇒ Ammonium Hydroxide: concentrated

⇒ 4-aminoantipyrine solution: Dissolve 2 g of 4-aminantipyrine in water and dilute to 100 mL. Prepare reagent fresh as used.

⇒ Potassium ferricyanide: Dissolve 8 g of K_3FeCN_6 in water and dilute to 100 mL. Filter if necessary. Prepare fresh daily.

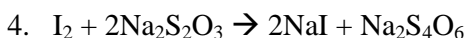
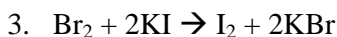
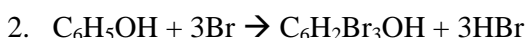
6. Procedure

- ⇒ calibration standards: Prepare a 100ml distilled water blank and series of 100ml phenol standards containing 0.5, 10, 20, 30,40, 50, 60, 70 ,80, 90, 100, 200, 300, 400 and 500 mg/l
- ⇒ Take sample of 100 ml, add 2 ml of 4-aminopyrine solution, mix well, add 2 ml potassium ferricyanide solution and mix well.
- ⇒ Prepare blank solution of 100 ml distilled water and add the same compound as you add for sample.
- ⇒ After 15 min. transfer the solution to absorption cells and read the absorbance of sample and standards against the reagent blank at 510 nm.

A.2 Phenol standardization method (Titration method)

Take 25 ml of the synthetic solution is pipette out into the 250 ml stopped conical flask. To each flask 2 ml of standard potassium bromate solution and 0.5 gm of potassium bromide and 5 ml of HCl are added. The reagents are mixed and they are allowed to stand for 15 min. About 2.5 gm of potassium iodide is added rapidly to each flask, and the flask is re-stoppered immediately. The contents are shaken with swirl to dissolve the solid. The liberated iodide is titrated with the standard (0.025 N) sodium thiosulphate until the solution is only slightly yellow, then 5 ml of starch indicator is added and titration is continued until the brown colour disappears. A blank is prepared exactly the same way, using distilled water. The blank is titrated with the sodium thiosulphate using starch solution as an indicator. Phenol (carboic acid) is in the form of colorless crystals, its melt at the most being pale yellowish. It turns reddish when exposed to light and air. It's soluble in water, alcohol, chloroform, ether, glycerin and alkaline sodium hydroxide.

The reactions occur during standardization



This standardization process is applied when the phenol concentration is more than 0.1 mg/l.

References:

- ⇒ N. F. Desai, "Profile in analysis of chemicals", second revised edition, pp. 219-220
- ⇒ Maiti, Handbook of methods in Environmental studies", Analysis of water and effluents, vol. 1, pp. 132-137
- ⇒ <http://www.epa.gov/std methods/Phenolic compounds/referred on 12/11/05>

APPENDIX: B

FIGURES -KINETICS

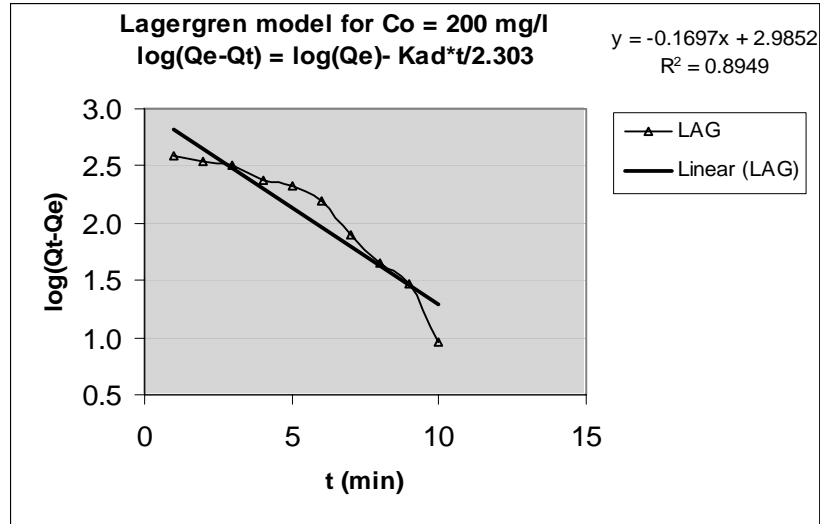


Figure B.1: Lagergren equation for Co = 200 mg/l

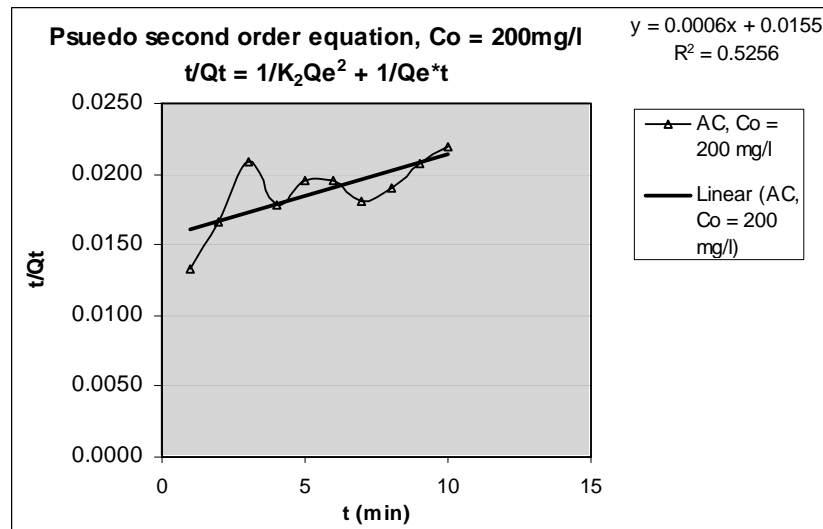


Figure B.2: Pseudo second order equation for Co = 200mg/l

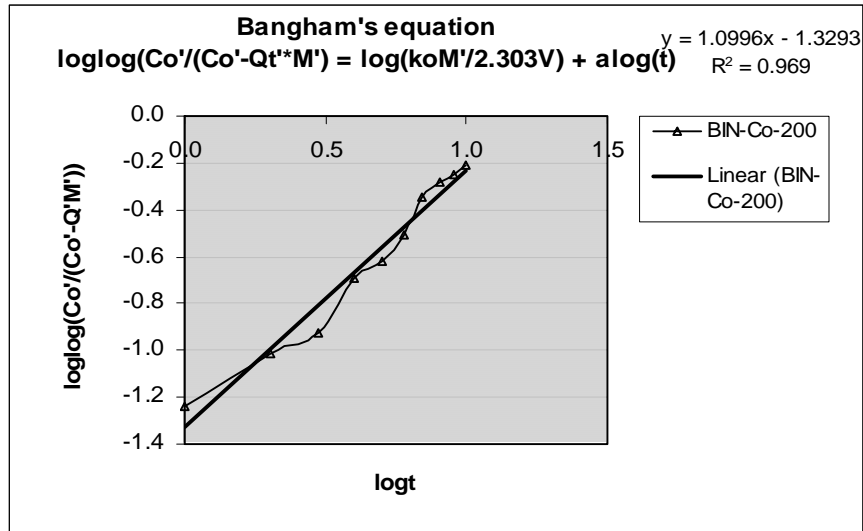


Figure B.3: Bangham's equation for intraparticle diffusion

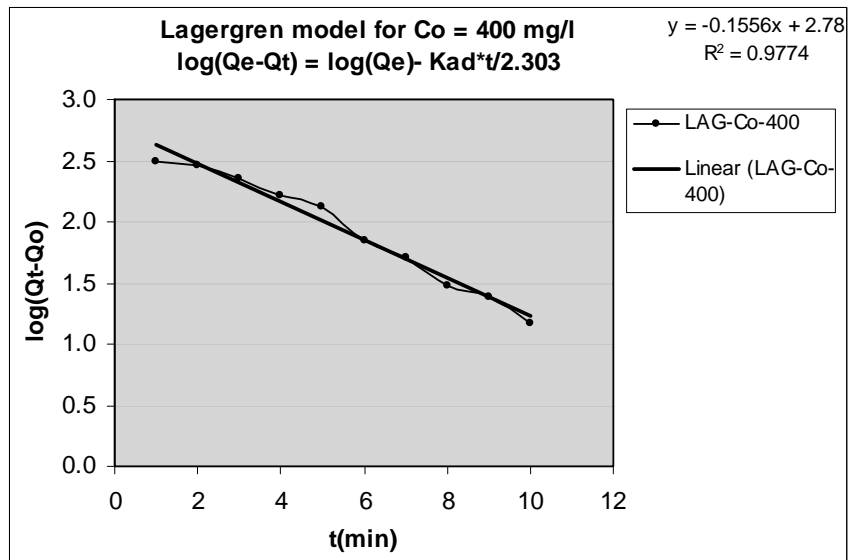


Figure B.4: Lagergren equation for Co = 400 mg/l

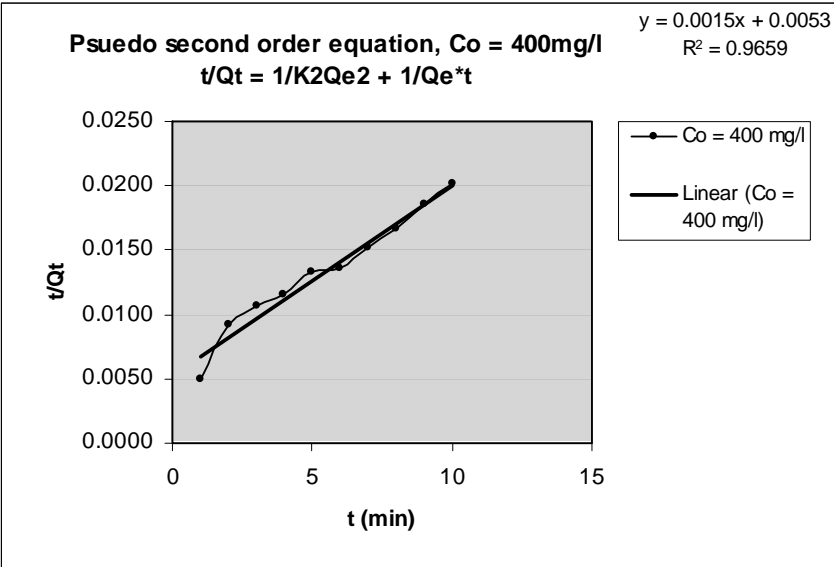


Figure B.5: Pseudo second order equation for Co = 400 mg/l

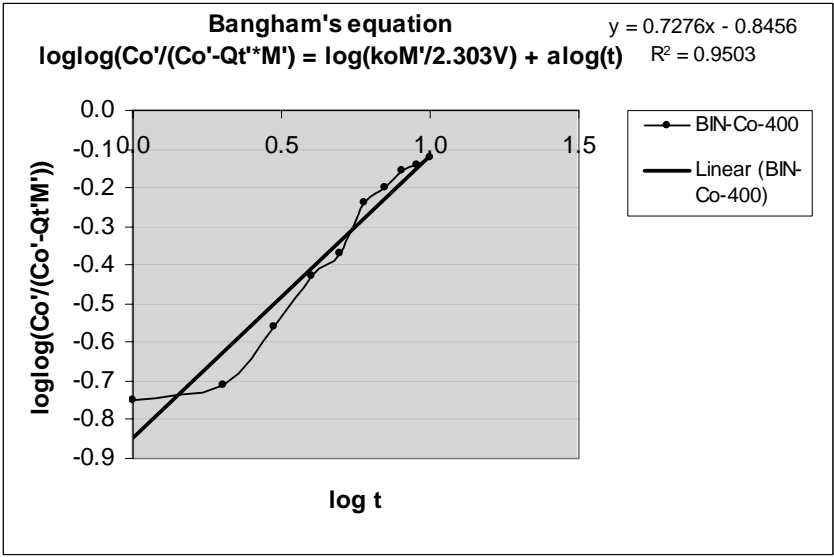


Figure B.6: Bangham's equation for Co=400mg/l

APPENDIX: C

FIGURES – TEMPKIN ISOTHERMS

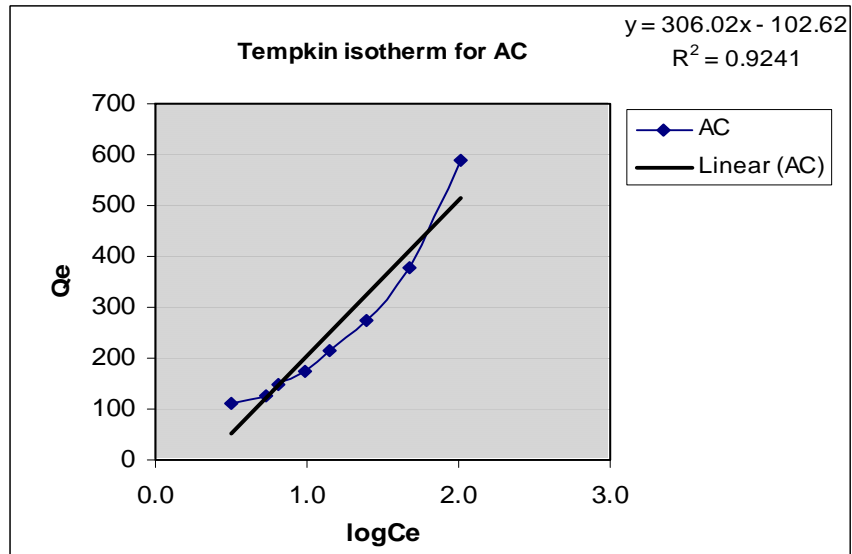


Figure C.1: Tempkin isotherm for Activated carbon

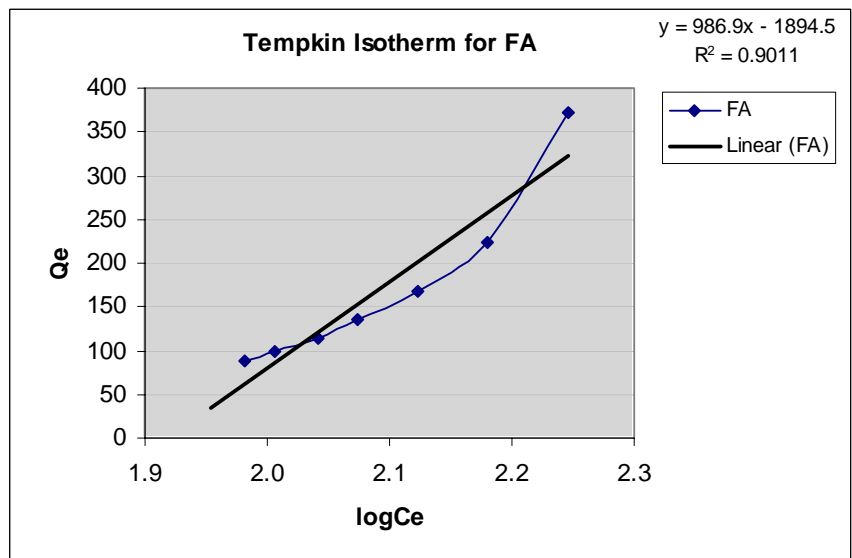


Figure C.2: Tempkin isotherm for Fly ash

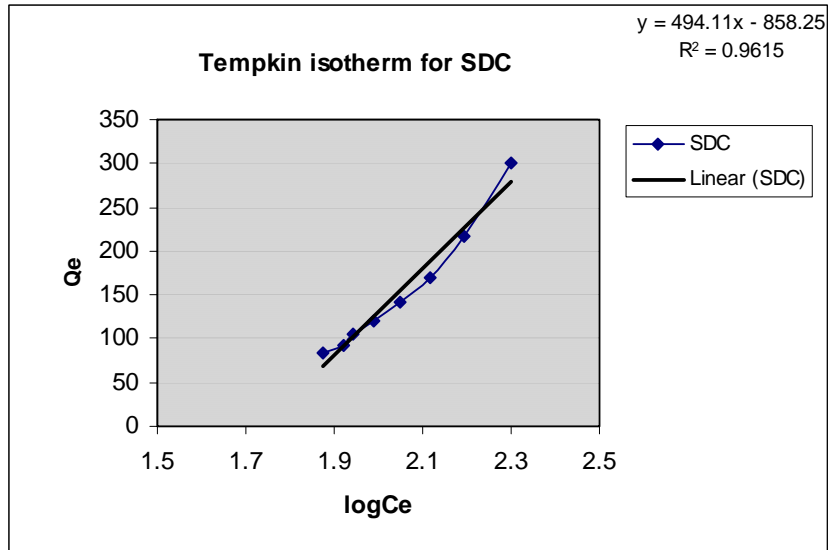


Figure C.3: Tempkin isotherm for saw dust carbon

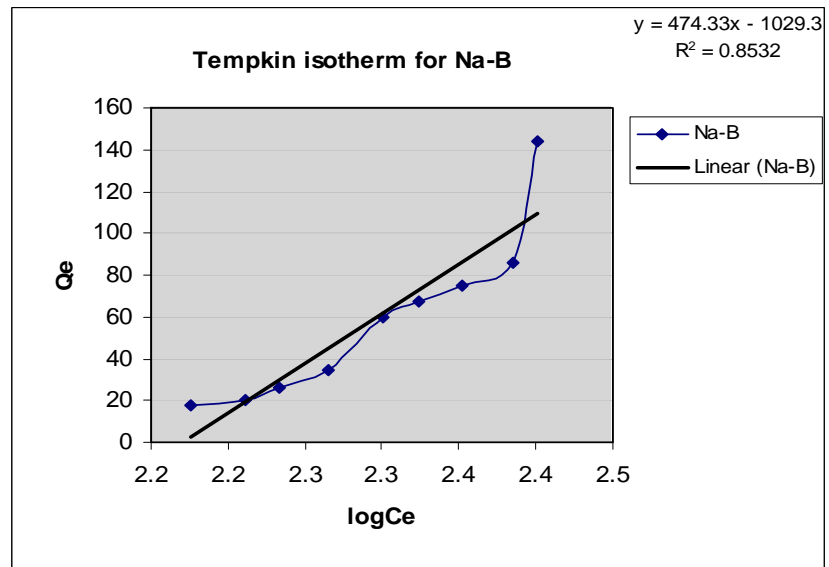


Figure C.4: Tempkin isotherm for Na-bentonite

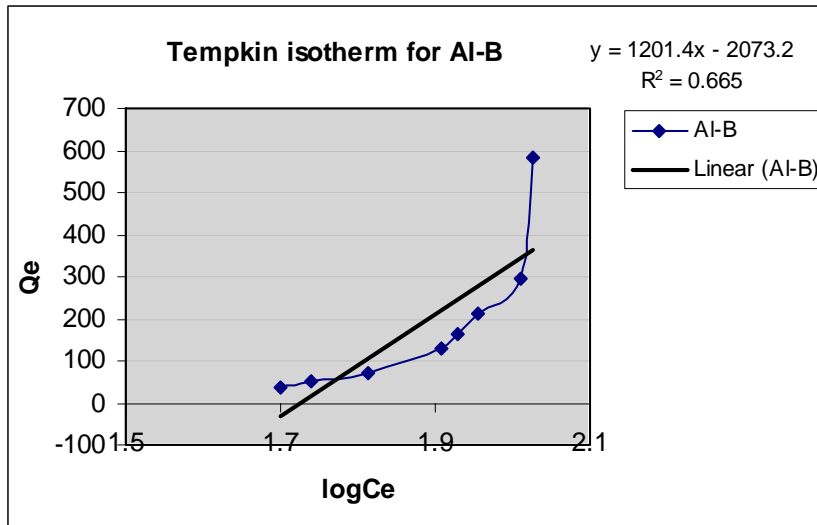


Figure C.5: Tempkin isotherm for Al-bentonite

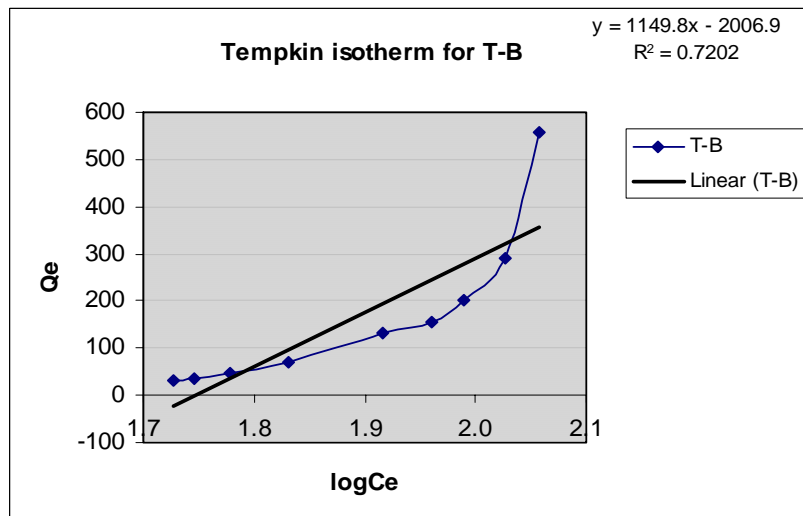


Figure C.6: Tempkin isotherm for T-bentonite

APPENDIX: D

FIGURES – EQUILIBRIUM CURVE

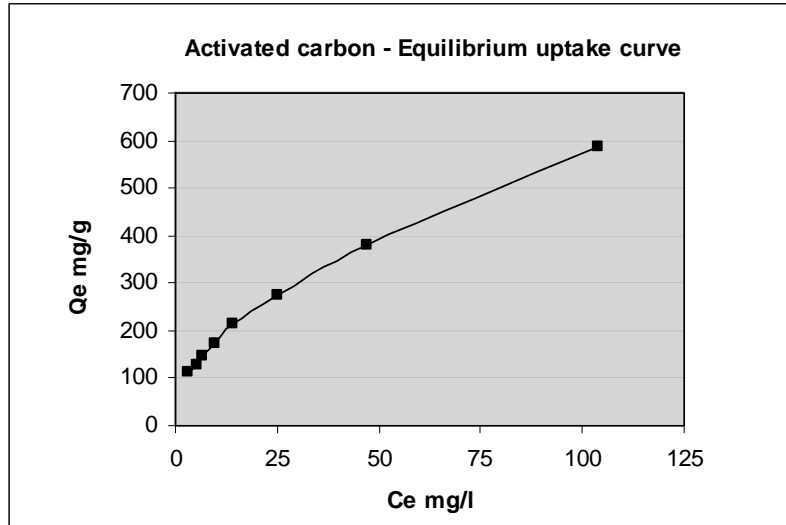


Figure D.1: Equilibrium uptake curve for Activated carbon

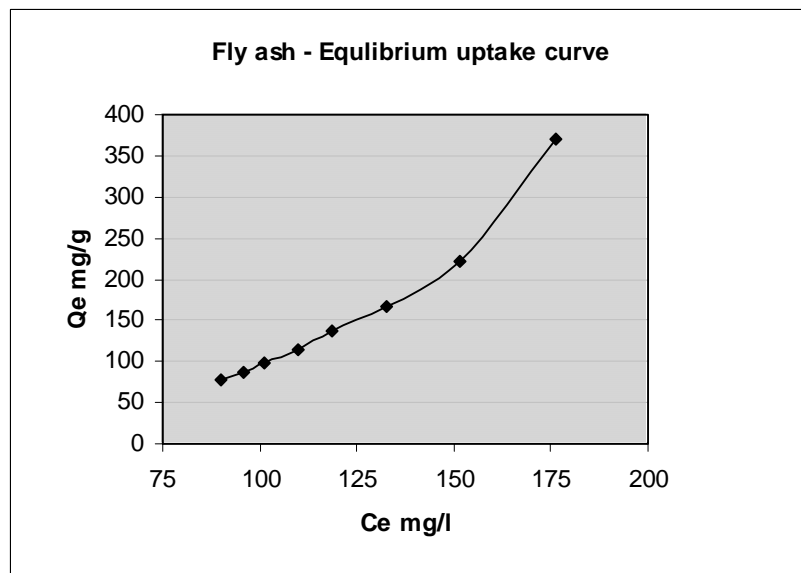


Figure D.2: Equilibrium uptake curve for Fly ash

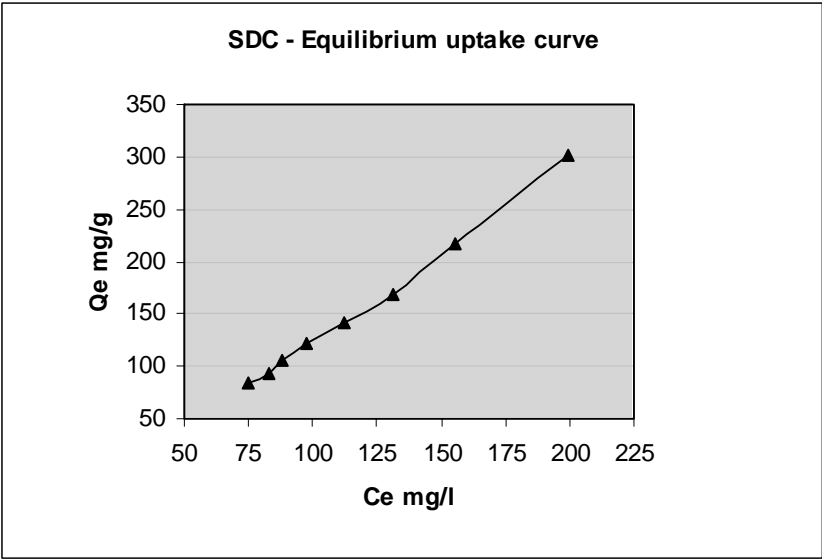


Figure D.3: Equilibrium uptake curve for saw dust carbon

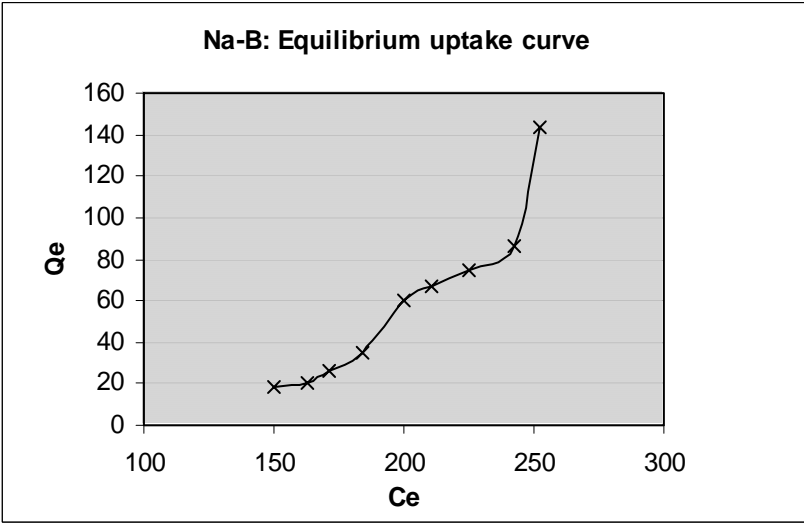


Figure D.4: Equilibrium uptake curve for Na-bentonite

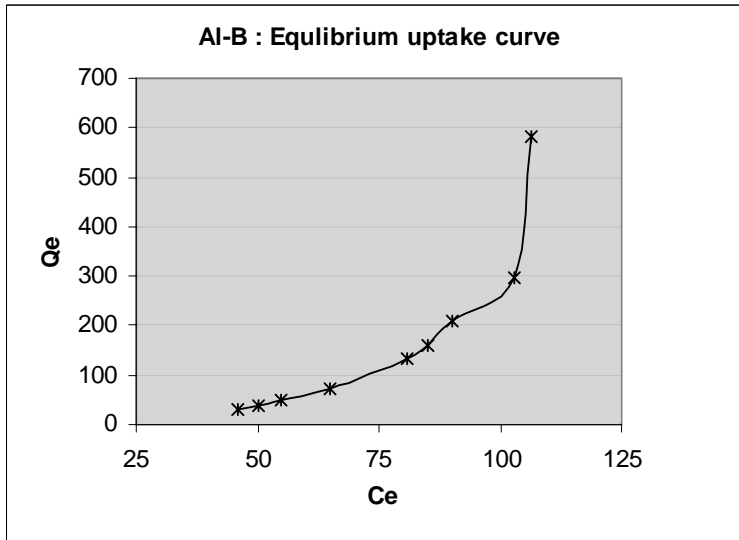


Figure D.5: Equilibrium uptake curve for Al-bentonite

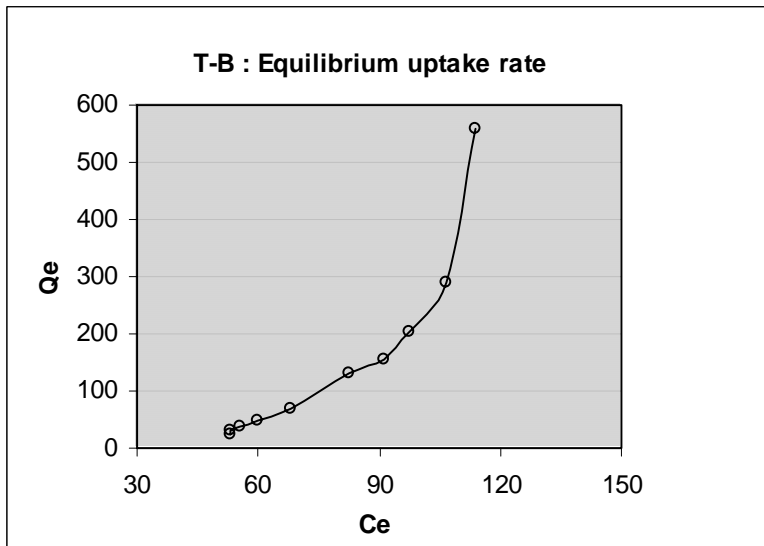


Figure D.6: Equilibrium uptake curve for T-bentonite

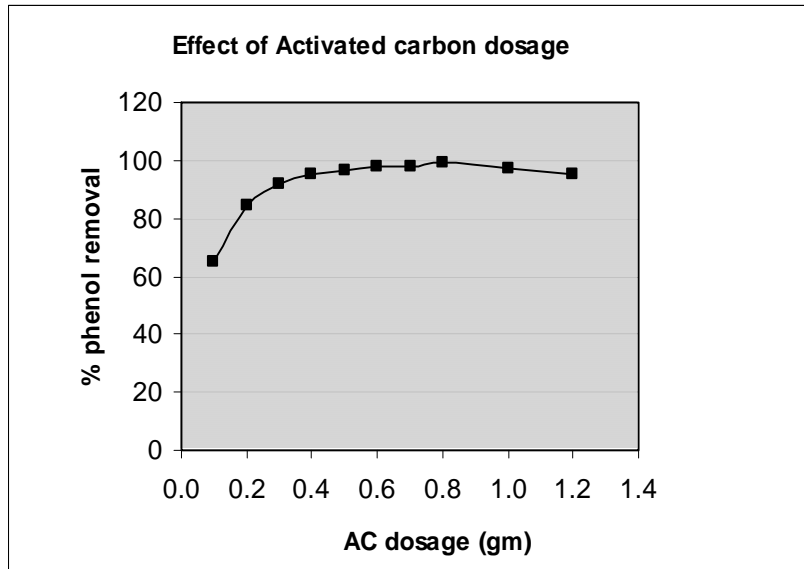


Figure.7: Effect of activated carbon dosage

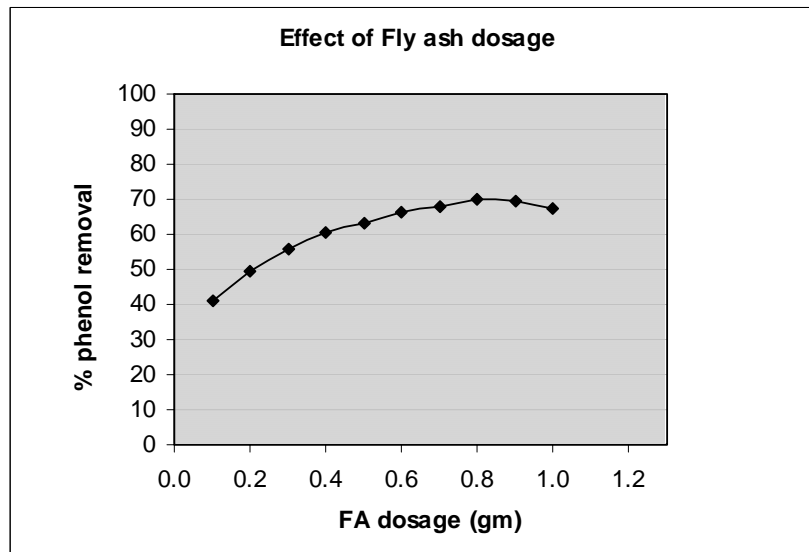


Figure D.8: Effect of fly ash dosage

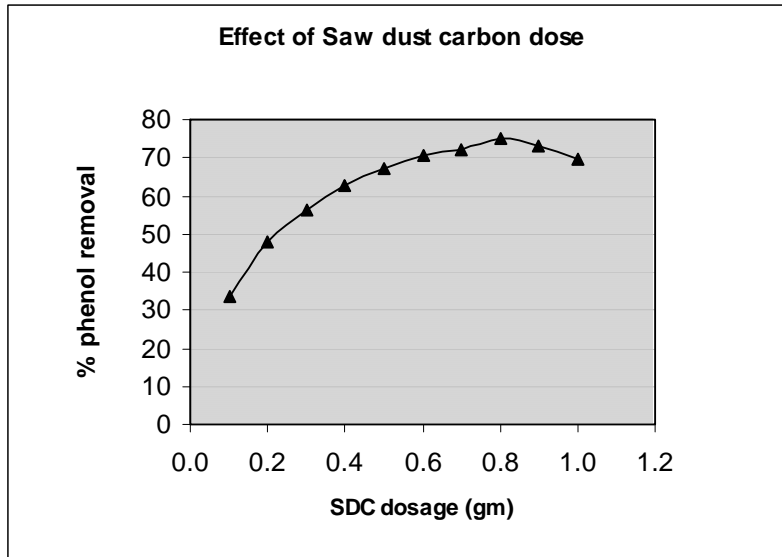


Figure D.9: Effect of saw dust carbon dosage

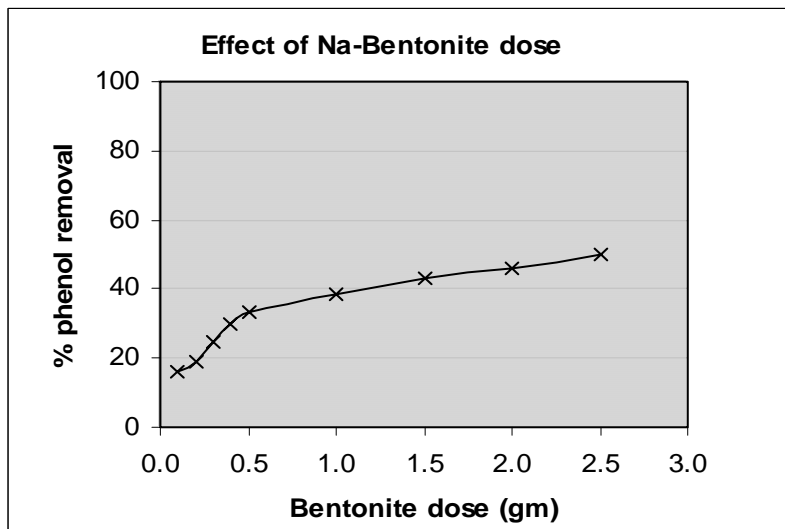


Figure D.10: Effect of Na-bentonite dosage

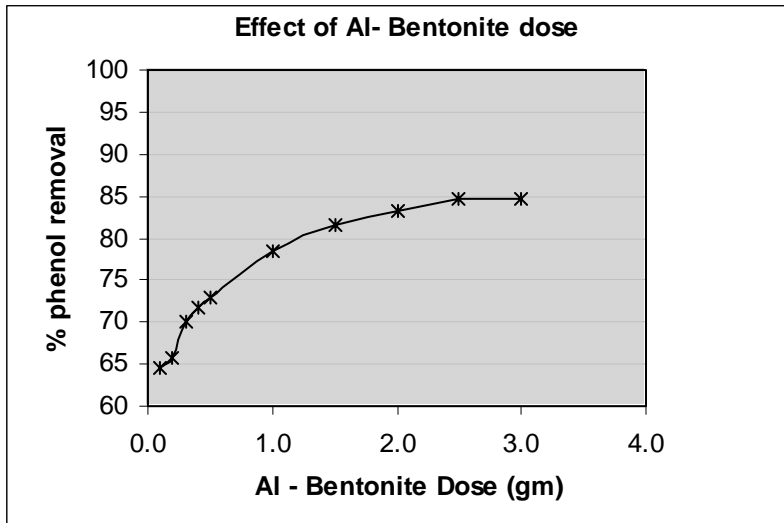


Figure D.11: Effect of Al-bentonite dosage

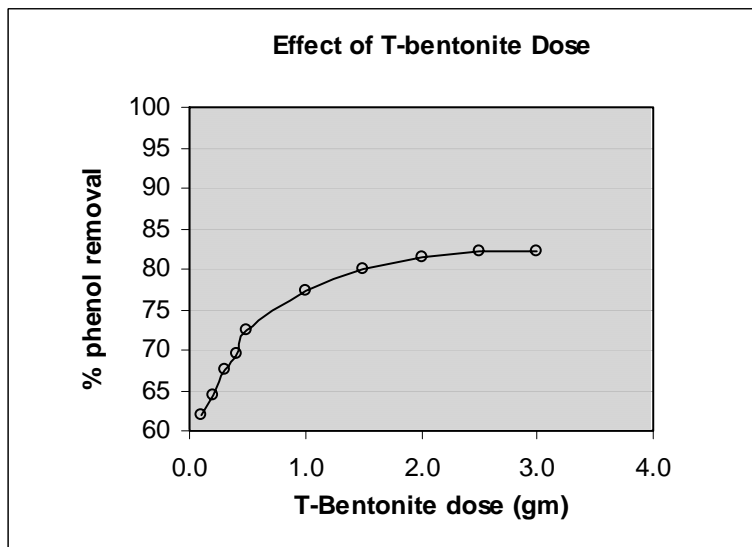


Figure D.12: Effect of T-bentonite dosage

ANNEXURE: A
DETAILED LITERATURE SURVEY

A.1 Phenol in effluent of Petrochemical industries, petroleum refineries, coke industries

H. Lounichi *et al.* (2004) [19] have used electro-activated carbon granules for the adsorption of the phenol. The electro-activation technique makes it possible to increase the number of active sites that improve the performance of the electro-activated granular carbon compared with conventional granular activated carbon. This new activation technique allowed enhanced adsorbing performance of the adsorbent. Two models were utilized to understand the improvement in the performance of electro-activated carbon granules. The first, a simple external resistance model based on film resistance, and second linear model, based on diffusion phenomena, was more representative in describing the experiment than the first model.

The Freundlich isotherm has been widely used in the design of activated carbon adsorption processes. The isotherm is easy to use and is applicable to a wide spectrum of organic compounds and adsorbents. The main drawback for the Freundlich isotherm is that it is an empirical formula requiring experiments to determine its coefficients. So to alleviate this drawback, a procedure is developed by E. G. Furuya *et al.* (1997) [12] to correlate the Freundlich coefficients with the basic properties of three components involved in adsorption (adsorbate, adsorbent and solvent). Chlorophenols and nitrophenols were used as the test adsorbate and GAC was used as the adsorbent.

Terasa J. Bandosz *et al.* (2003) [53] have investigated the role of surface chemistry in the adsorption of phenol on activated carbon. Activated carbon activated by using phosphoric acid and KOH was used for adsorption of phenol. They found that phenol adsorption from solution on carbons with acidic pH depends on the porosity, but more importantly, on the surface chemistry of the carbons. Phenol adsorption showed a strong dependence on the number of carboxylic groups.

N. Calace *et al.* (2002) [29] have studied the sorption capacity of paper mill sludge for phenols. Phenol, chlorophenols, di-chlorophenols and trichlorophenol were chosen for the sorption tests. Kinetic study shows that paper mill sludge has a potential for the removal of phenols from wastewaters over a range of concentration up to 800 mg/l. Hence, the paper mill sludge may be used as a low cost, natural abundant source for removal of phenols. Moreover, it may also be effective in removing other harmful species also such as heavy metals.

Waste slurry generated in fertilizer plants is used as an adsorbent to remove phenols in industrial effluents by Srivastava *et al.* (1995) [49]. They have successfully tried for the removal of a variety of substituted phenols from synthetic as well as live waste from oil refineries. They have studied the possible competition that can take place in such systems. The competitive effect on the uptake of various substituted phenols such as 2, 4, 6-trinitrophenol, 4-nitrophenol, 4-chlorophenol and 1, 3-dihydroxybenzene, on the carbonaceous adsorbent developed from fertilizer waste, has been studied.

Five organic phenolic compounds (phenol, o-chlorophenol, m-chlorophenol, p-chlorophenol and m-cresol) have been used to determine the adsorption isotherms for single and biphase systems from dilute aqueous solutions on activated carbon by Khan *et al.* (1997) [5]. All common types of reported isotherms, including Langmuir, Freundlich, BET (Brunauer, Emmett and Teller) and empirical types, were tried. For single solute systems the experimental data were found to be best represented by the Freundlich isotherm for all cases except for phenol, which followed the Langmuir isotherm. For biphase systems, the coefficients for all the most commonly used models were determined accurately applying a modified Rosenbrock method for non-linear optimization.

A.2 Activated carbon (AC) from various carbonaceous materials and other cheap adsorbents

W. Tanthapanichkoon *et al.* (2005) [61] have studied the adsorption – desorption characteristics of phenol and reactive dyes aqueous solution on mesoporous AC prepared from waste tires. Liquid phase adsorption desorption characteristics and ethanol regeneration efficiency of an AC prepared from waste tires and a commercial

AC were investigated. Water vapor adsorption experiments have been done which proved that both carbons showed hydrophobic characteristics. The prepared carbon possessed comparable phenol adsorption capacity as the commercial one but regeneration of former is less than later one.

A. H. Mahvi *et al* (2004) [1] show the potential of rice husk and rice husk ash for phenol removed in aqueous systems.

Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, concentration of phenol, dose of adsorbent and pH. Adsorption equilibrium of rice husk and rice husk ash was reached within 6 hr for phenolic concentration 150-500 $\mu\text{g/l}$ and 3 hr for phenol concentration 500-1300 $\mu\text{g/l}$ respectively. A comparative study showed that rice husk ash is very effective than rice husk for phenol removal. The studies showed that the rice husk ash can be used as an efficient adsorbent material for removal of phenolic compound from water and waste water.

Fabing Su *et al.* (2005) [15] have studied the phenol adsorption on zeolite templated carbon with different pore structure and surface properties. The structure and surface properties of the carbon samples were characterized using N_2 adsorption, water vapour adsorption, X-Ray photo electron spectrometer, thermogravimetric analysis (TGA). It was observed that thermal treatment under N_2 can significantly eliminate surface oxygen containing group, thus altering the adsorption capacity.

Possible reasons behind the experimental observations include formation of water molecules cluster, $\pi - \pi$ dispersive interaction, electron donor acceptor mechanism were discussed. Langmuir isotherms were developed for fitting the experimental data. The fertilizer waste slurry can be converted to cheap carbonaceous adsorbent material.

S.K. Srivastava *et al.* (1997) [49] worked on competitive adsorption of substituted phenols by activated carbon developed from the fertilizer waste slurry. These types of adsorbents are having good adsorptive properties for toxic metals and substituted phenols from oil refinery. The competitive effect on the uptake of various substituted phenols such as 2, 4, 6-trinitrophenol, 4-nitrophenol, 4-chlorophenol and 1, 3-

dihydroxybenzene has been studied and Langmuir model developed for bisolute system also Jain and Snoeyink (1973) modified model developed.

Erol Aryanci *et al.* (2005) [11] studied the behaviour of some phenolic compounds onto high specific area activated carbon cloth. Adsorption of phenol, Hydroquinone, m-cresol, p-cresol and p- nitro phenol from aqueous solution on to high specific area activated carbon cloth has been studied. Adsorption isotherms were derived at 30° C and the isotherm data were treated according to Langmuir, Freundlich and Tempkin isotherm equations.

Tempkin equation used:

$$Q_e = B_1 \log K_t + B_1 \log C_e \quad \dots (2.1)$$

Q_e = Amt of Phenolic compound adsorbed per unit mass of carbon cloth (mg/g)

B_1 and K_t are the constants of Tempkin isotherm.

The decreasing order of rate constants for the adsorption of phenolic compounds studied was determined as p-nitrophenol ~ m- cresol > p- cresol > hydroquinone ~ phenol.

R.S. Krishna *et al.* (2001) [35] prepared activated carbon from pyrolysis of coconut husk and evaluated the adsorption characteristics, for the removal of phenol from aqueous phase. The carbon showed low carbon content (53%) and produced high volatile matter (27%) and ash (13%).its phenol adsorption capacity was only about 10-15% of the adsorption capacity should by commercially available activated carbons.

They got very less surface area due to high volatile matter and ash content and low carbon content. This thing happened due to less temperature pyrolysis.

High temperature pyrolysis will increase surface area and hence the adsorptive efficiency of carbon.

Francisco Villacanas *et al.* (2005) [16] have done work on AC for removal of simple aromatic compound like phenol, aniline and nitro benzene.

But they did adsorption on modified Activated carbon. They tried to modify the surface properties by means of chemical treatment with HNO_3 and thermal treatment under a flow of H_2 . Although the texture properties were not significantly change after

these modification. Adsorption data were fitted to Langmuir model for all three adsorbate.

El-Nabarawy *et al.* (2000) [13] have done the study of removal of phenol from waste effluent using saw dust Sawdust and water hyacinth are waste products which have no economical application in Egypt. They even constitute a solid waste as far as the environment is concerned. As-received sawdust and water hyacinth were treated with phosphoric acid, phosphoric acid + urea or phosphoric acid + urea + dimethylformamide. The as-received and treated samples were used for the removal of Methylene Blue, iodine, phenol and ammonia from their aqueous solutions. The optimum conditions for the maximum adsorption of each pollutant were determined. The isotherms obtained obeyed the Freundlich and Langmuir equations in a satisfactory manner. The initial stages of adsorption follow first-order kinetics as predicted from the Lagergren equation. Sawdust and water hyacinth show promising potentialities for the removal of pollutants from water and can, at least, be used as precursors for the preparation of efficient adsorbents for the removal of pollutants from water.

Vimal C. Srivastava *et al.* 2006 have studied the removal of phenol by bagasse fly ash and activated carbon and also studied kinetics, equilibrium and thermodynamics. Equilibrium isotherms were analysed by Freundlich, Langmuir, Tempkin, Redlich-Peterson and toth isotherm models using non-linear regression technique.