ADSORPTION OF BENZALDEHYDE FROM WASTEWATER

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled **"ADSORPTION OF BENZALDEHYDE FROM WASTEWATER"** in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2005 to June 2006 under supervision of **Dr. B. Prasad**, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Ravi Kr Rajoriya

Date: June , 2006

Place: Roorkee **(RAVI KUMAR RAJORIYA)**

CERTIFICATE

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

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ABSTRACT

The deterioration of water quality started with fast industrialization and globalization. Untreated discharges from domestic and industrial activities resources and urban agglomerate into water bodies are the main sources of both punitively and qualitatively. Water is a fundamental component of the earth's eco-system and ensures a rich diversity of plant and animal life. Its quality affects biota-flora and fauna. Water resources need to be conserved and their quality should be preserved. Industrial wastewater is the discharge of industrial plants and manufacturing processes. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their contents of specific organic and inorganic substances. Amongst many pollutants affecting water quality are mining, petroleum processing, chemical and petrochemical units, steel and metal smelter plants, pulp and paper mills, textile, caustic, chlorine production units and agriculture industries.

Benzaldehyde is an aromatic aldehyde used in the food, beverage, pharmaceutical, perfume, soap, and dyestuff industries. Benzaldehyde occurs as a constituent of oils of bitter almond, peach and apricot kernel. It is usually prepared synthetically. It is a colorless liquid having an odour resembling that of bitter almond oil, and a burning taste. It is affected by light and it oxidizes in air to benzoic acid. Activated carbons are high porosity, high surface area materials used in industry for purification and chemical recovery operations as well as environmental remediation.

Present study deals with equilibrium and kinetic modeling for the adsorptive removal of benzaldehyde using granular activated carbon. Optimum conditions for benzaldehyde removal were found to be adsorbent dose of 4 g/l found for activated carbon. Equilibrium time was achieved 4 h. Equilibrium adsorption data was analyzed by Freundlich, Langmuir and Temkin isotherm equations, using regression and error analysis. Freundlich isotherm was found to best represent the data for benzaldehyde adsorption for activated carbon.

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NOMENCLATURE

C_i	Initial concentration of effluent
C_e	Concentration of adsorbate solution at equilibrium (mg/ l)
K	Adsorption rate constant (min^{-1})
K_a	Rate constant, liquid/mg of adsorbate, (l / mg)
K_L	Langmuir isotherm constant, (l / mg^{-1})
K_T	Temkin isotherm constant, (l / mg)
K_F	Freundlich isotherm constant $(mg / l)^{-1/n}$
n	Freundlich isotherm constant
Q_t	Amount of adsorbate adsorbed per unit amount of adsorbent at time t, (mg / g)
Q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg / g)
Q_m	Limiting adsorbing capacity, (mg / g)
R_L	Separation Factor
k_f	First order rate constant, (min^{-1})
k_s	Second order rate constant, (g $mg^{-1} min^{-1}$)
ΔG°	Gibbs free energy, (KJ / mol)
ΔH°	Enthalpy, (KJ / mol)
ΔS°	Entropy, (J K^{-1} mol^{-1})

CHAPTER #1

INTRODUCTION

1.1 GENERAL

The deterioration of water quality started with fast industrialization and globalization. Untreated discharges from domestic and industrial activities resources and urban agglomerate into water bodies are the main sources of both punitively and qualitatively. The principal sources of contaminants of water quality are mining, petroleum, chemical and petrochemical, steel, smelter plants, pulp and paper, textile, caustic, chlorine and agriculture industries. In many of these industries, hazardous wastes are also discharged. The wastewater gets into natural sources cause changes in the physicochemical composition of natural water, which ultimately becomes unsuitable for use. With the rapid growth of industrialization, the water pollution problem is mater of worth concern all over the world now. In brief Water pollution can be defined as "any biological, chemical, or physical change in water quality that has a harmful effect on living organisms or makes water unsuitable for desired uses." Such pollutants fall into three main categories: 1) biological, such as bacteria or viruses; 2) chemical, including organic and toxic substance; 3) physical, such as sediment, radioactive material, and heat.

Benzaldehyde is an aromatic aldehyde used in the food, beverage, pharmaceutical, perfume, soap, and dyestuff industries. Benzaldehyde occurs as a constituent of oils of bitter almond, peach and apricot kernel. It is usually prepared synthetically. It is a colorless liquid having an odour resembling that of bitter almond oil, and a burning taste. It is affected by light and it oxidizes in air to benzoic acid. (http://www.speclab.com/compound/m8315.htm)

There is considerable demand for chlorine free benzaldehyde as it is used in harmaceutical industry. As multinational is being coming up the competition is been developing and major challenge faced by the industry is purity of product (free from chlorine) Oxidation builds up the chlorination process material has large demand in soap and perfume industry.

Electroplating industry has great demand for benzaldehyde. Hence. benzaldehyde industry is an important raw material for many industries.

The leading manufacture of Benzaldehyde in India is,

Indian Organic Chemicals Ltd. Khopoli (Maharashtra state)

Estimated requirement of Benzaldehyde in India

Year	Quantity
1976-77	6000 Tons
1984-85	8000 Tons
1989-90	10000 Tons
1994-95	12000 Tons
1999-2000	14000 Tons

(http://www.omikron-online.de/cyberchem/aroinfo/fen_no.htm)

1.2 Elemental idea of Benaldehyde

Benzaldehyde (C_6H_5CHO) is the simplest and the most industrially useful member of the family of aromatic aldehydes. Benzaldehyde exists in nature, primarily in combined form such as glycoside in Almond, apricot, cherry and peach seeds. The characteristic benzaldehyde odour of oil of bitter almond occurs because of trace amounts of free benzaldehyde formed by hydrolysis of the glycoside amygdalin. Amygdalin was first isolated in 1830 from the seed of the bitter almond sometime later Liebeg and Wohler found that when amygdalin was hydrolyzed with water and emulsion.

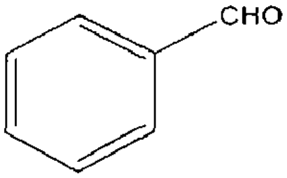

Fig: 1.1 Structural Formula of Benzaldehyde

Table 1.1: Properties of benzaldehyde

Common name	BENZALDEHYDE
Other name	Phenylmethanal Benzenecarboxaldehyde Benzoic aldehyde Benzene carbaldehyde
Molecular formula	C_6H_5CHO
Molecular mass	106.16 g/mol
Appearance	Clear, colorless liquid
Density	1.050 gm/cm^3@ 15°C
Vapour pressure	1 mm Hg at 26 C
Melting point	-26°C
Boiling point	179°C
Flash point	62°C
Auto-ignition temperature	190°C
Water Solubility	6.55 g/l at 25^{0}C, slight
Solubility in other :Solvents	Miscible with alcohol, ether, oils

(http://en.wikipedia.org/wiki/Benzaldehyde)

1.3 Production and uses

Benzaldehyde is produced by many processes like - chlorination of toluene to benzal chloride, which is then hydrolyzed by reaction with lime but the primary method of synthesis is by oxidation of toluene, where it is produced as a co product with benzoic acid.

1) Its more than 98% is used as an intermediate in production of pharmaceuticals, aromatic alcohols, hotographic chemicals, dyes, benzoic acid and cinnamic acid. Purified benzaldehyde used as an intermediate (60% on site and 38% off site) in closed systems and 1-2% is used as a food and fragrance additive.

2) It is used as a solvent for oils, resins, some cellulose ethers, cellulose acetate, and nitrate and is a useful pharmaceutical vehicle for administering bromides and other salts, especially when a low salt content is desired.

3) Benzaldehyde is widely used in flavors such as almond and cherry in various fragrances for soap and toiletries.

4) Benzaldehyde is a synthetic flavoring substance generally recognized as safe for foods.

5) It is used as a Bee repellant in the harvesting of honey.

6) It is used in denatured alcohol.

7) Intermediates for numerous derivatives.

8) Chemical intermediate for aromatic alcohol.

9) It is used in manufacturing of Benzoic acid, pharmaceuticals, and photographic chemical.

10) benzaldehyde is used in manufacturing of cinnamic and mandelic acids

11) Benzaldehyde is largely used as an intermediate for the manufacture of odorants and flavoring chemicals, mainly cinnamaldehyde, amyl cinnamaldehyde, hexyl cinnamaldehyde and cinnamyl alcohol.

12) Benzaldehyde is also used as starting material for pharmaceuticals (Ampicillin) and pesticides (Dibenzoquat).

13) Phenol Benzaldehyde resins have been utilized to prepare fireproof structural foam ferrocene polymers are also prepared from Benzaldehyde.

14) It is used in the production triphenylmethane green, which is obtained by condensation of benzaldehyde with dimethylaniline.

15) It is also used for extractive separation of isomeric amines.

16) Benzaldehyde most important use in organic synthesis where it is raw material for a large no of products. (http://ptcl.chem.ox.ac.uk/MSDS/toxicity_abbreviations.html)

1.4 Environmental Occurrence

Benzaldehyde is released to the environment in emissions from combustion processes such as gasoline and diesel engines, incinerators and wood burning. It is formed in the atmosphere through photochemical oxidation of toluene and other aromatic hydrocarbons. It occurs naturally in various plants. If released to the atmosphere, benzaldehyde will degrade by reaction with photo chemically produced hydroxyl radicals (half-life of 29.8 hr); direct photolysis may contribute to its atmospheric degradation.

1.5 Environmental Impact

Benzaldehyde is released to the environment in emissions from combustion processes such as gasoline and diesel engines, incinerators and wood burning. It is formed in the atmosphere through photochemical oxidation of toluene and other aromatic hydrocarbons. It occurs naturally in various plants. If released to the atmosphere, benzaldehyde will degrade by reaction with photo chemically produced hydroxyl radicals (half-life of 29.8 hr); direct photolysis may contribute to its atmospheric degradation. Physical removal from air by wet deposition can occur. If released to soil or water, the major degradation pathway is expected to be biodegradation. Physical transport from water can occur through volatilization. Estimated Koc values (9-71) suggest that benzaldehyde will leach in soil. Occupational exposure to benzaldehyde occurs through inhalation of vapor and dermal contact. The general population is

exposed to benzaldehyde through consumption of food (where it occurs either naturally or as an intentional food additive) and inhalation of contaminated air.
(http://msds.ehs.cornell.edu/msds/msdsdod/a127/m63056.htm)

1.6 Routes of exposure

The substance can be absorbed into the body by inhalation, through the skin and by ingestion. Since benzaldehyde is approved as a direct and indirect food additive, consumers can be exposed by the oral route. As it is also used as a solvent for resins, therefore consumers can also be exposed dermally and by inhalation.

1.7 Potential Health Effects

a) Inhalation

Benzaldehyde may cause irritation to the respiratory tract. Symptoms may include coughing, sore throat, labored breathing, and chest pain. High concentrations have a narcotic effect. Over exposure to benzaldehyde vapors is irritating to upper respiratory tract and produces central nervous system depression with possible respiratory failure.

b) Ingestion

It may cause sore throat, abdominal pain, nausea, central nervous system depression, convulsions, and respiratory failure. Estimated lethal dose 2 ounces.

c) Skin Contact

It May cause irritation with redness and pain , allergic skin reactions and may have a local anesthetic effect.

d) Eye Contact

It May cause irritation, redness and pain.

e) Chronic Exposure

Chronic exposure may cause skin effects.

1.8 First Aid Measures

a) Inhalation

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

b) Ingestion

If swallowed, do not induce vomiting. Give large quantities of water. Never give anything by mouth to an unconscious person. Get medical attention immediately.

c) Skin Contact

Immediately flush skin with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.

d) Eye Contact

In case of contact, immediately flush eyes with plenty of water for at least 15 minutes, lifting upper and lower eyelids occasionally. Call a physician if irritation persists.

(http://msds.ehs.cornell.edu/msds/msdsdod/a127/m63056.htm)

CHAPTER #2

LITERATURE REVIEW

2.1 GENERAL

The available literature on the removal of Benzaldehyde from waste water is not sufficient so help has been taken from the literatures of co-related works such as removal of aromatics and different other hydrocarbons from waste water. The literatures followed during the complete dissertation work have been presented in nutshell in table.2.1 and table.2.2.

Activated carbons are widely used as adsorbents for the treatment of polluted water or wastewater. In these wide applications of activated carbons, adsorption property and capacity of activated carbons plays an important role. Adsorption isotherms for benzaldehyde on activated carbon from supercritical carbon dioxide have been studied [Lucas et al., 2004]. Adsorption capacity of activated carbons mainly depends upon pore characteristics such as specific surface area, pore size, and its distribution. Commonly, most commercially available activated carbons are extremely micro porous and of high surface area, and consequently, they have high efficiency for the adsorption or removal of low molecular weight compounds. However, the adsorption of giant molecules exhibiting high molecular weight on micro porous activated carbon is very low. Also, adsorbent-grade activated carbon is cost-prohibitive and both regeneration and disposal of the used carbon is often very difficult. Consequently, many investigators have studied the feasibility of using low cost substances for the treatment of wastewater.

Shin et al., (1995) biotransformation of benzaldehyde to L-phenylacetylcarbinol (L-PAC) as a key intermediate for L-ephedrine synthesis has been evaluated using immobilized Candida utilis. During biotransformation, the benzaldehyde level and respiratory quotient significantly affected both L-PAC and by-product benzyl alcohol formation. By controlling the benzaldehyde level at 2 g/l, maintaining a respiratory quotient of 5-7 and pulse feeding glucose, a final concentration of 15.2 g/l L-PAC was achieved in a fed-batch process. This compares with previous published results of 10-12 g/l in batch culture and 10 g/l L-PAC in a semi continuous process with immobilized Saccharomyces cerevisiae. In a single stage continuous process with immobilized C. utilis, the steady state L-PAC concentration was significantly reduced because of the sustained toxic effects of benzaldehyde.

Sardar et al.(2000) studied the adsorption of benzaldehyde on Al(III) at 90 and 300 K has been investigated using ARUPS, HREELS and work-function measurements. Benzaldehyde adsorbs readily at both temperatures, with monolayer saturation reached at an exposure of 1.4 L. Bonding occurs via the aldehyde functional group rather than the ring p electrons. At 90 K, the functional group remains intact, while at 300 K, the CNO bond breaks, forming direct covalent bonds to the metal surface. At 90 K, the molecule lies flat, while at 300 K, the ring tilt depends on coverage, with the saturated monolayer containing considerably more material than at 90 K.

Affrossman et al (1987) found that the adsorptions of benzoic acid and of benzaldehyde on aluminium substrates are studied by XPS and SIMS. The negative and positive SIMS spectra and the XPS spectra of benzoic acid on plasma oxidized aluminium correlate with the adsorbate structure. Benzaldehyde adsorbed on plasma oxidised aluminium gives similar XPS and SIMS spectra to those of benzoic acid in agreement with the known oxidative properties of the surface. Decreasing the amount of oxygen on the substrate before adsorption of the aldehyde results in broad C ls spectra, which are difficult to interpret. The corresponding SIMS spectra show that only a fraction of the adsorbate is now in the form of the acid. SIMS fragments are observed at much higher masses than the acid ion. These are assigned to polymeric species formed by abstraction of oxygen or water from the adsorbed molecules to give hydrocarbon residues. The relative amount of acid and polymer depends on the amount of substrate oxygen.

Lichtenberger et al., (2006) found that the adsorption and reaction of 2-hydroxyacetophenone and benzaldehyde on MgO investigated via in situ FTIR spectroscopy in an attempt to gain a better understanding of the Claisen–Schmidt condensation reaction between these two molecules catalyzed by MgO. The results indicate that 2-hydroxyacetophenone adsorbs on MgO through abstraction of the phenolic hydrogen, forming a surface phenolate ion. Benzaldehyde adsorbs through its carbonyl bond and can be subsequently oxidized to form two different types of benzoate species. These benzoate species are inactive toward further reaction with 2-hydroxyacetophenone and/or its surface derivatives and accumulate on the MgO surface with time on stream. In contrast, the 2-hydroxyacetophenone-derived phenolate ion reacts with benzaldehyde, yielding an adsorbed chalcone-type product.

Kuiper et al. (1972) studied that infrared and laser Raman spectra indicate that the adsorption of benzaldehyde on alumina results in the formation of two adsorbed species, having a benzoate and a benzylalcoholate structure, respectively. By comparison with the benzoate the alcoholate is formed in only small quantities. The production of the benzoate is explained by the oxidative properties of the alumina surface. A possible explanation of the alcoholate formation is the occurrence of a Cannizzaro reaction, catalyzed by basic sites.

Giraudet et al. (2006) found that adsorption of volatile organic compounds (VOCs) by granular activated carbons (GACs) is a highly exothermic process and leads to temperature rises, which can be hazardous for high pollutant contents. This study points out the significant characteristics of VOCs and GACs on adsorption energies. For that purpose, adsorption energies were measured for a wide variety of VOCs, representative of different chemical groups, using eight different commercial GACs with different porous structures. Afterwards a statistical analysis was applied to the experimental database thus obtained, which enabled to enlighten the most significant variables, linked to either VOCs' molecular properties or intrinsic characteristics of GACs. Two statistical models have been tested: multi-linear regression (MLR) and neuron networks (NN), and their efficiencies were compared in terms of prediction skill. The best results have been obtained from the MLR approach, which discriminated five different properties of the system. These explicative variables were the polarizability, the heat of vaporization, the ionization potential and the surface tension for adsorbates and the average micropore radius for GACs. The MLR model enabled to compute integral adsorption enthalpies with a precision around 10%. Thanks to the properties discriminated, we came to some conclusions on the dominant mechanisms of adsorption.

Fuertes et al. (2002) found that activated carbon fibre monoliths (ACFMs) prepared from the rejects of polymeric fibres (Nomex^{TM}). These were carbonised, agglomerated with a phenolic resin and steam activated at burnoff degrees between 0 and 40%. Adsorption experiments with *n*-butane at 30 ^{0}C show that, at high adsorbate concentrations, the amount adsorbed is a function of pore volume, but at low concentrations this mainly depends on pore size distribution. The porosity of Nomex-based ACFMs is formed by narrow micropores, which permit higher amounts of vapour to be adsorbed in low concentrations compared to monoliths prepared from different commercial activated fibres and a commercial granular activated carbon, which exhibits wider pores. The agglomeration of Nomex-fibres to form ACFMs does not cause any loss in adsorption properties with respect to non-agglomerated activated fibres. From the adsorption experiments of different vapours on a Nomex-based ACFM (40% burn off) it was found that at high concentrations ($p/p_0=1$) the adsorbed volume was independent of the nature of the adsorbate and depended only on pore volume. However, at low vapor concentrations ($p/p_0=0.004$), the amount of adsorbed depended on the adsorbate being well correlated to the molecular parachor and the polarizability of the adsorbates.

Toles et al., (1997) found that almond and pecan shells chosen as hard, lignocellulosic precursors for the production of granular activated carbons (GACs) in order to create carbons for the adsorption of both organic compounds and metals. They were activated chemically, with H_3PO_4 or physically, with CO_2 under a variety of conditions. Following activation, a portion of the GACs were oxidized with air. The acid-activated samples had higher BET surface areas and greater product yields than the CO_2-activated carbons. Unoxidized, CO_2-activated carbons generally sequestered more Cu^{2+} from solution than the unoxidized acid-activated GACs, when evaluated in batch assays at pH 4.8. Oxidative treatment, however, improved Cu^{2+} adsorption in both types of carbon to levels significantly greater than comparable commercial carbons. Nutshell-based carbons were also examined for their ability to adsorb a variety of low molecular weight organic compounds with differing polarities. For CO_2 activated pecan shell carbons there was a distinct increase in organic uptake that was usually not altered by oxidation. Both acid- and CO_2 activated pecan shell carbons took up similar amounts of the non-polar benzene and toluene, but the CO_2 activated carbons took up more polar compounds. There were several GACs that outperformed commercial carbons in their ability to adsorb significant quantities of Cu^{2+} or organics on the same carbon. Our data show that nutshells provide a plentiful and inexpensive precursor for the production of GACs which may be competitive with commercial carbons in wastewater or potable water treatment.

Chen et al., (1996) found that the adsorption performance could be significantly improved by using small-size GAC, low pH, low temperature, and an increase in the dosage of GAC. The use of the Freundlich adsorption model had the potential in evaluating the behavior of GAC. The results reflected the batter adsorption efficiency of GAC in the higher initial concentration of total organic carbon (TOC) Earn the drinking water source. In addition, the adsorption capability and the Freundlich constant {n) increased with increasing operation time. In a single column study, a low flow rate led to an increase in adsorption capacity and breakthrough time and a decrease in the treated water volumes. In UC next step, the bed depth/ service time or BDST design method was used to predict the breakthrough profiles for TGC in the four serial columns. The column service time and treated water volumes were all reduced while high adsorption efficiency of GAC could be achieved. Furthermore, the operation at a low flow rate improved the adsorption capacity of GAC for the same TOC removal percentage.

Shen et al., (1994) the adsorption of molecules of organic or inorganic compounds in an aqueous solution onto granular activated carbon involves a sequence of steps including: transfer of the molecules from the bulk phase of solution through the relatively stagnant, layer of solution adjacent to the external surface and solution in macropores and micropores of the pellet of activated carbon and occupation of the active sites on the inside of the pellet by the molecules. The present work analyzes and models this sequence of steps by resorting to the stochastic population balance of the numbers of molecules of adsorbate in the three states. The first comprises the bulk phase of the solution; the second, the layer of solution adjacent to the external surface and the solution in the macropores; and the third, the active sites on the inside surfaces of the micropores. The master equation has been derived for the case of a single adsorbate compound. The equations for the means, variances, and covariances of the random variables have been obtained through the system size expansion of the master equation. At equilibrium, the equations for the means reduce to the equation of the Langmuir isotherm. The unknown parameters in the equations for the means have been estimated by comparing the calculated results with the experimental data. These parameters have been adopted to predict the evolution of variances and covariances of the numbers of adsorbate molecules in the three states.

Annisine et al., (1987) adsorption isotherms of acetone, propionaldehyde, methylisobutylketone and sucrose from aqueous solutions onto granular activated carbon have been determined. Multi-solute data have been compared with the theoretical prediction obtained from ideal adsorbed solution model. The agreement between calculated and observed results is satisfactory. Only the system sucrosemethylisobutylketone shows significant deviation between experimental and predicted values. Therefore the model can be successfully utilized in design of activated carbon units.

Snoeyink et al., (1985) the factors which affect removal of organic micropollutants by coagulation, sedimentation, filtration and activated carbon adsorption will be reviewed. Removal of specific compounds by coagulation, sedimentation and filtration is often slight; unless the pollutants adsorb on particles or associate with humic substances which are then coagulated. By comparison, removal of humic substances by these processes can be substantial, depending upon the water chemistry and the process conditions. Activated carbon may be applied in both the powdered (PAC) and granular (GAC) form. PAC and GAC have been used successfully throughout the world to remove odorous compounds. PAC has been used to a much smaller extent for removal of other micro pollutants, but there is much potential for improvement of the application procedure so that good results can be achieved. GAC is widely used to remove micro pollutants other than odor in Europe but has not been extensively used for this purpose in North America. The compounds which can be removed by GAC are presented and process monitoring procedures are discussed. Factors which limit its use include incomplete knowledge about which compounds must be removed and what effluent concentrations are acceptable.

Table 2.1: Various Experimental Works on Removal of Hydrocarbons and Related Compounds from Waste Effluents.

Reference	Operation	Results and conclusion
Valquiria.Ribeir. Gusmao et al.. [2006]	BTEX and ethanol removal in anaerobic denitrifying condition.	Removal efficiency is 99% at initial concentration of 26.5 mg/L of ETX by using denitrifying consortium. but the rate of the reaction is very slow.
Takahira.Suzuki et al.. [2005]	Removal of hydro carbons in a rotating biological contactor with biodrum.	A novel rotating biological contactor with biodrum was designed to remove hydrocarbon in waste water by using micro-alga protothecazopfic. Removal efficiency is 65%. but time taken was 30 days.
Srivastava et al., 2005	Removal of phenol by Bagasse fly ash and activated carbon in batch process	Adsorption kinetics was found to follow second order rate expression with initial sorption rate being highest for adsorption on BFA. Equilibrium adsorption data for phenol on all the adsorbents, viz., ACL, ACC and BFA were best represented by the Redlich–Peterson isotherm. Adsorption of phenol on BFA is favourably influenced by increase in the temperature of the operation. This shows that the overall sorption process is controlled by intra-particle diffusion of phenol. The negative value of Gibbs free energy indicates spontaneous adsorption of phenol on BFA
M.Blanchord et al. [2004]	Removal of poly cyclic aromatic hydrocarbon and polychloro biphenyl in waste water.	98% of PAH and 76% of PCB was removed.
A.Bernal et al [2005]	Combining anaerobic digestion and ozonation to remove PAH from urban sludge.	In this study combination of anaerobic digestion and ozonation process was used. 81% of PAH was removed with addition of hydrogen peroxide during ozonation.
Sanna.K.Marttinen et al [2003].	Occurrence and removal of organic pollutants in sewage and landfill leachates.	This process presented in 84% removal of DEHP adsorption on particle range 0.1-0.41 micrometer.
I.Alemzadeh et al [2001]	Biodegradation of toluene by an attached biofilm in a rotating biological contactor.	RBC was used to carry out the operation. The kinetics was found to be followed zero order mechanism.
William, T. Stringfellow et al [1997]	Evaluating the relationship between the sorption of PAH to bacterial biomass and biodegra-dation.	This process was meant for treating refinery waste water. The result study suggested that although biosorption decreases the rate of PAH biodegradation in the short term, it can also resulted in complete removal of PAH from waste water.

Wan, Liliao et al [1997]	Microbial removal of poly cyclic aromatic hydro carbons by Phanerochacle-chrysosporiun.	The biocarrier used in the investigation, was a mixed gel composed of alginate and activated carbon. The results showed that PAH were removed with an increased rate during the stationary growth phase and strain ATCC-*24725* exhibited the best PAH removal efficiency.
M. Kondo et al [1994]	Treatment of waste water from phenolic resinprocess by pervaporation.	PEBA(polyethylene black amide) membrane showed a substantial potential for application to phenol containg waste water treatment, subjected to the waste water being purified to the required quantity by vacuum distillation or other appropriate pre treatment. But time taken for the process was 72 hours.
J.H.Pardue et al [1988]	Removal of PCB from waste water in a simulated overland flow treatment system.	Overland flow treatment system proved to have a promising potential for removal of organic pollutants. The efficiency was found to be 100 % in 38 days time.
Richard, W. Wallirs et al [1986]	Liquid/ suspened solid phase partitioning of poly cyclicaromatic hydrocarbons in coal washing waste water.	Partitioning in the biological reactor of effluent stream was correlated with aqueous solubility and n-octanol/ water partition coefficient.
Farida. Y. Saleh et al [1982]	Selected organic pesticides, behavior and removal from domestic waste water by chemical and physical process.	Evaluation of effectiveness of physical and chemical waste water treatment process in removing selected organic pesticides from domestic waste. This result showed that application of several sequences of treatment process could produce a high quality effluent which is virtually free from detectable organic residue.
Dan, Wa et al [2006]	Removal of p-xylene from air streams in a hybrid biofilter.	Biofilter packed with pig compost and forest soil resulted in removal efficiency range from 47-80% at pH 6.3 in time 62 days.

Table 2.2: Various Adsorption Study Related with Organic Pollutants

Reference	Operation	Results and conclusion
Jeong, Hoon Bylon et al [2006]	Removal of volatile organic compound by spark generator carbon aerosol particles.	The study introduced an idea of removing benzene toluene and xylene in a controllable way using carbon particle produced by spark generator. BTX removal increased by 4% compared to conventional activated carbon.
C.Namosivayam et al [2006]	Removal of anions heavy metals, organic and dyes from waste water by adsorption onto $ZnCl_2$ activated coir pith carbon.	Coir pith was used to develop $ZnCl_2$ activated carbon. Result showed that the adsorbent was effective for removal of toxic pollutants with removal efficiency around 90%.
Xiao-Hong, Guan et al [2006]	Competitive adsorption of organic mater with phosphate on aluminum hydroxide.	The effect of ortho-phosphate for the adsorption of natural organic matter on aluminum hydroxide was investigated.
Vimal, C. Srivastava et al [2005]	Adsorptive removal of phenol by bagasse fly ash and activated carbon.	The study showed that BFA is an effective adsorbent for the removal of phenol from aqueous solution. Optimum condition for phenol removal were found to be pH=6.5 and adsorbent dose=10 g/L
Mall et al [1998]	Removal of 2.4-dichlorophenol by using BFA and RHFA.	The predicted applicability of BFA and RHFA in batch operation in various parameters such as effect of contact time, adsorbent dose, pH etc has been studied. Economic evaluation shows that their use will be viable.
Mall & Prasad [1998]	Removal of COD using pyrolysed bagasse char.	PBC was found effective for removal of COD from pulp and paper mill effluents in polishing stage.
S. Chang et al [2005]	A simplified model for trace organic removal by continuous flow PAC adsorption.	Mathematical model have been developed. The result indicated that the developed model provide reasonable representation of the trace removal by the adsorption process.
Y.H. Wang et al [2005]	Removal of trace organic compound from waste water by ultrasonic enhancement in adsorption.	The sorption used in the experiment was alumina with manganese nitrate. The process was found to be effective in temperature range 30-60 °C.
Kyuya, Nakagaua et al [2004]	Adsorption of phenol and reactive dye from aqueous solution on activated carbon, derived from solid waste.	Activated carbon produced from waste tyres and waste generated during lactic acid fermentation. This process is very effective for large capacity adsorption.

P. Duivedi et al [2004]	Comparative study of removal of volatile organic compounds by cryogenic condensation and adsorption by activated carbon fiber.	This paper describes studies and techniques for controlling emission of volatile organic compounds. Activated carbon fibers have shown to exhibit large adsorption for VOC than any other.
H.H.Tseng et al [2002]	The adsorption of PAH, BTEX and heavy metals on surfactants-modified desulphurization sorbents in a dry scrubber.	The adsorbent used in this process was $Ca(OH)_2$ modified with calcium lignosulfonate and sodium lingosulfonate. The process was followed by filtration in a dry scrubber fabric filter.
L.Nicolet & U.Rott.[1999]	Recirculation of activated carbon for the adsorption of dyes in municipal waste water plant.	Recirculation of PAC for several times results in removal of halogenated organic compounds which are not degraded by micro-organisms.
Zhang & Chuang [2001]	Adsorption of acidic bleach plant effluent by activated carbon and polymer resin as adsorbent.	The adsorption isotherm is described using freundlich isotherm equation. The pH of waste water solution influences significantly the adsorption capacity of activated carbon. The resin is more effective than activated carbon in color removal from effluents.
Mall et al [1998]	Adsorption of 2-chlorophenol and 4-chlorophenol using BFA and activated carbon adsorbent.	On the basis of investigation it has concluded that BFA can be a potential substitute for activated carbon. The process is more attractive in integrated sugar mill and paper mill complex.

The objectives of the present dissertation work can be put into a nutshell as:

- To study the effectiveness of granular activated carbon as adsorbent for removal of benzaldehyde through different parameter study such as effect of adsorbent dose, concentration, time and temperature.
- To find out the best suited kinetics and isothermal models for the above process
- To study the various thermodynamic properties such as: enthalpy, activation energy, entropy and free energy for the adsorption process.

CHAPTER #3

ADSORPTION FUNDAMENTALS

3.1 GENERAL

Adsorption is a surface phenomenon. The material adsorbed is called the adsorbate or solute and the adsorbing phase is the adsorbent. In the water purification, adsorbents are used to remove organic impurities, particularly those that are non-biodegradable or associated with taste, color, and odor. Although adsorption is applied in low concentration, recent physical-chemical processes use adsorption as a primary technique to remove soluble organics from the wastewater. The adsorption is called physical when relatively weak intermolecular forces cause the attachment and, chemical when chemical bonding like forces causes this attachment. During adsorption, the solid adsorbent becomes saturated or nearly saturated with the adsorbate. To recover the adsorbate and allow the adsorbent to be reused, it is regenerated by desorbing the adsorbed substances (i.e. the adsorbates). (http://www.faizkaskar.8k.com/p.html)

3.2 PHYSICAL ADSORPTION VS. CHEMISORPTION

Adsorption processes can be classified as either physical adsorption (van der Waals adsorption) or chemisorption (activated adsorption) depending on the type of forces between the adsorbate and the adsorbent. In physical adsorption, the individuality of the adsorbate and the adsorbent are preserved. In chemisorption, there is a transfer or sharing of electron, or breakage of the adsorbate into atoms or radicals, which are bound separately.

Physical adsorption from a gas occurs when the inter-molecular attractive forces between molecules of the solid adsorbent and the gas are greater than those between molecules of the gas itself. In effect, the resulting adsorption is like condensation, which is exothermic and thus is accompanied by the release of heat, similar in magnitude to the heat of condensation.

Physical adsorption occurs quickly and may be monomolecular (unimolecular) layer or monolayer, or two, three or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area.

In contrast, chemisorption is monolayer, involves the formation of chemical bonds between the adsorbate and adsorbent, often with a release of heat much larger than the heat of condensation. Chemisorption from a gas generally takes place only at temperatures greater than 200 ^{0}C, and may be slow and irreversible.
(http://www.dsm.com/en_US/html/dsp/products_sp_benzaldehyde.htm)

Most commercial adsorbents rely on physical adsorption; while catalysis relies on chemisorption. A comparison between physical adsorption and chemical adsorption is given in Table 3.1.

3.3 INTRAPARTICLE DIFFUSION PROCESS

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites with the particles. This can be broken conceptually into a series of consecutive steps.

1. Diffusion of adsorbate across a stationary solvent film surrounding each adsorbent
2. Diffusion through the macro pore
3. Diffusion through micro pore
4. Adsorption at an appropriate site

It is assumed that the fourth step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So, it can be assumed that the main resistance to adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the rate limiting step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system propose the term "intra-particle transport" which comprises of surface diffusion and molecular diffusion. Several researchers have shown that surface diffusion is the dominant mechanism and is the rate-determining step. A functional relationship common to most of the treatments of intra-particle transport is that the uptake varies almost proportionally with square root of time. (http://ntp.niehs.nih.gov/ntp/htdocs/structures/3d/TR378.mol)

3.4 STAGES IN ADSORPTION PROCESS

Adsorption is thought to occur in three stages, as the adsorbate concentration increases.

Stage I: First, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of the forces that hold it.

Stage II: As the fluid concentration is further increased, second, third etc., layers form by physical adsorption; the numbers of layers which can form are limited by the size of the pores.

Stage III: Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore.

3.5 ADSORPTION ISOTHERMS

When a solution is contacted with a solid adsorbent, molecules of adsorbate get transferred from the fluid to the solid until the concentration of adsorbate in solution as well as in the solid phase are in equilibrium. At equilibrium, equal amounts of solute eventually are being adsorbed and desorbed simultaneously. This is called adsorption equilibrium. The equilibrium data at a given temperature are represented by adsorption isotherm and the study of adsorption is important in a number of chemical processes ranging from the design of heterogeneous chemical reactors to purification of compounds by adsorption.

Many theoretical and empirical models have been developed to represent the various types of adsorption isotherms. Langmuir, Freundlich, Brunauer-Emmet-Teller (BET), Redlich-Peterson (R-P) etc. are most commonly used adsorption isotherm models for describing the dynamic equilibrium. The isotherm equations used for the study are described follows:

3.5.1 Langmuir Isotherm

This equation based on the assumptions that:

1. Only monolayer adsorption is possible.
2. Adsorbent surface is uniform in terms of energy of adsorption.
3. Adsorbed molecules do not interact with each other.
4. Adsorbed molecules do not migrate on the adsorbent surface

The adsorption isotherm derived by Langmuir for the adsorption of a solute from a liquid solution is:

$$Q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \tag{3.1}$$

where,

Q_e = Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium

Q_m = Amount of adsorbate adsorbed per unit amount of adsorbent required for monolayer adsorption (limiting adsorbing capacity).

K_A = Constant related to enthalpy of adsorption

C_e = Concentration of adsorbate solution at equilibrium

The Langmuir isotherm can be rearranged to the following linear forms:

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \tag{3.2}$$

Or

$$\frac{1}{Q_e} = \left(\frac{1}{K_A Q_m}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{Q_m}\right) \tag{3.3}$$

3.5.2 Freundlich Isotherm

The heat of adsorption in many instances decreases in magnitude with increasing extent of adsorption. This decline in heat of adsorption is logarithmic, implying that adsorption sites are distributed exponentially with respect to adsorption energy. This isotherm does not indicate an adsorption limit when coverage is sufficient to fill a monolayer .The equation that describes such isotherm is the Freundlich Isotherm, given as:

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{3.4}$$

where .

K_F and n are the constants

C_e = the concentration of adsorbate solution at equilibrium

By taking logarithm of both sides, this equation is converted into a linear form:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3.5}$$

Thus a plot between ln Q_e and ln C_e is a straight line. The Freundlich equation is most useful for dilute solutions over small concentration ranges. It is frequently applied to the adsorption of impurities from a liquid solution on to the activated carbon. A high K_F and high 'n' value is an indication of high adsorption through out the concentration range. A low K_F and high 'n' indicates a low adsorption through out the concentration range. A low 'n' value indicates high adsorption at strong solute concentration.

3.5.2 Redlich-Peterson isotherm

Redlich and Peterson (1959) model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The R–P equation is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the R–P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation.

It can be described as follows:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{3.6}$$

Where K_R is R–P isotherm constant (L/g), a_R is R–P isotherm constant (L/mg) and β is the exponent which lies between 1 and 0, where β=1

$$Q_e = \frac{K_R C_e}{1 + a_R C_e} \tag{3.7}$$

It becomes a Langmuir equation. Where β=0

$$Q_e = \frac{K_R C_e}{1+a_R} \quad (3.8)$$

i.e.the Henry's Law equation

Eq. (4.6) can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{Q_e} - 1\right) = \ln a_R + \beta \ln C_e \quad (3.9)$$

Plotting the left-hand side of equation (4.9) against ln C_e to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R andβ. Therefore, a minimization procedure was adopted to solve equation (4.9) by maximizing the correlation coefficient between the theoretical data for Q_e predicted from equation (4.9) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with any suitable computer programme.

3.5.4 The Temkin isotherm

It is given as
$$q_e = \frac{RT}{b}\ln(K_T C_e) \quad (3.10)$$

Which can be linear zed as

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (3.11)$$

$$\text{Where } B_1 = \frac{RT}{b}$$

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Temkin and Pyzhev, 1940; Kim et al. 2004). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_1 and K_T from the slope and the intercepyt. K_T is the equilibrium binding constant (l mol^{-1}) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption.

3.6 ADSORPTION PRACTICES

Adsorption systems are run either on batch or on continuous basis. Following text gives a brief account of both types of systems as in practice.

3.6.1 Batch Adsorption Systems

In a batch adsorption process the adsorbent is mixed with the solution to be treated in a suitable reaction vessel for the stipulated period of time, until the concentration of adsorbate in solution reaches an equilibrium value. Agitation is generally provided to ensure proper contact of the two phases. After the equilibrium is attained the adsorbent is separated from the liquid through any of the methods available like filtration, centrifugation or settling. The adsorbent can be regenerated and reused depending upon the case.

3.6.2 Continuous Adsorption Systems

The continuous flow processes are usually operated in fixed bed adsorption columns. These systems are capable of treating large volumes of waste wasters and are widely used for treating domestic and industrial wastewaters. They may be operated either in the up flow columns or down flow column. Continuous counter current columns are generally not used for wastewater treatment due to operational problems. Fluidized beds have higher operating costs. So these are not common in use. Wastewater usually contains several compounds which have different properties and which are adsorbed at different rates. Biological reactions occurring in the column may also function as filter bed retaining solids entering with feed. As a result of these and other complicating factors, laboratory or pilot plant studies on specific wastewater to be treated should be carried out. The variables to be examined include type of adsorbent, liquid feed rate, solute concentration in feed and height of adsorbent bed.

3.7 FACTORS CONTROLLING ADSORPTION

The amount adsorbed by an adsorbent from the adsorbate solution is influenced by a number of factors are given as:

1. Initial concentration
2. Temperature
3. pH
4. Contact time
5. Degree of agitation
6. nature of agitation

3.7.1 Initial Concentration

The initial concentration of pollutant has remarkable effect on its removal by adsorption. The amount of adsorbed material increases with the increasing adsorbate concentration as the resistance to the uptake to the solution from solution of the adsorbate decreases with increasing solute concentration. Percent removal increases with decreasing concentrations.

3.7.2 Temperature

Temperature is one of the most important controlling parameter in adsorption. Adsorption is normally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature of the system. Some of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbents.

3.7.3 PH

Adsorption from solution is strongly influenced by pH of the solution. The adsorption of cations increases while that of the anions decreases with increase in pH. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by pH of solution. Change in pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. It is an evident observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions.

3.7.4 Contact time

The studies on the effect of contact time between adsorbent and adsorbate have significant importance. In physical adsorption, most of the adsorbate species are adsorbed on the adsorbent surface with in short contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium. Strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of heavy metals is fast at the initial stages of the contact period, and there after it becomes slow near equilibrium.

3.7.5 Degree of agitation

Agitation in batch adsorbers is most important to ensure proper contact between the adsorbent and the solution. At lower agitation speed, the stationary fluid film around the particle is thicker and the process is mass transfer controlled. With the increase in agitation this film decreases in thickness and the resistance to mass transfer due to this film reduces and after a certain point the process becomes intra particle diffusion controlled. Whatever is the extent of agitation the solution inside the process remain unaffected and hence for intraparticle mass transfer controlled process agitation has no effect on the rate on the adsorption.

3.7.6 Nature of adsorbent

Many solids are used as adsorbents to remove the impurities from fluids. Commercial adsorbents generally have large surface area per unit mass. Most of the surface area is provided by a network of small pores inside the particles. Common industrial adsorbents for fluids include activated carbon, silica gel, activated alumina, molecular sieves etc. Adsorption capacity is directly proportional to the exposed surface. For the non-porous adsorbents, the adsorption capacity is directly proportional to the particle size diameter whereas for porous materials it is practically independent of particle size.

Activated carbon is the most widely used adsorbent for water purification. In the manufacture of activated carbon, organic materials such as coal nutshells, bagasse is first pyrolysed to a carbonaceous residue. Larger channels or pores with diameter 1000 degree Å are called macro pores. Most of the surface area for adsorption is provided by micropores; which are arbitrarily defined as pores with diameter from 10-1000 Å.

(http://ntp.niehs.nih.gov/ntp/htdocs/structures/3d/TR378.mol)

Table 3.1: Comparison of Physical and Chemical Adsorption

S. No.	**Physical Adsorption**	**Chemical Adsorption**
1.	Vander walls adsorption	Activated adsorption
2.	Heat of absorption = 5 kcal/mol	Heat of adsorption = 20-100 kcal/mol
3.	Adsorption only at temp less than the boiling point of the adsorbate	Adsorption can occur even at higher temperature
4.	No activated energy involved in the adsorption process	Activation energy may be involved
5.	Mono and multi layer adsorption	Almost mono layer adsorption
6.	Quantity adsorbed per unit mass is high i.e. entire surface is participating	Quantity adsorbed per unit mass is low i.e. only active surface sites are important
7.	Extent of adsorption depends upon the properties of adsorbent	Extent of adsorption depends on both adsorbate and adsorbent
8.	Rate of adsorption controlled by resistance mass transfer	Rate of adsorption controlled by resistance reaction

(http://www.inchem.org/documents/eintro/eintro/abreviat.htm)

Table 3.2: Various Commercial Adsorbents.

Adsorbent	**Properties& method of preparation**	**Application**
Silica gel	Hard, granular and very porous product made from gel precipitated by sodium silicate.	Drying of gases refrigerants, organic solvents. Desiccant in packing and double glazing. Due point control of natural gas.
Activated alumina	Hard, hydrated aluminum hydroxide which is activated by heating to drive moisture.	Dry of gases,organic solvents, transformer oils. Desiccant in packing and double glazing. Removal of HCl from hydrogen.
Carbon	Activated carbon is the residue obtained from various carbonaceous material like coal,wood,paper mills sludge, agro waste.	Nitrogen from air. Recovery of certain vapors. Purification of helium. Water purification.
Polymeric and Resin	These are hydrophobic adsorbents which are obtained from pyrolysis and activation of polymeric compounds.	Separation of fatty acids from water and toluene. Separation of aromatics from aliphatics. Removal of colour from syrups.
Fuller's Earth	These are natural clays The clay is heated and dried during which it develops a porous structure.	Treatment of edible oils. Removal of organic pigments. Refining of mineral oils.
Zeolites	It is insoluble and chemically stable aluminum silicate mineral that was formed from the glass component of volcanic ash.	Removing water from azeotropes. Sweetening sour gases and liquids. Purification of hydrogen. Separation of ammonia and hydrogen. Recovery of carbon dioxide. Separation of xylene and ethyl benzene.

Table 3.3: Typical Non Conventional Adsorbents.

Adsorbent	**Application**
Coal fly ash	Heavy metals, organic compounds. COD of waste water, phosphate, phenolic compounds.
Bagasse fly ash	Sugar and distillery effluents, heavy metals, chlorinated phenols.
Peat	Heavy metals, cyanide, phosphate, oil in water, color and dyes.
Lignite	Ammonia dyes.
Activated carbon from lignin sludge, bark, rice husk.	Color, heavy metals, dyes, distillery waste.
Coconut husk, peanut skin, bagasse pitch.	Heavy metals, dyes.
Hardwood, softwood, saw dust.	Heavy metals, dyes, COD.
Waste rubber.	Heavy metals.
Hematite, slag.	Heavy metals.
Tannery hair	TOC, soluble organic dyes, virus.
China clay, wollastonite.	Dyes, oxalic acid and Fluorides.

(http://www.inchem.org/documents/icsc/icsc/eics0102.htm)

EXPERIMENTAL PROGRAMME

4.1 GENERAL

In the present study, activated carbon has been utilized for the treatment of benzaldehyde bearing aqueous solution. Experimental details of the study have been presented in this chapter. These details include characterization of adsorbents, batch adsorption studies, and experimental details for the adsorption of benzaldehyde.

4.2 ANALYTICAL MEASUREMENTS

A double beam UV/VIS spectrophotometer (Perkin Eilmer 135) is used for the concentration measurement of benzaldehyde. For this purpose, first the wave length corresponds to maximum absorbance (λ_{max}) was determined from the plot between absorbance versus wavelength performed by taking a standard solution. λ_{max} for benzaldehyde was found to be 258nm. Throughout the further work this wave length is used for the concentration measurement. Then calibration curves were plotted between absorbance and concentration of standard benzaldehyde solution for further use (given in fig. 4.1).

4.3 BATCH EXPERIMENTAL PROGRAMME

Batch experimental programme was used throughout the experimental work i.e. to study the effect of important parameters like dose, Concentration, time and temperature at 30^{0}C. For each experimental run, 100ml of benzaldehyed solution of known concentration and a known amount of the adsorbent were taken in a 100 ml stoppered conical flask. This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of 160 rpm at 30^{0}C. Samples were withdrawn at appropriate time intervals. Some activated carbon particles remain suspended and do not settle down easily. Therefore, all the samples were centrifuged (Research Centrifuge, Remi scientific works, Mumbai) at 8000 rpm for 10 minute and analyzed for the residual benzaldehyde concentration. For the optimum amount of adsorbent per unit mass of adsorbate, a 100ml of benzaldehyde solution was contacted with different amounts of activated carbon respectively till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the benzaldehyde from the aqueous solution at different time intervals. For adsorption isotherms, benzaldehyde solution of different concentrations were agitated with the known amount of adsorbent till the equilibrium was achieved. The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 293, 303 and 313 K. Blank experimental runs, with only the adsorbent in 100 ml of double-distilled water, were conducted simultaneously at similar conditions to account for any benzaldehyde removal by the adsorbents and adsorbed by glass containers.

Table 4.1: Variation of Adsorbents with Concentration of Benzaldehyde.

Concentration (ppm)	Absorbance
1	0.1077
2	0.1715
4	0.3023
6	0.4539
8	0.6019
10	0.761
12	0.8713
15	1.126

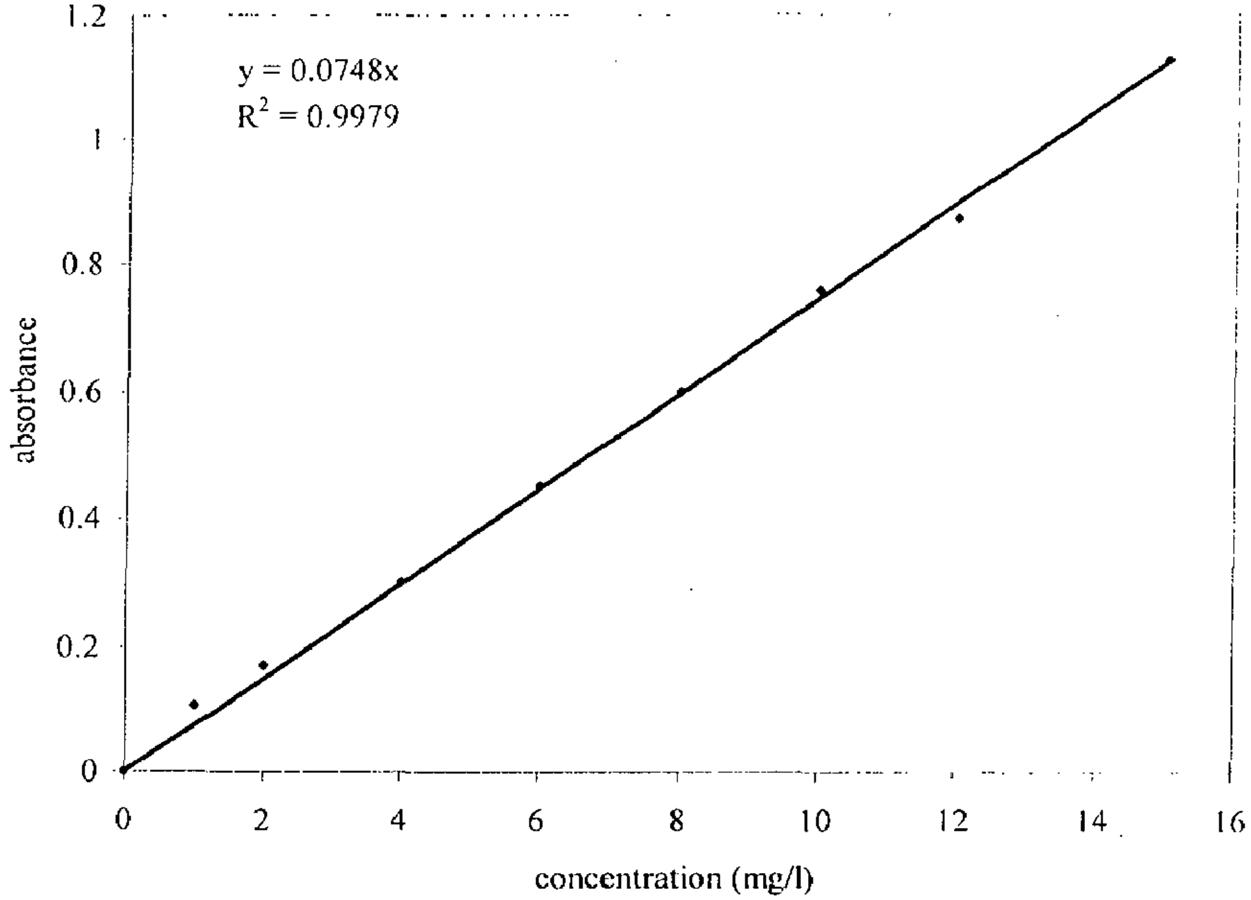

Fig.4.1 Variation of absorbance with concentration of benzaldehyde.

RESULT AND DISCUSSION

5.1 GENERAL

This chapter deal with the various results interpreted from the experimental data. These results include characterization of activated carbon and batch adsorption studies.

5.2 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

For structural characteristics, scanning electron microscope (SEM) analysis and was carried out. Scanning electron microscopic photograph (Figs.5.1) of activated carbon reveals their surface texture and porosity. The photomicrograph of activated carbon its fibrous structure of activated carbon. SEM of activated carbon (Fig. 5.1) shows fibrous structure with large pore size with strands in each fibre.

5.3 BATCH ADSORPTION STUDIES

In order to study the effect of different parameters the batch operations were found most suitable. Batch adsorption experiments were carried out in 100 ml stoppered conical flask for removal of benzaldehyde from synthetic solutions of known concentrations by using ACL. The effect of various operating parameters, viz. concentration, adsorbent dose and contact time is studied and presented here.

5.3.1 Effect of Adsorbent dose

The effect of activated carbon dose on the extent of solute adsorption was investigated by varying the dose from 0.05 to 1.2g per 100mL under the selected initial solute concentration (100mg/L). The agitation speed (160rpm) and temperature (397K) were selected for the experiment. It is observed that as the dose increases, the amount of solute adsorbed increases and reaches a maximum value corresponding to a certain dose (Fig.5.2). The minimum amount of adsorbent corresponding to the maximum adsorption is declared as the optimum dose. The optimum dose observed in the present study is 0.4g per 100mL of the solution of adsorbent dosage for activated carbon.

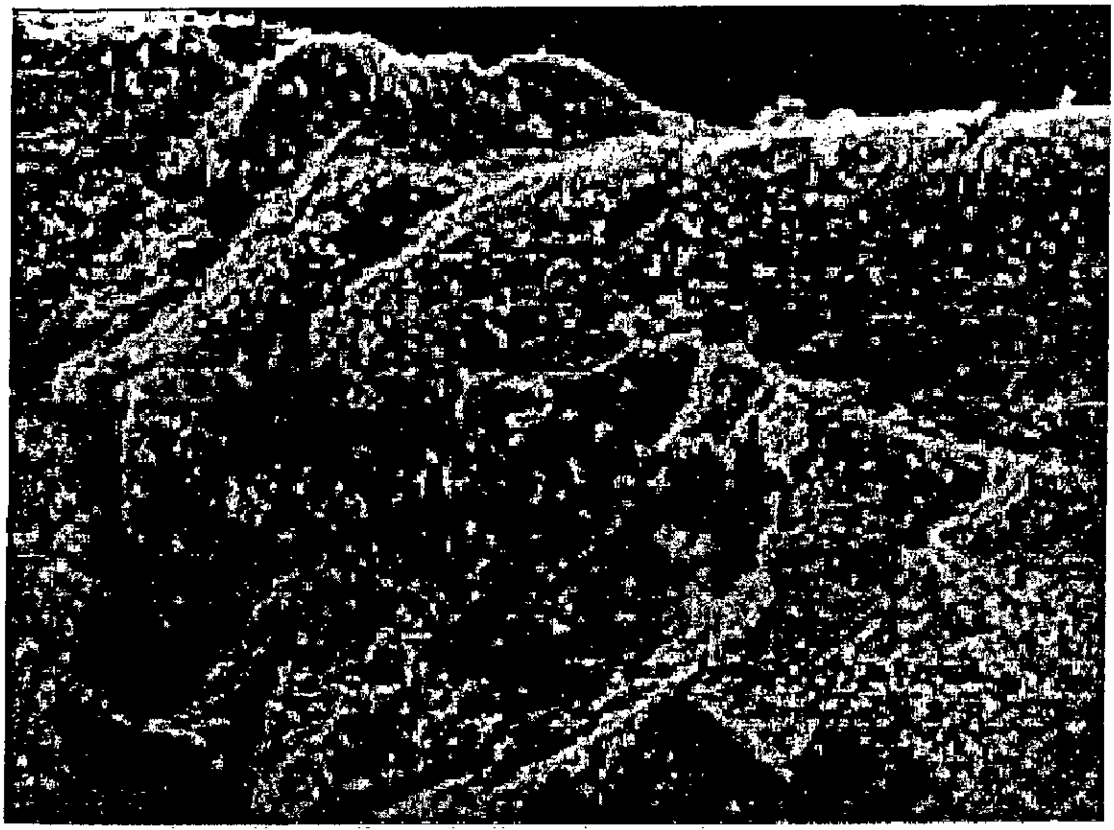

Fig.5.1 Scanning electron micro graph of activated carbon

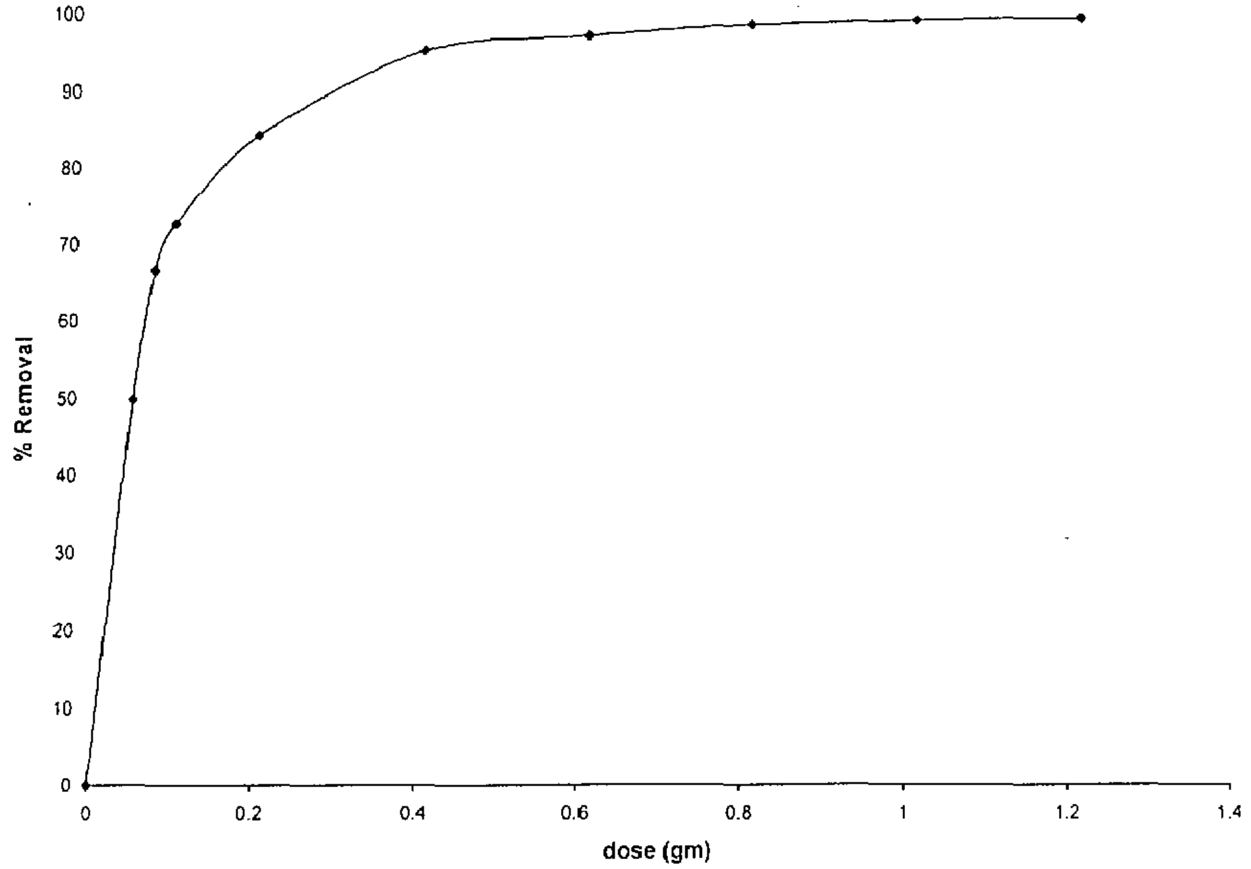

Fig.5.2 Effect of adsorbent mass on adsorption of benzaldehyde for activated carbon (Temp=30°C, Vol of sample=100 ml, C0=100mg/l)

5.3.2 Effect of contact time

The effect of contact time on the removal of benzaldehyde by activated carbon at C_0=100 mg l^{-1} are given in Figs.5.3. The contact time curves show rapid adsorption of benzaldehyde in the first 60-70 min, thereafter, the rate of adsorption rate decreases gradually and the adsorption reaches equilibrium around 4 hour.

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The effect of contact time for the adsorption of benzaldehyde by activated carbon was studied for a period of 10 h for initial benzaldehyde concentrations of 100mg/l at 25°C. Activated carbon dosage was 0.4g/100ml of benzaldehyde. The solutions were kept in contact with activated carbon for 10h, although no significant variation in residual benzaldehyde concentration was detected after 4 h of contact time. Thus, after 4 h of contact, a steady-state approximation was assumed and a quasi-equilibrium situation was accepted. The curves of contact time are single, smooth and continuous leading to saturation. These curves indicate the possible monolayer coverage of benzaldehyde on the surface of activated carbon.

Increase in contact time up to 10 h showed that the benzaldehyde removal by activated carbon increases only by about 0.5% over those obtained for 4 h. contact time. Aggregation of benzaldehyde with the increase in contact time makes it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites. This aggregation negates the influence of contact time as the mesopores get filled up and start offering resistance to diffusion of aggregated benzaldehyde in the adsorbents. This is the reason why an insignificant enhancement in adsorption is effected in 10 h as compared to that in 4 h. The difference in the adsorption values at 4 h and at 10 h is very small, further experiments were conducted for 4 h contact time only. The curves are single, smooth and continuous leading to saturation. The adsorption curves of contact time indicate the possible mono-layer coverage of benzaldehyde on the surface of activated carbon.

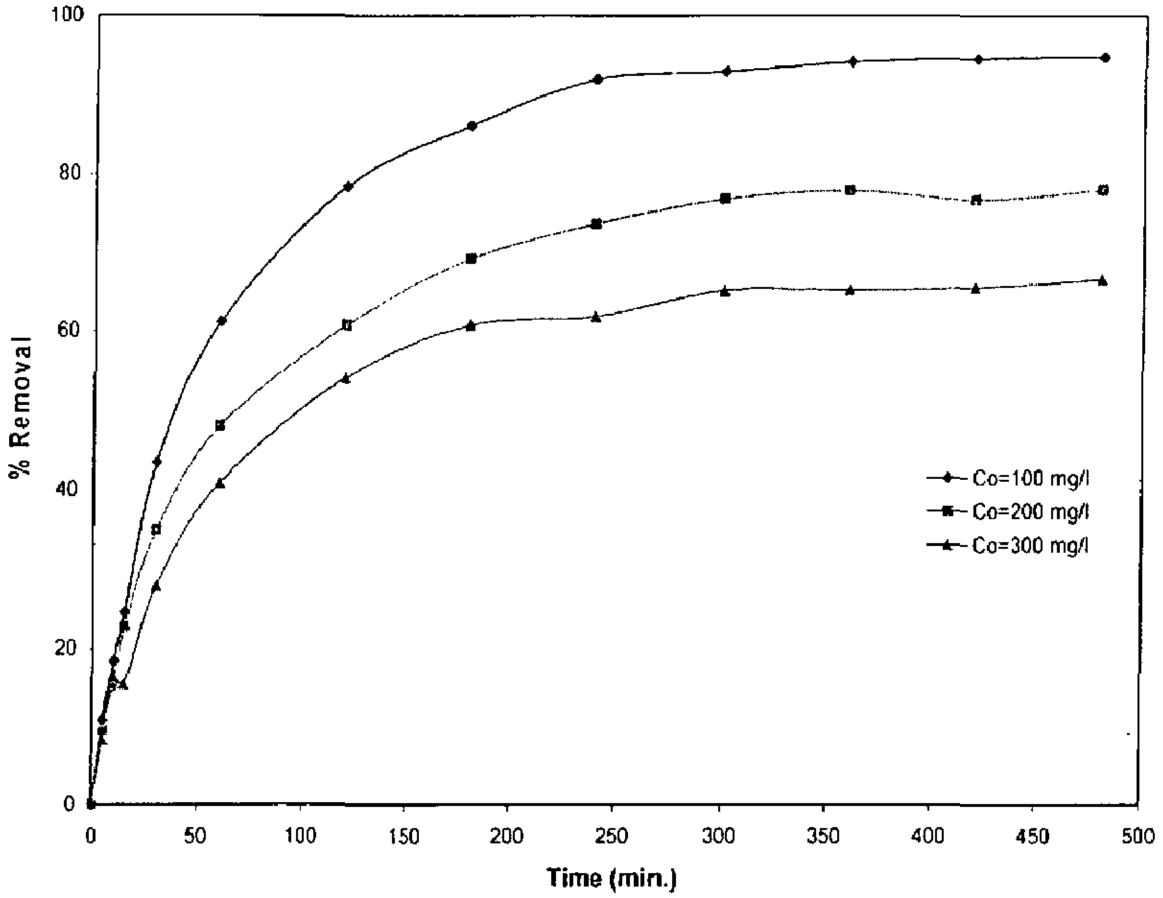

Fig.5.3 Effect of contact time on adsorption of benzaldehyde by activated carbon

5.4 ADSORPTION KINETICS STUDY

5.4.1 Pseudo-first-order model

The pseudo-first-order equation is given as:

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \qquad (5.1)$$

where, q_t is the amount of adsorbate adsorbed at time t (mg g^{-1}), q_e is the adsorption capacity at equilibrium (mg g^{-1}), k_f is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min). The integration of Eqn. (5.1) with the initial condition, q_t=0 at t=0 leads to following equation (Ho and McKay, 2000).

$$\log(q_e - q_t) = \log q_e - \frac{k_f}{2.303}t \qquad (5.2)$$

The values of adsorption rate constant (k_f) for benzaldehyde adsorption on activated carbon at C_0=100, 200 and 300mg/l were determined from the plot of log ($q_e - q_t$) against t (Fig. 5.4).

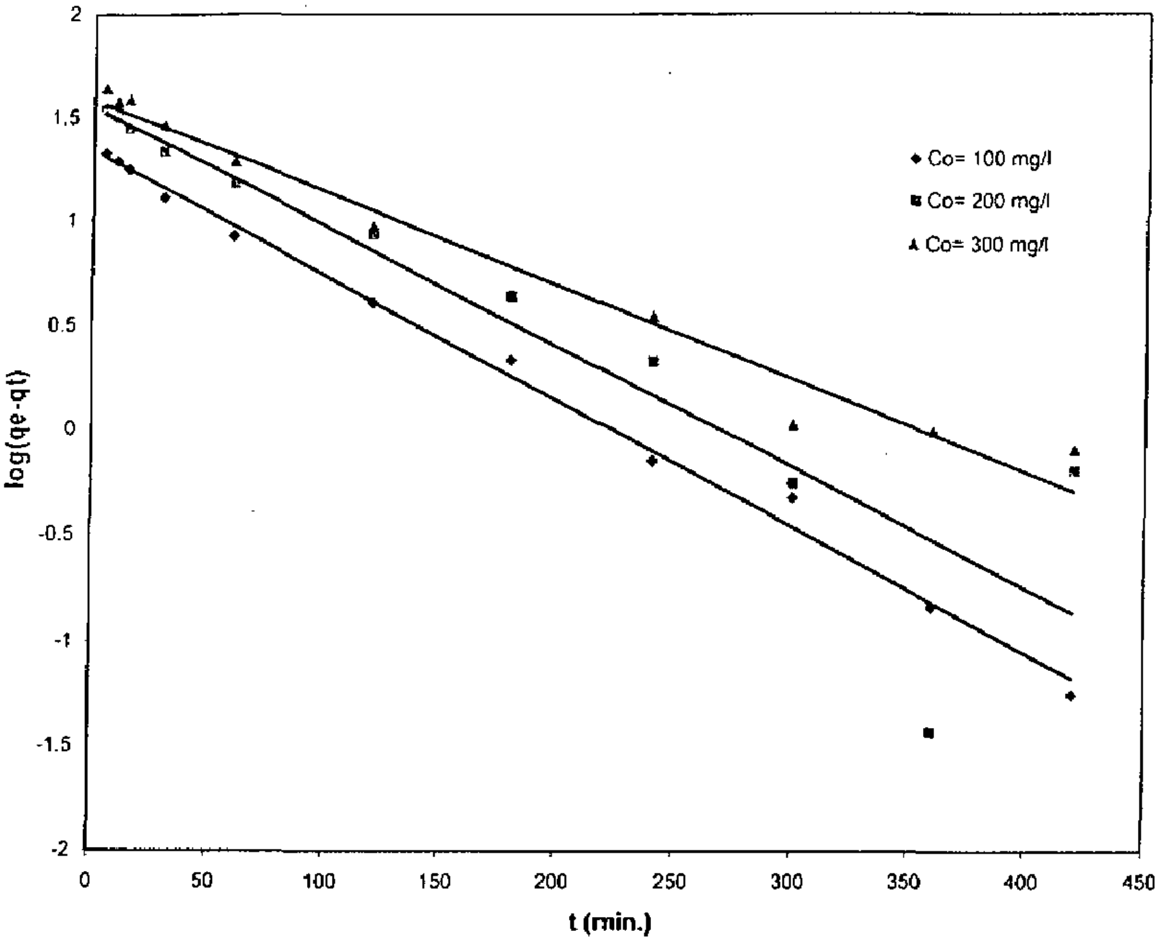

Fig. 5.4 Pseudo first order plot for the removal of benzaldehyde by activated carbon

5.4.2 Pseudo-second-order Model

The pseudo-second-order model is represented as (Ho and McKay, 1999):

$$\frac{dq_t}{dt} = k_S (q_e - q_t)^2 \qquad (5.3)$$

where, k_S is the pseudo-second-order rate constant (g/mg min).

Integrating Eqn. (5.3) and q_t =0 at t=0, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_S q_e^2} + \frac{1}{q_e} t \qquad (5.4)$$

The initial sorption rate, h (mg/g min), at t→0 is defined as

$$h = k_S q_e^2$$

Fig. 5.5 show the plot of t/q_t versus t at C_0= 100, 200 and 300mg/l. The q_e is obtained from the slope of the plot and the h value is obtained from the intercept. Since q_e is known from the slope, k_S can be determined from the h value. The k_S and h values as calculated from the figures are listed in Table 5.1. It can be seen from the table that the calculated correlation coefficients are also closer to unity for pseudo-second-order kinetics than that for the pseudo-first-order kinetic model. Therefore, the sorption of benzaldehyde can be approximated more appropriately by the pseudo-second-order kinetic model.

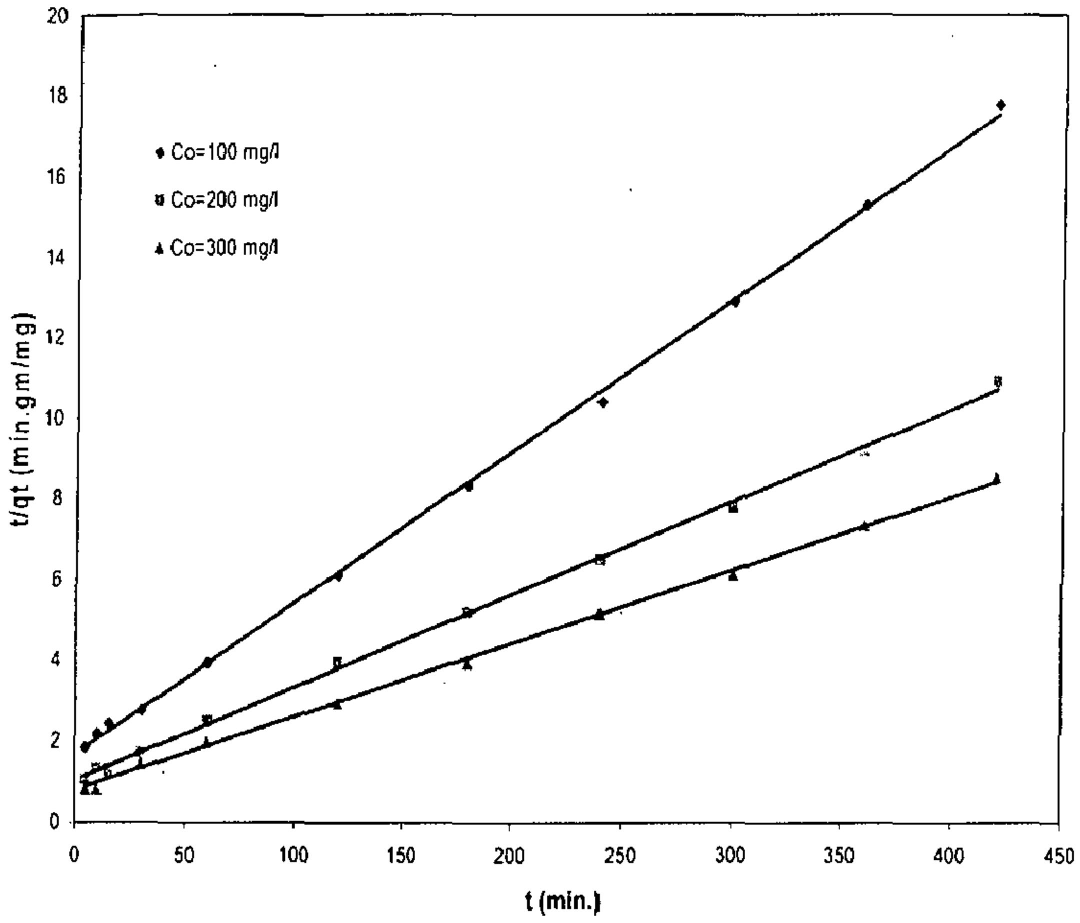

Fig. 5.5 Pseudo second order plot for the removal of benzaldehyde by activated carbon

5.5 INTRA-PARTICLE DIFFUSION STUDY

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

$$q_t = k_{id} t^{1/2} + I \tag{5.5}$$

where, k_{id} is the intra-particle diffusion rate constant (mg/g min$^{1/2}$) and I is the intercept (mg/g). Plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept I when adsorption mechanism follows the intra-particle diffusion process. Figs. 5.6 present a plot of q_t versus $t^{1/2}$ at C_0 = 100, 200 and 300 mg/l for benzaldehyde adsorption. The values of I (Table 5.1), gives an idea about the thickness of the boundary layer, i.e., the larger the intercept the greater is the boundary layer effect (Allen and Brown, 1995). The deviation of straight lines from the origin (Figs. 5.6) may be because of the difference between the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step (Poots et al., 1978). The values of intra-particle diffusion rate parameters are given in Tables 5.1.

5.5.1 Bangham's equation

Bangham's equation (Aharoni et al., 1979) is given as

$$\log\log\left(\frac{C_0}{C_0 - q_t m}\right) = \log\left(\frac{k_0 m}{2.303V}\right) + \alpha \log(t) \tag{5.6}$$

where, V is the volume of the solution (ml), and $\alpha\,(<1)$ and k_0 are constants. The double logarithmic plot, according to Eqn. 5.6 did not yield satisfactory linear curves for the benzaldehyde removal by the adsorbents shown in fig.5.7. This shows that the diffusion of adsorbate into the pores of the sorbent was not the only rate-controlling step (Tutem et al., 1998). It may be that both the film and pore diffusion were important to different extents in the removal process.

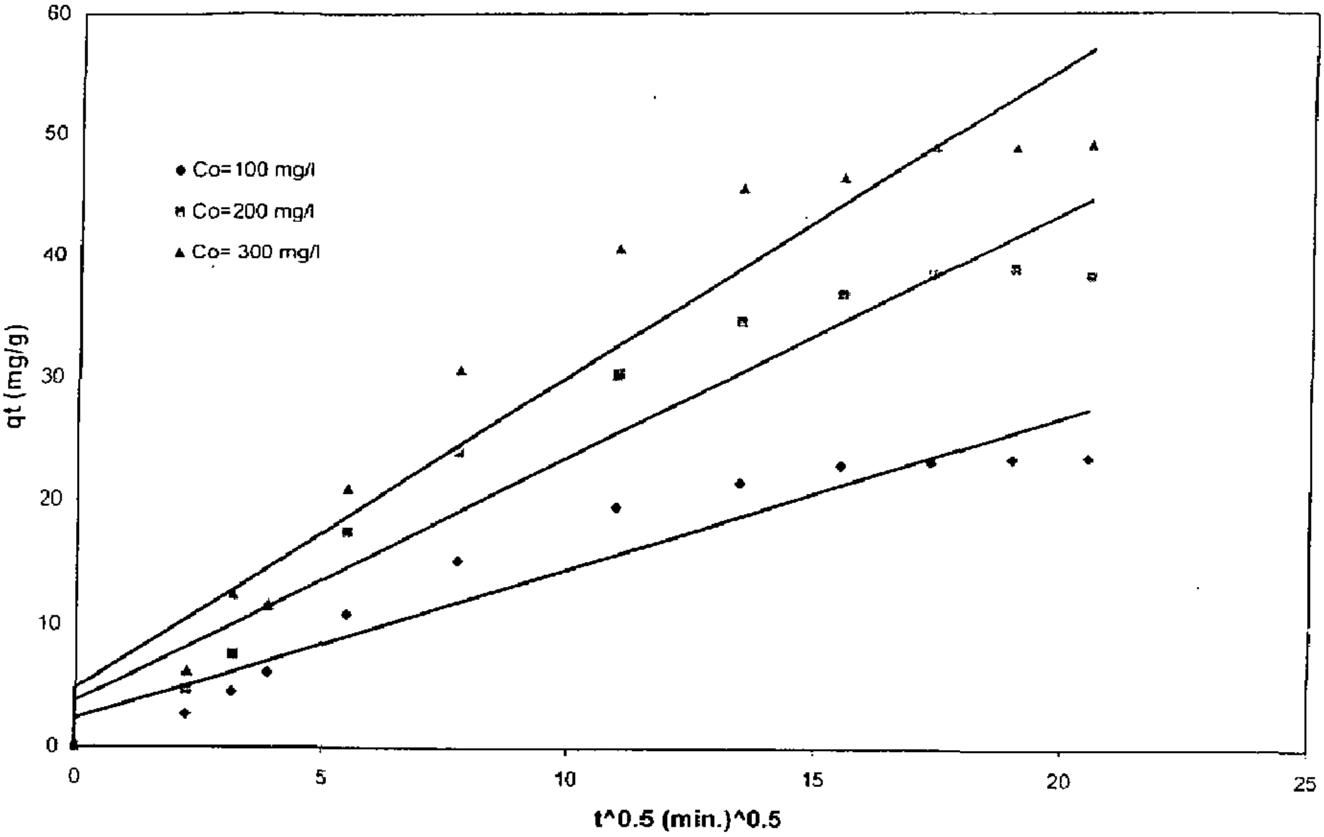

Fig. 5.6 Weber and Morris intra-particle diffusion plot for the removal of benzaldehyde by Activated carbon (T = 303 K, m = 4 g/l)

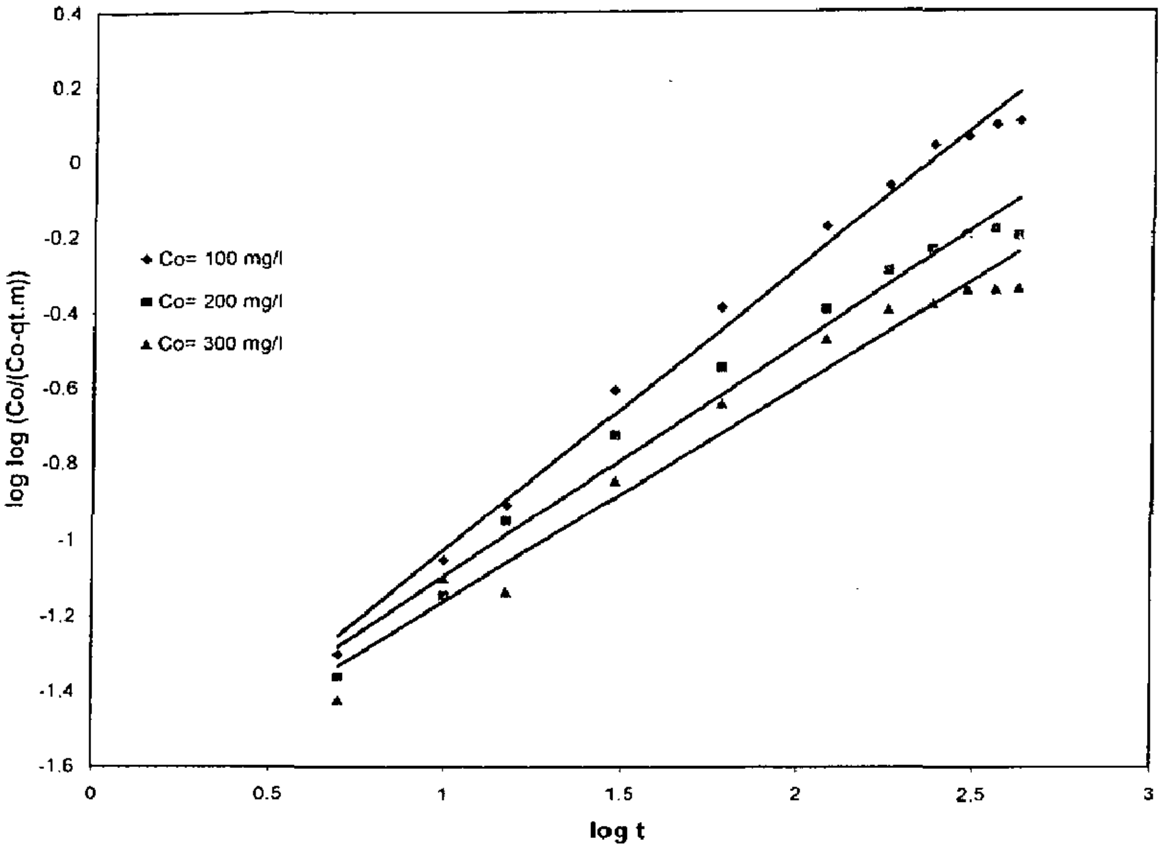

Fig. 5.7 **Bangham plot for the removal of benzaldehyde by activated carbon**

Table 5.1: Kinetic Prameters for the Removal of Benzaldehyde by Activated Carbon (C_0 = 100-300 mg/l, m = 4 g/l).

Pseudo-first-order model

C_0 (mg/l)	$q_{e,\exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	k_f (min)	R^2
100	23.7038	3.792024	0.013818	0.9953
200	39.01613	4.68703	0.0131271	0.849
300	49.93245	4.854955	0.0131332	0.9733

Pseudo-second-order model

C_0 (mg/l)	$q_{e,calc}$ (mg/g)	h (mg/g min	k_S (g/mg min)	R^2
100	26.5252	0.00085	1.21E-06	0.9993
200	43.29	0.0005174	2.76E-07	0.9989
300	54.94505	0.000418	1.38E-07	0.9982

Bangham model

C_0 (mg/l)	k_0 (g)	α	R^2
100	0.9728	0.7457	0.9909
200	1.1242	0.6134	0.9797
300	1.0741	0.5668	0.9689

W-M Intra-particle diffusion model

C_0 (mg/l)	k_{id} (mg/g min$^{1/2}$)	I_i (mg/g)	R^2
100	1.2324	2.2801	0.9201
200	1.9962	3.755	0.9351
300	2.5453	4.8492	0.9274

5.6 ADSORPTION EQUILIBRIUM STUDY

The presence of the amount of solute adsorbed per unit weight of the adsorbent as a function of the equilibrium concentration in bulk solution at constant temperature is termed the adsorption isotherm. In other words, the adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature. The adsorption isotherm in a batch equilibrium test is performed to determine suitability of adsorption treatment for a given application. Experimental isotherms are useful for describing adsorption capacity, i.e., for the selection of the most appropriate adsorbent and for the *preliminary determination of adsorbent dosage requirement. The isotherm plays a functional role* in predictive modeling procedure for analysis and design of adsorption systems. For mathematical modeling of the adsorption isotherm, several equilibrium models have been developed to describe adsorption isotherm relationships. Any particular one may fit experimental data accurately in one set of conditions, but fail entirely under another. No single model has been found to be generally applicable.

5.6.1 Freundlich and Langmuir isotherms:

Linearised form of Freundlich and Langmuir isotherm equations are given as

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \quad \text{(Linear form)} \tag{5.7}$$

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \quad \text{(Linear form)} \tag{5.8}$$

Figs.5.8 shows the Freundlich isotherm plots (ln Q_e vs ln C_e) for adsorption of benzaldehyde onto activated carbon at 293, 303 and 313K. Langmuir isotherm plot (C_e/Q_e versus C_e) are shown in Fig.5.9 for adsorption onto activated carbon. Freundlich and Langmuir isotherm parameter along with linear and non-linear correlation coefficients are given in table.5.2 activated carbon respectively. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L, which describes the type of pattern and is defined as $R_L=1/(1 + K_A C_0)$ indicates the nature of adsorption as

If	$R_L > 1$	Unfavorable
	$R_L = 1$	Linear
	$0 < R_L < 1$	Favourable
	$R_L = 0$	Irreversible

The value of R_L is found to be less than 1 for adsorption of benzaldehyde on activated carbon. So adsorption onto both the adsorbents is favorable. The values of 1/n were also found to be less than 1 showing favorable nature of adsorption.

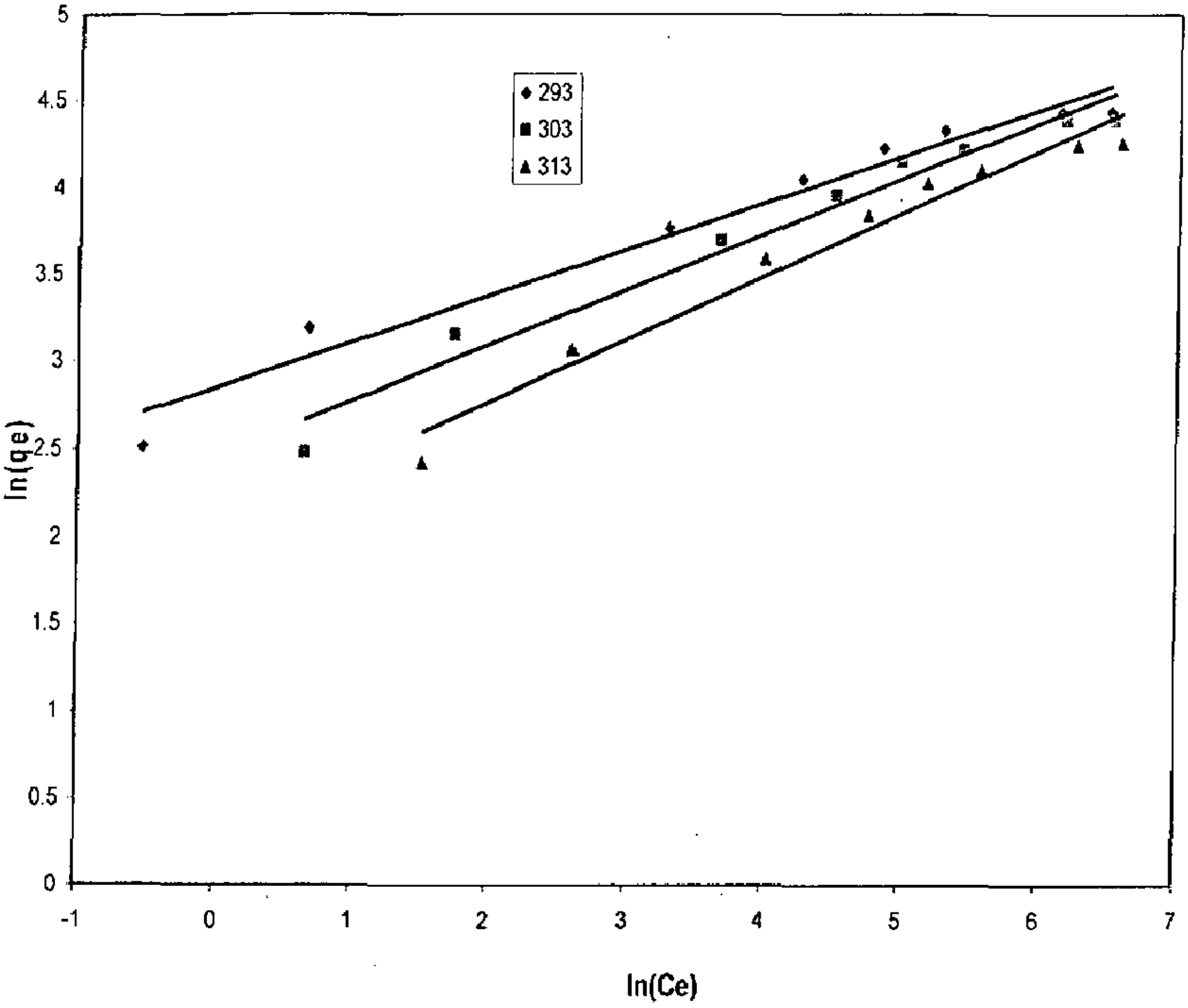

Fig.5.8 Freundlich isotherm for removal of Benzaldehyde by activated carbon

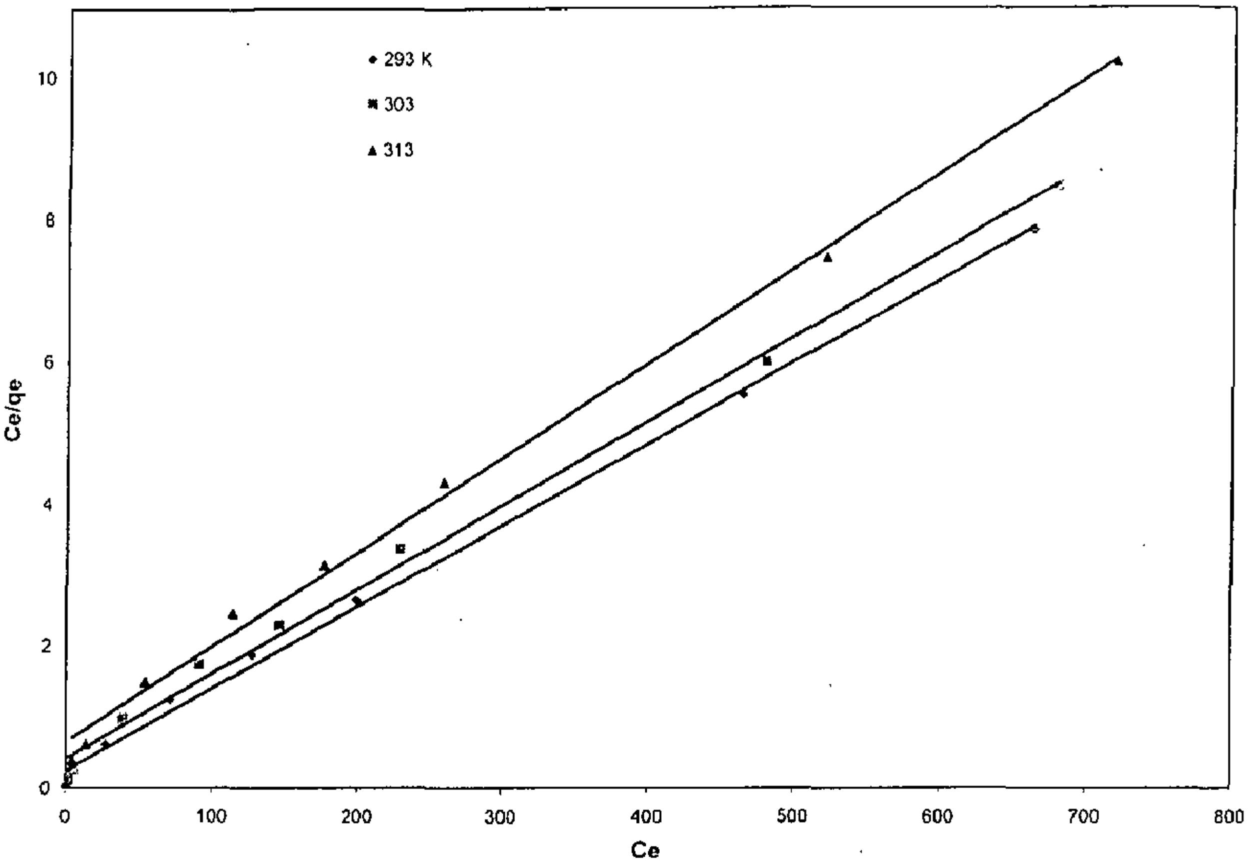

Fig.5.9 Langmuir isotherm for removal of Benzaldehyde by activated carbon

5.6.2 The Temkin isotherm:

It is given as

$$q_e = \frac{RT}{b}\ln(K_T C_e) \tag{5.9}$$

Which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{5.10}$$

$$\text{Where } B_1 = \frac{RT}{b}$$

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Temkin and Pyzhev, 1940; Kim et al. 2004). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_1 and K_T from the slope and the intercept, respectively. K_T is the equilibrium binding constant (l mol^{-1}) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. Fig.5.10 shows the Temkin isotherm plot for activated carbon. The Temkin isotherm parameters listed in Tables 5.2 activated carbon. It shows better only compared to Freundlich isotherm.

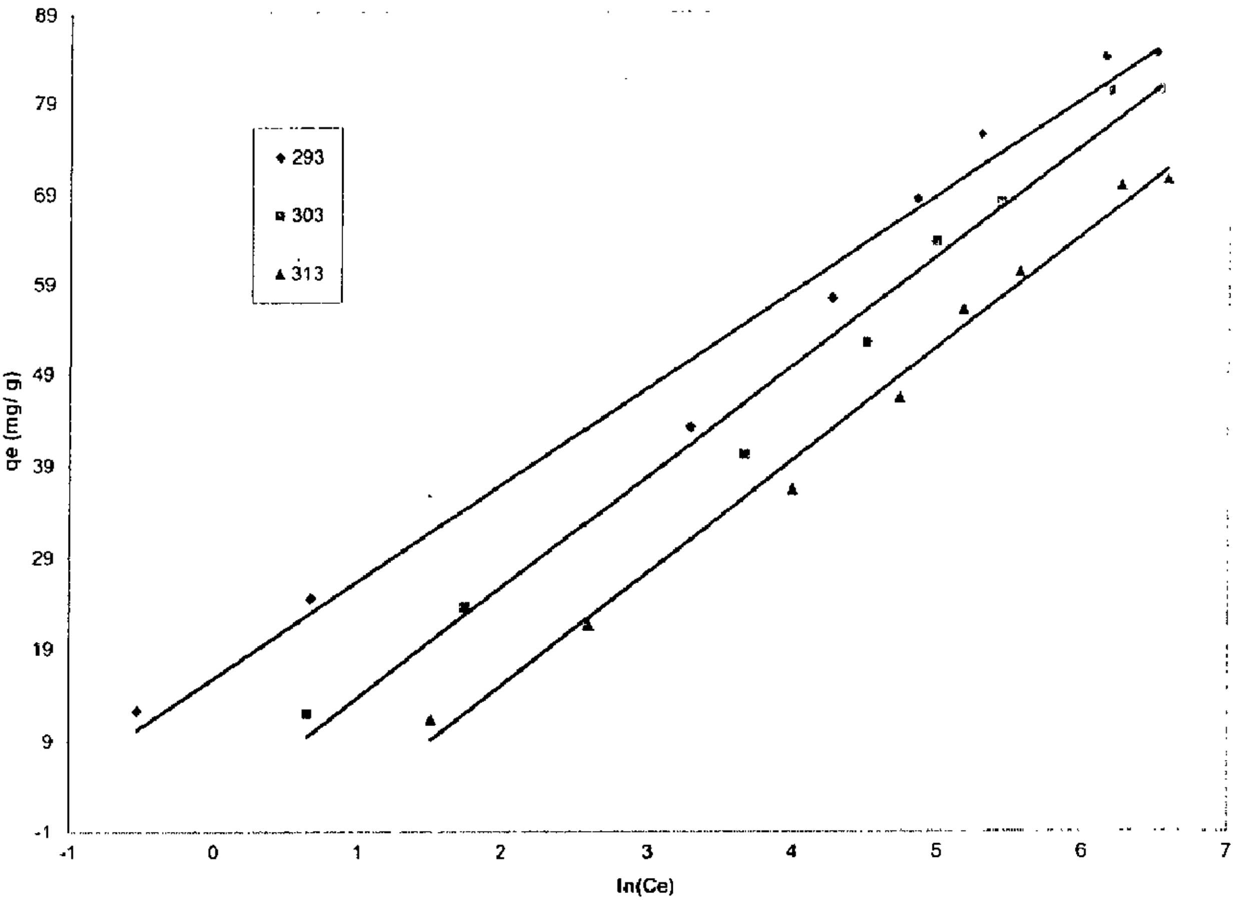

Fig.5.10 Tempkin isotherm for removal of Benzaldehyde by acticated carbon

Table 5.2: Isotherm Parameters for Adsorption of Benzaldehyde onto activated Carbon

Langmuir Isotherm

T (K)	K_L(l/mg)	q_m (mg/g)	R^2
293	0.0474	86.2069	0.9973
303	0.0288	84.03361	0.9952
313	0.020499	74.62687	0.9963

Freundlich Isotherm

T (K)	K_F ((mg/g)(mg/l)$^{-1/n}$)	1/ n	R^2
293	17.37444	3.767898	0.9671
303	11.85085	3.161555	0.9687
313	7.877417	2.791736	0.9659

Tempkin Isotherm

T (K)	K_T(l/mg)	B_1	R^2
293	4.452118	10.574	0.9814
303	1.150783	12.054	0.9844
313	0.462179	12.296	0.9902

5.7 ERROR ANALYSIS

Due to the inherent bias resulting from linearization, five different error functions of non-linear regression basin were employed in this study to find out the best-fit isotherm model to the experimental equilibrium data.

5.7.1 The sum of the squares of the errors (SSE)

This error function, SSE is given as

$$SSE = \sum_{i=1}^{n} \left(q_{e,calc} - q_{e,\exp}\right)_i^2 \tag{5.11}$$

Here, $q_{e,cal}$ and $q_{e,\exp}$ are, respectively, the calculated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg g^{-1}) and n is the number of data points. This most commonly used error function; SSE has one major drawback in that it will result in the calculated isotherm parameters providing a better fit at the higher end of the liquid phase concentration range. This is because of the magnitude of the errors, which increase as the concentration increases. The values of SSE are given in table.5.3 for activated carbon.

5.7.2 The sum of the absolute errors (SAE)

SAE is given as

$$SAE = \sum_{i=1}^{n} \left|q_{e,calc} - q_{e,\exp}\right|_i \tag{5.12}$$

The isotherm parameters determined by this method provide a better fit as the magnitude of the errors increase, biasing the fit towards the high concentration data.

5.4.2 The average relative error (ARE)

ARE (Kapoor and Yang, 1989) is given as

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{(q_{e,\exp} - q_{e,calc})}{q_{e,\exp}} \right|_i \tag{5.13}$$

This error function attempts to minimize the fractional error distribution across the entire concentration range. The values of ARE are given in Table 5.3 for activated carbon.

5.7.4 The hybrid fractional error function (HYBRID)

HYBRID is given as

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{(q_{e,\exp} - q_{e,calc})}{q_{e,\exp}} \right]_i \qquad (5.14)$$

This error function was developed (Porter and McKay, 1999) to improve the fit of the ARE method at low concentration values. Instead of n as used in ARE, the sum of the fractional errors is divided by (n-p) where p is the number of parameters in the isotherm equation.

5.7.5 Marquardt's percent standard deviation (MPSD)

MPSD (Marquardt, 1963) has been used by a number of researchers in the field (Wong et al., 2004, Seidel and Gelbin, 1988, Ng et al, 2003) to test the adequacy and accuracy of the model fit with the experimental data. It has some similarity to the geometric mean error distribution, but was modified by incorporating the number of degrees of freedom. This error function is given as;

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left(\frac{(q_{e,meas} - q_{e,calc})}{q_{e,meas}} \right)_i^2} \qquad (5.15)$$

The values of MPSD error functions are given in table 5.2.

5.7.6 Choosing best-fit isotherm based on error analysis:

The values of the five error functions are presented in table 5.3. By comparing the results of the values of the error functions, it is found that Langmuir isotherm best-fitted the isotherm data for benzaldehyde adsorption on activated carbon at 293K. However, Tempkin model best-fits the benzaldehyde adsorption isotherm data for the activated carbon 298K. It may, however, be noted that the non-linear correlation coefficients, R^2 and the error analysis values are similar for the Langmuir and Tempkin isotherms and hence any one of the isotherms could be used for benzaldehyde adsorption on activated carbon.

5.5 THERMODYNAMIC STUDY

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation

$$\Delta G^0 = -RT \ln K \qquad (5.16)$$

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (5.17)$$

Combining above two equations, we get

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \qquad (5.18)$$

Where ΔG^0 the free energy change (kJ/mol) is, ΔH^0 is the change in enthalpy (kJ/mol). ΔS^0 is the entropy change (kJ/mol K), T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol K). Thus ΔH^0 can be determined by the slope of the linear Van't Hoff plot i.e. as $\ln K$ versus $(1/T)$, using equation:

$$\Delta H^0 = \left[R\frac{d \ln K}{d(1/T)}\right] \qquad (5.19)$$

ΔG^0, ΔH^0 and ΔS^0 as calculated are given in Table 5.4 for adsorption of benzaldehyde onto activated carbon. The negative ΔH^0 value confirms the exothermic nature of the overall-sorption process. The adsorption process in the solid-liquid system is a combination of two processes:

- The desorption of the molecules of solvent (water) previously adsorbed
- The adsorption of adsorbate species. The benzaldehyde ions have to displace more than one water molecule for their adsorption and these results in the exothermicity of the adsorption process. The positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of the activated carbon towards benzaldehyde. Also, positive ΔS value corresponds to an increase in the degree of freedom of the adsorbed species. ΔG^0 Values were negative indicating that the sorption process led to a decrease in Gibbs free energy. Negative ΔG^0_{ads} indicates the feasibility and spontaneity of the adsorption process.

Table 5.3: Isotherm error analysis for adsorption of benzaldehyde onto activated carbon

Isotherm Temperature	HYBRID	MPSD	SSE	SAE	ARE
293K					
Langmuir	16.32	85.28825	691.9579	0.9239	26.1141
Freundlich	-3.05317	33.78722	260.8211	9.8219	9.4438
Temkin	-0.75705	30.76964	169.7203	7.2270	8.6004
303K					
Langmuir	12.47625	62.6629	310.5697	0.9013	19.1865
Freundlich	-0.89129	35.01909	258.5409	2.6042	9.7881
Temkin	1.910035	22.45629	63.0040	-0.2995	6.2767
313K					
Langmuir	-1.38694	44.66046	214.0466	18.8210	13.6744
Freundlich	-0.7467	35.87169	263.3080	3.3282	10.0264
Temkin	1.82353	22.03454	47.3960	-0.4621	6.1588

Table 5.4: Thermodynamics Study

Isotherm	ΔG^0 **(J/mol K)**			ΔH^0 **(KJ/mol)**	ΔS^0 **(KJ/mol K)**
	293 K	**303 K**	**313 K**		
Langmuir	-20.7634	-20.2169	-19.9994	-32.009	-38.5582
Temkin	-31.829	-29.5071	-28.107	-86.510	-187.115
Frendlich	-18.3186	-17.98	-17.5106	-30.133.9	-40.2556

CHAPTER #6

CONCLUSION AND RECOMMANDATIONS

6.1 CONCLUSIONS

The following major conclusions can be drawn from the present work are given below:

1. Activated carbon is viable alternatives for the removal of benzaldehyde from waste water through adsorption process as the removal efficiencies are around 98%.
2. Percent removal of benzaldehyde increases with the increase in adsorbent dose for activated carbon, however, it decreases with increase in benzaldehyde concentration for both the adsorbents.
3. Kinetic study shows that adsorption of benzaldehyde on activated carbon follow the first order kinetics.
4. Freundlich isotherm model best-fits the benzaldehyde adsorption isotherm data at all the temperatures.
5. Adsorption capacity of activated carbon for benzaldehyde removal decreases with increase in temperature for the adsorbent showing the exothermic nature of adsorption.
6. The results prove that granular activated carbon is good adsorbent for adsorption of benzaldehyde. Granular activated carbon can be used as a potential adsorbent for the removal of benzaldehyde.
7. The high negative value of ΔG for both the adsorbents suggest that the process is quite feasible on thermodynamic point of view.

6.2 RECOMMENDATIONS

1. Further pilot scale studies are required to evaluate the suitability of activated carbon for the adsorptive removal on plant scale.
2. Adsorption column studies shall be carried out at different inlet concentrations, different column diameter to get the characteristic dependence of the adsorption capacity and other parameters. Design parameter for scaled up adsorption column should thereafter be fixed for the removal of benzaldehyde form waste water.
3. Costing of the adsorption based on industrial scale treatment system shall be carried out to popularize the adsorption technique with activated carbon.
4. Many more combination of different adsorbents could be tried to get much better result.

REFERENCES

1. Annesine, M. C., Gironi, F., Ruzzi, M., and Tomei, C., "adsorption of organic compound onto activated carbon" War. Res. Vol. 21, No. 5, pp. 567-571, (1987).

2. Chen, P. H., Christina Hui Jenq, and Kuei Mei Chen "Evolution of granular activated carbon for removal of trace organic compounds in drinking water", vol. 22, no. 3, pp 343-359, (1996).

3. Fuertes, A.B., Marban, G., Nevskaia, D.M.,"Adsorption of volatile organic compounds by means of activated carbon fibre-based monoliths", Carbon 41, 87–96, (2003).

4. Giraudet, S.,Pre, P., Tezel, H., Le Cloirec, P., "Estimation of adsorption energies using physical characteristics of activated carbons and VOCs' molecular properties", Carbon 44, 1873–1883, (2006).

5. Ho Y.S., McKay G., Pseudo-second order model for sorption processes, Process Biochemistry. 34, 51-65, (1999).

6. Kuiper, A. E. T., Medema, J., and Van Bokhoven, J. J. G. M., "Infrared and Raman Spectra of Benzaldehyde Adsorbed on Alumina", JOURNAL OF CATALYSIS 29, 49-48, (1973).

7. Lichtenberger, J., Sirena, C., Michael D., "In situ FTIR study of the adsorption and reaction of 2-hydroxyacetophenone and benzaldehyde on MgO", Journal of Catalysis 238,165–176, (2006).

8. Poots V.J.P., Mckay G., Healy J.J., The removal of acid dye from effluent using natural adsorbents-II, Wood Water Research. 10, 1067, (1976).

9. Shinä, H.S., Rogers P.L., "Biotransformation of benzeldehyde to L-phenylacetylcarbinol. an intermediate in L-ephedrine production, by immobilized Candida utilis". Appl Microbiol Biotechnol, 44:7-14, (1995).

10. Sardar, S.A., Duschek, R., Blyth, R.I.R., Netzer, F.P., Ramsey M.G., "The bonding of aldehydes on aluminium: benzaldehyde on Al(111)", Surface Science 468, 10–16, (2000).

11. Shen, B.C., Fana, L.T., Chenb, W.Y., "Stochastic modeling of adsorption in a batch system" Journal of Hazardous Materials 38, 353-371, (1994).

12. Snoeyink, V. L., and Chen, A.S.C., "Removal of organic micropollution by coagulation and adsorption", The Science of the Total Environment, 47, 155-167, (1985)

13. Temkin, M.J., Pyzhev, V., Acta Physiochim. URSS 12, 217, (1940).

14. Toles, C. A., Marshall, W. E., and Johns, M. M., "Granular activates carbon from nutshells for the uptake of metals and organic compounds", Carbon Vol. 35, No. 9, pp. 1407-1414, (1997).

15. Tutem E., Apak R., Unal C.F., Adsorptive removal of chlorophenols from water by bituminous shale, Water Research 32, 2315, (1998).

16. Wong Y.C., Szeto Y.S., Cheung W.H., McKay G., Adsorption of acid dyes on chitosan—equilibrium isotherm analyses, Process Biochem. 39, 693, (2004).

17. http://www.speclab.com/compound/m8315.htm

18. http://www.omikron-online.de/cyberchem/aroinfo/fen_no.htm

19. http://en.wikipedia.org/wiki/Benzaldehyde

20. http://ptcl.chem.ox.ac.uk/MSDS/toxicity_abbreviations.html

21. http://msds.ehs.cornell.edu/msds/msdsdod/a127/m63056.htm

22. http://www.pesticideinfo.org/Docs/ref_general2.html

23. http://www.faizkaskar.8k.com/p.html

24. http://www.dsm.com/en_US/html/dsp/products_sp_benzaldehyde.htm

25. http://ntp.niehs.nih.gov/ntp/htdocs/structures/3d/TR378.mol

26. http://www.inchem.org/documents/eintro/eintro/abreviat.htm

27. http://www.inchem.org/documents/icsc/icsc/eics0102.htm

28. http://www.inchem.org/documents/jecfa/jeceval/jec_165.htm

29. http://www.inchem.org/documents/sids/sids/100527.pdf