EQUILIBRIUM AND KINETIC MODELING FOR THE ADSORPTIVE REMOVAL OF FURFURAL FROM AQUEOUS SOLUTION USING LOW-COST ADSORBENT

A DISSERTATION

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(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 **"EQUILIBRIUM AND KINETIC MODELING FOR THE ADSORPTIVE REMOVAL OF FURFURAL FROM AQUEOUS SOLUTION USING LOW-COST ADSORBENT"** 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 the supervision of **Dr. I. D. Mall**, 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.

Date: June 29, 2006
Place: Roorkee

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CERTIFICATE

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

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ASHWANI KUMAR SAHU

ABSTRACT

Furfural is a colourless, readily volatile oily liquid, with a pungent aromatic odour. Besides being used in solvent extraction processes in the petroleum refining industry, furfural has wide variety of other uses e.g. as solvent, ingredient of phenolic resins, chemical intermediate, weed killer, fungicide and also as a flavouring agent. Evaporation condensate from sulfite pulping processes used in the pulp and paper industry is a major source of furfural contamination in the effluent water streams. Levels of furfural in sulfite evaporator condensate, which represents about 15% of the wastewater flow from pulp mills, have been reported in the range of 10-1280 mg/l. Synthetic rubber plant wastewater has been found to have 1.7 g/l furfural. At the workplace, furfural may enter the body by the respiratory as well as the percutaneous route. Furfural is an irritant of the skin, mucous membranes and respiratory track. Concentration of 1.9 to 14 ppm produces symptoms of irritation in exposed persons. In large lube units, furfural contamination in effluent water streams may reach upto 2% (w/w) furfural. Solvent extraction may be used to recover furfural from wastewater, constraints affect the ease of solvent recovery and solvent solubility in the water streams. The polymeric adsorbent XAD-4 and XAD-7 have been used for removal of furfural from pretreated and hydrolyzed plant biomass. Biological treatments for the degradation of furfural which includes aerobic and anaerobic processes. However, these processes are costly and cannot be used by small industries to treat furfural-laden wastewater.

Present study deals with equilibrium and kinetic modeling for the adsorptive removal of furfural from aqueous solution using low-cost adsorbent viz. bagasse fly ash (BFA) and to explore the possibility of bagasse fly ash as a low cost adsorbent for the removal of furfural from aqueous solution. The economic feasibility and adsorptive capacity of bagasse fly ash has been also compared with activated carbon commercial grade. Proximate analysis of adsorbents showed 32.90 and 77.82 % fixed carbon in BFA and ACC, respectively. Aqueous solutions of different furfural concentrations were prepared in laboratory, using double distilled water. Batch studies were performed to evaluate the influence of various experimental parameters viz. initial pH, adsorbent dose, contact time, initial concentration and temperature on the removal of furfural.

Optimum initial pH(pH_0) of aqueous solution for furfural removal was found to be $pH_0 \approx 5.5$ for furfural-BFA system, whereas, in furfural-ACC system, change in removal was insignificant with variation in pH_0. Adsorbent dose (m) of 4 g/l and 10 g/l were found for BFA and ACC, respectively. Equilibrium time as achieved 4 h and 6 h for BFA and ACC, respectively. The adsorption of furfural onto both the adsorbents, BFA and ACC followed pseudo-second-order kinetics. Equilibrium adsorption data was analyzed by Freundlich, Langmuir, Dubinin–Raduskevich, Redlich–Peterson and Temkin isotherm equations, using regression and error analysis. Redlich-Peterson isotherm was found to best represent the data for furfural adsorption onto both the adsorbents. Adsorption of furfural on BFA and ACC is favourably influenced by a decrease in the temperature of the operation. The high negative value of change in Gibbs free energy (ΔG) indicates the feasible and spontaneous adsorption of furfural on BFA and ACC.

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NOMENCLATURE

BFA	Bagasse fly ash
ACC	Activated carbon commercial grade
C_0	Initial concentration of adsorbate solution (mg/ l)
C_e	Concentration of adsorbate solution at equilibrium (mg/ l)
$1/n$	Heterogeneity factor, dimensionless
a_R	Constant of Redlich-Peterson isotherm (l/mg)
h	Initial sorption rate (mg/g min)
I	Constant that gives idea about the thickness of boundary layer (mg/g)
k_0	Constant in Bangham equation
k_f	Rate constant of pseudo-first-order adsorption model (1/min)
k_{id}	Intra-particle diffusion rate constant (mg/g min$l^{1/2}$)
k_S	Rate constant of pseudo-second-order adsorption model (g/mg min)
K_F	Constant of Freundlich isotherm, (mg/g)/(l/mg)$^{1/n}$
K_L	Constant of Langmuir isotherm, l/mg
K_R	Constant of Redlich-Peterson isotherm, l/g
K_T	Temkin isotherm constant, (l/mg)
m	Mass of adsorbent per liter of solution, g/l
n	Freundlich isotherm constant
q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium (mg/g)
q_t	Amount of adsorbate adsorbed per unit amount of adsorbent at time t (mg/g)

$q_{e,cal}$	Calculated value of solid phase concentration of adsorbate at equilibrium, mg/g
$q_{e,\exp}$	Experimental value of solid phase concentration of adsorbate at equilibrium, mg/g
q_m	Maximum adsorption capacity of adsorbent, mg/g
R	Universal gas constant, 8.314 J/K mol
t	time, min
T	Absolute temperature, K
V	Volume of the solution, l
w	Mass of the adsorbent, g
ΔG^0	Gibbs free energy of adsorption, kJ/mol
ΔH^0	Enthalpy of adsorption, kJ/mol
ΔS^0	Entropy of adsorption, J/K mol
SSE	The Sum of the Squares of the Errors
SAE	The Sum of the Absolute Errors
ARE	The Average Relative Error
HYBRID	The Hybrid Fractional Error Function
MPSD	Marquardt's Percent Standard Deviation

Greek symbols

α	Bangham constant (<1)
β	Constant of Redlich-Peterson isotherm ($0<\beta<1$)

CHAPTER – I

INTRODUCTION

1.1 GENERAL

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. When toxic substances enter lakes, streams, rivers, oceans, and other water bodies, they get dissolved, suspended, or deposited on the bed. These result in the deterioration of water quality and cause water pollution which affect to the aquatic ecosystems. Pollutants can also seep down and affect the groundwater deposits.

The major sources of water pollution can be classified as municipal, industrial, and agricultural. Municipal wastewater consists of domestic and wastewater from commercial establishments. 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. In many of these industries, hazardous wastes are also discharged. The wastewater from these industries gets into natural sources, changing the physico-chemical composition of water and ultimately the source becomes unsuitable for use. Agriculture, including commercial livestock and poultry farming, is the source of many organic and inorganic pollutants in surface water and groundwater.

Furfural is produced from agro-industrial wastes and residues containing carbohydrates known as pentosans (http://dsir.nic.in/reports/techreps/tsr048.pdf). As no commercial synthetic routes have been found so far, all furfural manufacturing activity is based on pentosans containing residues that are obtained from the processing of various agricultural and forest products. World production of furfural is based on agro-industrial residues or wastes that are abundantly available in many developing countries and are often under utilized or unexploited. The manufacturing activity in the India started in the 1970s with the Southern Agrofurane Industries Ltd., Chennai. Furfural as a natural volatile compound has been identified in many foods, e.g., fruits, vegetables, bread, and beverages such as cognac, rum, malt whiskey, port wine, coffee [Maarsse and Visscher, 1989] and in several essential oil of plants, e.g., the pinaceae family, cajenne, trifolium, ambrette, angelica, ceylon cinnamon, lavender, tobacco, etc., fruit juices and vegetables [SGS, 1995]. Degradation of hemicelluloses feedstock during thermal/chemical treatment is another source of furfural as a by-product.

Furfural contamination is especially significant in large lube units, which may go upto 2% (w/w) in effluent water streams. Evaporation condensate from sulfite pulping processes used in the pulp and paper industry is another example of furfural contamination [DECOS, 1996; Rivard and Grohmann, 1991; Vinogradova *et al.*, 1968]. The furfural levels in sulfite evaporator condensate have been reported to range between 10-1280 mg/l [Ruus, 1964; CICAD, 2000]. Synthetic rubber plant wastewater has been found to have 1.7 g/l furfural [Keith, 1974; CICAD, 2000]. Chennai Petroleum Corporation Limited supplied (September, 1996) 12,937 MT of Naphtha, through Indian Oil Corporation Limited to a buyer, who rejected it due to furfural contamination. Company's failure to take effective action to prevent furfural contamination in Naphtha, resulted in loss of Rs. 8.47 crores during December 1996 to April 1999 (http://www.cag.gov.in/reports/commercial/2002_book3/chapter16.htm#16.2.1).

At the workplace, furfural can affect through the respiratory system and dermal route. Its contact with eyes and skin causes irritation. Short exposure to the respiratory system of furfural may cause irritation of nose, throat & lungs causing coughing and/or shortness of breath. Higher exposures can cause a build-up of fluid in the lungs (pulmonary edema), a medical emergency, with severe shortness of breath. Repeated exposure may cause loss of sense of taste, numbness of the tongue, headache, and tiredness. Long-term exposure may cause liver damage. Concentration of 1.9-14 ppm produces symptoms of irritation in exposed persons. Under the Clean Water Act, furfural is listed as a hazardous substance. It is also regulated by OSHA (http://nj.gov/health/eoh/rtkweb/0953.pdf).

1.2 CONSUMPTION PATTERN OF FURFURAL

Furfural is used as a selective solvent or extractant for several purposes, such as refining of petroleum oil, extraction of butadiene from C_4 streams and decolourizing of wood rosin *[Company A, 1980]*.

Oil refining process involves extraction of raw lubricating stock with furfural at temperatures generally below 121 °C to yield refined oil and an extract. The undesirable aromatic and olefinic components of the oil are selectively dissolved by furfural and separated from the desired paraffinic and naphthenic components. In practice, oil enters near the bottom of a counter-current extraction column, and furfural is applied at a point near the top. The extract is removed from the bottom of the column with the bulk of the furfural. Furfural is separated from the extracted material and recovered for reuse by flash distillation followed by steam distillation to remove the residual traces of furfural. Furfural water mixture from the steam distillation is readily separated in a decanter by drawing off the lower layer, which consists of about 92% furfural and 8% water. This layer is subsequently dried for reuse [Company A, 1980].

Furfural is an extractive distillation medium in the process for purification of butadiene and isoprene. The boiling points of C_4 hydrocarbons are almost same but vary in soluble characteristics. When distillation is carried out in the presence of furfural, the relative volatility of the several C_4 hydrocarbons is altered sufficiently to affect the separation. The same principle applies to C_5 streams containing isoprene. [Company A, 1980].

Furfural is also used to remove colour bodies from wood rosin to produce a light coloured product, capable of competing with gum rosin used in the soap, varnish and paper industries. Most of the colour bodies, which produce the characteristic ruby red colour of crude rosin, are removed by fractional steam distillation. Other undesirable colour bodies are extracted with furfural from a solution of the crude rosin in warm gasoline. Since furfural and gasoline are almost immiscible at low temperatures, furfural gasoline-rosin mixtures separate into two layers on cooling. Light coloured rosin is obtained on evaporation of the gasoline layer [Company A, 1980]. Table 1.1, shows the use of furfural in various processes.

Table 1.1. Industrial uses of furfural [CICAD, 2000] [Risk Assessment, 2004]

Area	Uses
Petrochemicals	As a selective solvent in the production of lubricating oils
Refractories	As a reactive wetting agent in the production of refractory components
Resin manufacture	Production of phenolic resins, production of cashew nutshell polymers
Abrasive materials	As a reactive wetting agent for the resin binder system in the production of abrasive wheels
Agricultural industry	Pesticides, others (clarifiers, refractories)
Chemical industry	Binders, intermediates
Personal/domestic	Cleaning & washing agent and disinfectants. Cosmetics, flavouring substances, pharmaceuticals
Mineral oil and fuel industry	Intermediates, lubricants and additives, solvents, surface active agent-wetting agents. Viscosity adjusters, others (clarifiers, refractories)

The demand estimates for furfural for its various applications developed in India are as follows in Table 1.2.

Table 1.2. Consumption pattern of furfural
(http://dsir.nic.in/reports/techreps/tsr048.pdf)

User Sector	Consumption (in tonnes)		
	1988-1989	1992-1993	1999-2000
Refinery	990	950	950
Grinding and Abrasive wheels	27	33	45
Pharmaceuticals	75	120	235
Phenolic resins	52	72	120
Total	**1,144**	**1,175**	**1,350**

1.3 TOXICITY OF FURFURAL

The highest reported emissions of furfural to the environment are from the wood pulp industry and lubricating oil processing unit, whereas its release to water from other uses is substantially lower. Levels reported in food are as follows: non-alcoholic beverages, 4 mg/l; alcoholic beverages, 10 mg/l; ice creams, 13 mg/kg; candy, 12 mg/kg; baked goods, 17 mg/kg; gelatins and puddings, 0.8 mg/kg; chewing gum, 45 mg/kg; and syrups, 30 mg/l [CICAD, 2000].

Furfural is an irritant to the skin, eyes, mucous membranes, and respiratory tract. It acts as a toxicant to the central nervous system, liver, kidney, blood, and bone marrow. The oral LD$_{50}$ in rats is 65 mg/kg; and the inhalation LD$_{50}$ in rats is 260 ppm [Cincinnati, 1991^{a}]. Cats exposed to 2800 ppm for 30 minutes developed fatal pulmonary edema [Hathaway et al., 1991]. Solutions to 10 percent and 100 percent furfural instilled in rabbits eyes causes pain in addition to transient swelling and redness of the lids and conjunctiva [Grant et al., 1986]. Chronic dietary exposure to furfural causes liver cirrhosis in rats [Bethesda, 1992]. Dogs exposed at 130 ppm for 6 hours a day for 4 weeks develops liver damage, but dogs exposed at 63 ppm did not [Cincinnati, 1994]. Rabbits exposed to furfural vapours for several hours daily develop liver and kidney lesions as well as changes in their blood profiles [Parmeggiani et al., 1983]. Furfural is mutagenic in at least one bacterial species [Cincinnati, 1991^{a}, http://www.osha.gov/SLTC/healthguidelines/furfural/recognition.html].

Furfural concentrations of 1.9-14 ppm causes headache, itching of the throat, redness and tearing of the eyes in some exposed workers [Cincinnati, 1991^{b}; Grant, 1986]. Workers exposed to furfural vapours in a plant with inadequate ventilation report numbness of the tongue and mucous membranes of the mouth, loss of taste sensation, and difficulty in breathing & damage to the eyesight of some individuals has also been reported [Cincinnati, 1991^{b}]. Exposures to high concentrations have produced pulmonary edema [Parmeggiani, 1983]. Chronic skin exposure may produce eczema, allergic skin sensitization, and photosensitization [Sittig, 1991]. Furfural may cause a disulfiram-type reaction, i.e., a worker exposed to furfural, who has consumed alcohol may experience warmth and redness of the fact, a throbbing sensation and pain in the head and neck, difficulty in breathing, nausea, vomiting, sweating, thirst, chest pain, uneasiness, weakness, dizziness, blurred vision, and confusion.

This effect may last from 30 minutes to several hours but does not appear to have residual side effects. By analogy with effects seen in animals, furfural may affect the central nervous system, liver, kidneys, blood, and bone marrow of humans; however, these effects have not been reported in exposed workers [http://www.osha.gov/SLTC/healthguidelines/furfural/recognition.html].

1.4 TREATMENT METHODS OF FURFURAL LADEN WASTEWATER

Furfural is biodegraded in aerobic systems using sewage sludge and in surface waters. In a flow through aerobic laboratory bioreactor degradation of furfural was reported using acclimated sewage sludge. Degradation also takes place under anaerobic conditions, with a range of bacteria and other microorganisms capable of degrading the compound as sole carbon source [CICAD, 2000].

Removal of furfural by distillation is not easy since when aqueous solutions of furfural are distilled at atmospheric pressure a minimum-boiling heteroazeotrope is formed, which contains 35% of furfural by weight [Coca *et al.*, 1980]. Furfural may be removed from aqueous solutions through solvent extraction method. But the operation is limited for the low content of solute.

Adsorption is well recognised as a unit operation for the removal of impurities from wastewater which otherwise cannot be removed efficiently. These include heavy metals, non-biodegradable organic compounds like phenols, toxic substances, dyes etc. It has been used for taste and odour control in water and wastewater treatment. Almost complete removal of impurities with negligible side effects explains its wide application. The polymeric adsorbent XAD-4 and XAD-7 have been used for removal of furfural from pretreated and hydrolysed plant biomass. However, these are expensive and its regeneration and reuse makes it more costly [Weil *et al.*, 2002].

1.5 FURFURAL PROPERTIES AND HEALTH EFFECTS

Various characteristics parameters of furfural and their details are summarised in Table 1.1. The molecular structure of furfural is shown in Fig. 1.1.

Potential Health Effects [http://www.jtbaker.com/msds/englishhtml/f8040.htm]:

Inhalation:

Causes irritation to the mucous membranes and upper respiratory tract. Symptoms may include sore throat, labored breathing, and headache. Higher concentrations act on the central nervous system and may cause lung congestion. Inhalation may be fatal.

Ingestion:

Highly toxic. It may cause gastrointestinal disorders, nerve depression and severe headache and may be fatal. Other effects are not well known.

Skin contact:

It is highly irritant to skin. It may cause dermatitis and possibly eczema, allergic sensitisation and photosensitisation. It may be absorbed through the skin with possible systemic effects.

Eye contact:

Vapours irritate the eyes, causing tearing, itching, and redness. Splashes may cause severe irritation or eye damage.

Chronic exposure:

It can cause numbness of the tongue, loss of sense of taste, headache. Other effects are not well known.

Aggravation of pre-existing conditions:

Persons with pre-existing skin disorders or eye problems, or impaired liver, kidney or respiratory function may be more susceptible to the effects of the substance.

Fire:

Flash point: 60 ^{O}C
Auto ignition temperature: 316 ^{O}C
Flammable limits in air % (v/v):
LEL: 2.1; UEL: 19.3
Oral LD_{50}, Redwing Blackbird: 98.0 mg/kg.
OSHA Permissible Exposure Limit (PEL): 5 ppm (TWA) skin
ACGIH Threshold Limit Value (TLV): 2 ppm (TWA) skin
(http://www.jtbaker.com/msds/englishhtml/f8040.htm)

Explosion:

Above flash point, vapour-air mixtures are explosive within flammable limits noted above. Furfural reacts violently with oxidants, strong acids and bases causing fire and explosion hazards. Sealed containers may rupture when they are heated. It is highly sensitive to static discharge.

Fire Extinguishing Media:

Water spray, dry chemical, alcohol foam, or carbon dioxide can be used as a fire extinguishing media. Water spray may be used to keep fire exposed containers cool. Water may be used to flush spills away from exposures and to dilute spills to non-flammable mixtures [http://www.jtbaker.com/msds/englishhtml/f8040.htm].

1.6 OBJECTIVES OF THE PRESENT STUDY

The objective of present work is to explore the possibility of bagasse fly ash as a low cost adsorbent for removal of furfural from aqueous solution. To evaluate the economic feasibility, adsorptive capacity of bagasse fly ash has been compared with commercial activated carbon. In this study the bagasse fly ash and activated carbon commercial grade were used to remove furfural. The whole study deals with equilibrium and kinetic modeling of adsorption. The experiments were carried out to study the following:

1. Characterization of Bagasse fly ash and activated carbon commercial grade which includes particle size distribution, chemical analysis and proximate analysis.
2. Study the effect of adsorbent dose, pH, contact time, initial concentration, and temperature on the removal of furfural from the wastewater in batch study for aqueous solution.
3. Study the kinetics of furfural removal using pseudo first order, pseudo second order, Bangham and Weber-Morris kinetic models.
4. Study of equilibrium data for removal efficiency of the adsorbent using Freundlich, Langmuir, Redlich-Peterson, Dubinin-Radushkevich and Temkin isotherm models.

CHAPTER – II

LITERATURE REVIEW

The majority of furfural released to the environment will be released to surface water. Release from the wood pulp industry seems to be the major source. Furfural has a low capacity for bioaccumulation. Binding to particulates in soil and aquatic sediments is expected to be very low, making furfural mobile in the environment. The compound is toxic to anaerobic degrading bacteria at concentrations above 1000 mg/l in unacclimated sludges (these concentrations have been reported in wood pulp waste), although acclimation allows full degradation at these concentrations. LC_{50} in fish range from 16- 32 mg/l [CICAD, 2000]. Various treatment methods are available for the removal of furfural from the wastewater. The critical literature review of all these methods is discussed in this chapter.

2.1 BIOLOGICAL REMOVAL

Furfural is readily biodegradable in aerobic systems using sewage sludge and in surface water. Degradation also takes place under anaerobic conditions, with a range of bacteria and other microorganisms capable of degrading the compound as sole carbon source. At higher concentrations (>1000 mg/l), furfural inhibits growth and metabolic activity of unadapted anaerobic cultures. However, acclimation increases the capacity of anaerobic sludge to degrade the compound [CICAD, 2000]. Virtually no degradation occurs in a solution of furfural in distilled water over 30 days, suggesting that hydrolysis is not an important process at environmental pH [Ettinger *et al.*, 1954].

2.1.1 Aerobic Process

Furfural is biodegraded in an aerobic batch culture at 200 mg COD/l, within 120 h, a degradation rate of 37 mg COD/(g.h) was analysed [Pitter, 1976]. Degradation also occurs at a concentration of 1000 mg/l [Rowe & Tullos, 1980]. Furfural was readily biodegradable in the Japanese Ministry of International Trade and Industry (MITI) test [Kawasaki, 1980; Wang *et al.*, 1994] screened a range of microorganisms for their ability to degrade furfural and reviewed the earlier literature; some strains of the aerobic bacteria *Escherichia coli*, *Pseudomonas putida*, and *Rhodococcus erythropolis* and the yeast *Hyphozyma rosoeniger* were able to degrade the compound to a greater or lesser degree [CICAD, 2000]. Inhibitory effects of furfural on *Pseudomonas putida* were seen at concentration of 0.1% and above, with complete inhibition at 1% with exposure for 30 min. [Kim *et al.*, 1983]. Furfural at 1 mg/l was degraded completely in water from the Great Miami, Little Miami, and Ohio rivers (USA) within 3 days under aerobic conditions [Ettinger *et al.*, 1954].

2.1.2 Anaerobic Process

Under anaerobic conditions, furfural was completely degraded to methane by unacclimated sewage sludge within 30 days at an initial concentration of 580 mg/l. The rate of methane production was initially slower than in controls, indicating some interference of the compound in the metabolism of the methanogenic bacteria [CICAD, 2000]. Using acclimated sludge (which had received furfural at 310 mg/l continuously for 8 months), full degradation occurred at 1160 mg/l. At 2320 mg/l, furfural was initially degraded rapidly, but then gas production slows for the remainder of the test [Benjamin et al., 1984]. A strictly anaerobic bacterium isolated from a fermentor degrading sulfite evaporator condensate from wood pulp production was able to use *furfural as sole carbon source; the organism was tentatively identified as Desulfovibrio* sp. [Brune et al., 1983]. *Methanococcus deltae* was found to be able to use furfural as sole carbon source, degrading the compound to furfuryl alcohol at initial concentrations of 5-10 mmol/l (480-960 mg/l); however, growth of the bacterium was inhibited at concentration of 20-25 mmol/l (1920-2400 mg/l). Other methanogenic bacteria (*Methanobacterium thermoautotrophicum*, *Methanosarcina barkeri*, and *Methanococcus thermolithotrophicus*) were unable to degrade the compound [Belay et al., 1997].

2.2 SOLVENT EXTRACTION

Solvent extraction recovery of furfural from aqueous solutions can be a suitable industrial method with low content of solute. Data on liquid-liquid extraction of furfural have been reported. In an attempt to find suitable solvents for extraction of furfural, liquid-liquid equilibrium data with trichloroethylene, perchloroethylene, 1,2dichloroethane, 1, 1,l-trichloroethane, and 1,1,2-trichloroethane as solvents were studied at 25 ^{0}C. Among the solvents studied, 1,2-dlchloroethane and trichloroethylene show the highest selectivity [Coca et al., 1980].

2.3 ADSORPTIVE REMOVAL

In the lube processing operation in petroleum industries, furfural is used as a solvent. After the extraction process, a lot of furfural goes with the wastewater stream. This furfural is quite expensive and toxic as well. Recovery of furfural from wastewater becomes very important. For that Agrawal et al. used adsorption process in which polymeric resin XAD-4 was used as an adsorbent. A study for different column lengths and different feed flow rates was done, keeping column diameter and concentration of feed nearly constant. For each set of conditions, break through time was determined by determination of length of MTZ. After that regeneration of column was done using acetone.

Weil et al., 2002, reported the removal of furfural by contacting a polymeric adsorbent, XAD-4, with biomass hydrolyzate containing furfural. Liquid Chromatographic analysis of the remaining effluent showed that furfural concentrations were less than 0.01 g/l compared to the initial concentrations which were in the range of 1-5 g/l. Fermentation of the resulting sugar with recombinant *E. coli* ethanologenic strain K011 confirmed that the concentration of furfural in the polymeric adsorbent treated hydrolyzate caused negligible fermentation inhibition. Fermentation of XAD-4 treated hydrolyzate with *E. coli* K011 was near as rapid as the control medium, formulated with reagent grade sugar of the same concentration. Ethanol yield for both fermentations were 90% of theoretical. Modeling of the adsorptive properties of this styrene based adsorbent indicates that it is suitable for on-off chromatography, and could be useful for removing small amounts of aldehydes that might otherwise inhibit fermentation.

2.4 SOURCES OF FURFURAL IN AQUEOUS EFFLUENT AND ITS TOXICITY

Furfural is found in a number of dietary sources. Because of its formation during the thermal decomposition of carbohydrates, furfural is found in numerous processed foods and beverages, including coffee, tea, beer, wine, milk products, and bread [Maga, 1979]. It is also found in some fruits and vegetables, and it is added as a flavouring agent to some foods. Furfural has also been found in the essential oils of camphor, citronella, sassafras, lavender, and lime. The highest reported emissions of furfural to the environment are from the wood pulp industry, whereas its release to water from other uses is substantially lower. The compound would be released to the atmosphere from wood fires, natural as well as anthropogenic source. Levels of furfural in sulfite evaporator condensate, which represents about 15% of the wastewater flow from pulp mills, have been reported to range between 10-1280 mg/l. The furfural is derived from pentosans in the wood pulp and is formed during the waste treatment in the evaporator. Although, furfural has been identified in vehicle exhaust, it was not detectable in air sampled from a road tunnel in the USA. The compound has been identified in smoke from burning wood.

Furfural has been identified but not quantified as a major flavour component in a range of food items, including beef, soya sauce, roasted nuts, fried bacon, nectarines, baked potatoes, clove oil, preserved mangoes, rum, roasted coffee, and blue cheese. Levels reported in food are as follows: non-alcoholic beverages, 4 mg/l; alcoholic beverages, 10 mg/l; ice creams, ices, etc., 13 mg/kg; candy, 12 mg/kg; baked goods (unspecified), 17 mg/kg; gelatins and puddings, 0.8 mg/kg; chewing gum, 45 mg/kg; and syrups, 30 mg/l [Pellizzari et al., 1982; CICAD, 2000].

Furfural-laden effluent discharged into receiving waters affects the aquatic flora and fauna, and causes many water borne diseases. Furfural is reported to cause allergy, dermatitis, skin irritation, cancer, and mutations in humans. The properties and the harmful effects of furfural are discussed in detail in Chapter 1.

2.5 ADSORPTION: BEST AVAILABLE TECHNIQUE

Biological treatments for the degradation of furfural have been used by many researchers, including aerobic and anaerobic processes. However, these processes are costly and cannot be used by small industries to treat furfural-laden wastewater. By comparing all methods, adsorption is the best available techniques for the treatment of furfural-laden wastewater. During recent years large number of adsorbents have been tried for the treatment of different kind of polluted water. Adsorption is a simple economically feasible process. The adsorption process provides an attractive alternative treatment, especially, if the adsorbent is cheap and readily available. The polymeric adsorbent XAD-4 and XAD-7 have been used for removal of furfural from pretreated and hydrolyzed plant biomass [Weil et al.]. However, these are expensive and its regeneration and reuse makes it more costly. Consequently, several low cost adsorbents like wood [Poots et al., 1976; Abo-Elala et al., 1987], coir pith [Navasivayam et al., 2001], coal fly ash [Rao et al., 1978; Gupta et al., 1985; Sharma et al., 2000], bagasse fly ash (BFA) [Mall et al., 1994; Swamy et al., 1997, ; Swamy et al., 1998; Mall et al., 1998] and coal-fired boiler bottom ash [Mall et al., 1994] have been used for the treatment of a wide variety of wastewater. A critical review on the utilisation of low cost adsorbents has been presented by Mall et al., 1996 and Bailey et al., 1999.

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 furfural 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. Activated carbon, commonly used adsorbent has its own limitations. Because of cost and 10-15 % loss in adsorption capacity during regeneration, the overall treatment process becomes costly and is a major constraint in its utilisation in developing countries. Consequently, many investigators have studied the feasibility of using low cost substances for the treatment of wastewater.

Bagasse fly ash has good adsorptive properties and has been used for the removal of COD and colour from sugar mill [Mall et al., 1994] and paper mill effluents [Srivastava et al., 2005]. Various researchers have utilised it for the adsorptive removal of phenolic compounds [Mall et al., 2003; Srivastava et al., 2005] furfural [Lataye et al., 2006] and dyes [Mall et al., 2005 a, b, 2006].

Table 2.1. Studies on removal of different compounds using various types of adsorbents used for adsorption and other treatment methods

References	**Adsorbent/Solvent**	**Adsorbate/Solute**	**Operations**	**Results and discussion**
Lucas et al., 2004	Activated carbon from supercritical carbon dioxide	Furfural and ethyl acetate	Continuous adsorption study	Fit of the adsorption isotherms showed that the Langmuir model could correlate the experimental data for ethyl acetate satisfactorily and with more simplicity versus other tested models, whereas, Freundlich isotherm is suitable to fit the adsorption data of furfural on activated carbon
Weil et al., 2005	XAD-4 and XAD-7	Furfural	Continuous adsorption study	Fermentation of the resulting hydrolysates with recombinant *E.coli* ethanologenic strain K011 confirmed that the concentration of furfural in the polymeric adsorbent treated hydrolysate causes negligible fermentation inhibition. Fermentation of XAD-4 treated hydrolysate with *E. coli* K011 was nearly as rapid as the control medium with ethanol yields at 90% of theoretical
Coca et al., 1980	Chlorinated hydrocarbons	Furfural	Solvent extraction	Liquid-liquid equilibrium data at 25 ^{0}C are reported for five ternary systems containing furfural, water and the chlorinated hydrocarbons trichloroethylene, perchloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethane. Among the solvents studied, 1,2-dichloroethane and trichloroethylene show the highest selectivity.

Table 2.1 (Contd...)

References	Adsorbent/Solvent	Adsorbate/Solute	Operations	Results and discussion
Agrawal et al., 2005	XAD-4	Furfural	Continuous adsorption study	A study of different column length and different feed flow rates were done, keeping column diameter and concentration of feed nearly constant. For each set of condition breakthrough curve was plotted. A comparison between the breakthrough times determined experimentally and by the determination of length of MTZ was done. Regeneration of column was done using acetone.
Srivastava et al., 2005	Bagasse fly ash and activated carbon	Phenol	Batch adsorption study	Adsorption kinetics was found to follow second order rate expression with initial sorption rate being highest for adsorption on BFA. The Redlich–Peterson isotherm, best represented equilibrium adsorption. 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
Srivastava et al., 2005	Poly aluminium chloride and bagasse fly ash	Pulp and paper mill wastewater	Batch adsorption study	Freundlich isotherm equation adequately describes the adsorption equilibrium data. Two-stage treatment using PAC as a coagulant in the first stage and BFA as an adsorbent in the second stage gives the combined COD and colour removal of nearly 84–96% and 91–98%, respectively, for different effluents. Two stage adsorptive treatment using BFA, in both the stages gives the combined COD and colour removal of about 71 and 69%, respectively

Table 2.1 (Contd...)

References	Adsorbent/Solvent	Adsorbate/Solute	Operations	Results and discussion
Lataye et al., 2006	Bagasse fly ash	Furfural (Py)	Batch adsorption study	The Langmuir equation is determined to best represent the equilibrium sorption data. Thermodynamic studies revealed that the adsorption of Furfural on BFA is endothermic in nature. The desorption of Py from Py-loaded BFA with several solvents shows that only 68.70% and 51% of Py could be recovered, using ethyl alcohol and 0.1 N H_2SO_4, respectively
Malik, 2003.	Activated carbon prepared from sawdust carbon (SDC) and rice husk carbon (RHC)	Acid dyes	Batch adsorption study	The isothermal data could be well described by the Langmuir and Freundlich equations. Kinetic parameters of adsorption such as the Langergren pseudo-first-order constant and the intraparticle diffusion rate constant were determined. For the present adsorption process, intraparticle diffusion of dye molecule within the particle has been identified to be rate limiting. The results indicate that SDC and RHC could be employed as low-cost alternatives to commercial activated carbon in wastewater treatment for the removal of acid dyes.

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, colour, and odour. Although adsorption is applied in low concentration. recent physico-chemical processes use adsorption as a primary technique to remove soluble organics from the wastewater. The adsorption is called physical when relatively weak inter-molecular forces cause the attachment and chemical when chemical bonding like forces causes 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).

3.1.1 Physical Adsorption vs. Chemisorption

Adsorption processes can be classified as either physical adsorption (Van der Waal's 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 electrons, 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 (uni-molecular) 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 °C, and may be slow and irreversible.

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.

Table 3.1. Comparison of Physical and Chemical Adsorption

Sl. No.	Physical Adsorption	Chemical Adsorption
1.	Van der wall's adsorption	Activated adsorption
2.	Heat of adsorption = 5 kcal/mol	Heat of adsorption = 20-100 kcal/mol
3.	Adsorption only at temperature less than the boiling point of the adsorbate	Adsorption can occur even at higher temperature
4.	No activation energy involved in the adsorption process	Activation energy may be involved
5.	Mono and multi-layer adsorption	Almost monolayer 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 involved
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

3.1.2 Intra-particle 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. They are:

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.

3.1.3 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 number 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.

3.2 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 as follows:

3.2.1 Langmuir Isotherm

This equation is based on the assumptions:

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 given by:

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

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

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

3.2.2 Freundlich Isotherm

The heat of adsorption in many instances decreases in magnitude with increase in 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 = Concentration of adsorbate solution at equilibrium.

By taking logarithm on 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 gives a straight line. The Freundlich equation is most useful for dilute solutions over small concentration range. It is frequently applied to the adsorption of impurities from a liquid solution onto the activated carbon. A high K_F and high 'n' value is an indication of high adsorption throughout the concentration range. A low K_F and high 'n' indicates a low adsorption throughout the concentration range. A low 'n' value indicates high adsorption takes place at strong solute concentration.

3.2.3 Redlich-Peterson Isotherm

Redlich and Peterson (1959) model combine 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 accordance 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 0 and 1.

- When β=1

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

It becomes a Langmuir equation.

- When β=0

$$Q_e = \frac{K_R C_e}{1 + a_R} \tag{3.8}$$

i.e., Henry's Law equation

Eqn. (3.6) can be converted to a linear form by taking logarithm on both the sides:

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

Plotting the left-hand side of equation (3.9) against ln C_e to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R and β. Therefore, a minimization procedure was adopted to solve equation (3.9) by maximizing the correlation coefficient between the theoretical data for Q_e predicted from equation (3.9) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and theoretical model predictions with any suitable computer programme.

3.2.3 The Temkin isotherm

It is given as:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \tag{3.10}$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{3.11}$$

where, $B_1 = \frac{RT}{b}$

Tempkin isotherm contains a factor that explicitly takes into the account of 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, upto 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.

3.2.4 Dubinin-Radushkevich (D-R) isotherm

It is given as:

$$q_e = q_s \exp(-B\varepsilon^2) \tag{3.12}$$

where, q_s is the D-R constant and ε can be correlated as

$$\varepsilon = \mathrm{RT}\ln\left(1 + \frac{1}{\mathrm{C_e}}\right) \tag{3.13}$$

The constant B gives the mean free energy E of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship [Hasany and Chaudhary, 1996]:

$$E = 1/\sqrt{2B}$$

3.3 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.

3.3.1 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, centrifuging or settling. The adsorbent can be regenerated and reused depending upon the case.

3.3.2 Continuous Adsorption Systems

The continuous flow processes are usually operated in fixed bed adsorption columns. These systems are capable of treating large volumes of wastewater and are widely used for treating domestic and industrial wastewater. They may be operated *either in the upflow columns or downflow 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.

3.4 FACTORS CONTROLLING ADSORPTION

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

1. pH.
2. Nature of adsorbent.
3. Contact time.

4. Initial concentration.
5. Temperature.
6. Degree of agitation.

3.4.1 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, 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 pyrolyzed to a carbonaceous residue. Larger channels or pores with diameter 1000 Å are called macro pores. Most of the surface area for adsorption is provided by micro pores, which are arbitrarily defined as pores with diameter from 10-1000 Å.

3.4.2 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 favourably 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.

3.4.3 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 within 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 larger 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 thereafter, it becomes slow near equilibrium.

3.4.4 Initial Concentration

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

3.4.5 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.

3.4.6 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.

CHAPTER – IV

EXPERIMENTAL PROGRAMME

4.1 GENERAL

In the present study, bagasse fly ash (BFA) and activated carbon commercial grade (ACC) have been utilized for the treatment of furfural-laden aqueous solution. Experimental details of the study have been presented in this chapter. These details include characterization of adsorbents and batch adsorption studies.

4.1.1 Characterization of Adsorbent

The physico-chemical characteristics of the BFA and ACC were determined using standard procedures are discussed below:

4.1.2 Proximate Analysis

Proximate analysis of the BFA and ACC were carried out as per IS 1350:1984.

4.1.3 Density

The Bulk density of BFA and ACC were determined using MAC bulk density meter.

4.1.4 Particle Size Analysis

Particle size analysis of the BFA and ACC was done using standard sieve as per IS 2720 (Pt 4): 1985.

4.1.5 Surface area measurement

The specific surface area, pore volume and pore diameter of the sample were measured by N_2 adsorption isotherm using an ASAP 2010 micrometric instrument and by Brunauer-Emmett-Teller (BET) method, using the software of micrometrics. Nitrogen was used as cold bath.

4.1.6 Scanning Electron Microscope (SEM)

SEM analysis of BFA and ACC were carried out before the adsorption of furfural from aqueous solution by using LEO 435 VP Scanning electron microscope.

4.2 ADSORBATE

Furfural supplied by S D Fine Chemicals, Mumbai (India) was used as adsorbate. Stock aqueous solution of 1000 mg/l was prepared by dissolving accurate quantity of furfural in distilled water. Further, the solutions of required concentration were prepared by using same stock solution.

4.2.1 Analytical measurement

The determination of the concentration of furfural was done by finding out the absorbance characteristic wavelength using UV/VIS spectrophotometer (Perkin Elmer 35). A standard solution of known concentration of furfural was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) was determined from this plot. The λ_{max} for furfural was found to be 275 nm. Calibration curve was plotted between the absorbance and the concentration of furfural solution. The linearity of calibration curve (Fig. 4.1) indicates the applicability of the Lambert-Beer's Law.

4.3 BATCH ADSORPTION EXPERIMENTS

To study the effect of various parameters like adsorbent dose (m), initial pH (pH_0), contact time (t) and initial concentration (C_0) on the adsorptive removal of furfural by BFA and ACC, batch experiments were conducted at $30 \pm 1^{\circ}C$. For each experimental run, 100 ml of furfural solution of known C_0, pH_0 and an optimum amount of the adsorbent were taken in a 250 ml stoppered conical flask. This mixture was agitated in a temperature controlled shaking water bath at a constant speed of 140 rpm at $30 \pm 1\ ^{\circ}C$. Samples were withdrawn at appropriate time intervals. Some BFA and ACC particles remain suspended and do not settle down easily. Therefore, all the samples were centrifuged (Research Centrifuge, Remi scientific works, Mumbai) at 7,000 rpm for 10 minutes and analyzed for the residual furfural concentration using double beam UV/VIS spectrophotometer. The effect of pH_0 on furfural removal was studied over a pH_0 range of 2-12. pH_0 was adjusted by the addition 0.1 N of H_2SO_4 or NaOH. For the optimum amount of m, a 50 ml furfural solution was contacted with different amounts of BFA and ACC till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the furfural from the aqueous solution at different time intervals. For adsorption isotherms, furfural solution of different concentrations were agitated with optimum dose of adsorbent till the equilibrium was achieved. The residual furfural concentration of the solution was then determined. Blank experimental runs with only adsorbent in 100 ml of distilled water, were conducted simultaneously at similar conditions to account for any leaching of the adsorbents. Batch tests were carried out to compare the adsorptive capacity and intensity of BFA and ACC.

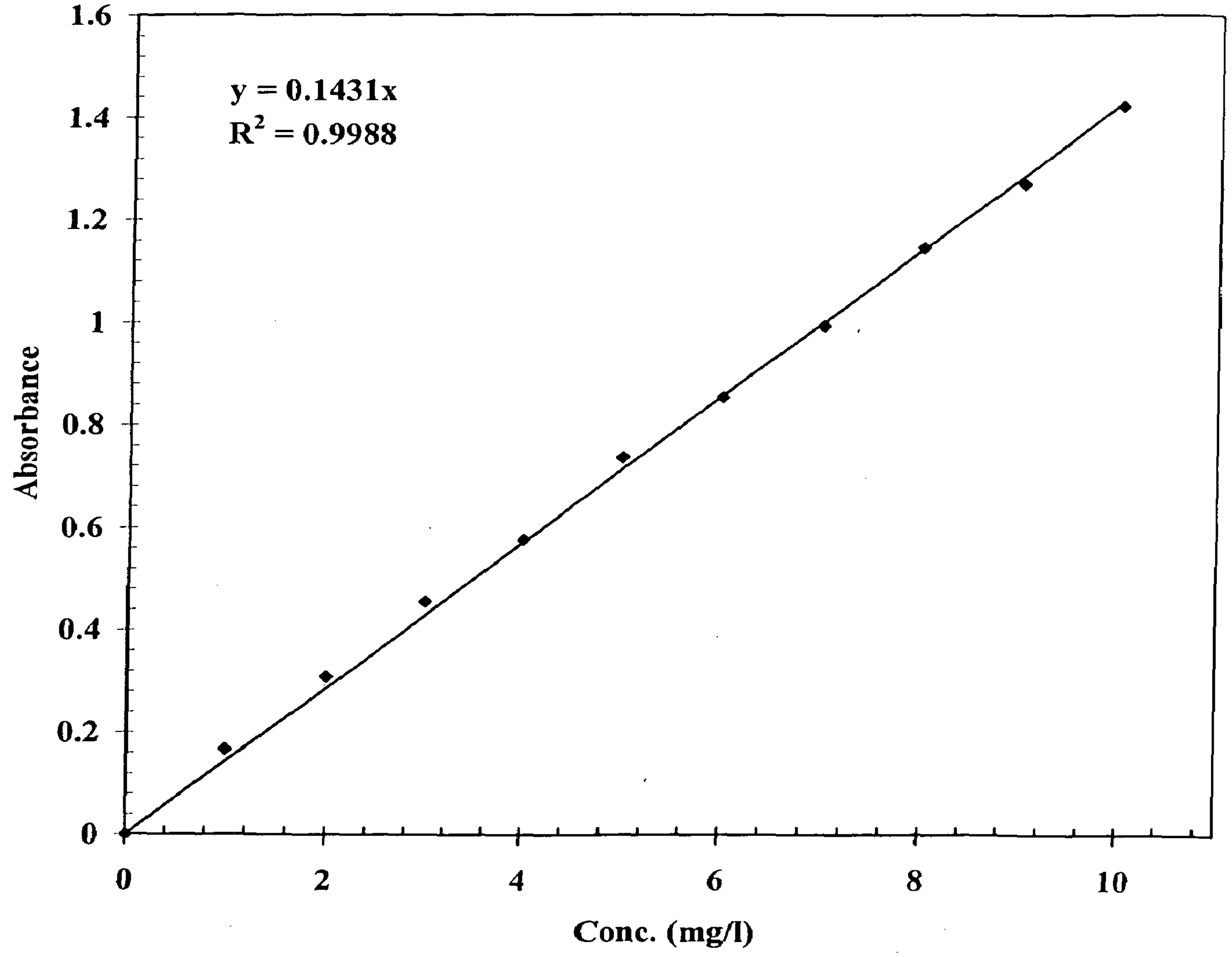

Fig. 4.1. Calibration Graph for determination of furfural concentration

CHAPTER – V

RESULTS AND DISCUSSION

5.1 GENERAL

The detailed discussion on the results of the experiments conducted for the removal of furfural by bagasse fly ash (BFA) and activated carbon commercial grade (ACC) is given in this chapter. These results include:

- Characterization of BFA and ACC.
- Batch adsorption studies.

5.2 CHARACTERISATION OF BAGASSE FLY ASH AND ACTIVATED CARBON COMMERCIAL GRADE

Characteristics of BFA and ACC include proximate and particle size analysis. Proximate analysis (Table 5.1) shows that the BFA has higher ash component as compared to ACC, however, amount of fixed carbon is comparatively higher in ACC. The physico-chemical characteristics of the adsorbents are given in Table 5.1. ACC has higher bulk density as compared to BFA, whereas, BFA has higher calorific value. BFA also has a large surface area of ~237.83 m^2/g which comprises mainly of pore surface area with average pore diameter of 22.49 Å (Table 5.1). The sieve analysis of BFA and ACC were presented in Table 5.2 and 5.3. Each adsorbent has different particle size distribution. This was because of the use of the adsorbents as procured. Average particle size of BFA was found to be 460.040 μm. For morphological characteristics, scanning electron microscope (SEM) analysis was carried out. Scanning electron micrograph (Figs. 5.1 and 5.2) of BFA and ACC reveal their surface texture and porosity. The micrograph of BFA shows its fibrous structure of BFA. SEM of BFA (Fig. 5.1) shows fibrous structure with large pore size with strands in each fibre. The size of the fibre and inter fibre space is lesser in ACC (Fig. 5.2). Number of pores in ACC is lesser than that in BFA.

5.3 BATCH ADSORPTION STUDY

In order to study the effect of different parameters the batch operations were performed. Batch adsorption experiments were carried out in 250 ml stoppered conical flask for removal of furfural from synthetic solutions of known concentrations by using BFA and ACC as adsorbents. The effect of various operating parameters, viz. adsorbent dose (m), initial pH (pH_0), contact time (t), initial concentration (C_0) and temperature (T) have been studied and presented here.

5.3.1 Effect of Adsorbent Dosage (m)

The effect of m on the removal of furfural by BFA and ACC at initial concentration $C_0 = 100$ mg/l is shown in Figs. 5.3 and 5.16, respectively. It can be seen that the furfural removal increases upto a certain limit and then it remains almost constant. Optimum m was found to be 4 g/l and 10 g/l for BFA and ACC, respectively. An increase in adsorption with the adsorbent dose can be attributed to greater surface area and availability of more adsorption sites. Further, in all the cases, equilibrium was found to be attained more rapidly at lower adsorbent age.

5.3.2 Effect of Initial pH (pH_0)

The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of the materials present in the solution. The hydrogen ion and hydroxyl ions are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. It is a common observation that the surface adsorbs anions favourably 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.

pH is also known to affect the structural stability of furfural. To study the effect of pH on the removal of furfural, a known concentration ($C_o = 100$ mg/l) was taken in a different 250 ml conical flask with varying pH from 2-12. The solution was kept for 1 h after the pH adjustment and, thereafter, the absorbance of the solution was found out. Figs. 5.4 and 5.17 show the furfural removal with and without BFA and ACC, respectively over a pH_0 range of 2-12. Furfural removal due to pH change alone as shown in Fig. 5.4 may be due to the structural changes being effected in the furfural molecules. Maximum furfural removal is observed at $pH_0 = 5.5$ using BFA. In furfural-ACC system, change in removal is insignificant with variation in pH; hence, remaining experiments were conducted at natural pH. The furfural removal at higher pH_0 is mainly due to the structural changes being effected in the furfural molecule. Further, all experiments were conducted with pH adjustment of 5.5.

5.3.3 Effect of Contact Time (t)

The effect of t on the removal of furfural by BFA and ACC at $C_0 = 100$, 200, 300 and 500 mg/l is given in Figs. 5.5 (a) and 5.18 (a), respectively. The contact time curves show rapid adsorption of furfural in the first 30 min., thereafter, the adsorption rate decreases gradually and the adsorption reaches equilibrium in 4 h for BFA and 6 h for ACC. Increase in contact time up to 7 days shows that the furfural removal by BFA and ACC increases only by about ~ 0.5% over those obtained for 4 h and 6 h contact time, respectively. Aggregation of furfural molecules 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 furfural molecules in the adsorbents. This is the reason, why an insignificant enhancement in adsorption is effected in 7 days as compared to that in 4 h and 6 h for BFA and ACC, respectively. The curves are single, smooth and continuous leading to equilibrium. The adsorption curves of contact time indicate the possible mono-layer coverage of furfural on the surface of BFA and ACC (Wong and Yu, 1999; Malik, 2003). Further experiments were conducted for 4 and 6 h, respectively, for furfural adsorption onto BFA and ACC.

5.3.4 Effect of Initial Furfural Concentration (C_0)

The effect of C_0 on the removal of furfural by BFA and ACC is shown in Figs. 5.5 (b) and 5.18 (b), respectively. It is evident from the figures that the amount of furfural adsorbed per unit mass of adsorbent (q_t) increased with the increase in C_0. q_t

increases with the increase in C_0 due to decrease in the mass transfer resistance. The rate of adsorption also increases with the increase in C_0 due to increase in the driving force.

5.3.5 Effect of Temperature

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. Figs. 5.6 and 5.19 show the adsorption isotherm, for furfural- BFA and furfural-ACC systems at 293, 303, 313 and 323 K. It shows that with the increase in temperature the adsorptivity of furfural increases. These figures also show that at lower adsorbate concentrations, q_e rises sharply and thereafter, the increase is gradual with solute concentration in the solution. Since sorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate-adsorbent system would result in decreased sorption capacity. The same behavior is observed for the adsorption of furfural onto BFA and ACC.

5.4 ADSORPTION KINETICS STUDY

5.4.1 Pseudo-first-order model

The pseudo-first-order equation is given as:

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

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).

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

The values of adsorption rate constant (k_f) for furfural adsorption on BFA and ACC at C_0=100, 200, 300 and 500 mg/l were determined from the plot of log ($q_e - q_t$) against t (Fig. 5.20).

5.4.2 Pseudo-second-order Model

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

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

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:

$$\frac{t}{q_t} = \frac{1}{k_S q_e^2} + \frac{1}{q_e} t \tag{5.4}$$

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

$$h = k_S q_e^2$$

Figs. 5.7 and 5.21 show the plot of t/q_t versus t for BFA and ACC, respectively, at $C_0 = 100$, 200, 300 and 500 mg/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 5.4 and 5.8 for both the adsorbents. 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 furfural by BFA and ACC can be approximated more appropriately by the pseudo-second-order kinetic model. It can be seen that the BFA has higher h and q_e values for furfural adsorption.

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. 5.8 and 5.22 present a plot of q_t versus $t^{1/2}$ at $C_0 = 100$, 200, 300 and 500 mg/l for furfural adsorption on BFA and ACC, respectively. The values of I (Table 5.4 and 5.8), 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.5.8 and 5.22) 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 5.4 and 5.8 for BFA and ACC, respectively.

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 α (<1) and k_0 are constants. The double logarithmic plot, according to Eqn. 5.6, did not yield satisfactory linear curves for the furfural removal by the adsorbents. 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.

5.6 ADSORPTION EQUILIBRIUM STUDY

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium characteristics of adsorption.

5.6.1 Freundlich and Langmuir Isotherms

Linearized 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. 5.10 and 5.24 show the Freundlich isotherm plots (ln Q_e versus $\ln C_e$) for adsorption of furfural, respectively, onto BFA and ACC at 293, 303, 313 and 323 K. Langmuir isotherm plot (C_e/Q_e versus C_e) are shown in Figs. 5.11 and 5.25, respectively for adsorption onto BFA and ACC. Freundlich and Langmuir isotherm parameter along with linear correlation coefficients are given in Tables 5.5 and 5.9, respectively. At all temperatures, Langmuir isotherm represents a better fit of the experimental data than Freundlich isotherm equation. The values of $1/n$ were also found to be less than 1 showing favourable nature of adsorption (Faust and Aly, 1978).

5.6.2 Redlich-Peterson Isotherm

Redlich and Peterson (1959) model has a linear dependence on concentration in the numerator and an exponential function in the denominator. 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:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \qquad (5.9)$$

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 0 and 1,

- When β=1

$$Q_e = \frac{K_R C_e}{1 + a_R C_e} \qquad (5.10)$$

It becomes a Langmuir equation.

- When β=0

$$Q_e = \frac{K_R C_e}{1 + a_R} \qquad (5.11)$$

i.e., Henry's Law equation

It can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_R + \beta \ln C_e \qquad (5.12)$$

Plotting the left-hand side of equation 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 by maximizing the correlation coefficient between the theoretical data for q_e predicted from equation and experimental data. Figs. 5.12 and 5.26 show the R-P isotherm plot for BFA and ACC, respectively, at 293, 303, 313 and 323 K. The R-P isotherm parameters and the correlation coefficients, R^2, for the R-P isotherms are listed in Tables 5.5 and 5.9 for BFA and ACC, respectively. Since, correlation coefficients for R-P plots are significantly higher than both the Langmuir and Freundlich plots. Therefore, R-P isotherm certainly best fits the equilibrium adsorption data of the three isotherms studied so far.

5.6.3 The Temkin Isotherm

It is given as:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \qquad (5.13)$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \qquad (5.14)$$

where, $B_1 = \frac{RT}{b}$

Temkin isotherm contains a factor that explicitly takes into account of 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, upto 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) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. Figs. 5.13 and 5.27 show the Temkin isotherm plot. The Temkin isotherm parameters are also listed in Tables 5.5 and 5.9. It shows comparable fit to Freundlich isotherm, and is poorly fitted to the equilibrium data when compared with R-P and Freundlich isotherm.

5.6.4 Dubinin-Radushkevich (D-R) Isotherm

It is given as (Dubinin and Radushkevich, 1947)

$$q_e = q_s \exp(-B\varepsilon^2) \tag{5.15}$$

where, q_s is the D-R constant and ε^2 can be correlated as:

$$\varepsilon = \mathrm{RT}\ln\left(1+\frac{1}{C_e}\right) \tag{5.16}$$

The constant B gives the mean free energy E of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship [Hasany and Chaudhary, 1996]:

$$\mathrm{E} = 1/\sqrt{2B}$$

D-R isotherm plots at 293, 303, 313 and 323 K are shown in Figs. 5.14 and 5.28, respectively. The estimated values of the D-R constants for the adsorption of furfural onto BFA and ACC respectively, are shown, in Tables 5.5 and 5.9. It may be observed that the sorption energy value is lower for adsorption of furfural at lower temperatures. The values of correlation coefficients are lowest in comparison to the values for all other isotherms investigated. Thus, the D-R equation does not represent the experimental data satisfactorily.

5.7 ERROR ANALYSIS

Due to the inherent bias resulting from linearization, five different error functions of non-linear regression basis 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:

$$SSE = \sum_{i=1}^{n}\left(q_{e,calc} - q_{e,\exp}\right)_i^2 \tag{5.17}$$

Here, $q_{e,cal}$ and $q_{e,\exp}$ are, respectively, the calculated and experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg/g) and n is the number of data points. This most commonly used error function; SSE has one major drawback is 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 5.6 and 5.10, both for BFA and ACC, respectively.

5.7.2 The Sum of the Absolute Errors (SAE)

SAE is given as:

$$SAE = \sum_{i=1}^{n} \left| q_{e,calc} - q_{e,\exp} \right|_i \tag{5.18}$$

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. The values of SAE are given in Table 5.6 and 5.10, both for BFA and ACC, respectively.

5.7.3 The Average Relative Error (ARE)

ARE (Kapoor and Yang, 1989) is given as:

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{(q_{e,\exp} - q_{e,calc})}{q_{e,\exp}} \right|_i \tag{5.19}$$

This error function attempts to minimize the fractional error distribution across the entire concentration range. The values of *ARE* is given in Table 5.6 and 5.10, both for BFA and ACC, respectively.

5.7.4 The Hybrid Fractional Error Function (HYBRID)

HYBRID is given as:

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{(q_{e,\exp} - q_{e,calc})}{q_{e,\exp}} \right]_i \tag{5.20}$$

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. The values of *HYBRID* error functions are given in Tables 5.6 and 5.10, both for BFA and ACC, respectively.

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; Srivastava et al., 2006 a, b, c) 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:

$$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{(q_{e,meas}-q_{e,calc})}{q_{e,meas}}\right)_i^2} \tag{5.21}$$

The values of *MPSD* error functions are given in Table 5.6 and 5.10, both for BFA and ACC, respectively.

5.7.6 Choosing Best-fit Isotherm Based on Error Analysis

The values of the five error functions are presented in Tables 5.6 and 5.10. By comparing the results of the values of the error functions, it is found that R-P isotherm is generally best-fitted the equilibrium data for furfural adsorption onto BFA and ACC at all temperatures. However, Freundlich model best-fits the furfural adsorption isotherm data onto BFA at 323 K. It may, however, be noted that the linear correlation coefficients, R^2 and the error analysis values invariably show that the R-P isotherm could generally be used for correlating furfural adsorption onto BFA and ACC.

5.8 THERMODYNAMIC STUDY

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

$$\Delta G^0 = -RT\ln K \tag{5.22}$$

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:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5.23}$$

Combining above two equations, we get

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \tag{5.24}$$

where, ΔG^0 is the free energy change (kJ/mol), 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 $(1/T)$ (Fig. 5.15 and 5.29), using equation:

$$\Delta H^0 = \left[R \frac{d \ln K}{d(1/T)} \right] \tag{5.25}$$

ΔG^0, ΔH^0 and ΔS^0 as calculated from Langmuir, Freundlich and R-P isotherms are given in Table 5.7 and 5.11, respectively, for adsorption of furfural onto BFA and ACC. The adsorption process in the solid-liquid system is a combination of two processes: (a) Desorption of molecules of solvent (water) previously adsorbed, and (b) Adsorption of adsorbate species. For significant adsorption to occur, the free energy changes of adsorption, ΔG^0, must be negative. The thermodynamics relation between ΔG^0, ΔH^0 and ΔS^0 suggests that either (i) ΔH^0 is positive and ΔS^0 is positive and that the value of $T\Delta S$ is much larger than ΔH^0, or (ii) ΔH^0 is negative and ΔS^0 is negative or that the value of ΔH^0 is more than $T\Delta S$. Furfural adsorption is exothermic in nature, giving a negative value of ΔH^0. For the negative values of ΔS^0 (furfural-BFA), the negative value of $T\Delta S$ has to be smaller than ΔH^0. The negative ΔH^0 o value confirms the exothermic nature of the overall-sorption process (Table 5.7 and 5.11). The negative value of ΔS^0 suggests decreased randomness at the solid/solution interface with some structural changes in the furfural and BFA, and a decrease in the degree of freedom of the adsorbed species. The positive value of ΔS^0 suggests increased uniformly randomness at the solid/solution interface and an affinity of the ACC towards furfural. Also, positive ΔS^0 value corresponds to an decrease in the degree of freedom of the adsorbed species (Raymon, 1988). Negative ΔG^0_{ads} indicates the feasibility and spontaneity of the adsorption process.

5.9 DESORPTION STUDY

Desorption study was carried for BFA. Fig. 5.30 shows the percent desorption with various solvents for the removal of from furfural loaded BFA. It is clear from the Fig. 5.30 that desorption is highest in ethyl alcohol. Desorption studies help in elucidating the mechanism of an adsorption process. If the furfural adsorbed onto the adsorbent can be desorbed by water, it can be said that the attachment of the furfural onto the adsorbent is by weak bonds. If the strong acid, such as HNO_3 and HCl, or strong bases, such as NaOH can desorb the furfural, it can be said that the attachment of the furfural onto the adsorbent is by ion exchange. If organic acids, for example, such as CH_3COOH, can desorb the furfural, it can be said that the adsorption of the furfural onto the adsorbent is by chemisorption. Various solvents, viz. H_2SO_4, HNO_3, HCl, NaOH, CH_3COOH, C_2H_5OH and water were used in the elution of furfural from the adsorbents. Furfural-loaded BFA was stirred with 50 ml of various eluents and the results are shown in Fig.5.30. A very low desorption is obtained with the mineral acids (HNO_3 and HCl), alkali (NaOH), organic acid (CH_3COOH) and water. Very low desorption of furfural indicates that some complex formation takes place between the active sites of BFA and the functional groups of furfurals. Therefore, the regeneration of BFA and the recovery of the furfural by desorption is ruled out. However, environmentally safe disposal of BFA and ACC loaded with the furfural is of prime importance.

5.10 COMPARATIVE ASSESSMENT OF BFA AS AN ADSORBENT

In the present study the BFA has been used for the removal of furfural from aqueous solution and tried to compare the performance with ACC. The optimum BFA dose was 4 g/l whereas the dose of ACC was 10 g/l, which is more than two times of the optimum dose of BFA. Further, the C_e versus q_e (Fig. 5.31) data of BFA indicate that the q_e can be as high as ~ 72.92 mg/g whereas the q_e value of ACC can be ~20.64 mg/g indicating a high adsorptive uptake of furfural by BFA as compare to ACC. It may also be seen in Table 5.12 that the removal of furfural by BFA is higher than that for ACC. Based on these experimental data and the fact that the BFA is available only at the transportation cost (Rs. 5000 per tonne), while ACC is available at the rate of ~ Rs. 40,000 per tonne, the BFA proves to be a very attractive adsorbent for the removal of furfural from aqueous solutions, even at very high concentration.

Table 5.1. Characteristics of BFA and ACC.

Characteristics	BFA	ACC
Proximate analysis		
Moisture (%)	5.65	4.39
Ash (%)	54.75	13.60
Volatile matter (%)	6.70	4.19
Fixed Carbon (%)	32.90	77.82
Bulk density (kg/m^3)	88.29	506.68
Average particle size (μm)	460.04	2311.56
Surface area of pores (m^2/g)		
(i) BET	237.83	171.05
(ii) BJH		
(a) adsorption cumulative	62.29	131.98
(b) desorption cumulative	36.19	94.33
BJH cumulative pore volume (cm^3/g)		
(i) Single Point Total	0.1337	0.1327
(ii) BJH adsorption	0.0526	0.1231
(iii) BJH desorption	0.0508	0.1081
Average pore diameter (Å)		
(i) BET	22.47	31.03
(ii) BJH adsorption	33.77	37.30
(iii) BJH desorption	56.12	45.86

Table 5.2. Particle size analysis of BFA.

Siveve sizes, micron	Avg. Size (d), micron	Wt Retaining	% weight retaining	Cumilative	% Cumulative	Weight passing	%Passing	Wt fraction, retaining xi	d^2	$xi*d^2$
>600	600	2.236	22.361	2.236	22.361	77.639	77.64	0.22361	360000	80499.6
600 - 500	550	3.032	30.321	5.268	52.682	47.318	47.32	0.30321	302500	91721.03
500 - 425	462.5	0.328	3.281	5.596	55.963	44.037	44.04	0.03281	213906.3	7018.264
425 - 300	362.5	1.709	17.091	7.305	73.054	26.946	26.95	0.17091	131406.3	22458.64
300 - 250	275	0.223	2.231	7.529	75.285	24.715	24.72	0.02231	75625	1687.194
250 - 180	215	0.956	9.561	8.485	84.846	15.154	15.15	0.09561	46225	4419.572
180 - 150	165	1.311	13.111	9.796	97.957	2.043	2.04	0.13111	27225	3569.47
150 - 125	137.5	0.070	0.701	9.866	98.658	1.342	1.34	0.00701	18906.25	132.5328
125 - 75	100	0.126	1.261	9.992	99.919	0.081	0.08	0.01261	10000	126.1
<75	75	0.008	0.081	10.000	100	0	0.00	0.00081	5625	4.55625
										211637
							Average particle size (µm)			**460.040**

Table 5.3. Particle size analysis of ACC.

Siveve sizes, micron	Avg. Size (d), micron	Wt Retaining	% weight retaining	Cumilative	% Cumulative	Weight passing	%Passing	Wt fraction, retaining xi	d^2	$xi*d^2$
>3350	3350	0.08	5.33	0.08	5.33	1.42	94.67	0.053333	11222500	598533.3
3350-1700	2525	1.032	68.80	1.112	74.13	0.388	25.87	0.688	6375625	4386430
1700-1000	1350	0.267	17.80	1.379	91.93	0.121	8.07	0.178	1822500	324405
1000-500	750	0.066	4.40	1.445	96.33	0.055	3.67	0.044	562500	24750
<500	500	0.055	3.67	1.5	100.00	0	0.00	0.036667	250000	9166.667
										5343285
							Average particle size (µm)			**2311.555**

Table 5.4. Kinetic parameters for the removal of furfural by BFA (C_0 = 100-500 mg/l, m = 4 g/l).

Pseudo-first-order model

C_o (mg/l)	$q_{e,\exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	k_f (/min)	R^2
100	24.9892	0.0854	0.0200	0.7993
200	45.8945	9.7791	0.0348	0.9818
300	59.9930	10.4135	0.0037	0.3344
500	80.1887	4.7632	0.0170	0.8402

Pseudo-second-order model

C_o (mg/l)	$q_{e,calc}$ (mg/g)	**mg/g min)**	k_S **(g/mg min)**	R^2
100	25.0000	625	1	**1**
200	46.5116	21.1864	0.0098	0.9999
300	59.1716	11.7925	0.0034	**0.9926**
500	80.6451	97.0874	0.0149	**1**

Bangham model

C_o (mg/l)	k_0 (g)	α	R^2
100	108.0274	0.1100	0.9706
200	27.992	0.1573	0.9125
300	22.2861	0.0828	0.4454
500	21.3567	0.0362	0.9719

W-M Intra-particle diffusion model

C_o (mg/l)	k_{id} (mg/g min$^{1/2}$)	**I_1 (mg/g)**	**R^2**
100	0.0104	24.8690	0.6295
200	0.6642	38.0120	0.8666
300	0.8180	46.4690	0.6337
500	0.4891	74.2500	0.8585

Table 5.5. **Isotherm parameters for the removal of furfural by BFA (C_0 = 50-1000 mg/l, m = 4 g/l).**

Frendlich Isotherm

Temp., K	K_F ((mg/g)(mg/l)$^{-1/n}$)	1/n	R^2
293	26.8670	0.1773	0.9557
303	20.7179	0.1952	0.9806
313	9.4678	0.3203	0.952
323	6.9699	0.3416	0.9771

Langmuir Isotherm

Temp., K	K_L (l/mg)	q_m (mg/g)	R^2
293	0.0488	81.9672	0.9901
303	0.0377	72.4638	0.9886
313	0.0244	69.9301	0.9922
323	0.0127	67.5676	0.9745

Dubnin-Radushkevich Isotherm

Temp., K	q_s (mg/g)	E (kJ/mol)	R^2
293	62.7212	4.0825	0.8964
303	51.4186	3.1623	0.7242
313	49.2495	0.3535	0.7683
323	41.4546	0.3535	0.6170

Temkin Isotherm

Temp., K	K_T (l/mg)	B_1	R^2
293	133.1260	6.7385	0.9699
303	45.6507	6.6778	0.9722
313	0.7961	10.6230	0.9957
323	0.4147	10.3360	0.9298

R-P Isotherm

Temp., K	K_R (l/g)	a_R (l/mg)$^{1/\beta}$	β	R^2
293	457.0069	11.7353	0.8952	0.9996
303	346.8524	14.0975	0.8379	0.9996
313	5.0752	0.1920	0.8551	0.9997
323	20.1019	2.4945	0.6827	0.9940

Table 5.6. **Values of five different error analyses of isotherm models for adsorption of furfural by BFA (C_0 = 50-1000 mg/l, m = 4 g/l).**

293 K

	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	1148.5240	-32.4694	32.6861	32.6461	106.7523
Freundlich	131.3678	0.6821	10.2895	-1.0876	36.8128
Temkin	127.5366	**0.0027**	6.4941	**0.1336**	23.2338
R-P	**108.1958**	-0.7218	**5.3370**	-0.4519	**19.0942**
D-R	975.0694	-9.6254	16.0856	-4.1235	57.5495

303 K

	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	863.0533	-23.5479	31.5976	27.9125	103.1973
Freundlich	77.6876	1.0615	6.2952	-0.3823	22.5225
Temkin	113.9604	16.0017	7.6744	-6.0634	27.4569
R-P	**39.4774**	**-0.3003**	**3.7776**	**-0.1806**	**13.5151**
D-R	1351.7170	-17.7893	25.1400	-4.8456	89.9437

313 K

	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	151.2038	-3.5089	14.3011	11.1566	46.7073
Freundlich	219.0646	2.0835	11.4010	-1.0238	40.7895
Temkin	11.7539	**-0.0175**	2.4945	0.1678	8.9247
R-P	**10.8387**	-0.0483	**1.9345**	**-0.0739**	**6.9210**
D-R	1016.2590	-16.1637	24.1161	-3.7210	86.2804

323 K

	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	239.6643	-0.4445	18.4319	9.6506	60.1985
Freundlich	77.5134	-0.2941	**6.5999**	**-0.4857**	**23.6125**
Temkin	164.8733	**-0.0017**	15.0744	1.7817	53.9318
R-P	**71.5293**	-0.9450	6.8516	-0.5383	24.5131
D-R	1384.4840	-17.1581	29.8047	-10.3632	106.6324

Table 5.7 Thermodynamics Study

Isotherm	ΔG^0 (J/mol K)				ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol K)
	293 K	**303 K**	**313 K**	**323K**		
Langmuir	-20.642	-20.695	-20.2425	-19.1336	-26.4105	-0.0194
Temkin	-39.913	-38.579	-29.3156	-28.5008	-193.8450	-0.5211
Frendlich	-19.1871	-19.1872	-17.7826	-17.5282	-39.5290	-0.0687
R-P	-26.0903	-26.2859	-16.16	-20.3727	-169.8500	-0.4852

Table 5.8. Kinetic parameters for the removal of furfural by ACC (C_0 = 100-500 mg/l, m = 10 g/l).

Pseudo-first-order model

C_o (mg/l)	$q_{e,\exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	k_f (/min)	R^2
100	8.9713487	7.7090	0.0088	0.9797
200	14.971349	17.5227	0.0097	0.9803
300	18.81202	17.8115	0.0117	0.9729
500	22.278127	19.0985	0.0088	0.9744

Pseudo-second-order model

C_o (mg/l)	$q_{e,calc}$ (mg/g)	**g/g min)**	k_S **(g/mg min)**	R^2
100	9.90099	0.1704	0.0018	**0.9954**
200	17.79359	0.2172	0.0007	0.9966
300	25.44529	0.2280	0.0004	**0.9912**
500	27.17391	0.3433	0.0005	**0.9930**

Bangham model

C_o (mg/l)	k_0 (g)	α	R^2
100	1.2324	0.6153	0.9857
200	0.6023	0.6740	0.9746
300	0.3620	0.7130	0.9727
500	0.4527	0.5884	0.9643

W-M Intra-particle diffusion model

C_o (mg/l)	k_{id} (mg/g $min^{1/2}$)	**I_1 (mg/g)**	**R^2**
100	0.3717	1.2016	0.9277
200	0.6665	1.0994	0.9304
300	0.8899	0.6194	0.9045
500	0.9998	1.7646	0.8916

Table 5.9. Isotherm parameters for the removal of furfural by ACC (C_0 = 50-1000 mg/l, m = 10 g/l).

Frendlich Isotherm

Temp., K	K_F ((mg/g)(mg/l)$^{-1/n}$)	1/n	R^2
293	4.0169	0.2926	0.8867
303	3.7173	0.2947	0.8682
313	3.4591	0.2907	0.8928
323	3.3391	0.2666	0.9099

Langmuir Isotherm

Temp., K	K_L (l/mg)	q_m (mg/g)	R^2
293	0.0559	22.6757	0.9999
303	0.0593	21.1864	0.9998
313	0.0451	19.9601	0.9999
323	0.0338	17.5747	0.9984

Dubnin-Radushkevich Isotherm

Temp., K	q_s (mg/g)	E (kJ/mol)	R^2
293	18.6342	0.3162	0.8202
303	17.8178	0.2673	0.8308
313	16.4069	0.2673	0.8102
323	14.2934	0.2673	0.8257

Temkin Isotherm

Temp., K	K_T (l/mg)	B_l	R^2
293	1.2341	3.5607	0.9545
303	1.1009	3.4158	0.9301
313	0.9925	3.1836	0.9548
323	1.1596	2.6274	0.9727

R-P Isotherm

Temp., K	K_R (l/g)	a_R (l/mg)$^{1/\beta}$	β	R^2
293	1.4298	0.0759	0.9703	0.9996
303	1.1029	0.0525	0.9970	0.9996
313	1.1366	0.0847	0.9354	0.9997
323	1.2383	0.1393	0.8948	0.9940

Table 5.10. Values of five different error analyses of isotherm models for adsorption of furfural by ACC (C_0 = 50-1000 mg/l, m = 10 g/l).

	SSE	SAE	ARE	HYBRID	MPSD
293 K					
Langmuir	0.7722	0.4193	2.1409	0.3242	6.9921
Freundlich	71.4181	0.1738	16.0063	-2.1818	57.2659
Temkin	14.2699	**0.0000**	9.1095	-3.5125	32.5911
R-P	**0.6805**	-0.0932	**1.7045**	**-0.1885**	**6.0981**
D-R	85.9622	-3.2548	18.5727	-5.4290	66.4477
303 K					
	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	2.5074	1.3675	4.1338	-3.6817	13.5010
Freundlich	74.1952	-0.0697	17.1184	-2.4195	61.2447
Temkin	19.0657	**-0.0020**	11.0000	-4.2603	39.3546
R-P	**1.0916**	-0.3108	**2.0972**	**0.0037**	**7.5033**
D-R	67.9177	-3.1065	18.1011	-3.9784	64.7605
313 K					
	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	**0.6227**	0.1437	**2.5143**	0.7892	**8.2116**
Freundlich	46.2339	0.1213	14.2833	-1.7953	51.1016
Temkin	9.9830	**-0.0012**	8.5031	-2.8638	30.4216
R-P	1.7229	-0.2315	2.7945	**0.0164**	9.9979
D-R	62.4179	-2.7284	17.3547	-4.3315	62.0902
323 K					
	SSE	SAE	ARE	HYBRID	MPSD
Langmuir	4.1186	-1.4931	7.6498	6.4374	24.9841
Freundlich	20.3391	0.0944	11.5721	-1.1905	41.4015
Temkin	3.8860	**0.0007**	5.7984	-1.8117	20.7451
R-P	**1.3842**	-0.1512	**2.3072**	**0.2416**	**8.2545**
D-R	38.6307	-1.4657	14.4434	-4.0911	51.6744

Table 5.11. Thermodynamics Study

Isotherm	**ΔG^0 (J/mol K)**				**ΔH^0 (KJ/mol)**	**ΔS^0 (KJ/mol K)**
	293 K	**303 K**	**313 K**	**323 K**		
Langmuir	-20.9240	-21.7870	-21.7923	-21.7116	-8.0606	44.3585
Temkin	-28.4607	-29.1444	-29.8366	-31.2075	-8.3059	68.7833
Frendlich	-14.5083	-14.8082	-15.1096	-15.4975	-5.6997	30.0628
R-P	-11.9920	-11.7473	-12.2134	-12.8337	-8.8674	10.2865

Table 5.12. Economic evaluation of both the adsorbent BFA and ACC
m (BFA) = 4 g/l, m (ACC)= 10 g/l

	% Removal of furfural (T = 303 K, C_0 = 100 mg/l)	**Adsorption capacity (mg/g)**	**Cost (Rs. per tonne)**
BFA	~97	72.92	5000.00
ACC	~88	20.64	40000.00

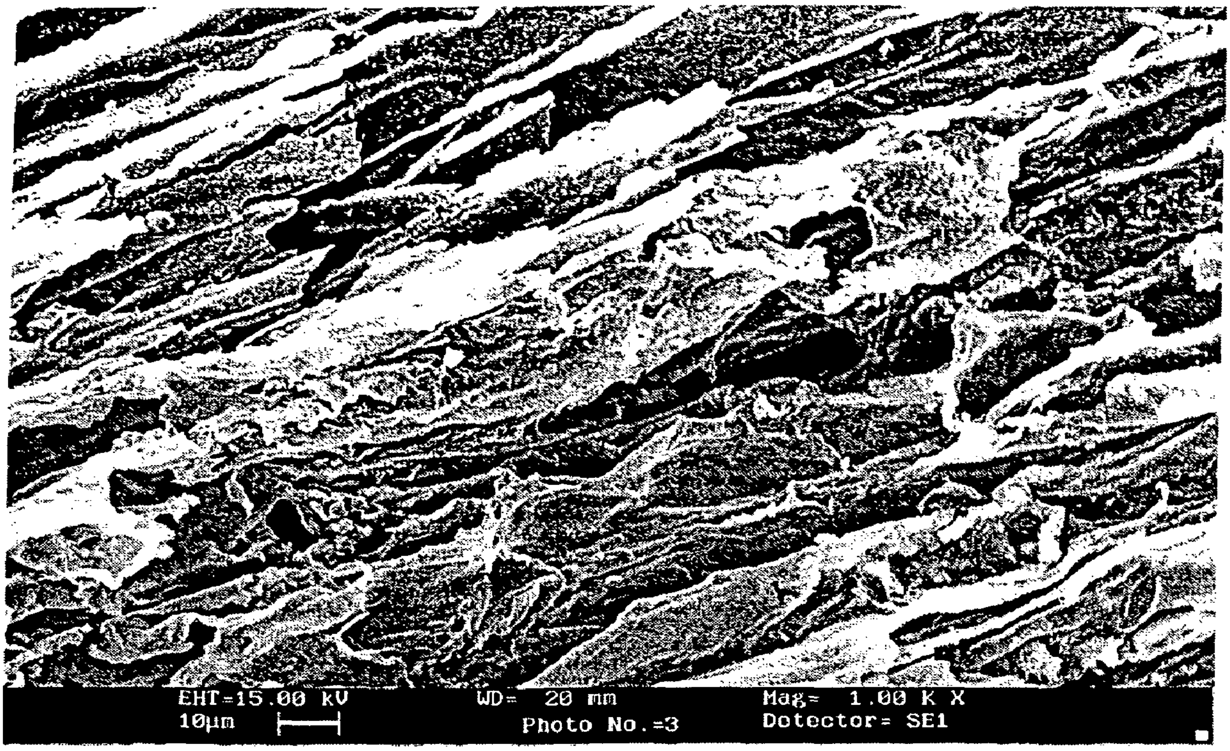

Fig 5.1. Scanning electron micrograph of bagasse fly ash at 1 KX

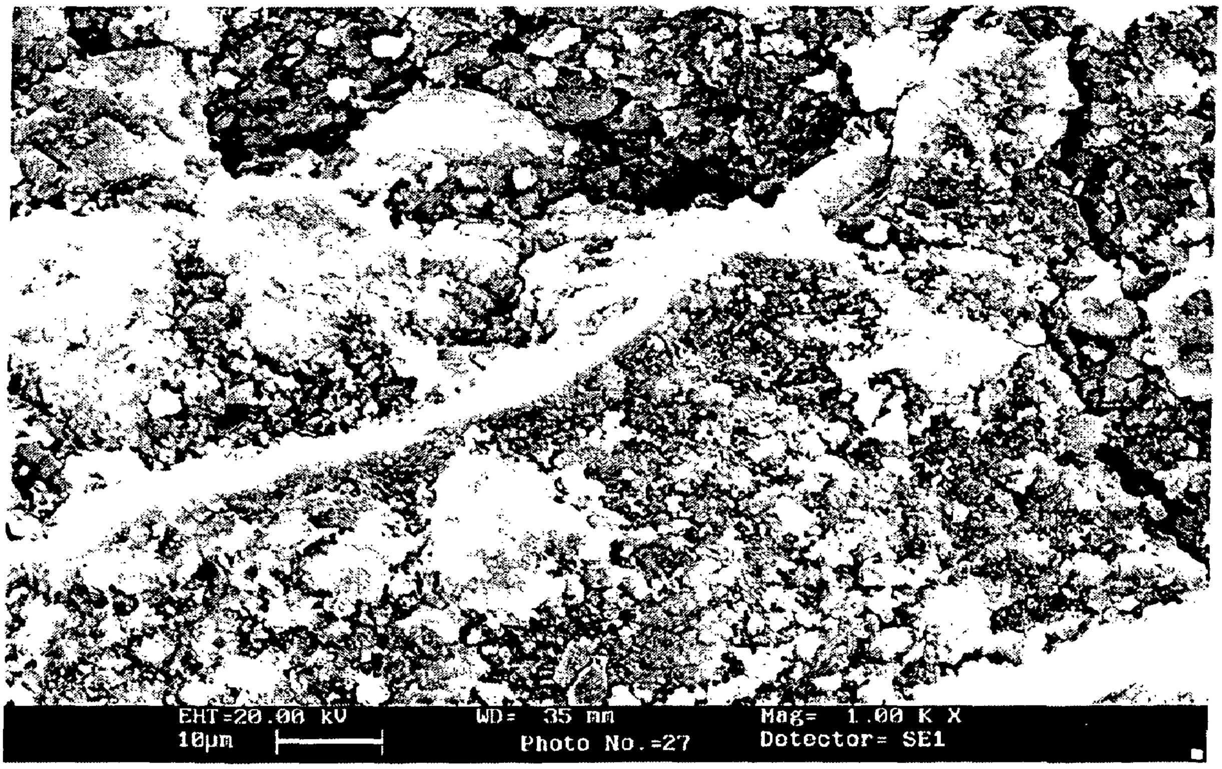

Fig 5.2. Scanning electron micrograph of activated carbon commercial grade at 1 KX magnification

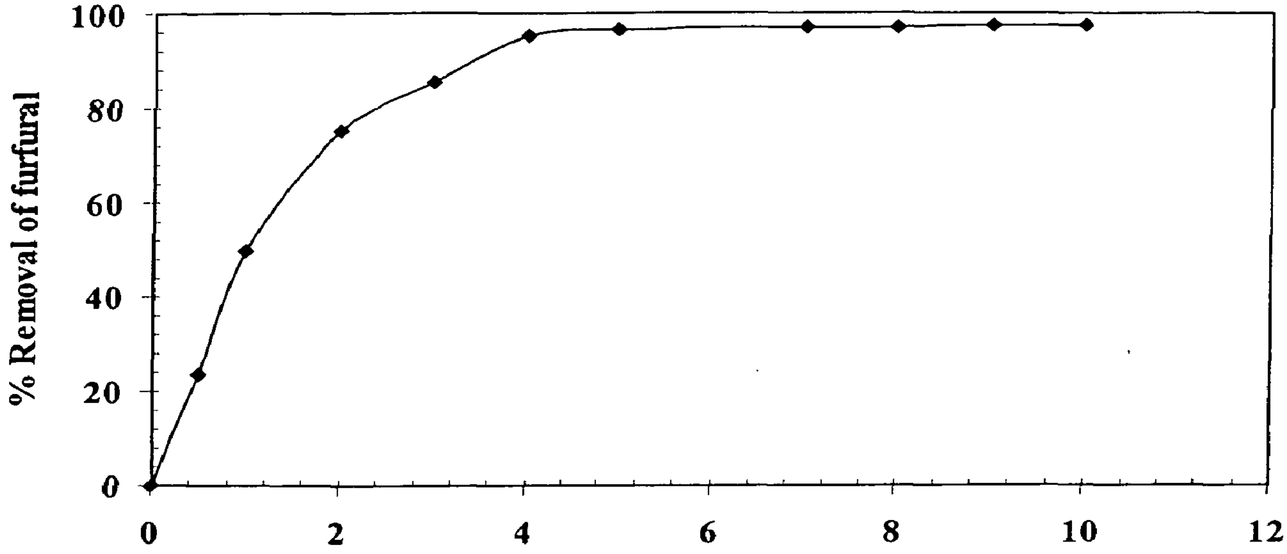

Fig. 5.3. Effect of adsorbent dose on the adsorption of furfural by BFA (T = 303 K, t = 6 h, C_0 = 100 mg/l).

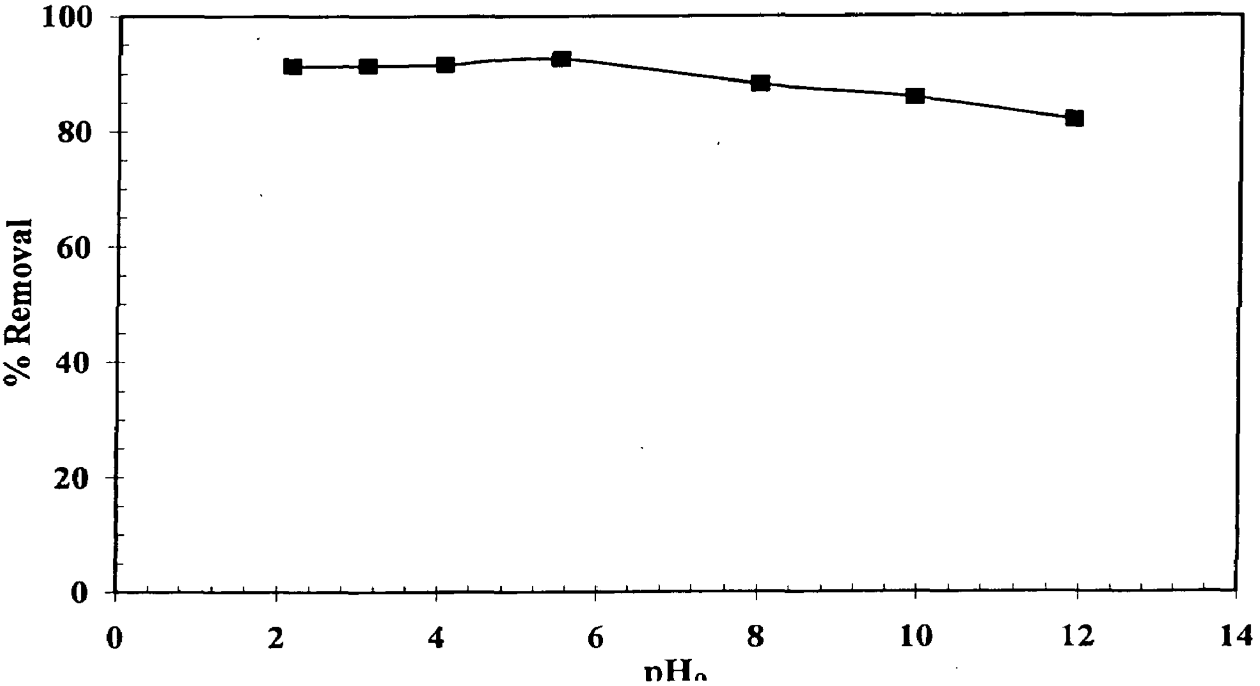

Fig. 5.4. Effect of pH_0 on the adsorption of furfural by adsorbent as BFA (T = 303 K, t = 6 h, C_0 = 100 mg/l).

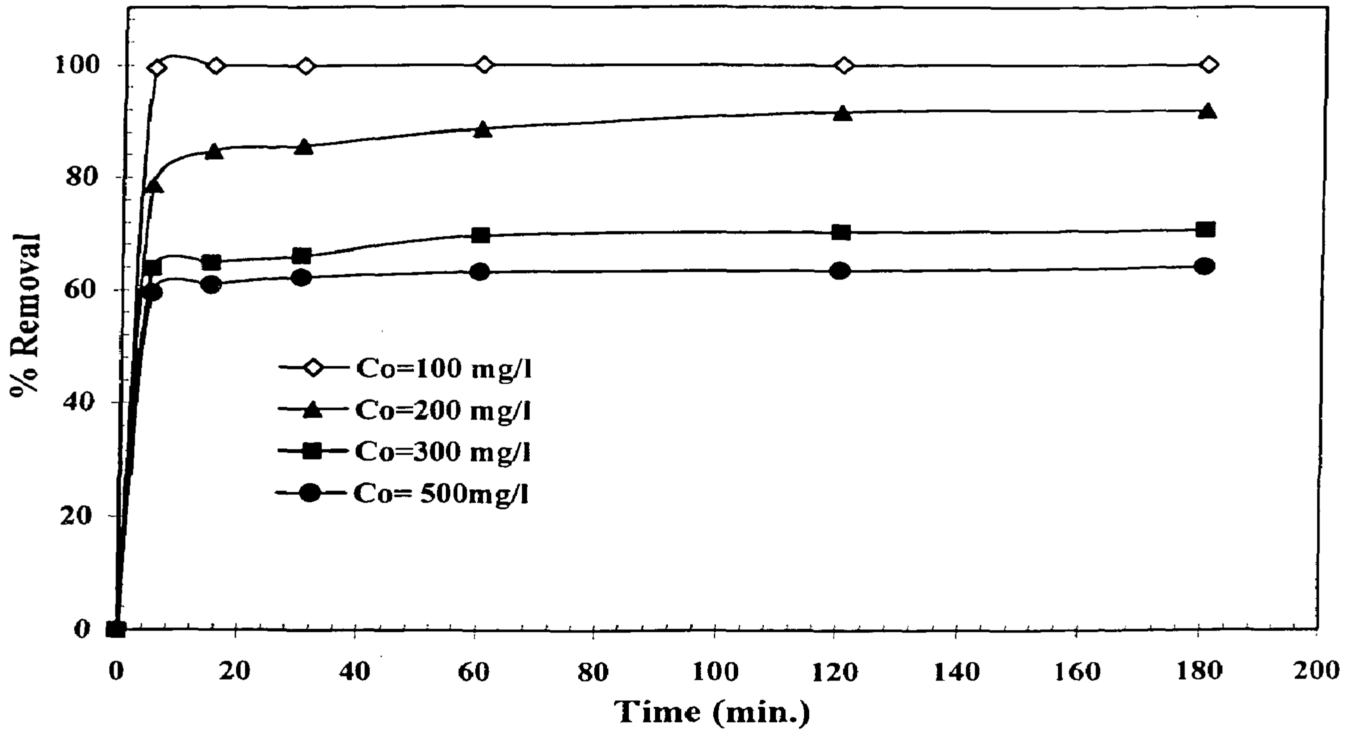

Fig. 5.5 (a). Effect of contact time on the % removal of furfural by BFA (T = 303 K, m = 4 g/l)

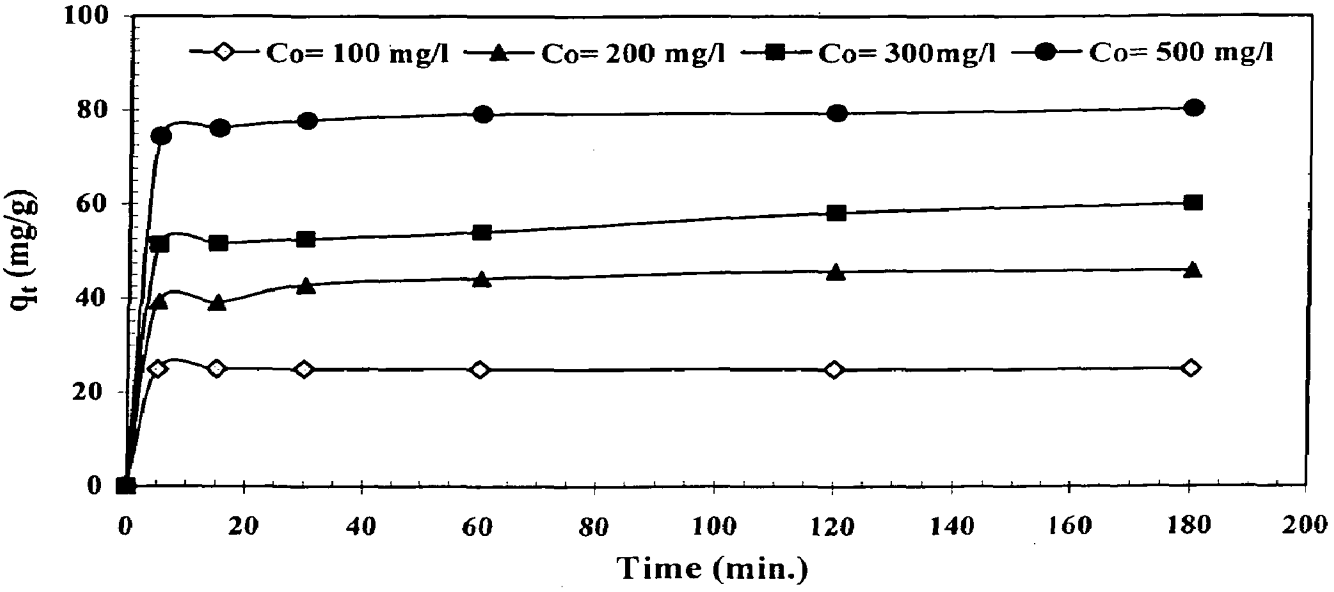

Fig. 5.5 (b). Effect of contact time on the removal of furfural by BFA (T = 303 K, m = 4 g/l).

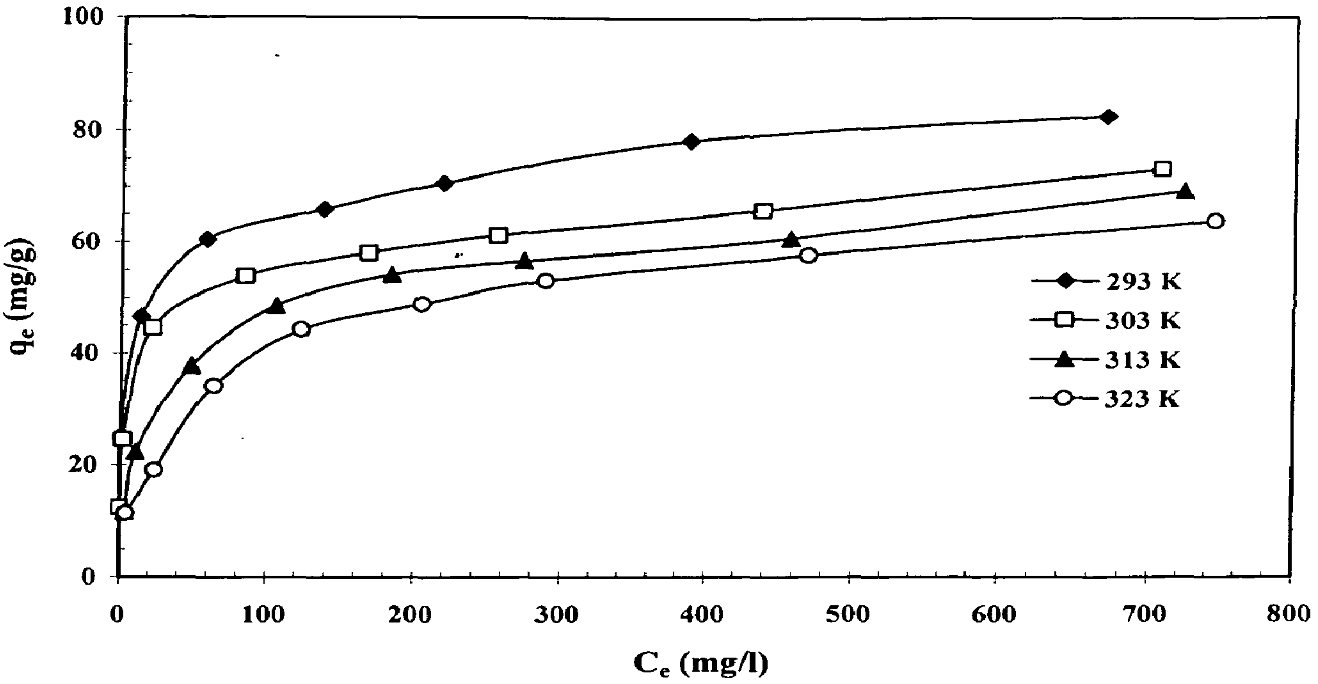

Fig. 5.6. Equilibrium adsorption isotherms at different temperature for furfural-BFA system. (*t* = 6 h, *m* = 4 g/l).

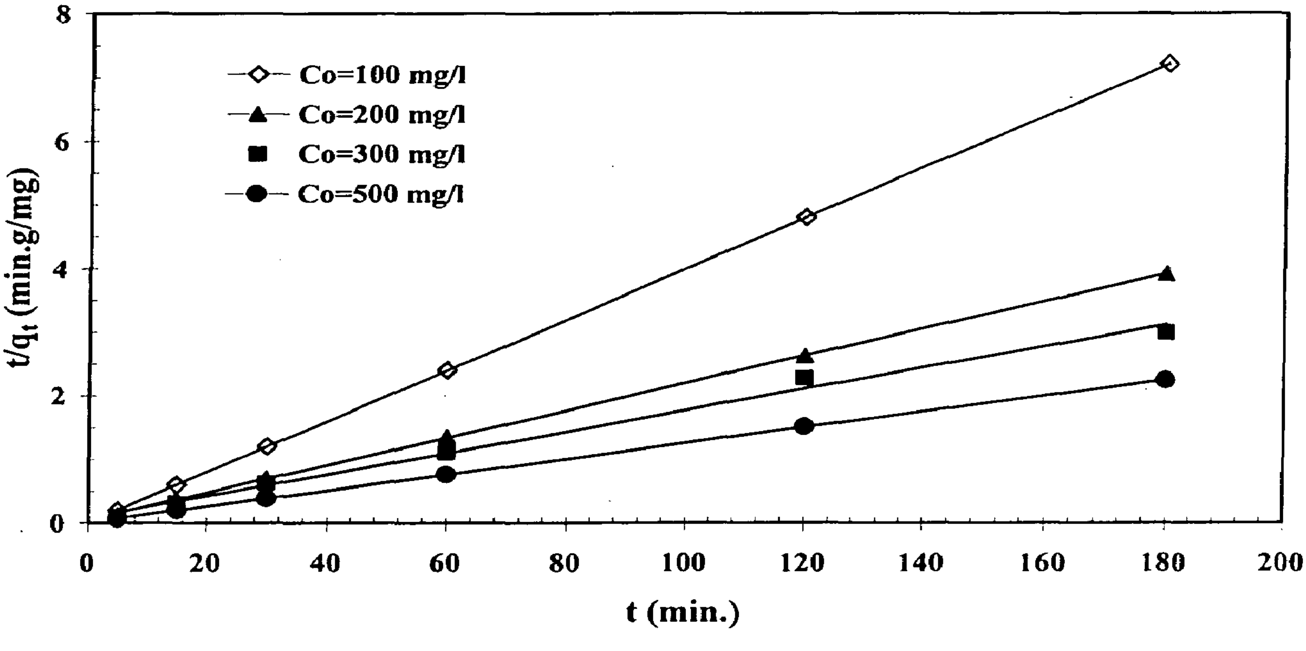

Fig. 5.7. Pseudo second order plot for the removal of furfural by BFA (*T* = 303 K, *m* = 4 g/l))

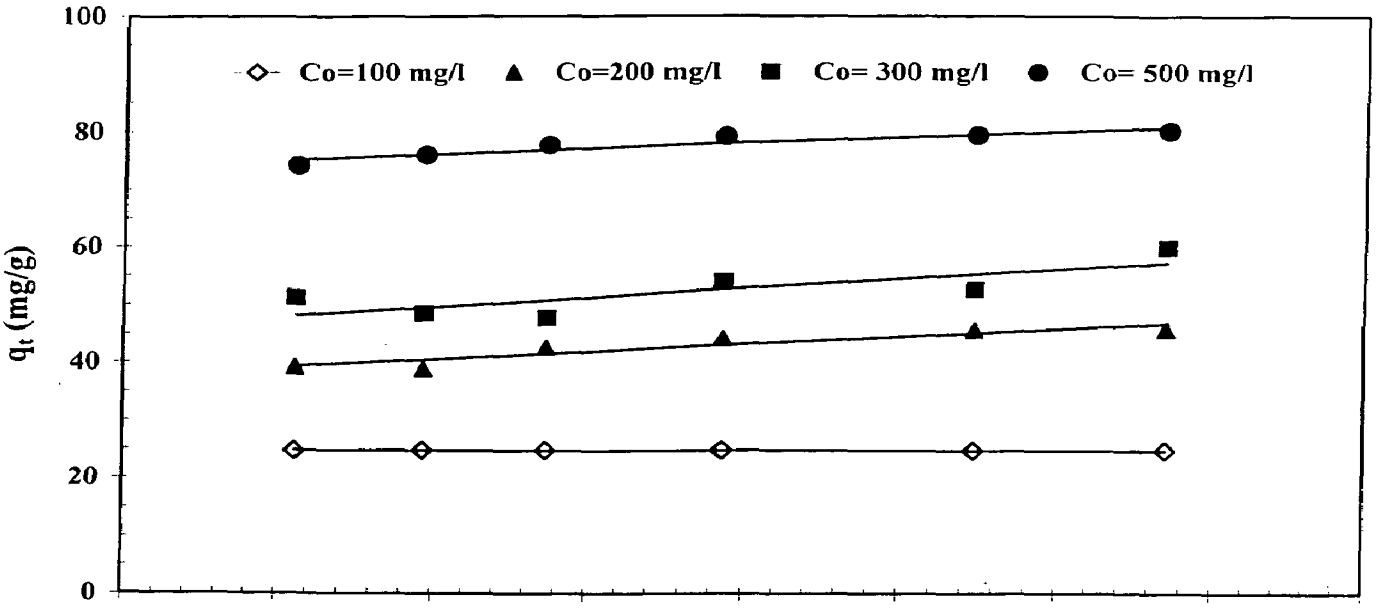

Fig. 5.8. Weber and Morris intra-particle diffusion plot for the removal of furfural by BFA (T = 303 K, m = 4 g/l).

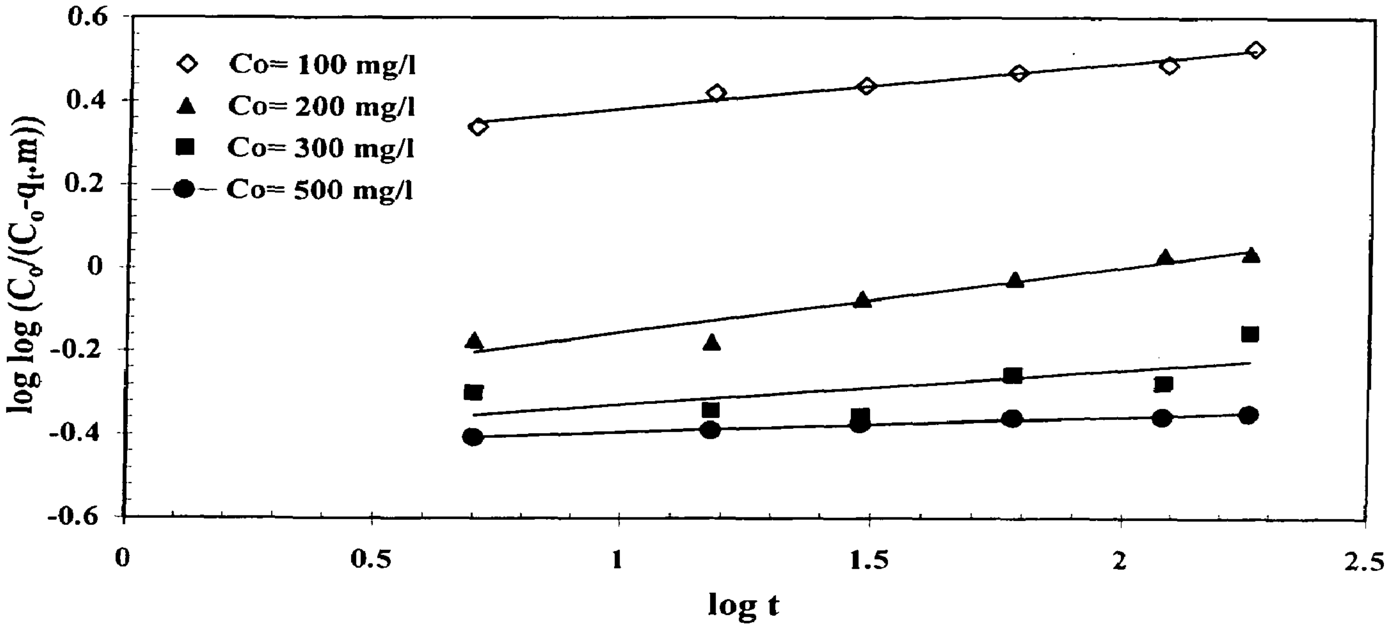

Fig. 5.9. Bangham plot for the removal of furfural by BFA (T = 303 K, m = 4 g/l).

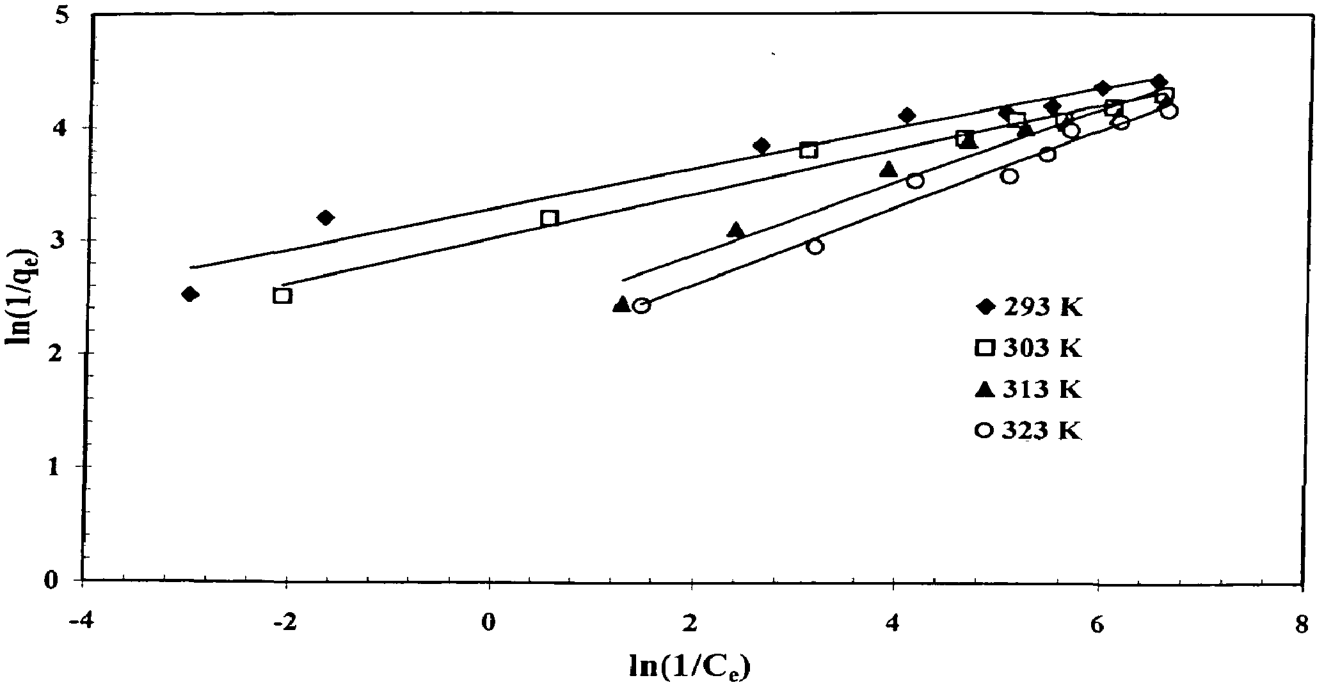

Fig. 5.10. Freundlich isotherm plots for the removal of furfural by BFA (t = 6 h, m = 4 g/l).

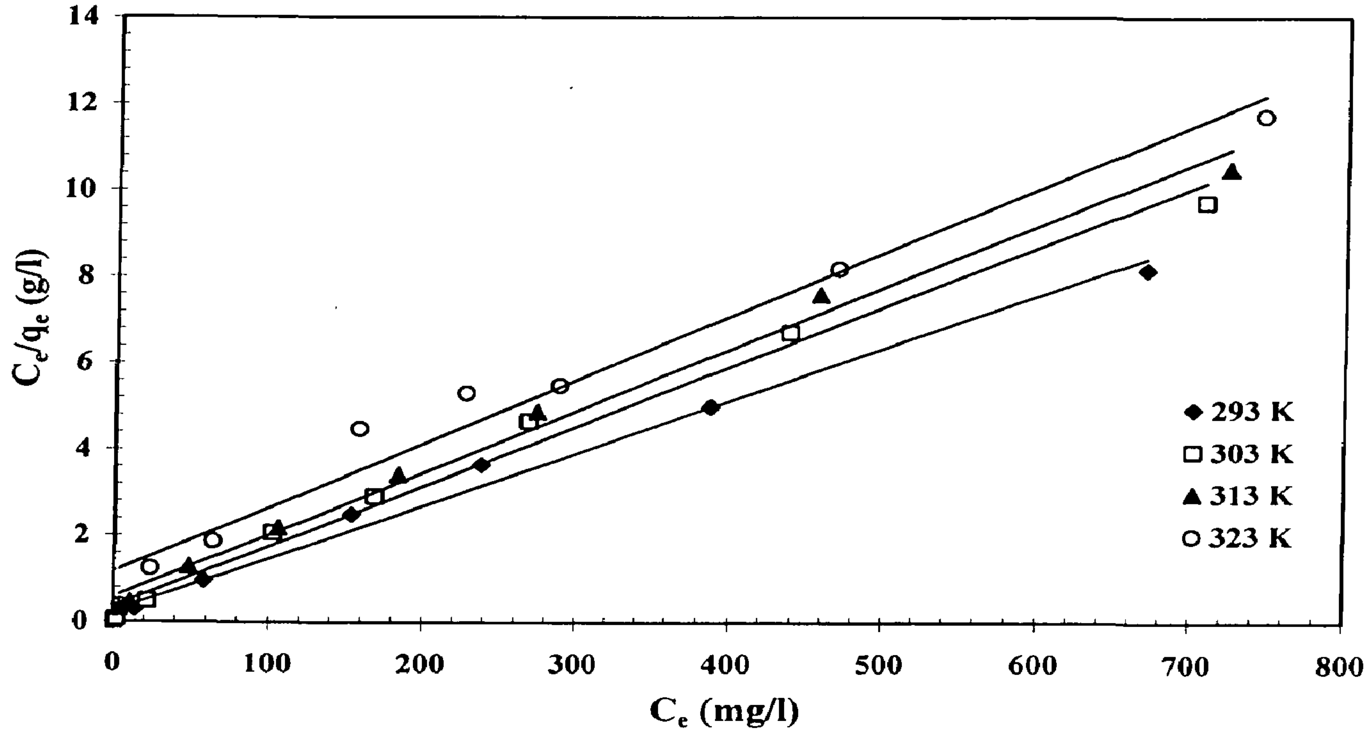

Fig. 5.11. Langmuir isotherm plots for the removal of furfural by BFA (t = 6 h, m = 4 g/l).

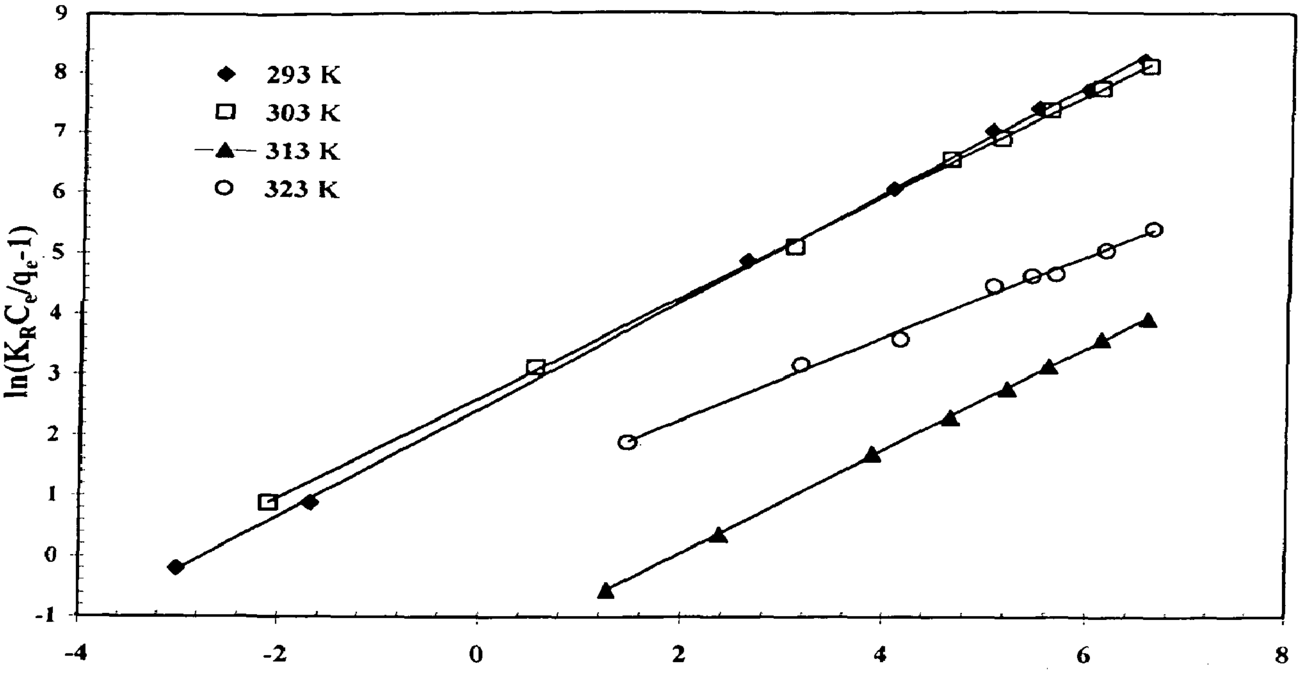

Fig. 5.12. **Redlich-Peterson isotherm plot for the removal of furfural by BFA (t = 6h, m = 4 g/l).**

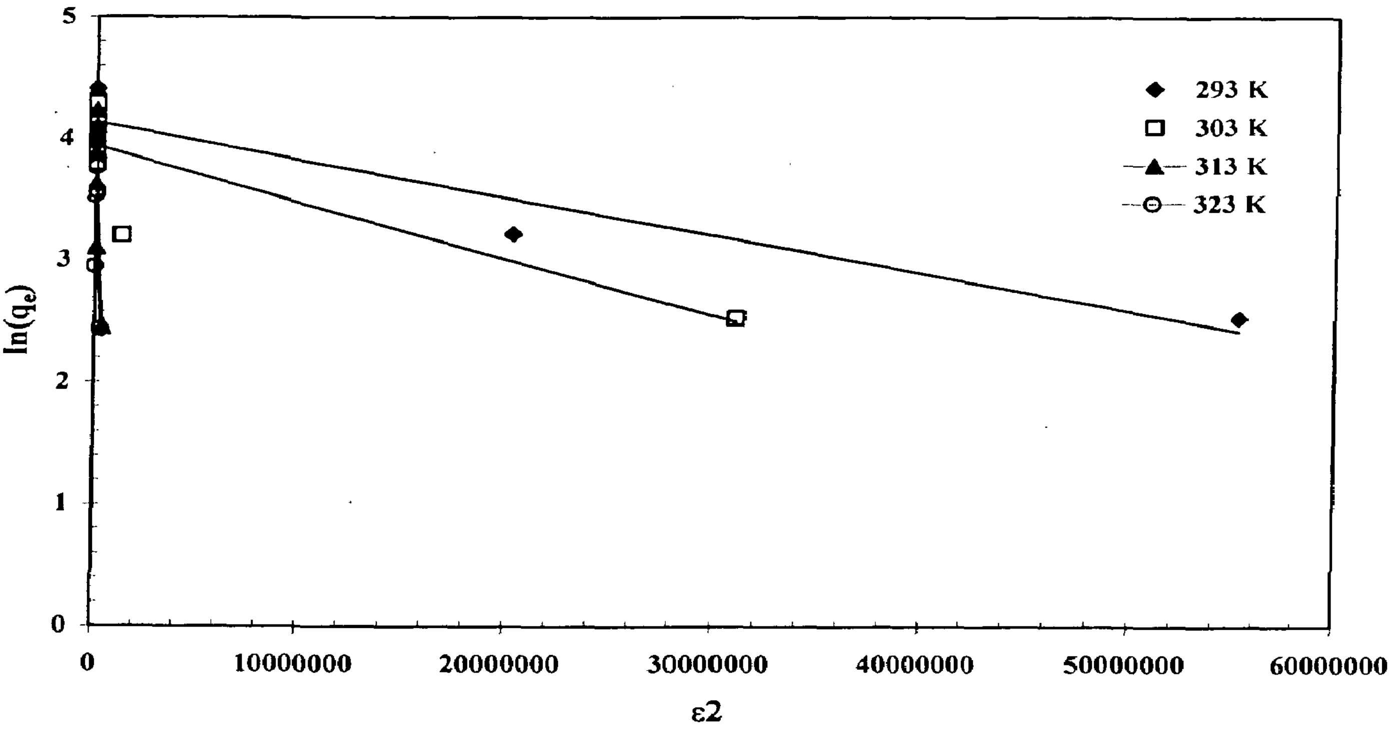

Fig. 5.13. **D-R isotherm plot for the removal of furfural by BFA (t = 6h, m = 4 g/l).**

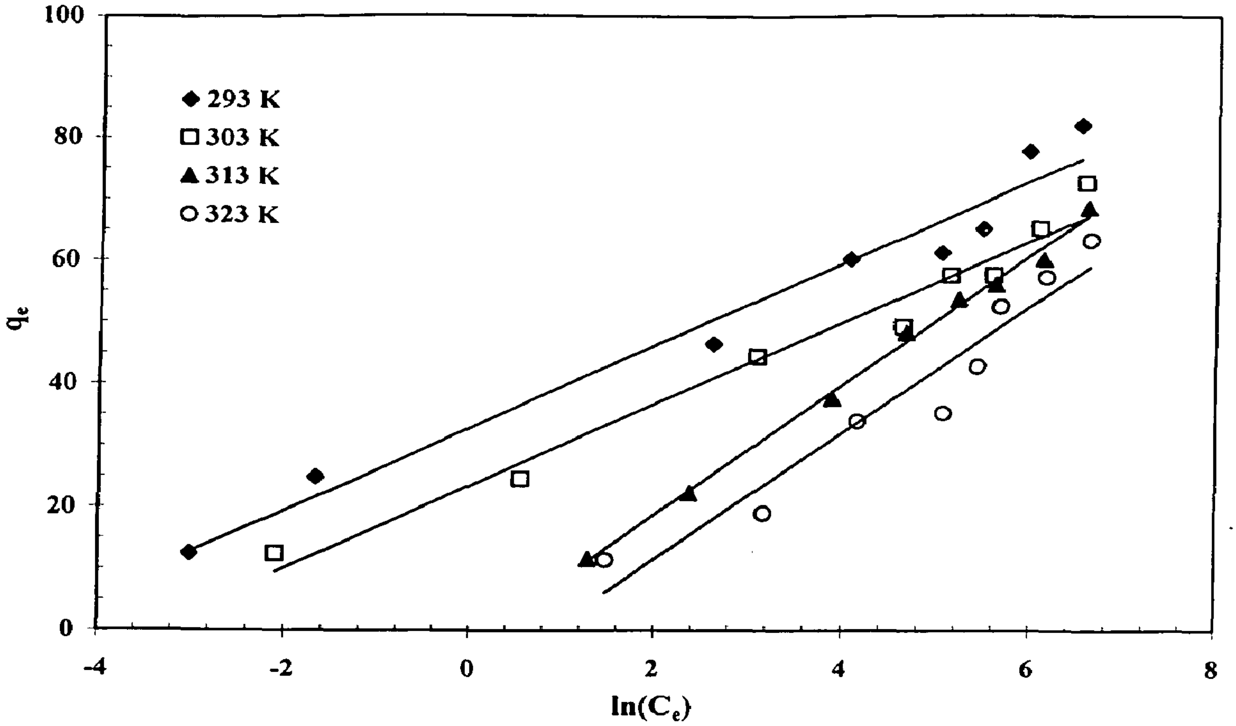

Fig. 5.14. Temkin isotherm plot for the removal of furfural by BFA (t = 6h, m = 4 g/l).

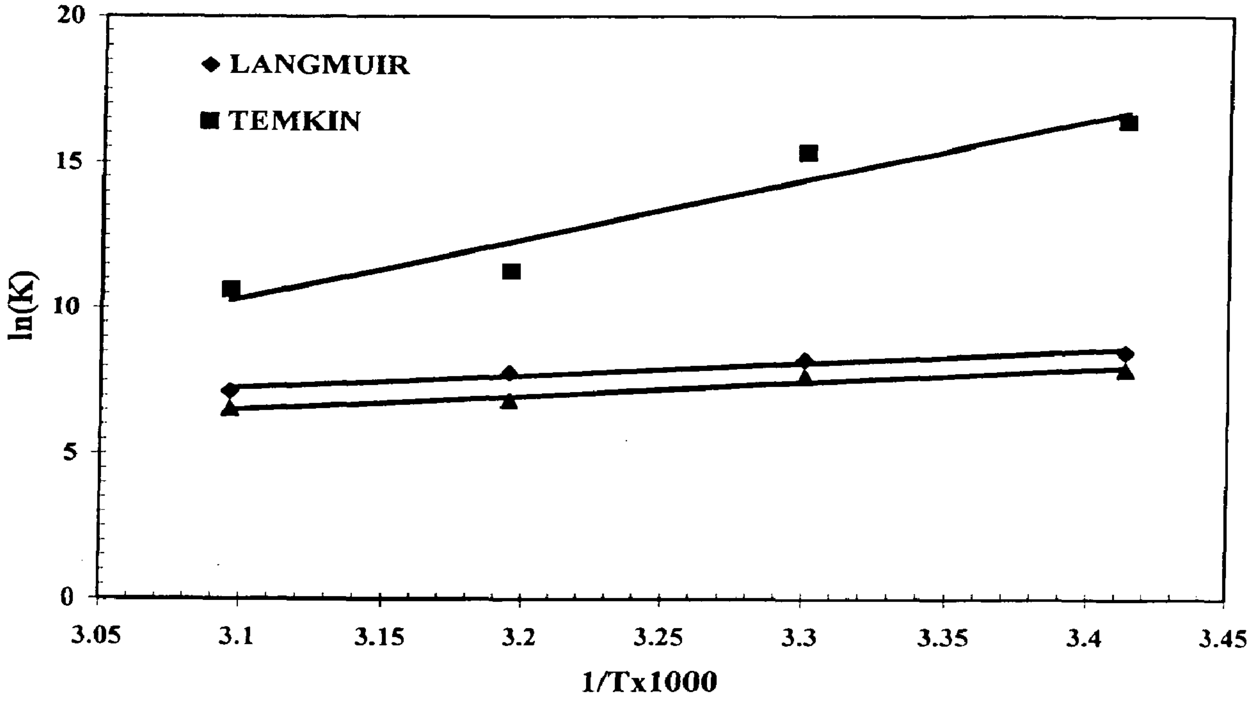

Fig. 5.15. Vant Hoff plot for the removal of furfural by BFA (t = 6h, m = 4 g/l).

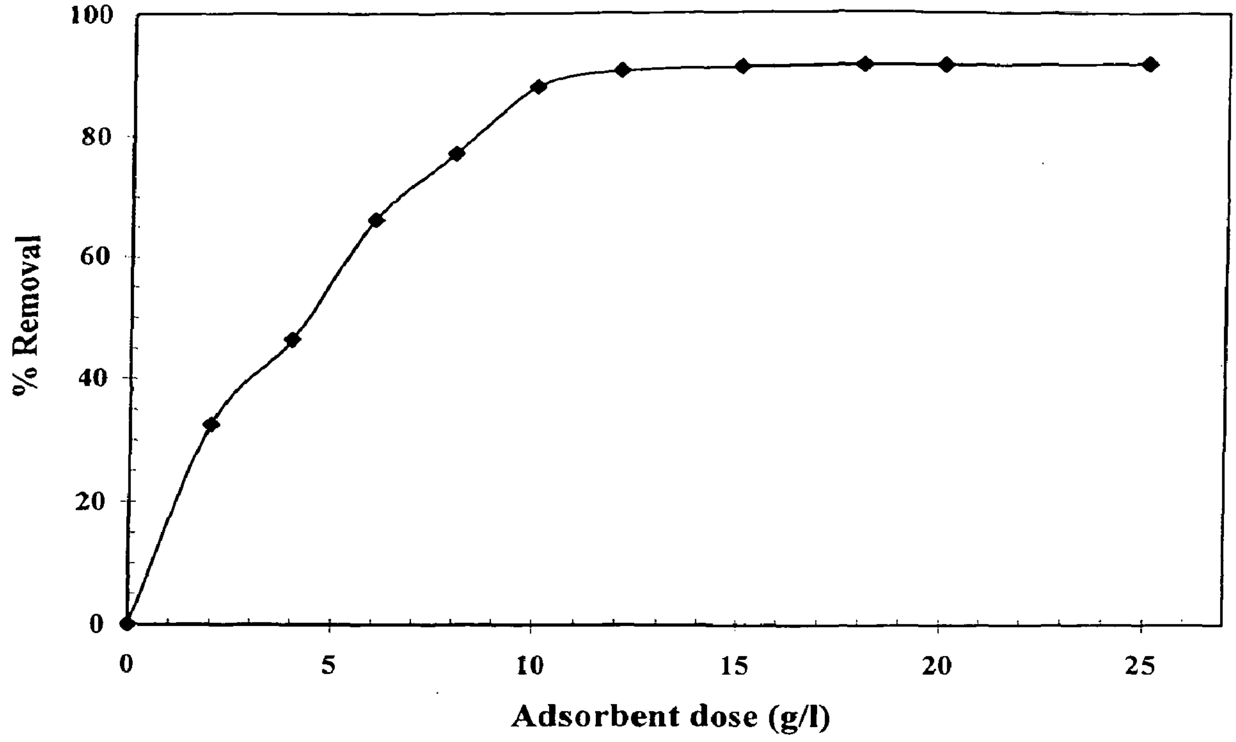

Fig. 5.16. Effect of adsorbent dose on the adsorption of furfural by ACC (T = 303 K, t = 6 h, C_0 = 100 mg/l).

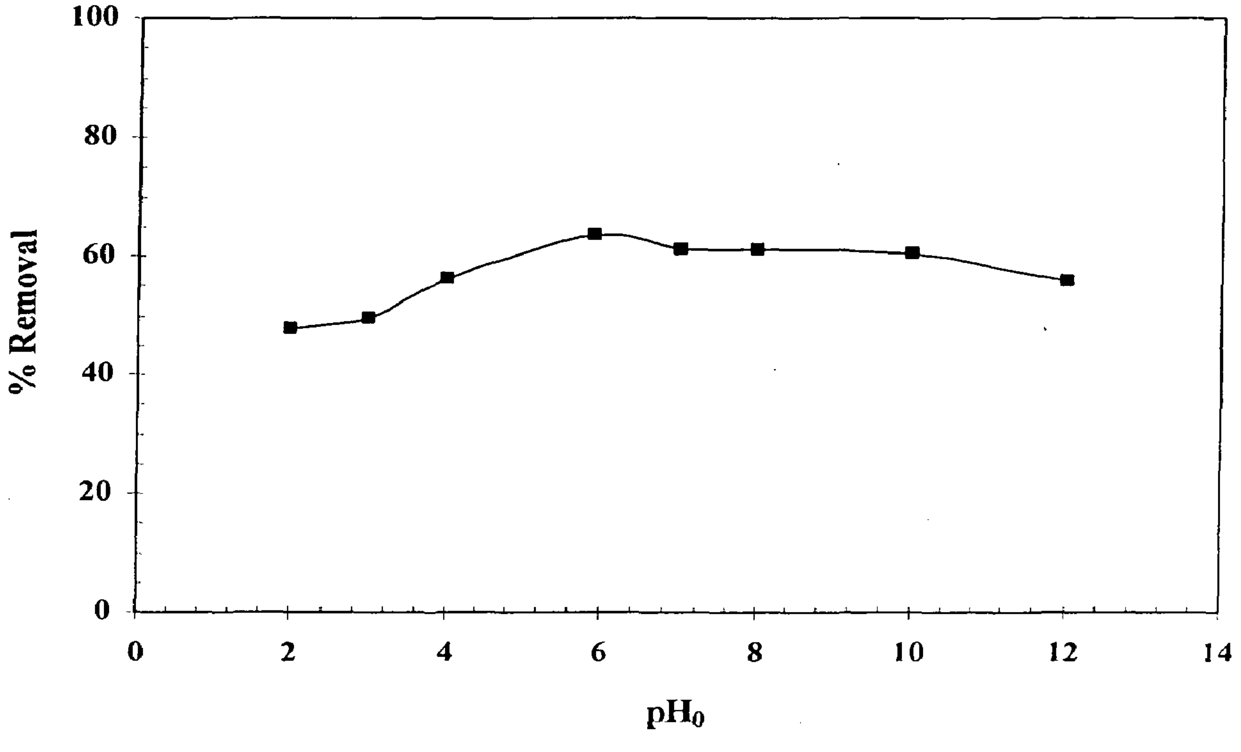

Fig. 5.17. Effect of pH_0 on the adsorption of furfural by adsorbent as ACC (T = 303 K, t = 6 h, C_0 = 100 mg/l, m = 5 g/l).

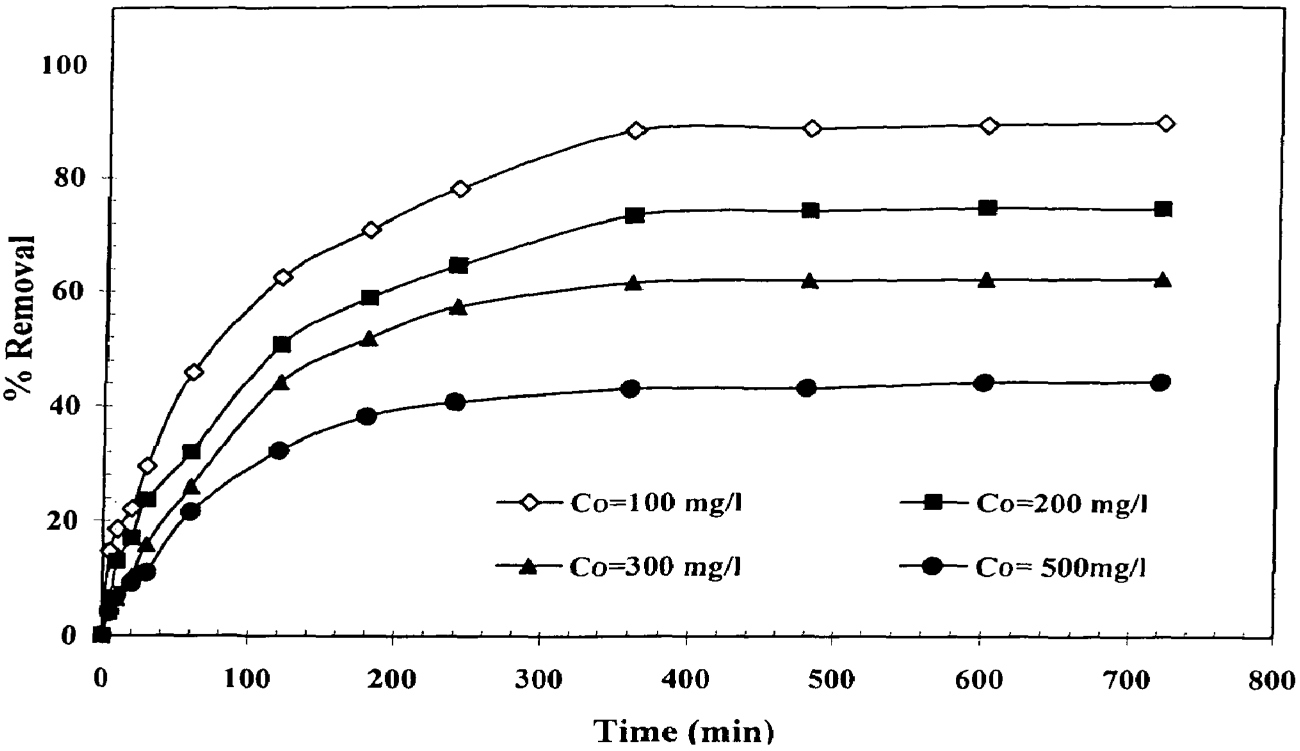

Fig. 5.18 (a). Effect of contact time on the % removal of furfural by ACC (T = 303 K, m = 10 g/l).

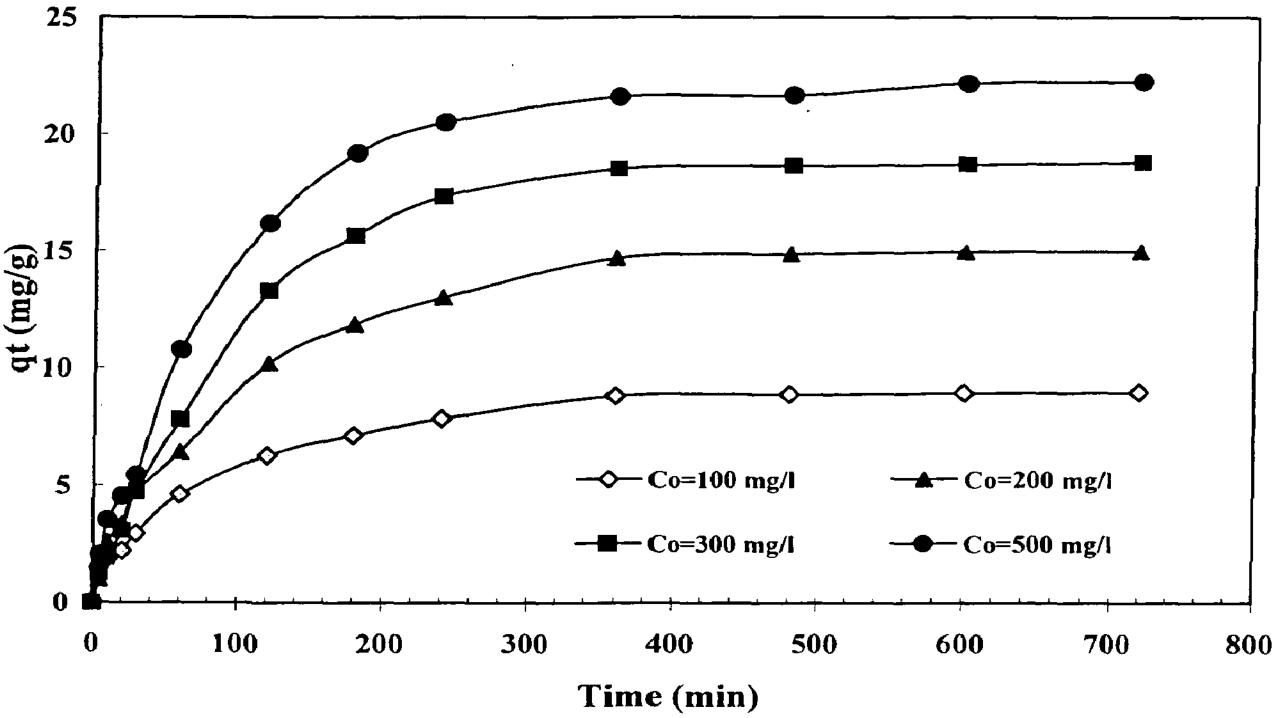

Fig. 5.18 (b) Effect of contact time on the removal of Furfural by ACC (T = 303 K, m = 10 g/l).

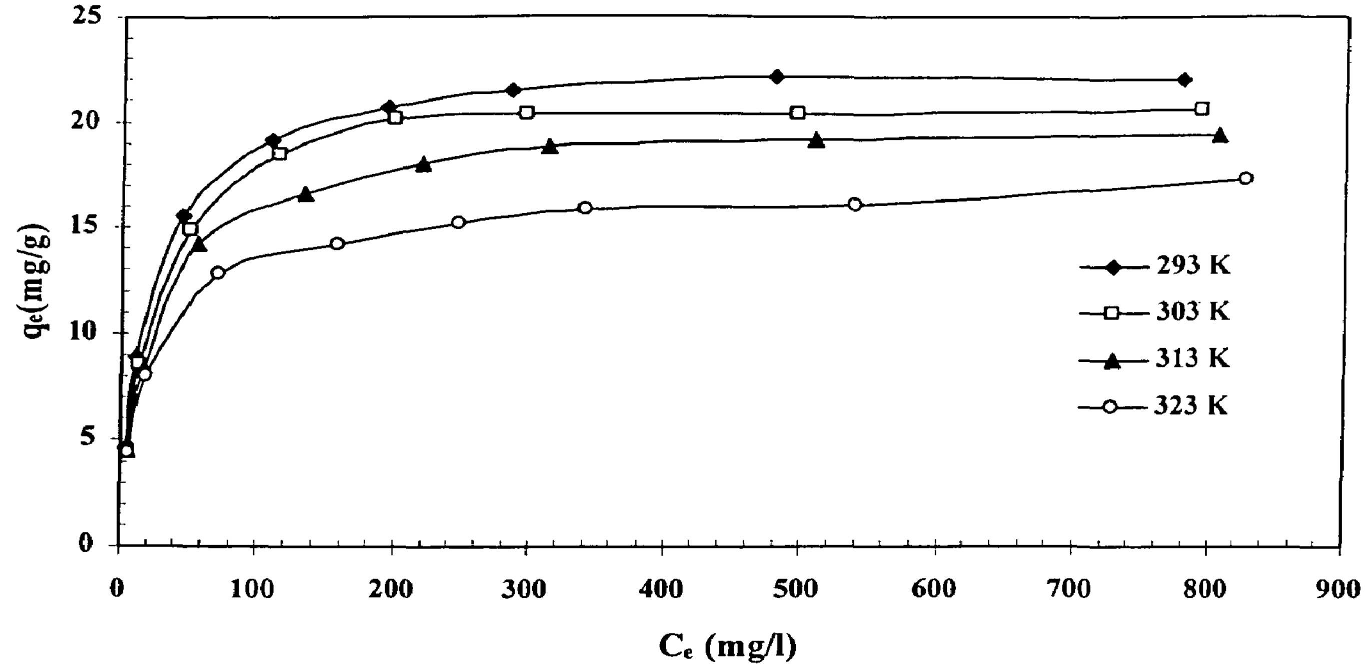

Fig. 5.19. Equilibrium adsorption isotherms at different temperatures for furfural-ACC system (t = 6 h, m = 10 g/l).

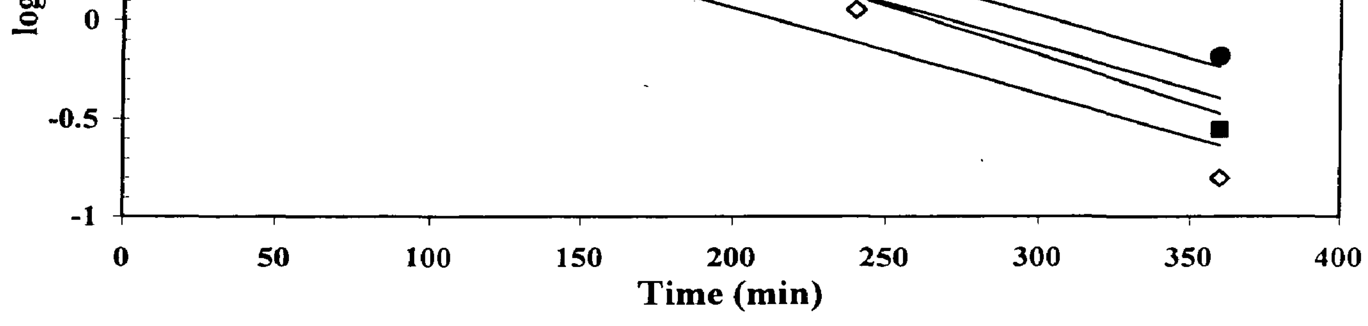

Fig. 5.20. Pseudo first order plot for the removal of furfural by ACC (T=323 K, m = 10 g/l)

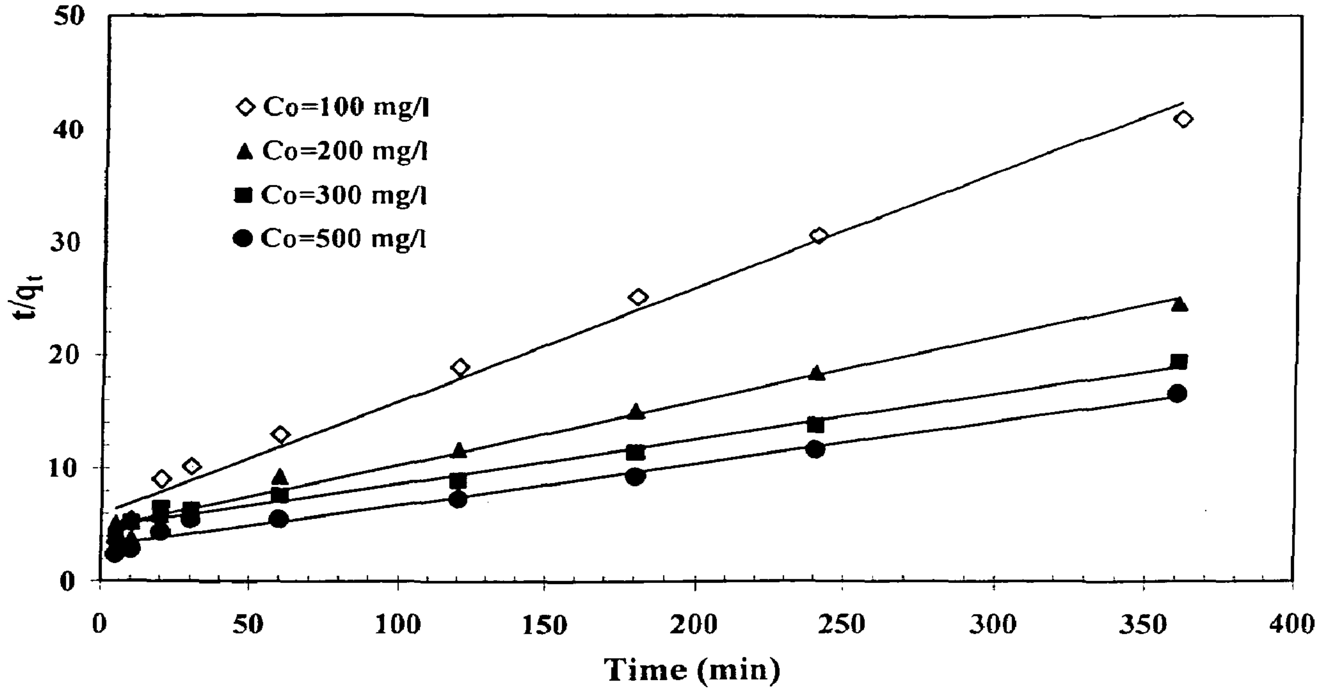

Fig. 5.21. Pseudo second order plot for the removal of furfural by ACC (T=323 K, *m* = 10 g/l)

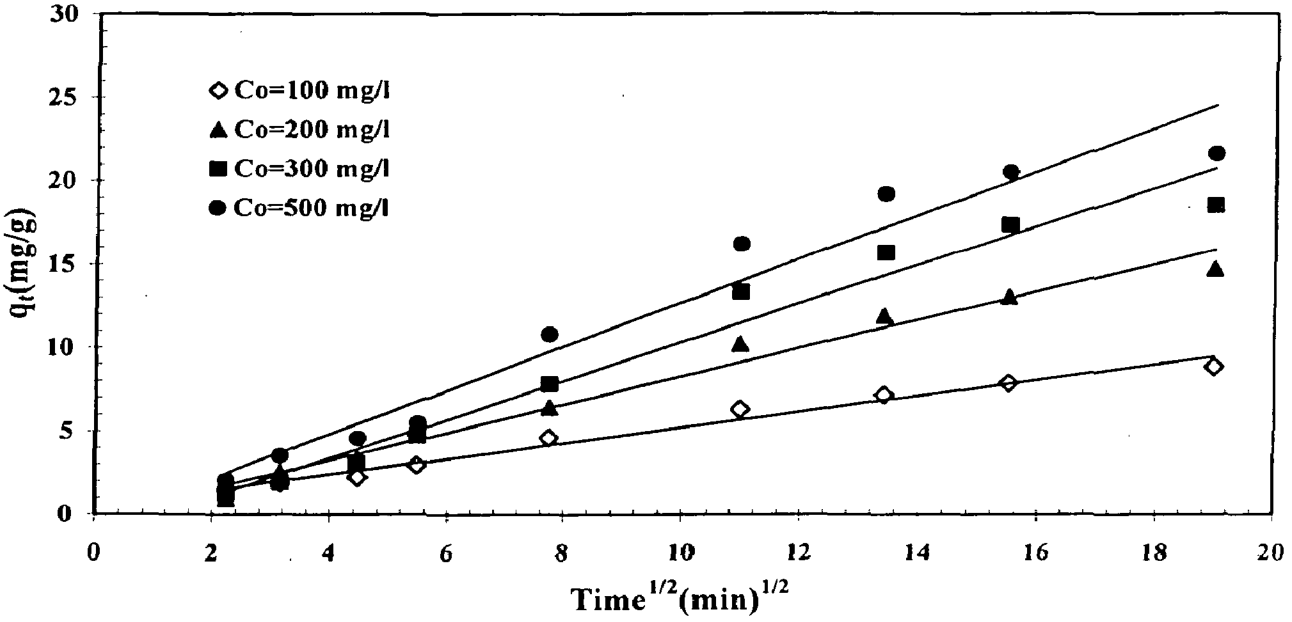

Fig. 5.22. Weber and Morris intra-particle diffusion plot for the removal of furfural by ACC (*T* = 303 K, *m* = 10 g/l).

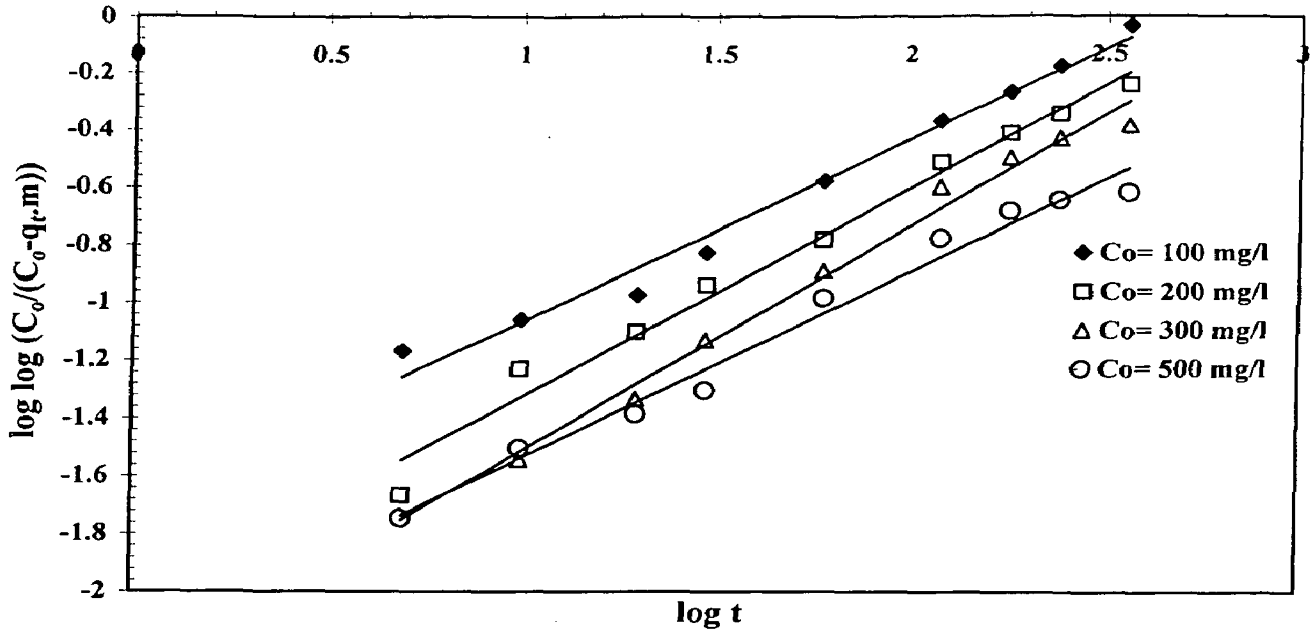

Fig. 5.23. Bangham plot for the removal of furfural by ACC
(T = 303 K, m = 10 g/l).

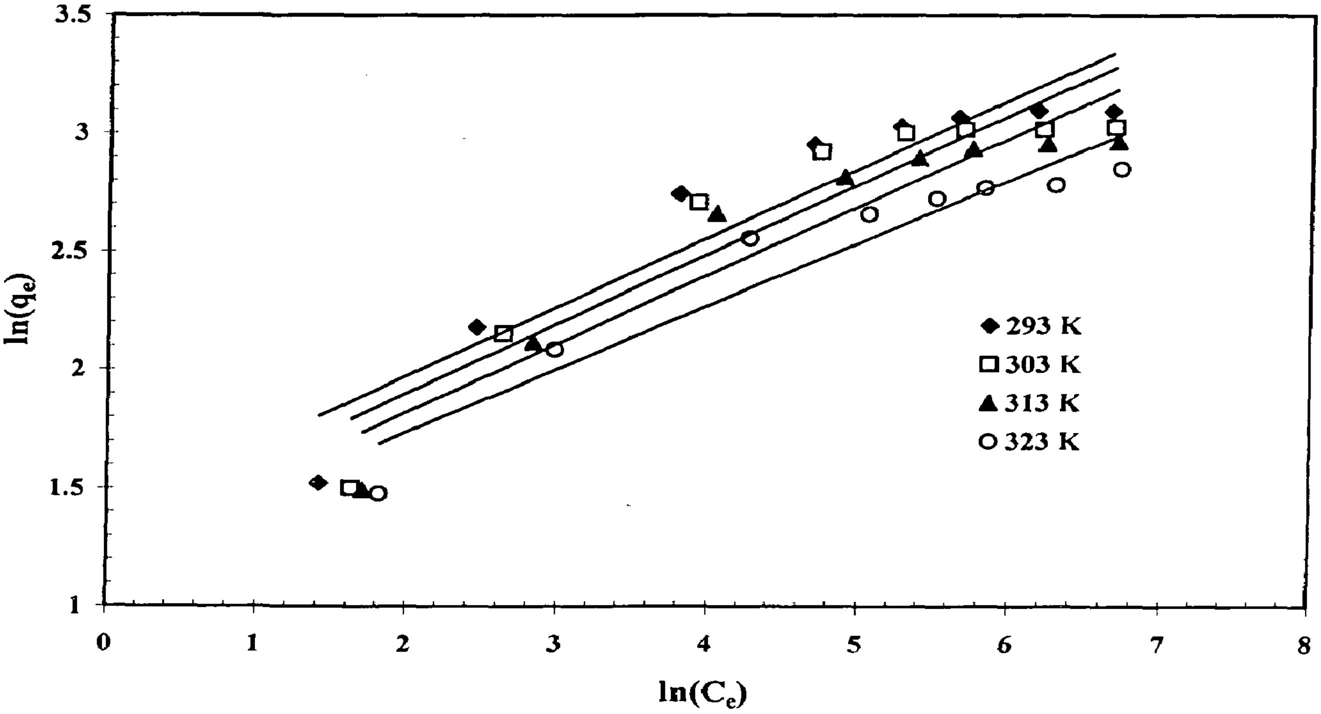

Fig. 5.24. Freundlich isotherm plots for the removal of furfural by ACC
(t = 6 h, C_0 = 50-1000 mg/l, m = 10 g/l).

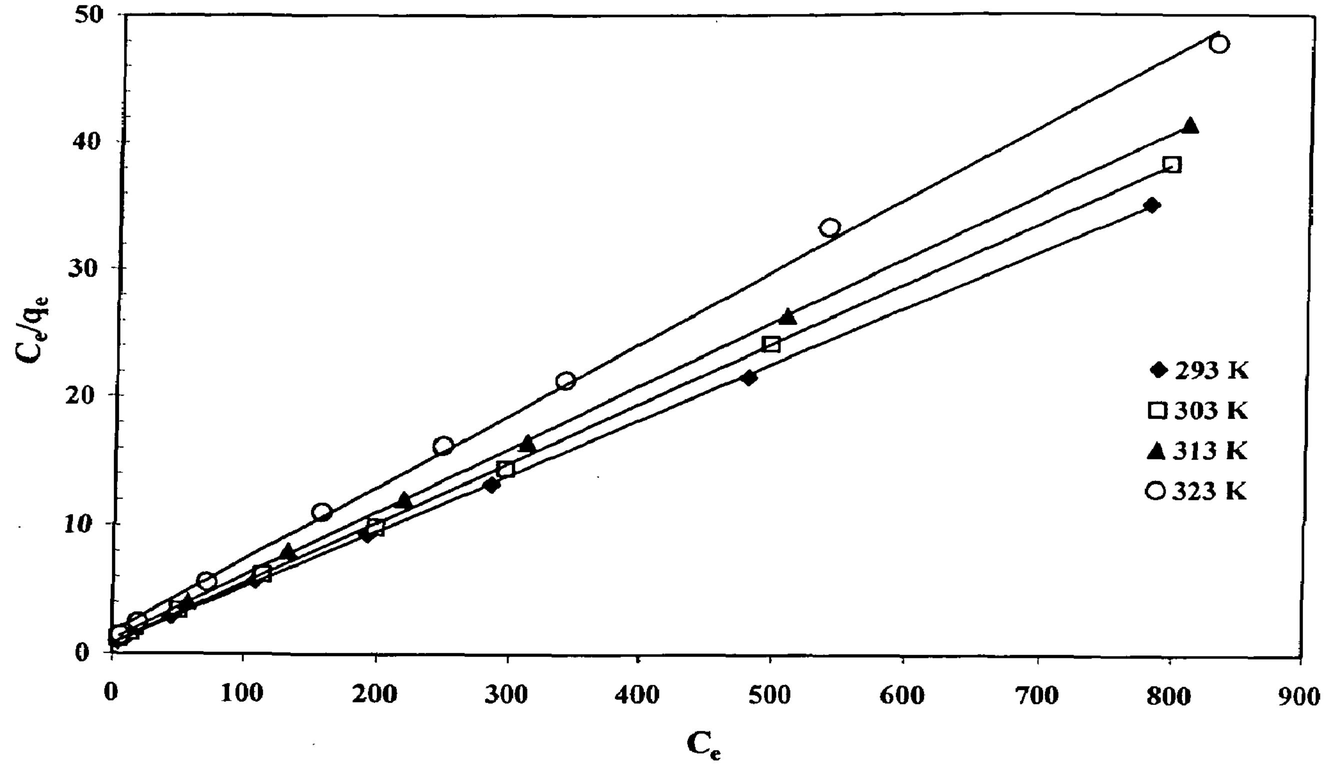

Fig. 5.25. Langmuir isotherm plots for the removal of furfural by ACC (t = 6 h, C_0 = 50-1000 mg/l, m = 10 g/l).

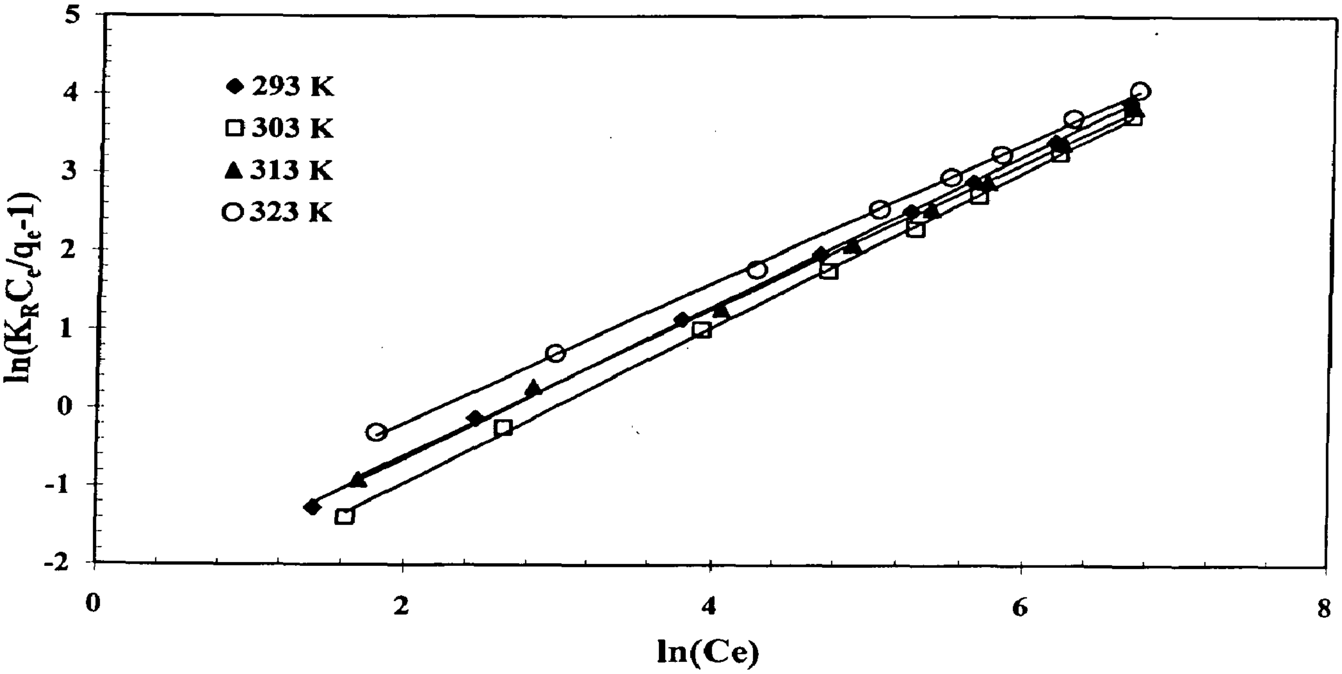

Fig. 5.26. Redlich-Peterson isotherm plot for the removal of furfural by ACC (t = 6h, C_0 = 50-1000 mg/l m = 10 g/l).

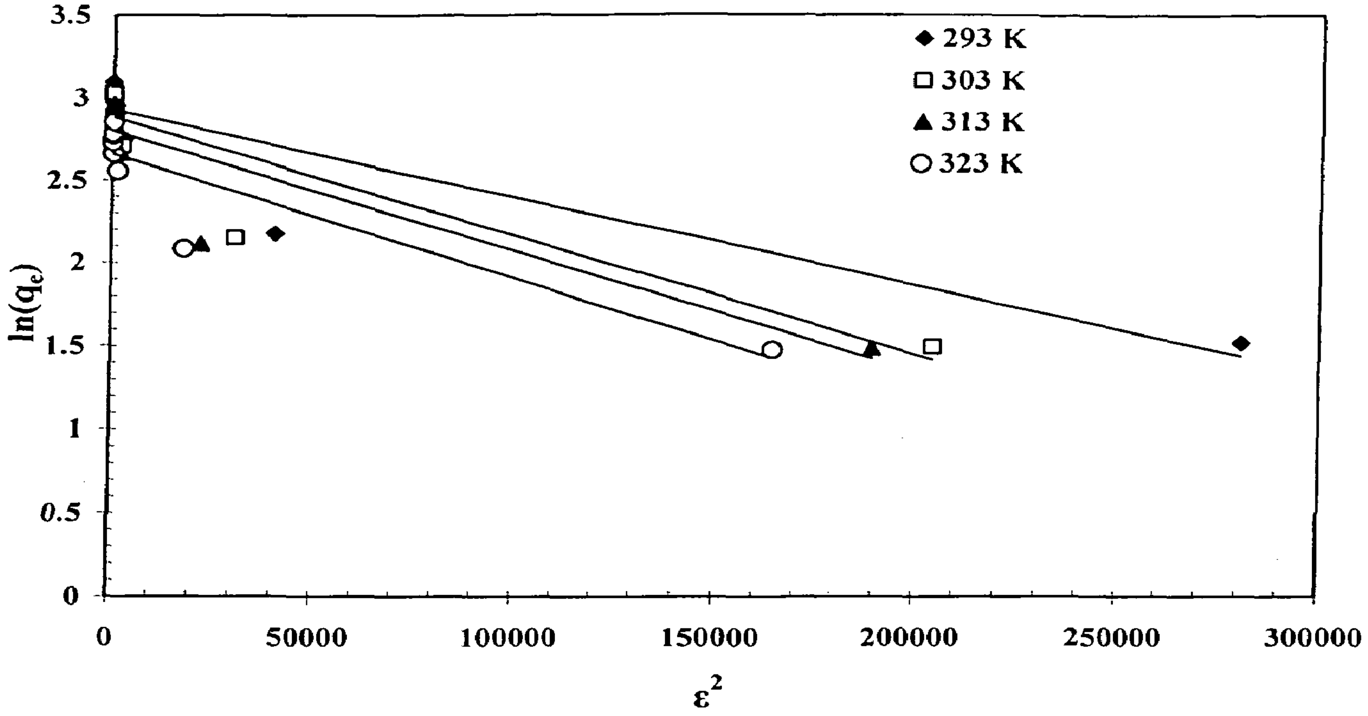

Fig. 5.27. D-R isotherm plot for the removal of furfural by ACC (t = 6h, C_0 = 50-1000 mg/l, m = 10 g/l).

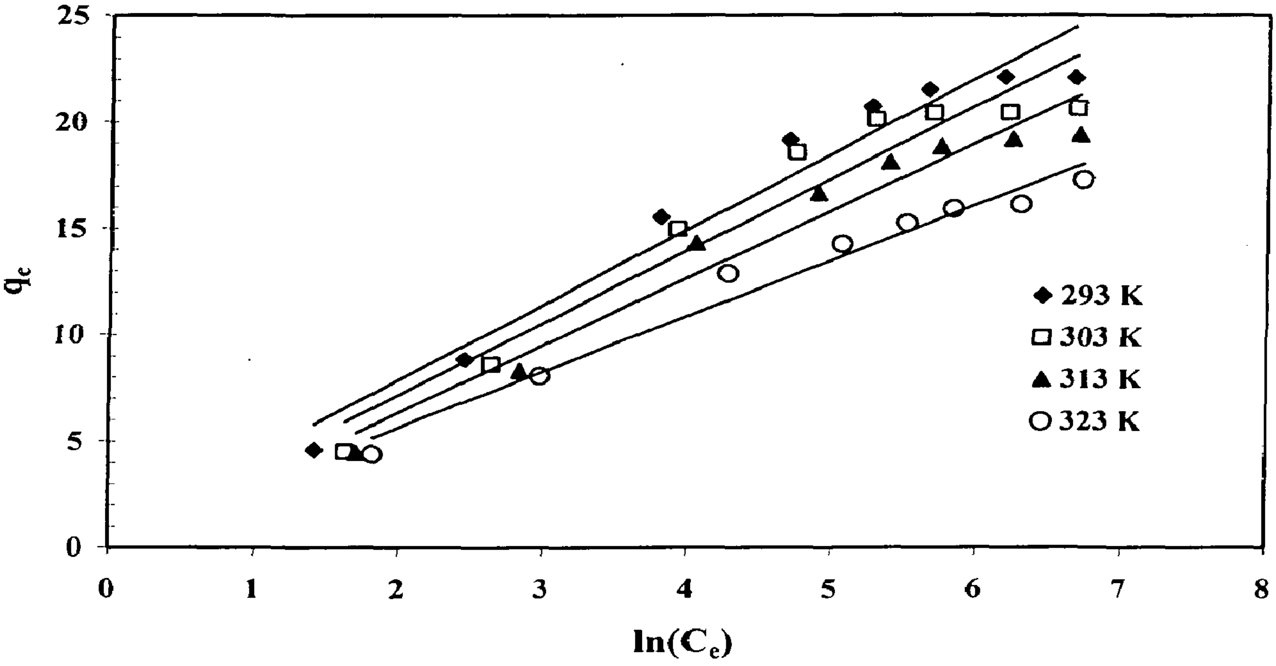

Fig. 5.28. Temkin isotherm plot for the removal of furfural by ACC (t = 6h, C_0 = 50-1000 mg/l, m = 10 g/l).

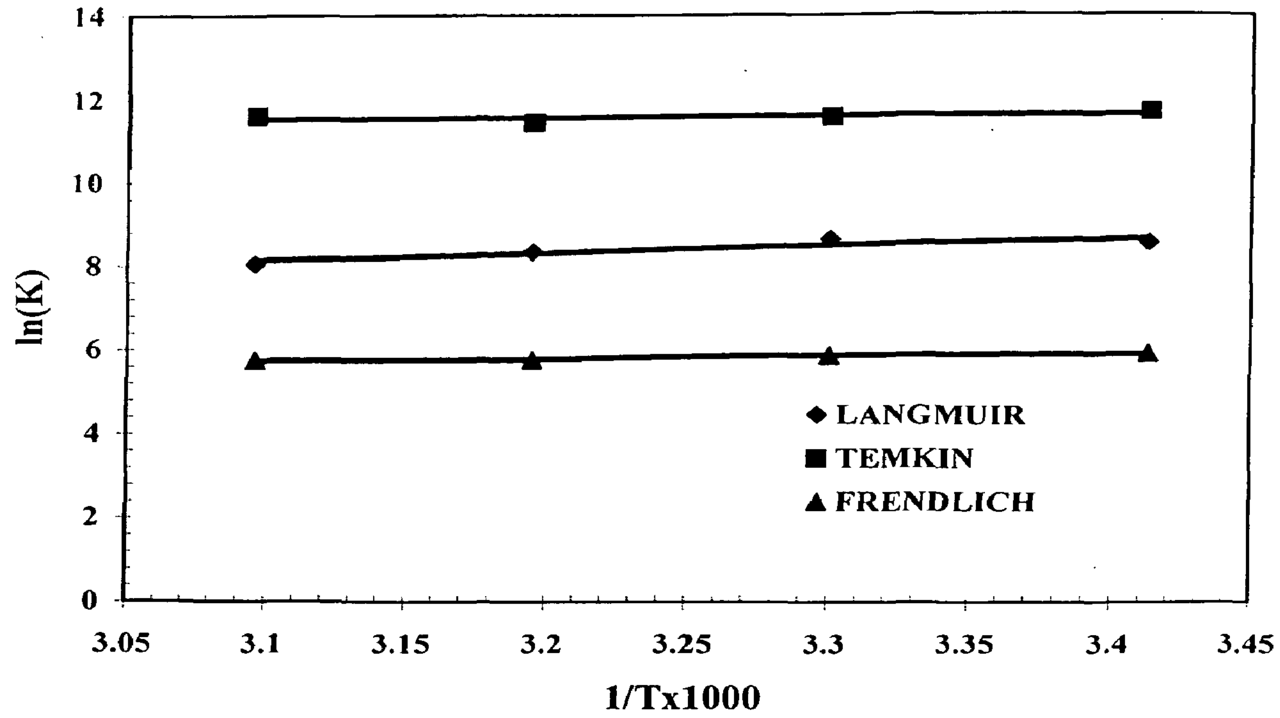

Fig. 5.29. **Vant Hoff plot for the removal of furfural by ACC (t = 6h, C_0 = 50-1000 mg/l, m = 10 g/l).**

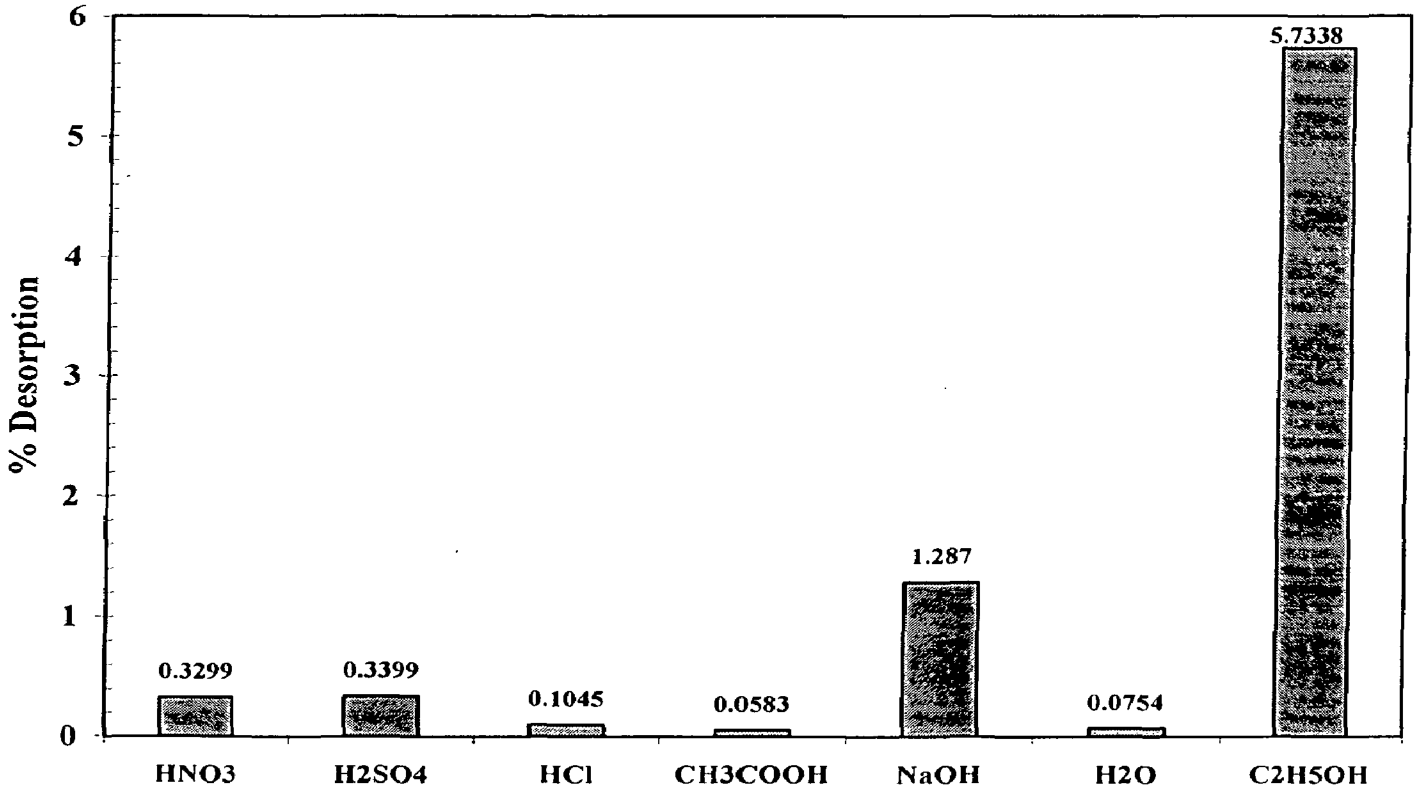

Fig. 5.30. **Plot of percent desorption from furfural loaded BFA (T = 303 K, m = 4 g, C_0 = 100 mg/l, t = 6h)**

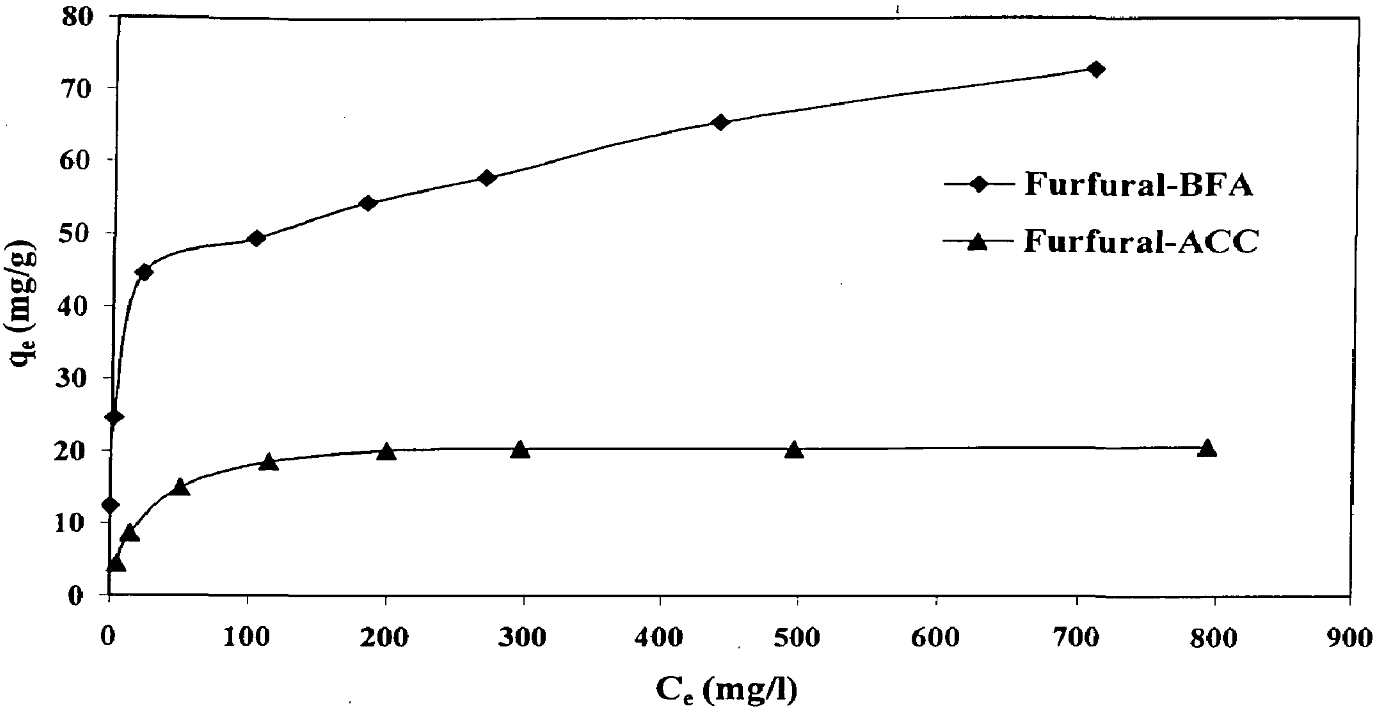

Fig. 5.31. Comparision of adsorption capacity for both the systems (T = 303 K, m (BFA)= 4 g/l, m (ACC)= 10 g/l C_0 = 100 mg/l, t = 6h)

CHAPTER – VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

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

1. Proximate analysis of adsorbents showed 32.90 and 77.82 % fixed carbon in BFA and ACC, respectively.
2. The morphologies of BFA and ACC were examined under scanning electron microscope. The BFA showed linear type of fibers with pores. Activated carbon is generally described as an amorphous form of graphite with a random structure of graphite has highly porous structure with a range of cracks and crevices reaching molecular dimensions.
3. Change in natural pH of the furfural solution alone caused furfural removal due to the structural changes being affected in the furfural-molecules. Adsorption of furfural on BFA is maximum at 5.5. Whereas ACC adsorbs maximum furfural at natural pH.
4. Initially, percent removal of furfural increases with the increase in adsorbent dose then approaches to constant level, for both BFA and ACC. The percent removal of adsorbate decreases with the increase in initial concentration whereas, the adsorbing capacity of the adsorbents increase with the initial concentration.
5. Kinetic study shows that the adsorption of furfural on both BFA and ACC follow the second order kinetics.
6. Weber-Morris plot reveals that the intraparticle transport (pore diffusion) is not the only rate-controlling step.
7. Redlich-Peterson model generally best-fits the furfural adsorption isotherm data on both the adsorbents at all the temperatures.

8. Adsorption capacity of BFA and ACC for furfural removal decreases with increase in temperature for both the adsorbents showing the exothermic nature of adsorption.
9. The results prove that BFA is a better adsorbent than ACC for adsorption of furfural. BFA can be used as a potential adsorbent for the removal of furfural.

6.2 RECOMMENDATIONS

1. BFA from different sugar mills shall be characterized for physical-chemical parameters and surface characteristics to arrive at average values for use in design.
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 furfural form wastewater.
3. Costing of the adsorption based on industrial scale treatment system shall be carried out to popularize the adsorption technique with BFA.

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