

ADSORPTIVE REMOVAL OF PARA-XYLENE FROM AQUEOUS SOLUTION USING LOW-COST ADSORBENT: EQUILIBRIUM, KINETICS AND THERMODYNAMICS

A DISSERTATION

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

MASTER OF TECHNOLOGY

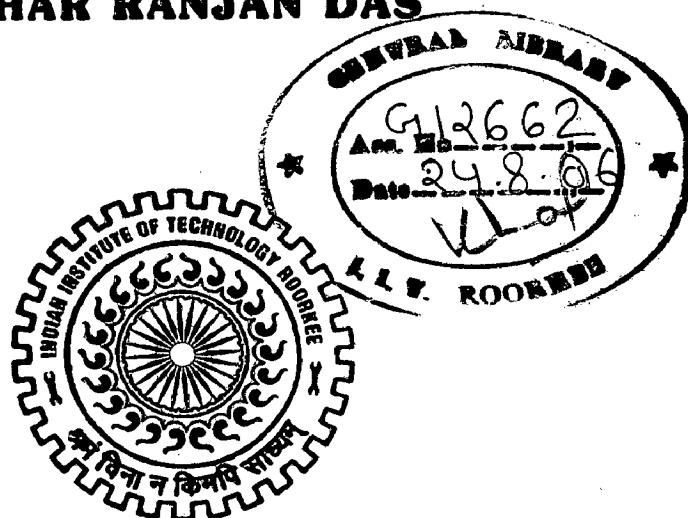
in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

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JUNE, 2006

CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled "ADSORPTIVE REMOVAL OF PARA-XYLENE FROM AQUEOUS SOLUTION USING LOW-COST ADSORBENT: KINETICS, EQUILIBRIUM AND THERMODYNAMICS" in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from June 2005 to June 2006 under supervision of Dr. I. D. Mall, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree.

Date: June , 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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ABSTRACT

The consequence of the rapid industrialization in developing countries since 20th century has emerged as a major threat to water pollution. Para-xylene is one of the most widely used chemical in chemical processes. It mainly used for preparation of tetraphthalic acid and diethyl tetraphthalate and as an antiknocking reagent in motor gasoline due to its high octane number (116.4). The huge demand of Para-xylene can be estimated from the fact that it is among the top 10 chemicals produced in U.S.A in terms of quantity according to the EPA source.

Due to such increasing demand of production of Para-xylene, its adverse effect on environment is now a matter of great concern. Its emission into environment is contributed by various sources such as point sources like chemical and petrochemical manufacture, polyester manufacture, manufacture of paints and dyes and natural sources like petroleum, coal tar, plant emission etc. For the health point of consideration, the adverse effect of Para-xylene on human being is mostly chronic in nature. Although its effect is restricted to irritating of skin, eyes and respiratory tract, but the major concern is its route of exposure that is through inhalation as it evaporates to atmosphere from liquid effluents. It has also high acute toxicity to aquatic life and causes injury to various agricultural and ornamental crops and is expected to moderately bioaccumulate in fish. From the various alternatives available for the removal of Para-xylene from waste water, adsorption process is one, worth to be considered due to its probing track records for the removal of various hydrocarbons and aromatic compounds

In the present study laboratory scale experiments have been carried out using the low cost bagasse fly ash as adsorbent for the removal of Para-xylene. Batch experiments were carried out to determine the effect of various factors such as contact time, pH, sorbent dose and temperature on adsorption process. Results obtained from these were interpreted in various ways like kinetic, isotherm and thermodynamic study to find out the economical and time appropriate feasibility of the process as well as various favorable conditions to carry out the process, then the

feasibility of using BFA as an adsorbent has been determined as compared commercial grade activated carbon through different parameters.

From the result it is found that there are not so much difference in adsorption mechanism as both BFA and ACC show first order reversible kinetics for the adsorption process and as far as isotherm model concerned, various error analysis resulted that Langmuir isotherm model is favored at low temperature range and Temkin isotherm model is favored at high temperature range in both cases.

It can be clearly envisaged that there is not so much difference in removal efficiencies for the two adsorbents. The removal efficiency is around 91 % for BFA and 94 % for ACC on double adsorption. After comparing both the aspects, economical (Cost of ACC is Rs. 40.00 / kg, where as for BFA it is only the transportation cost) as well as removal efficiency, it can be concluded that the negligible efficiency difference can be compromised for high economical gain, to make BFA as a promising alternate adsorbents for the high cost ACC.

ACKNOWLEDGEMENT

I express my deep sense of gratitude to my guide **Dr. I. D. Mall**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, for his keen interest, constant guidance and encouragement throughout the course of this work, his experience, assiduity and deep insight of the subject held this work always on a smooth and steady course. Useful criticism and constant help extended in the hours of need had been immensely useful.

Thanks are due to Dr. Shri Chand, Prof. and Head, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, for providing various facilities during this dissertation.

I am thankful to Shri B. K. Arora (Senior Technical Assistant) and Shri Ayodhya Prasad (Senior Lab. Attendant), Pollution Abatement Research Lab., Dept. of Chemical Engineering., IIT Roorkee, Roorkee for their continuous help during the experimental work.

I would like to thank Mr. Vimal Chandra Srivastava, Research Scholar, Pollution Abatement Research Lab. IIT Roorkee, Roorkee, for his support, advice and interest shown in my work. I am also thankful to Mr. Dilip Lataye and Mr. S. Mahesh, Research Scholars, Pollution Abatement Research Lab, IIT Roorkee, Roorkee, for their constant help and advice throughout my work.

It is very hard to express my feeling in proper words for my family members who, apart from providing me the best available education, have encouraged me in all my endeavors. I owe much of my academic success to them. I am greatly indebted to all my friends whose enthusiastic support, encouragement and help, made me come up with this report. Though it is not possible to mention everyone, none can be forgotten for their direct/indirect help.

NIHAR RANJAN DAS

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NOMENCLATURE

C_i	Initial concentration of effluent
C_e	Concentration of adsorbate solution at equilibrium (mg/l)
K	Adsorption rate constant (1/min)
K_a	Rate constant, liquid/mg of adsorbate, (l/mg)
K_L	Langmuir isotherm constant, (l/mg)
K_T	Temkin isotherm constant, (l/mg)
K_F	Freundlich isotherm constant, $((\text{mg/g})/(\text{mg/l})^{1/n})$
n	Freundlich rate constant
Q_t	Amount of adsorbate adsorbed per unit amount of adsorbent at time t , (mg/g)
STEL	Short time exposure limit
TWA	Time weight average
Q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg/g)
R_L	Separation Factor
k_f	First order rate constant, (1/min)
k_s	Second order rate constant, (g/mg min)
ΔG°	Gibbs free energy, (KJ/mol)
ΔH°	Enthalpy, (KJ/mol)
ΔS°	Entropy, (J/mol K)
SSE	Sum of the Squares of the Errors
SAE	Sum of the Absolute Errors
ARE	Average Relative Error
HYBRID	Hybrid Fractional Error Function
MPSD	Marquardt's Percent Standard Deviation

Due to such increasing demand of production of p-xylene, its adverse effect on environment is now a matter of great concern. Its emission into environment is contributed by various sources such as point sources like chemical and petrochemical manufacture, polyester manufacture, manufacture of paints and dyes and natural sources like petroleum, coal tar, plant emission etc [2]. For the health point of consideration, the adverse effect of xylene on human being is mostly chronic in nature. Although its effect is restricted to irritating of skin, eyes and respiratory tract, but the major concern is its route of exposure that is through inhalation as it evaporates to atmosphere from liquid effluents. It has also high acute toxicity to aquatic life. It causes injury to various agricultural and ornamental crops and is expected to moderately bioaccumulate in fish

As far as waste water treatment system is considered, biodegradation with activated seed is slow and not economically reliable, whereas sewage digestion process for this purpose is impaired by 0.1% conc. [1]. Among the various alternatives available for this purpose, adsorption is one which is worth to consider as various literature studies suggest the effectiveness of this process for aromatic compounds such as pyridine, phenol, dyes etc. with respect to both time and economy [4, 5, 6, 7, 8]. Till date the implementation of this method for the removal of p-xylene has not revealed to its full potential except very few [4].

Among the various adsorbents, activated carbon has been commercially used for the removal of the toxic effluents [10, 22, 24, 25, 26]. However, high cost activated carbon and significant amount of loss during regeneration make the utilization of the activated carbon prohibitive in developing countries [24]. This has led to search for cheaper carbonaceous substitutes to activated carbon. Recently large numbers of low cost adsorbents like bagasse fly ash, rice husk, coal fly ash, bagasse pith, etc. have been investigated for removal of phenol, pyridines, dyes, heavy metals, color and other organic pollutants [1, 2, 4, 22, 23, 25]. During recent years, possibilities of utilization of bagasse fly ash have been explored by various researchers as an alternate to activated carbon for removal of aromatic organic toxics [1, 2, 14, 22, 24, 26].

INTRODUCTION

Comprising over 70% of the Earth's surface, water is undoubtedly the most precious natural resource that exists on our planet. Without the seemingly invaluable compound comprised of hydrogen and oxygen, life on Earth would be non-existent: it is essential for everything on our planet to grow and prosper. With the rapid growth of industrialization, the water pollution problem is matter of worth concern all over the world now. In brief Water pollution can be defined as "any biological, chemical, or physical change in water quality that has a harmful effect on living organisms or makes water unsuitable for desired uses." Such pollutants fall into three main categories: 1) biological, such as bacteria or viruses; 2) chemical, including organic and toxic substance; 3) physical, such as sediment, radioactive material, and heat. To how much depth the problem has extended its root can be envisaged from a single fact: In the United States, approximately 44% of lakes, 37% of rives, and 32% of estuaries are unsafe for recreation due to toxic water pollutants [8].

Among the various toxic pollutants, Para-xylene is one of the most key pollutants as far as water pollution is concerned according to EPA sources [3]. As far as production source of Para-xylene is concerned, it is basically produced from the separation of mixed xylene. Commercially mixed xylene is produced from catalytic reforming, pyrolysis of gasoline, toluene disproportionate product and coke-oven light oil. Around 50-60% of this mixed xylene is used to make Para xylene (p-xylene). The huge demand of p-xylene can be estimated from the fact that it is among the top ten chemicals produced in USA in terms of quantity according to the EPA source. p-xylene is first converted to tetraphthalic acid and diethyl tetraphthalate, then to polyethylene tetraphthalate for ultimate use in fibers, films and resins. Some percentage of p-xylene used in solvent for paint and coating industries. However this use is declined particularly in U.S.A as environmental efforts to reduce hydrocarbon emission into air. Because of its high octane number (116.4), p-xylene also used in motor gasoline [12].

The primary source of this BFA ash is sugar industry which is one of the most important agro based industries in India, South America and Caribbean countries. BFA, a waste collected from the particulate collection equipment attached upstream to the stacks of bagasse fired boilers, causes disposal problems. It is mainly used for land filling, and partly used as filler in building materials and paper and wood boards.

The objective of this study is to investigate the feasibility of readily and cheaply available BFA as an adsorbent for the removal of Para-xylene, where as commercial grade ACC has been used as a standard adsorbent for the same process to verify the adsorption capacity and economical feasibility of BFA for industrial use. The experimental work has been carried out to achieve the objective through the following studies:

1. Characterization of Bagasse fly ash and commercial grade activated carbon, which includes chemical analysis, ultimate analysis and proximate analysis.
2. Study the effect of adsorbent dose, contact time, pH, initial concentration and temperature on the removal of Para-xylene from aqueous solution by batch process.
3. Study the adsorption kinetics of Para-xylene onto BFA and ACC
4. Study of equilibrium data for removal efficiency of the adsorbent using Freundlich, Langmuir, Dublin-Redushkevich and Temkin isotherms.
5. Study the various thermodynamic properties such as: enthalpy, activation energy, entropy and free energy for the adsorption process
6. Compare the feasibility of BFA as an alternate to ACC through various parameters.

PARA-XYLENE

2.1 GENERAL

Xylene is C₈ aromatic isomers having molecular formula C₈H₁₀. It exists in three isomeric forms: ortho- or o-xylene (1, 2-dimethylbenzene), meta- or m-xylene (1, 3-dimethylbenzene), and para- or p-xylene (1, 4-dimethylbenzene). These three isomers are different with respect to the position of methyl group on the benzene ring and among the three isomers, p-xylene accounts around 60% of the overall production. The structure and the properties of p-xylene are represented in Table 2.1 and Fig.2.1 respectively.

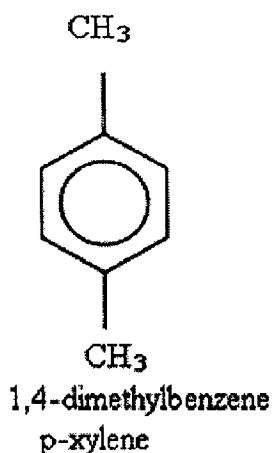


Fig. 2.1 Structure of p-xylene

Table.2.1: Properties of p-xylene [12,13].

Common name	p-xylene
Systematic name	1,4-Dimethyl benzene
Other name	p-xylol
Molecular formula	C ₈ H ₁₀
Molecular mass	106.16g/mol
Appearance	

Density	0.86g/cm ³
Solubility in water(20 °C)	170mg/l
Melting point	286K
Boiling point	411K
Flash point	300K
TWA(8 h)	80 ppm
STEL	150 ppm
Water Pollution Factors	BOD ₅ : 44% ThOD COD: 82% ThOD ThOD: 3.125.
Atmospheric Reaction	HC conc. Ranking: 0.5-1 NO _{ox} Ranking: 0.4

2.2 MAJOR INDUSTRIAL USES

- p-xylene is first converted to tetraphthalic acid and diethyl tetraphthalate, then to polyethylene tetraphthalate for ultimate use in fibers, films and resins.
- Some percentage of p-xylene used in solvent for paint and coating industries.
- Because of its high octane number (116.4), p-xylene also used in motor gasoline
- It also widely used as thinner and as a solvent for ink, rubber, adhesive and lacquers.

2.3 ENTRY INTO THE ENVIRONMENT

Since p- xylenes are a natural component of crude oil and coal distillates they may be introduced into the ground through petroleum seepage and weathering of exposed coal-containing strata, and into groundwater from petroliferous rocks. The magnitude of such releases to the environment is unknown (U.S. EPA, 1987).

p-xylenes enter water from the discharge of industrial and municipal effluents. In Ontario, p-xylenes were detected in effluents from a variety of industrial and municipal sources. The highest mean concentrations of p-xylenes in effluents

released into surface water were 2.2µg/L p-xylene in storm-water effluent from petroleum refineries and 3.3 µg/L m- and p-xylenes combined in effluents from a coke plant (OME, 1991).

p-xylenes can enter soil and water through spills of petroleum and other chemical products. Based on the reported number, [NATES, 1992], and the assumption that the mean concentration of p-xylenes in spilled petroleum products is 10%, approximately 600 tonnes per year could have remained in the environment. Also, p-xylenes can be released to soil from leaking underground storage tanks that contain gasoline, diesel fuel, or heating oil.

2.4 ROUTES OF EXPOSURE

2.4.1 Inhalation

Most exposures to p-xylene occur by inhalation and xylene is readily absorbed from the lungs. p-xylene's odor threshold is about 1 ppm, which is 100 times less than the OSHA PEL and generally provides adequate warning of acutely hazardous concentrations. Irritation of eye and throat occur at about 200 ppm. p-xylene vapor is heavier than air and may cause asphyxiation in enclosed, poorly ventilated, or low-lying areas.

Children exposed to the same levels of p-xylene vapor as adults may receive a larger dose because they have greater lung surface area: body weight ratios and increased minute volumes: weight ratios. In addition, they may be exposed to higher levels than adults in the same location because of their short stature and the higher levels of xylene vapor found nearer to the ground

2.4.2 Skin/Eye Contact

p-xylene is only mildly irritating to mucous membranes; however, p-xylene splashed in the eyes can result in corneal injury. Repeated or prolonged skin contact with liquid p-xylene can affect the skin, causing it to crack and peel. Percutaneous absorption is slow through intact skin; however, p-xylene absorbed through the skin

may contribute to body burden. Children are more vulnerable to toxicants absorbed through the skin because of their relatively larger surface area: body weight ratio.

2.5 HEALTH EFFECTS

2.5.1 CNS

Generally, symptoms of CNS toxicity are apparent immediately after inhalation of high xylene concentrations and 30 to 60 minutes after ingestion. Effects of mild CNS depression include headache, lightheadedness, dizziness, confusion, nausea, impaired gait, and blurred vision. More severe effects include tremors, rapid respiration, paralysis, loss of consciousness, coma, and death. Coma may be prolonged, although most victims regain consciousness rapidly after they are removed from exposure.

2.5.2 Respiratory

Acute exposure to xylene vapor may irritate the mucous membranes of the respiratory tract. With massive exposure, accumulation of fluid in the lungs and respiratory arrest may ensue. Pulmonary aspiration of toxic vomitus or ingested liquid xylene may cause inflammation of the lungs

Exposure to certain chemicals can lead to Reactive Airway Dysfunction Syndrome (RADS), a chemically- or irritant-induced type of asthma. Children may be more vulnerable because of relatively increased minute ventilation per kg and failure to evacuate an area promptly when exposed. Hydrocarbon pneumonitis may be a problem in children

2.5.3 Cardiovascular

Inhalation of massive doses of xylene can cause cardiac abnormalities. p-xylene lowers the threshold of the heart to the effects of epinephrine, partially disrupting the rhythm. Irregular heart rhythm leading to cardiac arrest has occurred in solvent abusers, often immediately after intense physical activity

2.5.4 Renal

Blood and protein in the urine can occur after massive inhalation. These effects usually are reversible if exposure is terminated

2.5.5 Metabolic

High-level p-xylene exposure may lead to acid-base imbalance. In solvent abusers, electrolyte and acid-base disturbances can cause renal-tubular acidosis, inadequate amounts of potassium in the blood, and low blood phosphate. Ethanol or aspirin may prolong the half-life of p-xylene in the body. Because of their higher metabolic rates, children may be more vulnerable to toxicants interfering with basic metabolism

Dermal p-xylene can cause skin inflammation and defatting, particularly after prolonged or repeated contact with the liquid. Redness of the skin and blisters may occur. Because of their relatively larger surface area: body weight ratio, children are more vulnerable to toxicants absorbed through the skin.

2.5.6 Hepatic

Reversible liver damage has been reported in some individuals exposed to p-xylene. Ocular high concentrations of p-xylene vapor may cause eye irritation, but ophthalmic injury is rare. When splashed in the eyes, p-xylene may cause burning pain, conjunctivitis, corneal vacuolation, and keratitis.

2.5.7 Gastrointestinal

If swallowed, xylene can irritate the stomach, causing nausea, vomiting, and diarrhea Potential Sequelae During recovery, patients may continue to experience impaired gait, lightheadedness, dilated and poorly responsive pupils, and decreased or absent deep-tendon reflexes. Anxiety, fatigue, and insomnia may last several days. No long-term effects due to acute xylene exposure have been reported

2.5.8 Chronic Exposure

2.5.8.1 Carcinogenicity

The International Agency for Research on Cancer has determined that p-xylene is not classifiable as to its carcinogenicity to humans. The EPA has determined that xylene is not classifiable as to its human carcinogenicity

2.5.8.2 Reproductive and Developmental Effects

p-xylene is not included in Reproductive and Developmental Toxicants, a 1991 report published by the United States General Accounting Office (GAO) that lists 30 chemicals of concern because of widely acknowledged reproductive and developmental consequences. Xylene has been reported to cross the placenta in humans. Limited human developmental data are available, but animal studies suggest that exposure to high doses of xylene may be fetotoxic

LITERATURE REVIEW

3.1 GENERAL

Due to the lack of adequate literature on the removal of p-xylene from waste water, help has been taken from the literatures of co-related works such as removal of aromatics and different other hydrocarbons from waste water. The literatures followed during the complete dissertation work have been presented in nutshell in Table.3.1 and Table.3.2.

Table.3.1: Various experimental works on removal of Hydrocarbons and related compounds from waste effluents.

Reference	Operation	Results and conclusion
Valquiria et al.[2006]	BTEX and Ethanol removal in anaerobic denitrifying condition.	Removal efficiency is 99% at initial concentration of 26.5 mg/L of ETX by using denitrifying consortium, but the rate of the reaction is very slow.
Suzuki et al.[2005]	Removal of hydrocarbons in a rotating biological contactor with biodrum.	A novel rotating biological contactor with biodrum was designed to remove hydrocarbon in waste water by using micro-alga protothecazopfic. Removal efficiency is 65%, but time taken was 30 days.
Blanchord et al.[2004]	Removal of poly cyclic aromatic hydrocarbon and polychloro biphenyl in waste water.	98% of PAH and 76% of PCB was removed.
Bernal et al.[2005]	Combining anaerobic digestion and ozonation to remove PAH from urban sludge.	In this study combination of anaerobic digestion and ozonation process was used. 81% of PAH was removed with addition of hydrogen peroxide during ozonation.
Sanna et al. [2003]	Occurrence and removal of organic pollutants in sewage and landfill leachates.	This process presented in 84% removal of DEHP adsorption on particle range 0.1-0.41 micrometer. Cont ...

Alemzadeh et al.[2001]	Biodegradation of toluene by an attached biofilm in a rotating biological contactor.	RBC was used to carry out the operation. The kinetics was found to be followed zero order mechanism.
William et al. [1997]	Evaluating the relationship between the sorption of PAH to bacterial biomass and biodegradation.	This process was meant for treating refinery waste water. The result study suggested that although biosorption decreases the rate of PAH biodegradation in the short term, it can also resulted in complete removal of PAH from waste water.
Wan et al. [1997]	Microbial removal of polycyclic aromatic hydrocarbons by Phanerochacle chrysosporium.	The biocarrier used in the investigation, was a mixed gel composed of alginate and activated carbon. The results showed that PAH were removed with an increased rate during the stationary growth phase and strain ATCC-24725 exhibited the best PAH removal efficiency.
Kondo et al. [1994]	Treatment of waste water from phenolic resin process by pervaporation.	PEBA (polyethylene black amide) membrane showed a substantial potential for application to phenol containing waste water treatment, subjected to the waste water being purified to the required quantity by vacuum distillation or other appropriate pre treatment. But time taken for the process was 72 hours.
Pardue et al. [1988]	Removal of PCB from waste water in a simulated overland flow treatment system.	Overland flow treatment system proved to have a promising potential for removal of organic pollutants. The efficiency was found to be 100 % in 38 days time.
Richard et al. [1986]	Liquid/ suspended solid phase partitioning of polycyclic aromatic hydrocarbons in coal washing waste water.	Partitioning in the biological reactor of effluent stream was correlated with aqueous solubility and n-octanol/ water partition coefficient.
Dan et al. [2006]	Removal of p-xylene from air streams in a hybrid biofilter.	Biofilter packed with pig compost and forest soil resulted in removal efficiency range from 47-80% at pH 6.3 in time 62 days.

Table.3.2. Various adsorption study related with organic pollutants.

Reference	Operation	Results and conclusion
Jeong et al. [2006]	Removal of volatile organic compound by spark generator carbon aerosol particles.	The study introduced an idea of removing benzene toluene and xylene in a controllable way using carbon particle produced by spark generator. BTX removal increased by 4% compared to conventional activated carbon.
Namosivayam et al. [2006]	Removal of anions heavy metals, organic and dyes from waste water by adsorption onto ZnCl ₂ activated coir pith carbon.	Coir pith was used to develop ZnCl ₂ activated carbon. Result showed that the adsorbent was effective for removal of toxic pollutants with removal efficiency around 90%.
Xiao-Hong et al. [2006]	Competitive adsorption of organic mater with phosphate on aluminum hydroxide.	The effect of ortho-phosphate for the adsorption of natural organic matter on aluminum hydroxide was investigated.
Srivastava et al.[2005]	Adsorptive removal of phenol by bagasse fly ash and activated carbon.	The study showed that BFA is an effective adsorbent for the removal of phenol from aqueous solution. Optimum condition for phenol removal were found to be pH=6.5 and adsorbent dose=10 g/L
Mall et al.[1998]	Removal of 2,4-dichlorophenol by using BFA and RHFA.	The predicted applicability of BFA and RHFA in batch operation in various parameters such as effect of contact time, adsorbent dose, pH etc has been studied. Economic evaluation shows that their use will be viable.
Mall et al. [1998]	Removal of COD using pyrolysed bagasse char.	PBC was found effective for removal of COD from pulp and paper mill effluents in polishing stage.
Chang et al.[2005]	A simplified model for trace organic removal by continuous flow PAC adsorption.	Mathematical model have been developed. The result indicated that the developed model provide reasonable representation of the trace removal by the adsorption process.
Wang et al. [2005]	Removal of trace organic compound from waste water by ultrasonic enhancement in adsorption.	The sorption used in the experiment was alumina with manganese nitrate. The process was found to be effective in temperature range 30-60 °C. cont...

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

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 4.1.

4.3 INTRAPARTICLE DIFFUSION PROCESS

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

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

It is assumed that the fourth step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So, it can be assumed that the main resistance to adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the rate limiting step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system propose the term “intra-particle transport” which comprises of surface diffusion and molecular diffusion. Several researchers have shown that surface diffusion is the dominant

ADSORPTION FUNDAMENTALS

4.1 GENERAL

Adsorption is a surface phenomenon. The material adsorbed is called the adsorbate or solute and the adsorbing phase is the adsorbent. In the water purification, adsorbents are used to remove organic impurities, particularly those that are non-biodegradable or associated with taste, color, and odor. Although adsorption is applied in low concentration, recent physical-chemical processes use adsorption as a primary technique to remove soluble organics from the wastewater. The adsorption is called physical when relatively weak intermolecular forces cause the attachment and, chemical when chemical bonding like forces causes this attachment.

During adsorption, the solid adsorbent becomes saturated or nearly saturated with the adsorbate. To recover the adsorbate and allow the adsorbent to be reused, it is regenerated by desorbing the adsorbed substances (i.e. the adsorbates).

4.2 PHYSICAL ADSORPTION VS. CHEMISORPTION

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

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

Physical adsorption occurs quickly and may be monomolecular (unimolecular) layer or monolayer, or two, three or more layers thick (multi-

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.

4.4 STAGES IN ADSORPTION PROCESS

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

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

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

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

4.5 ADSORPTION ISOTHERMS

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

Many theoretical and empirical models have been developed to represent the various types of adsorption isotherms. Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), Redlich-Peterson (R-P) etc. are most commonly used adsorption

isotherm models for describing the dynamic equilibrium. The isotherm equations used for the study are described follows:

4.5.1 Langmuir Isotherm

This equation based on the assumptions that:

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

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

$$Q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \quad (4.1)$$

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:

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \quad (4.2)$$

Or

$$\frac{1}{Q_e} = \left(\frac{1}{K_A Q_m} \right) \left(\frac{1}{C_e} \right) + \left(\frac{1}{Q_m} \right) \quad (4.3)$$

4.5.2 Freundlich Isotherm

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

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (4.4)$$

where ,

K_F and n are the constants

C_e = the concentration of adsorbate solution at equilibrium

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

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4.5)$$

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

4.5.3 Redlich-Peterson isotherm

Redlich and Peterson (1959) model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and

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

It can be described as follows:

$$Q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (4.6)$$

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

$$Q_e = \frac{K_R C_e}{1 + a_R C_e} \quad (4.7)$$

It becomes a Langmuir equation. Where $\beta=0$

$$Q_e = \frac{K_R C_e}{1 + a_R} \quad (4.8)$$

i.e. the Henry's Law equation

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

$$\ln \left(K_R \frac{C_e}{Q_e} - 1 \right) = \ln a_R + \beta \ln C_e \quad (4.9)$$

Plotting the left-hand side of equation (4.9) against $\ln C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, a_R , K_R and β . Therefore, a minimization procedure was adopted to solve equation (4.9) by maximizing the correlation coefficient between the theoretical data for Q_e predicted

from equation (4.9) and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with any suitable computer program.

4.5.4 The Temkin isotherm

It is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (4.10)$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (4.11)$$

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

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

4.5.5 Dubinin-Radushkevich (D-R) isotherm

It is given as:

$$q_e = q_s \exp(-B\varepsilon^2) \quad (4.12)$$

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

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (4.13)$$

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]:

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

4.6 ADSORPTION PRACTICES

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

4.6.1 Batch Adsorption Systems

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

4.6.2 Continuous Adsorption Systems

The continuous flow processes are usually operated in fixed bed adsorption columns. These systems are capable of treating large volumes of waste waters and are widely used for treating domestic and industrial wastewaters. They may be operated either in the up flow columns or down flow column. Continuous counter current columns are generally not used for wastewater treatment due to operational

problems. Fluidized beds have higher operating costs. So these are not common in use. Wastewater usually contains several compounds which have different properties and which are adsorbed at different rates. Biological reactions occurring in the column may also function as filter bed retaining solids entering with feed. As a result of these and other complicating factors, laboratory or pilot plant studies on specific wastewater to be treated should be carried out. The variables to be examined include type of adsorbent, liquid feed rate, solute concentration in feed and height of adsorbent bed.

4.7 FACTORS CONTROLLING ADSORPTION

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

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

4.7.1 Initial Concentration

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

4.7.2 Temperature

Temperature is one of the most important controlling parameter in adsorption. Adsorption is normally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature of the system. Some

of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to increase in number of adsorption sites caused by breaking of some of the internal bonds near the edge of the active surface sites of the adsorbents.

4.7.3 pH

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

4.7.4 Contact time

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

4.7.5 Degree of agitation

Agitation in batch adsorbers is most important to ensure proper contact between the adsorbent and the solution. At lower agitation speed, the stationary fluid film around the particle is thicker and the process is mass transfer controlled. With the increase in agitation this film decreases in thickness and the resistance to mass

transfer due to this film reduces and after a certain point the process becomes intra particle diffusion controlled. Whatever is the extent of agitation the solution inside the process remain unaffected and hence for intraparticle mass transfer controlled process agitation has no effect on the rate on the adsorption.

4.7.6 Nature of adsorbent

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

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

Table.4.1: Comparison of Physical and Chemical Adsorption

Sl. No.	Physical Adsorption	Chemical Adsorption
1.	Vander walls adsorption	Activated adsorption
2.	Heat of absorption = 5 kcal/mol	Heat of adsorption = 20-100 kcal/mol
3.	Adsorption only at temp less than the boiling point of the adsorbate	Adsorption can occur even at higher temperature cont...

4.	No activated energy involved in the adsorption process	Activation energy may be involved
5.	Mono and multi layer adsorption	Almost mono layer adsorption
6.	Quantity adsorbed per unit mass is high i.e. entire surface is participating	Quantity adsorbed per unit mass is low i.e. only active surface sites are important
7.	Extent of adsorption depends upon the properties of adsorbent	Extent of adsorption depends on both adsorbate and adsorbent
8.	Rate of adsorption controlled by resistance mass transfer	Rate of adsorption controlled by resistance reaction

Table.4.2: Various commercial adsorbents.

Adsorbent	Properties& method of preparation	Application
Silica gel	Hard, granular and very porous product made from gel precipitated by sodium silicate.	Drying of gases, refrigerants, organic solvents. Desiccant in packing and double glazing. Dew point control of natural gas.
Activated alumina	Hard, hydrated aluminum hydroxide which is activated by heating to drive moisture.	Dry of gases, organic solvents, transformer oils. Desiccant in packing and double glazing. Removal of HCl from hydrogen.
Polymeric and Resin	These are hydrophobic adsorbents which are obtained from pyrolysis and activation of polymeric compounds.	Separation of fatty acids from water and toluene. Separation of aromatics from aliphatics. Removal of colour from syrups. Cont...

Fuller's Earth	These are natural clays The clay is heated and dried during which it develops a porous structure.	Treatment of edible oils. Removal of organic pigments. Refining of mineral oils.
Zeolites	It is insoluble and chemically stable aluminum silicate mineral that was formed from the glass component of volcanic ash.	Removing water from azeotropes. Sweetening sour gases and liquids. Purification of hydrogen. Separation of ammonia and hydrogen. Recovery of carbon dioxide. Separation of xylene and ethyl benzene.

Table.4.3: Typical non conventional adsorbents.

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

EXPERIMENTAL PROGRAMME

5.1 GENERAL

In the present study, (BFA) and ACC have been utilized for the treatment of p-xylene bearing aqueous solution. Experimental details of the study have been presented in this chapter. These details include characterization of adsorbents, batch adsorption studies, and experimental details for the adsorption of p-xylene.

5.2 CHARACTERIZATION OF ADSORBENT

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

5.2.1 Proximate Analysis

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

5.2.2 Density

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

5.2.3 Surface area measurement

The specific surface area, pore volume and pore diameter of the sample were measured by N₂ adsorption isotherm using an ASAP 2010 micrometric instrument and by Brunauer-Emmett-Teller (BET) method, using the software of micrometric, Nitrogen was used as cold bath.

5.2.4 Scanning Electron Microscope (SEM)

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

5.3 ADSORBATE

p-xylene supplied by S.d Fine chemicals, Mumbai, India was used as adsorbate. Synthetic wastewater solutions of p-xylene of desired concentrations (25–150mg l⁻¹) were prepared by dissolving accurately weighed quantity of p-xylene in distilled water.

5.4 ANALYTICAL MEASUREMENTS

A double beam UV/VIS spectrophotometer (Perkin Eilmer 135) is used for the concentration measurement of p-xylene. For this purpose, first the wave length corresponds to maximum absorbance (λ_{\max}) was determined from the plot between absorbance versus wavelength performed by taking a standard solution. λ_{\max} for p-xylene was found to be 197nm. Throughout the further work this wave length is used for the concentration measurement. Then calibration curves were plotted between absorbance and concentration of standard p-xylene solution for further use (given in Fig.5.1).

5.5 BATCH EXPERIMENTAL PROGRAMME

Batch experimental programme was used throughout the experimental work i.e. to study the effect of important parameters like pH, dose, Conc, time and temperature at 30±1 °C. For each experimental run, 50ml of p-xylene solution of known concentration, pH and a known amount of the adsorbent were taken in a 100 ml stoppered conical flask. This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of 160 rpm at 30±1 °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 8000 rpm for 10 minute and analyzed

for the residual xylene concentration. The effect of pH on p- xylene removal was studied over a range of 2 to 12 was adjusted by the addition of dilute aqueous solutions of HCl or NaOH (0.10 M). For the optimum amount of adsorbent per unit mass of adsorbate, a 50ml of p-xylene solution was contacted with different amounts of BFA and ACC respectively till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the p- xylene from the aqueous solution at different time intervals. For adsorption isotherms, p-xylene solution of different concentrations were agitated with the known amount of adsorbent till the equilibrium was achieved. The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 293, 303 and 313 K. Concentration was varied from 25 mg/l to 150mg/l. Blank experimental runs, with only the adsorbent in 100 ml of distilled water, were conducted simultaneously at similar conditions to account for any p- xylene removal by the adsorbents and adsorbed by glass containers.

Table.5.1: Variation of absorbance with concentration of p-xylene.

Conc. (ppm)	Absorbance
1	0.1362
2	0.250
3	0.531
4	0.512
5	0.625

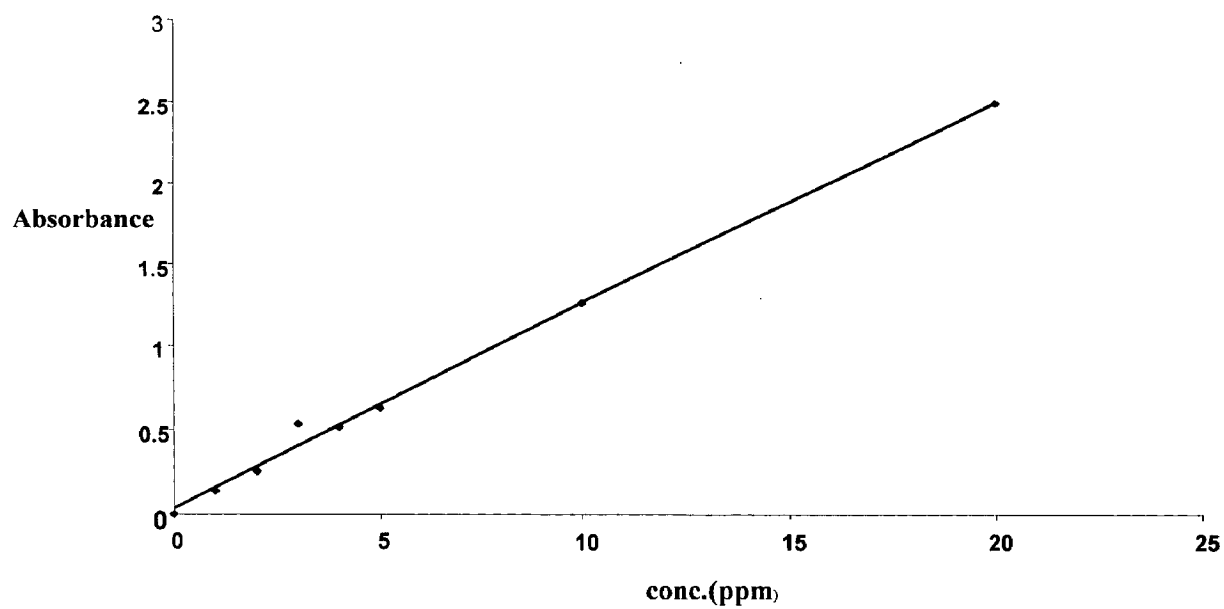


Fig. 5.1 Variation of absorbance with concentration of p-xylene

RESULT AND DISCUSSION

6.1 GENERAL

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

6.2 CHARACTERIZATION OF BAGASSE FLY ASH AND ACTIVATED CARBON

Physico-chemical characteristics of the two adsorbents are presented in Table.6.1 and 6.2 obtained by incineration of BFA and ACC consists mainly of carbon, silica, alumina, calcium oxide, etc. From Table.6.1, it is observed that the bulk density of BFA is lower than that of ACC. The specific surface areas of the adsorbents used in the present investigations are given in Table.6.1. From geometrical considerations of the particle shape, it is expected that the surface area per unit mass of BFA will be much lower than that of ACC. The morphologies of BFA and ACC were examined under scanning electron microscope. The SEMs of BFA and ACC as obtained are shown in Fig.6.1 and 6.2 respectively. The BFA has linear type of fibres with holes in it and at other places and has skeletal structure. Further, the number of pores in BFA shows the pore size distribution of BFA. The average pore size distribution of BFA is also much larger. Although, the detailed pore size analysis of the ACC is not available, it is expected that the pore size distribution shall be higher than BFA. It has both macro- and micro-pores. Major components identified in BFA are crystalline quartz, alumina, cristobalite, and calcium orthosilicate, whereas, tridymite and silicate carbon are the major components of ACC. Diffraction peaks corresponding to crystalline carbon were not observed in BFA and activated carbons. Nowackiite was also observed in ACC. The broad peaks in all the two samples indicate the presence of amorphous form of silica. From the micrographs and X-ray diffractograms, it is seen that the BFA and ACC

have heterogeneous surface. Proximate analysis of adsorbents showed 32.90, 77.82 fixed carbon in BFA, ACC respectively.

6.3 BATCH ADSORPTION STUDIES

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

6.3.1 Effect of initial pH

The adsorption of solute from water or wastewater is influenced by the pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization as well as the speciation of the solute. The adsorption pattern of p-xylene on BFA and ACC in the present case was studied varying the solution pH from 2 to 12. The adsorption was found to decrease both at the lower and higher pH values with somewhat higher adsorption in the intermediate pH region (Fig.6.4 and 6.5). This pH dependent behavior of p-xylene can be well explained considering the pH of BFA and ACC and the ionizing power (acidity, pKa) of the solutes. The oxides of metals present in fly ash form aqueous complexes with water and develop charged surface through amphoteric dissociation at varying pH values as shown in Fig.6.4 and 6.5. At low pH values a positive charge is developed at the oxides surface. At the same time at lower pH the presence of H⁺ suppresses the ionization of solute. The uptake of benzyl radical is more reduced, being even more weakly dissociated. From figure it has been clearly observed that the reaction is best suited at pH value around 6. So the further experiments were carried out for pH value of 6 for both BFA and ACC. The effect of pH can be studied in a nutshell as:

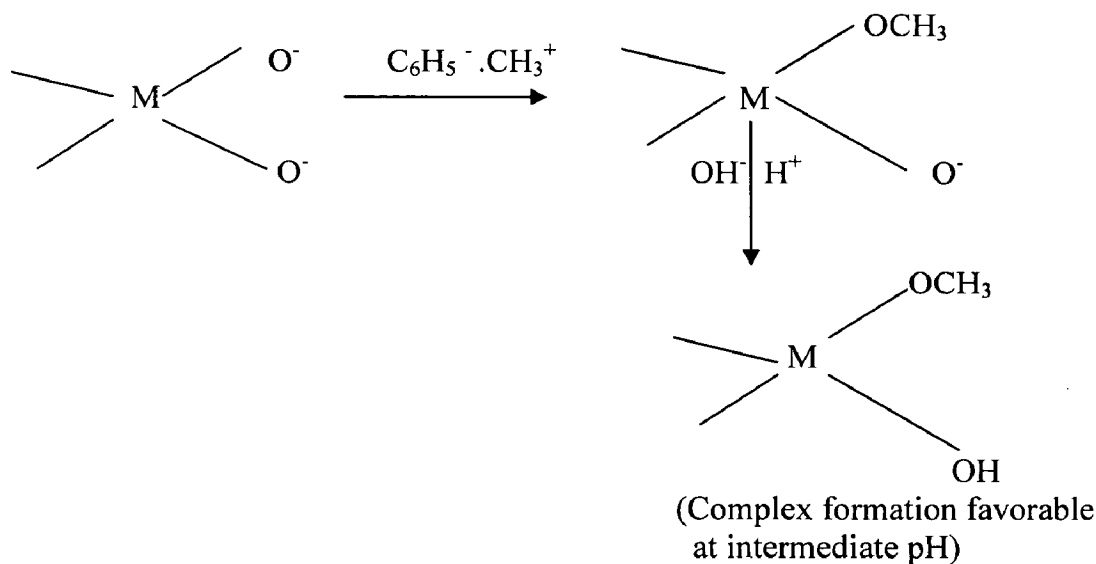


Fig.6.3. pH mechanism

6.3.2 Effect of Adsorbent dose

The effect of BFA and ACC dose on the extent of solute adsorption was investigated by varying the dose from 0.02 to 1g per 50 mL under the selected initial solute concentration (50mg/L). The agitation speed (160rpm) and temperature (303K) were selected for the experiment. It is observed that as the dose increases, the amount of solute adsorbed increases and reaches a maximum value corresponding to a certain dose (Fig.6.6 and 6.7). The minimum amount of adsorbent corresponding to the maximum adsorption is declared as the optimum dose. The optimum dose observed in the present study is 0.4g per 50 mL of the solution of adsorbent dosage for BFA, where as for ACC it is 0.6 gm/50 mL of solution. Further throughout the experiments this concentration has been followed.

6.3.3. Effect of contact time

The effect of contact time on the removal of p-xylene by BFA and ACC at $C_0=50, 100$ and 150 mg l^{-1} are given in Figs. 6.8 and 6.9 respectively. The contact time curves show rapid adsorption of p-xylene in the first 60-70 min, thereafter, the rate of adsorption rate decreases gradually and the adsorption reaches equilibrium around 80 min.

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The effect of contact time for the adsorption of p-xylene by BFA and ACC was studied for a period of 24 h for initial p-xylene concentrations of 50mg/l at 30°C. BFA and ACC dosage were 0.4 g/50 ml and 0.6g/50ml respectively of p-xylene, at optimum pH. The solutions were kept in contact with BFA and activated carbon for 24 h, although no significant variation in residual p-xylene concentration was detected after 70min of contact time. Thus, after 70min of contact, a steady-state approximation was assumed and a quasi-equilibrium situation was accepted. The curves of contact time are single, smooth and continuous leading to saturation. These curves indicate the possible monolayer coverage of p-xylene on the surface of BFA and ACC.

Increase in contact time up to 24 h showed that the p-xylene removal by BFA and activated carbon increases only by about 0.5% over those obtained for 70 min. contact time. Aggregation of p-xylene 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 p-xylene molecules in the adsorbents. This is the reason why an insignificant enhancement in adsorption is effected in 24 h as compared to that in 70 min. Since the difference in

the adsorption values at 70 min and at 24 h is very small, further experiments were conducted for 70 min contact time only. The curves are single, smooth and continuous leading to saturation. The adsorption curves of contact time indicate the possible mono-layer coverage of p-xylene on the surface of BFA and activated carbon. With double adsorption the removal percentage are 91 and 94 for BFA and ACC respectively.

6.3.4 Adsorption kinetics

Kinetics of adsorption plays a vital role to determine the time of completion of the reaction and the percentage of conversion. In other words it ultimately controls the process efficiency. The adsorption of organic compound from a liquid phase to a solid phase can be considered as a reversible process with equilibrium being established between the two phase. The kinetic model used in this study is based on the assumption of first order reversible process which has been found to be fitted into experimental data as shown from the Fig.6.10. The expression for the reversible kinetic can be found as follows:



The rate equation for the reaction can be written as:

$$\begin{aligned} (dC_B/dt) &= - (dC_A/dt) \\ &= k_1 (C_{A0} - C_{A0}X_A) - K_2 (C_{B0} + C_{A0}X_A), \end{aligned} \quad (6.2)$$

Where:

C_{A0} = initial concentration of solute in solution at time=0,

C_{B0} = initial concentration of solute on the sorbate at time=0,

C_A = concentration of solute in solution at any time during the reaction,

C_B = concentration of solute on the sorbate at any time during the reaction,

X_A = fraction adsorbed onto the sorbent,

k_1 = first-order adsorption rate constant, and

k_2 = first-order desorption rate constant.

At the equilibrium condition:

$$(dC_B/dt) = - (dC_A/dt) = 0 \quad (6.3)$$

And

$$X_{Ae} = (k_c - (C_{B0}/C_{A0})) / (1 + k_c) \quad (6.4)$$

Where:

X_{Ae} = fraction of solute adsorbed at equilibrium condition, and

k_c = equilibrium constant defined as:

$$k_c = (k_1/k_2) = (C_{B0} + C_{A0}X_{Ae}) / (C_{A0} - C_{A0}X_{Ae}). \quad (6.5)$$

In terms of equilibrium conversion, the differential form of the rate equation is:

$$(dX_A/dt) = (k_1 + k_2) (X_{Ae} - X_A). \quad (6.6)$$

Integration of equation (6), substituting (k_1/k_2) for k_2 , gives:

$$-\ln [1 - (X_A/X_{Ae})] = (k_1 + (k_1/k_c)) t$$

$$\ln [1 - (X_A/X_{Ae})] = -k't, \quad (6.7)$$

where:

k' = overall rate constant

$$= k_1 + k_2.$$

The overall rate constant (k') is calculated from the plot of $\ln[1 - (X_A/X_{Ae})]$ vs reaction time, which is summarized in Table 6.3.

6.3.5 Adsorption Equilibrium Study

The presence of the amount of solute adsorbed per unit weight of the adsorbent as a function of the equilibrium concentration in bulk solution at constant temperature is termed the adsorption isotherm. In other words, the adsorption isotherm is a functional expression for the variation of adsorption with concentration

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

6.3.5.1 Freundlich and Langmuir isotherms:

Linearised form of Freundlich and Langmuir isotherm equations are given as

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (\text{Linear form}) \quad (6.8)$$

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \quad (\text{Linear form}) \quad (6.9)$$

Figs.6.11 and 6.12 shows the Freundlich isotherm plots ($\ln Q_e$ vs $\ln C_e$) for adsorption of p-xylene, respectively, onto BFA and ACC at 293, 303 and 313K. Langmuir isotherm plot (C_e/Q_e versus C_e) are shown in Fig.6.13 and 6.14 respectively for adsorption onto BFA and ACC. Freundlich and Langmuir isotherm parameter along with linear and non-linear correlation coefficients are given in table.6.4 and 6.5 for BFA and ACC respectively. Comparison of correlation coefficient values (R^2) shows that R^2 values are close to unity for Langmuir isotherm for both BFA and ACC. The q_m value for both the adsorbent increase with temperature indicating endothermic nature of adsorption. Though adsorption is generally exothermic in nature but when, it is controlled by diffusion of adsorbates into the adsorbant, then it may be endothermic. This may be due to the endothermicity of the diffusion process [25].The essential characteristics of a

Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L , which describes the type of pattern and is defined as $R_L=1/(1 + K_A C_0)$ indicates the nature of adsorption as

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

The value of R_L is found to be less than 1 for adsorption of p-xylene on BFA and ACC. So adsorption onto both the adsorbents is favorable. The values of $1/n$ were also found to be less than 1 showing favorable nature of adsorption.

6.3.5.2 The Temkin isotherm:

It is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (6.10)$$

This can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (6.11)$$

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

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

respectively. K_T is the equilibrium binding constant (l mol^{-1}) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. Fig.6.15 and 6.16 show the Temkin isotherm plot for BFA and ACC respectively. The Temkin isotherm parameters listed in Tables 6.4 and 6.5 for BFA and ACC respectively. It shows better only compared to Freundlich isotherm.

6.3.5.3 Dubinin-Radushkevich (D-R) isotherm:

It is given as (Dubinin and Radushkevich, 1947)

$$q_e = q_s \exp(-B\varepsilon^2) \quad (6.12)$$

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

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6.13)$$

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:

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

The D-R equation does not represent the experimental data satisfactorily.

6.4 ERROR ANALYSIS

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

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

This error function, SSE is given as

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

Here, $q_{e,cal}$ and $q_{e,exp}$ are, respectively, the calculated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg g^{-1}) and n is the number of data points. This most commonly used error function; SSE has one major drawback in that it will result in the calculated isotherm parameters providing a better fit at the higher end of the liquid phase concentration range. This is because of the magnitude of the errors, which increase as the concentration increases. The values of SSE are given in table.6.6.and 6.7 both for BFA and ACC respectively.

6.4.2 The sum of the absolute errors (SAE)

SAE is given as

$$SAE = \sum_{i=1}^n |q_{e,calc} - q_{e,exp}|_i \quad (5.18)$$

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.

6.4.3 The average relative error (ARE)

ARE (Kapoor and Yang, 1989) is given as

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{(q_{e,exp} - q_{e,calc})}{q_{e,exp}} \right|_i \quad (6.14)$$

This error function attempts to minimize the fractional error distribution across the entire concentration range. The values of ARE are given in Table 6.6 and 6.7 both for BFA and ACC respectively.

6.4.4 The hybrid fractional error function (HYBRID)

HYBRID is given as

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,exp} - q_{e,calc})}{q_{e,exp}} \right]_i \quad (6.15)$$

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.

6.4.5 Marquardt's percent standard deviation (MPSD)

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

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{(q_{e,meas} - q_{e,calc})}{q_{e,meas}} \right)_i^2} \quad (6.16)$$

The values of MPSD error functions are given in table 6.6 and 6.7.

6.4.6 Choosing best-fit isotherm based on error analysis:

The values of the five error functions are presented in table 6.6 and 6.7. By comparing the results of the values of the error functions, it is found that Langmuir isotherm best-fitted the isotherm data for p-xylene adsorption on activated carbon

and BFA at 293K. However, Tempkin model best-fits the p-xylene adsorption isotherm data for the ACC and BFA 313K. It may, however, be noted that the non-linear correlation coefficients, R^2 and the error analysis values are similar for the Langmuir and Tempkin isotherms and hence any one of the isotherms could be used for p-xylene adsorption on ACC and BFA.

6.5 THERMODYNAMIC STUDY

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

$$\Delta G^0 = -RT \ln K \quad (6.17)$$

$$K = C_{Ae} / C_e$$

Where C_{Ae} and C_e indicate the equilibrium solute concentration on the adsorbent and in the solution, respectively. The equilibrium constant values corresponding to three different temperatures viz. 293, 303, and 313 K, at the studied temperature range, were calculated.

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:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6.18)$$

Combining above two equations, we get

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (6.19)$$

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

$$\Delta H^0 = \left[R \frac{d \ln K}{d(1/T)} \right] \quad (6.20)$$

ΔG^0 , ΔH^0 and ΔS^0 as calculated are given in Table 6.8 and 6.9, respectively, for adsorption of p-xylene onto BFA and ACC. The positive ΔH^0 value confirms the endothermic nature of the overall-sorption process. The adsorption process in the solid-liquid system is a combination of two processes: (a) The desorption of the molecules of solvent (water) previously adsorbed and (b) the adsorption of adsorbate species. The p-xylene ions have to displace more than one water molecule for their adsorption and these results in the endothermicity of the adsorption process. The positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of the ACC and BFA towards p-xylene. Also, positive ΔS value corresponds to an increase in the degree of freedom of the adsorbed species. ΔG^0 Values were negative indicating that the sorption process led to a decrease in Gibbs free energy. Negative ΔG_{ads}^0 indicates the feasibility and spontaneity of the adsorption process.

6.6 COMPARISON OF BFA AND ACC

The following table gives a clear comparison between BFA and ACC.

Table.6.(a): Comparison of BFA and ACC

Parameters	BFA	ACC
Adsorbent dosage	8 g/L	12 g/L
Optimal pH	6	6.5
Isotherm	Langmuir	Langmuir
Nature of reaction	Endothermic	Endothermic
Single adsorption removal efficiency	80 %	86 %
Double adsorption removal efficiency	91 %	94 %
Cost	Only transportation cost	Rs 40.00/kg
Cost for treatment of 1 lit solution	Negligible	Rs.0.48

Table.6.(b): Comparison of adsorption capacity (in mg/g)

Temperature (K)	BFA	ACC
293	17.986	20.260
303	22.420	21.459
313	33.784	31.948

From above table it is clear that after double adsorption the difference between the removal efficiency of BFA and ACC is not significant. But with respect to cost BFA is almost free, where as ACC is Rs. 40.00/kg. So from economical and as well as adsorption capacity point of view, it is well cleared that BFA is more feasible to be used as adsorbent for removal of p-xylene as compared to ACC.

Table 6.1: Characteristics of bagase fly ash

Proximate analysis	
Moisture (%)	5.65
Ash (%)	54.75
Volatile matter (%)	6.70
Fixed carbon (%)	32.90
Bulk density (kg/m³)	88.29
BJH cumulative pore volume (cc/g)	
(i)Single point total	0.1337
(ii)BJH adsorption	0.0526
(iii)BJH desorption	0.0508
Surface area of pores (m²/g)	
(i) BET	237.83
(ii) BJH	
(a) adsorption cumulative	62.29
(b) desorption cumulative	36.19
Average pore diameter (A^o)	
(i) BET	22.47
(ii) BJH adsorption	33.77
(iii) BJH desorption	56.12

Table 6.2: Characteristics of activated carbon

Proximate analysis	
Moisture (%)	4.39
Ash (%)	13.60
Volatile matter (%)	4.19
Fixed carbon (%)	77.82
Bulk density (kg/m³)	506.68
BJH cumulative pore volume (cc/g)	
(i) Single point total	0.1327
(ii) BJH adsorption	0.1231
(iii) BJH desorption	0.1081
Surface area of pores (m²/g)	
(i) BET	171.05
(ii) BJH	
(a) adsorption cumulative	131.98
(b) desorption cumulative	94.33
Average pore diameter (A^o)	
(i) BET	31.03
(ii) BJH adsorption	37.30
(iii) BJH desorption	45.86

Table.6.3: Values of rate constant at different initial conc. from kinetic study at 30°C.

Initial conc. of solute(mg/L)	k'(min⁻¹) For BFA	k'(min⁻¹) For activated carbon
50	0.067	0.071
100	0.085	0.088
125	0.110	0.192
150	0.113	0.231

Table.6.4: Isotherm parameters for adsorption of p-xylene onto BFA

Freundlich constants				
Temp (K)	K_F ((mg/g)/(mg/l) ^{1/n})	$1/n$	R_1^2 (linear)	R_2^2 (non-linear)
293	0.366	0.7086	0.9661	0.9746
303	0.631	0.5294	0.9695	0.9844
313	0.942	0.6659	0.9875	0.9741
Langmuir constants				
Temp (K)	K_L (l/mg)	q_m (mg/g)	R_L	R_1^2 (linear)
293	0.007	17.986	0.9982	0.9968
303	0.009	22.420	0.9900	0.9919
313	0.015	33.784	0.9876	0.9861
Tempkin constants				
Temp (K)	K_T (1/mg)	B_1	R_1^2 (linear)	R_2^2 (non-linear)
293	0.078	4.6867	0.9961	0.9960
303	0.080	9.2829	0.9909	0.9930
313	0.387	6.8343	0.9695	0.9528

Table.6.5: Isotherm parameters for adsorption of p-xylene onto activated carbon

Freundlich constants				
Temp (K)	K_F ((mg/g)/(mg/l) ^{1/n})	$1/n$	R_1^2 (linear)	R_2^2 (non-linear)
293	0.517	0.7150	0.9868	0.9643
303	0.459	0.6467	0.9512	0.9751
313	0.316	0.7232	0.9485	0.9748
Langmuir constants				
Temp (K)	K_L (l/mg)	q_m (mg/g)	R_L	R_1^2 (linear)
293	0.300	20.260	0.9919	0.9988
303	0.234	21.459	0.9530	0.9879
313	0.150	31.948	0.9609	0.9763
Tempkin constants				
Temp (K)	K_T (1/mg)	B_1	R_1^2 (linear)	R_2^2 (non-linear)
293	0.093	4.3536	0.9969	0.9936
303	0.078	4.6473	0.9912	0.9823
313	0.074	6.3386	0.9543	0.9421

Table.6.6: Isotherm error analysis for adsorption of p-xylene onto BFA

Isotherm Temperature	HYBRID	MPSD	SSE	SAE	ARE
293K					
Langmuir	0.1256	11.5723	89.6378	0.0021	3.0800
Freundlich	-1.0376	32.1827	131.6378	0.8621	9.2989
Temkin	0.1335	21.2331	127.5366	0.0026	5.9494
303K					
Langmuir	3.9125	12..1973	51.0533	1.0478	2.7595
Freundlich	-4.2822	22.5228	71.7588	1.0615	6.9250
Temkin	-5.0633	26.4866	113.6940	14.0016	6.7740
313K					
Langmuir	10.1656	46.7073	150.2803	-3.5089	12.4031
Freundlich	-1.0283	39.7825	219.6460	2.0834	10.4010
Temkin	0.1776	9.8247	11.5749	-0.7178	2.4294

Table.6.7: Isotherm error analysis for adsorption of p-xylene onto activated carbon

Isotherm Temperature	HYBRID	MPSD	SSE	SAE	ARE
293K					
Langmuir	0.01414	19.75232	90.52414	0.00085	7.08007
Freundlich	-1.0122	38.81276	133.3678	0.68210	12.28992
Temkin	0.01556	25.23314	129.53663	0.00263	8.49943
303K					
Langmuir	0.19125	17.19731	78.03513	0.54783	4.59759
Freundlich	-0.28422	24.52281	79.6981	1.06155	6.295
Temkin	-5.03384	29.8656	116.1604	16.1016	7.974
313K					
Langmuir	13.1526	46.70732	150.2038	-2.508925	14.3014
Freundlich	-1.0183	41.97825	217.0646	3.08743	10.9892
Temkin	0.2677	9.24743	11.75394	-1.11797	3.1286

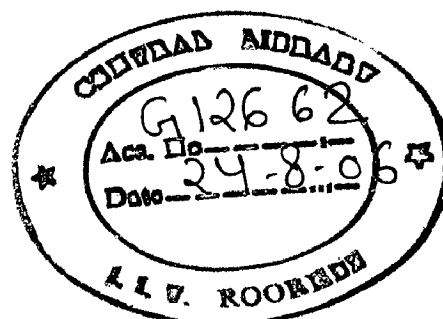


Table.6.8. Thermodynamics parameters for adsorption of p-xylene onto BFA

Temperature (K)	Kc	$\Delta G(\text{kJ/mol.K})$
293	2.34	-2.07
303	3.22	-2.94
313	3.80	-3.47
*$\Delta H = +21.4 \text{ J}$	$\Delta S = 0.0529 \text{ J/K}$	

Table.6.9. Thermodynamics parameters for adsorption of p-xylene onto activated carbon

Temperature (K)	Kc	$\Delta G(\text{kJ/mol.K})$
293	2.98	-2.659
303	3.67	-3.274
313	4.20	-3.734
*$\Delta H = +14.341 \text{ J}$	$\Delta S = 0.061 \text{ J/K}$	

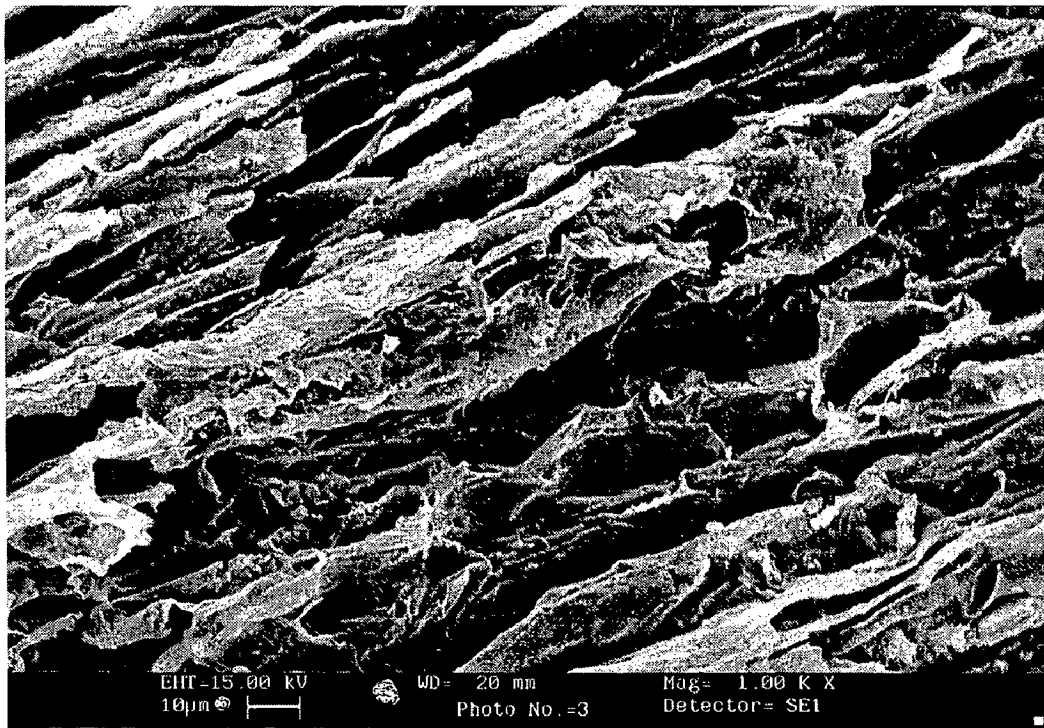


Fig. 6.1.Scanning electron micro graph of bagasse fly ash

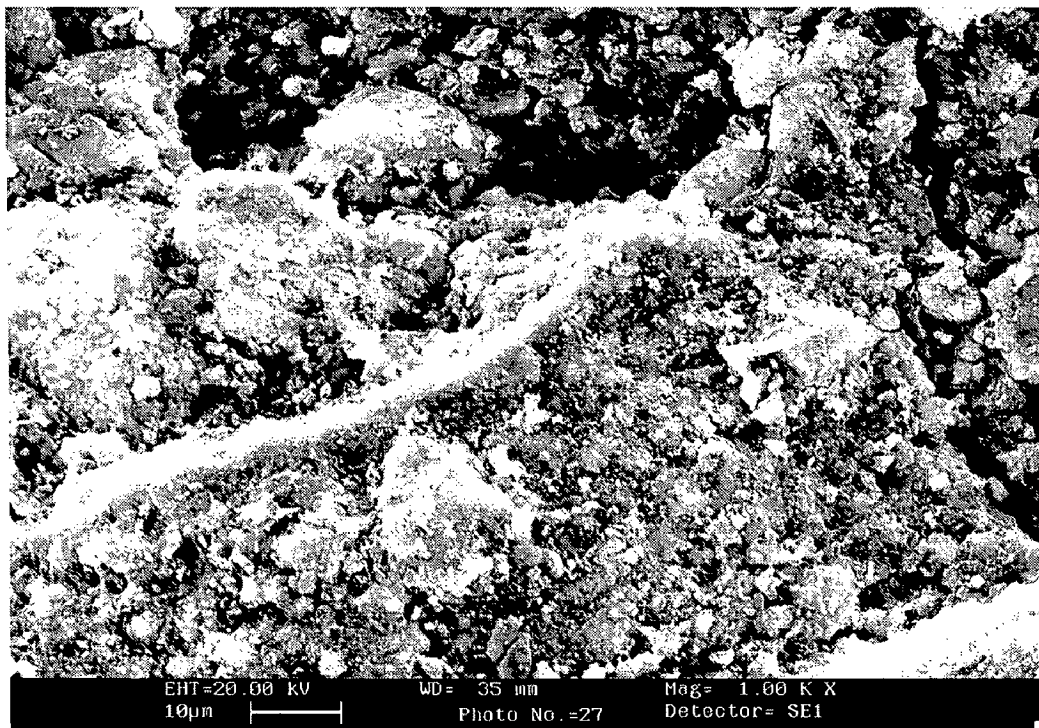


Fig. 6.2.Scanning electron micro graph of activated carbon

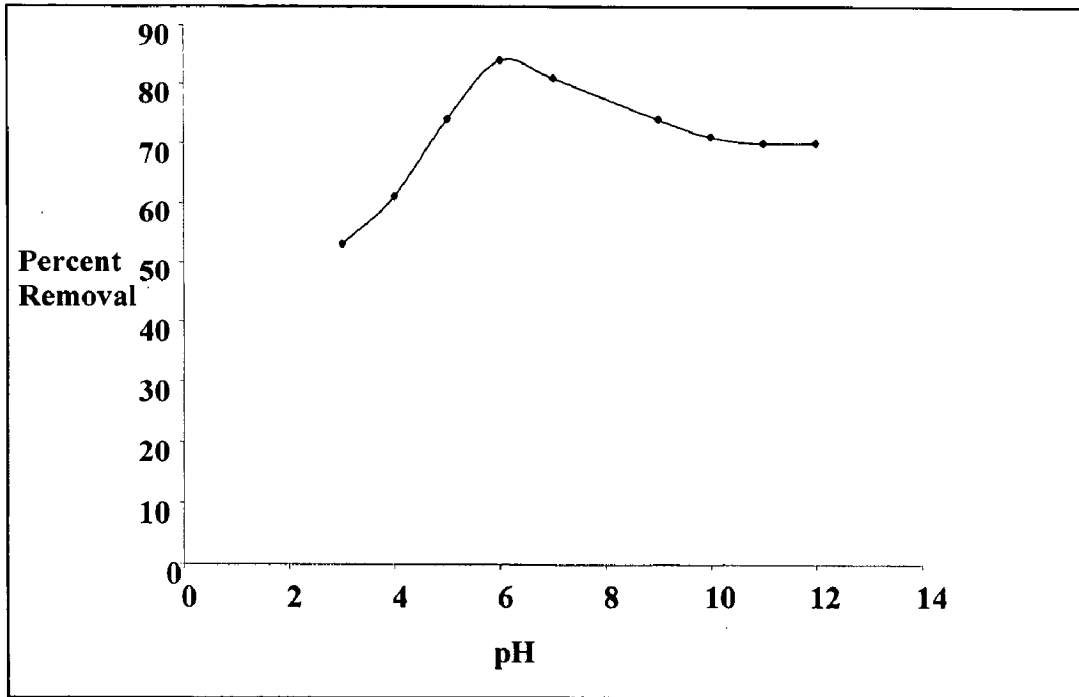


Fig. 6.4 Effect of pH on adsorption of p-xylene by BFA
 (Temp=30°C, Contact time=300min, $C_0=50\text{mg/l}$, BFA conc.=10 gm/L)

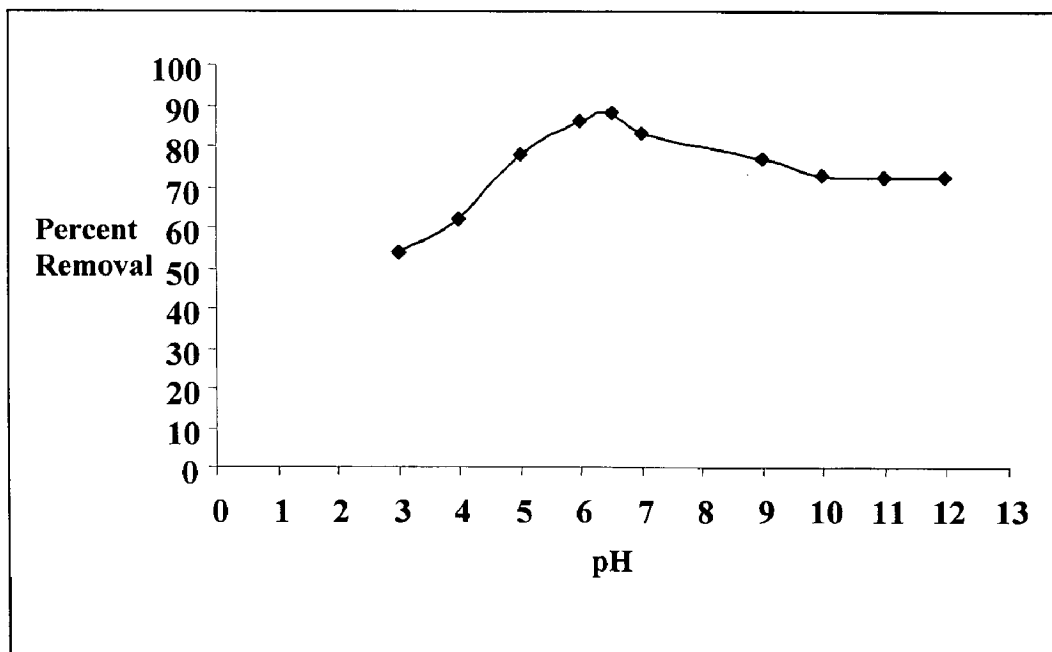


Fig. 6.5 Effect of pH on adsorption of p-xylene by ACC
 (Temp=30°C, Contact time=300min, $C_0=50\text{mg/l}$, ACC conc.=10 gm/L)

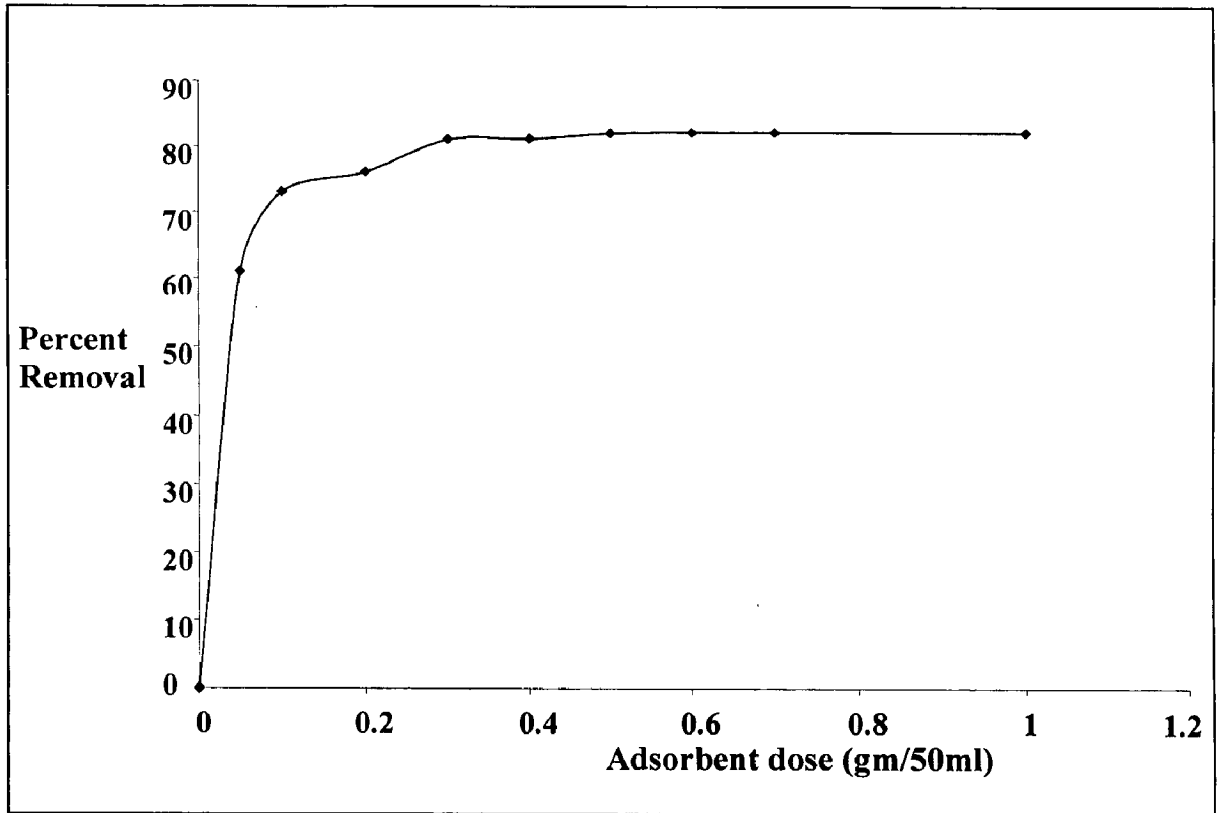


Fig. 6.6 Effect of adsorbent mass on adsorption of p-xylene for BFA
 (Temp=30°C, Vol of sample=50 ml, C0=50 ppm)

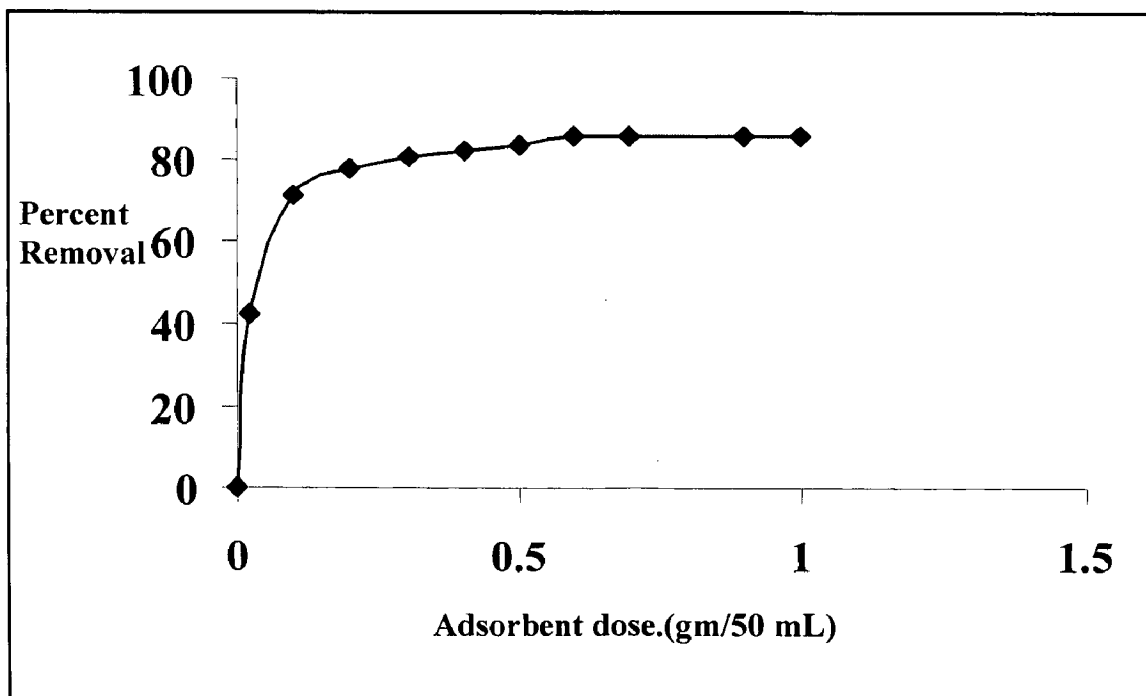
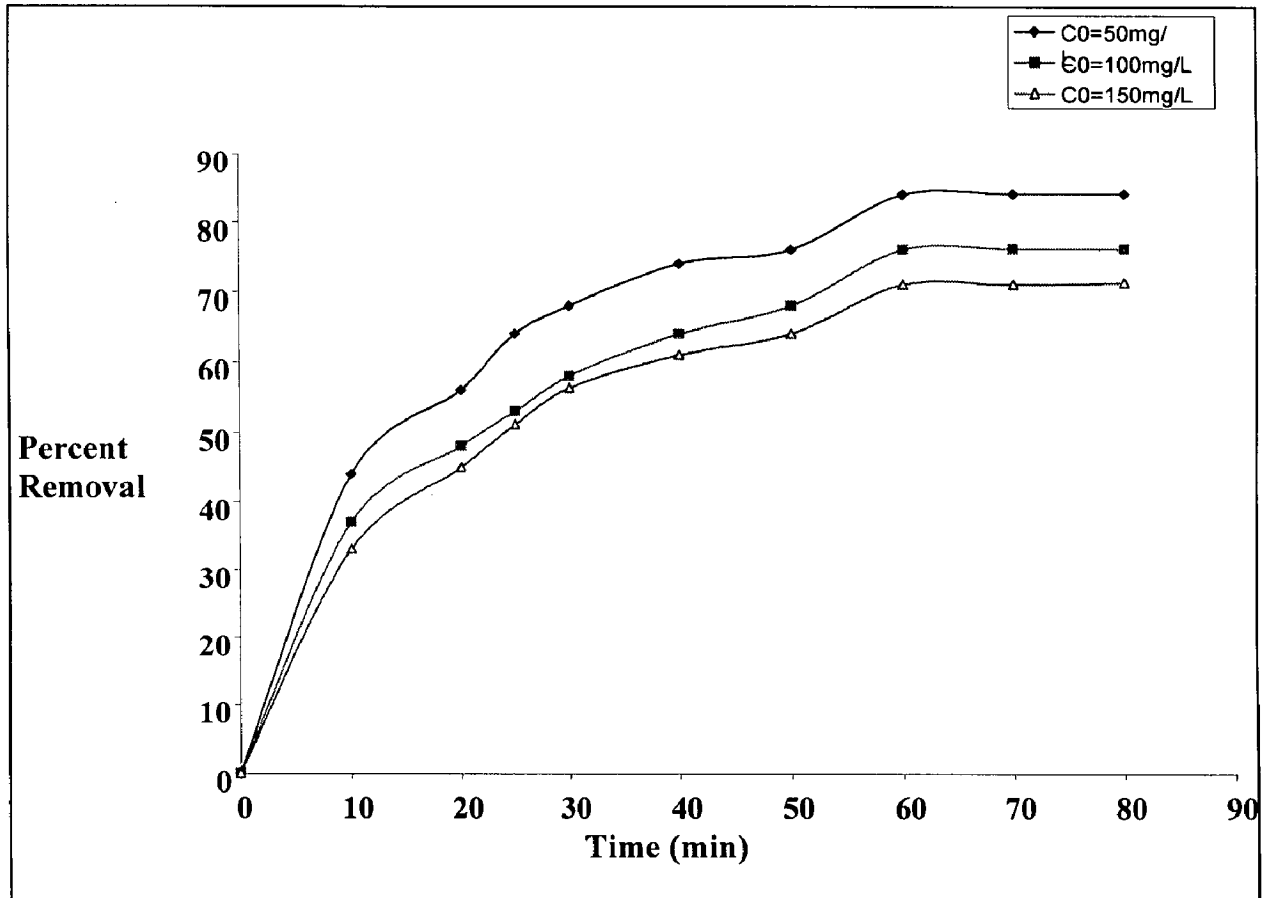
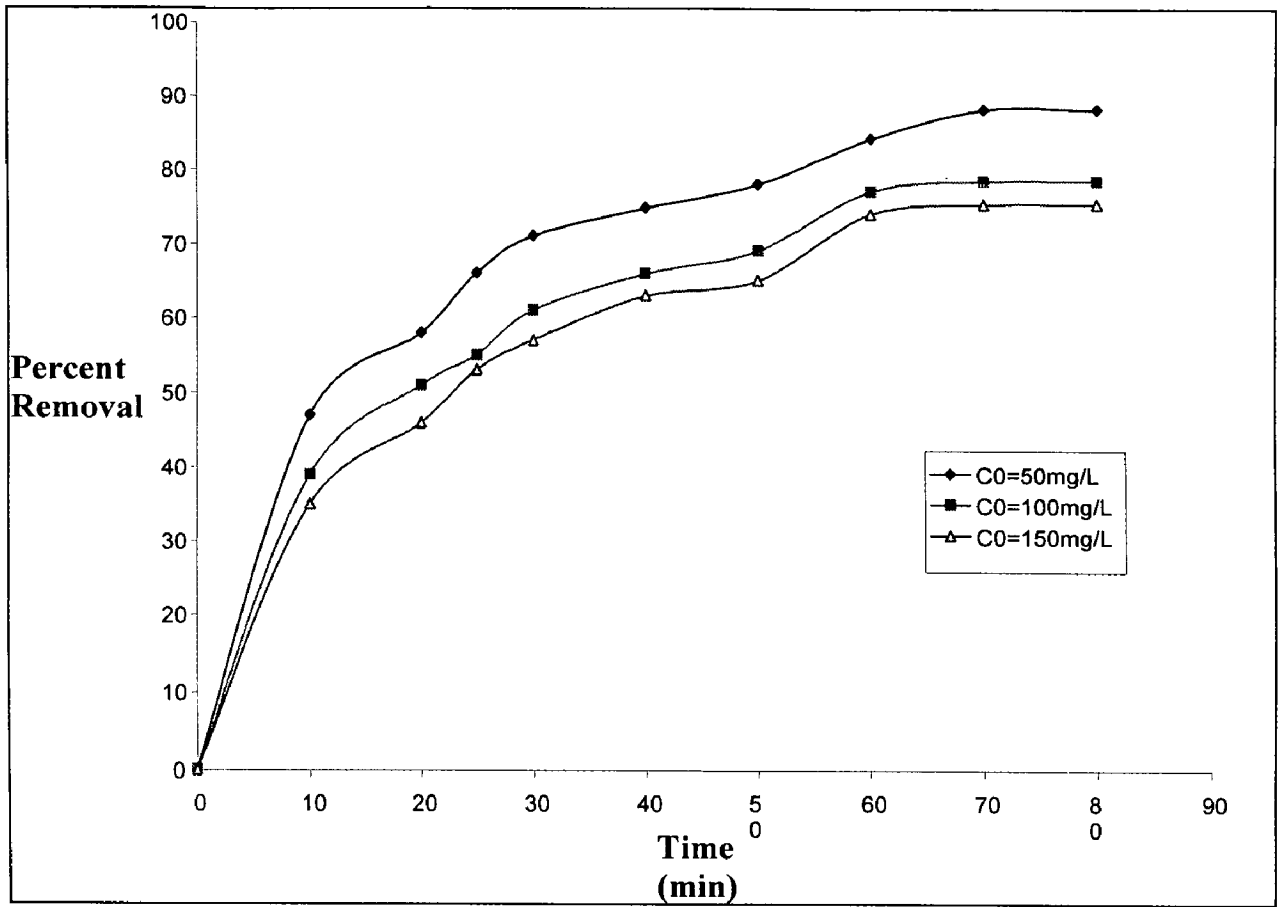


Fig. 6.7 Effect of adsorbent mass on adsorption of p-xylene for ACC
 (Temp=30°C, Vol of sample=50 ml, C0=50 ppm)



**Fig. 6.8 Effect of contact time on single adsorption of p-xylene by BFA
(Temp=30°C, Vol of sample=50 ml, Dose=8g/L)**



**Fig. 6.9 Effect of contact time on single adsorption of p-xylene by ACC
(Temp=30°C, Vol of sample=50 ml, Dose=12 gm/L)**

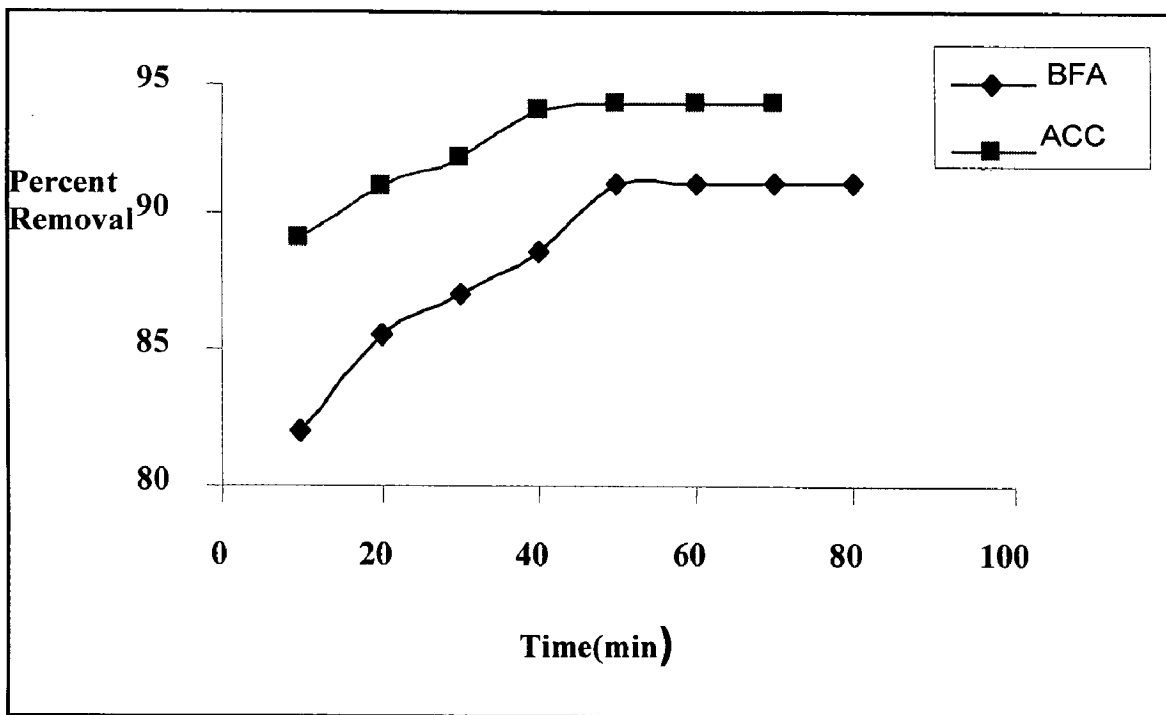


Fig. 6.9(i) Effect of contact time on double adsorption of p-xylene
(Temp=30°C, Vol of sample=50 ml, initial conc. p-xylene=50 ppm)

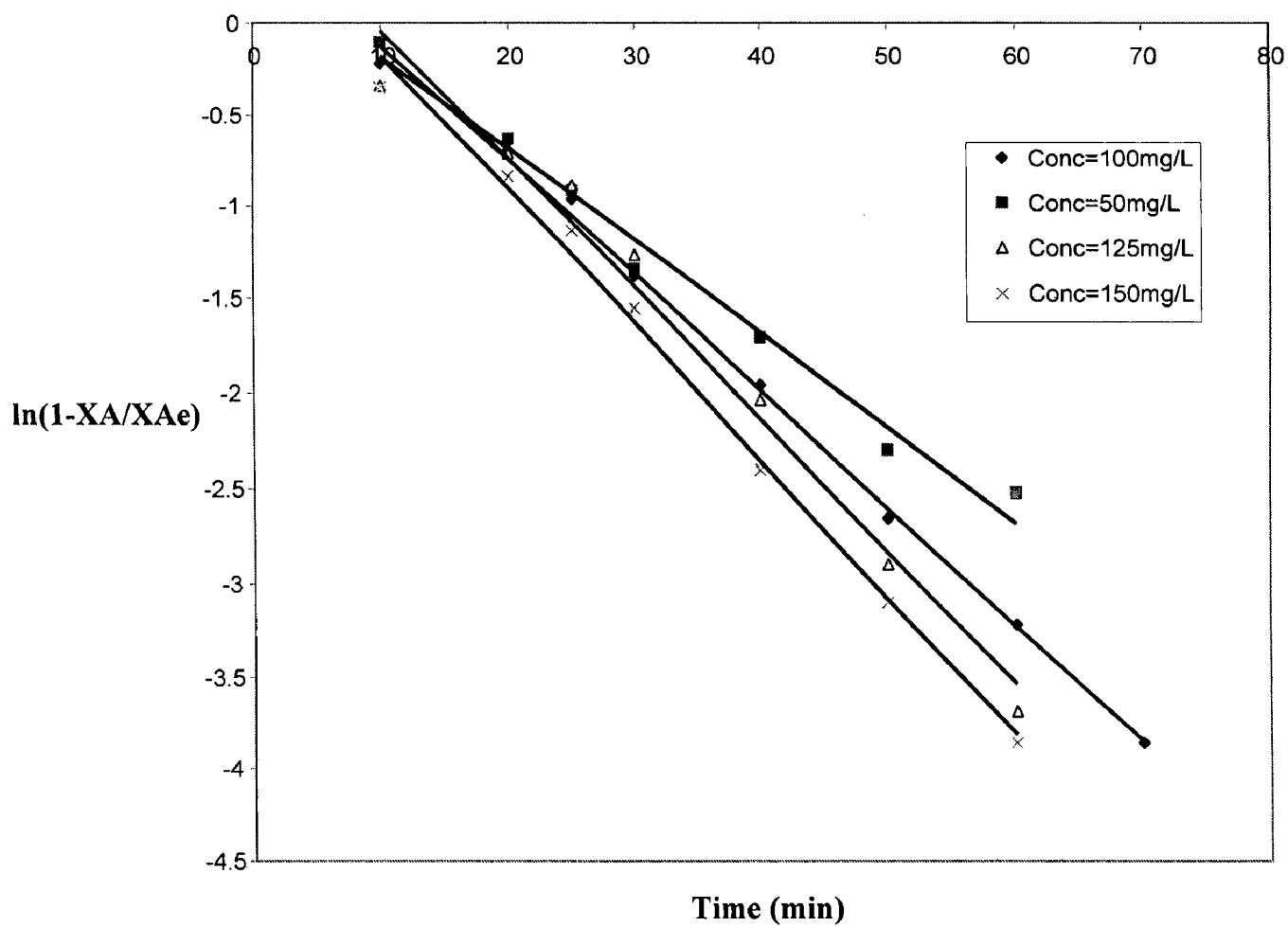


Fig. 6.10 First order reversible kinetic fit for p-xylene.

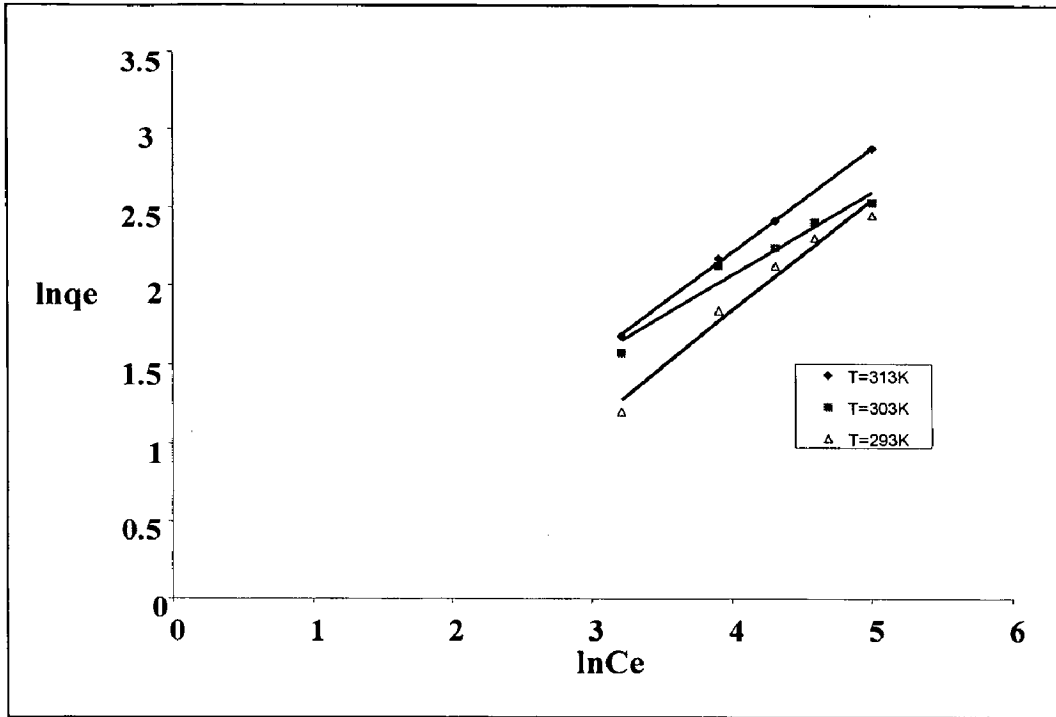


Fig. 6.11 Freundlich isotherm for removal of p-xylene by BFA

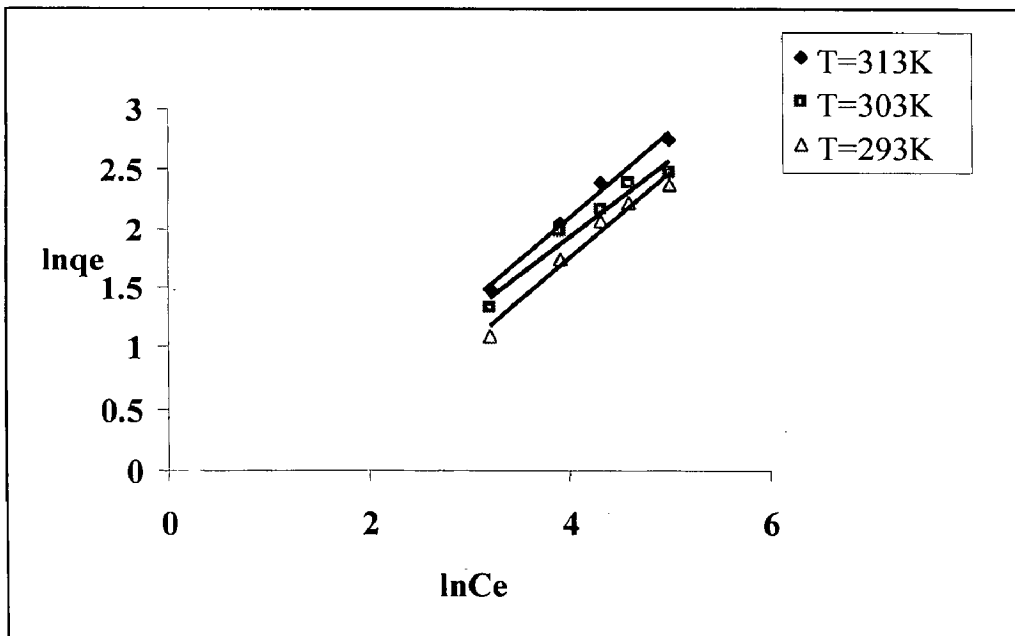


Fig. 6.12 Freundlich isotherm for removal of p-xylene by ACC

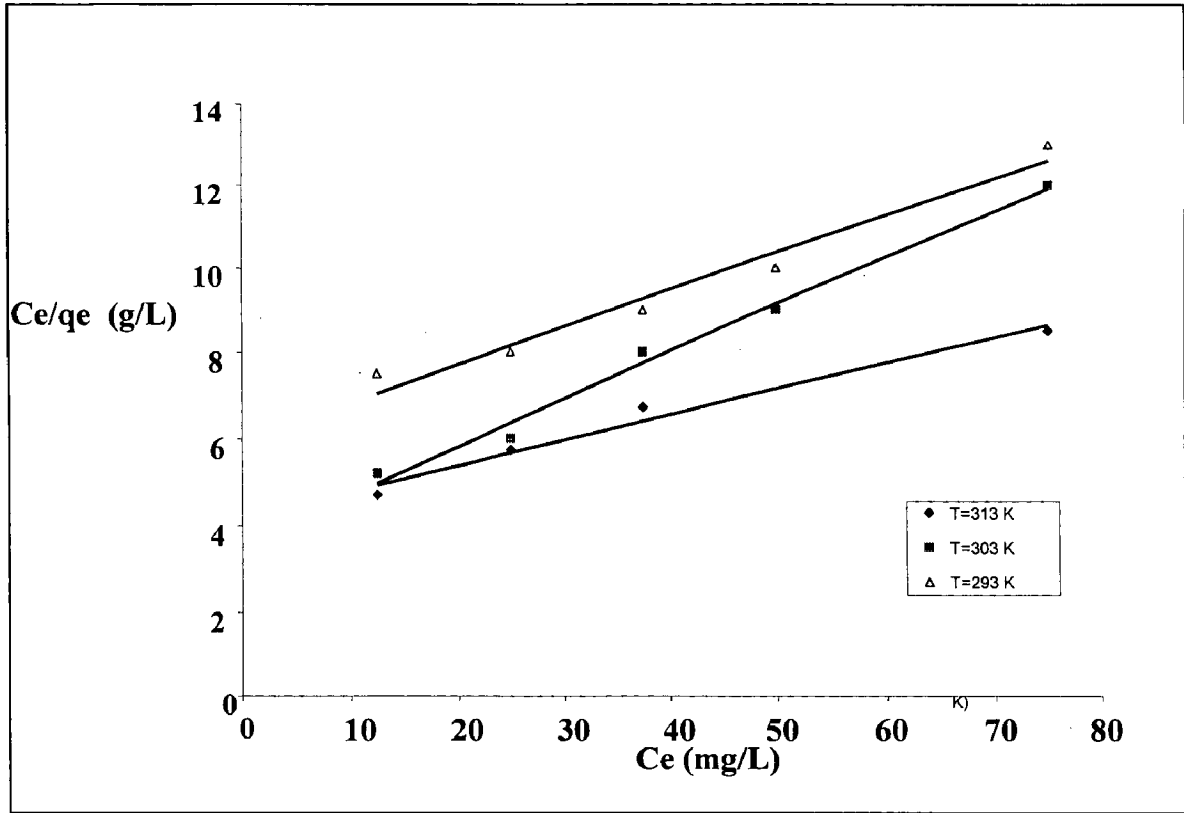


Fig. 6.13 Langmuir isotherm for removal of p-xylene by BFA

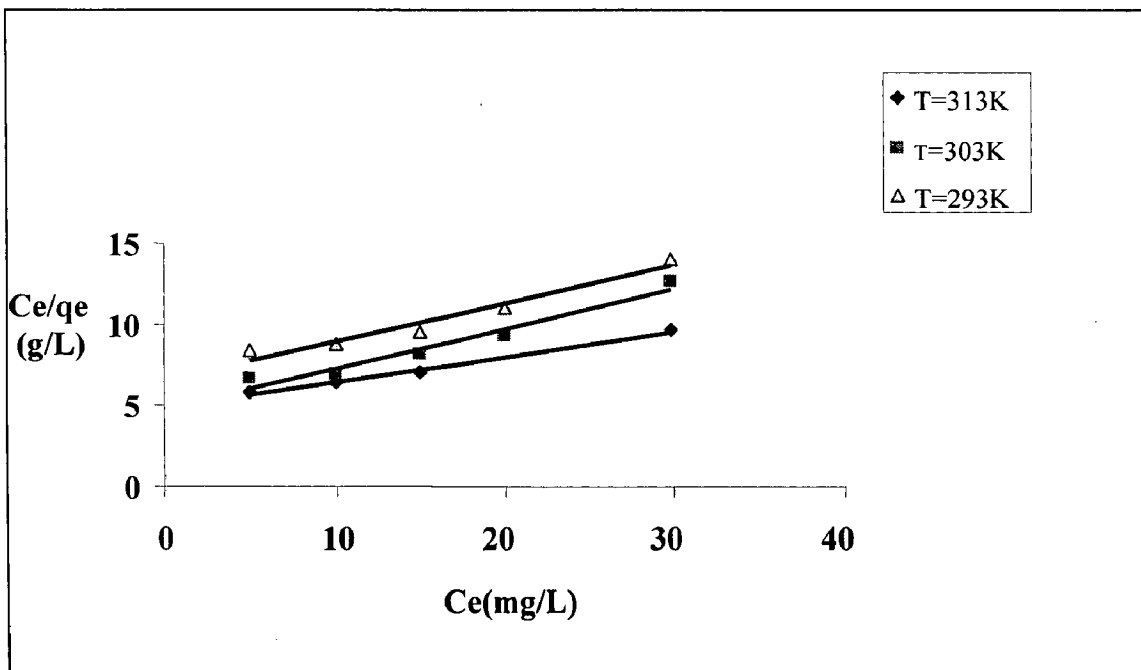


Fig. 6.14 Langmuir isotherm for removal of p-xylene by ACC

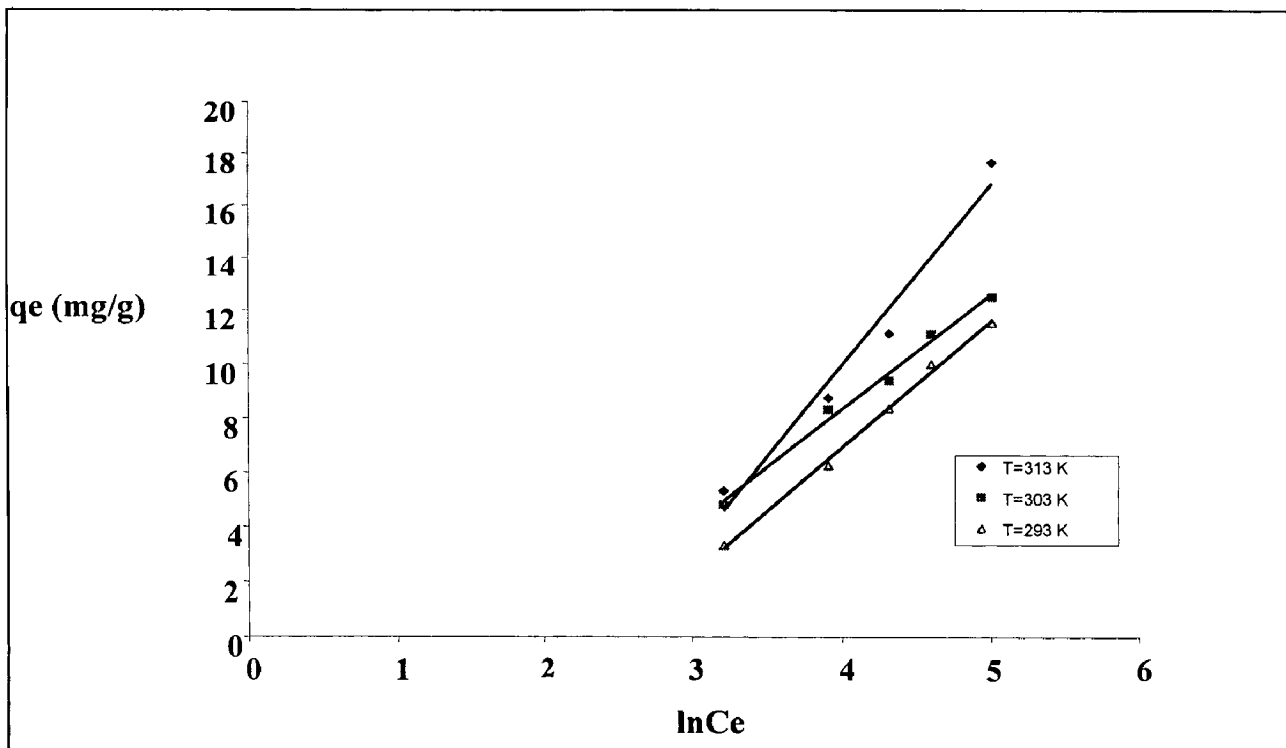


Fig. 6.15 Temkin isotherm for removal of p-xylene by BFA

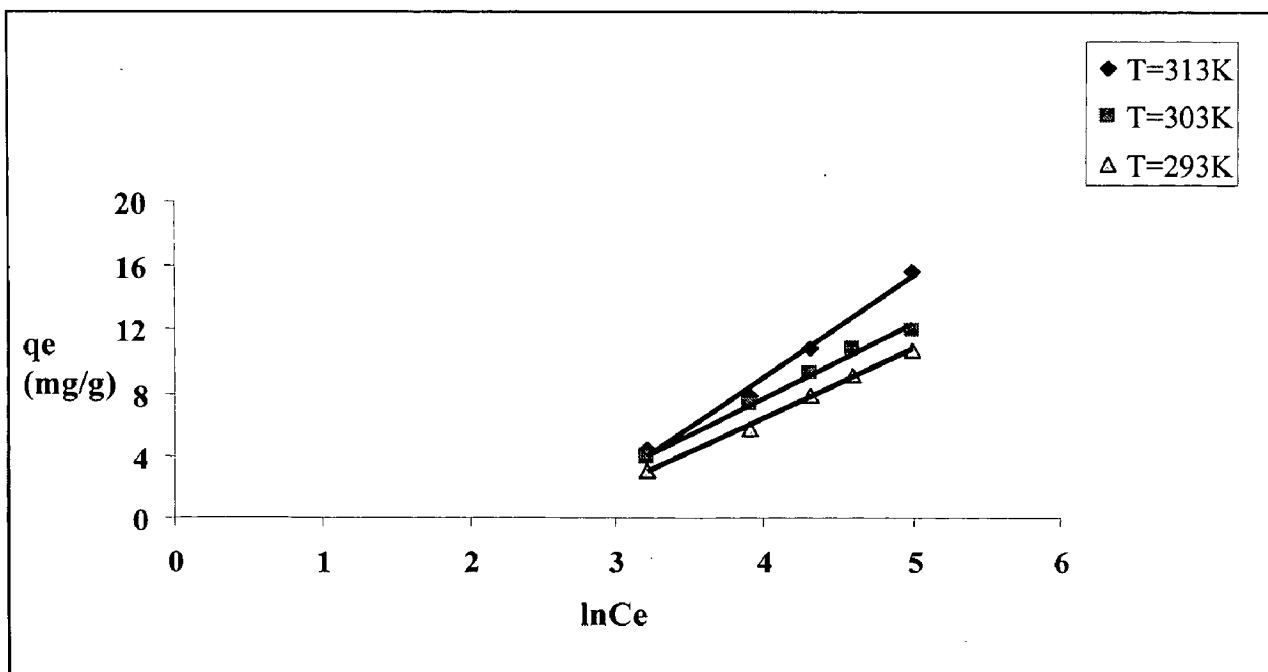


Fig. 6.16 Temkin isotherm for removal of p-xylene by ACC

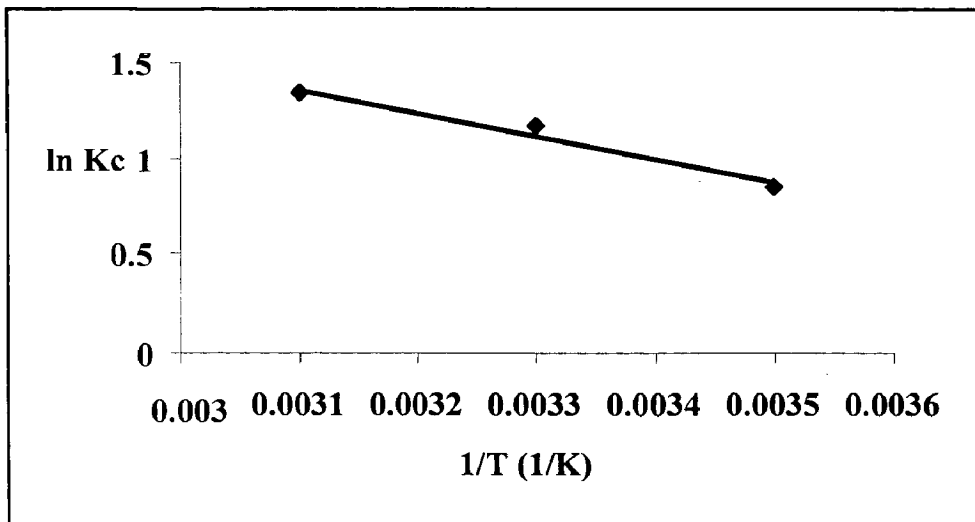


Fig. 6.17 Vanthoff's plot for adsorption of p-xylene onto BFA

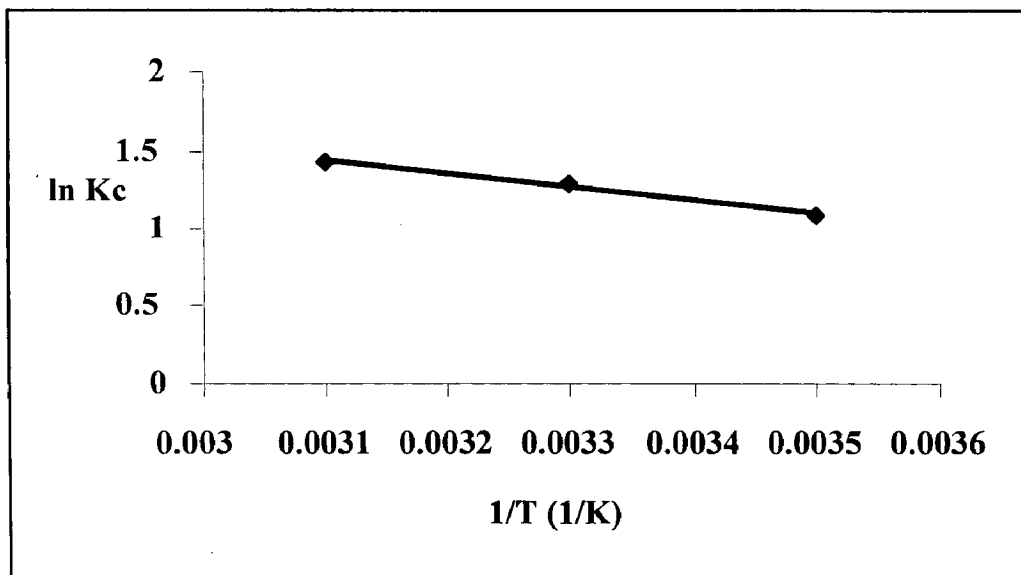


Fig. 6.18 Vanthoff's plot for adsorption of p-xylene onto ACC

CONCLUSIONS AND RECOMMENDATIONS

7.1. CONCLUSIONS

Based on the complete work the following major conclusions can be presented in a nutshell:

- BFA and activated carbon are viable alternatives for the removal of p-xylene from waste water through adsorption process as the removal efficiencies are around 80 % and 86 % for BFA and ACC respectively on single adsorption and 91% and 94% on double adsorption respectively for BFA and ACC.
- The time consumption for the process is approximately 70 min which suggests that the process is much faster than the conventional biodegradation process.
- As the difference between the removal efficiency of BFA compared to activated carbon is not so much significant, so the low cost BFA promises to have a very good potential to be used for the purpose.
- The various optimum condition for the process to be carried out are

pH=6; Time=70 min; adsorbent dose for BFA=8g/L and adsorbent dose for activated carbon=12g/L

- The adsorption process is found to be followed reversible first order kinetics
- Langmuir and Temkin models are best fitted for BFA and activated carbon respectively for the adsorptive removal.
- The high negative value of ΔG for both the adsorbents suggest that the process is quite feasible on thermodynamic point of view.
- From comparison study, it is cleared that BFA can be a substitutes to ACC for removal of p-xylene.

7.2. RECOMMENDATION

- Further pilot scale studies are required to evaluate the suitability of BFA and activated carbon for the adsorptive removal on plant scale.
- Column studies can be carried out to examine the effect of bed height, diameter, flow rate and concentration of adsorbate.
- Bagasse fly ash from different sugar mills can be characterized for physio-chemical parameters and surface characteristics, so the result can be correlated and may be utilized in effluent treatment.
- Many more combination of different adsorbents could be tried to get much better result.

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APPENDIX-A

Table A-1 Calibration curve for Para-xylene.

Sl. No.	Concentration (mg/l)	Absorbance
1.	1	0.136
2.	2	0.250
3.	4	0.512
4.	5	0.625
5.	10	1.256
6.	20	2.487

Table A-2 Effect of pH on the removal of Para-xylene with an initial concentration of 50 mg/l at 303 K using BFA.

Sl. No.	pH	% Removal of Para-xylene
1.	3	53.52
2.	4	61.54
3.	5	74.85
4.	6	84.07
5.	7	81.95
6.	9	74.32
7.	10	71.57
8.	11	70.00
9.	12	70.01

Table A-3 Effect of pH on the removal of Para-xylene with an initial concentration of 50 mg/l at 303 K using ACC.

Sl. No.	pH	% Removal of Para-xylene
1.	3	54.36
2.	4	62.01
3.	5	78.03
4.	6	86.72
5.	6.5	88.01
6.	7	83.12
7.	9	77.59
8.	10	73.48
9.	11	71.06
10.	12	71.06

Table A-4 Effect of Adsorbent dose on removal of Para-xylene using BFA.

Sl. No.	50 (mg/l)	
	Dose (g/l)	%Removal
1.	0.00	0.00
2.	0.01	41.03
3.	0.02	66.37
4.	0.10	73.12
5.	0.20	76.58
6.	0.30	81.01
7.	0.40	81.12
8.	0.50	81.12
9.	0.60	81.12
10.	0.70	81.12
11.	0.90	81.12

Table A-14 Effect of Contact time on removal of Para-xylene for different initial concentration at 303 K using ACC (12 g/l).

Sl. No.	Contact Time (min)	50 mg/l	100 mg/l	150 mg/l
		% Removal	% Removal	% Removal
1.	0	0.00	0.00	0.00
2.	10	47.30	39.56	35.53
3.	20	58.53	51.03	46.00
4.	25	66.18	55.43	53.28
5.	30	71.29	61.00	57.21
6.	40	74.79	66.07	63.70
7.	50	78.00	69.18	65.56
8.	60	84.12	77.00	73.00
9.	70	84.12	78.23	75.48
10.	80	84.12	78.23	75.48
11.	90	84.12	78.23	75.48