

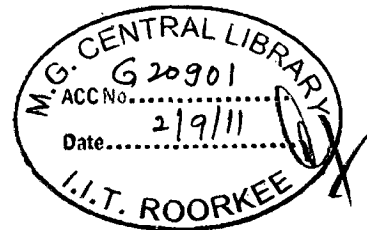
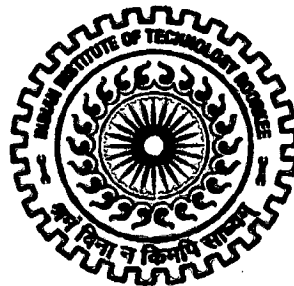
ADSORPTIVE REMOVAL OF PARA-XYLENE BY RICE HUSK ASH

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, 2011**



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CANDIDATE'S DECLARATION**

I hereby declare that the work, which is being presented in the dissertation entitled “**ADSORPTIVE REMOVAL OF PARA-XYLENE BY RICE HUSK ASH**” in the partial fulfilment of the requirements of the award of the Master of Technology in Chemical Engineering with specialization in “Industrial Pollution Abatement”, submitted in the Department of Chemical Engineering, Indian Institute of Technology, Roorkee, is an authentic record of my own work carried out during the period from July 2010 to May 2011 under 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, 2011

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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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Alok Kumar Gupta

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. It has also high acute toxicity to aquatic life 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 rice husk 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, adsorbent 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 RHA as an adsorbent has been determined.

Equilibrium contact was found to be 100 min for $C_0 \leq 150$ mg/l. Optimum removal of p-xylene onto RHA occurred at pH range 3.5 ± 0.2 . Optimum adsorbent dosage was found 9 g/l RHA. The para-xylene adsorption follows pseudo-second-order kinetics. The adsorption isotherm of para-xylene onto RHA was represented by various isotherm models in which the Freundlich isotherm fitting the experimental data. The negative values of (ΔS^0) , (ΔH^0) ; and (ΔG^0) indicated feasible, exothermic, spontaneous nature of para-xylene adsorption on RHA.

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NOMENCLATURE

C_0	Initial p-xylene concentration
C_e	Concentration of adsorbate at equilibrium (mg/l)
K	Adsorption rate constant (1/min)
K_L	Langmuir isotherm constant, (l/mg)
K_T	Temkin isotherm constant, (l/mg)
K_F	Freundlich isotherm constant, ((mg/g)/(mg/l)) ^{1/n}
$1/n$	Heterogeneity factor, dimensionless
Q_t	Amount of adsorbate adsorbed per unit amount of adsorbent at time t, (mg/g)
Q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg/g)
k_f	First order rate constant, (1/min)
k_s	Second order rate constant, (g/mg min)
h	Initial sorption rate, mg/g min
ΔG°	Gibbs free energy, (KJ/mol)
ΔH°	Enthalpy, (KJ/mol)
ΔS°	Entropy, (J/mol K)
R	Universal gas constant, 8.314 J/K mol
α	Bangham constant (<1)

INTRODUCTION

1.1 General

Para-xylene is one of the most key pollutants as far as water pollution is concerned according to EPA sources (Calley and Stafford., 1994). 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.

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 (Agarwal et al., 2006). 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. (Acharya et al., 2006). 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. Till date the implementation of this method for the removal of p-xylene has not revealed to its full potential except very few (Cheng et al., 2005).

Among the various adsorbents, activated carbon has been commercially used for the removal of the toxic effluents (Srivastava et al., 2006). However, high cost activated carbon and significant amount of loss during regeneration make the utilization of the activated carbon prohibitive in developing countries. 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.

Rice husks are agricultural waste, accounting for about one-fifth of the annual gross rice production (545 million metric tons) of the world (Feng et al., 2004). Rice husk is burned in the boiler of various industries to produce steam, thus, conserving both energy and resources. During the burning of rice husk, a waste called rice husk ash (RHA) is collected from the particulate collection equipment attached upstream to the stacks of rice husk-fired boilers. It has been previously used as an adsorbent to remove metal ions from aqueous solution (Srivastava et al., 2008), absorb oil on hard surfaces and potentially to filter arsenic from water.

1.2 Para-xylene

Xylene is a clear, colourless liquid. It is volatile, readily producing flammable and toxic concentrations at room temperature. Its vapour is heavier than air and may accumulate in low-lying areas. Xylene's odour generally provides adequate warning of hazardous concentrations (<http://en.wikipedia.org/wiki/Xylene>).

There are three possible xylene isomers: 1,2-, 1,3- and 1,4-dimethylbenzene; these will be referred to as the o- (ortho), m- (meta) and p- (para) xylene isomers, respectively. The molecular formula of the three xylene isomers is C_8H_{10} , and all are colourless liquids at room temperature. Pure p-xylene forms colourless plates or prisms at $13^\circ C$, whereas the other two isomers are liquids. The boiling points for the xylenes range from 137 to $144^\circ C$, and Kow's are 2.77, 3.20 and 3.15 for the o-, m- and p-isomers, respectively.

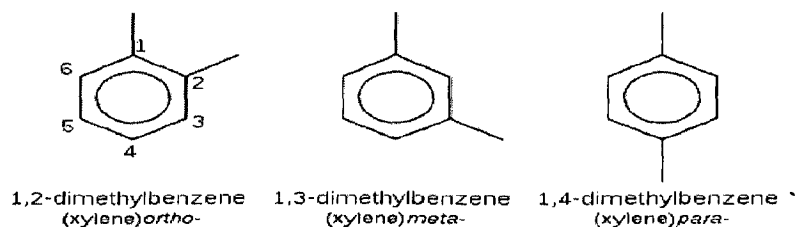


Figure 1.1-Isomers of xylene

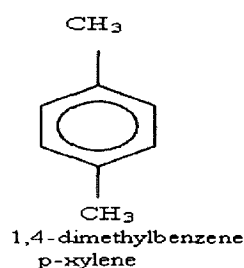


Figure 1.2- Structure of p-xylene

1.3 Properties of xylene

1.3.1 Chemical and Physical properties of xylene

Table 1.1 Chemical and Physical property

Parameter	Value	Reference
Synonyms	dimethylbenzene (1,2-; 1,3-; or 1,4-); xylol (mixture), m-, o-, or p-xylene (isomers); methyltoluene	Budavari et al. (1996)
CAS registry no.	1330-20-7 mixture 108-38-3 m-isomer 95-47-6 o-isomer 106-42-3 p-isomer	
Chemical formula	C_8H_{10}	Budavari et al. (1996)
Physical state	liquid	Budavari et al. (1996)
Molecular weight	106.17	Budavari et al. (1996)
Color	colorless	
Odor	sweet	
Vapor pressure at 20°C	6–16 mmHg mixture 5–6.5 mmHg individual isomers	ATSDR (1995)
Density	0.8642 g/cm ³ m-isomer 0.8801 g/cm ³ o-isomer 0.8611 g/cm ³ p-isomer	ATSDR (1995)
Melting point	-47.4°C m-isomer -25°C o-isomer 13–14°C p-isomer	Budavari et al. (1996)
Boiling point	139°C m-isomer 144.4°C o-isomer 138.37°C p-isomer	Budavari et al. (1996); ATSDR (1995)
Solubility in water	134–146 mg/L m-isomer	ATSDR (1995)

	178–213 mg/L o-isomer 185–198 mg/L p-isomer	
Odor threshold in air (absolute)	3.7 ppm m-isomer 0.08–0.17 ppm o-isomer 0.47 ppm p-isomer	ATSDR (1995)
TWA(8 h)	80 ppm	
STEL	150 ppm	

1.3.2 Reactivity

- Conditions contributing to instability: Heat, sparks, or open flame.
- Incompatibilities: Contact of xylene with strong oxidizers may cause fires and explosions.
- Hazardous decomposition products: Toxic gases (such as carbon monoxide) may be released in a fire involving xylene.
- Special precautions: Xylene attacks some coatings and some forms of plastic and rubber.

1.3.3 Flammability

The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to xylene.

- Flash point: 27 to 32°C (81 to 90 ° F).
- Autoignition temperature: 464 ° C (867 ° F).
- Flammable limits in air(% by volume) :lower=1,upper=7
- Extinguishant: Use foam, dry chemical, or carbon dioxide to fight fires involving xylene.

1.3.4 Warning properties

The odour threshold for xylene is 1 part per million (ppm) of air. Because this value is below the Occupational Safety and Health Administration (OSHA) current permissible exposure limit (PEL) of 100 ppm, xylene is considered to have adequate warning properties.

1.3.5 Eye irritation properties

The eye irritation threshold for xylene is 200 ppm (870 mg/m³)

(<http://www.osha.gov/SLTC/healthguidelines/xylene/recognition.html>)

1.3.6 Exposure Limits

The current OSHA PEL for xylene is 100 ppm (435 mg/m³ of air) as an 8-hour time-weighted average (TWA) concentration. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limits (RELs) for xylene are 100 ppm (435 mg/m³) as a TWA for up to a 10-hour workshift and a 40-hour workweek and 200 ppm (868 mg/m³)

for 10 minutes as a short-term limit . The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned xylene a threshold limit value (TLV) of 100 ppm (435 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek and a short-term exposure limit (STEL) of 150 ppm (655 mg/m³) for periods not to exceed 15 minutes . The OSHA and ACGIH limits are based on the risk of irritant, narcotic, and chronic effects associated with exposure to xylene, and the NIOSH limit is based on xylene's potential to cause central nervous system depression and respiratory irritation (<http://www.osha.gov/SLTC/healthguidelines/xylene/recognition.html>).

1.4 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.
- Xylene is often used as a solvent in the printing, rubber, and leather industries.
- It is used as a cleaning agent for steel and for silicon wafers and chips.
- 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 (ATSDR 2007).

1.5 Xylenes in 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. 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.

1.6 HEALTH HAZARD INFORMATION

1.6.1 Routes of exposure

Exposure to xylene can occur via inhalation, ingestion, eye or skin contact, and, to a small extent, by absorption through the skin. P-xylene vapor is heavier than air and may cause asphyxiation in enclosed, poorly ventilated, or low-lying areas.

1.6.2 Toxicology

1.6.2.1 Effects on Animals:

Xylene exposure produces central nervous system depression and irritation of the eyes and skin in animals. The meta isomer may be more acutely toxic than the o- or p-isomer: mice exposed for 24 hours to 2010 ppm of the m-isomer or to 3062 ppm of the o-isomer died, while exposure for the same period to 4912 ppm of the p-isomer did not cause death (Proctor et al., 1988). Rats exposed to a 1600-ppm concentration of xylene (isomer unspecified) for 2 or 4 days showed signs of irritation, became uncoordinated, lost weight, had an increased red blood cell count, exhibited signs of narcosis, and died (Proctor et al., 1988). In contact with the eye, xylene causes irritation of the conjunctiva, turbidity of the cornea, swelling, and tearing in rabbits (Clayton and Clayton., 1981).

1.6.2.2 Effects on Humans:

Xylene is an irritant of the eyes and mucous membranes at concentrations below 200 ppm, and it is narcotic at high concentrations (AIHA 1978; Proctor et al., 1988). The estimated oral LD(50) for humans is 50 mg/kg (EPA Health Advisory, 1987). Of three workers exposed to xylene concentrations of approximately 10,000 ppm for 18.5 hours, one died and two recovered slowly after a period of unconsciousness and retrograde amnesia; disturbances of liver and kidney function were noted in these workers (ACGIH 1986 ; Baselt 1980; Clayton and Clayton ., 1981). Ingestion of xylene causes gastrointestinal distress and may cause toxic hepatitis. Aspiration of xylene or acute exposure to high vapor concentrations of this substance may cause chemical pneumonitis, hemorrhage into the air spaces, and pulmonary edema (Clayton and Clayton 1981; Klaassen, Amdur, and Doull 1986). A worker exposed to the vapors of a solvent containing 75 percent xylene (approximate airborne xylene concentration of 60 to 350 ppm) developed giddiness, anorexia, and vomiting (Proctor et al., 1988). Chronic exposure to xylene may cause central nervous system depression, anemia, mucosal hemorrhage, bone marrow hyperplasia, liver enlargement, liver necrosis, and

nephrosis. Repeated contact of the skin with xylene causes drying and dermatitis (Clayton and Clayton 1981).

1.6.2.3 Signs and symptoms of exposure

- **Acute exposure:** The signs and symptoms of acute exposure to xylene include headache, fatigue, irritability, lassitude, nausea, anorexia, flatulence, irritation of the eyes, nose, and throat, and motor incoordination and impairment of equilibrium. Flushing, redness of the face, a sensation of increased body heat, increased salivation, tremors, dizziness, confusion, and cardiac irritability have also been reported.
- **Chronic exposure:** The signs and symptoms of chronic exposure to xylene may include conjunctivitis; dryness of the nose, throat, and skin; dermatitis; and kidney and liver damage.

1.7 EMERGENCY PROCEDURES:

In the event of an emergency, remove the victim from further exposure, send for medical assistance, and initiate the following emergency procedures:

- ❖ **Eye exposure:** If xylene or a solution containing xylene gets into the eyes, immediately flush the eyes with large amounts of water for a minimum of 15 minutes, lifting the lower and upper lids occasionally. Get medical attention as soon as possible.
- ❖ **Skin exposure:** If xylene or a solution containing xylene contacts the skin, the contaminated skin should be washed with soap and water. If irritation persists, get medical attention.
- ❖ **Inhalation:** If xylene vapors are inhaled, move the victim at once to fresh air and get medical care as soon as possible. If the victim is not breathing, perform cardiopulmonary resuscitation; if breathing is difficult, give oxygen. Keep the victim warm and quiet until medical help arrives.
- ❖ **Ingestion:** Do not induce vomiting. If xylene or a solution containing xylene is ingested, give the victim several glasses of water to drink. Get medical help immediately. Keep the victim warm and quiet until medical help arrives.
- ❖ **Rescue:** Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the

Material Safety Data Sheet required by OSHA's Hazard Communication Standard, 29 CFR 1910.1200). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment (<http://www.osha.gov/SLTC/healthguidelines/xylene/recognition.html>).

1.8 Objective

The objective of present study is to investigate the feasibility of readily and cheaply available RHA as an adsorbent for the removal of Para-xylene from aqueous solution. The experimental work has been carried out to achieve the objective through the following studies:

1. Characterization of RHA
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 RHA
4. Study of equilibrium data for removal efficiency of the adsorbent using Freundlich, Langmuir, Dublin-Rédushkevich, Temkin isotherms.
5. Study the various thermodynamic properties such as: enthalpy, entropy and free energy for the adsorption process

LITERATURE REVIEW

2.1 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 review also have been presented in tabular form in Table 2.1.

Banerjee et al. (1997) studied the kinetics of sorption of o-xylene on fly ash conducted in a controlled batch system. The effects of solute concentration, particle size of the adsorbent, and temperature on the adsorption rate were investigated. The results of this research demonstrate that the adsorption reaction can be approximated to first-order reversible kinetics. A significant correlation was observed between the rate of adsorption and the inverse of the square of the particle diameter. An examination of thermodynamic parameters shows that the adsorption of o-xylene by fly ash is an exothermic process and is spontaneous at the temperature investigated. Activation energies for the sorption process ranged between 3.1 and 4.3 kcal/mol. The rate at which o-xylene is adsorbed onto fly ash was found to be controlled by the diffusion process.

Daifullah and Mohamed (2004) studied the homogeneous degradation of benzene (B), toluene (T), ethylbenzene (E) and p-xylene (X) (BTEX) in aqueous solutions, at pH 3.0, of hydrogen peroxide (5.8mM) under UV irradiation in a photoreactor equipped with a 300 nm lamp of light intensity 3.5×10^{-5} E in $L^{-1} min^{-1}$. BTEX was substantially degraded by the H_2O_2/UV system, with >90% disappearing in 10min of irradiation. The decomposition of BTEX was studied either as single or as multi-component systems. The effects of irradiation time, amounts of H_2O_2 in molar ratios, rate of degradation and competition between components were thoroughly examined. It can be stated that the rate of BTEX degradation in mixture was higher than those for the individual components due to external effects of the absorption of UV light by the mixture, and their effects on enhancing the formation of $OH\cdot$ radicals. A theoretical model for the degradation pathway was proposed. The UV/H_2O_2 oxidation of BTEX contaminants has advantages in that fast kinetics, no sludge production, and a high degree of mineralization can be achieved. Besides, H_2O_2 is easy to handle and environmentally benign.

Morasch and Meckenstock (2005) suggested anaerobic degradation of p-Xylene by a sulfate-reducing enrichment culture. A strictly anaerobic enrichment culture was obtained with p-xylene as organic substrate and sulfate as electron acceptor from an aquifer at a former gasworks plant contaminated with aromatic hydrocarbons. P-xylene was completely oxidized to CO₂. The enrichment culture depended on Fe(II) in the medium as a scavenger of the produced sulfide. 4-Methylbenzylsuccinic acid and 4-methylphenylitaconic acid were identified in supernatants of cultures indicating that degradation of p-xylene was initiated by fumarate addition to one of the methyl groups.

Farhadian et al. (2008) studied benzene, toluene, and xylenes (BTX) removal from contaminated water by physical, chemical, and biological processes. Results showed that air sparging in polluted water can reduce mono aromatic compounds from 140,000 to about 5 µg/l in only 1 h process with a gassing rate of 0.33 VVM. This method cannot be considered as a green technology as pollutants are only transferred from the liquid phase to the gas phase. Current investigation showed that BTX are readily trapped by GAC particles with low further release in the liquid medium whereas they remain at least partially available for in situ biodegradation. BTX adsorption onto the GAC was shown to reach maximum solute retention close to 350, 250, and 150 (as mg/g GAC) for xylenes, toluene, and benzene, respectively. This approach, which could afford efficient biological active carbon regeneration, is very promising for the removal of BTX compounds from water without any further environment damage. Treatment efficiencies of 99% and above in terms of BTX disappearance from polluted water could be achieved by aeration and adsorption processes.

Jo et al. (2008) studied the removal of BTEX by microbes using response surface methodology. The removal of benzene, toluene, ethylbenzene and xylene (BTEX) as quaternary mixtures were studied in batch systems using a well-defined mixed microbial culture. The synergistic and antagonistic effects of total BTEX removal (BTEX_{T-RE}) due to the presence of mixed substrate was evaluated through experiments designed by response surface methodology (RSM). The low and high concentrations of individual BTEX were 15 and 75 mg l⁻¹, respectively. The results showed that, increasing the concentration of xylene increased the cumulative BTEX removal (BTEX_{T-RE}), however the reverse occurred when benzene concentrations were increased from low to high levels. A mixed response of increasing and decreasing trend in the BTEX_{T-RE} value was observed when either of toluene or ethylbenzene concentration was increased. When the concentrations of individual BTEX compounds were 30 mg l⁻¹, the BTEX_{T-RE} was about 58%. Complete BTEX_{T-RE} was achieved at optimal BTEX concentrations of 48.1, 45.6, 49.3 and 56.6 mg l⁻¹. The RSM approach was

found efficient in explaining the main, squared and interaction effects among individual BTEX concentrations on the BTEX_{T-RE} in a more statistically meaningful way.

Ke Gai (2009) used contact glow discharge for removal of p-xylene in aqueous solution with plasma. Anodic contact glow discharge plasma is promising, because doesn't need any evacuating system. Results indicate that the degradation rate can be effectively raised by decreasing the diameter of discharge electrode and electric conductivity of the aqueous solution, or by increasing the pH of the solution. The addition of H₂O₂, and especially FeSO₄ is found to significantly enhance p-xylene degradation, but the presence of Na₂CO₃, Ce(SO₄)₂ and n-butanol inhibited the degradation of p-xylene. Some major intermediate products were detected by HPLC.

Aivalioti et al. (2010) proposed the use of diatomite for removal of BTEX. The removal of BTEX (benzene, toluene, ethyl-benzene and xylenes) and MTBE (methyl tertiary butyl ether) from aqueous solution by raw (D_R) and thermally modified diatomite at 550, 750 and 950⁰ C (D₅₅₀, D₇₅₀ and D₉₅₀ respectively) was studied. Physical characteristics of both raw and modified diatomite such as specific surface, pore volume distribution, porosity and pH solution were determined, indicating important structural changes in the modified diatomite, due to exposure to high temperatures. The kinetics data proved a closer fit to the pseudo-second order model. Maximum values for the rate constant, k₂, were obtained for MTBE and benzene (48.9326 and 18.0996 gm⁻¹ h⁻¹, respectively) in sample D₅₅₀. The isotherm data proved to fit the Freundlich model more closely, which produced values of the isotherm constant 1/n higher than one, indicating unfavourable adsorption. The highest adsorption capacity, calculated through the values of the isotherm constant k_F, was obtained for MTBE (48.42mg kg⁻¹ (mg/L)ⁿ) in sample D₉₅₀. The highest adsorption percentages were achieved for p-xylene and ethyl-benzene and the lowest for MTBE and benzene. The adsorption kinetics of the examined contaminants onto the diatomite samples can be well described by the pseudo-second order reaction model.

Chen et al. (2010) studied the effectiveness of intrinsic bioremediation on the containment of petroleum hydrocarbons. In the first phase of their study at a gasoline spill site, evidences of the occurrence of intrinsic bioremediation within the BTEX (benzene, toluene, ethylbenzene, and xylenes) plume included (1) decreased BTEX concentrations; (2) depletion of dissolved oxygen (DO), nitrate, and sulfate; (3) production of dissolved ferrous iron, methane, and CO₂; (4) decreased pH and redox potential; and (5) increased methanogens, total heterotrophs, and total anaerobes, especially within the highly contaminated areas. In the second phase of this study, enhanced aerobic bioremediation process was applied at site to

enhance the BTEX decay rates. Air was injected into the subsurface near the mid-plume area to bio stimulate the naturally occurring microorganisms for BTEX biodegradation. Field results showed that enhanced bioremediation process caused the change of BTEX removal mechanisms from anaerobic biodegradation inside the plume to aerobic biodegradation. After this variation, field results showed that the percentage of total BTEX removal increased from 92% to 99%, and the calculated total BTEX first-order natural attenuation rates increased from 0.0092% to 0.0188% per day, respectively, after the application of enhanced bioremediation system from the spill area to the down gradient area (located approximately 300 m from the source area). Results also showed that the aerobic biodegradation was the dominant degradation processes of BTEX after the operation of enhanced aerobic bioremediation.

Jeong et al. (2008) used o-xylene-degrading microorganism *Rhodococcus* sp. BTO62 obtained from activated sludge from a wastewater treatment plant . A laboratory scale biofilter packed with biosol as packing material, which is made from foamed waste glass mixed with corrugated cardboard, was inoculated with strain BTO62 and operated to remove relatively high loading of o-xylene at different space velocities under non-sterile and sterile conditions. The o-xylene elimination capacity to maintain more than 90% removal efficiency was 41 g/m³/h under sterile condition, but it enhanced to 160 g/m³/h under non-sterile condition. This indicates possibilities of the role of other contaminants for degradation of o-xylene and the degradation of intermediate products of o-xylene by contaminants.

Gusmao et al. (2006) studied the BTEX and ethanol removal in horizontal-flow anaerobic immobilized biomass reactor, under denitrifying condition. The reactor was fed with hydrocarbons, separately (benzene at 13.8, 15.4 and 26.5 mg/L; toluene 30.8 mg/L; ethylbenzene 33.3 mg/L; xylene 32.1 mg/L), and also with a benzene, toluene, ethylbenzene and xylene (BTEX) mix solution of approximately 5.0 mg/L of each hydrocarbon. The hydrocarbons were dissolved in a solution containing ethanol. Organic matter removal efficiencies were of 95% with benzene and toluene amendments and about 76% with ethylbenzene, m-xylene and the BTEX-mix amendments. Hydrocarbons removal efficiencies were of 99% at an initial concentration of benzene 26.5 mg/L, toluene 30.8 mg/L, m-xylene 32.1 mg/L, ethylbenzene 33.3 mg/L and BTEX 26.5 mg/L.

Suzuki and Yamaya (2005) suggested the use of rotating biological contactor (RBC) with biodrum to remove hydrocarbons in wastewater from industrial discharges, and investigated its performance. The biodrum, a cylindrical mesh drum, filled with random packing of polyurethane foam cubes retaining petroleum-degrading achlorophyllous micro-alga *Prototheca zopfii* cells, was approximately 40% submergence in the culture. The amount of algal cells, immobilized in the 10-mm-cube pieces, was greater than in pieces of smaller pore size under the experimental conditions studied. A mixture of n-alkanes (C_{14} , C_{15} and C_{16}) was used as a model oil, and the influent hydrocarbons were removed by immobilized cells in the biodrum. The single-stage RBC system was operated at 25.8°C and at pH 7.0 in a batch mode. About 95% of hydrocarbons were removed during just 2 days of operation in the RBC with biodrum. The removal rate of a mixture of n-alkanes (C_{14} , C_{15} and C_{16}) observed in this system was 8.0 (kg-hydrocarbons/d per m^3). The removal rate for n-alkanes in the RBC with biodrum system was significantly increased as compared to those in the RBC system with polycarbonate biodisk.

Jeong et al.(2006) used bio-filter to remove p-xylene. *Pseudomonas* sp. NBM21 was isolated from an activated sludge of a wastewater treatment plant. NBM21 degraded p-Xyl, m-xylene, benzene and toluene, but not o-xylene, ethylbenzene (Eb) and styrene. NBM21 was inoculated to a biofilter with Biosol as a packing material and p-Xyl removal was operated for 105 d under sterile and nonsterile conditions. The maximum elimination capacities for p-Xyl at higher than 90% removal efficiency were 160 $g/m^3/h$ and 150 $g/m^3/h$ under nonsterile and sterile conditions, respectively. A high load of Eb adversely affected to the removal of xylene.

Shaoyong et al. (2009) used activated carbon (AC) supported Pd catalyst to develop a highly efficient in situ adsorption-catalysis system for the removal of low concentrations of o-xylene. The Pd/AC catalyst was first used as an adsorbent to concentrate dilute o-xylene at low temperature. After saturated adsorption, the adsorbed o-xylene was oxidized to CO_2 and H_2O by raising the temperature of the catalyst bed. The results showed that more than 99% of the adsorbed o-xylene was completely oxidized to CO_2 over a 5%Pd/AC catalyst at 140°C.

Wu et al. (2006) investigated the biofiltration technique for treatment of air stream containing p-xylene in a laboratory hybrid biofilter packed with a mixture of mature pig compost, forest soil and the packing material which was made of polyethylene (PE) and used in the moving bed biological reactor (MBBR) in wastewater treatment. Three flow rates, 9.17, 19.87 and 40.66 $m^3 m^{-2} h^{-1}$, were investigated for p-xylene inlet concentration ranging from 0.1 to 3.3 gm^{-3} . A high elimination capacity of 80 $gm^{-3} h^{-1}$ corresponding to removal

efficiency of 96% was obtained at a flow rate of $9.17 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ (empty bed residence time of 132 s). At a flow rate of $40.66 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ (empty bed residence time of 30 s), the maximum elimination capacity for p-xylene was $40 \text{ gm}^{-3} \text{ h}^{-1}$ and removal efficiencies were in the range of 47–100%.

Dwivedi et al. (2004) studied the removal of VOCs by cryogenic condensation and adsorption experimentally and theoretically. The condensation rate of VOC was shown to decrease with decrease in the effluent concentration suggesting difficulty in the separation at low concentration levels (<1%). The commercially obtained activated carbon fiber was shown to exhibit larger adsorption for VOC than granular activated carbon under identical operating conditions. The breakthrough time during adsorption was observed to considerably decrease with increase in the VOC concentration from 5000 to 50,000 ppm suggesting the utility of the adsorption method for controlling VOC from gaseous effluents at ppm and sub-ppm levels. The removal by cryogenic condensation was found to be effective at the relatively higher VOCs concentrations levels (>1%). The regeneration of ACF equilibrated with VOC was carried out by dc electrical heating. The regeneration time of 60min and temperature of 150 °C were determined to be effective in completely removing the adsorbate.

Table.2.1: Summary of various experimental works on removal of Hydrocarbons and related compounds from waste effluents

Reference	Operation	Results and conclusion
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.
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%.
Bernal et al. [2005]	Combining anaerobic digestion & 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.
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 prototheca zopfii. Removal efficiency is 65%, but time taken was 30 days.
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.
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
Dwivedi 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.
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.
Tseng et al. [2002]	The adsorption of PAH, BTEX and heavy metals on surfactants-modified desulphurization sorbents in a dry scrubber.	The adsorbent used in this process was Ca(OH) ₂ modified with calcium lignosulfonate and sodium lignosulfonate. The process was followed by filtration in a dry scrubber fabric filter.
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.

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ADSORPTION FUNDAMENTALS

3.1 General

Adsorption is a surface phenomenon. Adsorption is the process of attraction of atoms or molecules from an adjacent gas or liquid to an exposed solid surface. Such attraction forces (adhesion or cohesion) align the molecules into layers (films) onto the existent surface. The solute accumulated is called the adsorbate or solute and the adsorbing substance is the adsorbent (<http://en.wikipedia.org/wiki/Adsorption>). 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.

When adsorption occurs in aqueous solution, the adsorbate molecule is drawn from the bulk solution to the adsorbent phase. The net attractive forces involving the solute, solvent and adsorbent are assumed responsible for adsorption. In general, adsorption involves the accumulation of molecules from a solvent onto the exterior and interior surfaces of an adsorbent. This surface phenomenon is a manifestation of complicated interactions among the three components involved, i.e. the adsorbent, the adsorbate and the solvent.

3.2 PHYSICAL ADSORPTION v/s CHEMICAL ADSORPTION

Adsorption processes can be classified as either physical adsorption (van der Waals adsorption) or chemical adsorption (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 chemical adsorption, there is a transfer or sharing of electron, or breakage of the adsorbate into atoms or radicals, which are bound separately.

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

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

In contrast, chemisorption is monolayer, involves the formation of chemical bonds between the adsorbate and adsorbent, often with a release of heat much larger than the heat of condensation. Chemisorption from a gas generally takes place only at temperatures greater than 200 °C, and may be slow and irreversible.

3.3 INTRAPARTICLE DIFFUSION PROCESS

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

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

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

3.4 STAGES IN ADSORPTION PROCESS

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

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

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

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

3.5 ADSORPTION ISOTHERMS

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

Many theoretical and empirical models have been developed to represent the various types of adsorption isotherms. Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin etc. are most commonly used adsorption isotherm models for describing the dynamic equilibrium. The isotherm equations used for the study are described follows:

3.5.1 Langmuir Isotherm

This equation based on the assumptions that:

1. Only monolayer adsorption is possible.
2. Adsorbent surface is uniform in terms of energy of adsorption.
3. All the vacant sites are of equal size and shape on the surface of adsorbent.
4. Adsorbed molecules do not interact with each other.
5. 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: (<http://en.wikipedia.org/wiki/Adsorption>).

$$Q_e = \frac{Q_m K_A C_e}{1 + K_A C_e} \quad (3.1)$$

where,

Q_e is amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium.

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

K_A is the constant related to enthalpy of adsorption

C_e is the concentration of adsorbate solution at equilibrium.

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

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \quad (3.2)$$

or

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

3.5.2 Freundlich Isotherm

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

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (3.4)$$

where ,

K_F and n are the constants

C_e is the concentration of adsorbate solution at equilibrium

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

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3.5)$$

Thus a plot between $\ln Q_e$ and $\ln C_e$ is a straight line. The Freundlich equation is most useful for dilute solutions over small concentration ranges (<http://www.rpi.edu/dept/chem-eng/Biotech-Environ/Adsorb/equation.htm>). 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 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 at strong solute concentration.

3.5.3 Temkin isotherm

It is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (3.6)$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (3.7)$$

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

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. 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.

3.5.4 Dubinin-Radushkevich (D-R) isotherm

It is given as:

$$q_e = q_s \exp(-B\varepsilon^2) \quad (3.8)$$

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

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (3.9)$$

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)

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

3.6 Adsorption practices

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

3.6.1 Batch Adsorption Systems

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

3.6.2 Continuous Adsorption Systems

The continuous flow processes are usually operated in fixed bed adsorption columns. These systems are capable of treating large volumes of waste 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.

3.7 Factors controlling adsorption

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

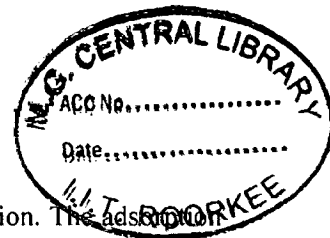
1. Initial concentration
2. Temperature
3. pH
4. Contact time
5. Degree of agitation
6. Nature of adsorbent
7. Solubility of solute in liquid

3.7.1 Initial Concentration

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

3.7.2 Temperature

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



3.7.3 pH

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

3.7.4 Contact time

The studies on the effect of contact time between adsorbent and adsorbate have significant importance. In physical adsorption, most of the adsorbate species are adsorbed on the adsorbent surface with in short contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium. Strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Contact time required to reach equilibrium may be depend upon concentration, temperature and pH of the solution; particle size and dose of adsorbent and agitation speed.

3.7.5 Degree of agitation

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

3.7.6 Nature of adsorbent

Many solids are used as adsorbents to remove the impurities from fluids. Commercial adsorbents generally have large surface area per unit mass. Most of the surface area is provided by a network of small pores inside the particles. Common industrial adsorbents for fluids include activated carbon (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.

3.7.7 Solubility of solute (adsorbate) in liquid

Substances slightly soluble in water will be more easily removed from water (i.e. adsorbed) than substances with high solubility. Also, non-polar substances will be more easily removed than polar substances since the later have a greater affinity for water.

Table.3.1: Comparison of Physical and Chemical Adsorption

S.No.	Physical Adsorption	Chemical Adsorption
1.	Van der Wall's adsorption	Activated Adsorption
2.	Heat of adsorption = 5kcal/mol	Heat of adsorption =20-100 kcal/mol
3.	Adsorption occurs only at temperature less than the boiling point of adsorbate	Adsorption occur even at higher temperature
4.	No activation energy is involved in adsorption process	Activation energy may be involved
5.	Adsorption occur in mono and multilayer	Adsorption occur almost in monolayer
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.	Rate of adsorption controlled by mass transfer resistance	Rate of adsorption is controlled by resistance reaction

EXPERIMENTAL PROGRAMME

4.1 GENERAL

In the present study, RHA has 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.

4.2 CHARACTERIZATION OF ADSORBENT

The physico-chemical characteristic of the RHA was determined using standard procedures as discussed below:

4.2.1 Proximate Analysis

Proximate analysis of the RHA was carried out using the procedure as per IS 1350:1984.

4.2.2 Density

The Bulk density of the RHA was determined using MAC bulk density meter.

4.2.3 Particle size analysis

Particle size analysis was made using standard sieve as per IS 2720 (Pt 4):1985.

4.2.4 Surface area measurement

The specific surface area of the RHA was measured by N₂ adsorption isotherm using an ASAP 2010 micrometric instrument and by Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938) using the software of micrometric, using nitrogen as cold bath.

4.2.5 Scanning Electron Microscope (SEM)

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

4.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectrometer (Thermo Nicolet, 6700, Australia) was used to determine the presence of functional groups in RHA at room temperature. Specimens of samples were first mixed with KBr and then ground in an agate mortar at an appropriate ratio 1/100 for the preparation of the pellets. Pellet (pressed-disk) technique was used for this purpose. The spectral range chosen was from 4000 to 400 cm^{-1} .

4.3 ADSORBATE

p-xylene supplied by Avra Synthetic Pvt. Ltd, Hyderabad, India was used as adsorbate. Synthetic wastewater solutions of p-xylene of desired conc. (50–150mg/l) were prepared by dissolving accurately weighed quantity of p-xylene in distilled water.

4.4 BATCH STUDY

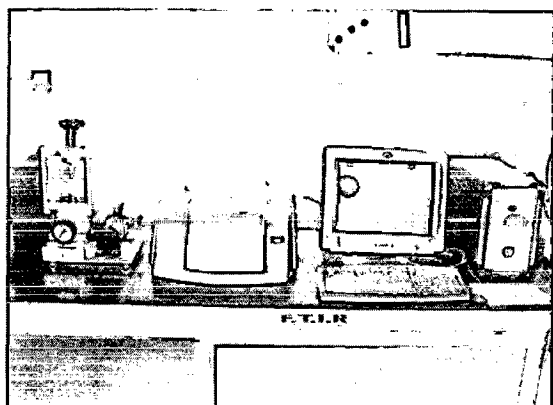
Batch study was undertaken for the optimization of process parameters and to extract design parameters like rate constants and isotherm constants. Considering the requirement of the sample for the analysis of the p-xylene, 100 ml of the sample volume was taken for each experiment. Experiments were conducted with adsorbent RHA.

4.4.1 Analytical instruments used for the present investigation

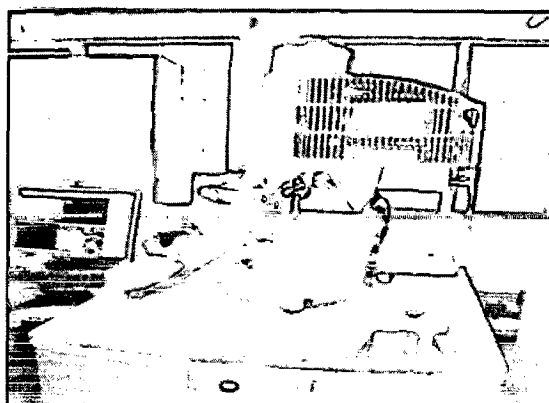
Analytical instruments used in the present study were UV/VIS spectrophotometer, Fourier transform infrared spectroscopy (FTIR), X-Ray diffractometer (XRD), scanning electron microscope (FE SEM) etc. Scanning electron microscopic (SEM) analysis of RHA was carried out by using a scanning electron microscope (Model SEM-501 Phillips, Holland). The photograph of the some analytical instruments used in the present investigation has been shown in Fig 4.1. The pH of the solution was measured with a pH Meter (EUTECH 510) using FET solid electrode calibrated with standard buffer solutions. FTIR (FTIR, Nicolet 6700, Australia) spectrometer was employed to determine the type of functional groups present on the adsorbents surface before and after adsorption and thus, to find out the component responsible for p-xylene adsorption.

4.4.2 Auxiliary equipments used for the present investigation

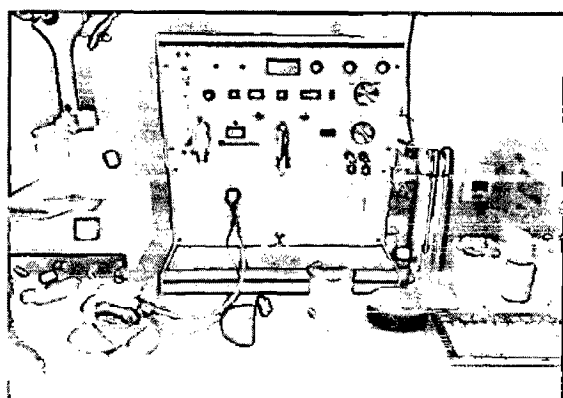
Auxiliary equipment used in the present study were pH meter, muffle furnace, centrifuge, autoclave, digital camera, weighing balance, orbital shaking incubator etc. The photograph of the some auxiliary instruments used in the present investigation has been shown in Fig 4.2.



FTIR, Thermo model AVATR 370 Australia

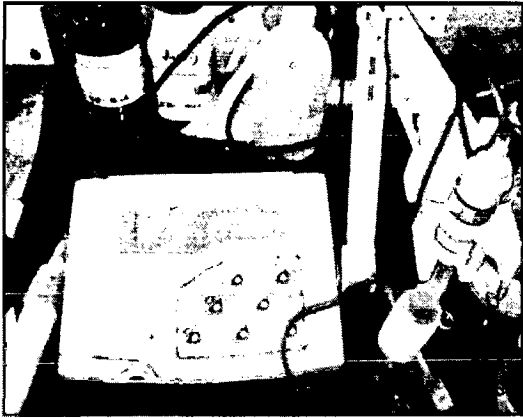


FE SEM, Quanta 200 F, Netherland

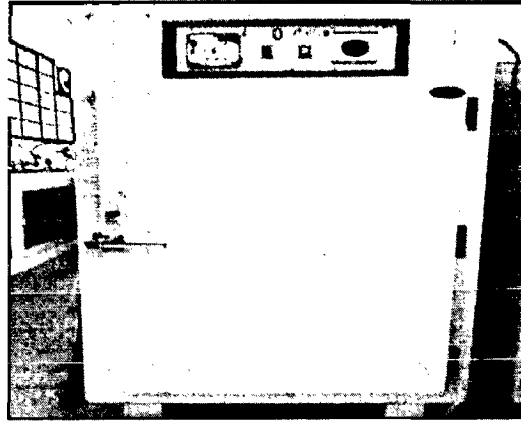


BET surface Area Analyzer

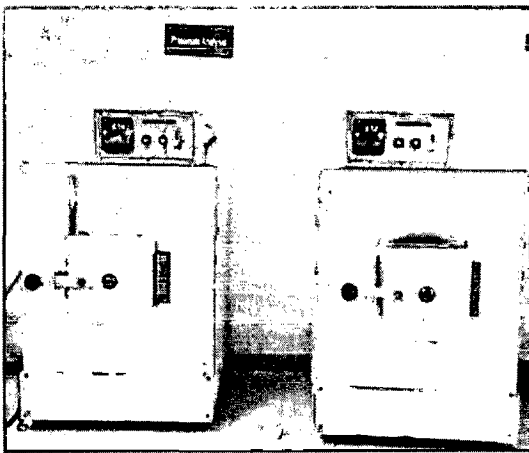
Figure 4.1 Analytical instruments used in the present investigation



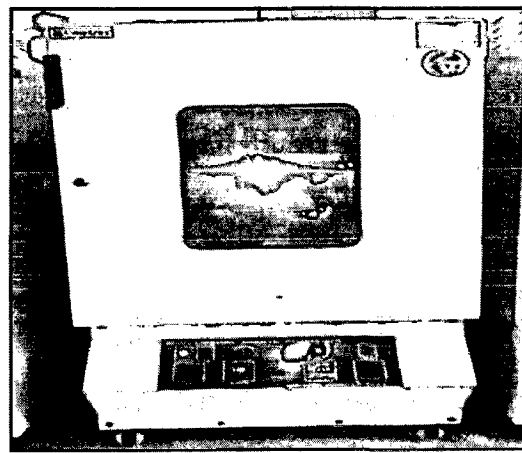
pH meter, EUTECH Instruments



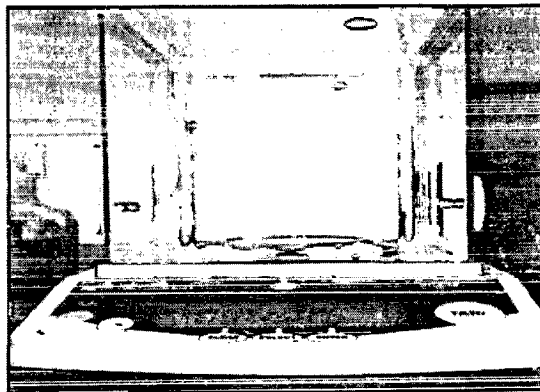
Oven



Muffle furnace



Orbital shaker incubator, Metrex, New Delhi



Weighing Balance, Denver Instruments

Figure 4.2 Auxiliary instruments used in the present investigation

4.5 ANALYTICAL MEASUREMENTS

A double beam UV/VIS spectrophotometer (UV 1800 Series) is used for the concentration measurement of p-xylene. For this purpose, first the wave length corresponds to maximum absorbance (λ_{max}) was determined. λ_{max} for p-xylene was found to be 212 nm. 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.4.3). The linearity of calibration curve Fig.4.3 indicated the applicability of the Lambert-Beer's Law.

4.6 BATCH EXPERIMENTAL PROGRAMME

Batch experimental programme was used throughout the experimental work i.e. to study the effect of important parameters like pH, dose, concentration, time and temperature. For each experimental run, 100 ml 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 150 rpm at 30 ± 1 °C. Samples were withdrawn at appropriate time intervals. Some RHA 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.

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.

The percentage removal of p-xylene, equilibrium adsorption uptake in solid phase q_e (mg/g) was calculated by using the following relationship:

$$\% \text{ Removal} = 100(C_o - C_e)/C_o \quad (4.1)$$

Amount of adsorbed p-xylene per g of solid,

$$q_e = (C_o - C_e) V/w \quad (4.2)$$

Where C_o is the initial concentration (mg/l), C_e is the equilibrium concentration (mg/l), V is the volume of the solution (ml) and w is the mass of adsorbent (g).

4.6.1 Effect of Adsorbent Dosage

To find the optimum adsorbent dosage the analysis was done at the different amount of adsorbent ranging from 3 to 12 g/l with initial adsorbate concentration 100 mg/l of p-xylene.

4.6.2 Effect of pH

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).

4.6.3 Effect of time

The kinetics of adsorption was determined by analyzing adsorptive uptake of the p- xylene from the aqueous solution at different time intervals. To investigate the kinetics of adsorption of p-xylene on the adsorbent various kinetic model, like pseudo –first order, pseudo-second order and intaparticle diffusion model were used .

4.6.4 Isotherm Study

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 313K. Concentration was varied from 50 mg/l to 150mg/l.

Table.4.1: Variation of absorbance with concentration of p-xylene.

Conc. (mg/l)	Absorbance
1	0.037
2	0.061
3	0.085
5	0.157
10	0.285
20	0.434
25	0.707
30	0.745
40	0.975
50	1.21

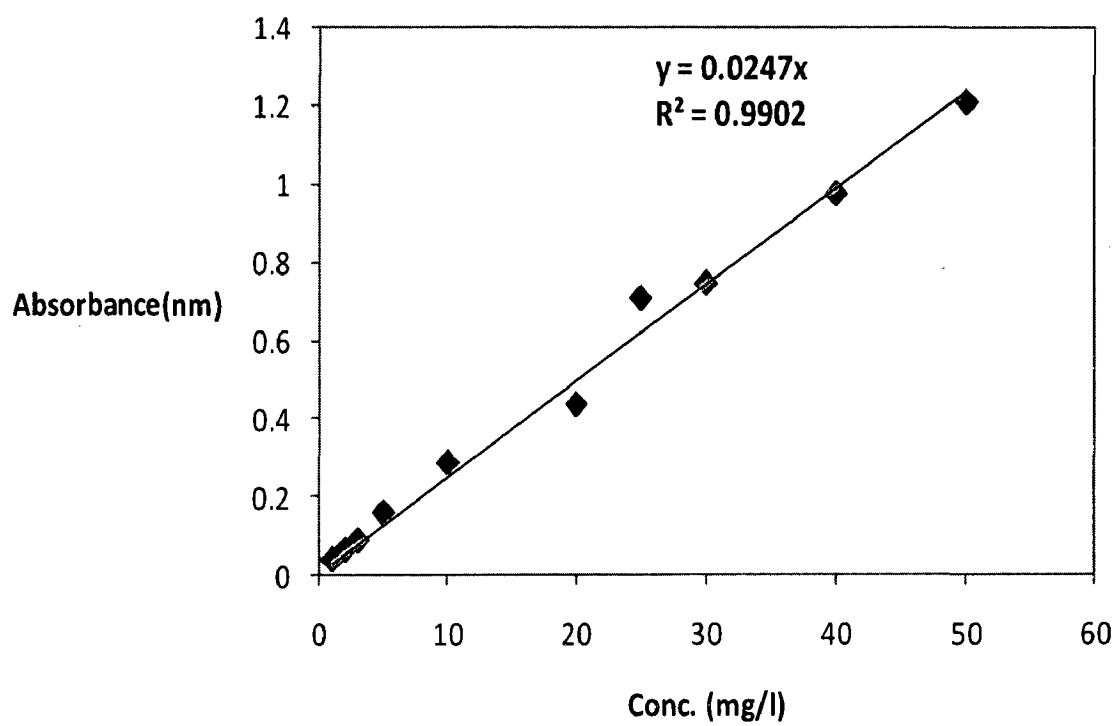


Figure 4.3-Calibration curve

RESULT AND DISCUSSION

5.1 General

This chapter deals with the various results interpreted from the experimental data. These results include characterization of RHA and batch adsorption studies.

5.2 Characterization of rice husk ash

Physico-chemical characteristics of the adsorbents are presented in Table.5.1. From Table.5.1, it is observed that the bulk density of RHA is 0.13 gm/ml. The specific surface areas of the adsorbents used is 27.4 m²/kg. The morphologies of RHA were examined under scanning electron microscope. SEM of RHA reveals its surface texture and porosity. The SEMs of RHA before adsorption and after adsorption are shown in Fig.5.3 and 5.4 respectively. Average particle size of RHA used was 212 μm. X-ray diffraction (XRD) analysis was carried out using Phillips (Holland) diffraction unit (Model PW 1140/90), using copper as the target with nickel as the filter media, and K radiation maintained at 1.542 Å. Goniometer speed was maintained at 1°/min. Major components identified in RHA are SiO₂, K₂O, MgO, Fe₂O₃, Al₂O₃ and CaO. The d-spacing values provided by the XRD spectra of RHA reflected the presence of Cristobalite (SiO₂), Margaritasite ((Cs,K,H₃O)₂(UO₂)₂V₂O₈·(H₂O)) and Macedonite (PbTiO₃).

5.3 FTIR spectroscopy of RHA

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. The FTIR technique is an important tool to identify the characteristic functional groups, which are instrumental in adsorption of p-xylene. The FTIR spectra of the blank and p-xylene loaded RHA is shown in Fig. 5.1 and 5.2 respectively. The Fourier Transform Infra Red (FTIR) spectra of the blank RHA indicated the presence of –CO-, -OH, -Si-OH, -Si-H and –C-OH groups on the surface of RHA.

Peaks around 1470 cm⁻¹ are indicative of –CH₂ and –CH₃ groups while those at 1380 cm⁻¹ are indicative of –CH₃ groups. The IR spectra indicated weak and broad peaks about 1600 cm⁻¹ corresponding to –C O and –C–OH groups stretching from aldehydes and ketones. The peak at 1300 cm⁻¹ band may be attributed to the aromatic CH and carboxyl-carbonate

structures and silanol groups. The silanol groups are in the form of silicon dioxide structure ($-\text{Si}-\text{O}-\text{Si}-\text{OH}$). This structure is similar to the silanol groups of silicic acid. The peaks at about 793 and 469 cm^{-1} indicate the presence of $\text{Si}-\text{H}$. With the loading of p-xylene the shifting of the peaks is seen from about 3948 , 3845 , 3740 , 3691 , 2653 , 1633 , 1489 , 1368 , 1013 , 679 and 453 cm^{-1} . This means that the functional groups at these wave numbers participate in the p-xylene adsorption. The shifting occurs both to higher and lower wave numbers. The shifting of all the bands is visible.

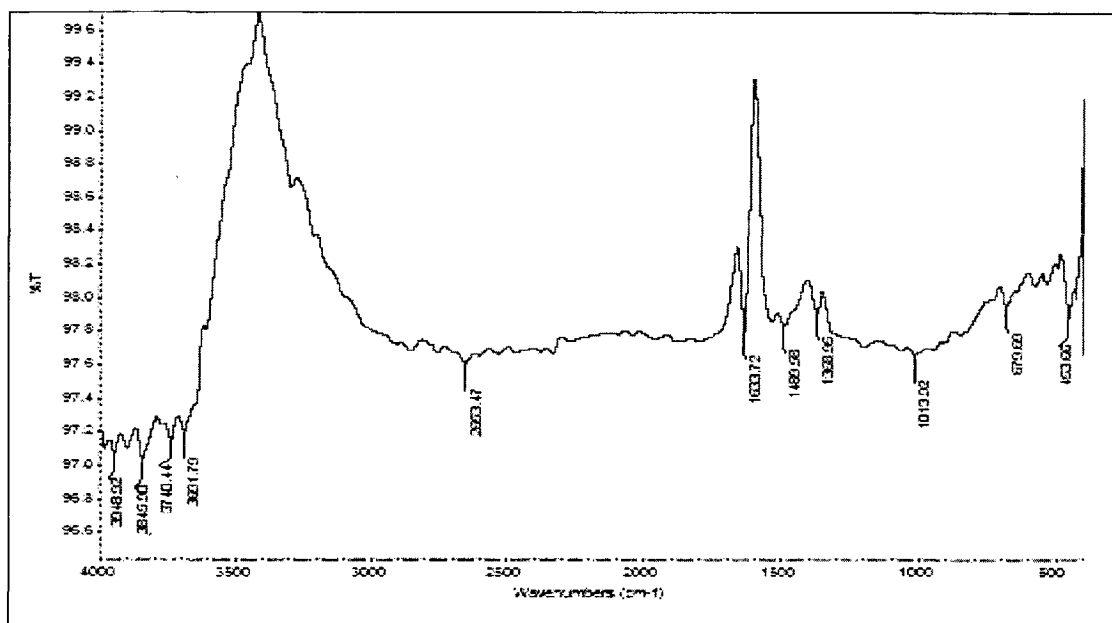


Figure 5.1: FTIR spectra of RHA-Blank

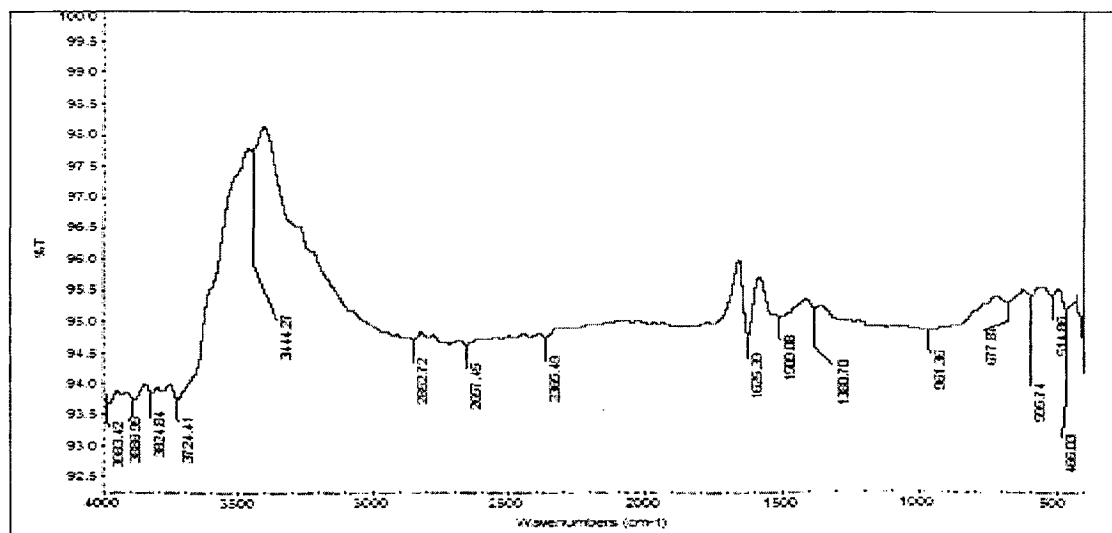


Figure 5.2 : FTIR spectra of p-xylene loaded RHA

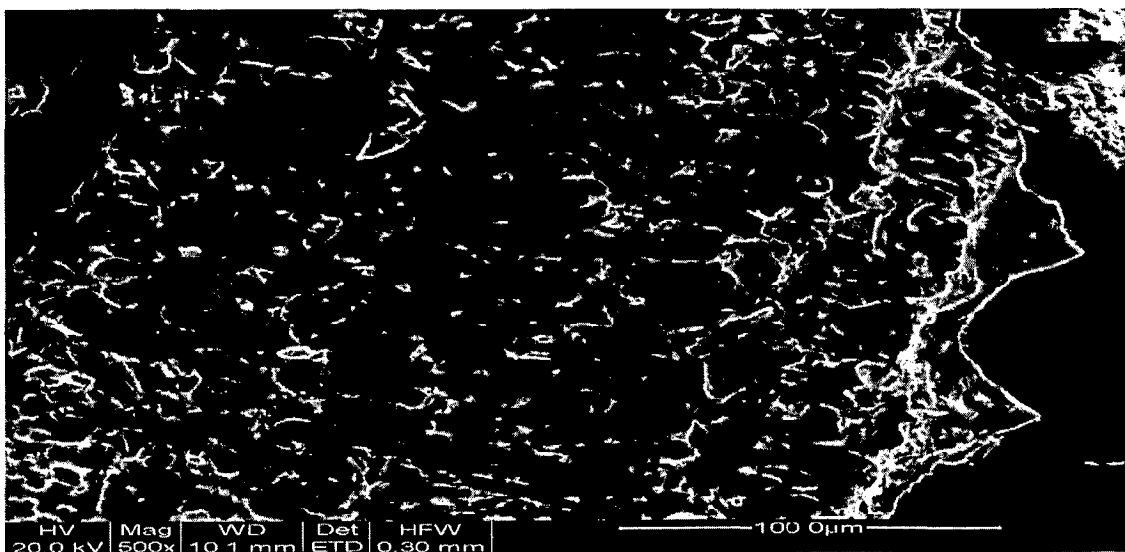


Figure 5.3: Scanning Electron Microscope (SEM) of Blank RHA

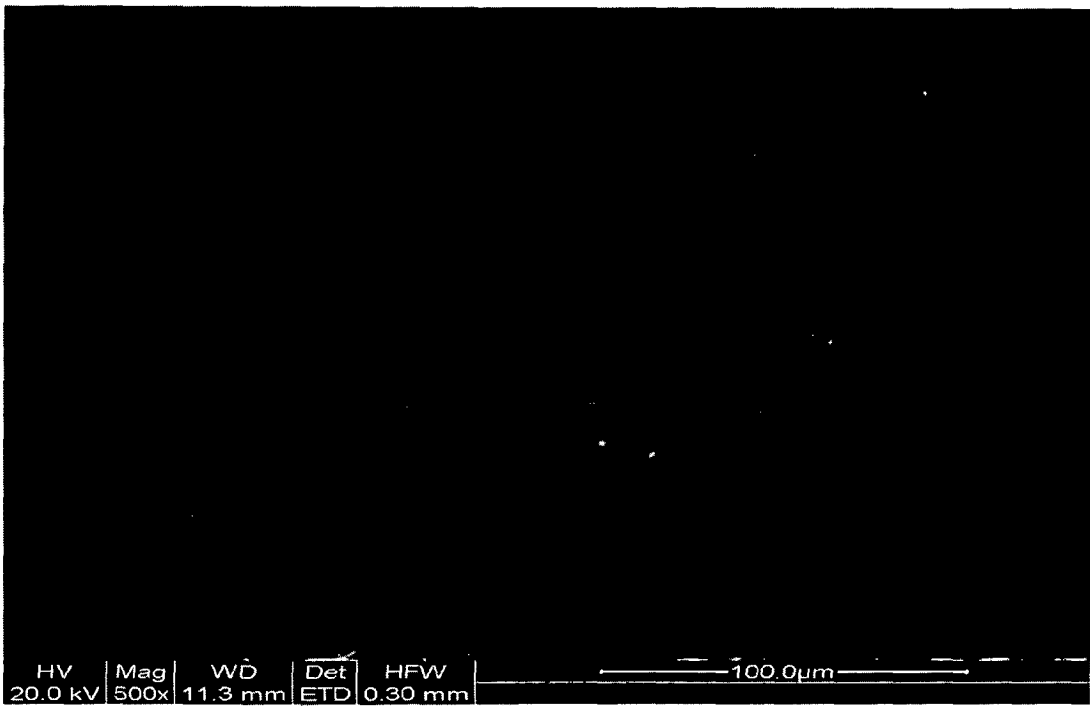


Fig 5.4 Scanning Electron Micrograph of p-xylene loaded RHA

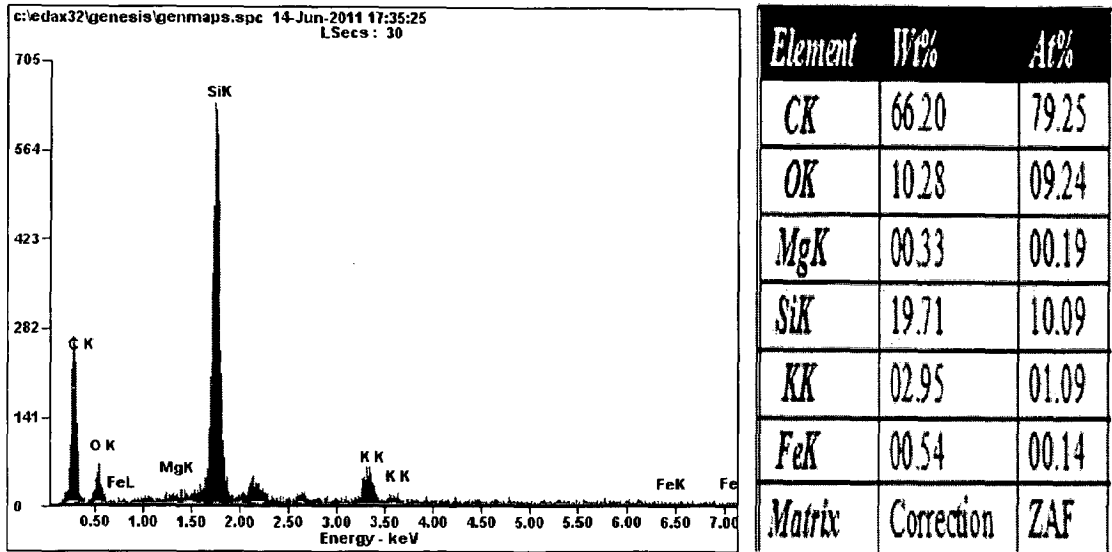


Figure 5.5:EDAX of blank RHA

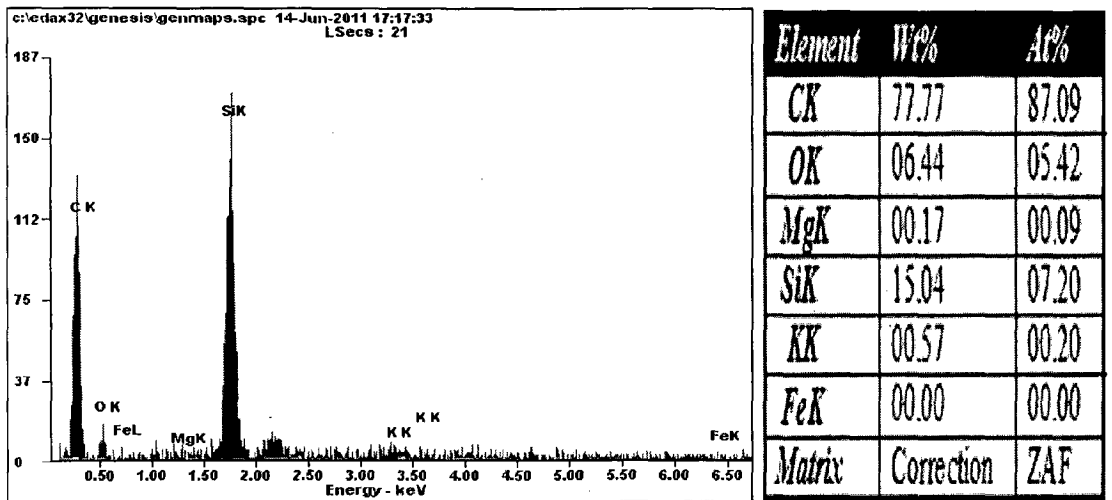


Figure 5.6:EDAX of p-xylene loaded RHA

5.4 Batch adsorption study

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 RHA. The effect of various operating parameters, viz. concentration, adsorbent dose, contact time and pH is studied and presented here.

5.4.1 Effect of Adsorbent dosage

The effect of RHA dose on the extent of solute adsorption was investigated by varying the dose from 0.3 to 1.2g per 100 mL under the selected initial solute concentration (100mg/L). The agitation speed (150rpm) 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.5.7). 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 0.9g per 100 mL of the solution of adsorbent.

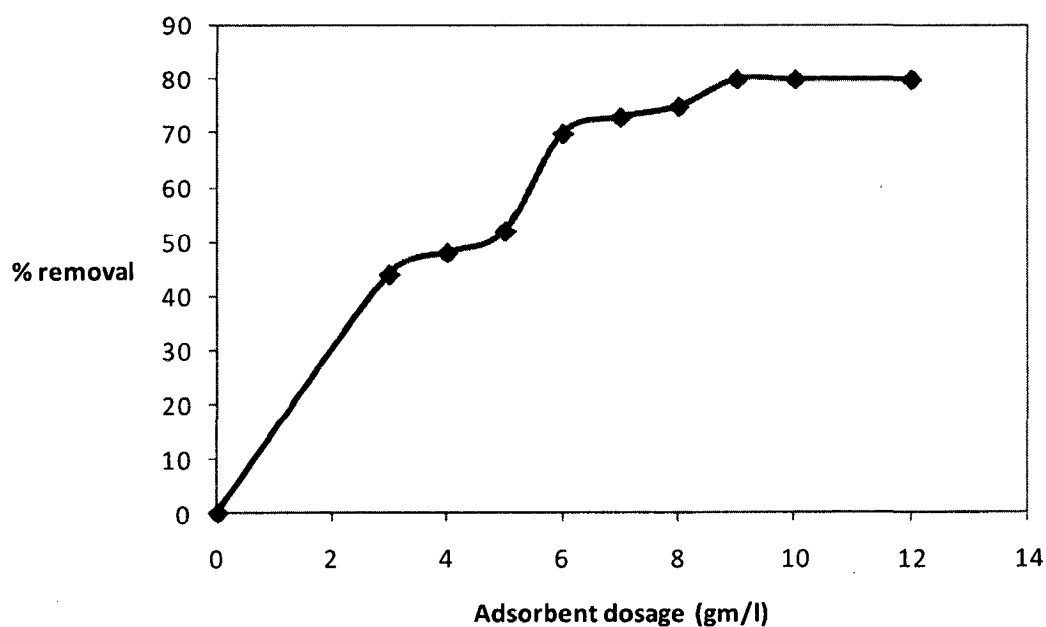


Figure 5.7 Effect of adsorbent dosage on percentage removal of p-xylene
Experimental conditions: $\text{pH}^i=6.1, C_o=100 \text{ mg/L}, t=4 \text{ h}, \text{temp. } T=30^\circ\text{C}$

5.4.2 Effect of initial pH

The adsorption pattern of p- xylene on RHA in the present case was studied varying the solution pH from 2 to 12. The adsorption was found to increase at the lower pH values. The adsorbent dosage was kept 9 g/l for para -xylene. The effect of pH on the removal of p-xylene was shown in the Fig.5.8. The effective pH for removal was found 3.5

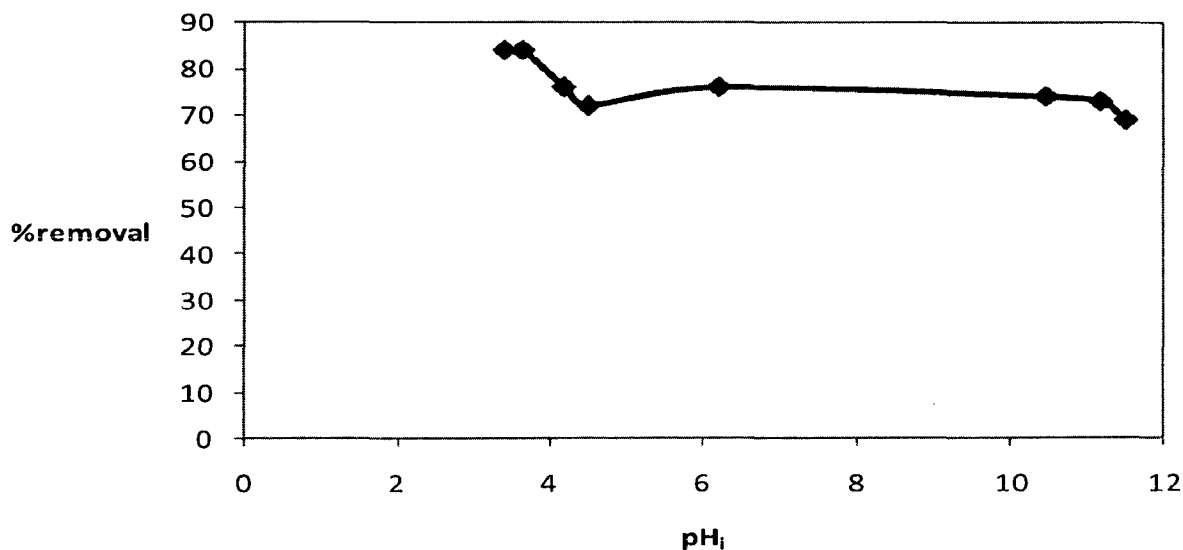


Figure 5.8 Effect of pH on percentage removal of p-xylene

Experimental conditions: adsorbent dosage, $m= 9\text{g/L}$, $C_0=100\text{ mg/L}$, $t= 4\text{ h}$, $T=30^\circ\text{C}$

5.4.3. Effect of contact time

The effect of contact time on the removal of p-xylene by RHA at $C_0=50, 100$ and 150 mg l^{-1} are given in Figs.5.8. The contact time curves show rapid adsorption of p-xylene in the first 40 min, thereafter, the rate of adsorption rate decreases gradually and the adsorption reaches equilibrium around 100 min.

The effect of contact time for the adsorption of p-xylene by RHA was studied for a period of 24 h for initial p-xylene concentrations of 100 mg/l at 30°C . RHA dosage was 0.9 g/100 ml of p-xylene, at optimum pH. The solutions were kept in contact with RHA 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 RHA.

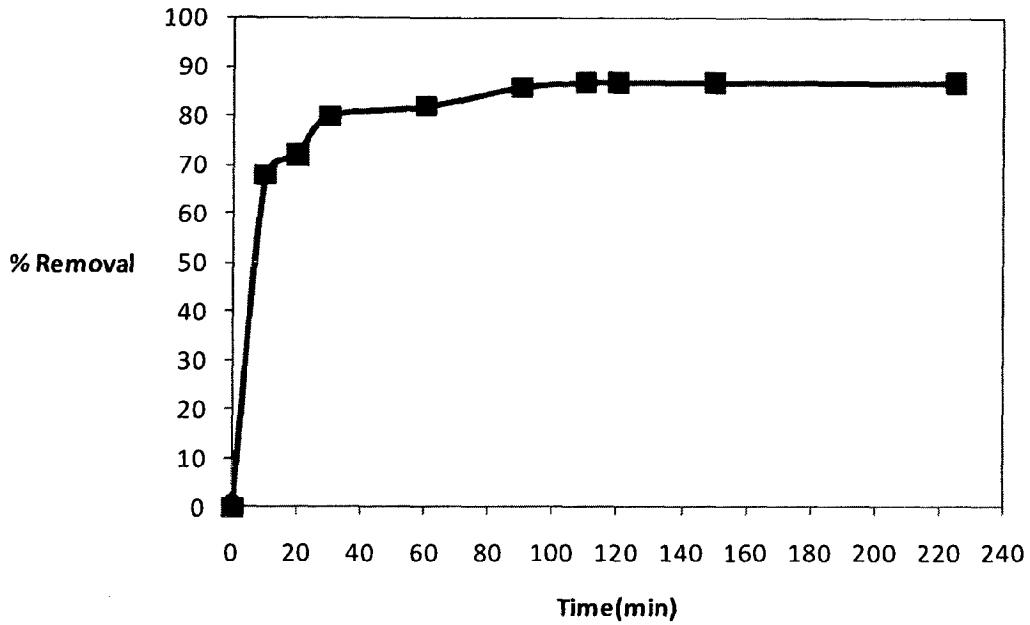


Figure 5.9 Effect of time on percentage percentage removal of p-xylene

Experimental conditions: adsorbent dosage, $m=9\text{g/L}$, $C_0=128\text{mg/L}$, $t=4\text{h}$, $T=30^\circ\text{C}$

5.4.4. Effect of concentration

Percentage removal of p-xylene from aqueous solution decreased as concentration increased from 50 to 150 mg/L at constant pH. With increase in the concentration, the percentage removal of the p-xylene from solution decreases.

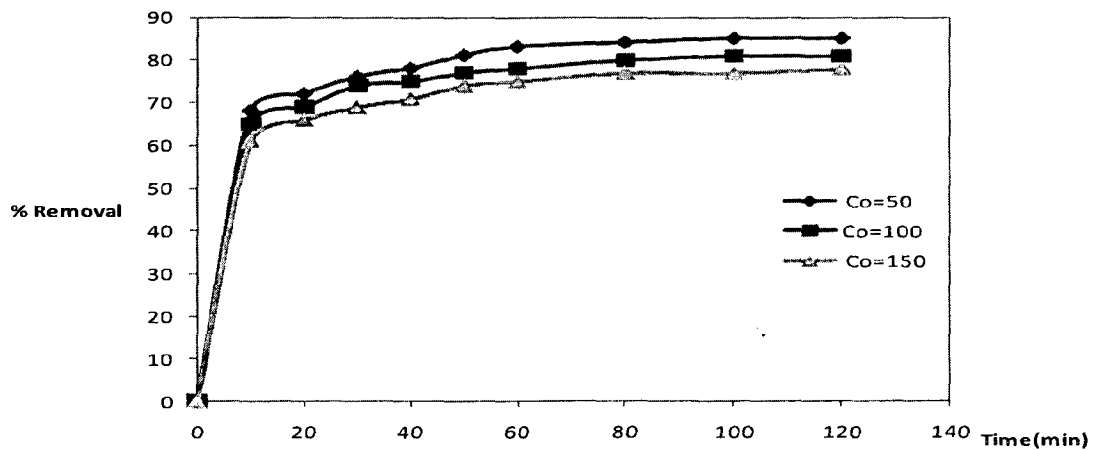


Figure 5.10 Effect of initial concentration on percentage removal of p-xylene

Experimental conditions: adsorbent dosage, $m=9\text{g/L}$, $t=2\text{h}$, $T=30^\circ\text{C}$

5.4.5. Effect of temperature

With the increase in temperature, percentage removal of p-xylene decrease. It was concluded that the adsorption reaction is exothermic.

Table 5.1: Characteristics of RHA

Proximate analysis	
Moisture (%)	2.4
Ash (%)	36.12
Volatile matter (%)	8.6
Fixed carbon (%)	52.88
Average particle size(μm)	212
Bulk density (kg/m^3)	130
BET Surface area(m^2/Kg)	27.46

5.5 Adsorption kinetics

In order to investigate the adsorption processes of p-xylene on RHA, four kinetic models were used, including pseudo-first order, pseudo-second order, Bangham and intra particle diffusion models.

5.5.1 Pseudo-first-order model:

The pseudo-first-order equation is given as

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

where, q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_f is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min). The integration of Eq. (1) with the initial condition, $q_t=0$ at $t=0$ leads to following equation (Mane et al., 2007).

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

The values of adsorption rate constant (k_f) were determined from the plot of $\log(q_e - q_t)$ against t (Figs. 5.11). The k_f values are given in Table 5.2.

Plot of $\log(q_e - q_t)$ versus t gives a straight line for first-order kinetics (Fig. 5.11). The trend shows that the predicted q_e values seem to be lower than the experimental values. The Lagergren first-order rate constant K_1 , q_e and R^2 determined from the model indicates that this model had failed to estimate q_e since the experimental value of q_e differs from estimated one. The pseudo-first-order Lagergren model parameters are given in Table 5.2.

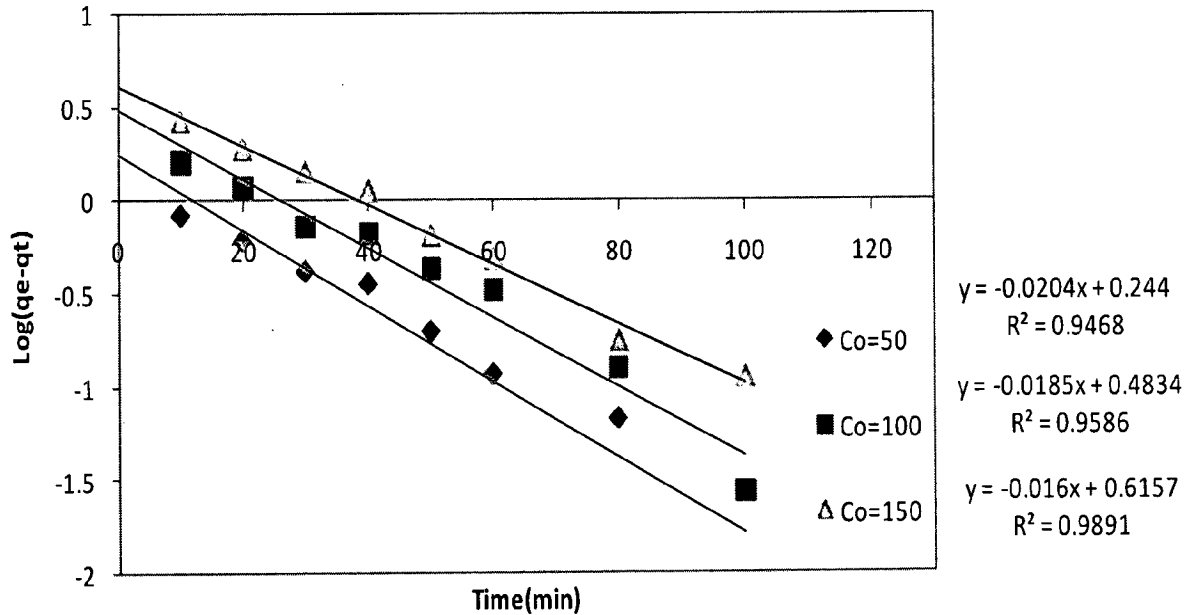


Fig. 5.11 Pseudo-first-order kinetic plots for the removal of p-xylene by RHA
Experimental conditions: $pH_0=3.5$, adsorbent dosage 9g/L, $T=30^{\circ}C$

5.5.2 Pseudo-second-order model:

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

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

Where, k_s is the pseudo-second-order rate constant (g/mg/min). Integrating Eq (5.3)

and noting that $q_t=0$ at $t=0$, the following equation is obtained:

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

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

$$h = k_s q_e^2 \quad (5.5)$$

Fig. 5.12 shows the plot of t/q_t versus t at $C_0=50, 100$ and 150 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 calculated correlation coefficients are also closer to unity and also $q_{e,calc}$ and $q_{e,expt}$ values are almost same for pseudo-second order kinetics than that for pseudo-first order kinetics model. Therefore the adsorption can be approximated more appropriated by the pseudo-second order kinetic model (Mane et al. 2007). The pseudo-second-order model parameters are given in Table 5.2.

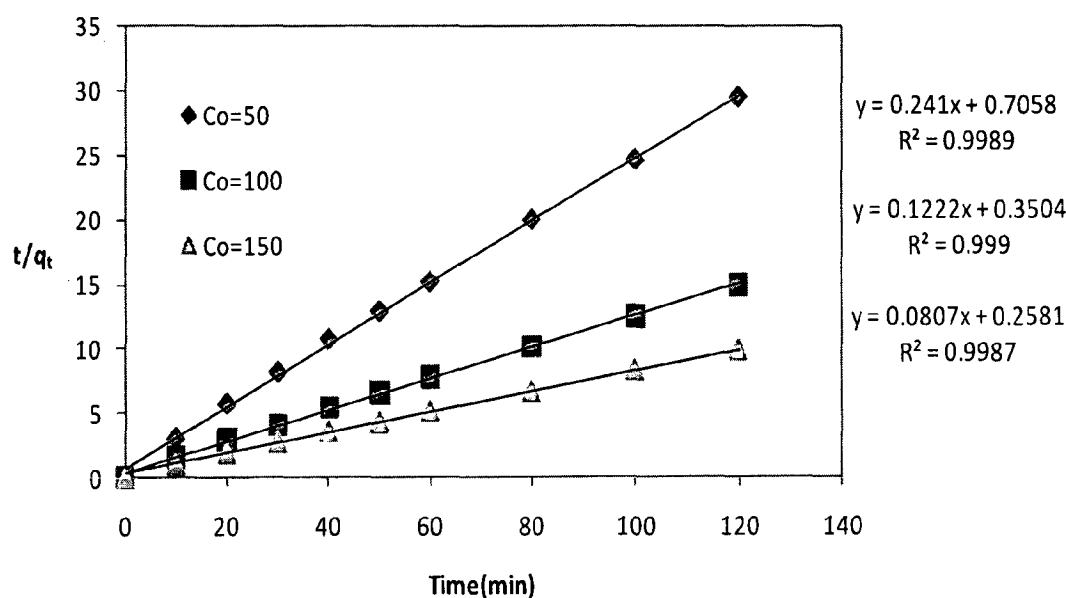


Figure 5.12 Pseudo-second-order kinetic plots for the removal of p-xylene by RHA
Experimental conditions: $pH_0=3.5$, adsorbent dosage $9g/L$, $T=30^{\circ}C$

5.6 INTRA-PARTICLE DIFFUSION STUDY

5.6.1 Weber-Morris intra-particle diffusion equation :

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model: (Weber and Morris, 1963)

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

Where, k_{id} is the intra-particle diffusion rate constant ($mg/g \text{ min}^{1/2}$) 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. Figure 5.13 present a plot

of q_t versus $t^{1/2}$ at $C_0=50, 100, 150$ for P-xylene adsorption on RHA . The deviation of straight lines from the origin 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. The values of intra-particle diffusion rate parameters are given in Table 5.2.

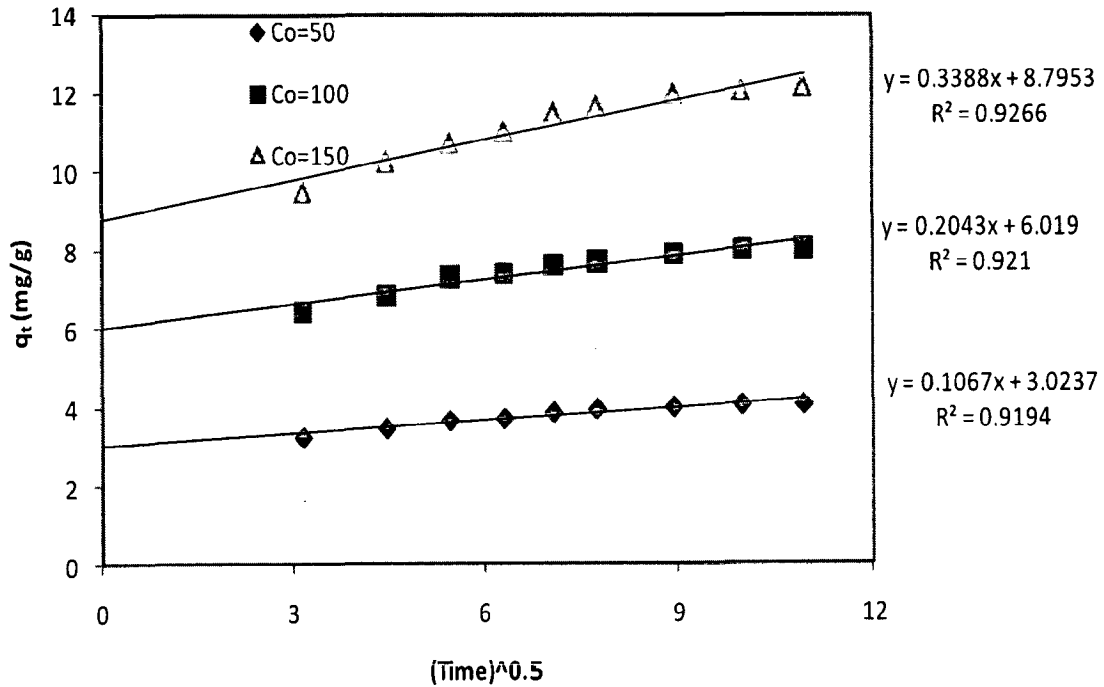


Fig. 5.13 Weber and Morris intra particle diffusion plots for the removal of p-xylene by RHA
Experimental conditions: pH=3.5, adsorbent dosage 9g/L, T=30⁰C

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

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

where V is the volume of the solution (ml), and $\alpha (<1)$ and k_0 are constants.

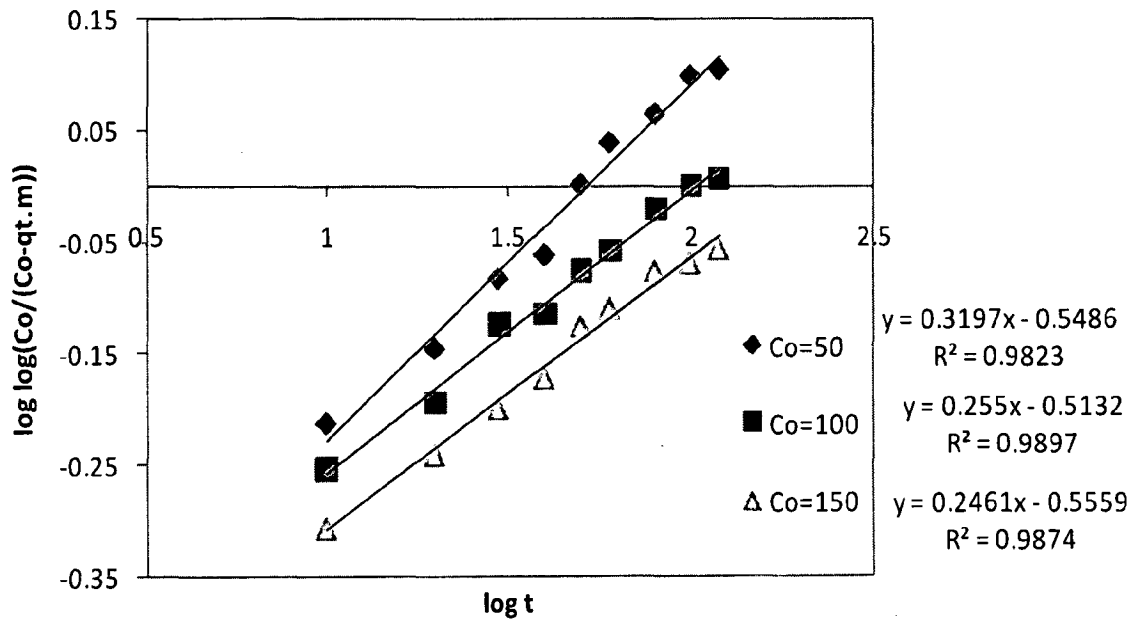


Fig. 5.14 Bangham plots for the removal of p-xylene by RHA
Experimental conditions: pH=3.5, adsorbent dosage 9g/L, T=30⁰C

5.7 Adsorption equilibrium study

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

5.7.1 Freundlich and Langmuir isotherms:

Linearised form of Freundlich and Langmuir isotherm equations are given as

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{Linear form}) \quad (5.8)$$

$$\frac{C_e}{Q_e} = \frac{1}{K_A Q_m} + \frac{C_e}{Q_m} \quad (\text{Linear form}) \quad (5.9)$$

Figs. 5.15 shows the Freundlich isotherm plots ($\ln Q_e$ vs $\ln C_e$) for adsorption of p-xylene, onto RHA at 293, 303 and 313K. Langmuir isotherm plot (C_e/Q_e versus C_e) are shown in Fig. 5.16 for adsorption onto RHA. Freundlich and Langmuir isotherm parameter along with linear and non-linear correlation coefficients are given in Table 5.3 for RHA. Comparison of correlation coefficient values (R^2) shows that R^2 values are close to unity for Freundlich isotherm. The q_m value decrease with temperature indicating exothermic nature of adsorption.

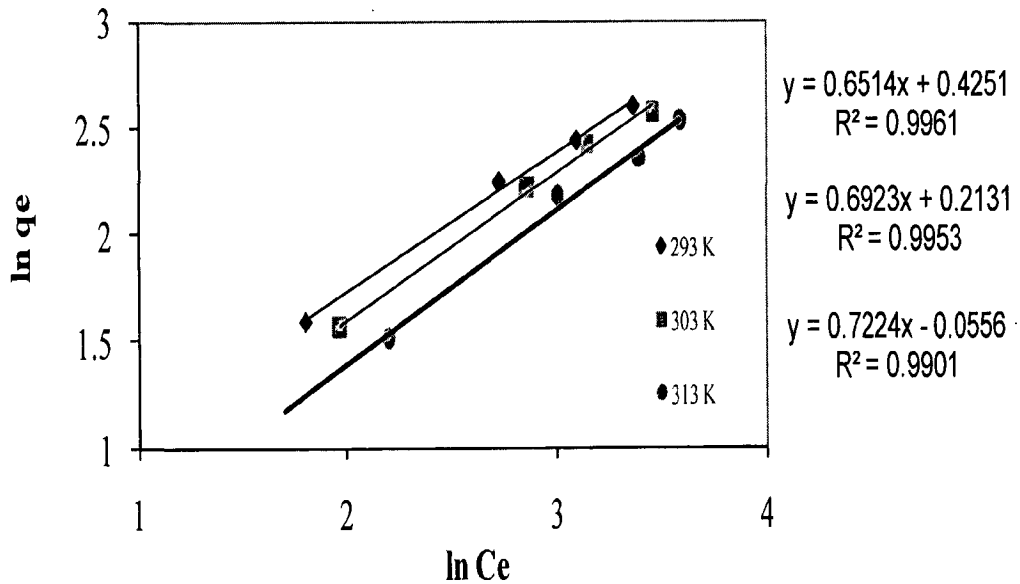


Figure 5.15 Freundlich isotherm plots for adsorption of p-xylene by RHA
Experimental conditions: pH 3.5, adsorbent dosage 9g/L, contact time 240 min

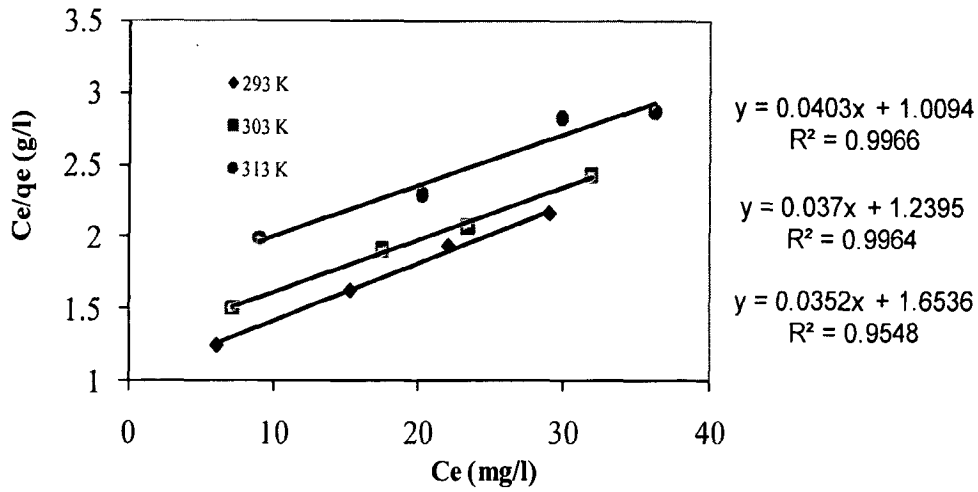


Figure 5.16 Langmuir isotherm plots for adsorption of p-xylene by RHA
Experimental conditions: pH 3.5, adsorbent dosage 9g/L, contact time 240 min

5.7.2 The Temkin isotherm:

It is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (5.10)$$

This can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (5.11)$$

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) corresponding to the maximum binding energy and constant B_1 is related to the heat of

adsorption. Fig.5.17 show the Temkin isotherm plot for RHA. The Temkin isotherm parameters listed in Table 5.2 for RHA.

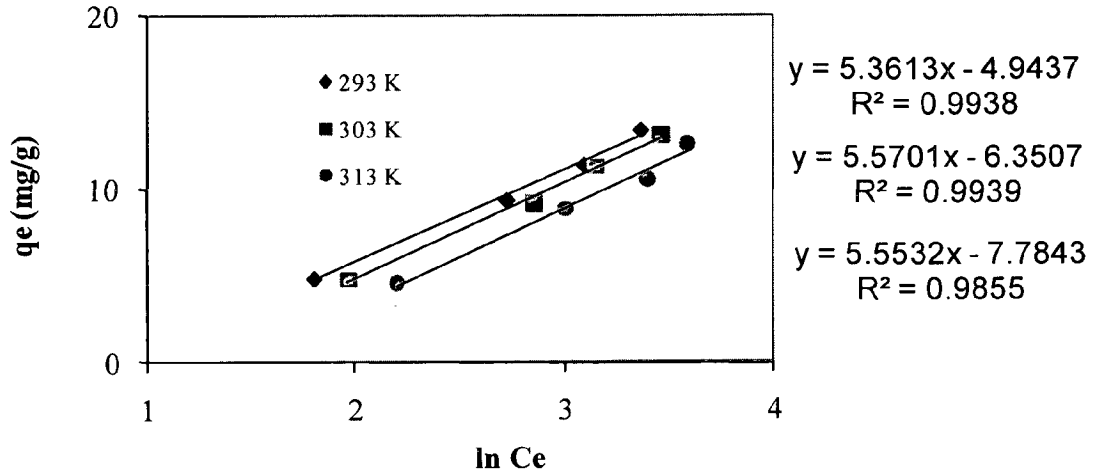


Figure 5.17 Temkin isotherm plots for adsorption of p-xylene by RHA
Experimental conditions: pH 3.5, adsorbent dosage 9g/L, contact time 240 min

5.7.3 Dubinin-Radushkevich (D-R) isotherm:

It is given as (Dubinin and Radushkevich, 1947)

$$q_e = q_s \exp(-B\epsilon^2) \quad (5.12)$$

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

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (5.13)$$

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:

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

D-R isotherm plots at 293,303 ND 313K are shown in Fig. The values of correlation coefficient are the lowest in comparison to the values for all other isotherms investigated. Thus, D-R equation does not represent the experimental data satisfactorily.

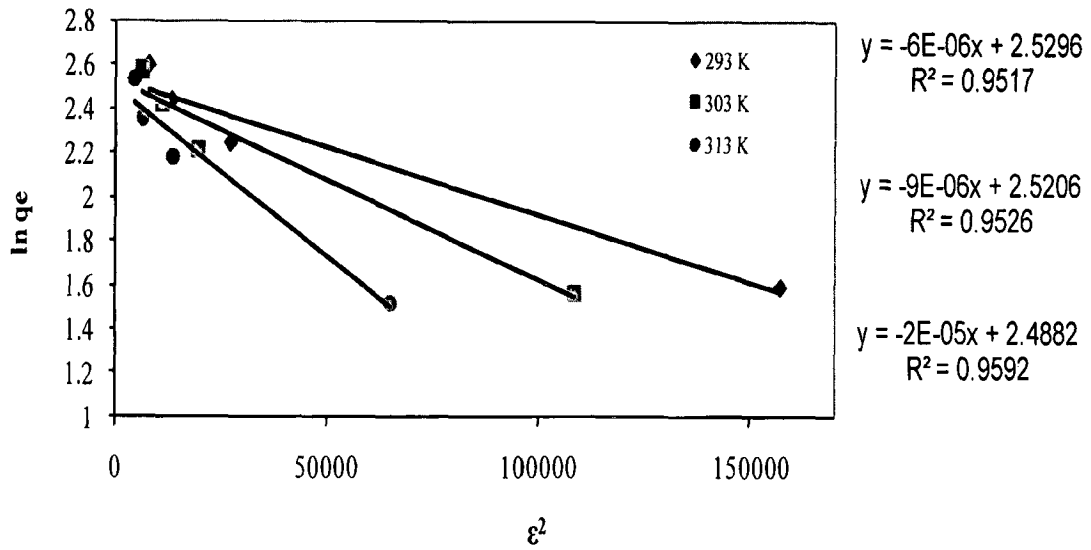


Fig. 5.18 Dubinin-Radushkevich isotherm plots for adsorption of p-xylene by RHA
Experimental conditions: pH 3.5, adsorbent dosage 9g/L, contact time 240 min

It was found that the adsorption equilibrium data was better fitted by the Freundlich isotherm and Langmuir isotherm although it can also be modelled by the Temkin isotherm, in the concentration range studied.

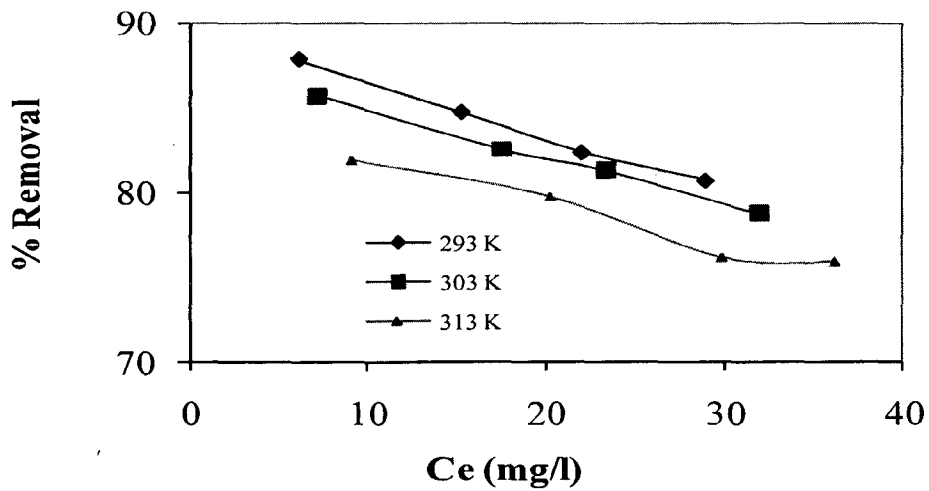


Fig. 5.19 Effect of concentration on percentage removal of p-xylene
Experimental conditions: pH 3.5, adsorbent dosage 9g/L, contact time 240 min

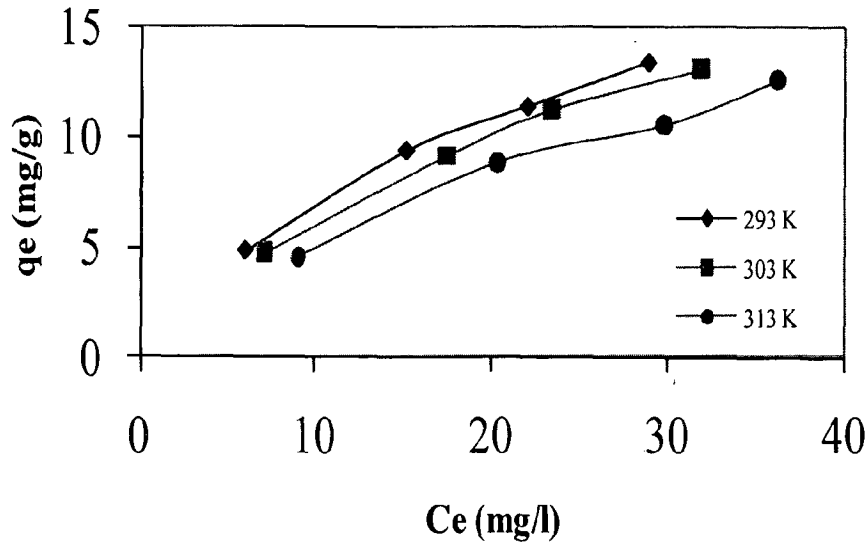


Figure 5.20 Effect of concentration on uptake of RHA

Experimental conditions: pH 3.5, adsorbent dosage 9g/L, contact time 240 min

5.8 Error analysis

Due to the inherent bias resulting from linearization, 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. Based on the error functions and their limitations, the hybrid fractional error function (HYBRID) was chosen along-with Marquardt's percent standard deviation (MPSD).

5.8.1 The hybrid fractional error function (HYBRID)

HYBRID is given as

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

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

5.8.2 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:

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

The values of MPSD error functions are given in Table 5.4.

5.8.3 Choosing best-fit isotherm based on error analysis:

The values of the error functions are presented in Table 5.3. By comparing the results of the values of the error functions, it is found that both Langmuir and Freundlich isotherm best-fitted the isotherm data for p-xylene adsorption on RHA at all temperature.

5.9 Thermodynamic study

The effect of temperature on the adsorption of p-xylene on RHA was investigated by conducting experiments for different initial p-xylene concentrations at 298, 308, and 318 K. Fig. 5.19 indicates that on increasing the temperature percentage removal of p-xylene decreases. This shows that the process is exothermic in nature.

The thermodynamic parameters Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations: (Gupta et al., 2011)

$$\text{Log}(q_e m / c_e) = \Delta S^\circ / 2.303R + -\Delta H^\circ / 2.303RT \quad (5.16)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5.17)$$

where m is the adsorbent dose (g L^{-1}), C_e is concentration of q_e solution at equilibrium (mgL^{-1}), q_e is the amount of p-xylene at equilibrium in unit mass of adsorbent (mg/g), q_e/C_e is called the adsorption affinity. ΔH° , ΔS° and ΔG° are change in enthalpy (KJ mol^{-1}), entropy ($\text{J mol}^{-1} \text{K}^{-1}$) and free energy (KJ mol^{-1}), respectively, R is the gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH° and ΔS° were obtained from the slopes and intercepts of the Van't Hoff plots of $\log(q_e m / C_e)$ vs. $1/T$, respectively, thereafter

ΔG° values were determined from Eq. 10. The values of thermodynamic parameters are presented in Table 5.5. The negative values of ΔG° and ΔH° indicate that adsorption process is spontaneous and exothermic in nature.

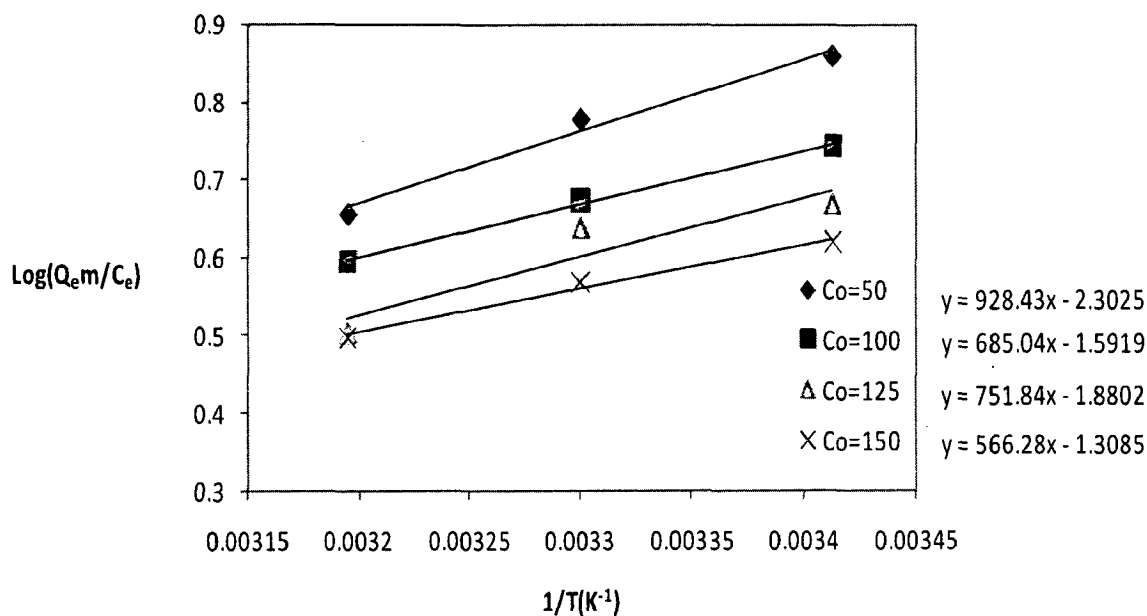


Fig. 5.21 Van't Hoff plots for the determination of (ΔG°), (ΔH°) and (ΔS°)

The negative ΔH° value confirms the exothermic nature of the overall-sorption process. The negative values of ΔH° and ΔS° support the fact that the reaction is spontaneous at low temperature. Negative value of free energy change ΔG_{ads}° indicates the feasibility and spontaneous nature of the adsorption process. The negative values of ΔS° shows that the p-xylene molecules are organized on the adsorbent surface in less randomly fashion than in solution. It suggests decreased randomness during adsorption.

Table 5.2 Kinetic parameters for adsorption of p-xylene by RHA
(pH=3.4, T=303K, Co=50, 100 and 150 mg/l, RHA dose=9 g/l)

Pseudo-first order						
C_o (mg/l)	$Q_{e, \text{expt}}$ (mg/g)	$Q_{e, \text{calc}}$ (mg/g)	k_f (1/min)	R_1^2 (linear)	R_2^2 (non-linear)	
50	4.07	1.75	0.0469	0.9468	-0.9730	
100	8.04	3.04	0.0426	0.9586	-0.9790	
150	12.15	4.12	0.0368	0.9891	-0.9945	
Pseudo-second order						
C_o (mg/l)	$Q_{e, \text{expt}}$ (mg/g)	$Q_{e, \text{calc}}$ (mg/g)	h (mg/g min)	k_s (g/mg min)	R_1^2 (linear)	R_2^2 (non-linear)
50	4.07	4.14	1.42	0.0823	0.9989	0.9998
100	8.04	8.18	2.85	0.0426	0.9990	0.9998
150	12.15	12.39	3.87	0.0252	0.9987	0.9998
Bangham						
C_o (mg/l)	k_o (g)	α	R_1^2 (linear)		R_2^2 (non-linear)	
50	6.5	0.32	0.9823		0.9911	
100	7.1	0.25	0.9897		0.9948	
150	6.4	0.24	0.9874		0.9936	
Intra-particle diffusion						
C_o (mg/l)	k_{id} (mg/g min ^{1/2})	I (mg/g)	R_1^2 (linear)		R_2^2 (non-linear)	
50	0.11	3.0	0.9266		0.9588	
100	0.201	6.1	0.9210		0.9596	
150	0.34	8.8	0.9194		0.9626	

Table.5.3: Isotherm parameters for adsorption of p-xylene onto RHA
(pH=3.5, T=293,303 and 313 K, Co=50 -150 mg/l, RHA dose=9 g/l, t=4 h)

Freundlich constants				
T (K)	K_F (mg/g)/(mg/l) ^{1/n}	1/n	R ₁ ² (linear)	R ₂ ² (non-linear)
293	1.53	0.6514	0.9961	0.9980
303	1.24	0.6923	0.9953	0.9976
313	0.95	0.7224	0.9901	0.9950
Langmuir constants				
T (K)	K _L (l/mg)	Q _m (mg/g)	R ₁ ² (linear)	R ₂ ² (non-linear)
293	0.04	24.8	0.9966	0.9983
303	0.03	27.0	0.9964	0.9981
313	0.02	28.4	0.9548	0.9771
Dubnin-Radushkevich constants				
T(K)	Q _s (mg/g)	E (kJ/mol)	R ₁ ² (linear)	R ₂ ² (non-linear)
293	12.5	0.28	0.9517	-0.9755
303	12.4	0.23	0.9526	-0.9760
313	12.0	0.15	0.9592	-0.9793
Temkin constants				
T(K)	K _T (l/mg)	B ₁	R ₁ ² (linear)	R ₂ ² (non-linear)
293	0.40	5.36	0.9938	0.9968
303	0.32	5.57	0.9939	0.9969
313	0.25	5.55	0.9855	0.9927

Table 5.4: Isotherm error analysis for adsorption of p-xylene onto RHA

293K		
	HYBRID	MPSD
Freundlich	4.050	3.379
Langmuir	1.729	1.476
D-R Isotherm	12.890	12.174
Temkin	5.085	3.642
303K		
	HYBRID	MPSD
Freundlich	5.054	3.746
Langmuir	1.596	1.378
D-R Isotherm	12.990	4.930
Temkin	12.143	4.085
313K		
	HYBRID	MPSD
Freundlich	6.184	5.374
Langmuir	5.335	4.232
D-R Isotherm	22.197	21.9987
Temkin	5.894	4.689

Table 5.5 : Thermodynamics parameters for adsorption of p-xylene by RHA

Co(mg/l)	-ΔH° (kJ/mol)	-ΔS° (J mol⁻¹ K⁻¹)	-ΔG° (kJ/mol)		
			298K	303K	313K
50	17.7	44.09	4.86	4.42	3.98
100	13.1	30.49	4.19	3.88	3.58
125	14.4	36.01	3.85	3.49	3.13
150	10.8	25.06	3.50	3.25	3.00

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions were drawn from the present study:

- RHA is feasible alternatives for the removal of p-xylene from waste water through adsorption process as the removal efficiency is around 80 % for RHA.
- The time consumption for the process is approximately 60 min .
- The various optimum condition for the process to be carried out are
pH=3.5±0.2; Time=60 min; adsorbent dosage =9 g/L
- The adsorption process is found to be followed pseudo second order kinetics, an indication of chemisorptions mechanism, fitted better with the experimental data than the intra-particle diffusion and pseudo first- order model.
- Freundlich and Langmuir isotherm are best fitted for the adsorptive removal.
- The adsorption capacity was found to decrease with increasing temperature, indicating the exothermic nature of the process.
- The negative value of ΔG suggest that the process is quite feasible on thermodynamic point of view.

6.2. Recommendation

- Further pilot scale studies are required to evaluate the suitability of RHA for the adsorptive removal on plant scale.
- Packed bed studies can be carried out to examine the effect of bed height, diameter, flow rate and concentration of adsorbate.
- Many more combination of different adsorbents could be tried to get much better result.

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