

# DETOXIFICATION OF PULP AND PAPER MILL EFFLUENT USING ADSORPTION

**A DISSERTATION**

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

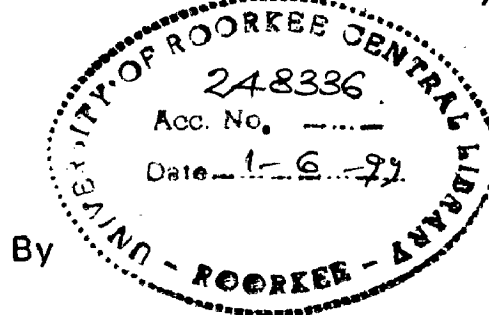
*of*

**MASTER OF ENGINEERING**

*in*

**CHEMICAL ENGINEERING**

**(With Specialization in Industrial Pollution Abatement)**



By

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**MARCH, 1999**

## **CANDIDATE'S DECLARATION**

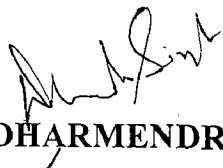
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I hereby declare that the work which is being presented in the dissertation entitled "**DETOXIFICATION OF PULP AND PAPER MILL EFFLUENT USING ADSORPTION**", in partial fulfilment of the requirements for the award of the degree of **MASTER OF ENGINEERING** in Chemical Engineering with specialization in **INDUSTRIAL POLLUTION ABATEMENT**, submitted in the Department of Chemical Engineering, University of Roorkee, is an authentic record of my own work carried out by me, under the supervision and guidance of **Dr. I. D. Mall**, Assistant Professor, Department of Chemical Engineering, University of Roorkee, Roorkee, from July 1998 to March 1999.

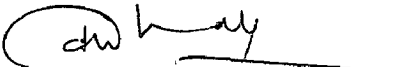
The matter embodied in this dissertation has not been submitted by me for the award of any other degree.

**Date :** March 31, 1999

**Place :** Roorkee

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

  
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(DHARMENDRA SINGH)

## ABSTRACT

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Paper industry has played an important role in the development of human civilization. Worldwide demand for paper is likely to rise continuously due to both the population growth and the improvement in quality of life. There is huge consumption of water in the paper industry resulting in equal amount of waste water and it is amongst the highly polluting industries. It is included in the list of industries notified by the Ministry of Environment and Forest, Government of India, requiring Environmental Impact Assessment and clearance.

There are various toxic compounds present in the effluent emanating from the pulp and paper mills employing chlorine or chlorine dioxide in the bleaching process. Now environmental concern has shifted from traditional parameters e.g. BOD, COD, TSS to chlorinated organic compounds containing large number of chlorinated phenols. These compounds are highly irritant and suspected carcinogens.

Chemical and biological methods are being used for the treatment of pulp and paper mill effluent. Adsorption by activated carbon has been commonly used for effective and efficient removal of the pollutants. However, due to 10-15 % loss during regeneration and high cost of activated carbon, various low cost adsorbents are being tried.

In the present work bagasse flyash and rice husk flyash have been used as low cost adsorbents for removal of some of the chlorinated phenols present in the bleach plant effluent. Detailed studies have been done using these adsorbents for the removal of 2,4 dichlorophenol and tetrachlorocatechol, two of the toxic compounds present in pulp and paper mill effluent. The experiments were conducted by varying the parameters affecting adsorption - adsorbent dose, pH, contact time and initial concentration. The results obtained were compared with those of using activated carbon as adsorbent for economic evaluation of the process. Adsorption studies were also carried out for removal of 4 chlorophenol and 2, 4, 6 trichlorophenol.

The results and comparisons show that bagasse flyash and rice husk flyash can be used as efficient and economically viable adsorbents for toxicity removal.

## NOMENCLATURE

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$C_e$	Concentration of adsorbate solution at equilibrium, ( $\text{mg l}^{-1}$ )
$k$	Adsorption rate constant, ( $\text{min}^{-1}$ )
$k'$	Intraparticle diffusion rate constant, ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )
$K_A$	Langmuir isotherm constant, ( $\text{l mg}^{-1}$ )
$K_F$	Freundlich isotherm constant, ( $(\text{mg l}^{-1})^{-1/n} \cdot 10^{-3}$ )
$n$	Freundlich isotherm constant
$q$	Amount of adsorbate adsorbed per unit amount of adsorbent at time $t$ , ( $\text{mg g}^{-1}$ )
$q_e$	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, ( $\text{mg g}^{-1}$ )
$q_m$	Limiting adsorbing capacity, ( $\text{mg g}^{-1}$ )
$t$	Time, (min)

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## INTRODUCTION

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### 1.0 GENERAL

Paper industry has been playing an important role in the development of human civilization and per capita consumption of paper is a major indicator of the level of civilization. It assumes nearly 3.5% of the world's industrial production and 2% of the world's trade. Worldwide demand for paper is projected to continue to rise due to both, the population growth and the development of higher living standards [Gopalratnam, 1997]. Current paper production all over the world is around 270 million tonnes with per capita consumption of 45 kg. Indian paper industry has been growing at the rate of 5.5% per annum. With the present installed capacity of 4.4 million tonnes, the installed capacity is likely to be 5.0 million tonnes in 2000 A.D. The present per capita consumption in India is 3 kg which is likely to be 4 kg by 2000 A.D.

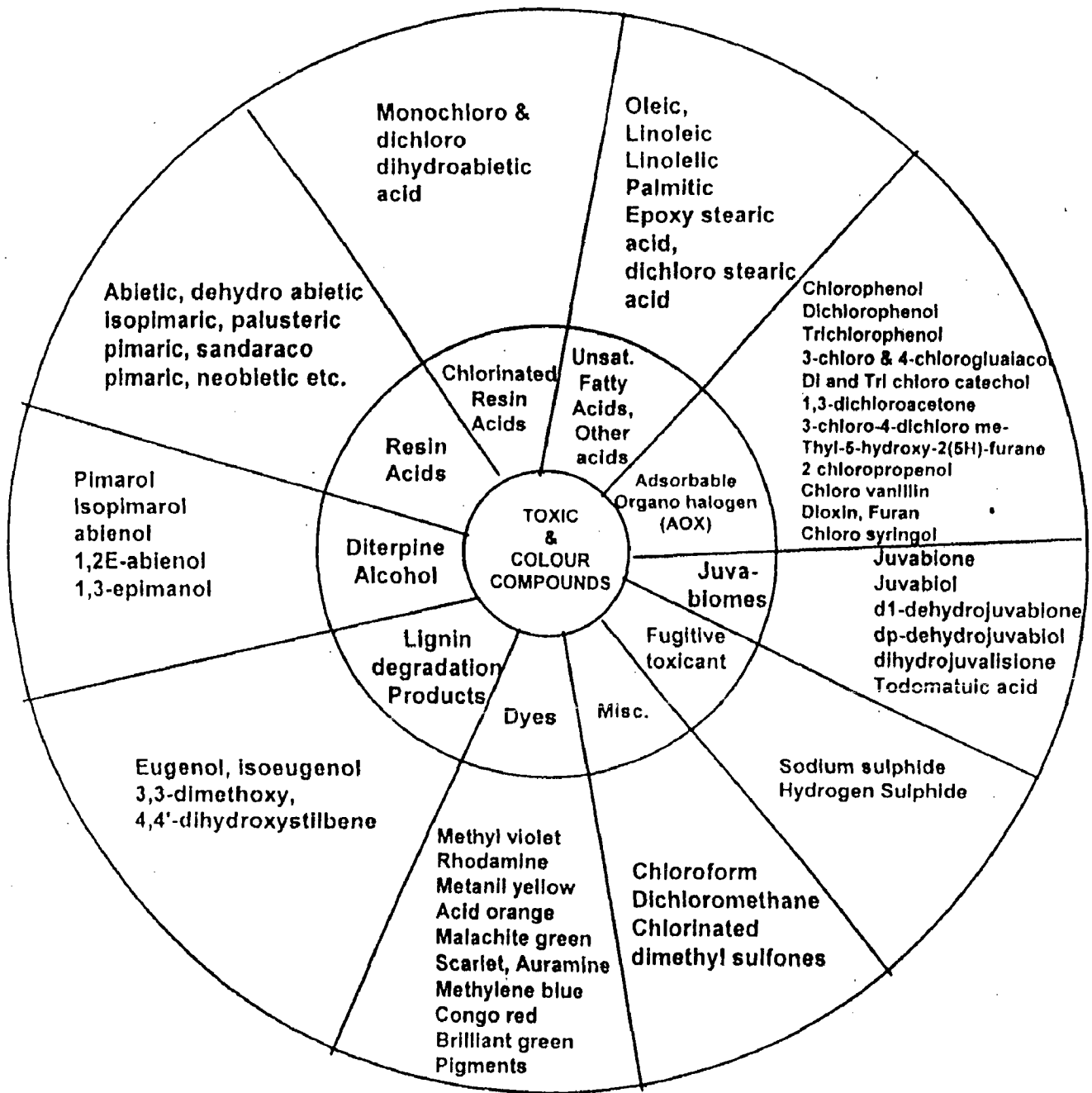
Paper industry consumes huge amount of water and present intake of Indian pulp and paper industry is considerably higher than the figure in developed countries. With projected capacity of 5.0 million tonnes by 2000 A.D., the water requirement of the industry is likely to be about 1250 million cubic meter with generation of almost equal amount of wastewater, having BOD, COD, colour, odour, pH, suspended solids, foam and toxic compounds comprising chlorinated organics.

### 1.1 WASTEWATER GENERATION PATTERN AND CHARACTERISTICS OF WASTEWATER

Paper industry consumes huge amount of water at various stages of operation. During the processing of pulp and paper the pulp is diluted and then thickened about ten times at various stages. The water use pattern in paper industry vary widely depending upon the type of paper mills – small or large, waste paper based, agro based or large integrated mills based on wood, bamboo or waste paper. The water consumption per tonne of the pulp varies from 100 to 350 m<sup>3</sup>.



**Fig. 1.1 Waste Water Sources in Pulp and Paper Mill**



**Fig. 1.2 Major Toxic and Colour Compounds in Pulp and Paper Mill Effluent**

Wastewater generation from paper mills which vary widely ranging from 100 to 350 m<sup>3</sup> per tonne of paper has been the cause of major concern because of colour and toxicity. Wastewater sources, pollution load and their characteristics from a pulp and paper mill are given in Table 1.1 and Fig. 1.1. A relatively large amount of pollutants have been identified in pulp and paper mill effluent. Major toxic and colour compounds identified in pulp mill effluent are given in Fig. 1.2 [Sastry, 1986; Kinae et al, 1981; Walden and Howard, 1981; Walden and Howard, 1997].

**Table 1.1 : Characteristics of Wastewater from Pulp and Paper Mill**

Parameter	Pollution Load		
	<i>Large Integrated Mill</i>	<i>Agro Based Mill</i>	<i>Waste Paper Based Mill</i>
kg/tonne of paper :			
COD (mg/l)	150-300	1000-2000	50-100
BOD (mg/l)	50-80	200-400	20-50
Suspended solids (mg/l)	150-300	300-400	250-350
Wastewater generation m <sup>3</sup> /tonne of paper	200-350	200-250	70-150
Lignin kg/tonne of paper	40-50	200-350	–
Sodium kg/tonne of paper	–	60-150	–

In exercise of the power conferred by section 6 and 25 of Environmental Protection Act 1986 , standards for emission or discharge for environmental pollutants and for minimization of wastewater generation, have been set up for protecting and improving the quality of environment. Permissible limits for discharge of total organic chlorine compounds have also been included. The MINAS for pulp and paper industry are given in Table 1.2 [CPCB, 1995]. Decolourisation and detoxification of pulp and paper mill effluent are the two major problems which are posing serious environmental threat.

**Table 1.2 : MINAS for Pulp and Paper Mills**

**MINAS for Small Pulp and Paper Mill**

<i>Parameter</i>	<i>Discharged on to surface water</i>	<i>Disposal on land</i>
pH	5.5-9.0	5.5-9.0
Suspended solids, mg/l	100	100
BOD, mg/l	30	100

**MINAS for Large Pulp and Paper Mills, Capacity > 24,000 Tonnes/annum**

<i>Parameter</i>	<i>Concentration</i>
pH	7.5-8.5
Suspended Solids, mg/l	50
BOD, mg/l	30
COD, mg/l	350
TOCl, kg/tonne of paper	2

**Total wastewater generation per tonne of paper**

<i>For capacity above 24,000 tonnes/annum :</i> 200 cubic metre (100 cubic metre for mills established after 1992).
<i>For capacity below 24,000 tonnes/annum :</i> Agro Based : 200 cubic metre (150 cubic metre for mills established after 1992). Waste paper Based : 75 cubic metre ( 50 cubic metre for mills established after 1992).

**MINAS for Caustic Chlorine Plant**

<i>Parameter</i>	<i>Concentration</i>
pH	5.5-9.0
Mercury in the final effluent, mg/l	0.01
Mercury bearing wastewater generation	10 kilo-litre/tonne of caustic produced

**1.1.1 Toxicity of Pulp and Paper Mill Effluent**

As the demand for a bleached chemical pulp with a high and stable brightness, good cleaning and good strength properties increased , so did the need to improve production capacity and upgrade existing bleach plants. In the quest to improve the efficiency of pulp bleaching, methods to curtail the effluent load emanating from the bleach plant are also being considered.

With the discovery of dioxins and furans in bleach plant effluent, now the environmental concern has shifted from traditional BOD, COD, TSS, colour to

chlorinated organic compounds [Wilson, 1992]. There is a growing concern over the use of chlorine chemicals in bleached pulp, which has led to products offered as total chlorine free (TCF) or elemental chlorine free (ECF) pulp and paper [Clapp et al., 1996].

Most of the chlorinated organic substances in the effluent originate in the chlorination and alkali extraction stages of a kraft bleach plant. These effluent contain a broad range of chlorinated organics extending from lower molecular weight to high molecular weight compounds such as chloroform to complex lignin derivatives. The formation of these substances is mainly attributed to the consumption of elemental chlorine originating from chlorine and/or chlorine dioxide [Kringstad and Lindstorm 1984].

External treatment at bleach kraft pulp mills has most commonly involved, aerobic treatment of the combined mill effluent in either aerated lagoons or activated sludge plants. The removal of chlorinated phenols in these processes typically ranges from 50-70% [Wayne et al., 1993].

### 1.1.2 Colour in Pulp and Paper Mill Effluent

Effluent colour has been a major nuisance as even after primary and secondary treatment considerable colour persists in the effluent. Various sources of colour in pulp and paper mill effluent are given in Table 1.3. . Caustic extraction stage is responsible for 60-70% of kraft mill effluent colour loading

**Table 1.3 : Sources of Colour in Pulp and Paper Mills**

<b>Units</b>	<b>Sources</b>
Digester House	Leakage from pulp gland, non-return valves, spills from liquor storage tanks and entrainment with back pressure relief gases
Washing and Screening	Leakages from pump glands, pipe lines, overflows, carryover during washing, screening and centricleaner rejects, unbleached pulp decker wash.
Bleaching section	Chlorination stage, caustic extraction stage, hypochlorite stage liquors

Stock preparation	Unbleached pulp decker wash, centricleaner reject, save all discharge of dye colour, wastewater from hog pit pulp washer, dye effluent spillage
Paper machine	Wastewater from wire part and mould part during coloured paper manufacturing
Deinking plant	Deinking plant wastewater containing printing ink, dye colour.
Recovery plant	Leakages from black liquor green liquor and fresh liquor overflows and spills, entrainment from evaporators, evaporator boil out, condenser water, clarifier etc.

A large variety of coloured papers are being manufactured using various types of dyes-acid, basic, direct dyes, optical whitening. Some of the commonly used dyes are methyl violet, rhodamine, malachite, methylene blue, scarlet red, auramine, brilliant green etc. and their quantities varies from 0.6-0.9 kg per tonne of paper depending on the specific requirement of coloured paper [Mall and Upadhyay, 1994]. The dyes bearing wastewater also contain a wide spectrum of heavy metal and other toxic organic pollutants. Dyes are highly persistent as the manufacturer always go for the most stable dye, making the recycling of wastewater more difficult. A number of dyes have been found to be human carcinogens [ Goel and Gupta, 1985].

## 1.2 OBJECTIVES OF THE PRESENT STUDY

Biological processes are cost effective in comparison to physico-chemical processes, however biological process may not be sufficient for the removal of toxicity to desired permissible limits. In general, aerobic microbial processes become less effective in biodegrading compounds as the degree of chlorination increases .Therefore tertiary treatment of the segregated bleach plant effluents which contain a majority of the chlorinated compounds is a potential option for the removal of chlorinated organics.

Some of the tertiary treatment processes for treatment of pulp and paper mill effluent are adsorption, membrane separation process using ultrafiltration, reverse osmosis, coagulation and precipitation , biological treatment using special microbes etc.



Amongst various tertiary treatment processes, adsorption has been found to be most efficient for the removal of most organic compounds in wastewater especially at lower concentrations.

Activated carbon has been most commonly used in adsorption. However, high cost of activation and 10-15% loss in regeneration, have been major deterrents in utilisation of activated carbon in developing countries. During recent years, low cost adsorbents like flyash, rice husk carbon, wood, bagasse flyash, bottom ash etc. have been used for treatment of wide variety of wastewaters. A critical review of this has been presented by Mall et al. [1996].

The present study has been taken with the objective to investigate the suitability of low cost adsorbents for removal of some of the chlorinated phenolic compounds present in bleach plant effluent. Adsorption capacity of these low cost adsorbents have also been compared with that of activated carbon.

## TOXICITY OF PULP AND PAPER MILL EFFLUENT

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### 2.0 GENERAL

In this chapter the toxic constituents and their sources in the pulp mill effluents are discussed. This is preceded by a brief introduction to the process technology used in paper manufacturing.

### 2.1 PROCESS TECHNOLOGY FOR PULP AND PAPER MANUFACTURE

Pulp and paper making process is a combination of five major steps, namely

Raw material preparation	Debarking and chipping
Pulping	Separation of fibres, screening and bleaching
Stock preparation	Imparting suitable properties for making paper
Paper making	Conversion of pulp from stock preparation into a sheet of paper
Chemical recovery	Concentration of spent liquor, burning and causticising of liquor

Various process technologies involved in pulping processes are kraft pulping, soda and lime pulping, sulfite pulping, NSSC, mechanical-pulping-stone ground, thermo-mechanical, cold soda refiner, mechanical pulping, and refiner mechanical pulping. Various bleaching sequences used in Indian paper industry are CEH, CEHH, CEHD.

All the large integrated paper mills in India are based on kraft pulping process. The raw materials used are bamboo, wood and waste paper. The small paper mills which account for about 50% of total production are based on soda pulping processes and use agricultural residues and waste paper. The newsprint mills are based on kraft pulping and various mechanical processes utilising bamboo, wood, bagasse, etc. The

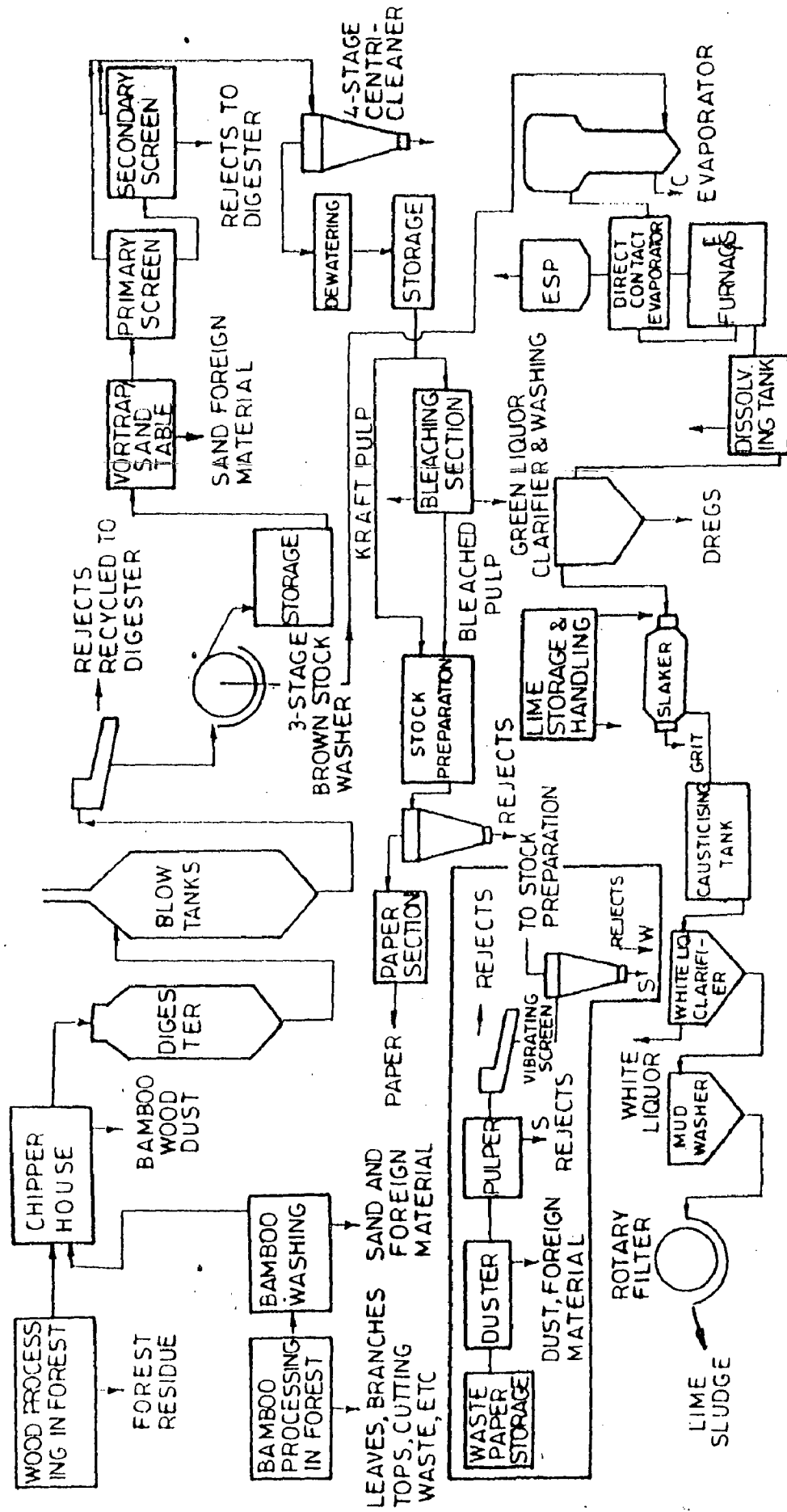


Fig. 2.1 Pulp and Paper Manufacturing Process

other raw materials used are caustic soda, chlorine, salt cake, talcum powder, rosin, mineral acids, dyes, pigments, etc. Process flow diagram for manufacture of pulp and paper is shown in Fig. 2.1.

Utilisation of more and more waste paper in order to meet the demand of raw material has triggered the development of deinking processes which have found wide applications. The processes involved in deinking are flotation and washing. Deinking processes also cause serious pollution problems, resulting in toxicity.

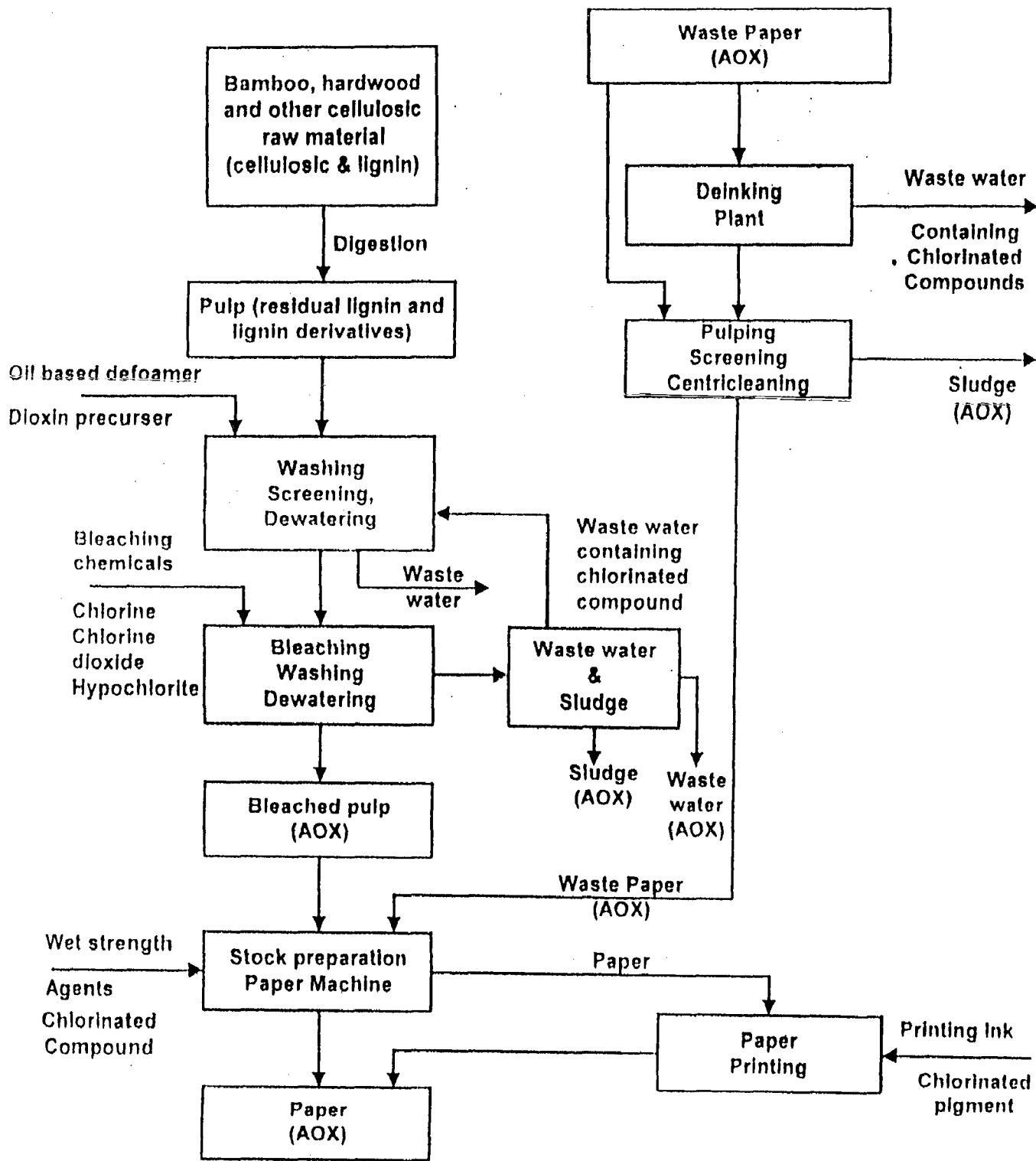
## **2.2 TOXICITY OF PULP AND PAPER MILL EFFLUENT**

Toxicity of pulp mill effluent has been a cause of major concern due to presence of large number of high molecular weight organic compounds including the AOX(adsorbable organic halides).Pulping and bleaching operations account for the greatest concentration of coloured lignin derivatives and toxic compounds. Discharge of colour and toxic compounds to water stream is more serious in India due to non-recovery of chemicals from black liquor in small paper mills, partial/non-treatment of effluents and use of non-conventional raw materials.

### **2.2.1 Chlorinated Organics Sources, Formation and Toxic Effects**

It has been well established that a series of chlorophenols are formed during bleaching process. The nature and extent of formation of chlorinated organics is determined primarily by the residual lignin content in the pulp and the type of bleaching chemical employed. Chlorinated organics discharged from a bleached kraft operation consist of a complex mixture of organic compounds. The major fraction being of high molecular weight compounds. These substances may differ significantly in molecular weight and content of functional groups.

The formation of AOX and other chlorinated polyphenols is largely dependent on the type of bleaching chemicals besides residual lignin. The formation of chlorinated phenols is strongly affected by the chlorine multiple. The AOX formed increases exponentially above a chlorine multiple of 0.05 which corresponds to about 10-15 kg. of chlorine/tonne of pulp having Kappa no. 20.This is one reason why the AOX



**Fig. 2.2 Pathways for AOX in Pulp and Paper Manufacture**

formation is more predominant in bleaching sequences involving elemental chlorine like  $\text{Cl}_2$ ,  $\text{Ca}(\text{OCl})_2$  etc.

The formation of AOX and chlorinated organic compound is largely dependent upon the type of bleaching sequences and AOX formation is roughly determined from the charge of chlorine, chlorine dioxide and hypochlorite [Srinath and Bowen, 1995].

$$\text{AOX} = k_1 [C+D/k_2]$$

$$\text{AOX} = 0.11 [1 + 0.5 H + 0.2 D]$$

$$\text{AOX} = \text{AOX concentration}$$

$$k_1 = 0.1$$

$$k_2 = 5$$

C = Chlorine charge (as kg active chlorine/ tonne of pulp)

D = Chlorine dioxide charge (as kg active chlorine/ tonne of pulp)

H = Sodium hypochlorate charge (as kg active chlorine/ tonne of pulp).

Pathways for AOX in the process of pulp and paper manufacture are shown in Fig. 2.2 [Welker and Schmitt, 1997]. Although, in developed countries, considerable efforts has been made for reducing the toxicity of pulp and paper mill effluent, however, the problem has yet to be tackled effectively in India, as conventional bleaching process CEH or CEHH sequences utilising chlorine and hypochlorate are being used by majority of the paper mills in India. With high chlorine consumption, the situation is alarming as AOX formation is more predominant in bleaching sequences involving elemental chlorine. Economic feasibility of various ECF and TCF technology for small capacity mills which are located all over the country with wide variation in raw materials and process conditions is to be evaluated. The regulatory values for AOX are given in Table 2.1 [Mall, 1997].

**Table 2.1: Regulatory Values of AOX**

<i>Country</i>	<i>AOX Kg/AD Tonne</i>	<i>Target</i>
Austria	0.5	
Finland	1.4	1995
Germany	1.0	1989
Canada		
Alberta	1.0	(new mills)
British Columbia	2.5	(by 1992)
		(by 1995)
Ontario	1.5	(by 2002)
Quebec	No AOX (2002)	(by 1992)
Australia	2.5	(by 1994)
Yearly moving average	1.5	
Weekly maximum	1.0	
Sweden	2.5	
	1-2	(1993)
	1-0.5	(1995)
	0.3-0.5	(2000)
Portugal	1.5	
Helsinki Convention	2-3	
India TOCI	2.0	

### 2.2.2 Toxic Constituents

Chlorinated organic matter emitted from kraft mills employing chlorine or chlorine dioxide in the bleaching process has increasingly become an important environmental concern. Virtually all of the chlorinated organic matter produced at bleached kraft pulp mills originate in the bleaching process with the initial chlorination and extraction stages contributing the largest quantities. These wastewaters contain a broad range of chlorinated organics extending from low molecular weight compounds such as chloroform to complex lignin derivatives [Kringstad and Lindstorm, 1984]. A class of compounds of particular interest is the chlorinated phenolics since they have been shown to be deleterious to the environment. For example, trichloroguaiacol and

**Table 2.2 : Toxic Compounds Detected in Bleach Plant Effluent**

Toxic compounds detected in Bleach plant effluents						
Raw material	Bleaching stage					
Bamboo	C Stage	2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 2,6-Dichlorophenol 2,5-Dichlorophenol				
	E Stage	2,4-Dichlorophenol 3,4-Dichlorophenol 3,4-Dichloroguaiacol 6-Chloroguaiacol 2,4,6-Trichlorophenol 2,3,4-Trichlorophenol 4,6-Dichloroguaiacol 3,4-Dichloroguaiacol 2,3,4-Trichlorophenol 3,4,6-Trichloroguaiacol 3,4,5-Trichloroguaiacol 3,6-Dichlorocatechol 3,5-Dichlorocatechol 3,4,6-Trichlorocatechol 3,4,5-Trichlorocatechol 3,4,6-Trichlorocatechol 2-Chlorosyringaldehyde Pentachlorophenol Tetrachloroguaiacol Trichlorosyringol Tetrachlorocatechol 2,6-Dich.syringaldehyde				
Wheat Straw	C Stage	2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 2,6-Dichlorophenol 2,5-Dichlorophenol				
	E Stage	2,4-Dichlorophenol 2,3-Dichlorophenol 3,4-Dichlorophenol 6-Chloroguaiacol 2,4,6-Trichlorophenol 2,3,4-Trichlorophenol 4,6-Dichloroguaiacol 3,4-Dichloroguaiacol 2,3,4-Trichlorophenol 3,4,6-Trichloroguaiacol 3,5-Dichlorocatechol 3,6-Dichlorocatechol 3,4,6-Trichlorocatechol 3,4,5-Trichlorocatechol 3,4,6-Trichlorocatechol 2-Chlorosyringaldehyde Pentachlorophenol Tetrachloroguaiacol Trichlorosyringol Tetrachlorocatechol 2,6-Dich.syringaldehyde				
Bagasse	C Stage	2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 2,6-Dichlorophenol 2,5(2,4)-Dichlorophenol				
	E Stage	3,4-Dichlorophenol 6-Chloroguaiacol 2,4,6-Trichlorophenol 2,3,5-Trichlorophenol 2,4,5-Trichlorophenol 2,3,4-Trichlorophenol 4,5-Dichloroguaiacol 3,6-Dichlorocatechol Trichlorophenol 4,6-Dichloroguaiacol 3,4-Dichloroguaiacol 4,5-Dichloroguaiacol 3,4,5-Trichloroguaiacol 3,4,6-Trichloroguaiacol 6-Chlorovanillin 3,4,5-Trichloroguaiacol 4,5,6-Trichloroguaiacol 3,4,6-Trichlorocatechol 5,6-Dichlorovanillin 2-Chlorosyringaldehyde Pentachlorophenol 3,4,5-Trichlorocatechol Trichlorosyringol Tetrachlorocatechol 2,6-Dich.syringaldehyde				
Soft Wood	Mixed	2-Chlorophenol 3-Chlorophenol 4-Chlorophenol 2,6-Dichlorophenol 2,4-Dichlorophenol				
	Effluent	3,5-Dichlorophenol 2,3-Dichlorophenol 2,4,6-Trichlorophenol 2,3,6-Trichlorophenol 2,4,5-Trichlorophenol 3,4,5-Trichlorophenol 2,3,5,6-Trichlorophenol 2,3,4,5-Trichlorophenol Pentachlorophenol 4-Chloroguaiacol 4-Chloroguaiacol 4,6-Dichloroguaiacol 3,4,5-Trichloroguaiacol 3,4,5-Trichloroguaiacol 4,5,6-Trichloroguaiacol 3,4,5,6-Tetrachloroguaiacol 4-Chlorocatechol 3,5-Dichlorocatechol 4,5-Dichlorocatechol 3,4,5,6-Tetrachlorocatechol 3,4,5-Trichlorovanillin 5,6-Dichlorovanillin				
Khai Grass	C Stage	4-Chlorocatechol 2-Chlorophenol 3-Chlorophenol 2,6-Dichlorophenol 2,5-Dichlorophenol				
	E Stage	2,4-Dichlorophenol 6-Chloroguaiacol 2,4,6-Trichlorophenol 2,3,5-Trichlorophenol 2,3,4-Trichlorophenol 4,6-Dichloroguaiacol 3,4-Dichloroguaiacol 4,5-Dichlorocatechol 3,6-Dichlorocatechol 3,4,6-Trichloroguaiacol 6-Chlorovanillin 3,4,5-Trichloroguaiacol 3,4,5-Trichlorocatechol 3,4,5-Trichlorocatechol Tetrachloroguaiacol 2,6-Dichlorocatechol 2,6-Dichlorocatechol 3,4,5-Trichlorocatechol Tetrachloroguaiacol 3,4,5-Trichlorocatechol Tetrachlorocatechol 2,6-Dichlorocatechol 2,3,4-Trichlorophenol 3,5-Dichlorocatechol 3,6-Dichlorocatechol 3,4,6-Trichlorocatechol 3,4,5-Trichlorocatechol 3,4,6-Trichlorocatechol Tetrachlorocatechol				
<b>Acids</b>						
	Nonadecanoic	Heptadecanoic	Oleic	Linolenic	Stearic	Pimaric
	Isopimaric	Dihydroisopimaric	Arachidic	Neobiotic	Docosahexaenoic	Henicosanoic
	Chlorodehydroabietic I	Chlorodehydroabietic II	Tricosanoic	12,14-Dichlorohydroabietic	Lignoceric	
	9,10,12,13-Tetrachlorostearic					



**Table 2.3 : Characteristics of 2 Chlorophenol and 4 Chlorophenol**

S. No.	Parameters	2 Chlorophenol	4 Chlorophenol
1	Formula	C <sub>6</sub> H <sub>4</sub> OHCl	C <sub>6</sub> H <sub>4</sub> OHCl
2	Description	Light amber liquid	Light pale yellow crystals
3	Toxicity	Mildly irritating to skin and can cause CNS depression, kidney and liver damage has been reported in experimental animals, harmful to respiratory system	High irritant, high ingestion, high inhalation and can cause kidney and liver damage, harmful to respiratory system
4	Acute Oral LD <sub>50</sub> mg/kg Male Mice Female Mice	347 345	1373 1422
5	Odour threshold	0.00033 – 0.002 mg/l	0.033 – 0.25 mg/l
6	Taste threshold	0.0001 – 0.006 mg/l	1 – 1.35 mg/l
7	Fire Hazards	Moderate when exposed to heat or flame	Moderate when exposed to heat or flame
8	Disastrous Hazards	Dangerous, can react with oxidising material	Dangerous
9	Disaster	When heated to decomposition emits highly toxic fumes and can react vigorously with oxidising agent	

**Table 2.4 : Characteristics of 2, 4 Dichlorophenol, 2, 6 Dichlorophenol and 3, 5 Dichlorophenol**

S. No.	Parameters	2, 4 Dichlorophenol	2, 6 Dichlorophenol	3, 5 Dichlorophenol
1	Formula	C <sub>6</sub> H <sub>3</sub> OH Cl <sub>2</sub>	C <sub>6</sub> H <sub>3</sub> OH Cl <sub>2</sub>	C <sub>6</sub> H <sub>3</sub> OH Cl <sub>2</sub>
2	Description	Colourless crystals	Needles	-
3	Mol. wt.	163	163	163
4	m. p.	45°C	56 - 58°C	67 - 69°C
5	b. p.	210°C	211°C	233°C
6	Flash pt.	237°F (113°C)	-	-
7	Sp. gr.	1.383 at 60°C/ 25°C	-	-
8	Solubility	4,500 mg/l at 25°C, 4600 mg/l at 20°C	-	-
9	Toxicity	Cancer suspect agent toxic moderately toxic by skin absorption Causes burns	Corrosive	Irritant
10	Acute Oral LD <sub>50</sub> mg/kg			
	Male Mice	1276	2198	2643
	Female Mice	1352	2120	2389
11	Odour threshold	Av. 0.21 mg/l Range 0.02 - 1.35 mg/l	0.003 mg/l	-
12	Taste threshold	0.008 - 0.02 mg/l	0.002 mg/l	-
13	Conc. causing taste in fish	0.005 mg/l	-	-
14	TOC	0.002 mg/l	-	-

**Table 2.5 : Characteristics of 2, 4, 5 Trichlorophenol and 2, 4, 6 Trichlorophenol**

S. No.	Parameters	2, 4, 5 Trichlorophenol	2, 4, 6 Trichlorophenol
1	Formula	C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> OH	C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> OH
2	Description	Colourless needles or grey flakes	Colourless needles or yellow solid. Strong phenolic odour.
3	Mol. wt.	197.5	197.5
4	m. p.	67 - 69°C	68°C
5	b. p.	248°C/ 740 mm	244.5°C
6	Sp. gr.	1.678 at 25° / 4° C	1.490 at 75° / 4° C
7	Vap. Pressure	1 mm at 72°C	1 mm at 76.5°C
8	Solubility	Practically insoluble in water	800 mg/l at 25°C 2430 mg/l at 96°C (practically insoluble in water)
9	Toxicity	No adverse effect at 500 mg/kg body wt. Cancer suspect agent, irritant	Cancer suspect agent, Toxic Irritating to eyes & skin
10	Acute Oral LD <sub>50</sub> mg/kg	0.821 g/ kg body wt.	820 mg/ kg, (in rats)
11	Odour threshold	0.011 - 0.333 mg/l	0.10 to > 1.0 mg/l

**Table 2.6 : Characteristics of 3, 4, 5, 6 Tetrachlorocatechol and Pentachlorophenol**

S. No.	Parameters	3, 4, 5, 6 Tetrachlorocatechol	Pentachlorophenol
1	Formula	$C_6Cl_4(OH)_2$	$C_6Cl_5OH$
2	Description	Colourless anhydrous crystals	White monoclinic, crystalline solid, technical grade dark grey to brown
3	Mol. wt.	265.91	266.35
4	m. p.	193 - 195°C	188 - 191°C
5	b. p.		310°C (decomposes)
6	Sp. gr.		1.978 at 25° / 4° C
7	Vap. density		9.20
8	Vap. Pressure		0.00011 mm at 20°C
9	Solubility		5 mg/l at 0°C, 14 mg/l at 20°C, 35 mg/l at 50°C, 85 mg/l at 70°C
10	Toxicity	Toxic, Irritant	Painful irritation to the eyes and upper respiratory tract at 1.0 mg/m <sup>3</sup>
11	Acute Oral LD <sub>50</sub> mg/kg Rabbit Rat		70-100 mg/kg 27-28 mg/kg
12	96 hr LC <sub>50</sub>	For sockeye salmon 0.48 mg/l	For goldfish small size 0.247 mg/l large size 0.190 mg/l

tetrachloroguaiacol are known to have median lethal concentrations (96-h LC<sub>50</sub>) to rainbow trout falling within the ranges of 0.1-1.0 and 0.2-0.4 mg/L, respectively [Leach, 1980]. In addition, these compounds are known to exert sublethal chronic toxicity at lower concentrations. Table 2.2 shows the various toxic compounds identified in the bleach plant effluent using bamboo, bagasse, wheat straw, soft wood and grass as raw materials. Characteristics of some of the chlorinated phenolic compounds are given in Tables 2.3-2.6 [Aldrich, 1990; Fawell, 1989; Sax, 1963; Verschueren, 1977].

Of the 30 chlorophenolic compounds on the analytical target list, only 20 were detected regularly by Wayne et al [1993] in the influents or effluents from the reactors. Typical concentration of chlorinated phenolic compounds in bleach plant effluent are given in Table 2.7 [Wayne et al., 1993].

**Table 2.7 : Concentration of Chlorophenolics in Bleach Plant Effluent**

Compound	Mean concentration (µg/L)	Compound	Mean concentration (µg/L)
2-chlorophenol	13.9	4-chloroguaiacol	12.0
4-chlorophenol	23.4	4,5-dichloroguaiacol	57.8
2,6-dichlorophenol	8.3	3,4,5-trichloroguaiacol	237.9
2,4-dichlorophenol	22.1	4,5,6-trichloroguaiacol	38.8
3,5-dichlorophenol	3.9	3,4,5,6-tetrachloroguaiacol	171.8
2,4,6-trichlorophenol	41.6	4-chlorocatechol	20.4
2,4,5-trichlorophenol	6.3	3,5-dichlorocatechol	29.3
pentachlorophenol	2.6	4,5-dichlorocatechol	66.1
6-chlorovanillin	82.1	3,4,5-trichlorocatechol	186.6
5,6-dichlorovanillin	53.8	3,4,5,6-tetrachlorocatechol	96.9

The chlorinated catechols, guaiacols, and vanillins, with individual compound concentrations in the range of 50-250 µg/L, were reported to be present in the greatest quantities. The chlorinated phenols, with the exception of 2,4,6-trichlorophenol, were generally present at lower concentrations. The chlorinated phenolics constituted approximately 1% of the total chlorinated organic matter as measured by the adsorbable organic halogen (AOX) method. The measured influent and effluent chlorophenolic concentrations exhibited substantial variability.

## DETOXIFICATION STRATEGIES

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### 3.0 GENERAL

All detoxification strategies are based on controlling, reducing or eliminating the chlorine and precursors agents responsible for formation of chlorinated organic compounds. The detoxification can be done either by doing changes in the mill process and introducing new technologies or by external control measures by treatment of the toxic effluents.

### 3.1 MILL PROCESS CHANGES

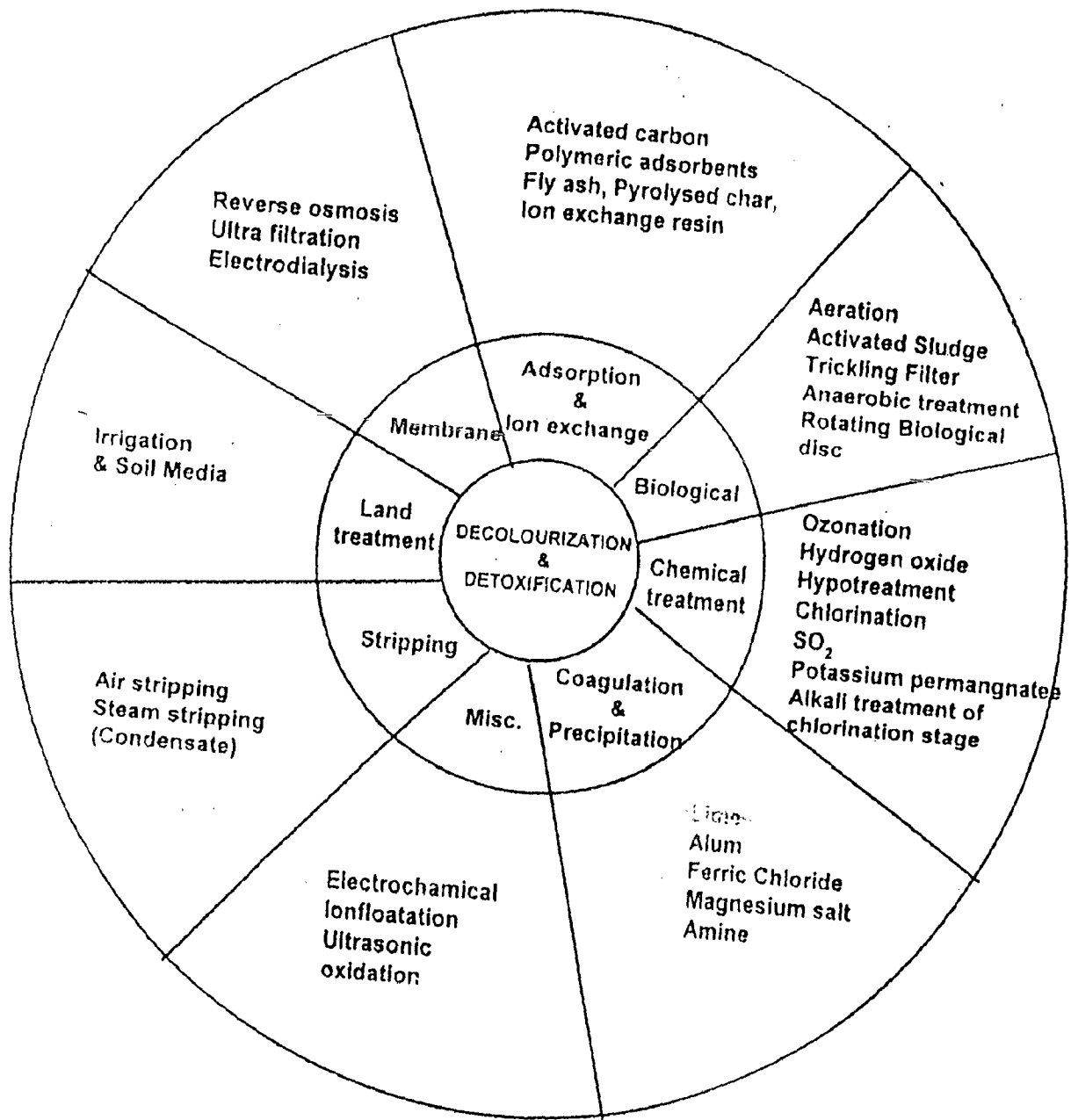
A variety of process changes have been made or are being considered for reduction of toxicity. These changes can be grouped into three major categories:

1. Control outside contamination : Polychlorinated phenolics preservative and oil based defoamers should be avoided as these are responsible for formation of toxic chlorinated compounds.

2. Remove more lignin before bleaching : by (i) improved brown stock washing (ii) use of additive such as anthroquinone and polysulphides, (iii) oxygen delignification, and (iv) extended delignification.

3. Modification of bleaching process chemicals : A number of options exist for mills to lower the amount of chlorinated organics found during bleaching :

- Increasing chlorine dioxide substitution in the chlorination stage
- Lower chlorine factors by
  - (i) increasing chlorine dioxide usage in subsequent stages
  - (ii) using hydrogen peroxide and/or oxygen in early stage.
- Split the chlorine charge amount in several mixtures, increasing the chlorination stage process.
- Lower the final bleached pulp brightness targets.



**Fig. 3.1 Waste Water Treatment Technologies for Decolourisation and Detoxification in Pulp and Paper Mills**

Use of Xylanose enzymes to enhance the bleaching of kraft pulp has been reported. Some of the potential oxidative enzymes are lacasse, lignin peroxidase and manganese peroxide. Some of the benefits of enzyme treatment are saving in bleaching chemical (8 to 15%), improved effluent quality (reduction of AOX 12-25%), decrease in effluent colour, increased brightness, tear strength, pulp throughput [Totan et al, 1995].

With the development of twin roll DPA press, high consistency screening, oxygen delignification and bleaching and ECF & TCF technology, there has been considerable reduction in effluent load with low toxicity and colour. They have resulted in (i) high degree of delignification with higher yield, (ii) saving in bleaching chemicals with less fibre degradation, (iii) better strength of paper, (iv) reduced space, manpower and utility [Mall, 1997].

### **3.2 EXTERNAL CONTROL MEASURES**

Several methods have been used for reducing the bleach plant effluent toxicity as shown in Fig. 3.1. These include physico-chemical treatment processes, chemical oxidation and biological degradation.

The biological treatment methods include activated sludge and its modifications, trickling filters, aerated lagoons and waste stabilization ponds. The chemical oxidation methods use hydrogen peroxide or ozone for oxidation of phenol, and phenolic derivatives.

The physico-chemical processes include adsorption, ion exchange and chemical precipitation. For high strength and low volumes of wastewaters, adsorption using granular/powdered activated carbon has been widely used [Stenzel, 1993; Sorial et al., 1993 and Nabll et al., 1994].

### **3.3 LOW COST ADSORBENTS**

The high cost of activated carbon and loss during regeneration have been the major impediments in its use especially in developing countries [Kumar et al., 1987]. This has led to a search for low cost adsorbents like bagasse flyash, rice husk



flyash, brick kiln ash, cinder, coconut shells, coal flyash, bentonite etc. [Sengupta et al., 1982; Panday et al., 1984; Gupta et al., 1990; Mall et al, 1994; Pandey, 1998; Swamy, 1998].

Bagasse flyash as an adsorbent has been widely used by investigators for treatment of wastewaters. Mall et al. [1994] have used it for removal of organics from cane sugar mill effluents. This has also been used for removal of COD and colour and for treating pulp and paper mill effluent [Mall and Kumar, 1997; Mall and Prasad, 1997]. Pandey [1998] has used bagasse flyash as an adsorbent to remove herbicide 2,4-D. Swamy [1998] has used it for the removal of phenol, resorcinol and o-cresol.

## ADSORPTION FUNDAMENTALS

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### 4.0 GENERAL

In this chapter a brief introduction to the adsorption is presented together with references to waste water treatment using adsorption.

### 4.1 BASIC CONCEPTS

When two phases, at least one of which is liquid or gaseous, come into contact, the composition of these phases close to the phase boundary will differ from the composition observed in regions distant from that boundary i.e. within the bulk of the phases. This will occur even though the phases may be in equilibrium. The increase in concentration in the region where the phases are in mutual contact relative to the concentration in the bulk of the phase is called *adsorption*. Conversely, a concentration decrease may be observed in, for example, solution of electrolytes. This phenomenon is called *negative adsorption*. The phase in the surface of which a substance from the other phase accumulates is termed the *adsorbent* and the adsorbed substance is called the *adsorbate*.

Adsorption is said to be monomolecular when only one layer of particles (molecules, atoms or dissociated fragments) is involved. When adsorbate concentration may vary over a larger distance from the phase boundary the multimolecular adsorption is involved.

Adsorption may be either physical or chemical. The latter is also known as chemiadsorption. In physical adsorption the electron cloud of the substance adsorbed interacts as a whole with the adsorbent and only its polarisation occurs. In chemiadsorption, on the other hand, electron transfer and sharing of electrons (formation of a new molecular orbital) takes place between the adsorbate and the adsorbent as in the case of normal chemical compounds. These two types of adsorption are accompanied by different thermal effects. When adsorbed particles are able to

migrate along the adsorbent surface, mobile adsorption is involved. When migration does not occur, adsorption is said to be immobile.

Physical adsorption is independent of the nature of the adsorbent surface, covering surfaces of rather different chemical character with roughly equal numbers of layers at the same pressure. At temperature close to the boiling point of the adsorbate, physical adsorption is reversible. The molecules do not dissociate on physical adsorption. Physical adsorption take place without any activation energy and it's rate should always be proportional to the first order of pressure. Comparison of physical and chemical adsorption is given in Table 4.1.

**Table 4.1 : Comparison of Physical and Chemical Adsorption**

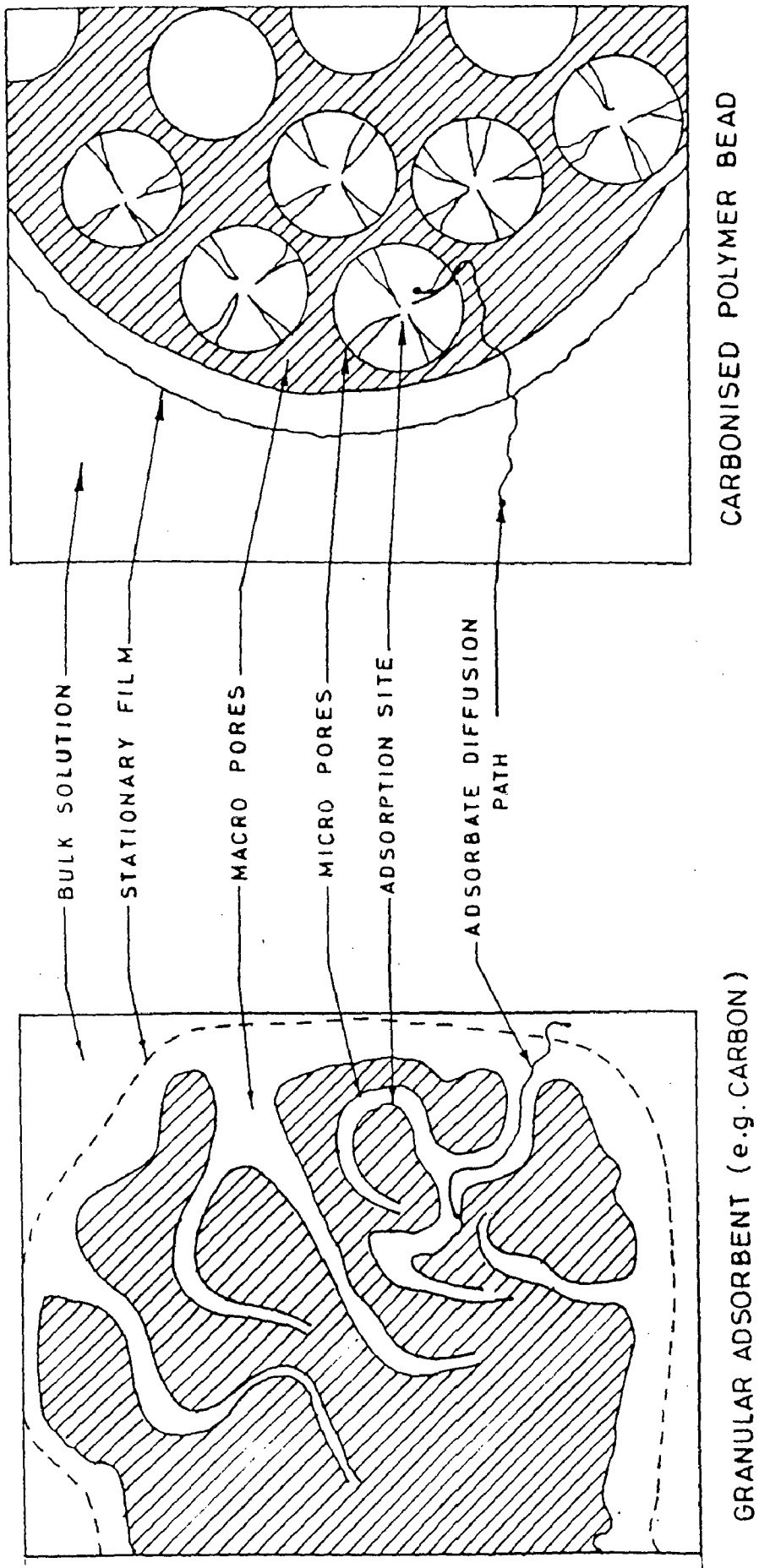
<i>Sl. No.</i>	<i>Physical Adsorption</i>	<i>Chemical Adsorption</i>
1	Heat of adsorption = 5 kcal/mole	Heat of adsorption = 20-100 kcal/mole
2	Adsorption only at temp less than the boiling point of the adsorbate	Adsorption can occur even at higher temp
3	No Activated Energy involved in the adsorption process	Activation Energy may be involved
4	Mono and multi layer adsorption	Almost monolayer adsorption
5	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
6	Extent of adsorption depends upon the properties of adsorbent.	Extent of adsorption depends on both adsorbate and adsorbent
7	Rate of adsorption controlled by resistance mass transfer	Rate of adsorbent controlled by resistance reaction.

## 4.2 ADSORPTION PRACTICES

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

### 4.2.1 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 which depends on the kinetics of adsorption. Agitation is generally provided to ensure proper contact of



**Fig. 4.1 The Dynamic Adsorption Process Showing Partial Cross-Section of Adsorbent and a Portion of the Surrounding Solution.**

the two phases. After the equilibrium is attained the adsorbent is separated from the liquid through any of the methods available like filtration, centrifugation or settling. The adsorbent can be regenerated and reused depending upon the case.

#### **4.2.2 Continuous Adsorption Systems**

In continuous flow systems the solution to be treated is passed through a bed of adsorbent which is either fixed, moving or fluidised state. These columns may be used in several stages if necessary. Continuous counter current columns are generally not used for waste water treatment due to operational problems. Fluidised beds have higher operating costs. In certain cases the column may also function as filter bed retaining suspended solids entering with the feed.

### **4.3 INTRA-PARTICLE DIFFUSION PROCESS**

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites. This process 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 pores to the immediate vicinity of the internal adsorbent surface
3. Adsorption at an appropriate site

It is assumed that the third step occurs very rapidly in comparison to the second step. If the system is agitated vigorously, the exterior diffusional 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 "intraparticle 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 [Allen et al.,1989; Singh et al.,1988; Gupta et al 1990]. A

functional relationship common to most of the treatments of intraparticle transport is that the uptake varies almost proportionally with square root of time.

#### 4.4 ADSORPTION EQUILIBRIA

Adsorbate molecules are simultaneously adsorbed and desorbed from the adsorbent surface. At equilibrium the rate of adsorption equals that of desorption. This equilibrium is of dynamic nature in the sense that the state of equilibrium changes with the change in the several parameters. Equilibrium behaviour is best described by isotherms of adsorption. As the name indicates an isotherm is a plot of amount of solute adsorbed per unit amount of adsorbent against the corresponding equilibrium concentration in the solution phase, temperature remaining constant. Vital conclusions can be drawn from these isotherms which are useful in the designing of adsorption systems.

A number of isotherm equations have been proposed like Freundlich, Langmuir, Brunnauer-Emmett-Teller (BET), Redlich-Peterson, Toth, Radke-Prausnitz etc. Out of these the Freundlich and Langmuir isotherm equations have been widely used by many researchers. These two equations have satisfied the data for various organic contaminants and conventional or unconventional adsorbents.

##### 4.4.1 Langmuir Isotherm

The Langmuir isotherm is based on the following assumptions:

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

Langmuir isotherm is obtained from a kinetic derivation of equilibrium between condensation and evaporation of adsorbed molecules. This gives

$$q_e = \frac{q_m \cdot K_A \cdot C_e}{1 + K_A \cdot C_e}$$

where,  $q_e$  is the amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium;  $C_e$  the concentration of adsorbate solution at equilibrium;  $K_A$  the adsorption

coefficient (a measure of the adsorption energy) and  $q_m$  the amount of adsorbate adsorbed per unit amount of adsorbent required for monolayer adsorption (limiting adsorbing capacity).

The above equation can also be written as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_A \cdot q_m} \left( \frac{1}{C_e} \right)$$

The constants  $K_A$ ,  $q_m$  can be evaluated from a plot between  $1/q_e$  and  $1/C_e$  which gives a straight line.

#### 4.4.2 Freundlich Isotherm

The Freundlich isotherm is expressed as :

$$q_e = K_F C_e^{1/n}$$

where,  $K_F$  is the adsorption coefficient which is a measure of adsorption capacity or fundamental effectiveness of the adsorbent. It is directly related to the standard free energy change. Empirical constant 'n' is a measure of the adsorption intensity. The model can be linearised logarithmically as :

$$\log q_e = (1/n) \log C_e + \log K_F$$

Thus a plot between  $\log q_e$  and  $\log C_e$  is a straight line.

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 studied concentration range. A low 'n' value indicates high adsorption at strong solute concentration.

### 4.5 FACTORS CONTROLLING ADSORPTION

The amount adsorbed by an adsorbent from adsorbate solution is influenced by a number of factors as given below.

#### 4.5.1 Nature of Adsorbent

Both the physical state and chemical nature of adsorbent is important. Adsorbent differs in their specific surface area and affinity for adsorbate. Adsorption capacity is directly proportional to the exposed surface. For the non-porous adsorbents,

of equilibrium. Available adsorption results reveal that the uptake of adsorbate species are fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant.

A study by Deepak et al. [1981] showed these results for adsorption of phenol on activated carbon as well as on unconventional adsorbents. This may be due to the fact that a large number of active surface sites are available for adsorption at initial stages and the rate of adsorption is a function of available vacant sites concentration of available vacant sites decreases and there is repulsion between solute molecules thereby reducing the adsorption rate.

#### **4.5.4 Initial Concentration**

It is generally observed that the removal by adsorption decreases with increasing initial concentration of the adsorbate solution. Khanna and Malhotra [1997], Prakash and Solanki [1993] and Swamy [1998] have reported higher adsorption capacity at lower initial adsorbate solution concentration. Khanna and Malhotra [1977] have suggested that this is due to competition among adsorbate molecules to occupy the vacant active sites of the adsorbent.

#### **4.5.5 Temperature**

Temperature dependence of adsorption is of complex nature. Adsorption processes are generally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature. This trend may be explained on the basis of rapid increase in the rate of desorption or alternatively explained on the basis of Le-Chatelier's principle.

Some of the adsorption studies show increased adsorption with increasing temperature. This increase in adsorption is mainly due to an 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 adsorbent.



#### **4.5.6 Degree of Agitation**

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

## EXPERIMENTAL WORK

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### 5.0 GENERAL

In the present work, 2,4 dichlorophenol and tetrachlorocatechol two of the toxic components present in pulp and paper mill effluent were taken for detailed batch adsorption studies. 4 chlorophenol and 2,4,6 trichlorophenol were also taken for determining the removal efficiency by low cost adsorbents. Batch adsorption experiments were done using activated carbon, baggase flyash and rice husk flyash.

### 5.1 ADSORBATE

Synthetic wastewater solutions were prepared of the above mentioned toxic compounds. Stock solutions of 1 g/l of each were prepared with distilled water, except 2,4,6 trichlorophenol and tetrachlorocatechol which were intially dissolved in acetone and then diluted by adding distilled water. These solutions were used after dilution by adding distilled water as required.

#### 5.1.1 Analytical Measurement

The determination of the concentration of synthetic wastewater solutions was done by finding out the absorbance characteristic wavelength of these using UV-spectrophotometer (Schimadzu, Japan). A standard solution of each compound was taken and the absorbance was observed at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance ( $\lambda_{\max}$ ) was determined from this plot. This was found to be 284, 260, 213 and 230 nm for 2,4 dichlorophenol, tetrachlorocatechol, 2,4,6 trichlorophenol and 4 chlorophenol. Calibration curves were plotted between absorbance and solution concentration of these compounds.

The linearity of calibration curve indicates applicability of the Lambert-Beer's Law. The linear portion of the standard calibration curves were used for the determination of residual concentration of the toxic compounds.

For the calibration curve the concentration range was taken as 0.5 mg/l to 20 mg/l for 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol and 0.5 mg/l to 10 mg/l for 2,4,6-trichlorophenol and tetrachlorocatechol.

## **5.2 ADSORBENTS AND THEIR CHARACTERIZATION**

Three adsorbents namely activated carbon, bagasse flyash and ricehusk flyash were used in the experiments. The adsorptive capacities of bagasse flyash and rice husk flyash which are low cost adsorbents were compared with that of activated carbon.

The physico-chemical characteristics of the three adsorbents were determined using standard procedures as discussed below :

### **5.2.1 Proximate Analysis**

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

### **5.2.2 Density**

Bulk densities of bagasse flyash and activated carbons were determined by following the method prescribed for coal and coke as per IS 1350:1984.

### **5.2.3 Particle Size**

Particle size analysis of the bagasse flyash and the activated carbons was made using standard sieve analysis as per IS 2720 (Pt 4) : 1985.

### **5.2.4 X-ray Diffraction Analysis**

X-ray diffraction analysis of rice husk flyash, bagasse flyash and the activated carbons have been carried out by using Phillips (Holland) diffraction unit (Model PW 1140/90) using copper target with nickel as filter media and K radiation maintained at 1.542 Å. Goniometer and chart speed were maintained at 1° min<sup>-1</sup> and 1 cm min<sup>-1</sup>, respectively.

### 5.2.5 Scanning Electron Microscopy (SEM)

SEM analysis of rice husk flyash, bagasse flyash and the activated carbon were carried out by using LEO 435 VP.

## 5.3 EXPERIMENTAL PROCEDURE

Before using the adsorbent mass for experimental work, it was washed thoroughly with distilled water to remove finer particles and oven dried for 48 hours at 100°C to remove free moisture.

Detailed batch experiments were conducted for 2,4 dichlorophenol and tetrachlorocatechol to study the effect of important parameters - adsorbent dose, initial concentration, pH and contact time. For each experimental run, 50 ml of synthetic waste water solution of known concentration, pH and the known amount of the adsorbents were taken in a 100 ml stoppered conical flask. This mixture was agitated at a constant speed in a temperature controlled shaking water bath maintained at  $30^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . Samples were withdrawn at appropriate time intervals and these were filtered and analysed for the remaining 2,4 dichlorophenol and tetrachlorocatechol concentration using UV-spectrophotometer (Schimadzu, Japan) at 284 nm and 260 nm wavelength respectively. The pH of the adsorbate solutions were adjusted using 1 N ( $36.5 \text{ g l}^{-1}$ ) HCl or 1 N ( $40 \text{ g l}^{-1}$ ) NaOH. The optimum values of adsorbent dose, pH and contact time were thus determined. Adsorption studies were also carried out for the removal of 2,4,6 trichlorophenol and 4 chlorophenol.

For adsorption isotherms, synthetic waste water solutions of different concentrations were agitated with known amount of adsorbent till the equilibrium was achieved. After filtering the residual concentration in the supernatant solution was subsequently determined.

## RESULTS AND DISCUSSIONS

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### 6.0 GENERAL

The detailed discussion on the results of the experiments conducted under the present study are given in this chapter.

These results include

- (i) Characterization of adsorbents
- (ii) Batch adsorption studies
- (iii) Effect of various operating parameters

The characteristics of 2,4 dichlorophenol, tetrachlorocatechol, 2,4,6 trichlorophenol and 4 chlorophenol used in the experiments are given in Tables 2.4 - 2.6.

Experimental data and calculated values required for different plots are given in Appendix – A.

### 6.1 CHARACTERIZATION OF ADSORBENTS

Activated carbon, bagasse flyash and rice husk flyash are the three adsorbents used in the present investigation. Characteristics of adsorbents used include bulk density, particle size and proximate analysis. For structural and morphological characteristics, X-ray diffraction and scanning electron microscope analysis were also carried out.

Characteristics of the three adsorbents are given in Table 6.1 and the particle size distribution are given in Table 6.2 - 6.4.

From Table 6.1, it can be seen that the bulk density of bagasse flyash and rice husk flyash are lower than that of activated carbon. The bulk density of bagasse flyash and rice husk flyash depends upon the combustion efficiency of the boilers in the sugar and rice mills. Table 6.1 also shows that the amount of fixed carbon is very low in rice husk flyash in comparison to activated carbon and bagasse flyash.

The particle size distribution of bagasse flyash and rice husk flyash vary widely from boiler to boiler depending upon make, operational features and



Fig. 6.1(a) Scanning Electron Micrograph of Activated Carbon at 1.73 K Magnification



Fig. 6.1(b) Scanning Electron Micrograph of Activated Carbon at 2.97 K Magnification

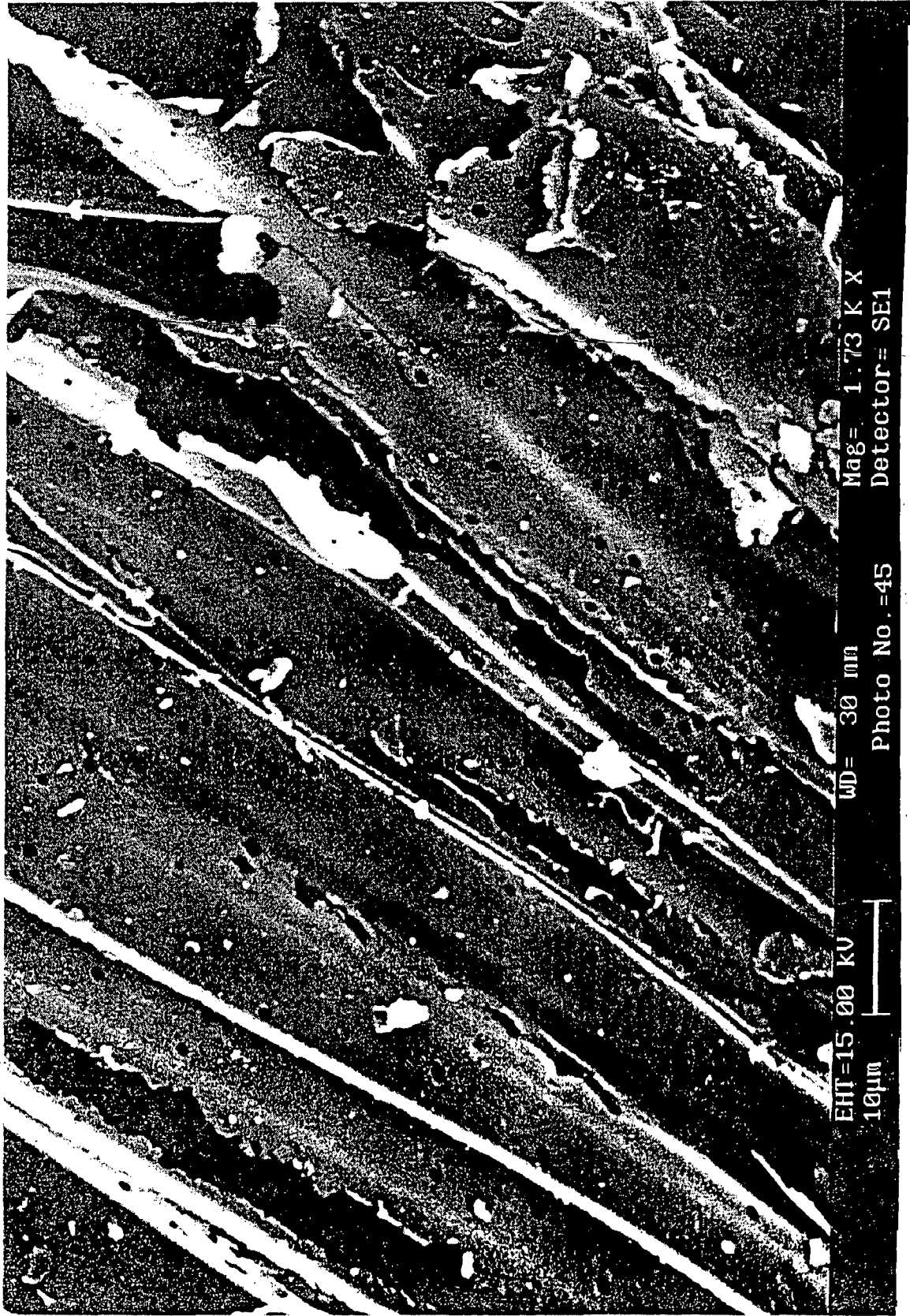


Fig. 6.2(a) Scanning Electron Micrograph of Bagasse Flyash at 1.73 K Magnification





Fig. 6.2(b) Scanning Electron Micrograph of Bagasse Flyash at 2.97 K Magnification

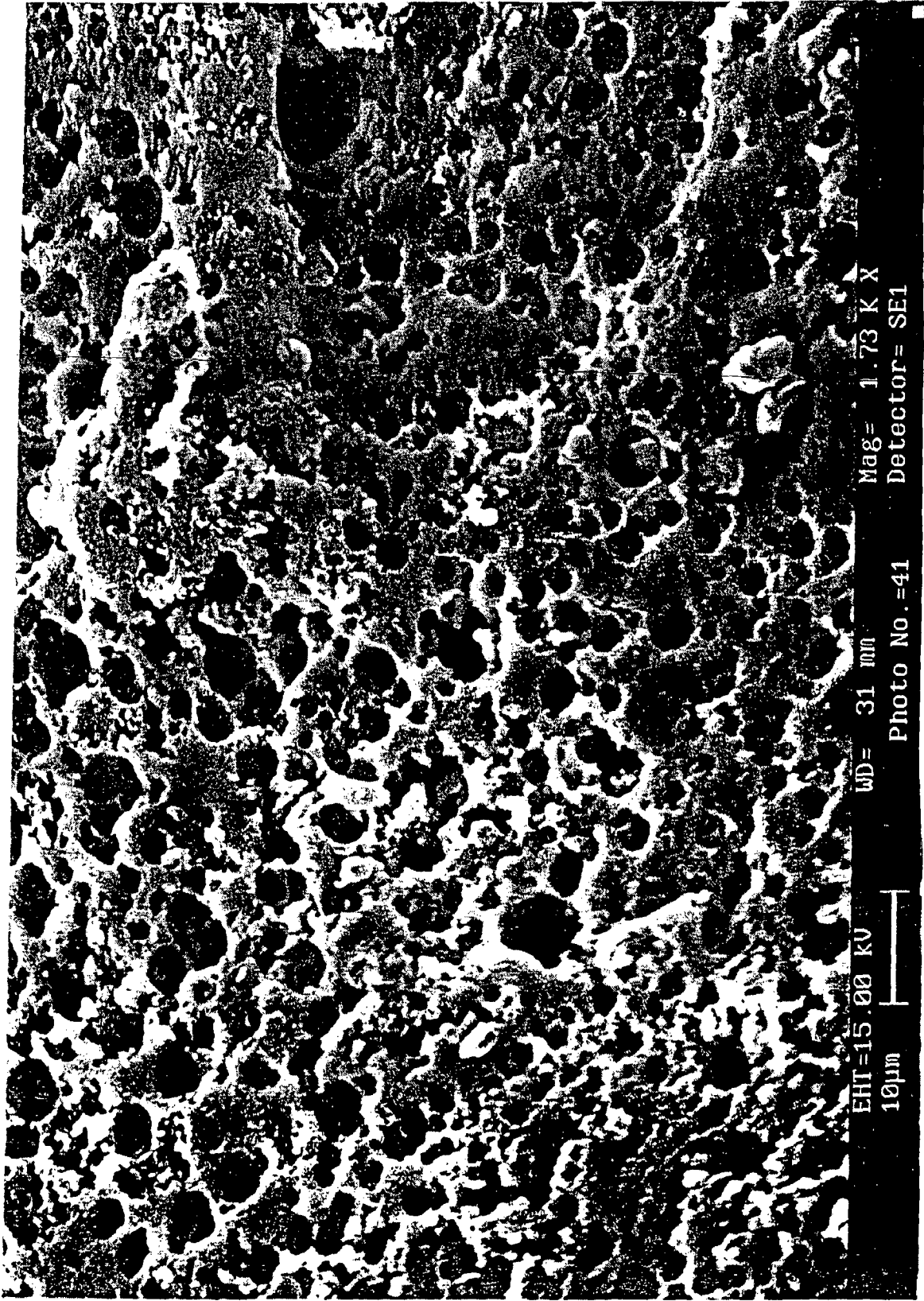


Fig. 6.3(a) Scanning Electron Micrograph of Rice Husk Flyash at 1.73 K Magnification

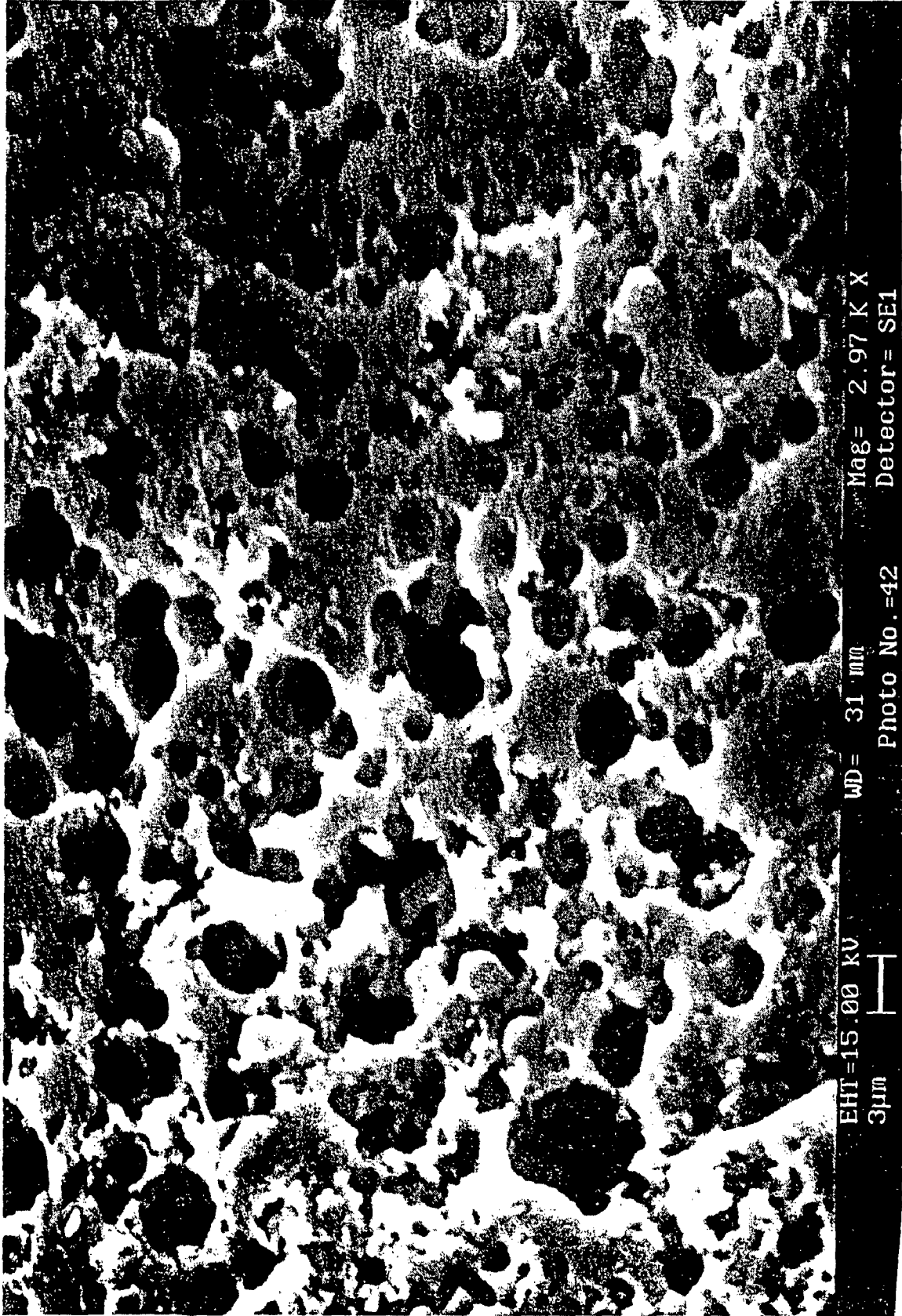


Fig. 6.3(b) Scanning Electron Micrograph of Rice Husk Flyash at 2.97 K Magnification

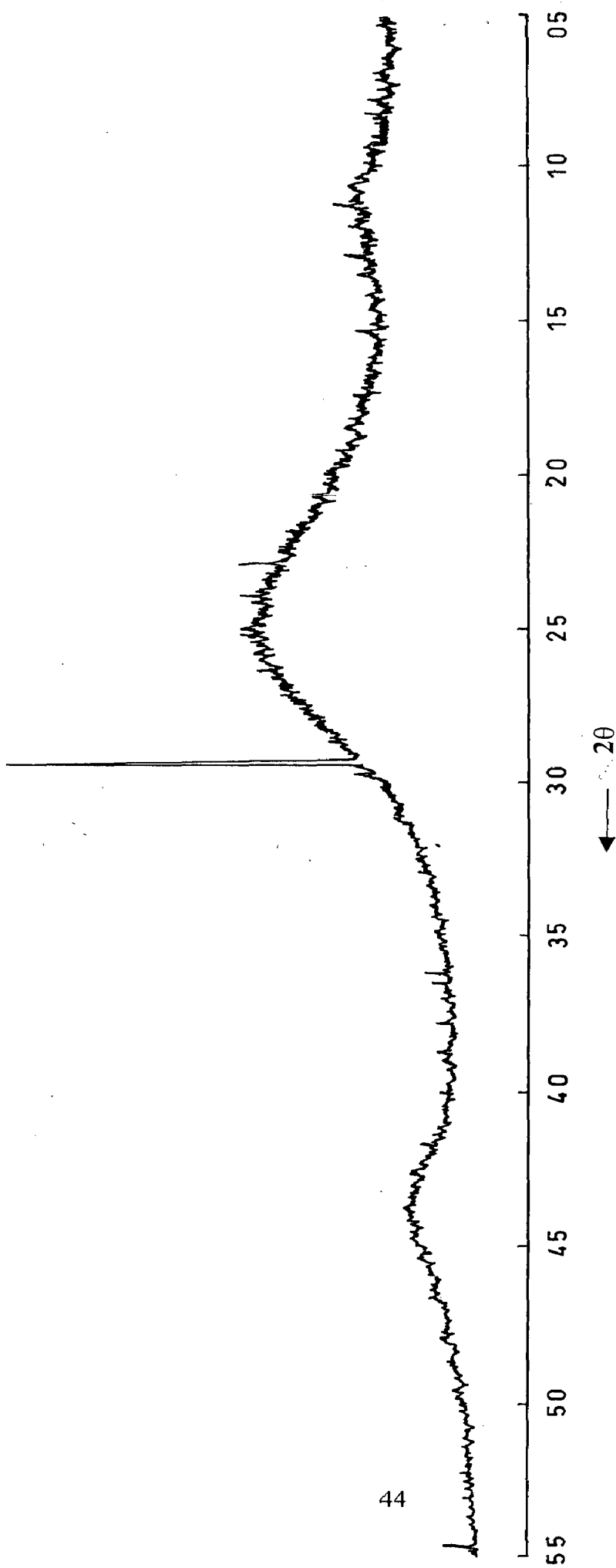
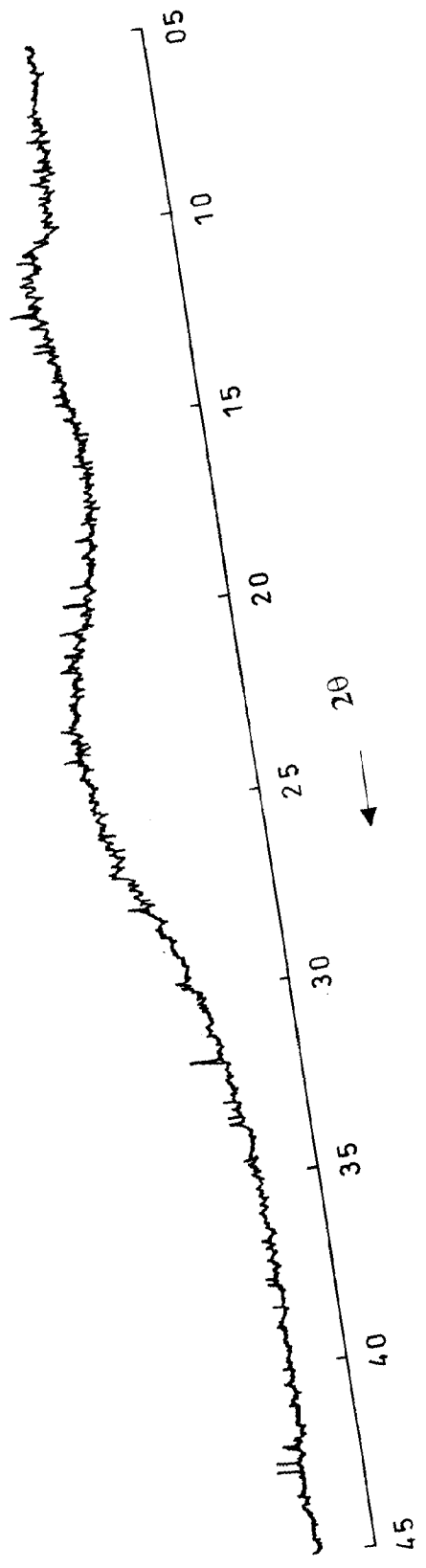


Fig. 6.4 X-ray Diffraction Pattern of Activated Carbon



**Fig. 6.5** X-ray Diffraction Pattern of Bagasse Flyash

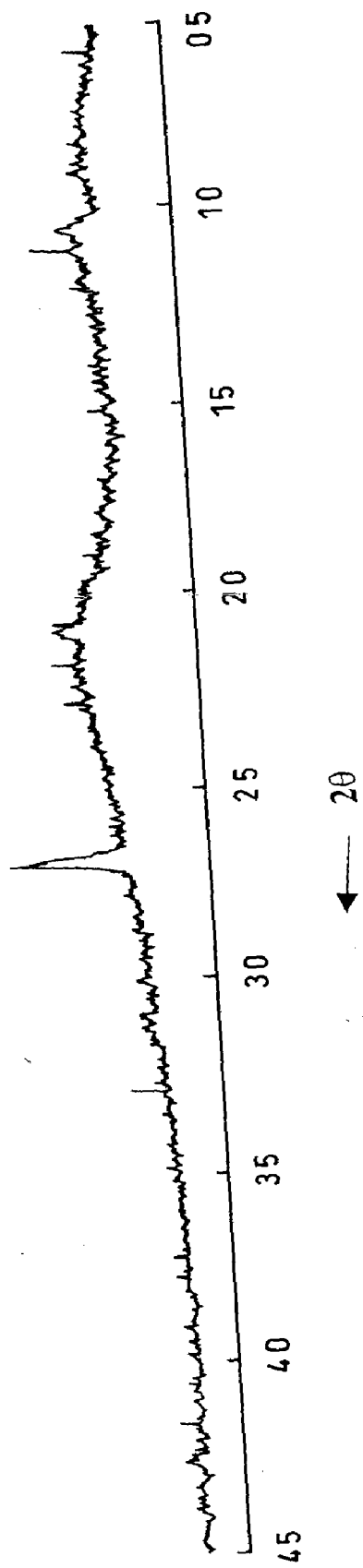


Fig. 6.6 X-ray Diffraction Pattern of Rice Husk Flyash

efficiency of boilers, variety of sugarcane or rice paddy, and the flyash collection devices used.

The electron micrographs of bagasse flyash, rice husk flyash and activated carbon obtained under scanning electron microscope (SEM) are shown in Figs. 6.1 – 6.3. These micrographs show different morphology for bagasse flyash, rice husk flyash and activated carbon. The bagasse flyash at places has strands similar to fibre in the original material. After burning some pores have been developed in the strands. But their number is much less than those observed in rice husk flyash and activated carbon. The SEM micrograph of rice husk flyash shows that it has a larger number of pores than activated carbon.

X-ray diffraction patterns for bagasse flyash, rice husk flyash and activated carbon as shown in Fig. 6.4 – 6.6, show different patterns. The X-ray diffraction patterns of bagasse flyash and activated carbon have broad peaks corresponding to silica, whereas there are no broad peaks in X-ray diffraction patterns of rice husk flyash, showing crystalline structure of the minerals.

In activated carbon the major peaks indicate the presence of silica in form of tridymite and alpha cristobalite. For bagasse flyash the major peaks were from the presence of silica in the form of tridymite, alpha cristobalite and keatite. In case of rice husk flyash the major peak indicated the presence of silica in the form of alpha quartz. Besides these, other peaks indicated the presence of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{CaO}$ .

## 6.2 BATCH ADSORPTION STUDIES

Detailed adsorption studies have been conducted for the removal of 2,4 dichlorophenol and tetrachlorocatechol from synthetic wastewaters having known concentration of these toxic compounds, which is much more than normally encountered in pulp and paper mill effluent. Effect of various operating parameters, viz. concentration, adsorbent dose, contact time and pH is studied and presented here.

### 6.2.1 Effect of Adsorbent Dose

The effect of adsorbent dose on removal of 2,4 dichlorophenol and tetrachlorocatechol is shown in Fig. 6.7 and Fig. 6.8. It can be seen from these that the percentage removal increases up to a certain limit and then it remains almost constant. For larger concentration of adsorbent the adsorption sites larger and the adsorbate molecules have to travel considerable distance in order to reach these sites. Similar results were obtained by Cloutier et al. [1985] for adsorption of 2,4 D from wastewater on peat and by Swamy [1998] for removal of phenols using activated carbon and bagasse flyash. For further experiments adsorbent dose concentration was taken as  $20 \text{ g l}^{-1}$ .

### 6.2.2 Effect of pH

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of different pollutants [Elliot and Huang, 1981]. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of 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. Adsorption of various anionic and cationic species on such adsorbents has been explained on the basis of the competitive adsorption of  $\text{H}^+$  and  $\text{OH}^-$  ions with adsorbates [Khanna and Malhotra, 1997]. It is a common observation that the surface adsorbs anions favourably at lower pH due to presence of  $\text{H}^+$  ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of  $\text{OH}^-$  ions.

In the present study, in case of both 2,4 dichlorophenol and tetrachlorocatechol the percentage removal was higher in the acidic range. The effect of pH is shown in Figs. 6.9 and 6.10. In further experiments pH was kept at 4.5 for 2,4 dichlorophenol and 5.0 for tetrachlorocatechol.



### 6.2.3 Effect of Contact Time

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficacy of that adsorbent for its use in wastewater treatment.

Fig. 6.11 and 6.12 show the effect of contact time on removal of 2,4 dichlorophenol and tetrachlorocatechol respectively. It is found that rate of removal is very rapid during initial 30 minutes and thereafter it starts decreasing and there is no significant change after 180 minutes in case of 2,4 dichlorophenol and after 300 minutes in case of tetrachlorocatechol. This can be explained on the basis of the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules of the solid and bulk phases.

In further experiments the contact time was taken as 240 minutes for 2,4 dichlorophenol and 360 minutes for tetrachlorocatechol.

### 6.2.4 Effect of Initial Concentration

A given mass of adsorbent can adsorb only a fixed amount of adsorbate. So the initial concentration of adsorbate solution is very important. The amount adsorbed decreases with increasing adsorbate concentration as the resistance to the uptake of solute from solution of adsorbate decreases with increasing solute concentration. The rate of adsorption is increased because of the increasing driving force .

The effect of initial concentration for 2,4 dichlorophenol and tetrachlorocatechol are shown in Figs. 6.13 and 6.14 respectively. From these figures, it is evident that percentage removal is decreasing with the increasing initial concentration of adsorbate solution. However, uptake of chlorinated phenolics was found to increase with increase in initial concentration.

Percentage removal by the various adsorbents was found to be in the following order :

Activated carbon > Bagasse flyash > Rice husk flyash

### 6.3 KINETICS OF ADSORPTION

The Lagergren equation as shown below has been used by a number of investigators [ Panday et al., 1986, Mall et al., 1996, Kumar et al., 1995].

$$\frac{q_e - q}{q_e} = \exp(-kt)$$

where  $q_e$  = Amount of adsorbate adsorbed at equilibrium, mg/g

$q$  = Amount of adsorbate adsorbed at time  $t$ , mg/g.

$k$  = Adsorption rate constant,  $\text{min}^{-1}$

$t$  = Time, min.

This equation can also be expressed as

$$\log(q_e - q) = \log q_e - \frac{k}{2.3} t$$

The plot of  $\log (q_e - q)$  against time is shown in Figs. 6.15 and 6.16. The straight line plots shows the validity of Lagergren equation. The correlation coefficients ( $r$ ) obtained after fitting experimental data to Lagergren equation are given Appendix B. This follows that the adsorption kinetics can be fairly assumed to be of first order. Table 6.5 gives the value of adsorption rate constant ( $k$ ) for 2,4 dichlorophenol and tetrachlorocatechol respectively with different adsorbents.

### 6.4 INTRA-PARTICLE DIFFUSION STUDY

A functional relationship commonly used to describe the intraparticle transport is the plot between mass of solute adsorbed per unit mass of adsorbent ( $q$ ) and square root of contact time ( $t^{0.5}$ ). The linear nature of the plot shows that the controlling mechanism for adsorption is intraparticle diffusion [Allen et al., 1989]. These plots for 2,4 dichlorophenol and tetrachlorocatechol are shown in Figs. 6.17 and 6.18 respectively. The plots of 2,4 dichlorophenol and tetrachlorocatechol were linear over a wide range of contact period. The correlation coefficients ( $r$ ) for fitting the experimental data to straight line are given in Appendix B. Thus indicating that controlling step is intraparticle diffusion. The values of intraparticle diffusion rate parameters (in  $\text{mg g}^{-1} \text{min}^{-0.5}$ ) are given in Table 6.6 for 2,4 dichlorophenol and tetrachlorocatechol.



## 6.5 ADSORPTION ISOTHERM EQUATIONS

Various isotherm equations have been used to describe the equilibrium nature of adsorption. Some of these equations are Freundlich, Langmuir, Redlich-Peterson, Radko-Praunitz and Toth equations. Out of these Freundlich and Langmuir isotherm equations are widely used by researchers in the field of environmental engineering. The Freundlich isotherm is represented by the following equation ;

$$q_e = K_F C_e^{1/n}$$

which can also be written as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

The Langmuir isotherm is represented by the following equation

$$q_e = \frac{q_m K_A C_e}{1 + K_A C_e}$$

which can also be written as

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_A q_m} \left( \frac{1}{C_e} \right)$$

Figs. 6.19 and 6.20 give the plot of  $\log q_e$  against  $\log C_e$  for 2,4 dichlorophenol and tetrachlorocatechol respectively. Similarly Figs. 6.21 and 6.22 give the plot of  $1/q_e$  against  $1/C_e$  for these two chemicals. The experimental data fairly fit the straight line as shown by correlation coefficients ( $r$ ) given in Appendix B.

The values of parameters for Freundlich and Langmuir isotherms are given in Tables 6.7 and 6.8.

## 6.6 TOXICITY REMOVAL USING ADSORPTION

While the detailed batch studies were done for 2,4 dichlorophenol and tetrachlorocatechol, the removal of 4 chlorophenol and 2,4,6 trichlorophenol with initial concentration of 5 mg/l and adsorbent dose concentration of 20 g/l and contact time of 6 hrs was also done, keeping other parameters same as in case of 2,4 dichlorophenol.

The percentage removal of these two toxic compounds, present in pulp and paper mill effluent, together with those of 2,4 dichlorophenol and tetrachlorocatechol are given in Table 6.9.

## **6.7 ECONOMIC EVALUATION OF THE PROCESS**

The economics of the treatment process using activated carbon, bagasse flyash and rice husk flyash is presented in Table 6.10. Though the percentage removal by activated carbon is higher than that of rice husk flyash and bagasse flyash, the overall cost of treatment with bagasse flyash and rice husk flyash is lower, as these adsorbents are available almost free of cost involving only handling charges.

**Table 6.1 Characteristics of adsorbents**

Characteristics	Ricehusk flyash	Bagasse flyash	Activated carbon
Bulk density (kg/m <sup>3</sup> )	224.2	118.6	617.5
Moisture (%)	4.75	4.59	9.36
Volatile matter (%)	8.25	17.82	19.18
Ash (%)	81.57	46.84	34.05
Fixed carbon (%)	5.43	30.75	37.41

**Table 6.2 Particle size analysis of activated carbon**

Particle size (mm/ $\mu$ m)	Weight (%)
> 2.0 mm	11.1
2.0 mm – 1.4 mm	42.5
1.4 mm – 1.18 mm	9.2
1.18 mm – 1.0mm	20.2
1.0 mm – 710 $\mu$ m	13.1
< 710 $\mu$ m	3.9

**Table 6.3 Particle size analysis of bagasse flyash**

Particle size ( $\mu$ m)	Weight (%)
> 710	3.8
710-500	2.5
500-400	13.2
400-300	17.3
300-212	28.2
212-100	24.7
< 100	10.3

**Table 6.4 Particle size analysis of rice husk flyash**

Particle size ( $\mu$ m)	Weight (%)
> 710	10.1
710-500	2.9
500-400	9.7
400-300	20.3
300-212	13.2
212-100	34.5
< 100	9.3

**Table 6.5 Adsorption rate constant k for adsorbents in 2,4 dichlorophenol and tetrachlorocatechol adsorption from Lagergren equation**

Adsorbent	Lagergren constant ,k (min <sup>-1</sup> )	
	2,4 dichlorophenol	Tetrachlorocatechol
Activated carbon	0.01863	0.01012
Bagasse flyash	0.02254	0.01081
Rice husk flyash	0.02047	0.01035

**Table 6.6 Intraparticle diffusion rate parameter k' from Weber -Morris plot**

Adsorbent	k' (mg g <sup>-1</sup> min <sup>-0.5</sup> )	
	2,4 dichlorophenol	Tetrachlorocatechol
Activated carbon	0.06500	0.0116
Bagasse flyash	0.0622	0.0106
Rice husk flyash	0.0574	0.0091

**Table 6.7 Isotherm parameters for different 2,4 dichlorophenol - adsorbent systems at 30°C**

Isotherm equation parameters	Activated carbon	Bagasse flyash	Rice husk flyash
<b>Freundlich isotherm</b>			
K <sub>F</sub> ((mg l <sup>-1</sup> ) <sup>-1/n</sup> x 10 <sup>-3</sup> )	0.78886	0.52747	0.32337
n	2.74725	2.45942	1.91718
<b>Langmuir isotherm</b>			
q <sub>m</sub> (mg g <sup>-1</sup> )	1.83117	1.44676	1.54392
K <sub>A</sub> (l mg <sup>-1</sup> )	0.717999	0.54649	0.22350

**Table 6.8 Isotherm parameters for different tetrachlorocatechol - adsorbent systems at 30°C**

Isotherm equation parameters	Activated carbon	Bagasse flyash	Rice husk flyash
<b>Freundlich isotherm</b>			
K <sub>F</sub> ((mg l <sup>-1</sup> ) <sup>-1/n</sup> x 10 <sup>-3</sup> )	0.23372	0.18009	0.13916
n	2.38265	2.42718	1.95274
<b>Langmuir isotherm</b>			
q <sub>m</sub> (mg g <sup>-1</sup> )	0.32666	0.27592	0.24540
K <sub>A</sub> (l mg <sup>-1</sup> )	2.70505	2.29284	1.83898

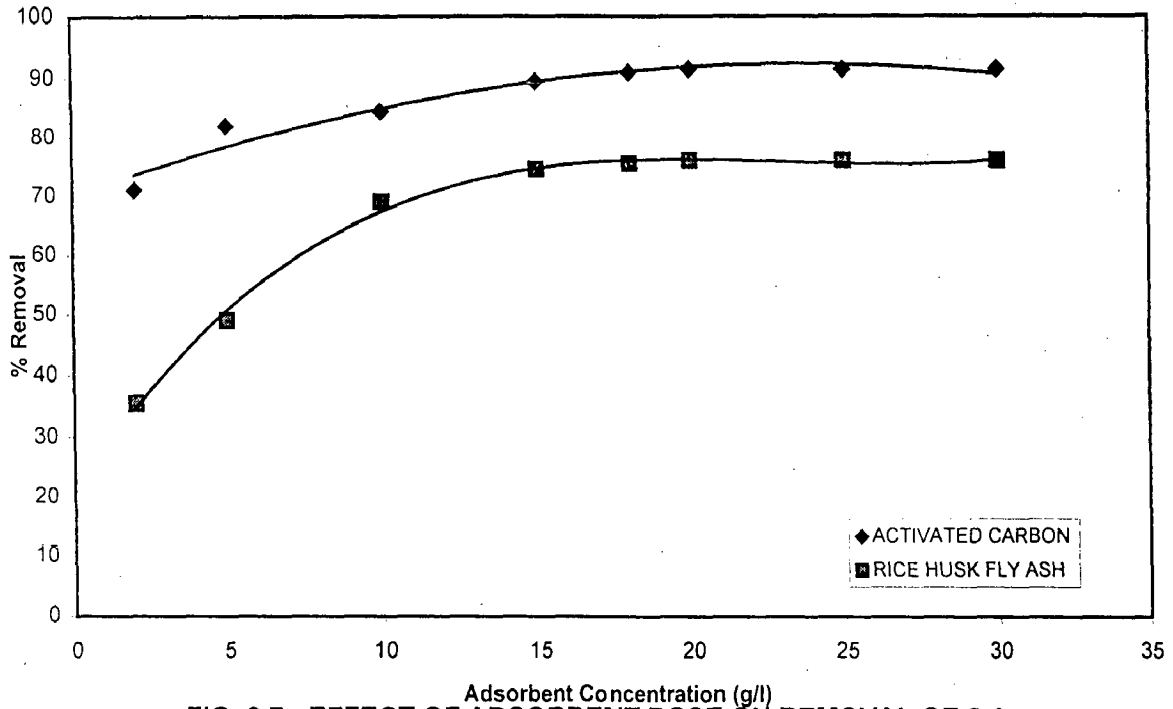
**Table 6.9 Percentage removal of various toxic compounds with initial concentration of 5 mg/l and 6 hr contact time**

Toxic compounds	% Removal		
	Activated carbon	Bagasse flyash	Rice husk flyash
4 chlorophenol	100.0	98.5	91.0
2,4 dichlorophenol	100.0	97.5	89.5
2,4,6 trichlorophenol	95.5	91.5	87.0
Tetrachlorocatechol	86.0	79.0	72.0

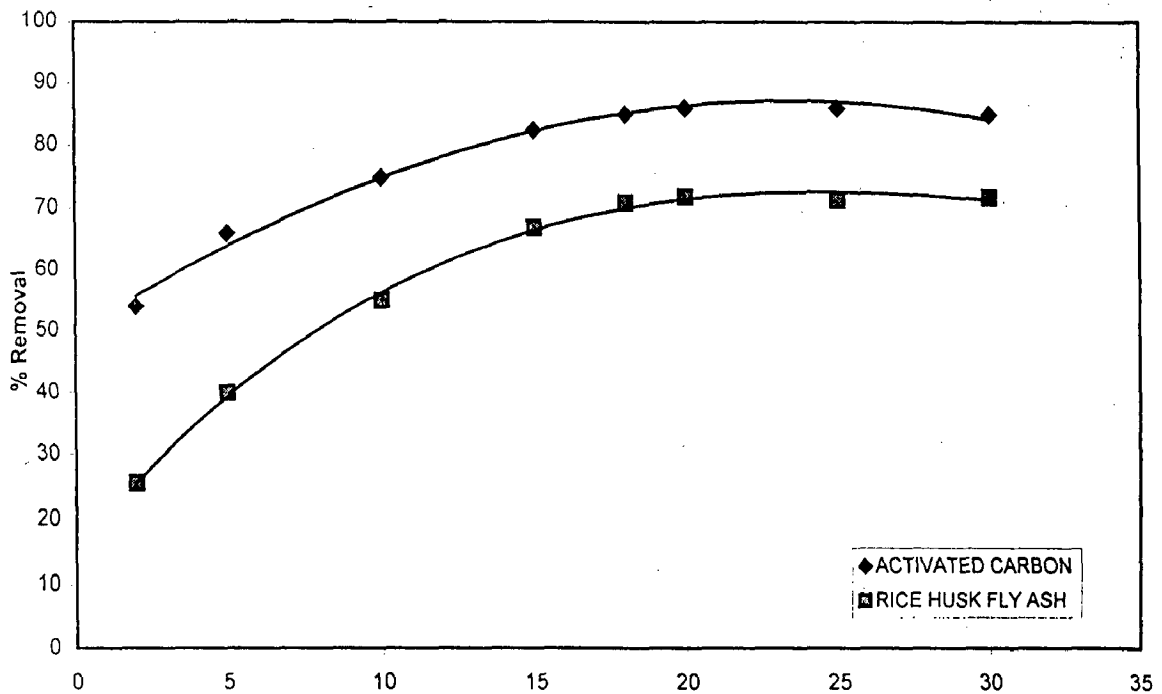
**Table 6.10 Economic evaluation of various adsorbents**

Adsorbent	Cost of adsorbent (Rs/Ton)
Activated carbon	60,000 – 70,000
Bagasse flyash	5,000*
Rice husk flyash	5,000*

\* Handling charges

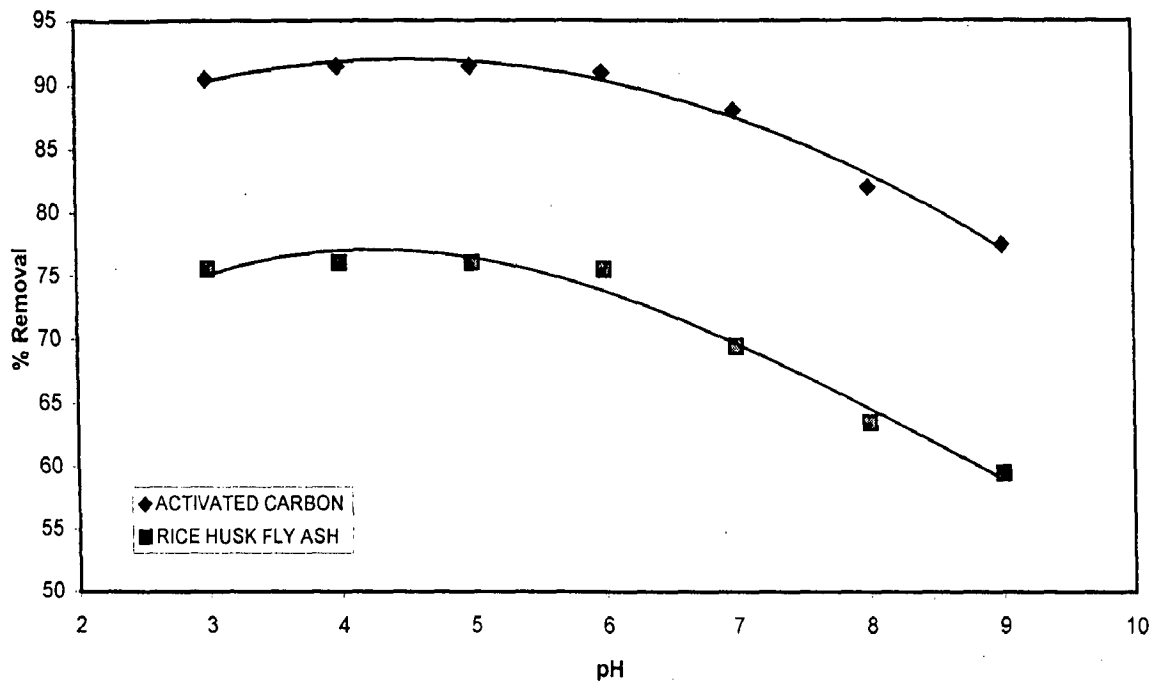


**FIG. 6.7 : EFFECT OF ADSORBENT DOSE ON REMOVAL OF 2,4 DICHLOROPHENOL**  
 Initial conc. = 20 mg/l, Contact time = 4 hr,  
 Temperature = 30°C

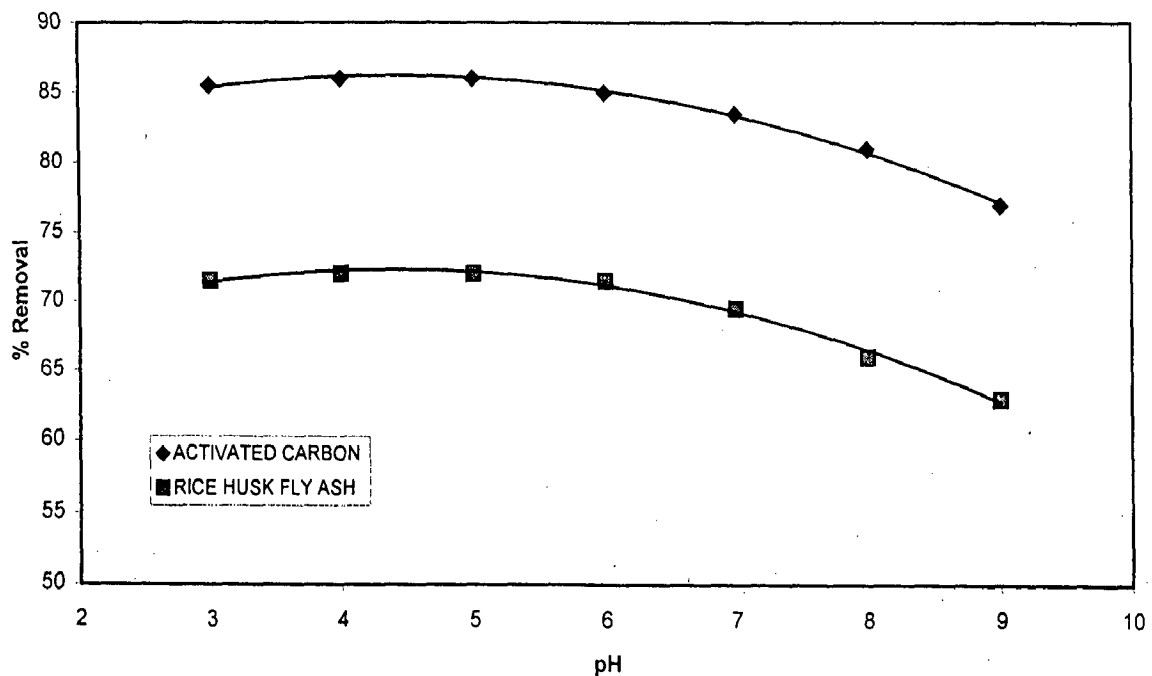


**FIG. 6.8 : EFFECT OF ADSORBENT DOSE ON REMOVAL OF TETRACHLOROCATECHOL**  
 Initial conc. = 5 mg/l, Contact time = 6 hr,  
 Temperature = 30°C





**FIG. 6.9 : EFFECT OF pH ON REMOVAL OF 2,4 DICHLOROPHENOL**  
 Initial conc. = 20 mg/l, Adsorbent conc. = 20 g/l,  
 Contact time = 4 hr, Temperature = 30°C



**FIG. 6.10 : EFFECT OF pH ON REMOVAL OF TETRACHLOROCATECHOL**  
 Initial conc. = 5 mg/l, Adsorbent conc. = 20 g/l,  
 Contact time = 6 hr, Temperature = 30°C

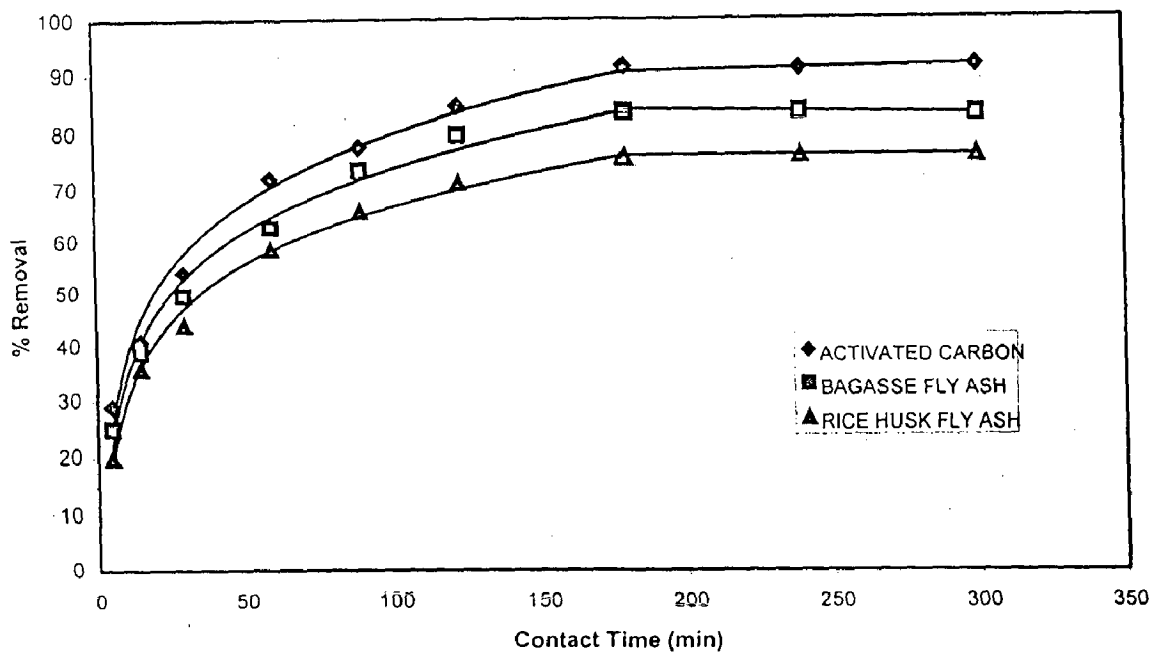


FIG. 6.11 : EFFECT OF CONTACT TIME ON REMOVAL OF 2,4 DICHLOROPHENOL  
 Initial conc. = 20 mg/l, Adsorbent conc. = 20 g/l,  
 Temperature = 30°C

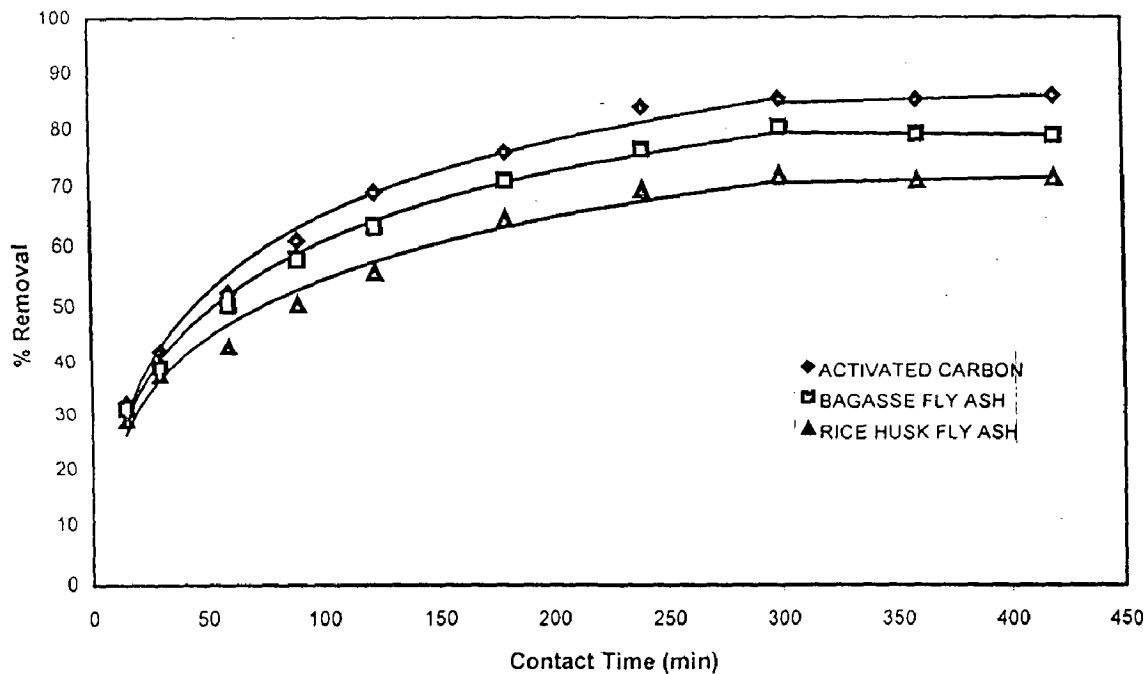
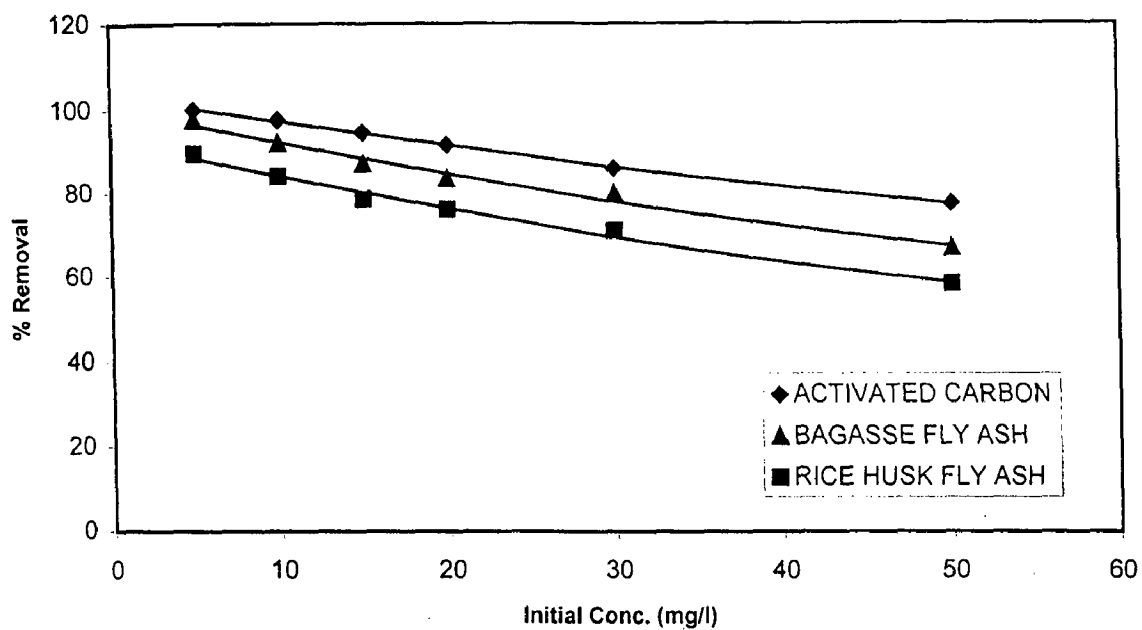
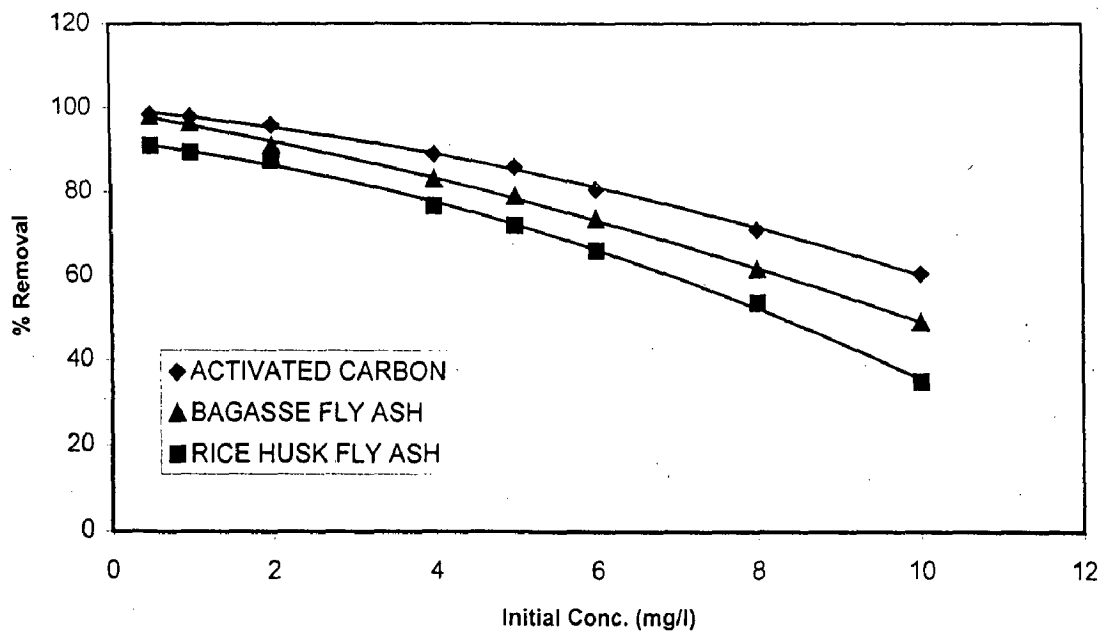


FIG. 6.12 : EFFECT OF CONTACT TIME ON REMOVAL OF TETRACHLOROCATECHOL  
 Initial conc. = 5 mg/l, Adsorbent conc. = 20 g/l,  
 Temperature = 30°C



**Fig. 6.13 : EFFECT OF INITIAL CONCENTRATION ON REMOVAL OF 2,4 DICHLOROPHENOL**  
 Adsorbent conc. = 20 g/l, Contact Time = 4 hr,  
 Temperature = 30°C



**Fig. 6.14 : EFFECT OF INITIAL CONCENTRATION ON REMOVAL OF TETRACHLOROCATECHOL**  
 Adsorbent conc. = 20 g/l, Contact Time = 6 hr,  
 Temperature = 30°C

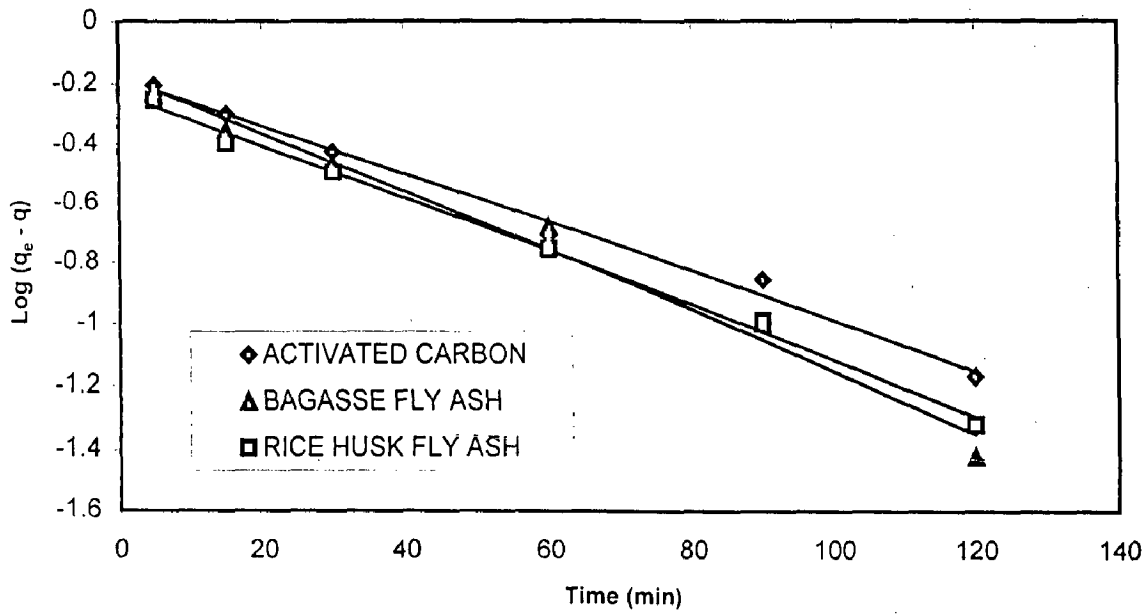


Fig. 6.15 : LAGERGREN PLOT FOR REMOVAL OF 2,4 DICHLOROPHENOL

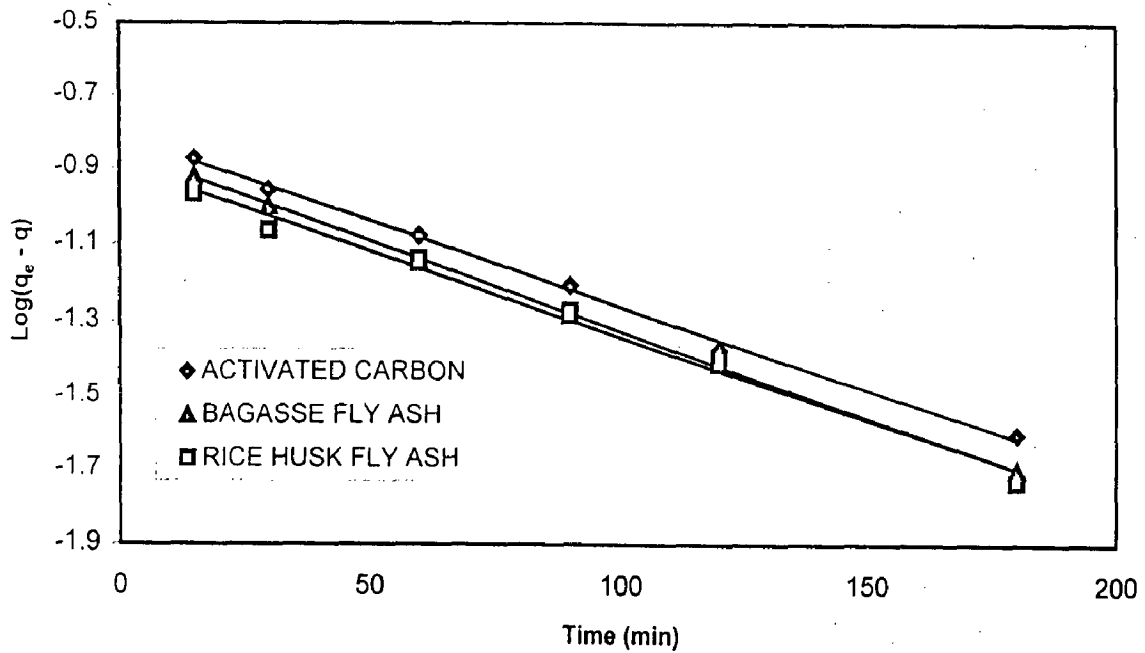


Fig. 6.16 : LAGERGREN PLOT FOR REMOVAL OF TETRACHLOROCATECHOL

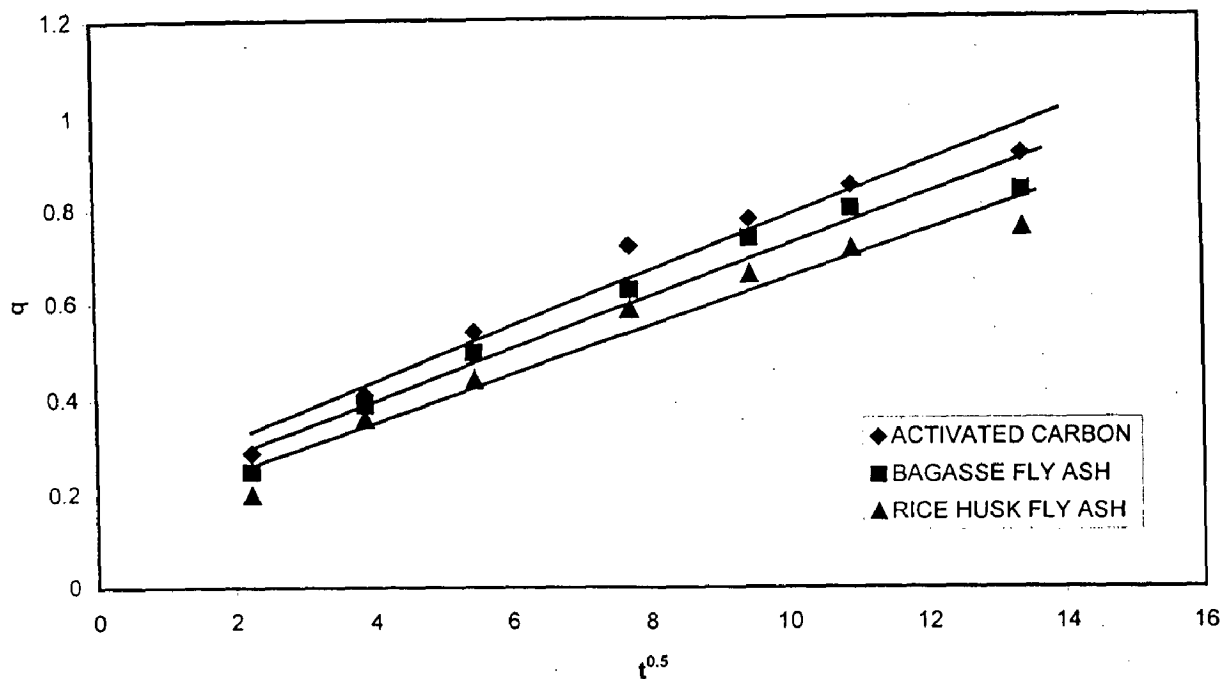


FIG. 6.17 : WEBER AND MORRIS INTRAPARTICLE DIFFUSION PLOT FOR REMOVAL OF 2,4 DICHLOROPHENOL USING ADSORPTION

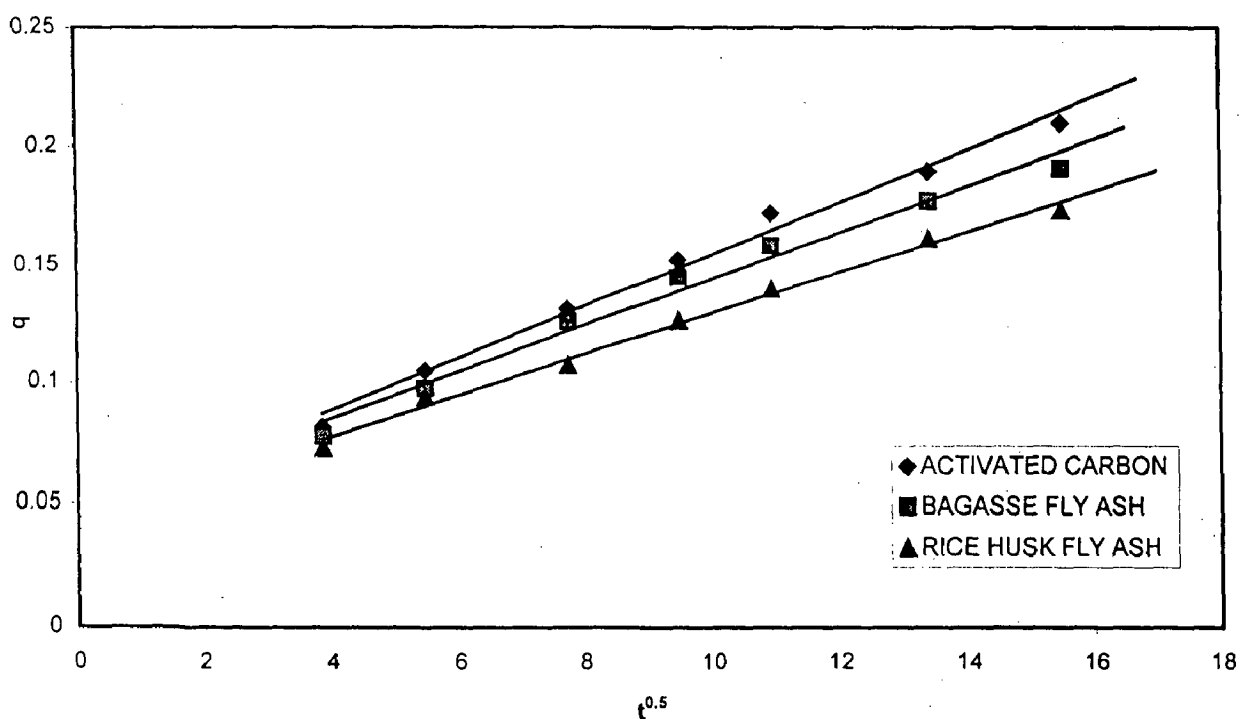


FIG. 6.18 : WEBER AND MORRIS INTRAPARTICLE DIFFUSION PLOT FOR REMOVAL OF TETRACHLOROCATECHOL USING ADSORPTION

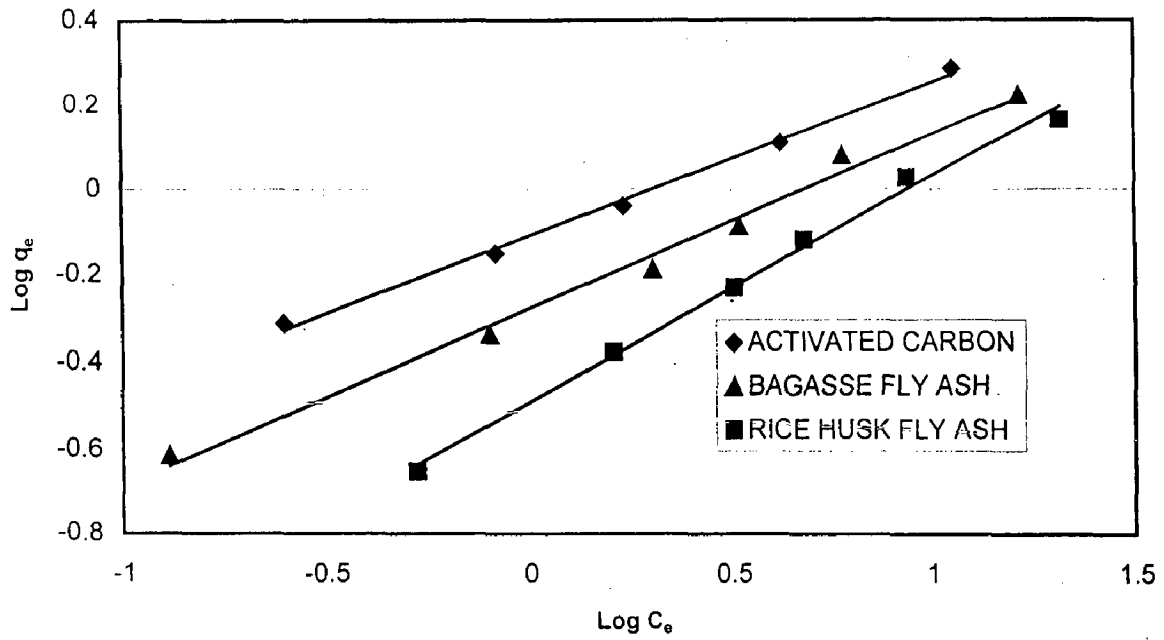


Fig. 6.19 : FREUNDLICH ISOTHERM FOR REMOVAL OF 2,4 DICHLOROPHENOL USING ADSORPTION

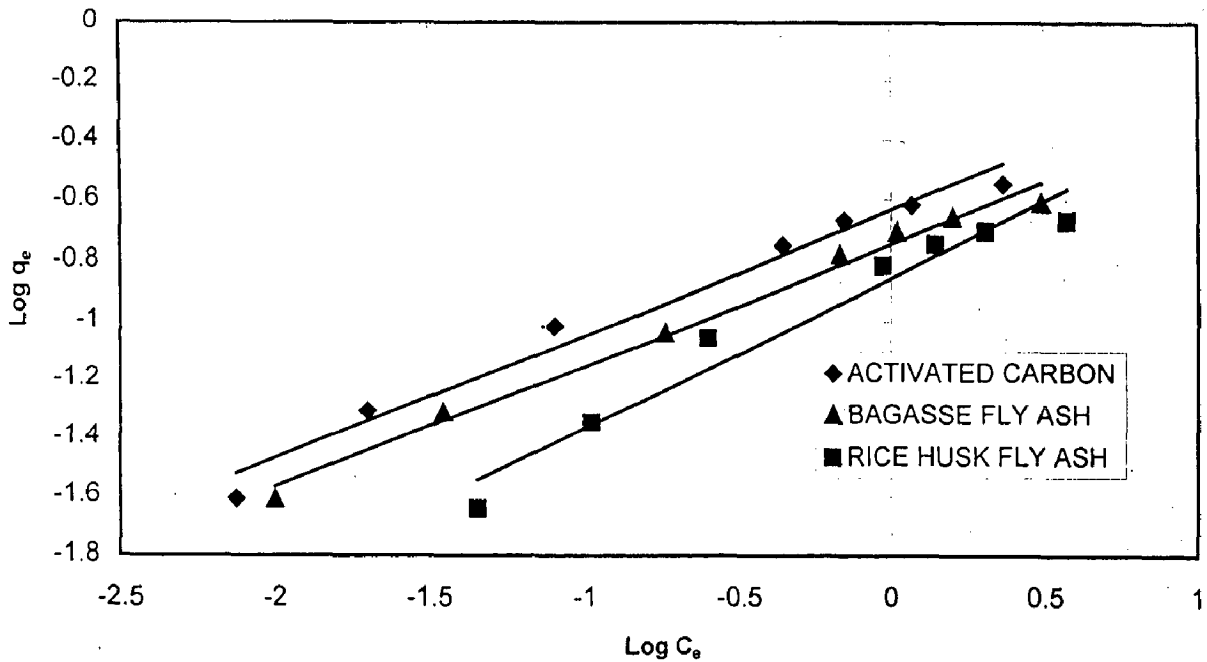


Fig. 6.20 : FREUNDLICH ISOTHERM FOR REMOVAL OF TETRACHLOROCATECHOL USING ADSORPTION

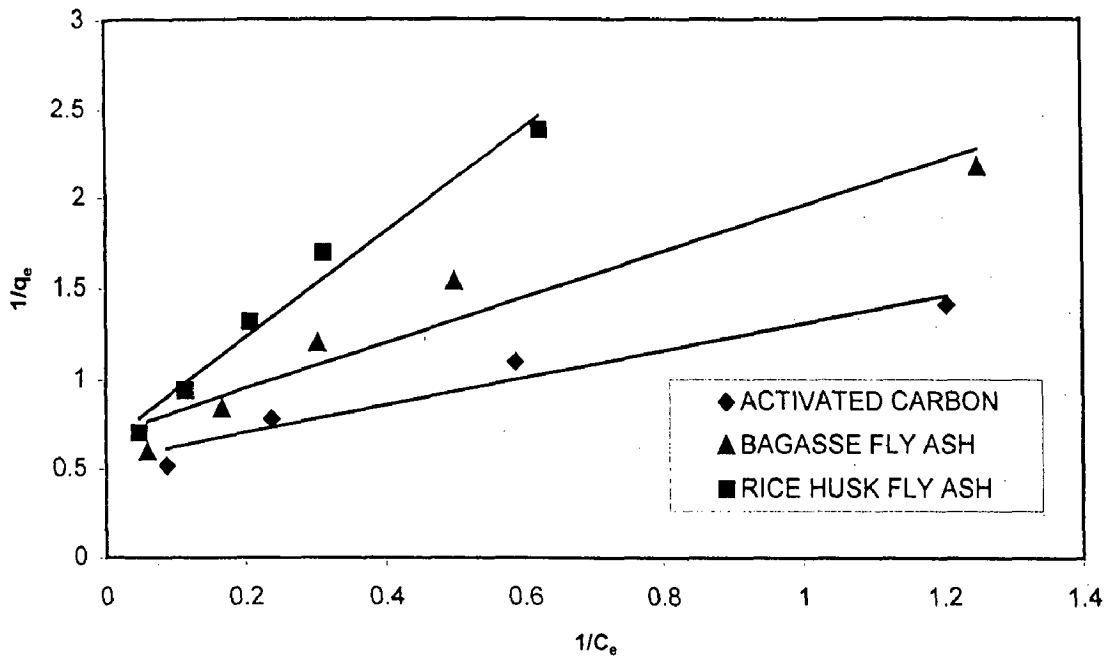


Fig. 6.21 : LANGMUIR ISOTHERM FOR REMOVAL OF 2,4 DICHLOROPHENOL USING ADSORPTION

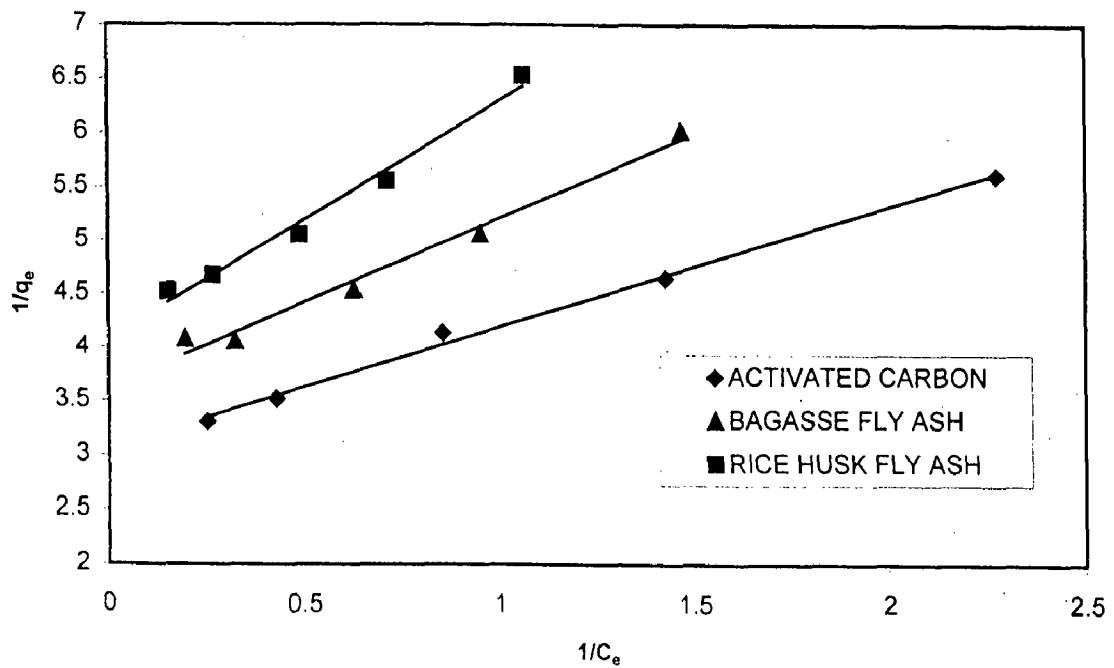


Fig. 6.22 : LANGMUIR ISOTHERM FOR REMOVAL OF TETRACHLOROCATECHOL USING ADSORPTION

## CONCLUSIONS AND RECOMMENDATIONS

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### 7.1 CONCLUSIONS

The following major conclusions can be made from the present study :

- Percentage removal of 2,4 dichlorophenol and tetrachlorocatechol increases with adsorbent concentration till it attains equilibrium.
- Removal of 2,4 dichlorophenol and tetrachlorocatechol is found to be rapid in initial stages followed by slow adsorption upto saturation indicating that the controlling step is the boundary layer diffusion.
- The percentage removal of 2,4 dichlorophenol and tetrachlorocatechol increases with decrease in initial concentration of adsorbate.
- Kinetics of removal follows first order rate expression.
- Equilibrium data confirms applicability of Freundlich and Langmuir isotherm equations.
- Weber and Morris plot reveals that the intra-particle transport (pore diffusion) is the rate controlling step.
- Percentage removal using various adsorbents was found in the following order  
Activated carbon > Bagasse Flyash > Rice husk flyash
- Both bagasse flyash and rice husk flyash were found to be cost effective adsorbents.

### 7.2 RECOMMENDATIONS

- Further pilot plant column studies are required to evaluate the suitability of bagasse flyash and rice husk flyash on plant scale.
- Further studies on other toxic constituents of pulp and paper mill effluents like trichlorophenols, pentachlorophenol and tetrachloroguaiacol need to be done for detoxification of pulp and paper mill effluent.



## REFERENCES

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1. Aldrich, Catalog Handbook of Fine Chemicals (1990).
2. Allen, S.J., McKay, G. and Khader, K.Y.H., "Intra-Particle Diffusion of Basic Dye during Adsorption onto Sphagnum Peat", *Environ. Pollut.* Vol. 56, 39-50 (1989).
3. Clapp, R.T., Truemper, C.A., Aziz, S. and Reschke, T., "AOX content of Paper manufactured with Chlorine Free Pulps", *Tappi*, Vol. 79, No. 3, 111 (1996).
4. Cloutier, J.N., Leduy, A. and Ramalho, R. S., "Peat Adsorption of Herbicide 2,4 - D from Wastewaters", *The Canad. J. Chem. Engg.*, Vol. 63, 250-257 (1985).
5. CPCB, "Pollution Control Acts, Rules and Notifications, Issue thereunder" Central Pollution Control Board, Ministry of Environment & Forest, Govt. of India, New Delhi (1995).
6. Deepak, D., Shankaranarayana, K.R. and Chandramalik, V.S., "Removal of Phenol from Wastewater by Adsorption on Flyash and Soil", *Asian Environment*, 37-42 (1981).
7. Elliott, H.A. and Huang, C.P., "Adsorption Characteristics of some Cu (II) Complexes on Alumino Silicates", *Water Res.*, Vol. 15, 849-854 (1981).
8. Fawell, J. K. and Hunt, S., "Environmental Toxicology : Organic Pollutants", Ellis Harvard Ltd., John Wiley & Sons, New York (1989).
9. Goel, K.A. and Gupta, K., "Acute Toxicity of Metanil Yellow to Heteropneustes Fossils", *Indian J. Environment Health* Vol. 27, No. 3, 266-269, (1985).

10. Gopalratnam, N., Keynote address , Workshop on cleaner production in Pulp and Paper Mills, held at New Delhi, organised by UNEP Bangkok and Central Pollution Control Board, April 25-26 (1997).
11. Gupta, G.S., Prasad, G. and Singh, V.N.,“ Removal of Chrome Dye from Aqueous Solutions by Mixed Adsorbents : Flyash and Coal ”, Water Res., Vol.24, 45-50 (1990).
12. Khanna, P. and Malhotra, S.K.,“ Kinetics and Mechanism of Phenol Adsorption on Flyash”, Ind. J. Environ. Health, Vol. 19, 224-237 (1997).
13. Kinae, N. Hashizumē, T., Makita, T., Tumita, I., Kimura, I. and Kanamori, H.,“Studies on the Toxicity of Pulp and Paper Mill Effluents - I, Mutagenicity of the Sediment Samples derived from Kraft Papermills”, Water Research Vol. 15, 17 (1981).
14. Kringstad, K.P. and Lindstrom, K.,“Spent Liquors from Pulp Bleaching”, Environ. Sci. & Techno. Vol. 16, No. 18, 236 (1984).
15. Kumar, R., Mishra, I.M. and Mall, I.D.,“ Treatment of Pyridine bearing Wastewater using Activated Carbon”, Research and Industry, Vol. 40, 33-35 (1995).
16. Kumar, S., Upadhayay, S.N. and Upadhayay, Y.D.,“ Removal of Phenols by Adsorption on Flyash”, J. Chem. Tech. Biotechnol., Vol.37, 281-290 (1987).
17. Leach, J. M.,“Water Chlorination, Environmental Impact and Health Effects”; Ann Arbor Science Publishers; Ann Arbor, MI, Vol. 3, 325 (1980).
18. Mall, I. D., Mishra, N. and Mishra, I.M.,“Removal of Organic Matter from Sugar Mill using Bagasse Flyash and Activated Carbon ” Research and Industry, Vol. 39, 115-119 (1994).

19. Mall, I.D. and Upadhyay, S.N., "Treatment of Dyes bearing Wastewater from Paper Mill Effluent using Low Cost Adsorbents", IPPTA convention issue, 33 (1994).
20. Mall, I. D., Upadhyay, S.N. and Sharma, Y. C., "A Review on Economical Treatment of Wastewaters and Effluents by Adsorption", Intern. J. Environmental Studies, Vol. 51, 77-124 (1996).
21. Mall, I. D., "Wastewater Management – A Critical Approach" Proceedings of PAPEREX 97, 3<sup>rd</sup> International Conference on Pulp and Paper Industry held at New Delhi, 351-376 (1997).
22. Mall, I. D. and Kumar, V., "Removal of Organic Matter from Distillary Effluent using Low Cost Adsorbents", Chem. Engg. World., Vol. XXXII, 89-96 (1997).
23. Mall, I. D. and Prasad, J., "Environmental Management in Pulp and Paper Industry using Low Cost Effluent Treatment Technology", IPPTA (1997).
24. McKay, G., Otterburn M.S. and Sweeney A.G., "The Removal of Colour from Effluent using various Adsorbents – IV, Silica : Equilibria and Column Studies", Water Res., Vol. 14, 21-27 (1980).
25. Nabli, S.A. and Gligis, F.N., "Dissolved Oxygen Effect on Equilibria and Kinetics of Phenolics Adsorption by Activated Carbon", Environ. Sci. Tech., Vol. 28, 216-221 (1994).
26. Panday, K.K., Prasad, G. and Singh, V.N., "Adsorption of Cu (II) from Aqueous Solutions on Flyash - Chinaclay ", J. Chem. Tech. Biotechol., Vol. 34a, 367-371 (1984).
27. Panday, K.K., Prasad, G. and Singh, V.N., "Mixed Adsorbents for Cu (II) Removal from Aqueous Solutions ", Environ. Tech. Letts., Vol. 7, 547-554 (1986).

28. Pandey, Piyush M., "Studies on Herbicides – 2,4 D Removal from Wastewaters using Adsorption ", M.E. Thesis, Univ. of Roorkee, Roorkee, India (1998).
29. Powder Diffraction File (PDF), JCPDS International Centre for Diffraction Data, Swarthmore Pennsylvania, USA (1979).
30. Prakash, A. and Solanki, S., "Sorption and Desorption Behaviour of Phenol and Chlorphenols on Guar Derivatives : Reclamation of Textile Effluents", Research and Industry, Vol. 38, 35-39 (1993).
31. Sastry, C.A., "Colour Removal from Pulp and Paper Mill Wastewaters", Indian J. of Environment Protection, Vol. 6, No. 2, 105-112 (1986).
32. Sax, N. I., "Dangerous Properties of Industrial Materials", 2<sup>nd</sup> Edition, Reinhold, New York (1963).
33. Sengupta, D.P., Kumar, S., Upadhyay, S.N. and Upadhyay, Y.D., "Chromium Removal using Flyash as an Adsorbent", Inst. of Public Health Engg., India, Vol. 4, 125-131 (1982).
34. Sharma, C., Mohanty, S., Kumar, S. and Rao, N. J., "Gas Chromatographic Analysis of Chlorphenolics Resin and Fatty Acids in Effluents from Bleaching Processes of Agriculture Residues", Intern. J. Environ. Anal. Chem., Vol. 64, 289 (1996).
35. Singh, A.K., Singh, D.P., Panday, K.K. and Singh, V.N., "Wollastonite as Adsorbent for removal of Fe(II) from Water", J. Chem. Tech. Biotechnol., Vol. 42, 39- 49 (1988).
36. Sorial, G.A., Suidan, M.T., Vidic, R.D. and Maloney, S.W. " Competitive Adsorption of Phenols and GAC II : Adsorption Dynamics under Anoxic Conditions" J. Env. Engg. Div. ASCE, Vol. 119, 1044-1058 (1993).

37. Srinath, S.A. and Bowen, I.J., "Environmental Issues and Technology in Pulp and Paper Industry", A Tappi Press Anthology of Published Papers, 1991-1994, Ed. Joyee T.W., Tappi Press (1995).
38. Stenzel, H.M., "Removal of Organics by Activated Carbon Adsorption, Process Water Treatment / Reuse", Chem. Engg. Prog., 36-43 (1993).
39. Swamy, M.M., "Studies on the Treatment of Phenolic Wastewaters using Adsorption and Immobilized Whole Cells", Phd. Thesis, Univ. of Roorkee, Roorkee, India (1998).
40. Totan, J.S., Ulsan, D. and Dines, R.E., "Survey of Xylanase Enzyme usage in Bleaching in Canada", Pulp and Paper, Canada, Vol. 96, No. 12, 107 (1995).
41. Verschneren, K., "Handbook of Environmental Data on Organic Chemicals", Van Nostrand Reinhold Comp., London (1977).
42. Walden, C.C. and Howard, T.E., "Toxicity of Pulp and Paper Mill Effluents - A Review" Pulp and Paper Canada, Vol. 82, No. 4, T143 (1981).
43. Walden, C.C. and Howard, T.E., "Toxicity of Pulp and Paper Mill Effluents" Tappi, Vol. 60, No. 1 (1997).
44. Wayne, J. Parker, Graham, J.F. and Eric R. Hall., "Removal of Chlorophenols and Toxicity during High Rate Anaerobic Treatment of Segregated Kraft Mill Bleach Plant Effluents", Environ Sci. Technol. (1993).
45. Welker, A. and Schmitt, T., "A basic Investigation in Origins of AOX-Substances in Paper Sludges", Water Research, Vol. 31, No. 4, 805 (1997).
46. Wilson, D.G., "Decrease AOX with various External Effluent Treatments", Pulp and Paper, Canada, Vol. 93, No. 12, T372 (1992).

## APPENDIX - A

### A-1 Effect of adsorbent dose on removal of 2,4 dichlorophenol using activated carbon as adsorbent

Adsorbent dose concentration (g l <sup>-1</sup> )	% Removal	Uptake of adsorbate per unit weight of adsorbent (mg g <sup>-1</sup> )
2	71.0	7.100
5	82.0	3.280
10	84.5	1.690
15	89.5	1.193
18	91.0	1.011
20	91.5	0.915
25	91.5	0.732
30	91.5	0.610

### A-2 Effect of adsorbent dose on removal of 2,4 dichlorophenol using ricehusk flyash as adsorbent

Adsorbent dose concentration (g l <sup>-1</sup> )	% Removal	Uptake of adsorbate per unit weight of adsorbent (mg g <sup>-1</sup> )
2	35.5	3.5500
5	49.0	1.9600
10	69.0	1.3800
15	74.5	0.9933
18	75.5	0.8389
20	76.0	0.7600
25	76.0	0.6080
30	76.0	0.6080

### A-3 Effect of pH on removal of 2,4 dichlorophenol using activated carbon and ricehusk flyash as adsorbent

pH	% Removal	
	Activated carbon	Ricehusk flyash
3	90.5	75.5
4	91.5	76.0
5	91.5	76.0
6	91.0	75.5
7	88.0	69.5
8	82.0	63.5
9	77.5	59.5

**A-4 Effect of contact time on removal of 2,4 dichlorophenol using various adsorbents**

Time (min)	Activated carbon		Bagasse flyash		Ricehusk flyash	
	% Removal	Amount adsorbed/g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)
5	29.0	0.2900	25.0	0.2500	20.0	0.2000
15	41.0	0.4100	39.0	0.3900	36.0	0.3600
30	54.0	0.5400	49.5	0.4950	44.0	0.4400
60	72.0	0.7200	62.5	0.6250	58.5	0.5850
90	77.5	0.7750	73.5	0.7350	65.5	0.6550
120	84.5	0.8450	79.5	0.7950	71.0	0.7100
180	91.5	0.9150	83.5	0.8350	75.5	0.7550
240	91.0	0.9100	83.5	0.8350	76.0	0.7600
300	91.5	0.9150	83.0	0.8300	76.0	0.7600

**TableA-5 Effect of initial concentration on removal of 2,4 dichlorophenol using various adsorbents**

Initial concentration (mg/l)	Activated carbon		Bagasse flyash		Ricehusk flyash	
	% Removal	Amount adsorbed /g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)
5	100.0	0.2500	97.5	0.2438	89.5	0.2238
10	97.5	0.4875	92.0	0.4600	84.0	0.4200
15	94.5	0.7088	87.0	0.6525	78.5	0.5888
20	91.5	0.9150	83.5	0.8350	76.0	0.7600
30	86.0	1.2900	80.0	1.2000	71.0	1.0650
50	77.5	1.9375	67.0	1.6875	58.5	1.4625

**Table A-6 Lagergren plot for the removal of 2,4 dichlorophenol using various adsorbents**

Time (min)	log (q <sub>c</sub> -q)		
	Activated carbon	Bagasse flyash	Ricehusk flyash
5	-0.2041	-0.2328	-0.2518
15	-0.2967	-0.3516	-0.3979
30	-0.4260	-0.4698	-0.4949
60	-0.7100	-0.6819	-0.7570
90	-0.8539	-1.0000	-0.9914
120	-1.1550	-1.4202	-1.3188

**Table A-7 Freundlich isotherm for adsorption of 2,4 dichlorophenol using activated carbon as adsorbent**

$\log C_e$	$\log q_e$
-0.6021	-0.3120
-0.0835	-0.1495
0.2304	-0.0385
0.6232	0.1106
1.0510	0.2872

**Table A-8 Freundlich isotherm for adsorption of 2,4 dichlorophenol using bagasse flyash as adsorbent**

$\log C_e$	$\log q_e$
-0.9031	-0.6131
-0.0969	-0.3372
0.2900	-0.1854
0.5185	-0.0783
0.7782	0.0792
1.2175	0.2272

**Table A-9 Freundlich isotherm for adsorption of 2,4 dichlorophenol using ricehusk flyash as adsorbent**

$\log C_e$	$\log q_e$
-0.2998	-0.6502
0.2041	-0.3768
0.5085	-0.2301
0.6812	-0.1192
0.9395	0.0273
1.3170	0.1651

**Table A-10 Langmuir isotherm for adsorption of 2,4 dichlorophenol using activated carbon as adsorbent**

$1/C_e$	$1/q_e$
1.2121	1.4109
0.5882	1.0929
0.2381	0.7752
0.0889	0.5161



**Table A-11 Langmuir isotherm for adsorption of 2,4 dichlorophenol using bagasse flyash as adsorbent**

$1/C_e$	$1/q_e$
1.2500	2.1739
0.5128	1.5326
0.3030	1.1976
0.1667	0.8333
0.0606	0.5926

**Table A-12 Langmuir isotherm for adsorption of 2,4 dichlorophenol using ricehusk flyash as adsorbent**

$1/C_e$	$1/q_e$
0.6250	2.3810
0.3101	1.6985
0.2083	1.3158
0.1149	0.9390
0.0482	0.6638

**Table A-13 Weber and Morris intraparticle diffusion plot for removal of 2,4 dichlorophenol using various adsorbents**

Time (min)	$\sqrt{\text{Time}}$ ( $\text{min}^{-0.5}$ )	Amount adsorbed per unit weight of adsorbent (mg/g)		
		Activated carbon	Bagasse flyash	Ricehusk flyash
5	2.2361	0.2900	0.2500	0.2000
15	3.8730	0.4100	0.3900	0.3600
30	5.4772	0.5400	0.4950	0.4400
60	7.7460	0.7200	0.6250	0.5850
90	9.4868	0.7750	0.7350	0.6550
120	10.9545	0.8450	0.7950	0.7100
180	13.4164	0.9150	0.8350	0.7550

**A-14 Effect of adsorbent dose on removal of tetrachlorocatechol using activated carbon as adsorbent**

Adsorbent dose concentration ( $\text{g l}^{-1}$ )	% Removal	Uptake of adsorbate per unit weight of adsorbent ( $\text{mg g}^{-1}$ )
2	54.0	1.350
5	66.0	0.660
10	75.0	0.375
15	82.5	0.275
18	85.0	0.236
20	86.0	0.215
25	85.5	0.171
30	86.0	0.143

**A-15 Effect of adsorbent dose on removal of tetrachlorocatechol using ricehusk flyash as adsorbent**

Adsorbent dose concentration ( $\text{g l}^{-1}$ )	% Removal	Uptake of adsorbate per unit weight of adsorbent ( $\text{mg g}^{-1}$ )
2	25.5	0.638
5	40.0	0.400
10	55.0	0.275
15	67.0	0.223
18	71.0	0.197
20	72.0	0.180
25	71.5	0.143
30	72.0	0.120

**A-16 Effect of pH on removal of tetrachlorocatechol using various adsorbents**

pH	% Removal	
	Activated carbon	Ricehusk flyash
3	85.5	71.5
4	86.0	72.0
5	86.0	72.0
6	85.0	71.5
7	83.5	69.5
8	81.0	66.0
9	77.0	63.0

**A-17 Effect of contact time on removal of tetrachlorocatechol using various adsorbents**

Time (min)	Activated carbon		Bagasse flyash		Ricehusk flyash	
	% Removal	Amount adsorbed /g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)
15	32.5	0.0812	31.0	0.0775	29.0	0.0725
30	42.0	0.1050	39.0	0.0975	37.5	0.0938
60	52.5	0.1312	50.5	0.1263	43.0	0.1075
90	61.0	0.1525	58.0	0.1450	50.5	0.1263
120	69.0	0.1725	63.5	0.1588	56.0	0.1400
180	76.0	0.1900	71.0	0.1775	64.5	0.1613
240	84.0	0.2100	76.5	0.1913	69.5	0.1738
300	85.5	0.2138	80.5	0.2013	72.0	0.1800
360	85.5	0.2138	79.0	0.1975	71.0	0.1775
420	86.0	0.2150	79.0	0.1975	71.5	0.1788

**TableA-18 Effect of initial concentration on removal of tetrachlorocatechol using various adsorbents**

Initial concentration (mg/l)	Activated carbon		Bagasse flyash		Ricehusk flyash	
	% Removal	Amount adsorbed /g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)	% Removal	Amount adsorbed /g adsorbent (mg/g)
0.5	98.5	0.0246	98.0	0.0245	91.0	0.0228
1.0	98.0	0.0490	96.5	0.0483	89.5	0.0448
2.0	96.0	0.0960	91.0	0.0910	87.5	0.0875
4.0	89.0	0.1780	83.0	0.1660	76.5	0.1530
5.0	86.0	0.2150	79.0	0.1975	72.0	0.1800
6.0	80.5	0.2415	73.5	0.2205	66.0	0.1980
8.0	71.0	0.2840	61.5	0.2460	53.5	0.2140
10.0	60.5	0.3025	49.0	0.2450	35.0	0.1750

**Table A-19 Lagergren plot for the removal of tetrachlorocatechol using various adsorbents**

Time (min)	log (q <sub>e</sub> -q)		
	Activated carbon	Bagasse flyash	Ricehusk flyash
15	-0.87354	-0.72125	-0.96859
30	-0.95861	-1.00000	-1.06449
60	-1.07676	-1.14752	-1.13966
90	-1.20412	-1.27984	-1.27003
120	-1.37161	-1.41229	-1.39794
180	-1.60210	-1.69897	-1.72816

**Table A-20 Freundlich isotherm for adsorption of tetrachlorocatechol using activated carbon as adsorbent**

$\log C_e$	$\log q_e$
-2.1249	-1.6086
-1.6990	-1.3098
-1.0969	-1.0177
-0.3565	-0.7496
-0.1549	-0.6676
0.0682	-0.6171
0.3655	-0.5467

**Table A-21 Freundlich isotherm for adsorption of tetrachlorocatechol using bagasse flyash as adsorbent**

$\log C_e$	$\log q_e$
-2.0000	-1.6108
-1.4559	-1.3165
-0.7447	-1.0410
-0.1675	-0.7799
0.0212	-0.7044
0.2014	-0.6566
0.4886	-0.6091

**Table A-22 Freundlich isotherm for adsorption of tetrachlorocatechol using ricehusk flyash as adsorbent**

$\log C_e$	$\log q_e$
-1.3468	-1.6430
-0.9788	-1.3492
-0.6021	-1.0580
-0.0269	-0.8153
0.1461	-0.7447
0.3096	-0.7033
0.5705	-0.6696

**Table A-23 Langmuir isotherm for adsorption of tetrachlorocatechol using activated carbon as adsorbent**

$1/C_e$	$1/q_e$
2.2727	5.6180
1.4286	4.6512
0.8547	4.1408
0.4310	3.5211
0.2532	3.3058

**Table A-24 Langmuir isotherm for adsorption of tetrachlorocatechol using bagasse flyash as adsorbent**

$1/C_e$	$1/q_e$
1.4706	6.0241
0.9524	5.0633
0.6289	4.5351
0.3247	4.0650
0.1961	4.0816

**Table A-25 Langmuir isotherm for adsorption of tetrachlorocatechol using ricehusk flyash as adsorbents**

$1/C_e$	$1/q_e$
1.0638	6.5359
0.7143	5.5556
0.4902	5.0505
0.2688	4.6729
0.1538	5.7143

**Table A-26 Weber and Morris intraparticle diffusion plot for removal of tetrachlorocatechol using various adsorbents**

Time (min)	$\sqrt{\text{Time}}$ ( $\text{min}^{-0.5}$ )	Amount adsorbed per unit weight of adsorbent (mg/g)		
		Activated carbon	Bagasse flyash	Ricehusk flyash
15	3.8730	0.0812	0.0775	0.0725
30	5.4772	0.1050	0.0975	0.0938
60	7.7460	0.1312	0.1263	0.1075
90	9.4868	0.1525	0.1450	0.1263
120	10.9545	0.1725	0.1588	0.1400
180	13.4164	0.1900	0.1775	0.1613
240	15.4919	0.2100	0.1913	0.1738

## APPENDIX - B

**Table B-1 Correlation coefficient (r) for fitting experimental data to straight line for Lagergren plot for 2,4 dichlorophenol and tetrachlorocatechol.**

Adsorbent	Correlation coefficient (r)	
	2,4 dichlorophenol	Tetrachlorocatechol
Activated carbon	0.9962	0.9986
Bagasse flyash	0.9923	0.9998
Rice husk flyash	0.9977	0.9933

**Table B-2 Correlation coefficient (r) for fitting experimental data to straight line for Weber-Morris plot for 2,4 dichlorophenol and tetrachlorocatechol.**

Adsorbent	Correlation coefficient (r)	
	2,4 dichlorophenol	Tetrachlorocatechol
Activated carbon	0.9816	0.9947
Bagasse flyash	0.9807	0.9919
Rice husk flyash	0.9750	0.9964

**Table B-3 Correlation coefficient (r) for fitting experimental data to Freundlich isotherm equation for 2,4 dichlorophenol and tetrachlorocatechol**

Adsorbent	Correlation coefficient (r)	
	2,4 dichlorophenol	Tetrachlorocatechol
Activated carbon	0.9982	0.9891
Bagasse flyash	0.9954	0.9947
Rice husk flyash	0.9977	0.9780

**Table B-4 Correlation coefficient (r) for fitting experimental data to Langmuir isotherm equation for 2,4 dichlorophenol and tetrachlorocatechol**

Adsorbent	Correlation coefficient (r)	
	2,4 dichlorophenol	Tetrachlorocatechol
Activated carbon	0.9887	0.9915
Bagasse flyash	0.9653	0.9918
Rice husk flyash	0.9719	0.9977