DECOLORISATION OF PULP & PAPER MILL EFFLUENT : REMOVAL OF DYES

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

NITIN KUMAR AGARWAL

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF ROORKEE
ROORKEE-247 667 (INDIA)

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the dissertation entitled **"DECOLORISATION OF PULP & PAPER MILL EFFLUENT: REMOVAL OF DYES"** in partial fulfilment of the requirement 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, Roorkee is an authentic record of my own work carried out during the period from July 1999 to March 2000 under the supervision of **Dr. I. D. Mall.**

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

Nitin Agrawal

Date :31st **March 2000** **(NITIN KUMAR AGARWAL)**

Place : Roorkee

CERTIFICATE

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

(I. D. MALL)
Assistant Professor
Deptt. of Chemical Engg.
University of Roorkee
Roorkee – 247 667
India

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Nitin Agrawal

NITIN KUMAR AGARWAL

ABSTRACT

Consumption of paper is the indication of the growth of civilization, industrialization of country. Higher the consumption higher is the growth rate. Due to increase in population in India the demand of paper is increasing rapidly and paper mills are producing more paper. There are many small paper mills in India, which are contributing in disposal of waste paper by recycling it. A wide variety of colored paper is made using various types of dyes. In spite of all precautions, some dyes remain untreated and come out of the mill with liquid effluent making it toxic and colored. The intake of dye by human being is harmful for their health. So removal of these dyes is essential.

There are many processes for removal of color due to dye. Adsorption is widely used process due to its simplicity. Usually activated carbon is used for adsorption. But due to its high cost there was a need of low cost adsorbent.

In present study Bagasse fly ash is used as a low cost adsorbent and their results were compared with the activated carbons (Laboratory grade, commercial grade) and coal ash. Auramine, Congo Red, Malachite Green, Orange-G, Methyl Violet, Rhodamine–B dyes that are commonly used in paper mills were used as adsorbates. Batch studies were conducted to see the effect of contact time, adsorbent dose, initial concentration of dyes and pH. The results were fitted in Langmuir and Freundlich isotherms. It was found that the bagasse fly ash is good adsorbent. Column studies were conducted on the removal of Methyl Violet and Rhodamine-B. Colored effluent from a large integrated mill was also treated using bagasse fly ash for removal of COD and color.

NOMENCLATURE

C_{Ab}	Desired concentration of adsorbate at break through, (mg l^{-1})
C_e	Concentration of adsorbate solution at equilibrium, (mg l^{-1})
k	Adsorption rate constant, (min^{-1})
k'	Intraparticle diffusion rate constant, (mg g^{-1} $min^{-0.5}$)
K_a	Rate constant,(l liquid / mg of adsorbent, (mg l^{-1})
K_A	Langmuir isotherm constant, (l mg^{-1})
K_F	Freundlich isotherm constant, ((mg l^{-1}) $^{-1/n}$$*10^{-3}$)
N_0	Adsorptive capacity of the adsorbent (mg l^{-1})
n	Freundlich isotherm constant
q	Amount of adsorbate adsorbed per unit amount of adsorbent at time t, (mg g^{-1})
q_e	Amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium, (mg g^{-1})
q_m	Limiting adsorbing capacity, (mg g^{-1})
u	linear velocity of the feed solution in the bed(ms^{-1})
t	Time, (min)
Z	Depth of adsorbent bed in the column (m)
Z_0	Critical depth (m)

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Chapter - 1

INTRODUCTION

1.0 GENERAL

Paper industry is one of the major polluting industries and is amongst top twenty-nine industries for which environmental impact assessment has been made mandatory. There are around 340 mills in India of them 30 are large mills, 80 are medium sized and rest are small mills. The total effective capacity of mills in India is around 2.6 million tonnes per annum. Paper industry consumes large amount of water (about 50 – 300 cu. m. per tonne of paper) and generates an equal amount of wastewater having high BOD, COD, pH, turbidity, high temperature, colour. Large number of malodorous sulphur compounds is also released in the environment. The large mills have already set up their recovery plants and effluent treatment plants comprising primary and secondary treatment units. Some of the mills are based on only waste paper and rag. In these mills, coloured effluent discharged is mainly due to presence of colour due to dyes.

1.1 LIQUID WASTE GENERATION IN PULP & PAPER INDUSTRY

Paper industry consumes a lot of water at different stages of process. The over all consumption of water varies according to the size of the mill and the raw material used. It varies from 50-300 m^3 per ton of paper depending upon type of raw material and process technology. Wastewater generation and characteristics of effluent from large integrated mill, agro based paper mill and waste paper mill is given in Table 1.1 [Mall & Prasad, 1998].

Being a large mill with different types of stages, the paper industry discharges a lot of liquid effluent from different stages of the process. The sources of liquid waste are shown in the Table 1.2.

Agro paper mills which utilize agricultural residues like wheat straw, rice straw, bagasse etc. are responsible for large scale pollution as these mills do not have recovery system and discharge highly colored effluent containing lignin, alkalinity, suspended solids, foam etc.

Table 1.1: Characteristics of Wastewater from Pulp and Paper Mill

Parameter	Pollution Load		
	Large Integrated Mill	Agro Based Mill	Waste Paper Based Mill
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^3/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	–

Table 1.2 : Waste water sources in pulp and paper mill.

SECTION	SOURCE
Raw material preparation	Conveying wash of wood/bamboo, depithing, debarking, chip washing.
Pulping	Digester steam condensate, leakage from digester condensate, floor washings, screening and washing.
Bleaching	Bleaching stages, bleach liquor pump leakage, bleach liquor spillage, and floor washing.
Stock preparation	Refiner/beater, centricleaners, save all spillage floor washing
Paper machine	White water over flow, condensate, floor washing, cooling water.
Power plant	Coal washing, condensate, and cooling tower, blow down.
Recovery plant	Lime slacker, evaporator, condensate cooling water in furnace, caustisizing, clarifiers, and blow down.

1.2 COLOUR IN PULP & PAPER MILL EFFLUENT

The final effluent of the pulp and paper industry is dark brown in colour, which is totally unacceptable to the public for any type of use. The coloured water creates panic in the general public and it is discarded for even irrigation purpose.

The intensity of colour depends on type of raw materials, efficiency of washing, bleaching severity, extent of recycling, requirement of coloured paper etc. In paper industry coloured discharge may be either because of lignin and lignin derivatives or due to dyes and pigments from coloured paper manufactures.

Table 1.3: Sources of colour in pulp and paper mills

Units	**Sources**
Digester House	Leakage from pulp gland, non-return valves, spills from liquid of storage tanks and entrainment with backpressure relief gases.
Washing and Screening	Leakage from pump glands, pipelines, 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 rejects, save all discharge of dye colour, wastewater from hog pit pulp washer, dye 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	Leakage from black liquor, green liquor and fresh liquor overflows and spills, entrainment from evaporators, evaporator boil out, condenser water, dreg clarifier etc.

The problem of dye based coloured effluent is more important from Indian context as share of agro based and waste paper is more than 50%. Share of the mills based on waste paper and hand made paper is about 27% and these mills are not having pulping units and source of color is mainly dyes bearing wastewater. The dyes and color discharged to the wastewater offer toxicity and a large number of dyes have been carcinogenic and their removal is essential. Apart from producing environmental pollution problem, the colour bearing wastewaters also affect badly the recycling and reuse in the plant. Although no standards for colour has been given in MINAS Table 1.4 [CPCB, 1995] but the colour in the effluent is increasing attention in public.

1.3 TOXICITY OF COLOUR AND DYES

The colour and dyes discharged to water streams were often thought to contribute negatively only to the aesthetic value of water. However, biologists are increasingly concerned about the effect of reduced light transmittance on organic productivity as well as toxic effects of colour due to lignin degradation products and dyes [Goel and Gupta 1985,Rosehart 1985]. Presence of dyes is highly persistent as the manufacturers always go for the most stable dye. Most of the dye bearing wastewater has high COD to BOD ratio and affect the water stream used for drinking and also the aquatic life.

Coloured dye wastes contain a spectrum of heavy metals and other toxic organic pollutants. The discharge of coloured wastes is not only aesthetically displeasing but it also offers considerable resistance to biodegradation and upsets aquatic life and at the same time the colour imparted is also very undesirable to the wastewater from recycling point of view. A large number of dyes have been found to be human carcinogens. [Barnes , D at al , 1984]. Goel and Garg [1980], Miller and Miller [1953] have reported toxicity of the Azo dyes. Many of the azo dyes have been reported to be carcinogenic. LC_{50} of basic violet have been to be 0.047 mg/l [Barnes et al, 1984]. Toxicity of metanil yellow to fish has been reported by Goel and Gupta [1985].

Table 1.4 : MINAS for PULP and PAPER Mills

MINAS FOR SMALL PULP AND PAPER MILL

Parameter	Discharged on to surface water	Disposal on land
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

Parameter	Concentration
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

For capacity above 24,000 tonnes/annum:

200 cubic meter (100 cubic metre for mills established after 1992).

For capacity below 24,000 tonnes/annum:

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

Parameter	Concentration
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

1.4 OBJECTIVE OF PRESENT STUDY

Biological processes are cost effective in comparison to physico-chemical processes, however, biological process may not be sufficient for the removal of colour to desired permissible limits. In general, aerobic microbial processes are less effective in biodegrading compounds. Therefore, tertiary treatment of the coloured effluents is a potential option for removal of coloured organic.

Some of the tertiary treatment processes for treatment of pulp and paper mill effluent are adsorption, membrane separation process, ultra filtration, 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, has been major deterrent in utilisation of activated carbon in developing countries. During recent years, low cost adsorbents using flyash, rice husk carbon, wood, bagasse fly ash, bottom ash etc. have been used for treatment of wide varieties of wastewater.

The present study has been taken with the objective to investigate the suitability of bagasse fly ash, the low cost adsorbent for the removal of dye from white water and comparing it with activated carbon available for laboratory use and for commercial use and coal ash from integrated paper mills.

Chapter –2

LITERATURE REVIEW

2.0 GENERAL

In this chapter a detailed study of literature on the removal of color and dye from aqueous solutions by adsorption has been reported. The work done on the removal of dye using various types of adsorbents has been summarized in table 2.1. Further discussion on the process in pulp and paper industry is given with details of dyes used in the industry.

Table 2.1: Studies on Dye Removal Using Activated Carbon and Non-Conventional Adsorbents

References	Adsorbent	Adsorbate	Operating Conditions	Conclusion
Ajay K. Vanjara (1998)	Refuse derived fuel (RDF)	Methylene blue	Batch study	RDF proved good adsorbent and followed Langmuir isotherm
Allen et al. (1989)	Sphagnum peat	Astrazone Yellow 7GL	Batch agitated vessel	Intraparticle diffusion in the peat pore structure is proposed as a mass transfer mechanism.
Asfour et al. (1985)	Hardwood sawdust	Basic dye (Astrazone blue)	Batch, C_i. 100mg/l C_i: 70 mg/l	48 mg g^{-1} at C_i of 100 mg/l and 70 mg g^{-1} at C_i of 70 mg/l
Balasubramanian & Muralisankar (1987)	Coal fly ash and tea waste ash	Dye effluent	Batch and column	Color removal more complete for fly ash than for tea waste ash.
Fasoli and Genon (1970)	Activated carbon from pyrolysed sludge	Methylene blue	Batch	Freundlich isotherm
Gupta et al. (1987)	Coal (Singrauli) 53 μm	Chrome dye (Metomega chrome orange)	C_i:5-20 mg l^{-1} Temp.:30 to 50° C	100% at C_i:5 and 80.77% at C_i: 20 mg l^{-1} decrease in removal 97.66 to 71.09 with rise in temp. 30 to 50°C.
Gupta et al. (1988a)	Fly ash	Chrome dye (Metomega chrome orange)	Batch C_i:5-20 mg l^{-1} PH:3.0-11.8 Dp:53-300 μm	Higher removal at low pH concentration and particle size. Rate controlling step is mainly intraparticle diffusion.
Gupta et al. (1988b)	Fly ash	Omega chrome red dye	Batch C_i : mg l^{-1} PH : .4.2,T:30°C Dose : 1.0 g Volume : 50 ml	98.85% removal of dye in the acidic range.

Gupta et al. (1988c)	China clay	Chrome dye Batch	Batch	First order reaction, diffusion controlled
Hwang M.C. et al. (1993)	Polyamide-epi chlorohydrin cellulose (PAE-cell) & Commercial Activated Carbon	Yellow MR, cyanine, Red PG, Red RS	Continuous	PAE-cell was found to be better adsorbent than commercial activated carbon
Jain Ruby et al. (1999)	Charcoal	Remazol Turquoise blue and Direct violet	Batch study	Charcoal proved to be an effective adsorbent for removal of dyes
Khare et al. (1987)	Fly ash	Victoria blue	Batch C_i:1.0x10^{-1}M Dose : 1.0 g in 50 ml Ph : 8.0,T:25°C	96 % removal
Khattri et al. (1998)	Mixture of alumina and clay (1:2)	Methylene blue, Malachite green, crystal violet, Rhodamine B	Batch 2.0 g adsorbent 200 ml aqueous solution of dye shaking 200 rpm	Maximum removal occurs in initial 35-40 min. with increase in initial concentration from 6-12 mg/l of dye the % removal decreased. Optimum pH 7.2 and temperature 25°C.
Khattri et al. (1999)	Sagaun sawdust	Methylene blue, Malachite green, crystal violet, Rhodamine B	Batch 0.5 g adsorbent 200 ml aqueous solution of dye	Maximum removal for Methylene blue 86%, Malachite green 83%, Rhodamine B 58%, Crystal violet 89%. At concentration 6 mg/l pH 7.5 and 30°C.
Mall et al. (1995)	Bottom ash	Methylene blue, Malachite green	Batch and column tests	Removal to the extent of 95 to 100 percent in low concentration ranges and increase in agitation gives higher removal
Mall et al. (1994)	Fly ash Bottom ash	Methylene blue, Methyl violet, Scarlet, RhodamineB, Acid orange, Sunfast yellow, Malachite green	Contact time of 30-45 min. and pH 8 and 5.6	Higher carbon content bottom ash proved more powerful adsorbent than fly ash. Rhodamine was most poorly adsorbed dye
McKay et al. (1980a)	Sorbsil silica	Astrazone blue	Batch	Equilibrium time increases with increasing in concentration. Adsorption increases with decrease in particle size. The rate-controlling step is mainly intraparticle diffusion. Adsorption increased with increase in temp. However adsorption capacity decreased with increase in time.
Mckay et al. (1980b)	Silica	Astrazone blue (Basic blue 69)	Batch, Fixed and Fluidized C_i:200 mgl^{-1} PH:5.1	Results indicate that silica has the ability to remove considerable quantities of Astrazone blue dye ,BDST model is inapplicable.

Mckay et al. (1980c)	Wood dp:150-25 μm S_s 6. M^2g^{-1} D_P=355-500 μm : 4.5 m^2g^{-1} D_c:710-100μm S_s:3.8 m^2g^{-1}	Astrazone blue and telon blue	-	Adsorption of telon blue increased whereas of astrazone blue decreased with rise of solution temperature
McKay et al. (1981)	Peat	Astrazone blue	-	Adsorption increases with temp. increase, film diffusion to be the rate-controlling step.
McKay et al. (1986)	Wood bark, rice husk, coal, bentonite clay, hair and cotton waste	Sandolan, Rhodamine, Safranine, Congo Foron Bril red, Methylene blue, Solar blue, Foron blue	Batch C_i:50-1000 mg l^{-1} 1 gm adsorbent in 100 ml of dye solution.	None of the adsorbents adsorbed sandolan blue or sandolan Rhodamine, Bentonite was best overall, followed by tree bark, cotton waste and rice husk.
Namasivayam, C. et al. (1994)	Bio gas slurry	Methylene blue (basic dye) Acid violet (acid dye)	Batch study	Adsorption follows first order rate expression. Methylene blue, showed 95% removal in the pH range of 4 to 10.5, whereas acid violet showed a maximum removal of 99% at pH 2.3 and decreased to 77% with a pH increase to 11.2.
Poots et al. (1976)	Peat (d_p:150-250 μm to 710-1000 μm and S_s:6.4-3.8 m^2g^{-1})	Telon blue (acid blue 25)	Batch and column	Peat found suitable for Acid blue dye removal, t_e = 2 hr
Poots et al. (1978)	Wood (d_p:150-250 μm to 355-500and 710 - 1000 μm and S_s:6.4-3.8 m^2g^{-1})	Telon blue (acid blue 25)	Batch and column	Equilibrium time more than 6 hrs. higher compared to peat (2 hr).
Ray, A.K., Mohanty, P. and Utgata, T. (1998)	Wood meal, bagasse pith, saw dust	Methyl violet, Victoria blue	Batch study	Adsorption rate of Victoria blue is much higher than methyl violet. Bagasse pith has been found to be the best adsorbent compared to saw dust and wood meal. Saw dust will be the next preferred one.
Rao et al (1978)	Fly ash (acidified with chlorinated effluent of Kraft mill)	Colour from pulp mill effluent	Batch	93 % colour removal and 73 % COD removal.
Shah and Bhattacharya (1988)	Fly ash	Bleach plant effluent	Batch	92.5 % colour removal with acid treated fly ash, COD removal 63 %.
Singh et al. (1984)	Wollastonite	Congo red	Batch	95% removal at pH:3.0, 50°C and C_i:25 ppm

2.1 PROCESS TECHNOLOGY OF PULP AND PAPER INDUSTRY

2.1.1 Process

Pulp and papermaking process is a combination of four major steps, namely.

Raw material preparation	Debarking and chipping
Pulping	Separation of fibres, screening & 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, sulphite pulping, 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, and CEHD. Some of the large integrated mills have also gone for oxygen delignification.

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 news print mills are based on Kraft pulping and various mechanical processes utilising bamboo, wood, Bagasse, etc. The other raw materials used are caustic soda, chlorine, salt cake, talcum powder, rosin, mineral acids, dyes, pigments, etc. Process flow diagrams for manufacture of pulp from Kraft pulping process and soda pulping process for agricultural residues are shown in Fig. 2.1 and 2.2.

Deinking Process

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 colour and toxicity.

Dyeing of Paper

Various types of dyes and pigments are used for making coloured paper. In general there are four main methods employed for dyeing of paper Beater Dyeing Process, Dip Dyeing Process, Surface Dyeing (Calender staining) and Various Printing Processes.

2.1.2 Dyes used in paper industry (William, 1996)

Dye is used in the stock preparation section. The use of dye is to accomplish following two general goals:

- Produce paper having a given colour or shade.
- Produce white paper having a desired tint.

To achieve these goals the paper maker has to set many parameters in accordance with the goal. For colouring the paper following types of colouring material is used.

1. Coloured pigments.
2. Acid dyes
3. Basic dyes
4. Direct dyes
5. Fluorescent dyes

These categories differ according to chemical and physical properties, fastness, and affinity for paper making fibres, effective pH range and solubility. Water-soluble direct dyes are the most commonly used dyes in the paper industry. Some dyes are given normally used in the paper industry in Table 2.2 (Mall et al., 1994)

Acid dyes

Acid dyes are all water-soluble salts (usually sodium or potassium salts) of coloured aromatic organic acids, which dissociate in water to from coloured anions.

Properties of acids dyes:

1. High water solubility.
2. Neutral or slightly alkaline water solution.
3. Fair to good light fastness.
4. Low affinity for wood fibres.
    - Dye retention aids must be used
    - White water will usually be coloured.
5. Contribute to two-sidedness
6. Sensitive to heat (migrate on dryers).
7. Excellent for calender dyeing.

Basic dyes

Basic dyes are the salts (chlorides, hydrochlorides, sulphates and oxalates) of colour bases. Basic dyes constitute the only class of dyes generally applied to paper whose members are soluble to any appreciable extent in methyl-, ethyl-, or isopropyl alcohol, as well as compounds having similar solvent characteristics, among which are oils and waxes.

Direct dyes

Direct dyes are sodium salts of dye acids. Chemically they are similar to acid dyes, and are known as direct dyes because of their affinity for cellulose, which distinguishes them from acid dyes which have no affinity for cellulose. The aqueous solutions of the dyes are often highly colloidal rather than true solutions and some direct dyes may even form gel when the solution is left standing. The classification of acid dyes and direct dyes is often arbitrary and dyes are frequently encountered that have more affinity for cellulose than the average acid dye and less than the average direct dye. These are usually classified as acid dyes. The properties of direct dye are:

1. Strong affinity for cellulose. Retention can be improved by

- The use of alum or other retention aids.
- Heating the stock after adding the dye.
- Adding a cationic group to the acid dye molecule.

2. Superior light-fastness.
3. Intermediate factorial values.
4. Amendable to a wide range of pH.

Fluorescent dye

These dyes are referred to as "Paper whites" or "optical brightness" and are used by paper makers to brighten white papers. They are very effective when used with highly bleached pulps, but are ineffective when applied to unbleached pulps and ground wood.

Fluorescent dyes absorb light in the ultraviolet region of the spectrum (below 370 nm) and re-emit the light in the visible blue range (435nm), giving a fluorescent effect that produces a bright white in daylight, masking the inherent yellowness of the bleached pulp.

Table 2.2: Dyes used in paper industry

Sl No.	Dyes	Quality of Paper	Consumption in Coloured Paper Board, kg per tonne of paper
1.	Methylene Blue	File board, maplitho	2.5 - 3.5
2.	Rhodamine	File board, pink coloured poster, maplitho, duplex board, cover paper	1.5 - 2.0
3.	Methyl Violet	Violet poster, maplitho paper, cream wove, coloured wove	8.0 - 9.0
4.	Scarlet Red	File board	0.6 - 1.0
5.	Acid Orange	Buff board, buff manila board	5.0 - 6.0
6.	Malachite Green	File board, coloured	1.0 - 2.0
7.	Metanil Yellow	File board, coloured poster	2.5 - 4.5
8.	Sunfast Yellow	File board, coloured poster, buff manila board	4.0 - 5.0
9.	Auramine	File board	0.5 - 1.0
10.	Brilliant Green	Cover paper	0.8 - 1.0

It should be noted that the direct dyes has more affinity to cellulosic fibre than the basic dyes and acidic dyes. So retention problem is more in basic dyes and acidic dyes. This leads to the more colored white water formation and thus requires treatment before recycling when the shade of the paper has to be changed or dye has to be changed.

2.2 COLOUR

2.2.1 Colour measurement and representation

Colour can be defined of two types;

1. **True Colour**

   Is the colour of water from which the turbidity has been removed.

2. **Apparent Colour**

   It not only includes colour due to substance in solution, but also that due to suspended matter. Apparent colour is determined on the original sample without filtration or centrifugation.

Now these are three methods of colour measurement;

1. Visual comparison method.
2. Spectrophotometric method.
3. Tristimulus filter method.

It should be noted that colour is pH dependent and when representing colour, pH should be indicated.

Out of the above methods spectrophotometric method is very useful. We can use it in two ways. First we can give the colour in the Hazen unit. 1 Hazen unit is corresponding to the colour of 1 mg/l solution of Pt-Co. We can make some different unit standard solutions by varying concentration of the Pt-Co solution.

Now we take the transmittance of the solution by spectrophotometer and make a calibration chart. Now the sample is taken, the turbidity is removed and then transmittance is checked. This will give the colour unit of the sample.

Secondly if one do not require colour unit and only change is to be measured then there is no need to prepare calibration chart with Pt-Co solution. The calibration chart can be prepared by the sample only and at any stage we can check the concentration of the sample.

The colour can also be represented as the load in kg per tonne of the effluent or kg per tonne of product produced.

2.2.2 Colour Removal Methods

The colour of the effluent can be controlled by either process modification or end of pipeline treatment. There are many methods suggested for the colour removal. Some of them are given below.

2.2.2.1 Biochemical treatment

The removal of colour by using biological treatment is widely used. The use of wood rotting fungus [Fuming Zhang et al,1999], white Rot fungi [Knapp et al, 1999] has been used for effective colour removal.

2.2.2.2 Coagulation and sedimentation

Coagulation followed by sedimentation is an effective means of removing certain constituents of wastewater including dyes, though large amounts of sludge produced and other operational difficulties make the process less attractive. The removal is also low as compared to other advanced processes.

Primary coagulants like alum, lime, ferric chloride and similar inorganic salts can remove dyes through coagulation but the dose of the coagulant and the subsequent sludge production is quite high.

Use of synthetic organic polymers at optimum pH reduces the amount of sludge. The polymers act as coagulation aids in conjunction with primary coagulants. For disperse dyes and water soluble anionic dyes, cationic polymers have been found to be effective. Some water insoluble dyes are coagulated by polyacrilamides. Coagulation sedimentation on systems is operated on both batch and continuous basis. Some work is done by Hwang et al. al.[1993]

2.2.2.3 Chemical oxidation

Chemical oxidants can remove the colour of dyes by oxidation. Even if the oxidation is not complete it renders the products more biodegradable for subsequent treatment. Several oxidants have been employed for this purpose but the most important are chlorine and ozone.

Chlorination

The use of chlorine and related compounds for bleaching purposes is nothing new. Chlorine and sodium hypochlorite can decolourise some dyes and have been used for the same purpose. Chlorination does not remove dyes but only oxidise them to become colourless. Chlorination is often not environmentally acceptable since the chlorinated products are themselves harmful if discharged in to the river. The effort to take care of the chlorinated compounds makes the process too complex to be cost effective.

Ozonation

Ozone is one of the strongest oxidising agents and only hydrogen peroxide in the presence of UV radiation can surpass its oxidising power.

Reduction of COD and BOD is less in ozonation but the colour removal is complete. Investigators have reported various doses of ozone ranging from 45 mg/l to 1000 mg/l. Application of ozone in more than one stage are generally more effective.

Overall operational control and precise regulation of parameters are vital as ozone is costly to produce and at the same time toxic and corrosive. The gas is produced on site by passing dry air or oxygen through a high voltage electric field. The power consumption is high in production of ozone. Half-life of ozone in pure water is about 25 min. and the contact time and the pH is important. Temperature and pressure governs the solubility of ozone. Deep chambers and proper agitation are necessary to ensure good mixing and full use of ozone. Proper attention is also to be paid to the residual gas either by recycling the gas or by destroying it.

However, due to various economic and operational constraints ozonation in its present state is not used widely. The know-how is limited and several side effects are associated with the process.

2.2.2.4 Ion exchange

Ion exchange resins and macroreticular resins have been used to remove dyes from solution. Resins can be used alone or along with coagulants. They can be regenerated upon exhaustion.

Several combinations of these resins have been tried. Macroreticular resin followed by anion resin has been found to remove acidic, basic, reactive and direct dyes whereas disperse dyes posed some difficulties. Dye removal as high as 98% has been observed. Resins can be regenerated by treatment with methanol. Anion resins may need sulphuric acid for regeneration. Polyamides, polyester and mixed dyes have also been removed by ion exchange mechanisms.

2.2.2.5 Reverse osmosis, membrane separation

Reverse osmosis and membrane separation is relatively recent developments in the field of wastewater treatment. Cellulose acetate membranes have been found to remove COD and colour satisfactorily. Experiments have been conducted on zirconium oxide-polyacrylic acid membranes on stainless steel tubes. In such applications the recovered water may be reused in the process. However, these processes are still in their infancy and not popularly acknowledged.

2.2.2.6 Adsorption

Adsorption is well recognised as a unit operation for the removal of impurities present in trace amounts from wastewater which otherwise cannot be removed efficiently. These include heavy metals, non-biodegradable organic compounds like phenols, toxic substances, dyes etc. It has been used for taste and odour control in water and wastewater treatment. Almost complete removal of impurities with negligible side effects explains its wide application in tertiary treatment stages and polishing stages.

Large numbers of adsorbents are available which can be utilised for treatment of dye bearing wastewater. Some are charcoal [Jain et al, 1999], refuse derived fuel [Vanjara & Ajay K, 1998], saw dust [Khattri et al, 1999], clay [Khattri et al 1998], Eucalyptus bark [Moris et al, 1999], coal ash [Mall et al, 1994] etc. (Table 2.1).

A comparative study has been done by Marmagne et al, [1996] for removal of colour and COD using different methods of treatment as coagulation-flocculation, membrane-treatment, activated carbon treatment and ozonation

2.3 PROBLEMS ASSOCIATED WITH TREATMENT OF DYE BEARING WASTE WATER

Due to low biodegradability of dyes, dye removal in the conventional secondary biological process is not used. Physicochemical methods have been commonly used for treatment of dyes bearing wastewater. Although coagulation and flocculation are commonly used methods for removal of dyes, however, these methods have their own limitations. Coagulation and flocculation employing coagulants like Fe, Ar or Mg salts for removal of organic colour is commonly used. The resulting sludge is normally disposed off without much concern to groundwater contamination. Adsorption process have been gaining importance for removal of dyes. However, because of higher cost of the activated carbon is restricted for specific cases. During recent years large number of low cost adsorbents have been tried for treatment of dyes (Table 2.1).

The removal is must for the further reuse of the effluent. Also due to toxicity and colour it comes in priority for removal. Membrane process also are effective in removal of dyes, however, due to relatively high investment and membrane fouling problem, its application is respected.

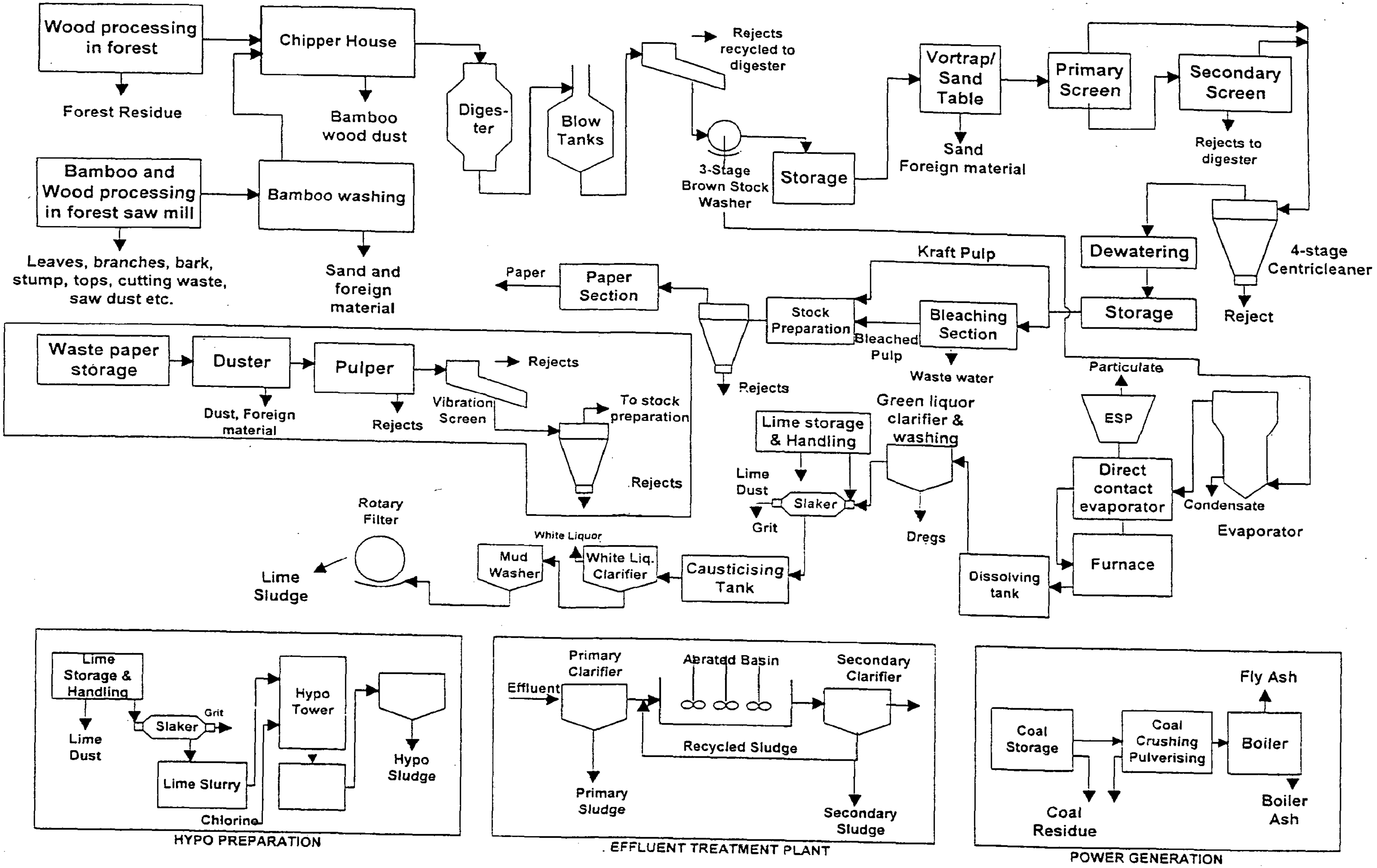


Fig. 2.1 Process of pulp and paper manufacture in large integrated kraft mill

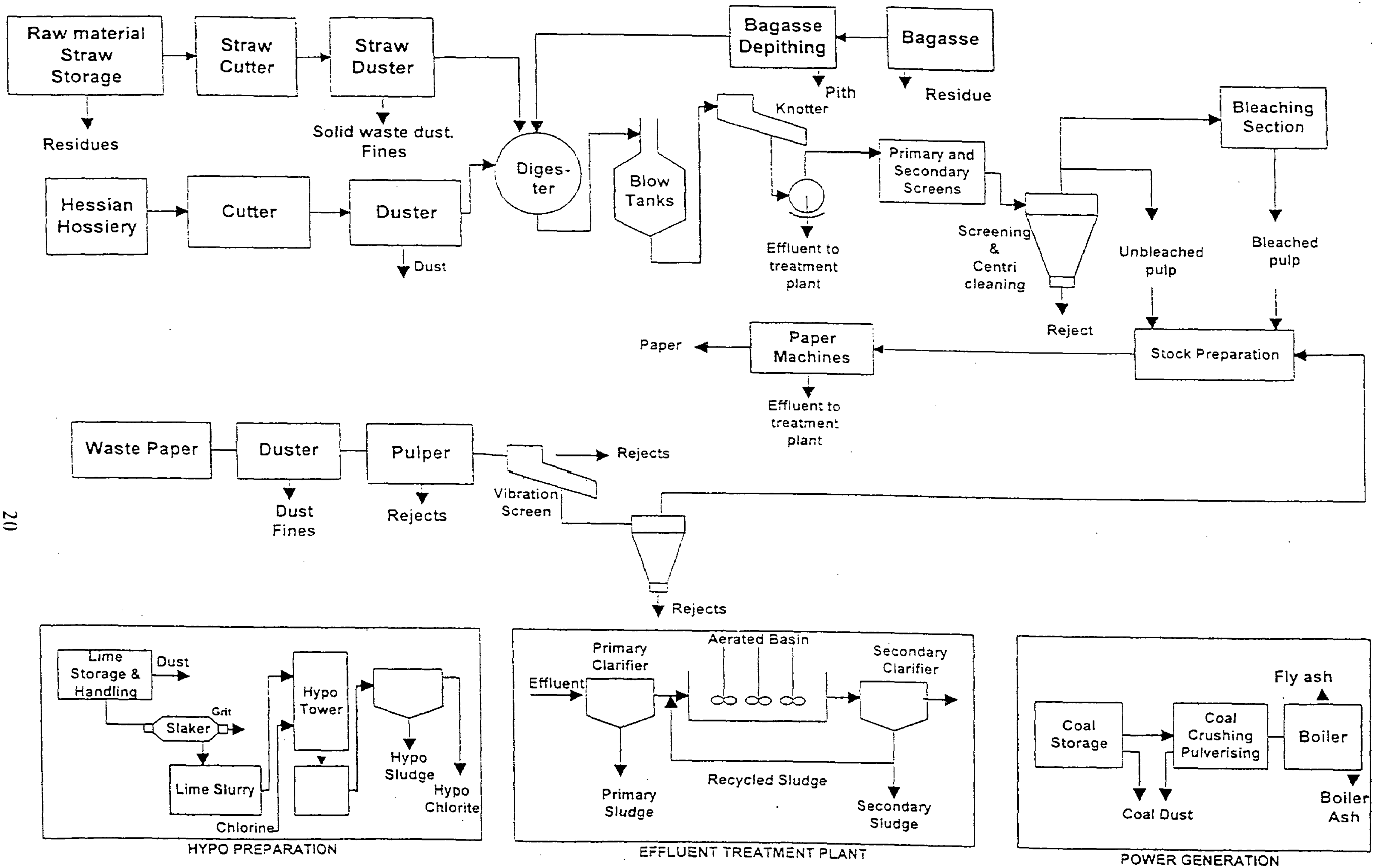


Fig. 2.2 Process of pulp and paper manufacture in agro based paper mill

Chapter - 3

ADSORPTION FUNDAMENTALS

3.0 BASIC CONCEPTS

When two phases, at least one of which is liquid or gas, come into contact, the composition of these phases close to the phase boundary will differ from the composition observed in regions distant from the boundary i.e. within the bulk of the phases. This will occur even though the phases may be in equilibrium. This 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.

Penetration of particles of one phase deep into the other phase, resembling dissolution to some extent is called absorption. This process may also be accompanied by adsorption, if the particles are irregularly distributed around the phase boundary the majority being concentrated close to the phase boundary. In cases where absorption is combined with adsorption the process involved is most often called sorption.

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 large distance from the phase boundary the multi-molecular adsorption is involved.

Adsorption may be either physical or chemical. The latter is also known as chemisorption, depending on what process cause the adsorption. In physical adsorption the electron cloud of the substance adsorbed interacts as a whole with the adsorbent and only its polarisation occurs. In chemisorption, 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. Different thermal effects accompany these two types of adsorption. 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. Sometimes catalyst is also used.

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 takes place without any activation energy and its rate should always be proportional to the first order of pressure. A comparison between physical adsorption and chemical adsorption is given in table 3.1.

Table 3.1: Comparison of Physical and Chemical Adsorption

S. No.	Physical Adsorption	Chemical Adsorption
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.

3.1 ADSORPTION PRACTICES

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

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

3.1.2 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 wastewater 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.

3.2 Intra-particle diffusion process

The rate of adsorption is determined by the rate of transfer of the adsorbate from the bulk solution to the adsorption sites. 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 diffusion film around the adsorbent will be very thin, offering negligible resistance to diffusion. So it can be assumed that the main resistance to adsorption shall lie in the pore diffusion step. Weber and Morris while referring to the rate limiting step of organic materials uptake by granulated activated carbon in the rapidly mixed batch system propose the term "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.

3.3 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, and 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.

3.3.1 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

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

Where, q_e is the amount of adsorbate adsorbed per unit amount of adsorbent at equilibrium; Ce 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

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

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.

3.3.2 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.

3.4 FACTORS CONTROLLING ADSORPTION

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

3.4.1 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, the adsorption capacity is inversely proportional to the particle diameter whereas for porous material it is practically independent of particle size. However, for porous substances particle size affects the rate of adsorption. For substances like granular activated carbon the breaking of large particles to form smaller ones opensup previously sealed channels making more surface accessible to adsorbent.

Pores may be characterised according to their sizes. Macropores have specific areas in the range of 0.5 to 2 m^2/g. though their contribution to total adsorption is inappreciable, they play a vital role in making the internal parts of the particle available for adsorption. Pores having specific area in the range of 20-40 m^2/g are known as transitional pores and adsorb relatively large molecules or particles of colloidal nature. For micropores the concept of specific area is not important, as the mechanism of adsorption is one of the volume filling rather than the layer to layer filling for macro and transitional pores.

3.4.2 pH of Solution

The surface charge as well as the degree of ionization are affected by the pH of the solution [Elliot and Huang, 1981]. Since the hydrogen and hydroxyl ions adsorbed readily on the adsorbent surface the adsorption of other molecules and ions is effected by pH. It is a common observation that a surface adsorbs anions favourably at low pH and cations in high pH range.

3.4.3 Contact Time

In physical adsorption ; most of the adsorbate species are sorbed on the adsorbent surface with in an initial contact time. The uptake of adsorbate is fast in the initial stages of the contact period and becomes slow near equilibrium .In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption results reveal that the uptake of 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. 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 site. Concentration of available vacant sites decreases and there is repulsion between solute molecules thereby reducing the adsorption rate.

3.4.4 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.

3.4.5 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.

3.4.6 Degree of Agitation

Agitation in batch adsorption is important to ensure proper contact between the adsorbent and the solution. At lower agitation 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 remains unaffected and hence, for intraparticle mass transfer controlled process agitation has no effect on the rate of adsorption.

3.5 BREAK THROUGH CURVE

For fixed bed adsorption with activated carbon or fly ash the waste water to be treated is passed through a stationary bed of the carbon. An unsteady state condition prevails in that the carbon remove-increasing amount of impurities from solution during operation.

Fig 3.2 shows the adsorption pattern, which normally obtains for a fixed bed unsteady state adsorber. The solute or impurity is adsorbed most rapidly and effectively by the upper few layers of fresh carbon during the initial stages of operation. These upper layers come in contact with initial concentration Co and adsorb maximum amount of solute, remaining amount of solute is then removed by lower part of bed. The primary adsorption zone is concentrated near the top of the column. As feed continues to flow into the column, the top layers of the carbon become practically saturated with solute and less effective for adsorption . Thus primary adsorption zone moves downward through the column to regions of fresher adsorbent. The plot of C/Co Vs Time shows the increase in the ratio of effluent to influent concentrations as the zone moves through the column. The break point on this curve represents that point in operation where for all practical purposes, the column is in equilibrium with the influent water and further little removal will take place. This curve is called break through curve. The nature of breakthrough curve depends on solute concentration, pH, particle size etc.

As a general rule, the time to break point is decreased by:

1) Increased particle size of the carbon.
2) Increased concentration of solute in the influent.
3) Increased pH of the solution.
4) Increased flow rate.
5) Decreased bed height.

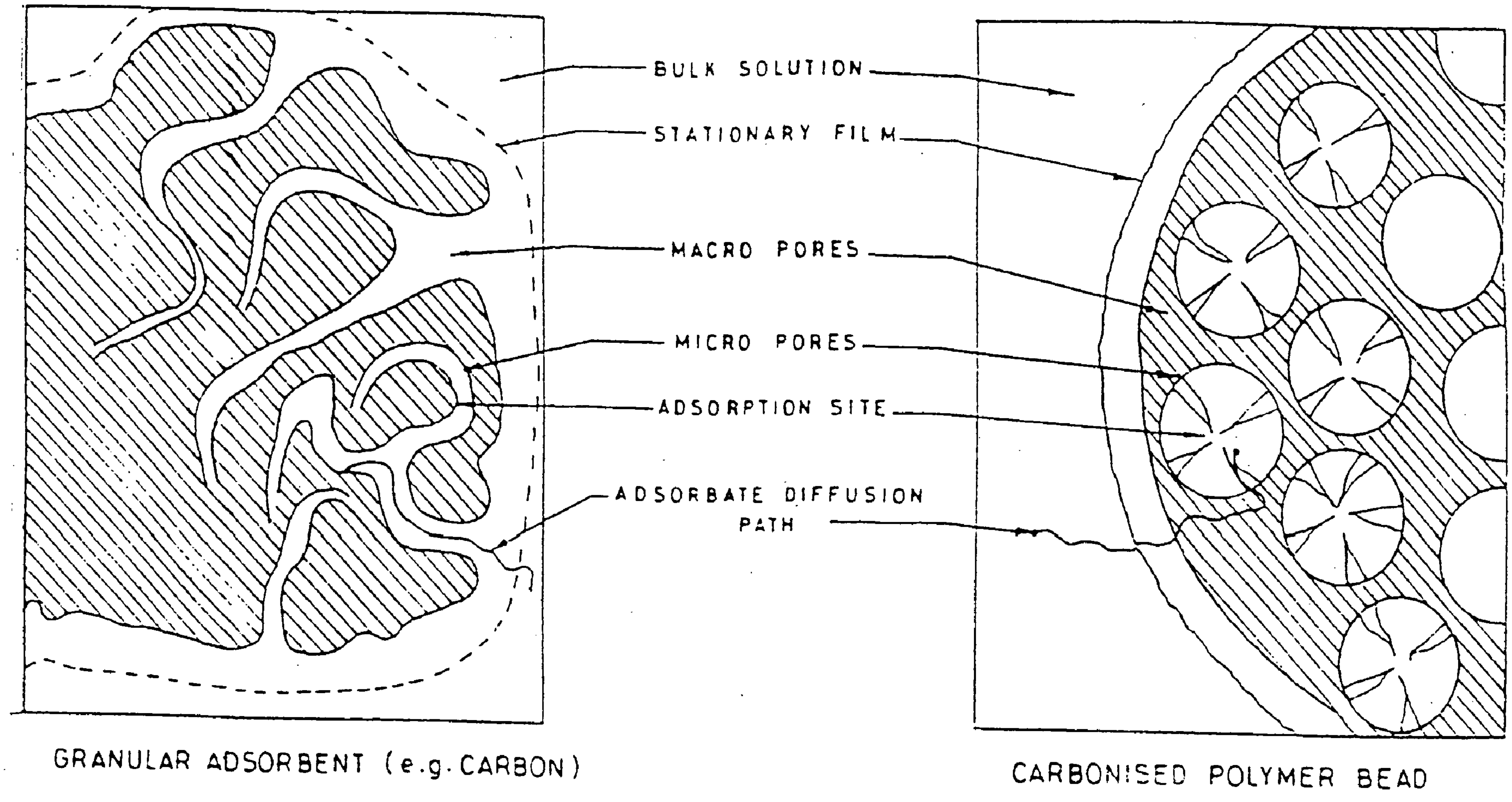


Fig. 3.1 The dynamic adsorption process showing partial cross-section of adsorbent and a portion of the surrounding solution

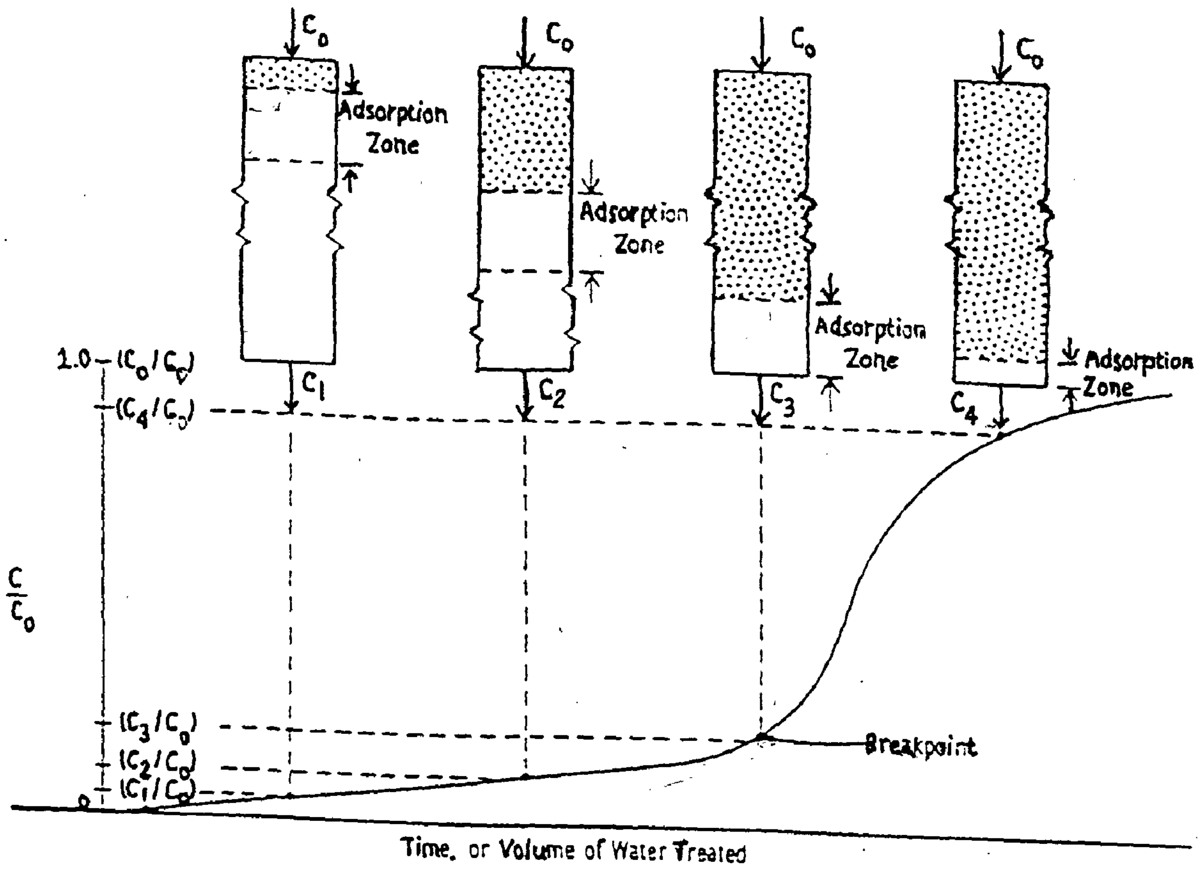


Fig. 3.2 Idealised breakthrough curve for fixed bed adsorber

Chapter - 4

EXPERIMENTAL PROGRAMME

4.0 GENERAL

Experimental details on the adsorption studies and the analysis for the removal of dyes using bagasse fly ash (BFA) and activated carbon (ACC and ACL) as adsorbents have been presented in this chapter. This includes batch adsorption studies under different operating condition. It also includes the adsorption of dyes in fixed bed of BFA column.

4.1 ANALYSIS OF A TYPICAL PAPER MILL EFFLUENT

Characterisation of a typical paper mill wastewater has been carried out. Samples were taken from chlorination stage, extraction stage, a combined effluent from bleach plant , and white water from paper machine section . These samples were characterised for BOD, COD, pH, Turbidity and conductivity. Further the COD were taken after the adsorption of effluent on different adsorbents.

4.2 ADSORPTION STUDIES

Two inactivated adsorbents bagasse fly ash and coal fly ash were used in the present investigation and their adsorptive capacity were compared with activated carbon laboratory grade and commercial grade.

4.2.1 Adsorbents

Three adsorbents, Activated carbons, commercial grade (ACC) and laboratory grade (ACL) and bagasse fly ash (BFA) were used in the experiments. For comparison with other adsorbents fly ash (CFA) from an integrated mill was taken.

4.2.2 Characterization of Adsorbents

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

4.2.2.1 Proximate Analysis

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

4.2.2.2 Density

Bulk densities of bagasse flyash, coal flyash and activated carbons were determined by using MAC bulk density meter.

4.2.2.3 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.

4.2.2.4 X-ray Diffraction Analysis

X-ray diffraction analysis of coal fly ash, 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^{-1} and 1 cm min^{-1}, respectively.

4.2.2.5 Scanning Electron Microscopy (SEM)

SEM analysis of coal flyash, bagasse flyash and the activated carbons were carried out by using LEO 435 VP Scanning electron microscope.

4.2.3 Adsorbate

Synthetic waste water solution s were prepared of Auramine, Congo Red, Rhodamine-B, Methyl Violet, Orange -G, Malachite Green, Methylene Blue, Brilliant green dyes.

4.2.3.1 Analytical measurements

The determination of the concentration of dyes (Auramine, Congo Red , Rhodamine-B , Methyl Violet , Orange -G, Malachite Green , Methylene Blue , Brilliant green)was done by finding out the absorbance characteristic wavelength of these using UV-spectrophotometer (Schimadzu, Japan). A standard solution of each dye was taken and the transmittance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum transmittance (λ_{max}) was determined from this plot. The λ_{max} for Auramine, Congo Red, Rhodamine-B, Methyl Violet, Orange -G, Malachite Green, Methylene Blue , Brilliant green was found to be 432, 500, 555, 580, 476, 618, 660 and 624 respectively. 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 portions of the standard calibration curves were used for the determination of residual concentration dye. Table 4.1 shows the operating range of the calibration equation.

4.2.4 Experimental Programme

4.2.4.1 Batch studies

To study the effect of important parameters like adsorbent dose , initial dye concentration ,pH , contact time etc. batch experiments were conducted. For each experimental run 50 ml of dye solution of known concentration , pH and the known amount of the adsorbents were taken in a 100ml stoppered conical flask . This mixture was agitated in a temperature controlled shaking water bath at a constant speed of 145 revolutions per minutes (rpm) at 30 ± 1°C. Samples were withdrawn at appropriate time intervals and these were centrifuged using Research Centriguge (Remi scientific works Mumbai), at 10000 rpm for 30 min. and analysed for remaining dye concentration using UV - spectrophotometer (Schimadzu , Japan)at 432, 500, 555, 580, 476, 618, 660, and 624 nm wave length. The pH of the adsorbate solution were adjusted using HCl or NaoH.

For adsorption isotherms, dye solutions of different concentrations were agitated with known amount of adsorbents till the equilibrium was achieved. For optimum amount of adsorbent per unit mass adsorbate, a 50 ml dye solution was contacted with different amounts of adsorbents (BFA, CFA, ACC, ACL) till equilibrium was attained . The residual dye concentration was then determined. Batch tests were carried out to compare the adsorptive capacity and intensity of BFA, CFA, ACC, ACL.

4.2.4.2 Column studies

For packed columns adsorption test, plexiglass columns of 25-mm diameter and 1000 mm length were used. Methyl Violet and Rhodamine-B having initial concentration of 40mg/l and 20mg/l respectively,were used for column studies. The bed heightswere taken 30 cm, 45cm and 60 cm .A constant head was maintained to over come the disturbances due to fluctuations in flow rate.

Table 4.1: Operating range for different dyes for estimating Concentration from calibration curve

Dye	Type of dye	Calibration equation	Operating range
Auramine	Direct	$y = -9.4283x + 100$	$0 < x < 10$
Congo Red	Direct	$y = -8.8345x + 100$	$0 < x < 5$
Malachite Green	Basic	$y = -17.12x + 100$	$0 < x < 5$
Orange-G	Direct	$y = -7.0856x + 100$	$0 < x < 6$
Rhodamine-B	Basic	$y = -38.575x + 100$	$0 < x < 1.5$
Methyl Violet	Basic	$y = -21.619x + 100$	$0 < x < 2$
Methylene Blue	Basic	$y = -26.193x + 100$	$0 < x < 2.5$

y = Transmittance (%)

x = Concentration of dye (mg/l)

Chapter – 5

RESULTS AND DISCUSSIONS

5.0 GENERAL

The detailed discussion on the results of the experiments conducted is given in this chapter. These results include

1. Characterization of paper mill effluent.
2. Characterization of adsorbents.
3. Batch adsorption studies
4. An adsorptive study with continuous flow of wastewater through fixed beds of bagasse fly ash.

5.1 CHARACTERIZATION OF PAPER MILL EFFLUENT

The characteristics of wastewater samples of a paper mill collected at four different locations (combined bleach plant effluent, chlorination stage, extraction stage, white water) and analyzed for BOD, COD, color, turbidity, pH are presented in Table 5.9.

5.2 CHARACTERIZATION OF ADSORBENTS

Activated carbons (laboratory grade , commercial grade), Bagasse flyash and coal ash from a large integrated mill were the four adsorbents used in the present investigation. Characteristics of adsorbents used include, bulk density, particle size, proximate analysis and chemical analyses. For structural and morphological characteristics, X-ray diffraction and scanning electron microscope analysis were also carried out.

Physico-chemical characteristic of bagasse fly ash, coal fly ash and Activated carbons are given in Table 5.1 and the particle size distribution is given in Table 5.2- 5.4. From Table 5.1, it is observed that bagasse fly ash has the lowest bulk density among the adsorbents. The bulk density of bagasse flyash varies from boiler to boiler to boiler depending upon makes operational features and efficiency of boilers, variety of sugarcane. Table 5.1 also shows that the amount of fixed carbon is very low in coal fly ash in comparison to activated carbons and bagasse flyash.

The Scanning electron micrograph of bagasse fly ash shows fibrous structure with large pore size with strands in each fibre. Laboratory grade activated carbon also shows similar structure like bagasse flyash, which may be due to inhirent fibre structure in the oreginal raw material. The size of the fibre and inter fibre space are similar to bagasse flyash. Coal flyash has particulate structure in a matrix which could be of relatively low melting aluminium silicate. Commercial activated carbon has structure similar to activated carbon labotatory grade and partially similar to bagasse flyash. However the fibrous nature of the structure is not so predominant in the micrograph which may be due to its large size

X-ray diffraction patterns for Bagasse flyash, Coal flyash from a large integrated mill. , ACC and ACL are shown in fig. 5.5 to 5.8 . Major components identified in Bagasse flyash are $CaSiO_3$, Al_2O_3, and $Ca_8Si_5O_{18}$. Where as $CaSiO_3$, Al_2O_3 are present in ACC, ACL and CFA (Powder Diffraction Files , 1979) . Diffraction peaks corresponding to crystalline carbon were not observed in Bagasse fly ash and Activated carbons. The other peaks indicate the presence of Fe_2O_3, MgO and CaO. The broad peaks in bagassse fly ash and activated carbons is due to presence of silica, no such peaks were present in coal fly ash.

5.3 BATCH ADSORPTION STUDIES

Detailed adsorption studies have been conducted for the removal of Auramine , Congo red, Malachite green, Orange- G , Methyl violet, Rhodamine -B from synthetic wastewater having known concentration of these dyes , 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.

5.3.1 Effect of Adsorbent Dose

The effect of adsorbent dose on removal of Auramine , Congo Red, Malachite Green, Orange- G , Methyl Violet, Rhodamine -B is shown in Fig. 5.9, 5.21, 5.29, 5.39, 5.47, 5.55 respectively .The calculated values are given in Appendix A. 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 are more and the adsorbate molecules have to travel considerable distance in order to reach these sites. So no effect does it make on further increase in adsorbent dose. Similar results were obtained by Mall et al [1995] for adsorption of Methylene Blue, Methyl Violet, Rhodamine –B , Malachite Green on fly ash and bottom ash and Khattri et al [1998] for removal of dyes.

5.3.2 Effect of pH

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionisation and speculation of different pollutants. 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 H^+ and 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 H^- ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions.

In the present study, the effect of pH on removal of Auramine and Rhodamine –B is negligible as shown in Fig. 5.12 and 5.58 respectively. The removal of Congo Red and Orange –G is more in acidic range as shown in fig. 5.24 and 5.42 respectively. Malachite green and Methyl Violet gives higher removal in higher pH range as shown in fig 5.42, 5.47 respectively. The calculated values are given in Appendix A.

5.3.3 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. 5.10, 5.22, 5.32, 5.40, 5.48 and 5.56 show the effect of contact time on removal of Auramine, Congo Red, Malachite Green, Orange- G, Methyl Violet, Rhodamine -B respectively. The calculated values are given in Appendix A. It is found that rate of removal is very rapid during initial 30 –45 minutes and thereafter it starts decreasing and there is no significant change after 180 minutes. 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 some time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules of the solid and bulk phases.

5.3.4 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 removal of Auramine, Congo Red, Malachite Green, Orange- G, Methyl Violet, Rhodamine -B are shown in Fig. 5.11, 5.23, 5.33, 5.41, 5.49 and 5.57 respectively. The calculated values are given in Appendix A. From these figures, it is evident that percentage removal is decreasing with the increasing initial concentration of adsorbate solution.

A comparison has been made between different adsorbents on the removals of dyes and shown in Table 5.10 and 5.11. It may also be observed that removal of Congo Red, Orange- G and Rhodamine- B dyes was less than other dyes requiring higher dose of adsorbent for removal of dyes to same level. Adsorption studies reveals that dye removal efficiency of various adsorbents were in following order. Bagasse flyash> Coal flyash> Lab grade Activated carbon >Commercial grade Activated carbon.

5.4 KINETICS OF ADSORPTION

The Lagergren equation as shown below has been used by a number of investigators [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, 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. 5.13, 5.25, 5.35, 5.43, 5.51 and 5.59. The straight-line plots show the validity of Lagergren equation. The correlation coefficients (r) obtained after fitting experimental data to Legergren equation are given in Appendix C. This follows that the adsorption kinetics can be fairly assumed to be of first order. Table 5.6 gives the value of adsorption rate constant (k) for different dyes with different adsorbents.

5.5 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 Auramine, Congo Red, Malachite Green, Orange- G, Methyl Violet, Rhodamine -B are shown in Figs. 5.20, 5.28, 5.38, 5.46,5.54 and 5.62 respectively. The plots 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 C. Thus indicating that controlling step is intraparticle diffusion. The values of intraparticle diffusion rate parameters (in mg g^{-1} $min^{-0.5}$) are given in Table 5.7.

5.6 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. 5.15,5.14,5.16, 5.26, 5.36, 5.44, 5.52 and 5.60 give the plot of Log q_e against log C_e for Auramine, Congo Red, Malachite Green, Orange- G, Methyl iolet, Rhodamine -B. Similarly Figs. 5.18, 5.19, 5.17, 5.27, 5.37, 5.45, 5.53 and 5.61 give the plot of $1/q_e$ against $1/C_e$ for these dyes. The experimental data fairly fit the straight line as shown by correlation coefficients (r) given in Appendix C.

The values of parameters for Freundlich and Langmuir isotherms are given in Table 5.8. Adsorptive capacities of the various adsorbents were in the following order. BFA>CFA>ACL>ACC.

Inspite of smaller size , (as per SEM) adsorption capacity in the coal flyash was also high which may be due to higher surface area because of high fineness and high carbon content.

5.7 ADSORPTION OF DYES IN THE FIXED BED OF BAGASSE FLYASH

The most important criterion in the design of a column adsorber is the prediction of column break through or the shape of the adsorption wave front, which determines the operating life span of the bed. The factors that effect the column breakthrough include both the operating variables as well as characteristic of the adsorbate and adsorbent. Here we have used bagasse fly ash as adsorbent and Methyl Violet and Rhodamine –B as adsorbate. The column diameter was taken 25 mm. The initial concentration for Methyl violet was taken 40 mg/l, pH 7.5, Temperature 25° C and for Rhodamine-B, the initial concentration was kept 20 mg/l, pH 7.0 and temperature 25° C. The three bed heights were taken as 30 cm, 45 cm and 60 cm. The flow rate was kept 75ml/min. fig 5.63 and 5.64 presents the breakthrough curves (C/Co Vs time) for Methyl Violet and Rhodamine –B .

5.7.1 Effect of Bed Height

From Fig 5.63 and 5.64 it is found that profile of the break through curve varies with bed height. As the bed height increases the curve becomes less steep. A plot between bed height (Z) and service time (t) that verifies Bohart -Adams Equation is drawn in Fig 5.65.

Bohart -Adams Equation:

$$t = \frac{N_0}{C_{A0}u} Z - \frac{1}{C_{A0}k_a} \ln\left(\frac{C_{A0}}{C_{Ab}} - 1\right)$$

Or

$$t = m_a Z + C$$

Where C_{Ab} = desired concentration of adsorbate at break through, (mgl^{-1})

K_a = rate constant, (l liquid/mg of adsorbent)

N_0 = adsorptive capacity of the adsorbent, (mgl^{-1})

Z = depth of the adsorbent bed in the column (m)

u = linear velocity of the feed solution in the bed (ms^{-1})

t = service time of column under above conditions,(s).

5.8 ECONOMIC EVALUATION OF ADSORBENTS

Economic evaluation of the process has been given in Table 5.13 and 5.14. It may be seen that cost of bagasse fly ash, coal fly ash is almost free except handling charges. While the adsorptive capacities of bagasse fly ash is higher than the Activated carbons (laboratory and commercial grade)

Table 5.1: Characteristic of adsorbents

CHARACTERISTIC	ACL	ACC	BFA	CFA
Bulk Density (Kg/m^3)	588.23	740.74	133.33	333.33
Moisture(%)	8.61	9.07	7.64	6.92
Volatile matter (%)	16.62	17.32	17.37	9.28
Ash(%)	2.67	5.49	26.425	51.97
Fixed carbon	72.1	68.12	48.565	31.83

Table 5. 2: Particle size analysis of activated carbon commercial grade.

Particle size	Weight (%)
>2.0 mm	7.62
2.0 mm – 1.7 mm	24.53
1.7 mm – 1.4 mm	43.04
1.4 mm – 1.18 mm	10.83
1.18 mm – 1.0 mm	5.15
1.0 mm – 850 μ m	6.77
< 850 μ m	2.06

Table 5.3: Particle size analysis of activated carbon laboratory grade.

Particle size	Weight (%)
> 4.0 mm	14.00
4 mm –3.35 mm	5.38
3.35 mm- 2.8 mm	23.55
2.8 mm – 2.0 mm	50.55
2.0 mm – 1.7 mm	3.33
1.7 mm – 1.4 mm	2.68
<1.4 mm	0.51

Table 5.4: Particle size analysis of bagasse flyash

Particle size	Weight (%)
> 1.4 mm	0.96
1.4 mm – 1.18 mm	1.40
1.18 mm – 1.0 mm	2.09
1.0 mm – 850 μm	1.97
850 μm – 212 μm	21.95
212 μm – 180 μm	39.92
<180 μm	31.71

Table 5.5: Chemical analysis of BFA and CFA

% Chemical composition	Coal fly ash (CFA)	Bagasse fly ash (BFA)
LOI	48.8	49.7
SiO_2	30.7	36.3
Al_2O_3	12.3	5.2
Fe_2O_3	4.0	3.8
CaO	2.2	3.0
MgO	1.6	1.6

Table 5.6: Adsorption rate constant k for adsorbents in dye adsorption from Lagergren equation

DYE	LAGERGREN CONSTANT, k (min $^{-1}$)		
	BFA	ACC	ACL
AURAMINE	0.0225	0.0264	0.0258
CONGO RED	0.0159	0.0193	0.0209
MALACHITE GREEN	0.0154	0.0269	0.0172
METHYL VIOLET	0.0184	-	-
RHODAMINE-B	0.0184	-	-
ORANGE - G	0.0081	-	-

Table 5.7: Intraparticle diffusion rate parameter k' from Weber Morris plot

DYE	k' ($mg\ g^{-1}\ min^{-0.5}$)		
	BFA	ACC	ACL
AURAMINE	0.1355	0.0106	0.0881
CONGO RED	0.3544	0.4632	0.3243
MALACHITE GREEN	0.0067	0.0044	0.0199
METHYL VIOLET	0.9606	-	-
RHODAMINE-B	0.0586	-	-
ORANGE - G	0.2832	-	-

Table 5.8: Isotherm parameter for different dye- adsorbent system at 30° C

DYE	ADSORBENT	FREUNDLICH ISOTHERM		LANGMUIR ISOTHERM	
		$K_F\ (mg/l)^{-1/n}$	n	$q_m(mg/g)$	$K_A(mg^{-1})$
AURAMINE	BFA	17.8772	1.8305	59.8802	0.8392
	ACC	1.4325	2.6940	1.2888	12.9967
	ACL	7.6085	3.9401	12.7226	2.0363
CONGO RED	BFA	18.3105	1.4641	10.8696	5.5422
	ACC	0.4066	4.6970	0.6062	2.2055
	ACL	0.9320	2.5517	1.7665	1.3020
MALACHITE GREEN	BFA	12.3937	4.3516	15.7978	3.7456
	ACC	1.1803	2.7571	1.5108	4.0959
	ACL	5.5744	1.9120	10.6838	1.1415
METHYL VIOLET	BFA	13.1100	4.2845	25.0000	0.7767
ORANGE -G	BFA	2.8629	2.7248	5.5127	1.3816
RHODAMINE - B	BFA	5.9415	3.2103	12.8535	0.8616

Table 5.9: Characterization of actual paper mill effluent.

S. No.	Sample	Color	pH	Conductivity	Turbidity (NTU Units)	BOD (mg/l)	COD (mg/l)	% Color removal	Wt (g)	% COD Removal		
										ACL	BFA	CFA
1	**Paper mill combined effluent**	Dirty Yellow	7.7	1.333 μ mho	15	255	476	100.00	0.1	70.6	80.3	89.7
								-	0.3	75.0	92.6	95.6
									0.5	77.9	95.6	98.5
2	**Chlorinated pulp back water**	Light yellow	1.92	245 mv	3.3	318	602	82.00	0.5	-	28.0	-
								-	1.0	-	-	58.0
									2.0	46.5	-	-
3	**Alkaline extraction stage back water**	Brown	12.75	-292mv	5.8	2100	3500	20.00	0.5	-	35.0	-
								-	1.0	-	-	50.0
									2.0	46.0	-	-
4	**White Water**	Light green	4.45	119 mv	27.4	98	182	100.00	0.5	-	92.3	-
								-	1.0	-	-	92.3
									2.0	100.0	-	-
									0.2	-	61.5	-

BFA = BAGASSE FLY ASH

ACL = ACTIVATED CARBON LABORATORY GRADE

CFA = COAL FLY ASH

Volume taken for COD removal = 100 ml.

Table 5.10: CHARACTERIZATION OF DYES WITH COMPARISON ON COLOR REMOVAL WITH DIFFERENT ADSORBENTS.

PROPERTY DYE	λ max (nm)	pH	CONDUCTIVITY (μmho)	C. O. D. (mg/l)	% REMOVAL OF COLOR			
					BFA 0.1 g /mg of Dye	CFA 0.1 gm/mg of Dye	ACL 1.0 g/mg of Dye	ACC 1.0 g/mg Dye
ORANGE– G C.I.No.16230 Y=-7.0856X+100	476	7.7	69	14	68.95	56.6	81.94	42.42
BRILLIANT GREEN C. I. No. 42040 Y=-18.165X+100	624	8.0	132.2	7	100.0	91.9	98.84	95.43
METHYL VIOLET C. I. No. 42535 Y=-21.619X+100	580	7.5	143.6	28	98.47	94.54	100.00	94.22
RHODAMINE– B GR C. I. No. 45170 Y=- 38.575X+100	555	7.0	90.0	28	76.8	76.2	98.20	59.30
MALACHITE GREEN C. I. No. 42000 Y=-17.12X+100	618	7.3	140.3	34.54	97.95	100.0	100.00	96.26
CONGO RED C. I. No. 22120 Y=-8.8345X + 100	500	7.5	155.0	13.776	80.19	98.64	86.87	56.08
AURAMINE C. I. No. 41000 Y=-9.4283X+100	432	7.2	33.0	27.6	97.45	97.56	97.88	93.31
METHYLENE BLUE Y=-26.193X+100	660	7.3	96.2	22.0	99.31	79.96	99.46	92.78

Table 5.11: A comparison of adsorbent dose of different adsorbents for higher removal of dyes.

DYE	BAGASSE FLY ASH		COAL FLY ASH		ACTIVATED CARBON (LAB)		ACTIVATED CARBON (COMMERCIAL)	
	g/mg of Dye	% Removal	g/mg of Dye	% Removal	g/mg of Dye	% Removal	g/mg of Dye	% Removal
ORANGE –G	1.0	100.00	1.0	96.75	2.0	96.33	4.0	66.27
BRILLIANT GREEN	0.1	100.00	0.1	91.90	1.0	98.84	1.0	95.43
METHYL VIOLET	0.1	98.47	0.1	94.54	1.0	100.00	1.0	100.00
RHODAMINE –B	0.5	100.00	0.4	99.12	1.0	98.2	4.0	88.83
MALACHITE GREEN	0.1	97.95	0.1	100.00	1.0	100.00	1.0	96.26
CONGO RED	1.0	99.43	0.1	98.64	1.5	100.00	4.0	98.07
AURAMINE	0.1	97.45	0.1	97.56	1.0	97.888	1.0	93.31
METHYLENE BLUE	0.1	99.31	0.4	100.00	1.0	99.46	4.0	100.00

Table 5.12: Values of adsorptive capacity and critical bed height for Bagasse flyash.

ADSORBENT(S)	N_0 (mg/l)	Z_0 (cm)
Methyl Violet	1230.63	0.9574
Rhodamine -B	746.27	6.5789

Table 5.13: Economic Evaluation based on adsorptive capacity of adsorbents for some dyes.

DYE	ADSORPTIVE CAPACITY (mg dye / adsorbent)		
	Bagasse flyash	Activated Carbon (Laboratory grade)	Activated Carbon (Commercial grade)
Auramine	59.88	12.72	1.29
Congo Red	10.87	1.77	0.61
Malachite Green	15.80	10.68	1.51
Cost Rs. Per tonne	**1000**	**40,000-50,000**	**30,000**

Table 5.14: Economic Evaluation based on comparative study.

DYE	% REMOVAL OF COLOR			
	BFA (0.1 g/mg of dye)	**CFA (0.1 g/mg of dye)**	**ACL (1.0 g/mg of dye)**	**ACC (1.0g/mg of dye)**
Auramine	97.45	97.56	97.88	93.31
Congo Red	80.19	98.64	86.87	56.08
Malachite Green	97.95	100.0	100.0	96.26
Orange - G	68.95	56.6	81.94	42.42
Methyl Violet	98.47	94.54	100.0	94.22
Rhodamine –B	76.8	76.2	98.2	59.3
Methylene Blue	99.31	79.96	99.46	92.76
Brilliant green	100.0	91.9	98.84	95.43
ACTUAL EFFLUENT	% COD REMOVAL			
	BFA (0.5g/100ml effluent)	**CFA (0.5g/100ml effluent)**	**ACL (0.5g/100ml effluent)**	**ACC (0.5g/100ml effluent)**
Paper mill combined effluent	95.6	98.5	77.9	-
Cost	1000	1000	40,000 – 50,000	30,000

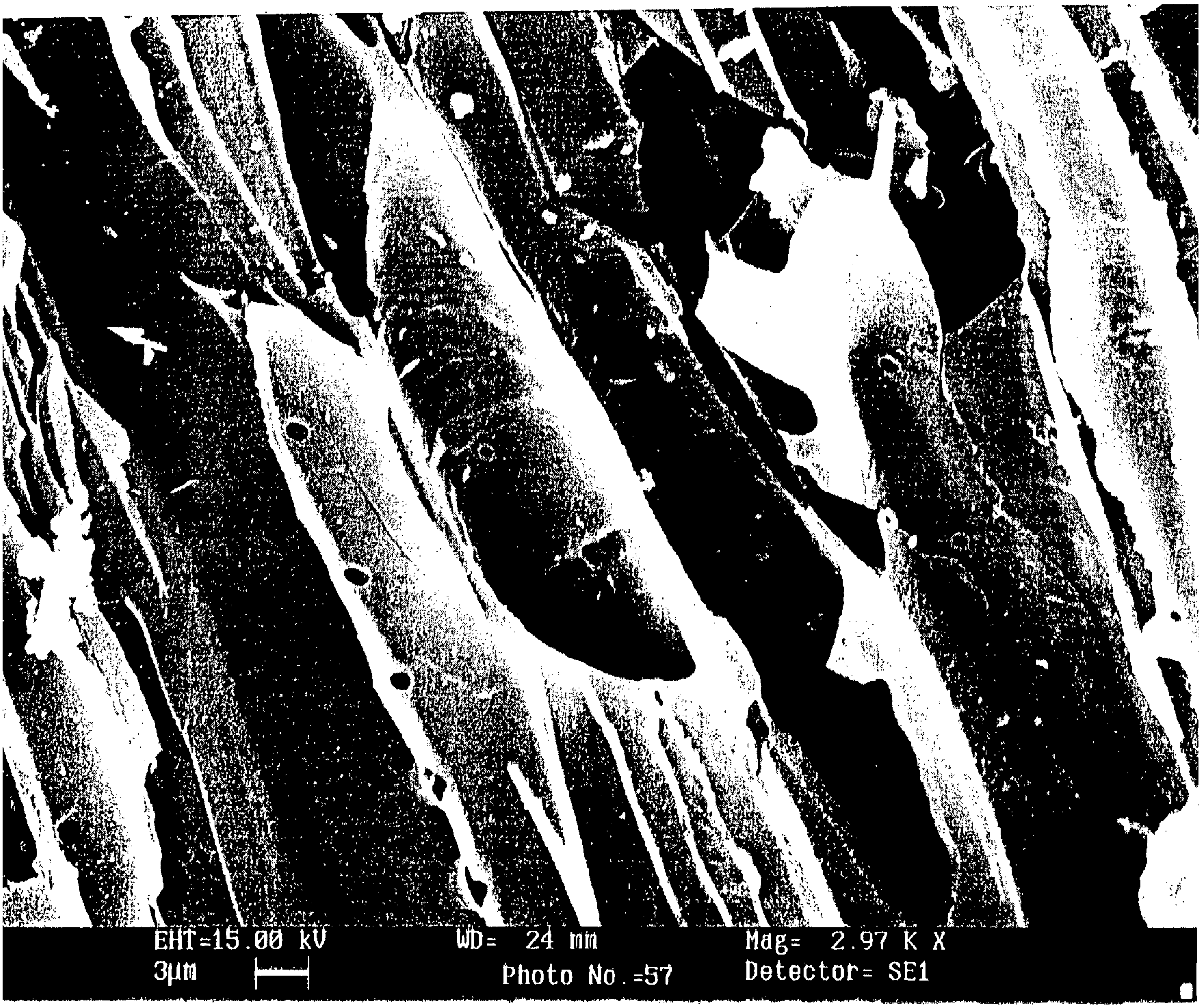


Fig. 5.1 Scanning electron micrograph of activated carbon (laboratory grade) at 2.97K magnification

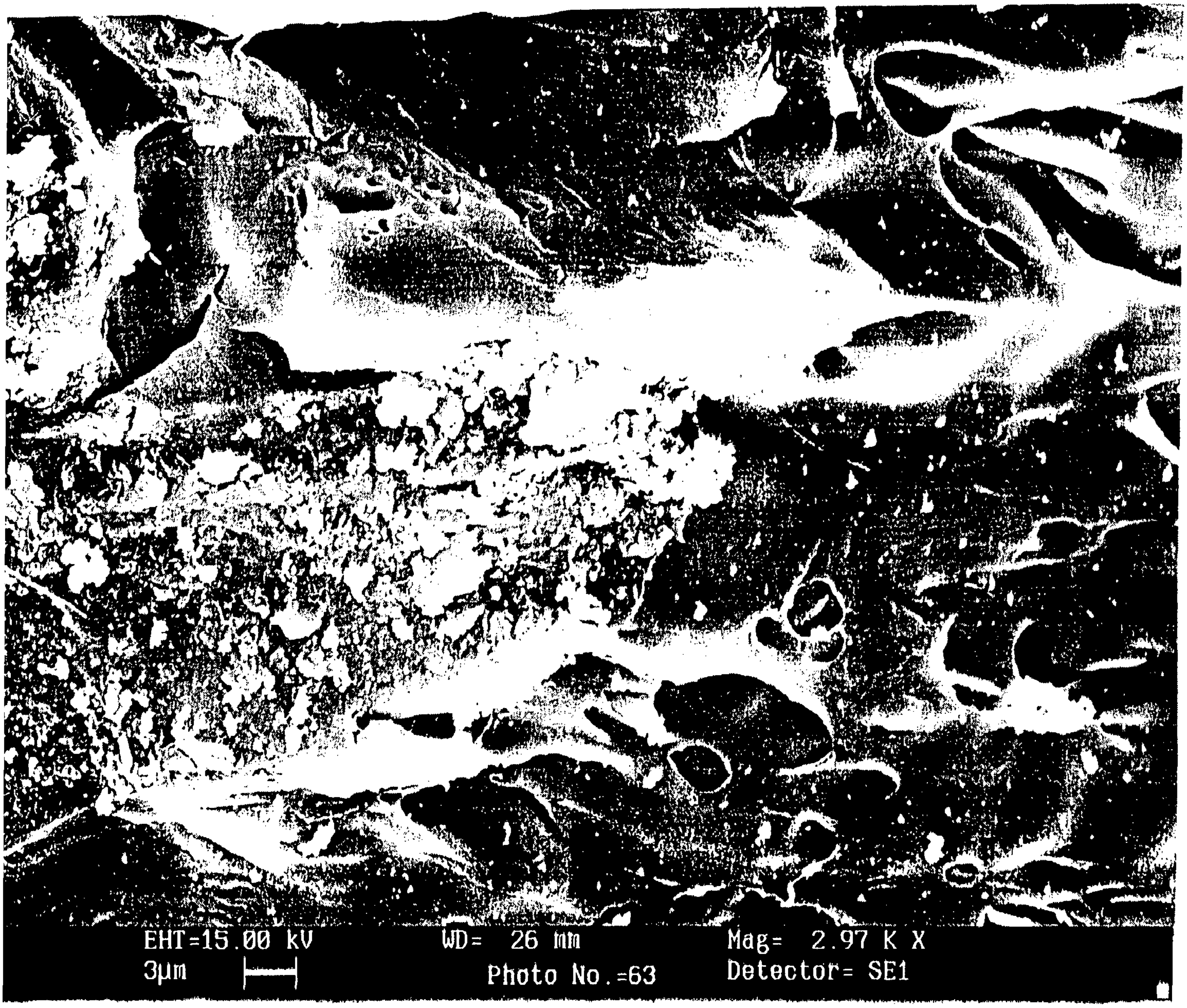


Fig. 5.2 Scanning electron micrograph of activated carbon (commercial grade) at 2.97K magnification

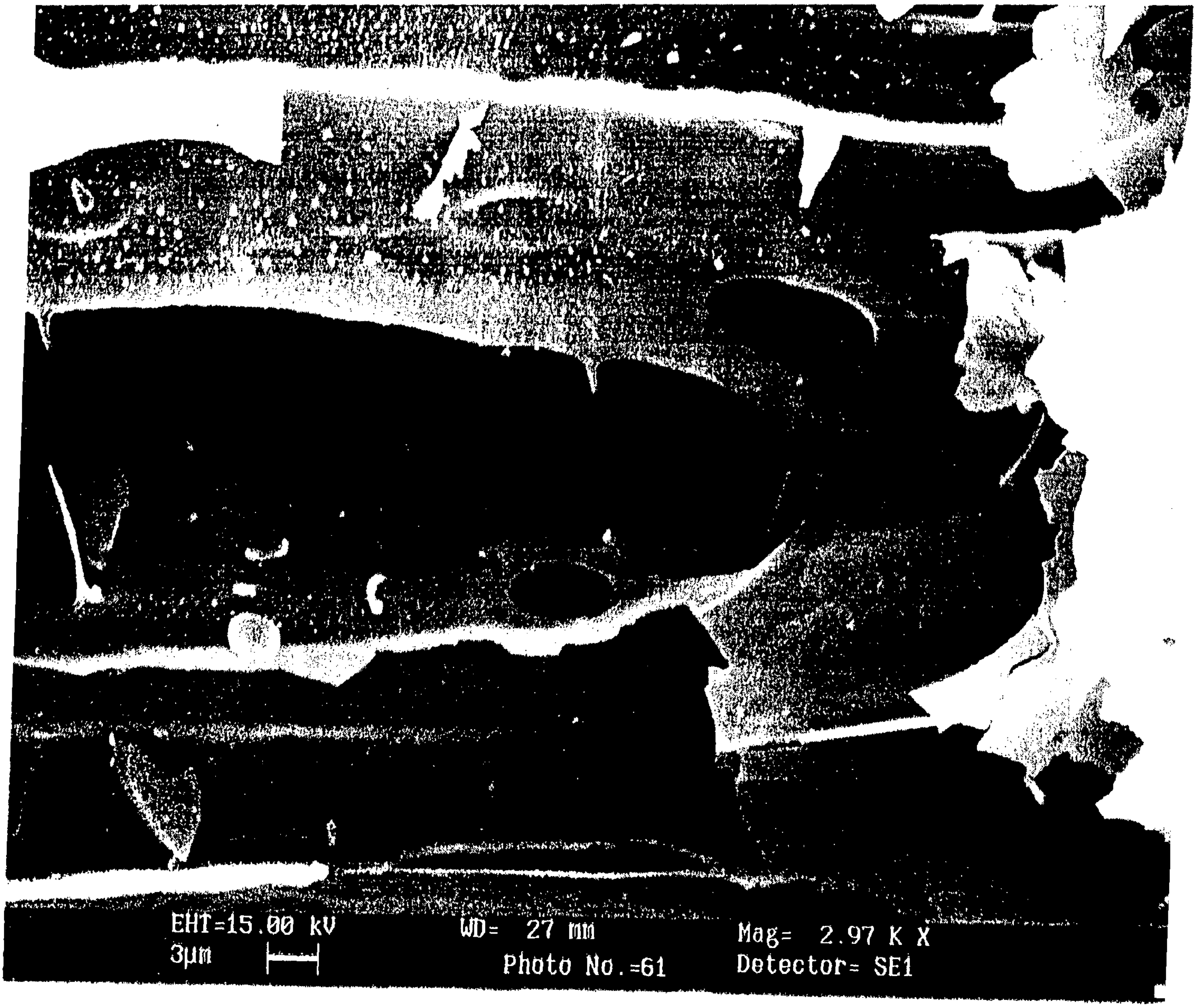


Fig. 5.3 Scanning electron micrograph of bagasse fly ash at 2.97K magnification

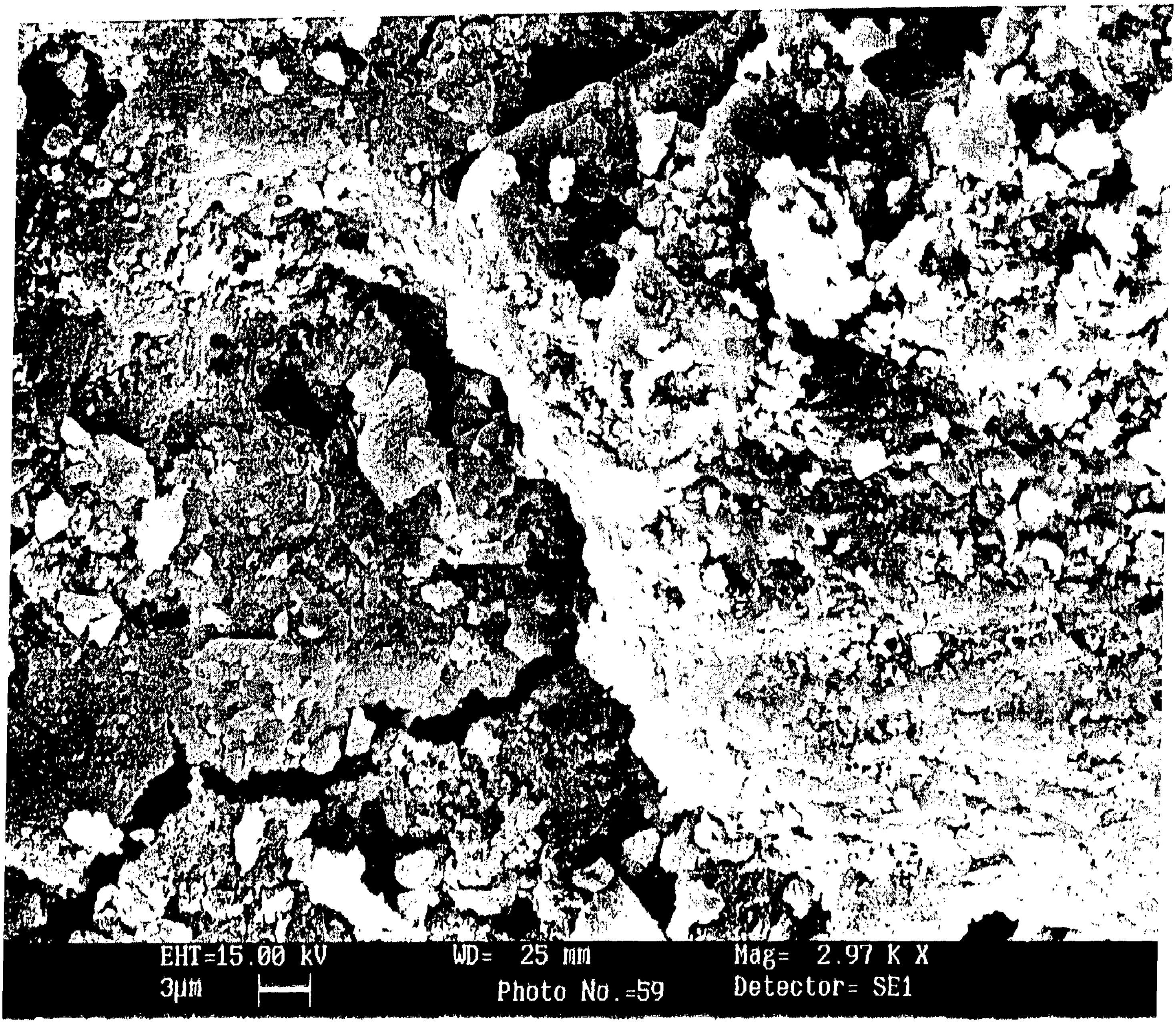


Fig. 5.4 Scanning electron micrograph of coal ash at 2.97K magnification

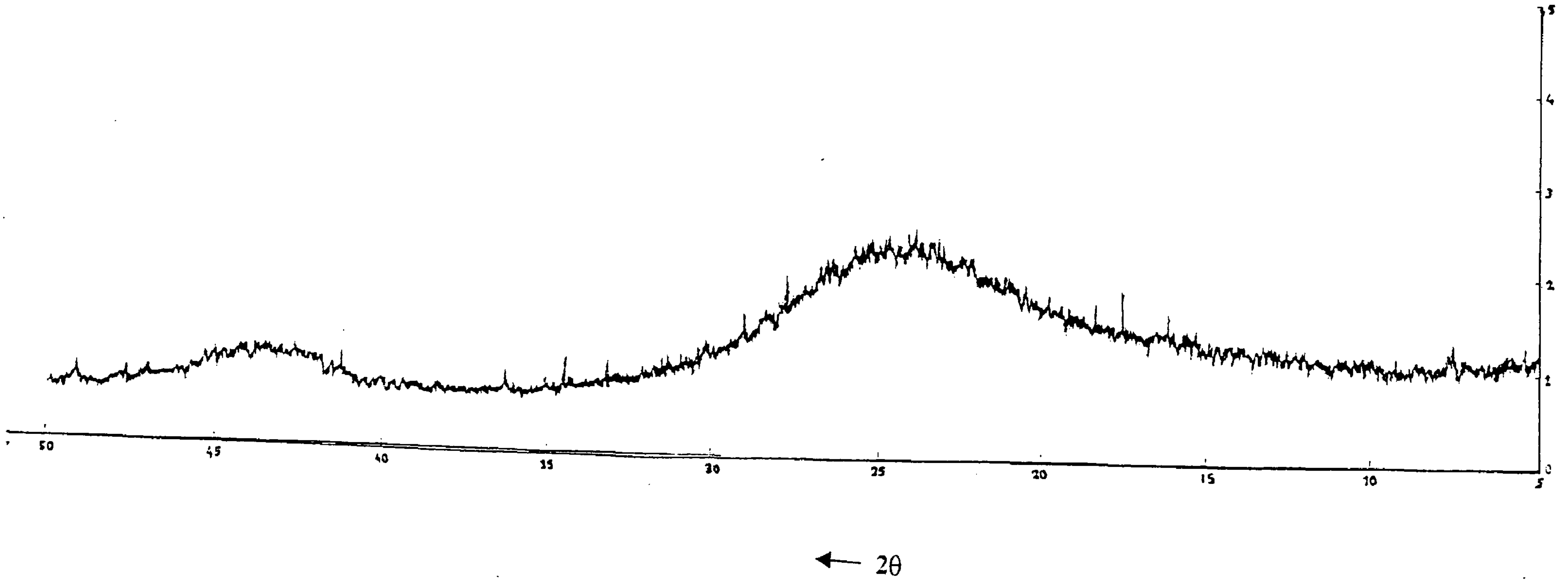


Fig. 5.5 X-ray diffraction pattern for the activated carbon (laboratory grade)

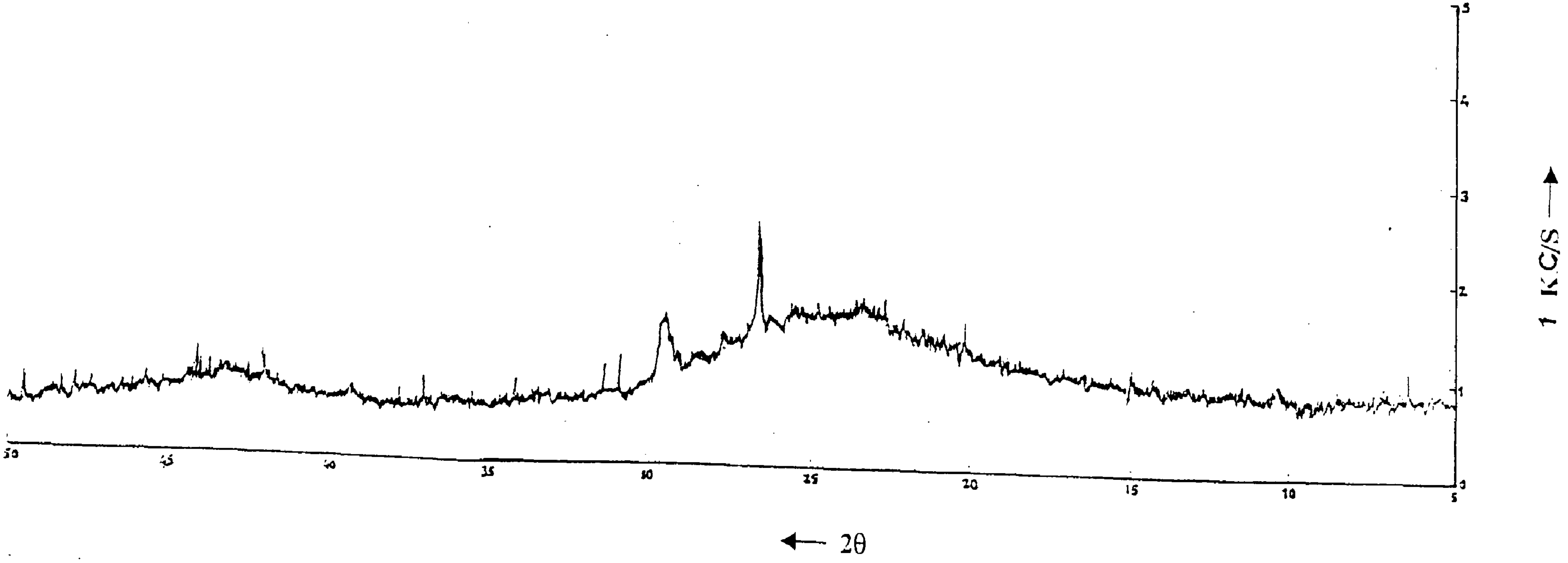


Fig. 5.6 X-ray diffraction pattern for the activated carbon (commercial grade)

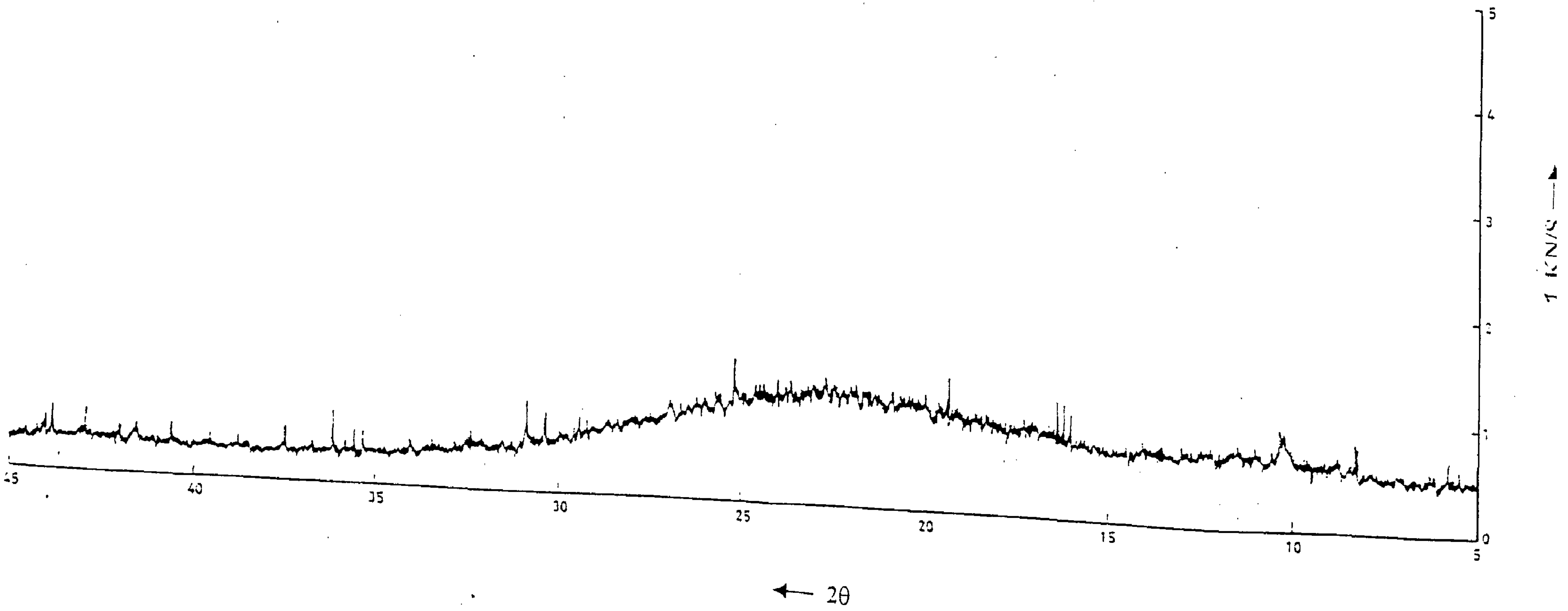


Fig. 5.7 X-ray diffraction pattern for the bagasse fly ash

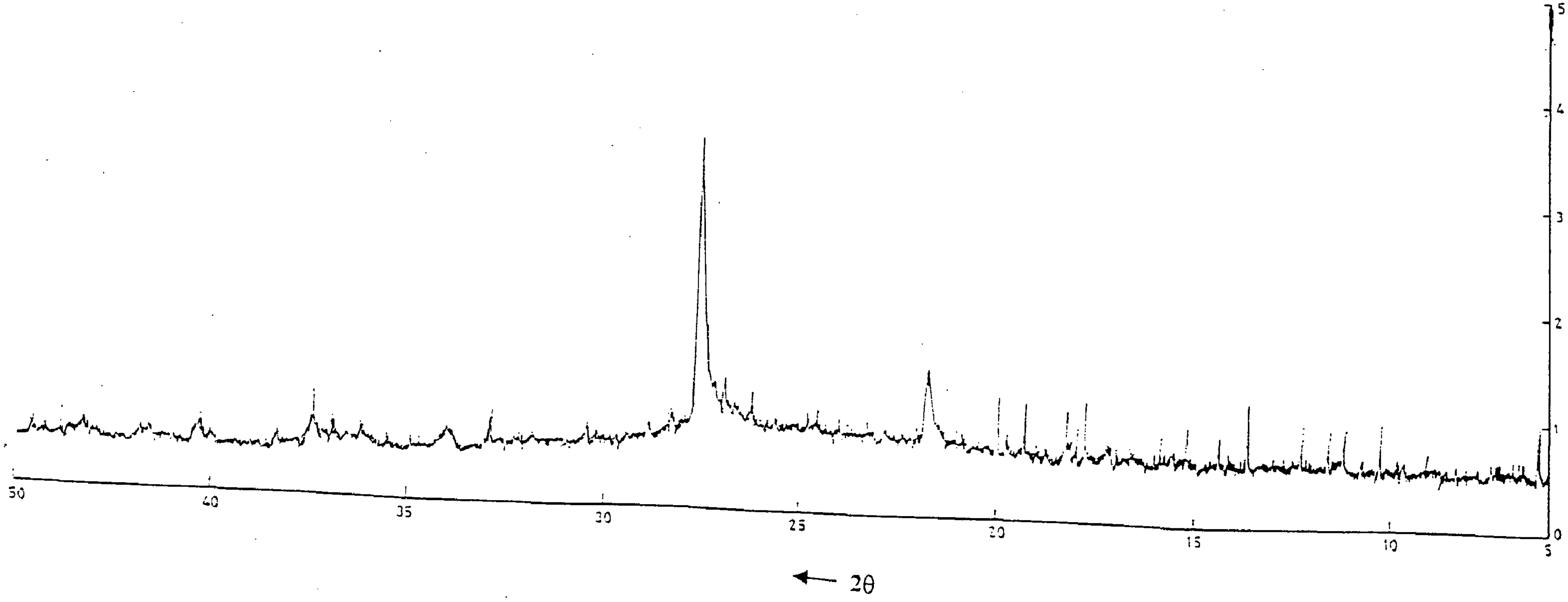


Fig. 5.8 X-ray diffraction pattern for the coal ash

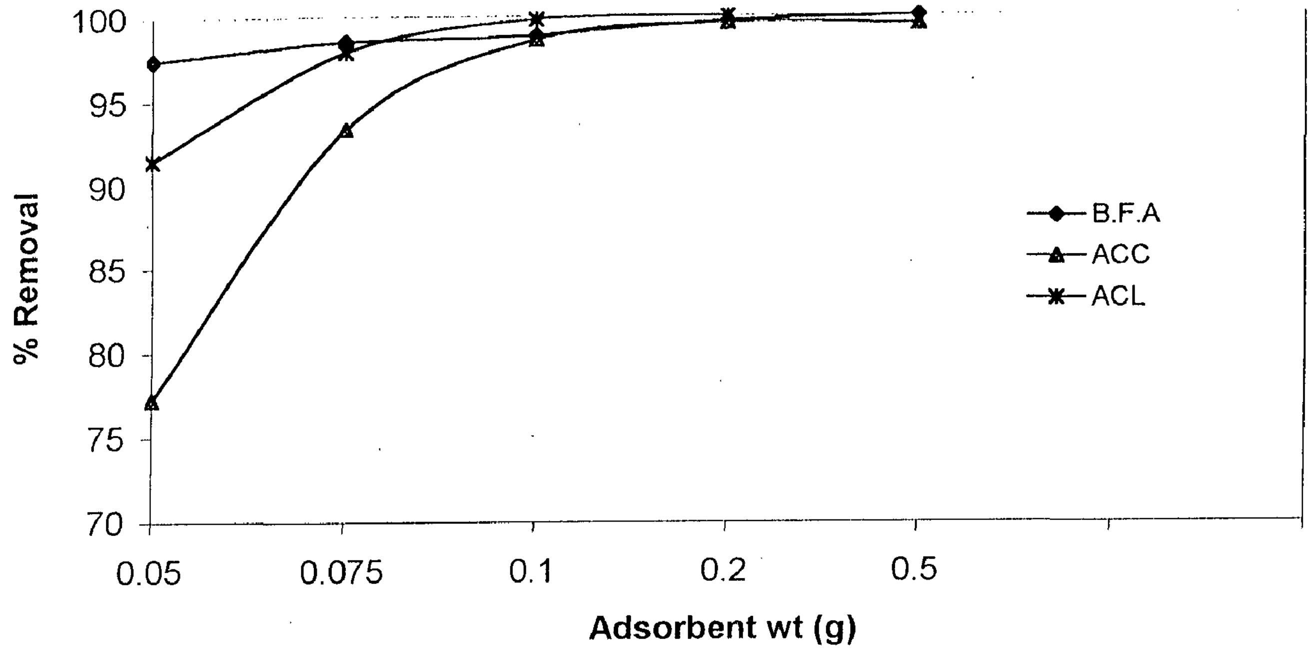


FIG 5.9 EFFECT OF ADSORBENT DOSE ON REMOVAL OF AURAMINE

Initial concentration = 10 mg/l ,Volume=50 ml, contact time = 5.0 hr,

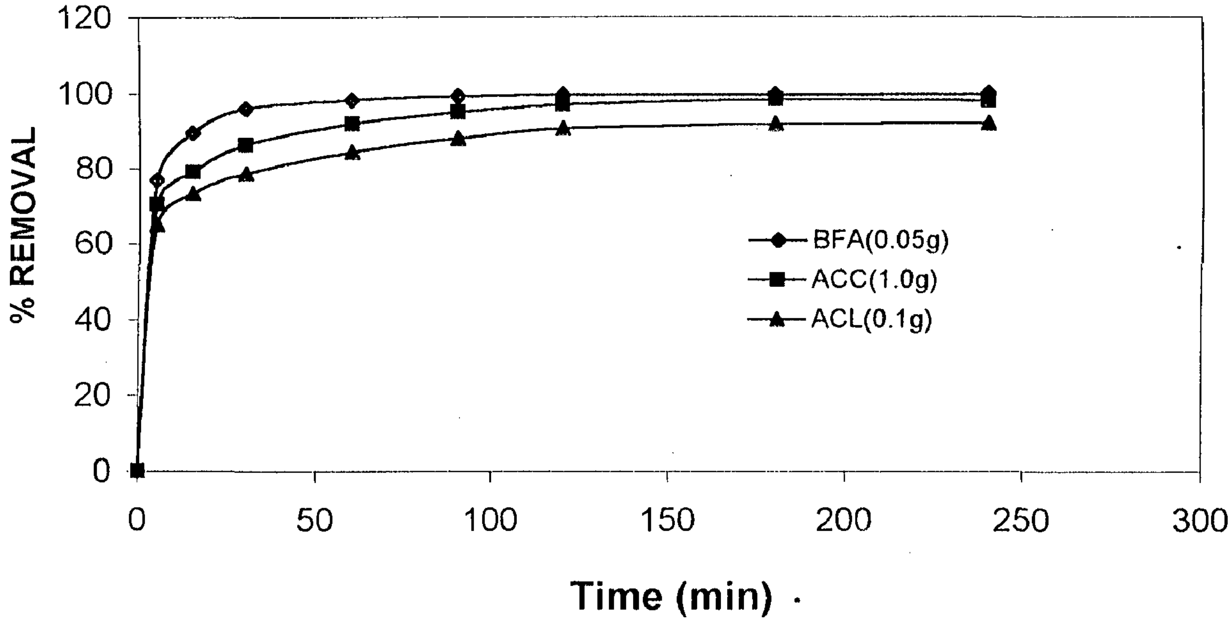
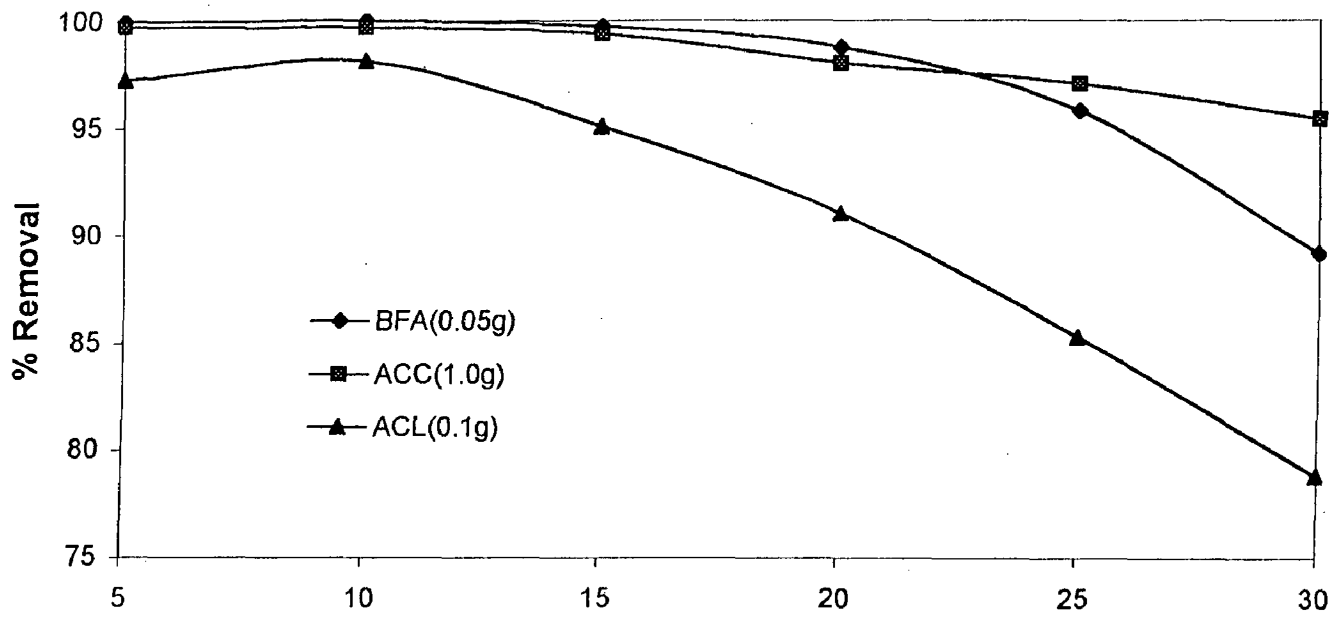


FIG 5.10 EFFECT OF CONTACT TIME ON REMOVAL OF AURAMINE



Concentration of Dye (mg/l)

FIG 5.11 EFFECT OF INITIAL CONCENTRATION ON REMOVAL OF AURAMINE

Volume= 50ml, Time=5.0 hr,pH=7.2

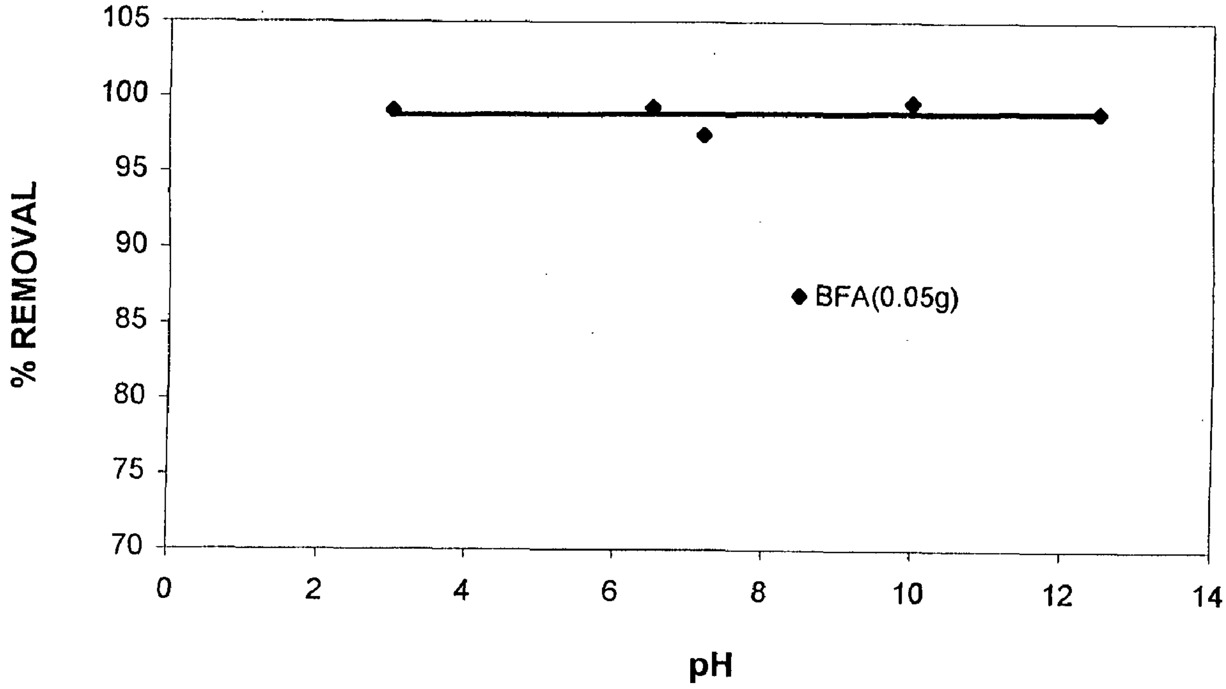


FIG 5.12 EFFECT OF PH ON REMOVAL OF AURAMINE

Initial concentration = 10 mg/l, Volume = 50ml

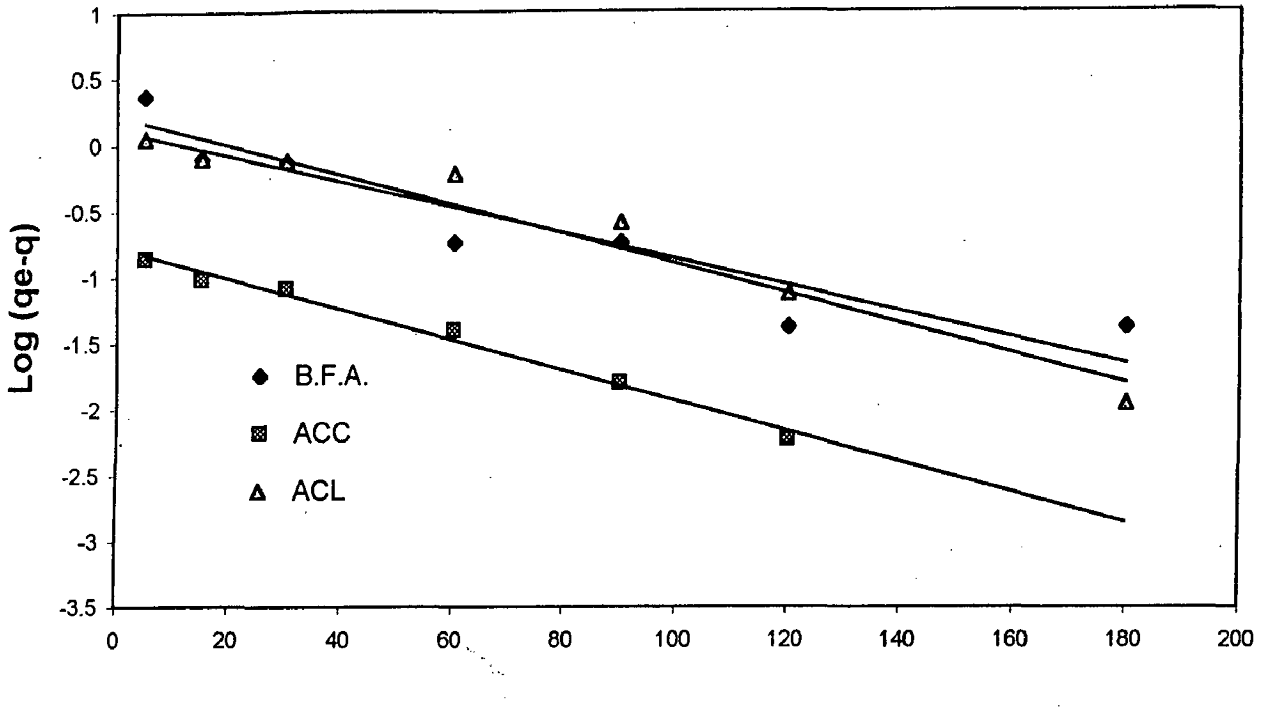


FIG 5.13 LAGREGREN PLOT FOR REMOVAL OF AURAMINE

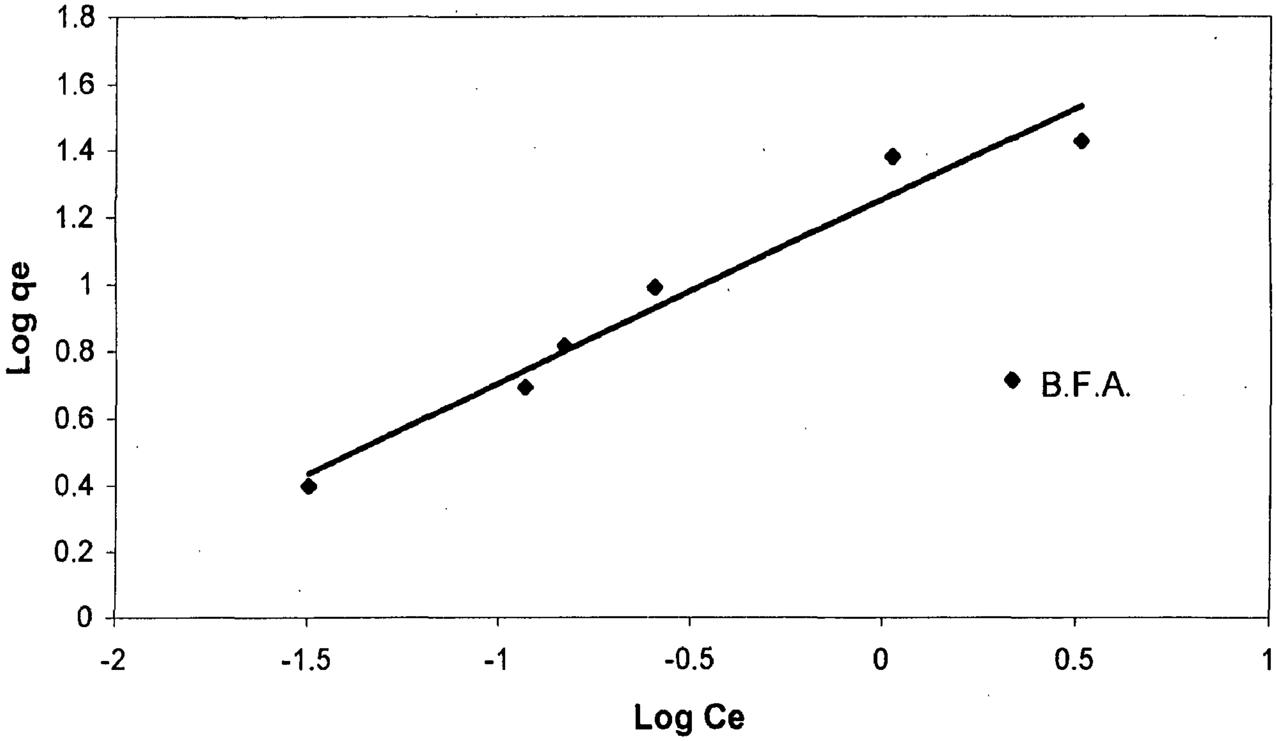


FIG 5.14 FREUNDLICH ISOTHERM FOR REMOVAL OF AURAMINE

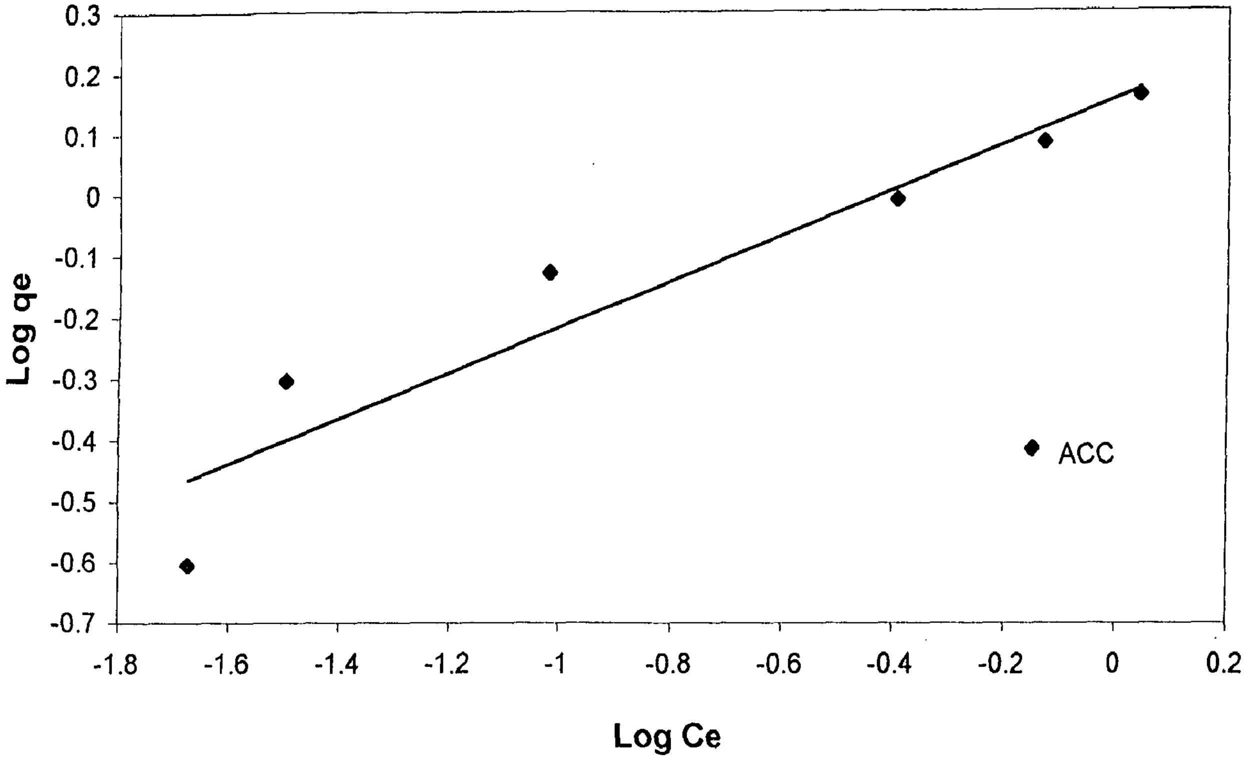


FIG 5.15 FREUNDLICH ISOTHERM FOR REMOVAL OF AURAMINE

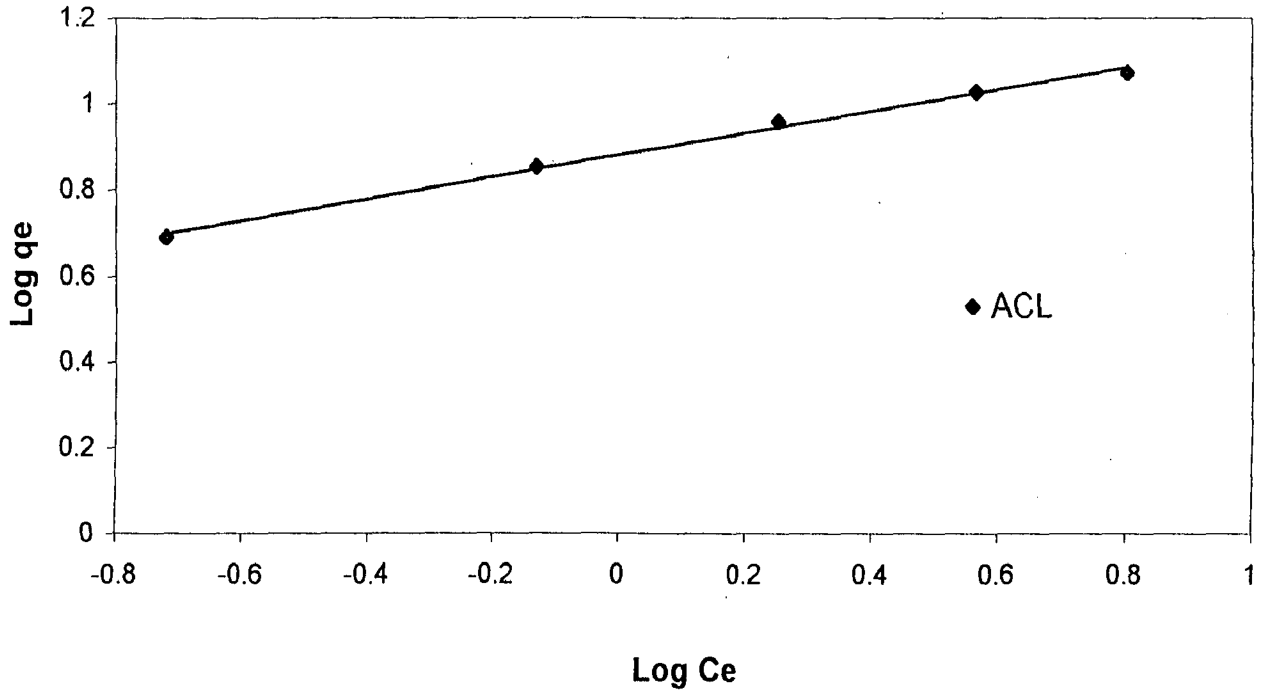


FIG 5.16 FREUNDLICH ISOTHERM FOR REMOVAL OF AURAMINE

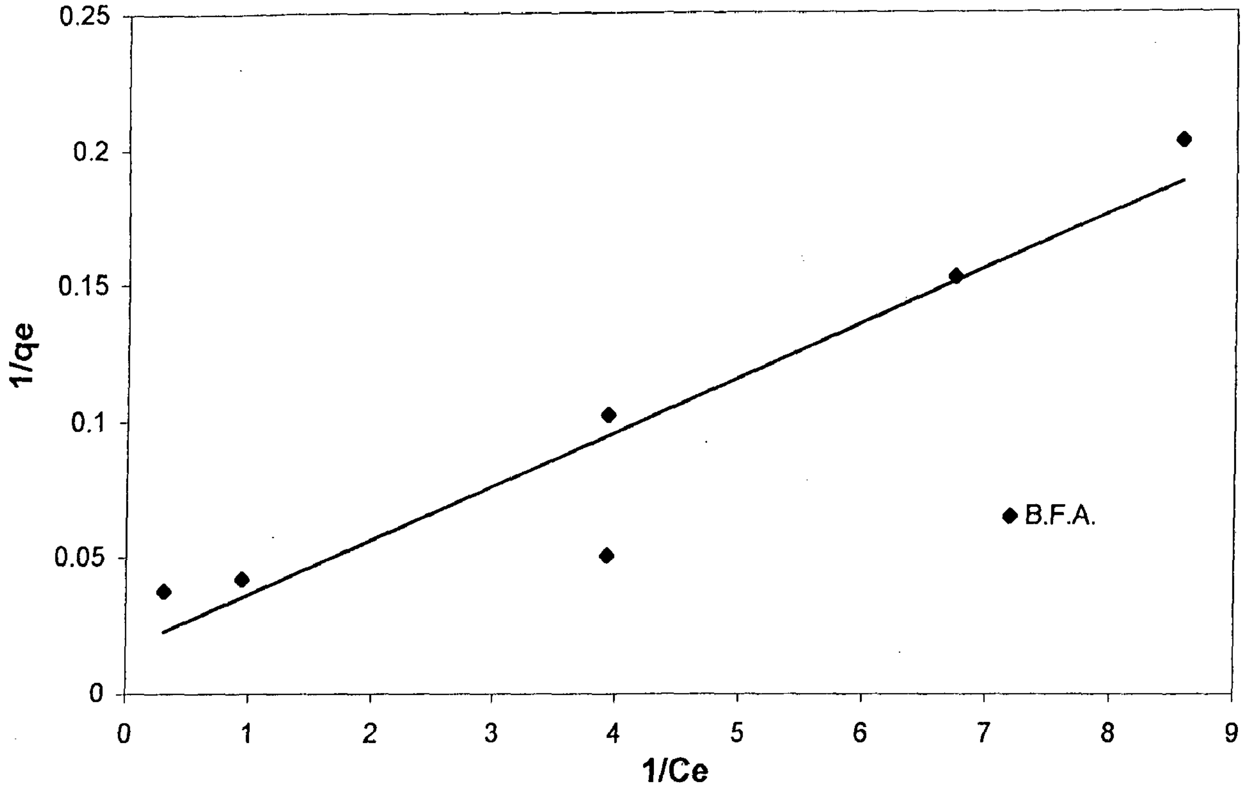


FIG 5.17 LANGMUIR ISOTHERM FOR REMOVAL OF AURAMINE

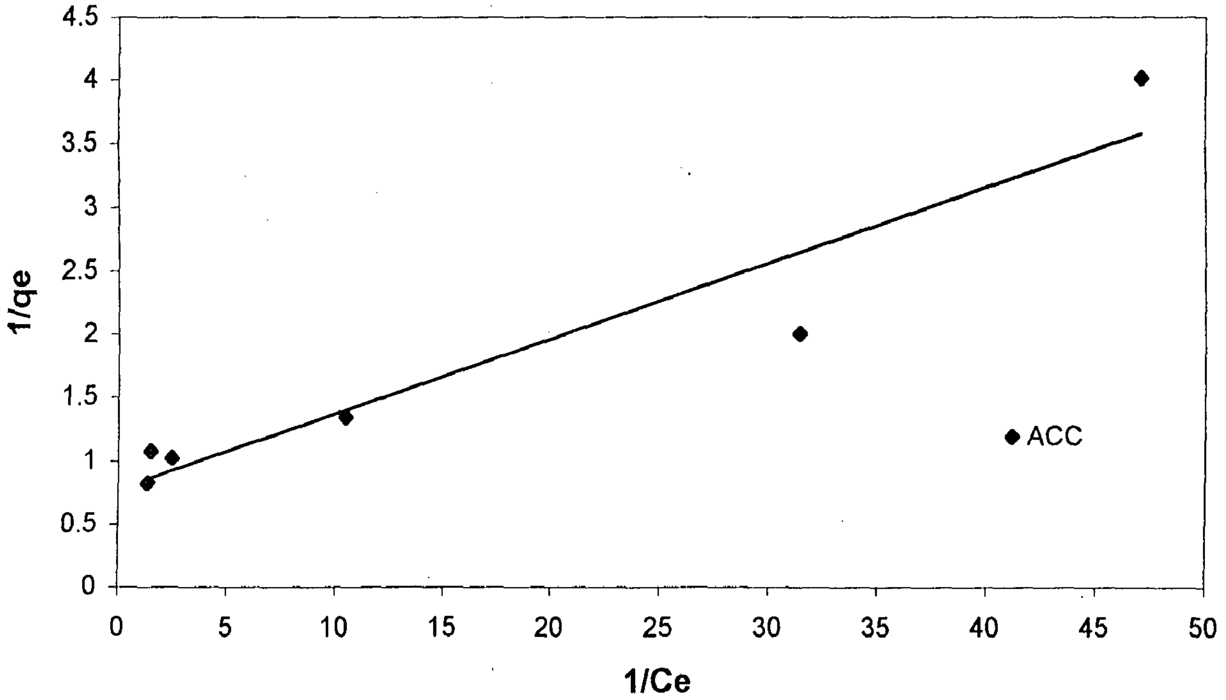


FIG 5.18 LANGMUIR ISOTHERM FOR REMOVAL OF AURAMINE

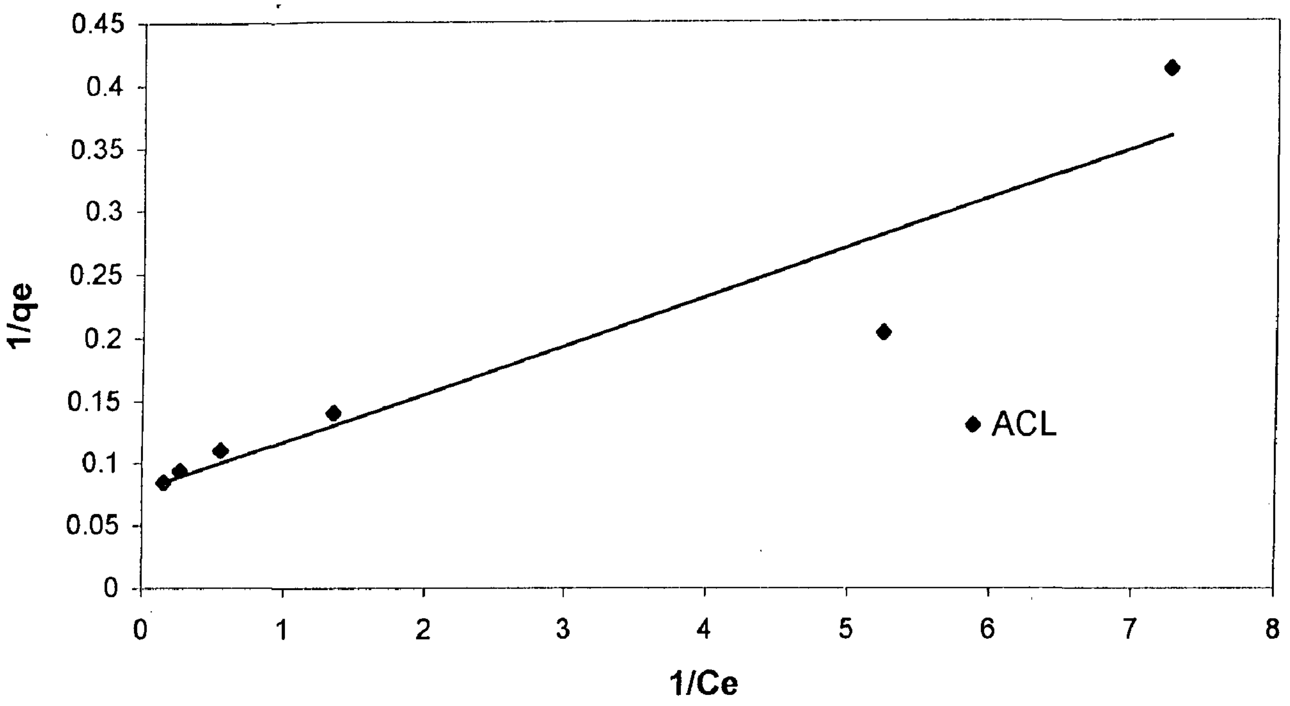


FIG 5.19 LANGMUIR ISOTHERM FOR REMOVAL OF AURAMINE

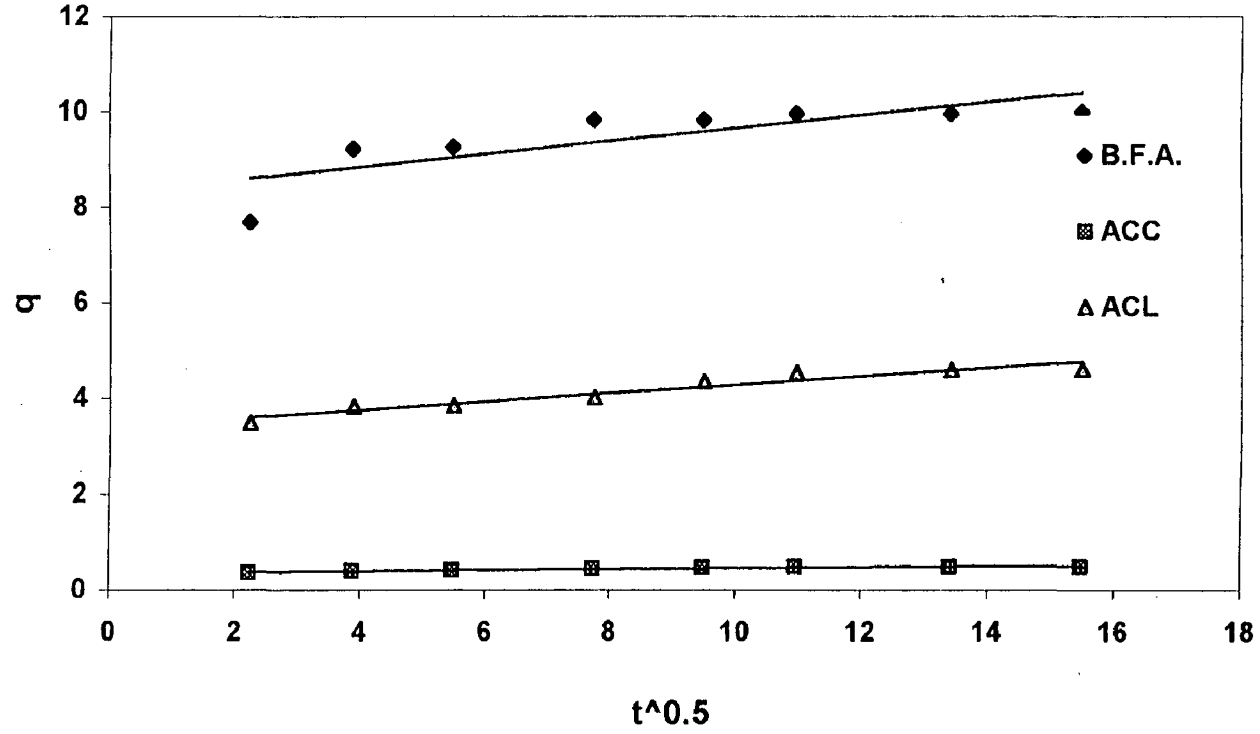


FIG 5.20 WEBER AND MORRIS INTRAPARTICLE DIFFUSION PLOT FOR REMOVAL OF AURAMINE

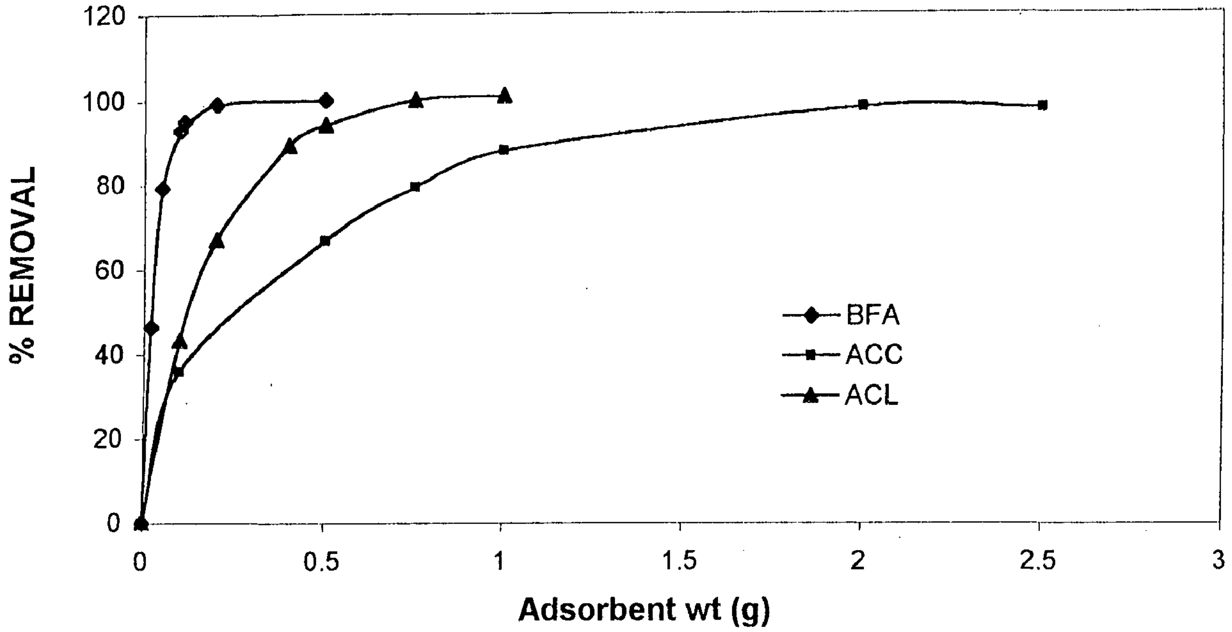


FIG 5.21 EFFECT OF ADSORBENT DOSE ON REMOVAL OF CONGO RED

Initial concentration = 10 mg/l,Time =5 hr,pH=7.5

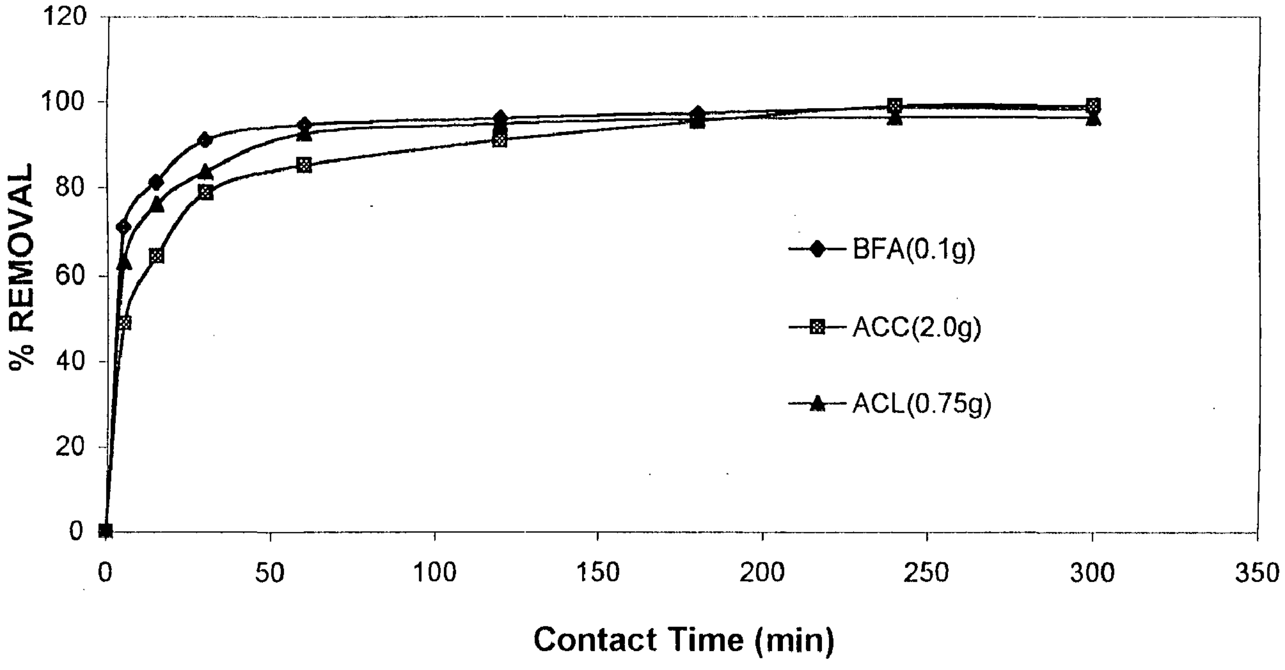


FIG 5.22 EFFECT OF CONTACT TIME ON REMOVAL OF CONGO RED

Initial concentration=10 mg/l, pH=7.5

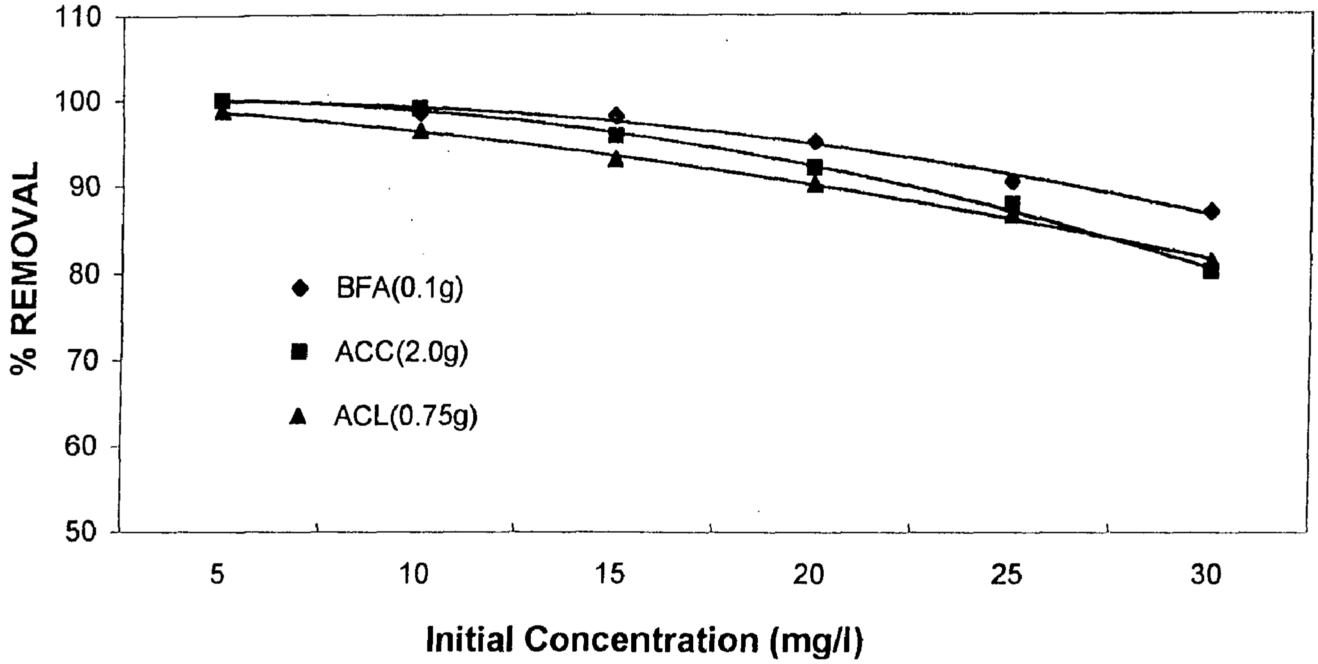


FIG 5.23 EFFECT OF INITIAL CONCENTRATION OF CONGO RED ON ITS REMOVAL

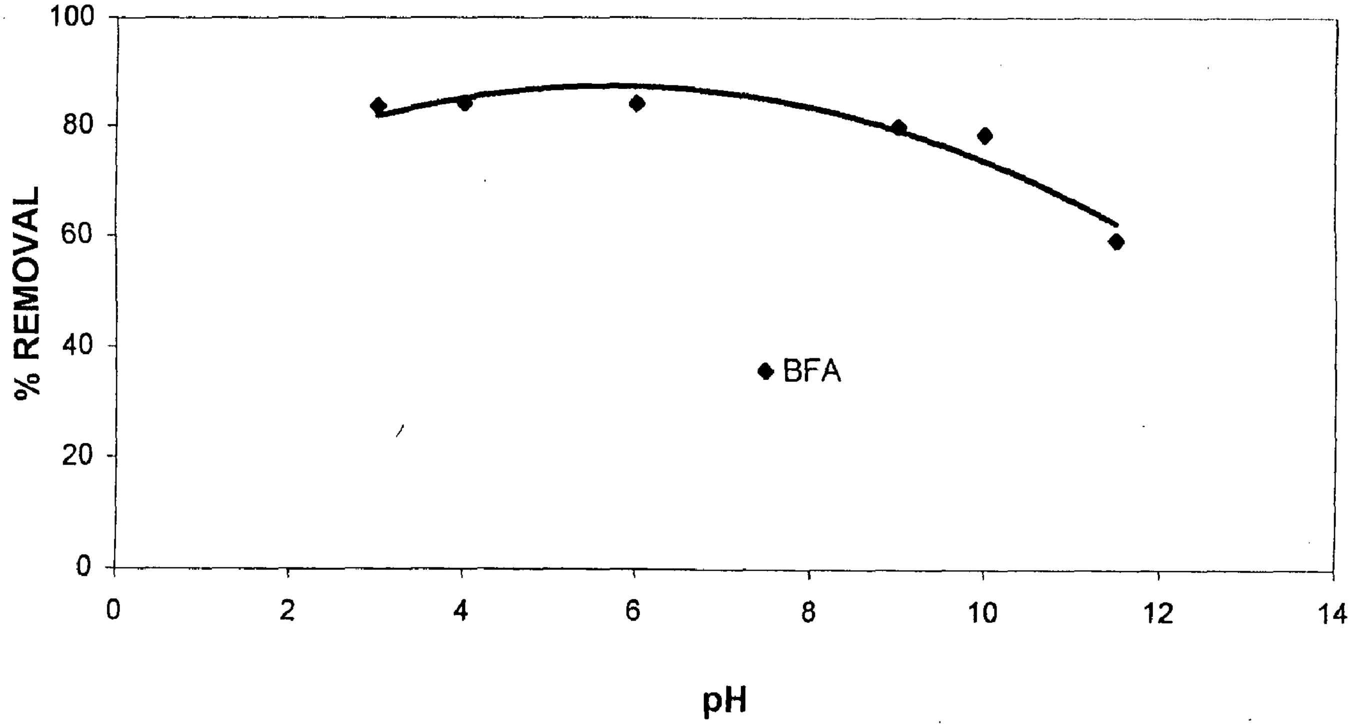


FIG 5.24 EFFECT OF pH ON REMOVAL OF CONGO RED

Initial concentration=10mg/l, BFA=0.05g, Vol=50 ml

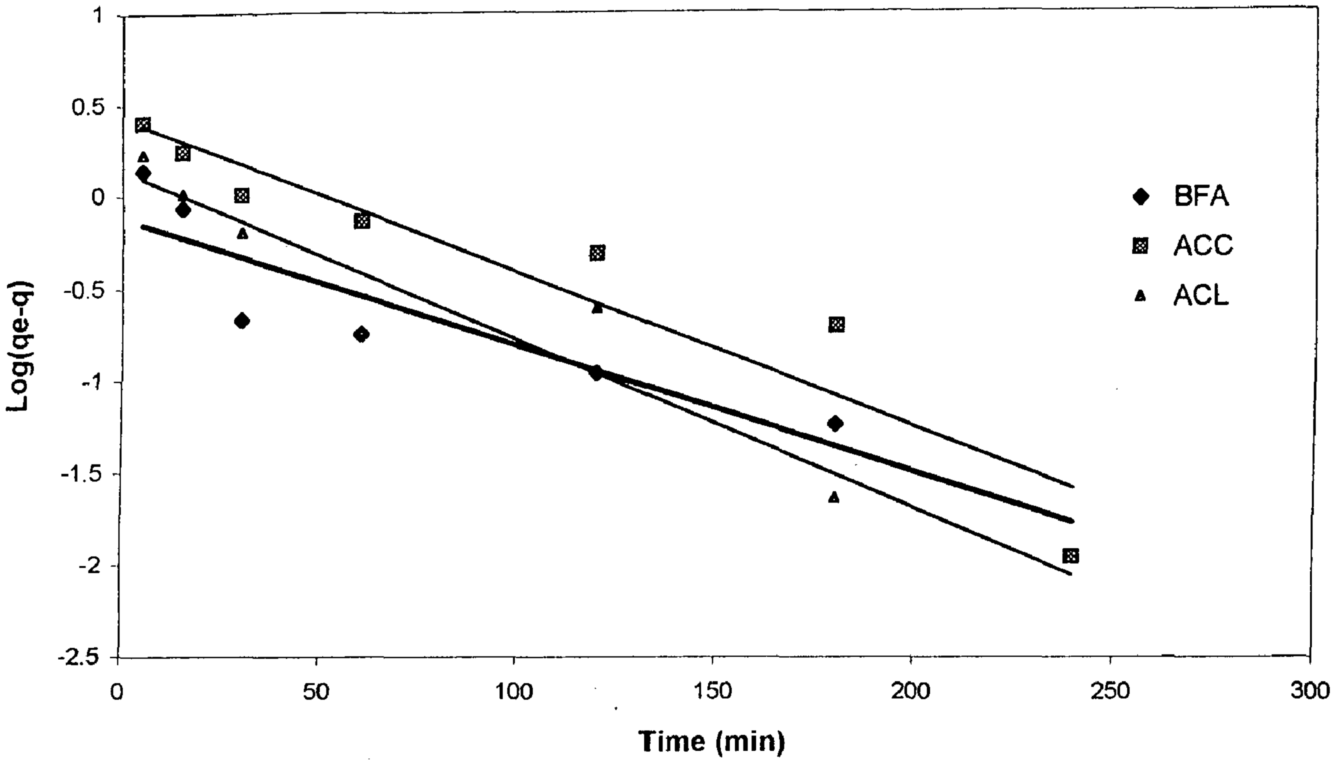


FIG 5.25 LAGERGREN PLOT FOR REMOVAL OF CONGO RED

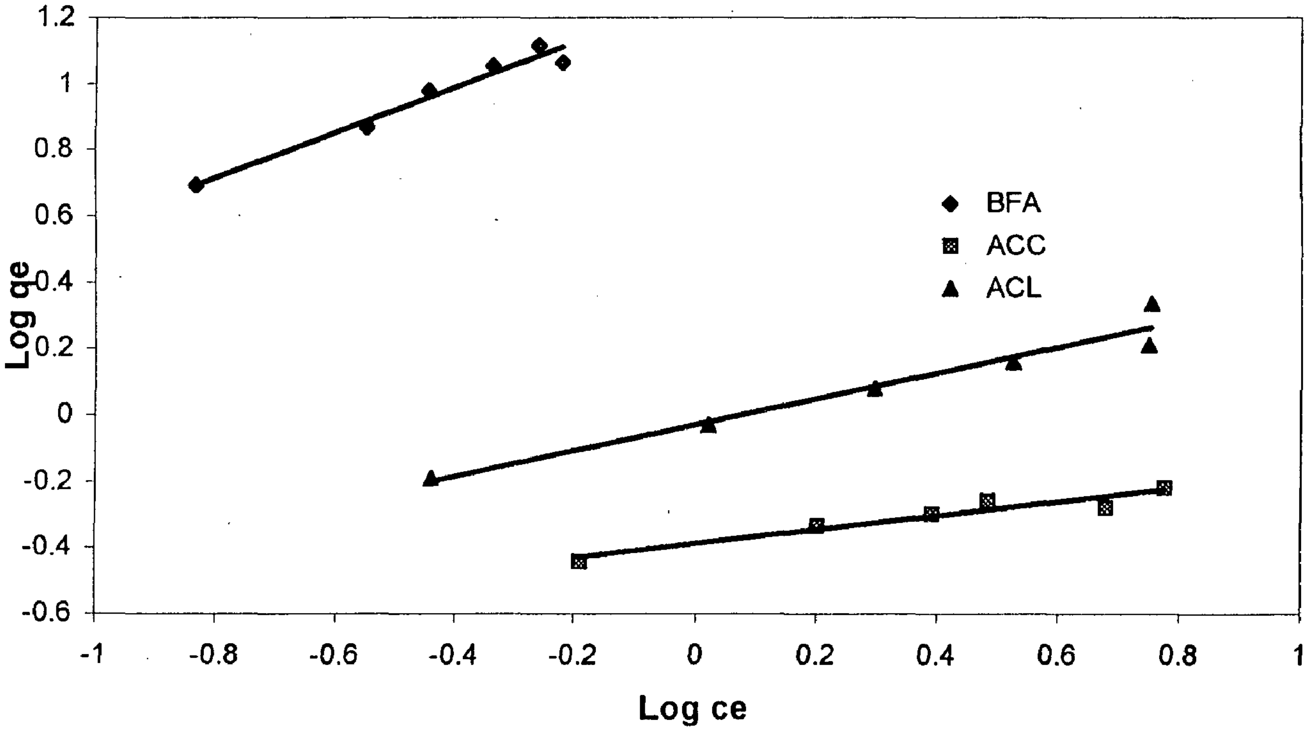


FIG 5.26 FREUNDLICH ISOTHERM FOR REMOVAL OF CONGO RED

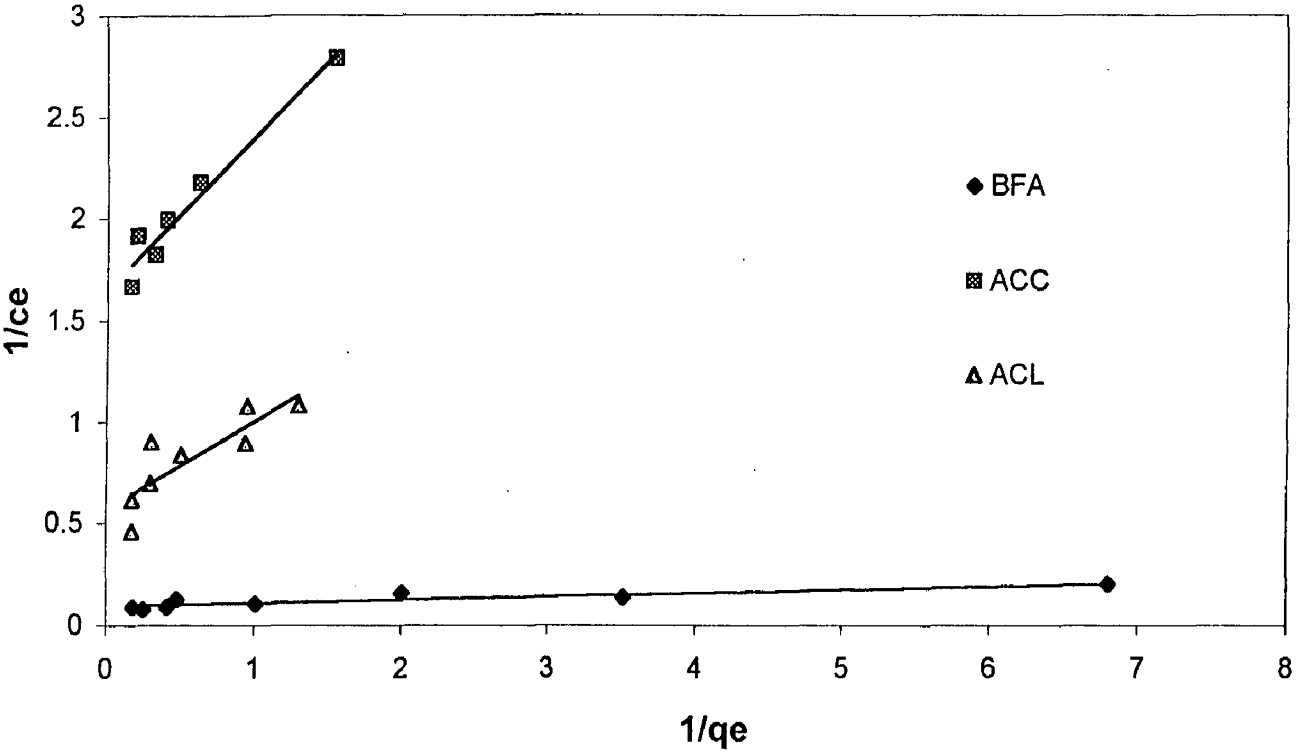


FIG 5.27 LANGMUIR ISOTHERM FOR REMOVAL OF CONGO RED

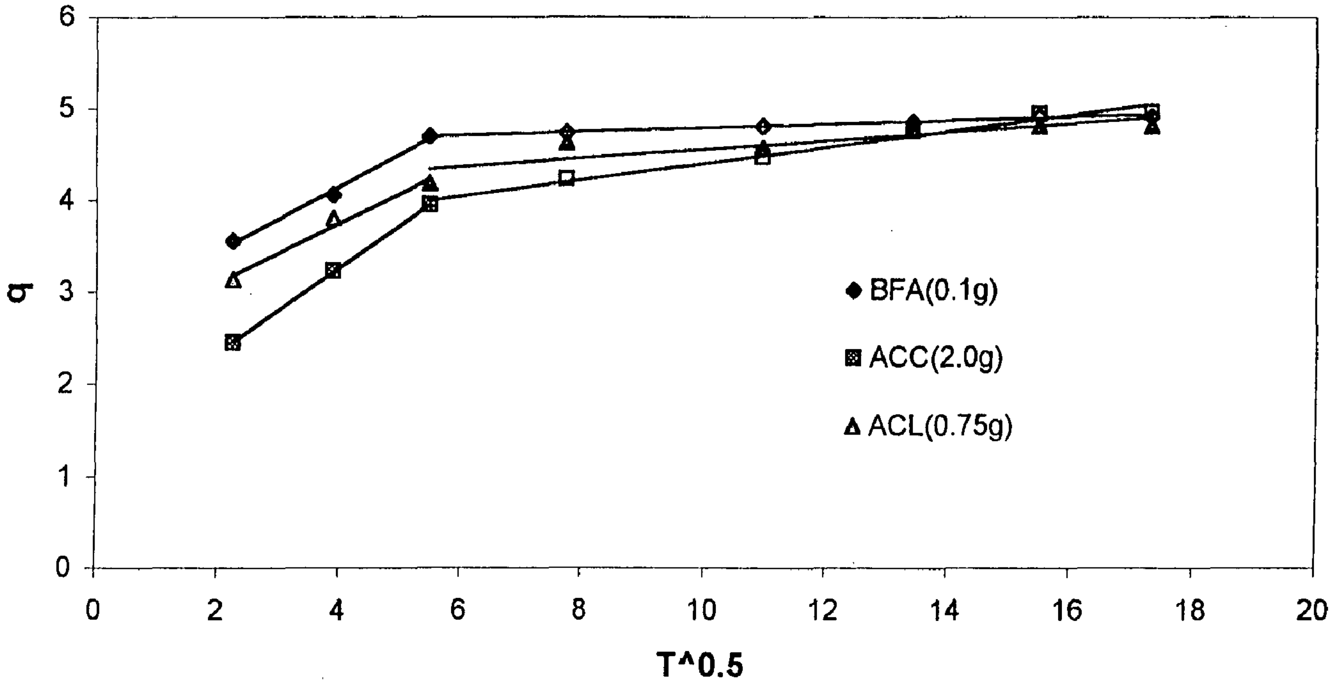


FIG 5.28 WEBER AND MORRIS INTRA PARTICLE DIFFUSION PLOT FOR REMOVAL OF CONGO RED

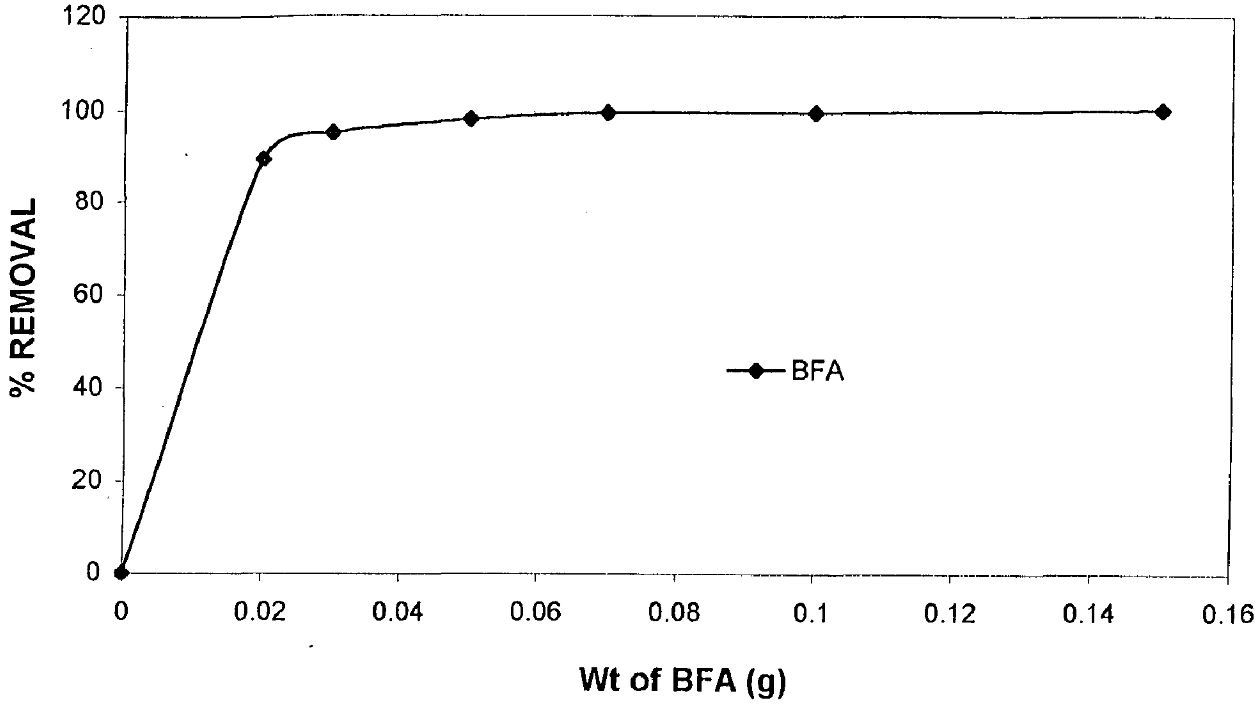


FIG 5.29 EFFECT OF ADSORBENT DOSE ON REMOVAL OF MALACHITE GREEN

Initial concentration =10 mg/l, Time=5 hr, pH= 7.3

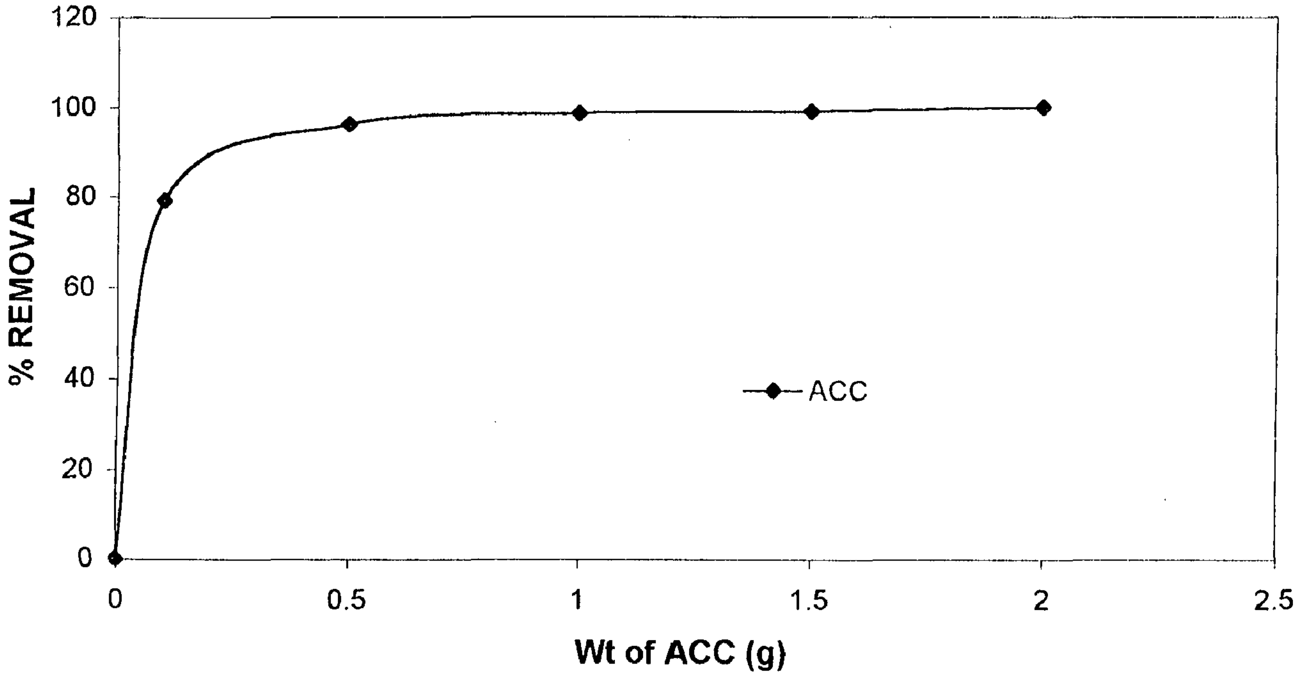


FIG 5.30 EFFECT OF ADSORBENT DOSE ON REMOVAL OF MALACHITE GREEN

Initial concentration =10 mg/l, Time=5 hr, pH= 7.3

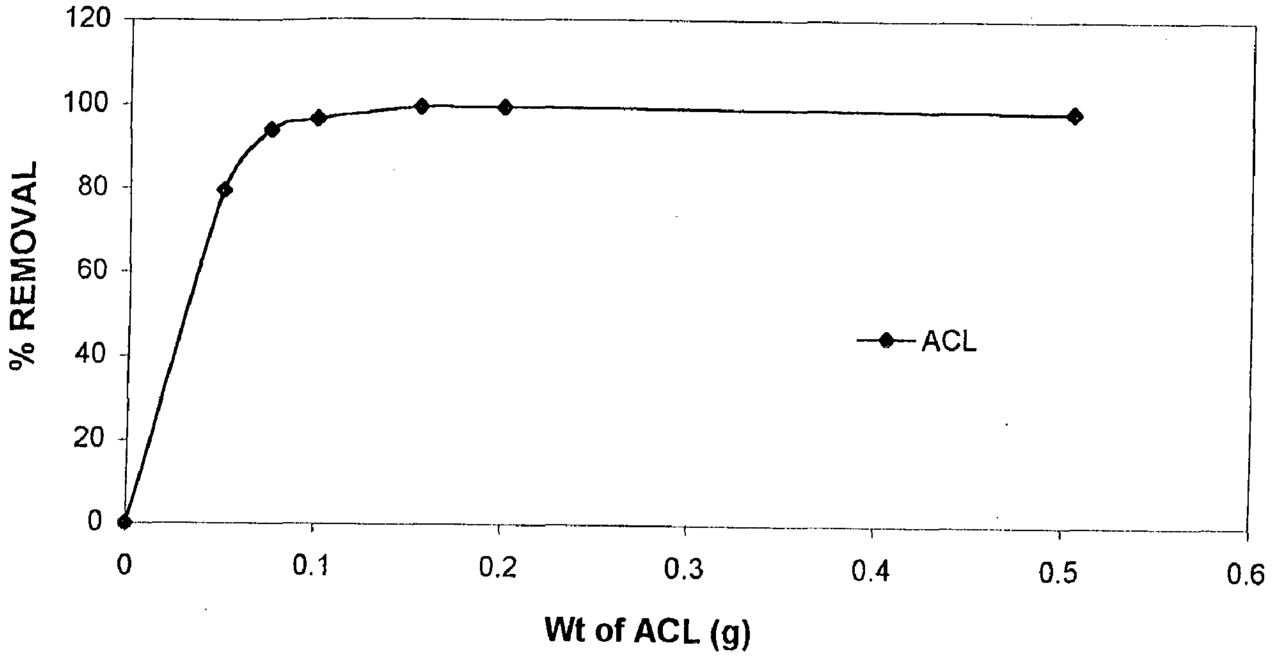


FIG 5.31 EFFECT OF ADSORBENT DOSE ON REMOVAL OF MALACHITE GREEN

Initial concentration =10 mg/l, Time=5 hr, pH= 7.3

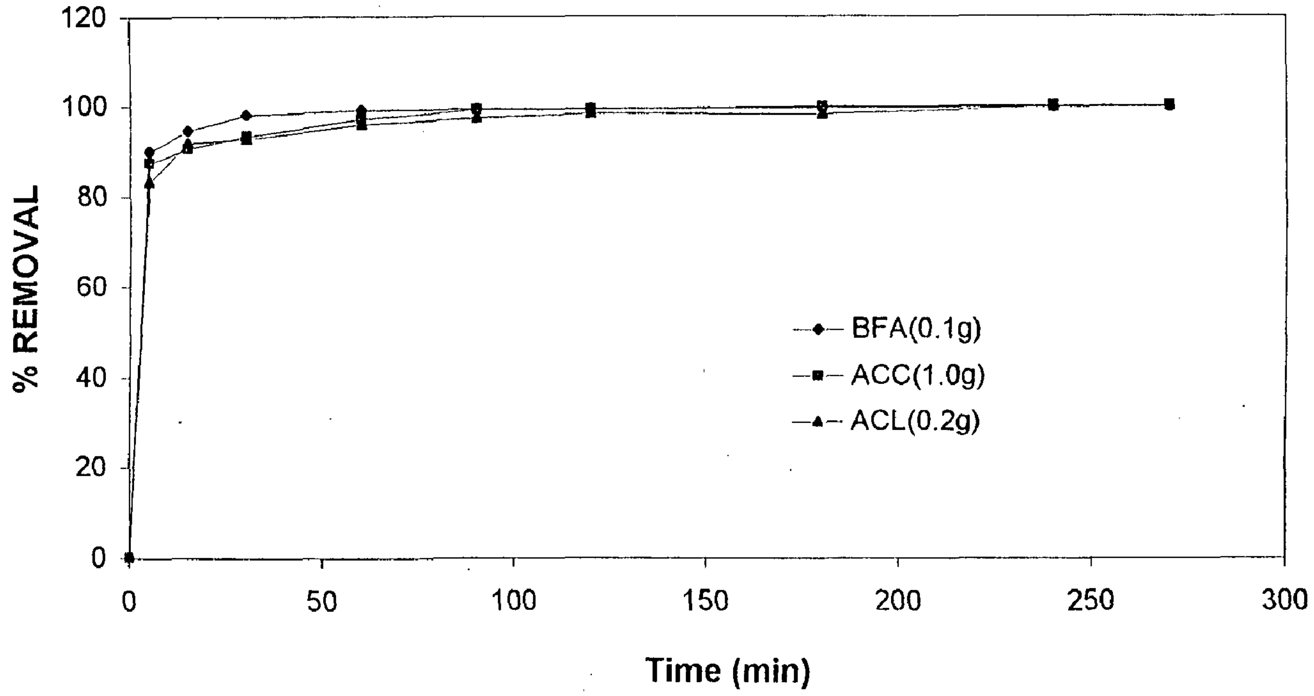


FIG 5.32 EFFECT OF CONTACT TIME ON REMOVAL OF MALACHITE GREEN

Initial concentration = 10 mg/l,pH=7.3

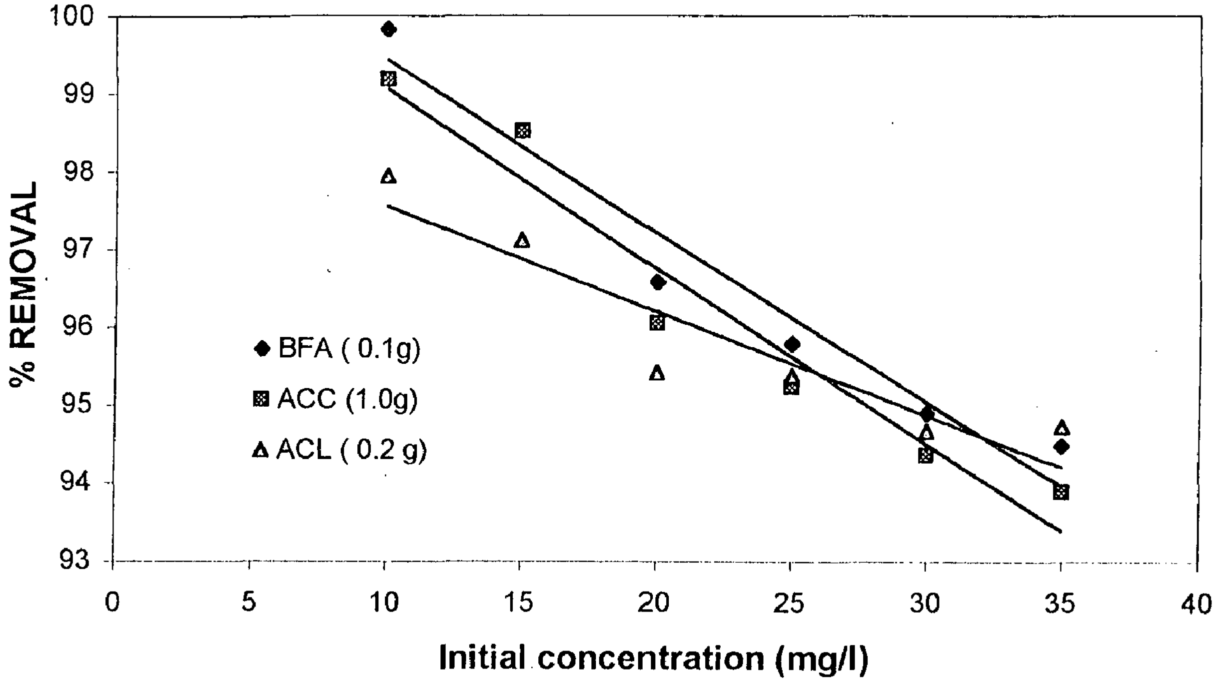


FIG 5.33 EFFECT OF INITIAL CONCENTRATION OF MALACHITE GREEN ON IT'S REMOVAL

Contact time 5.0 hr pH = 7.3

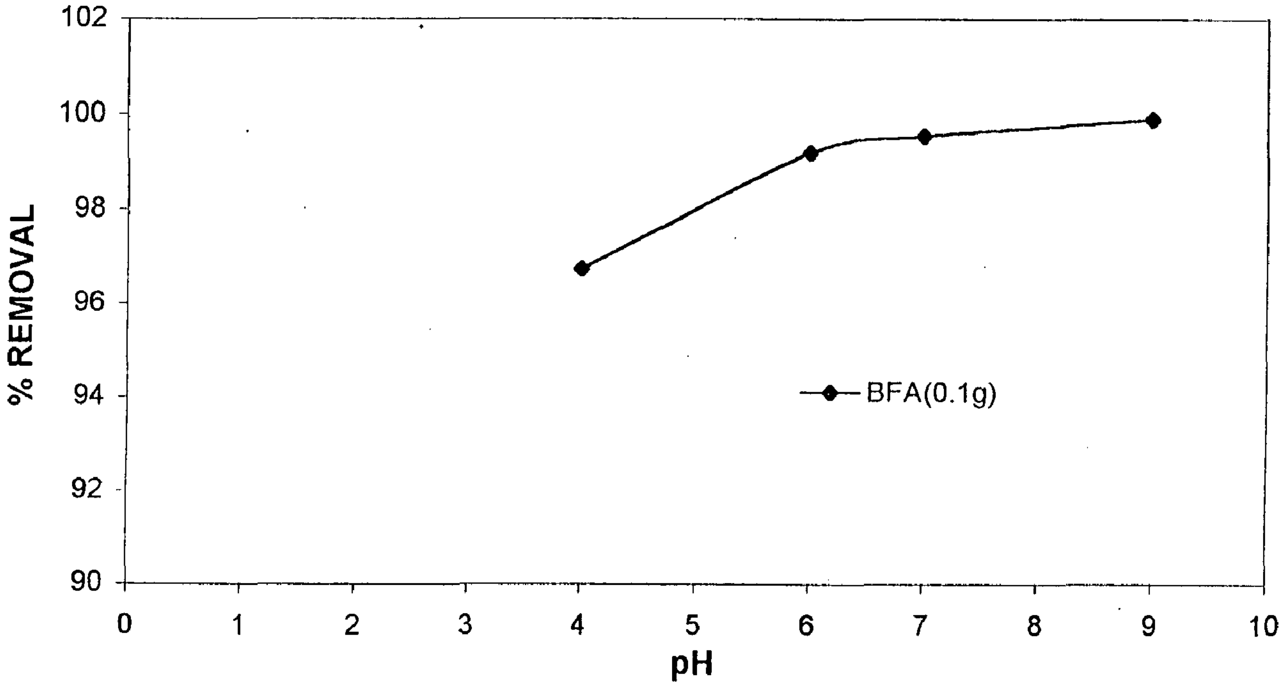


FIG 5.34 EFFECT OF PH ON REMOVAL OF MALACHITE GREEN

Initial concentration = 10 mg/l,Time=5 hr

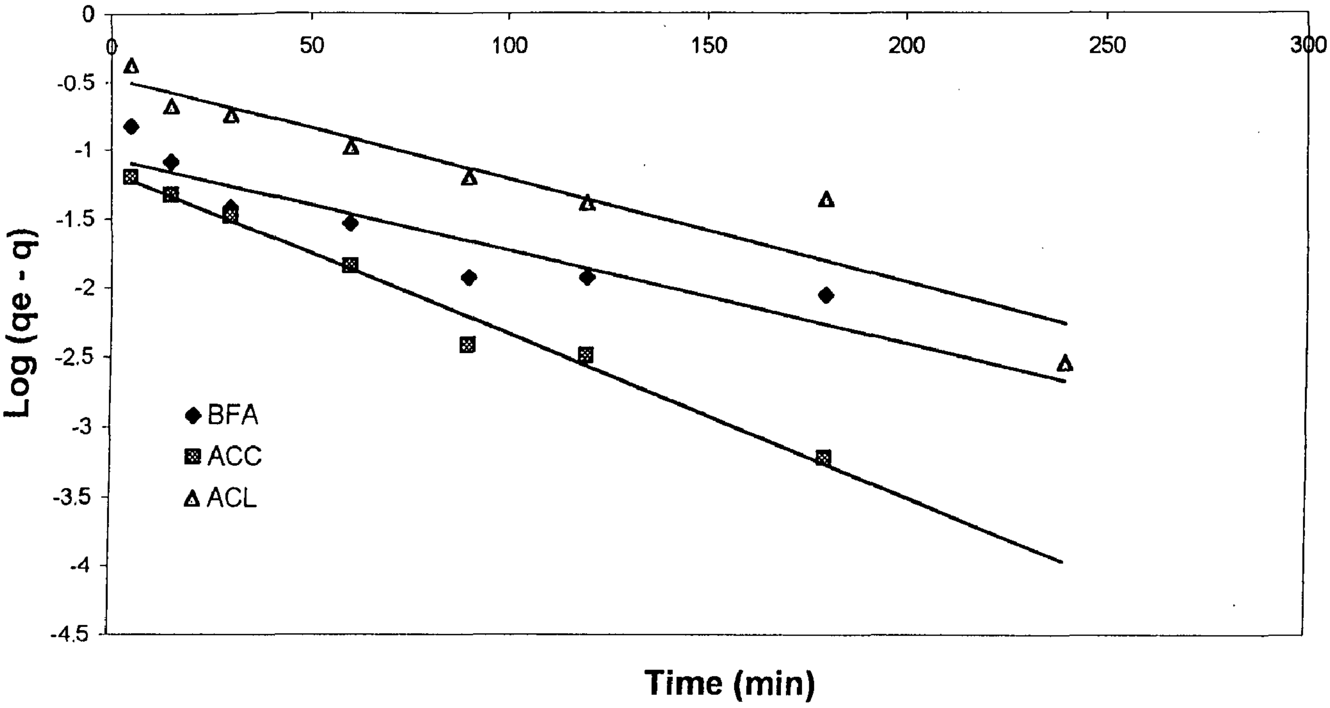


FIG 5.35 LAGERGREN PLOT FOR REMOVAL OF MALACHITE GREEN

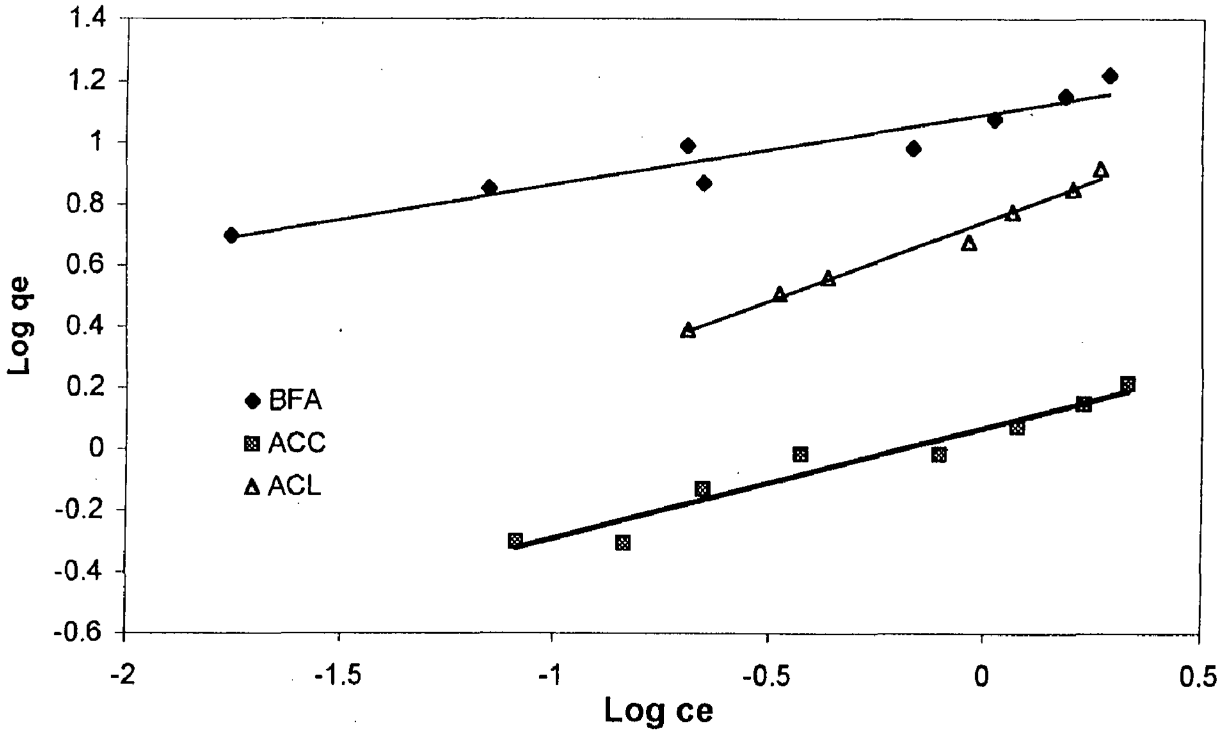


FIG 5.36 FREUNDLICH ISOTHERM FOR REMOVAL OF MALACHITE GREEN

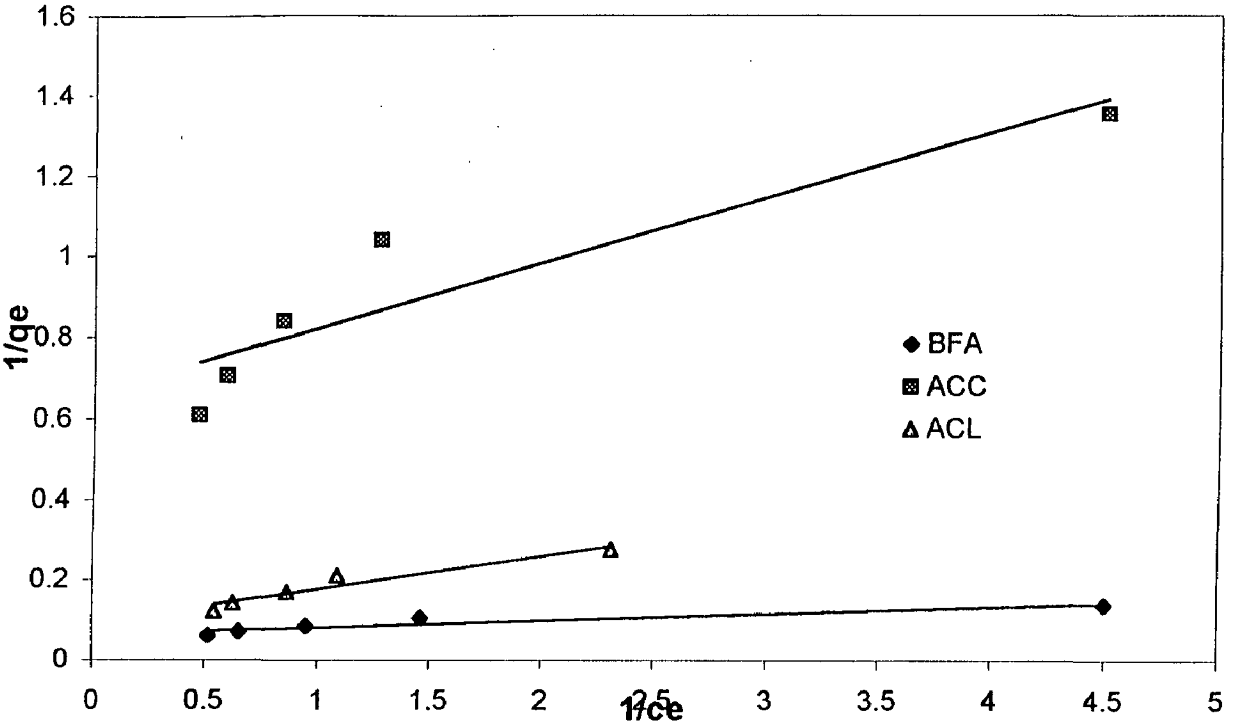


FIG 5.37 LANGMUIR ISOTHERM FOR REMOVAL OF MALACHITE GREEN

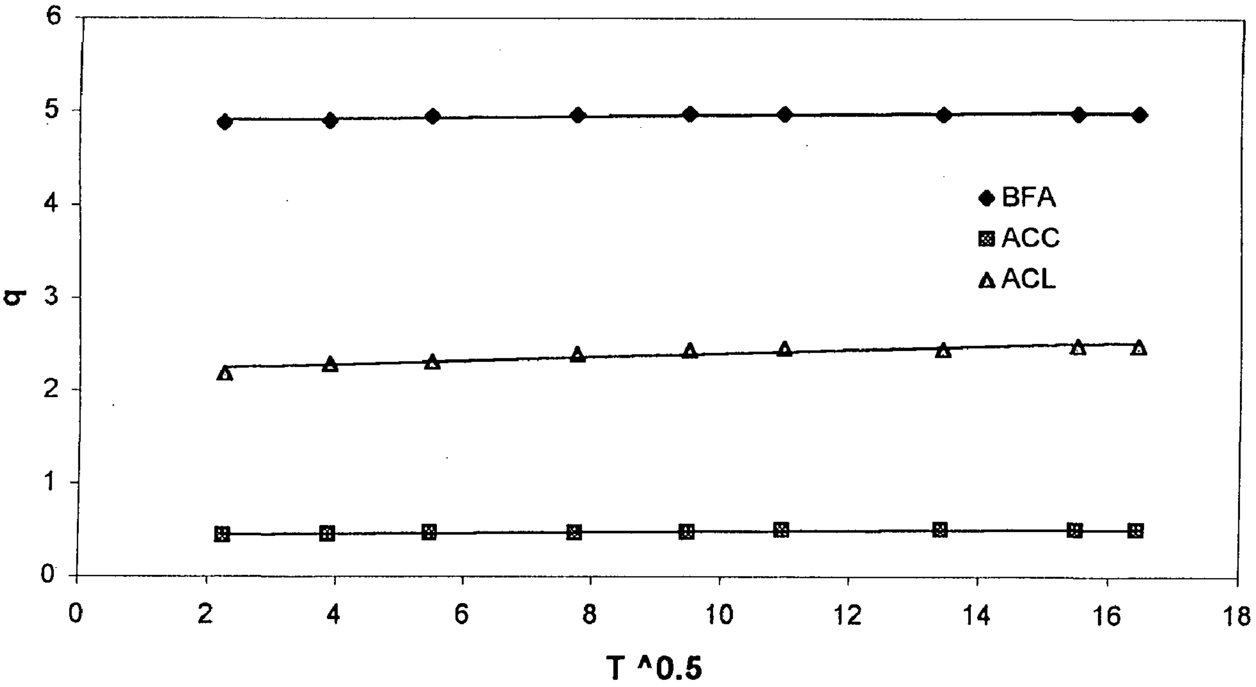


FIG 5.38 WEBER AND MORRIS INTRAPARTICLE DIFFUSION PLOT FOR REMOVAL OF MALACHITE GREEN

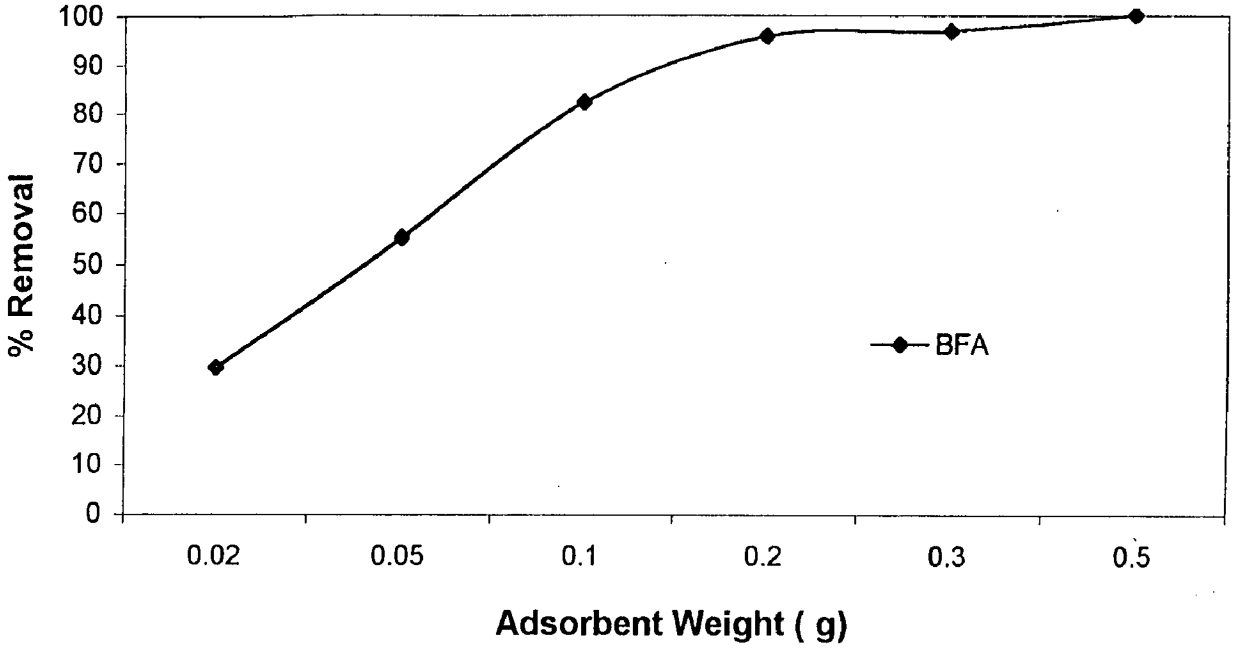


FIG 5.39 EFFECT OF ADSORBENT DOSE ON REMOVAL OF ORANGE-G

Initial concentration = 10 mg/l , Time = 5 hr, pH = 7.7

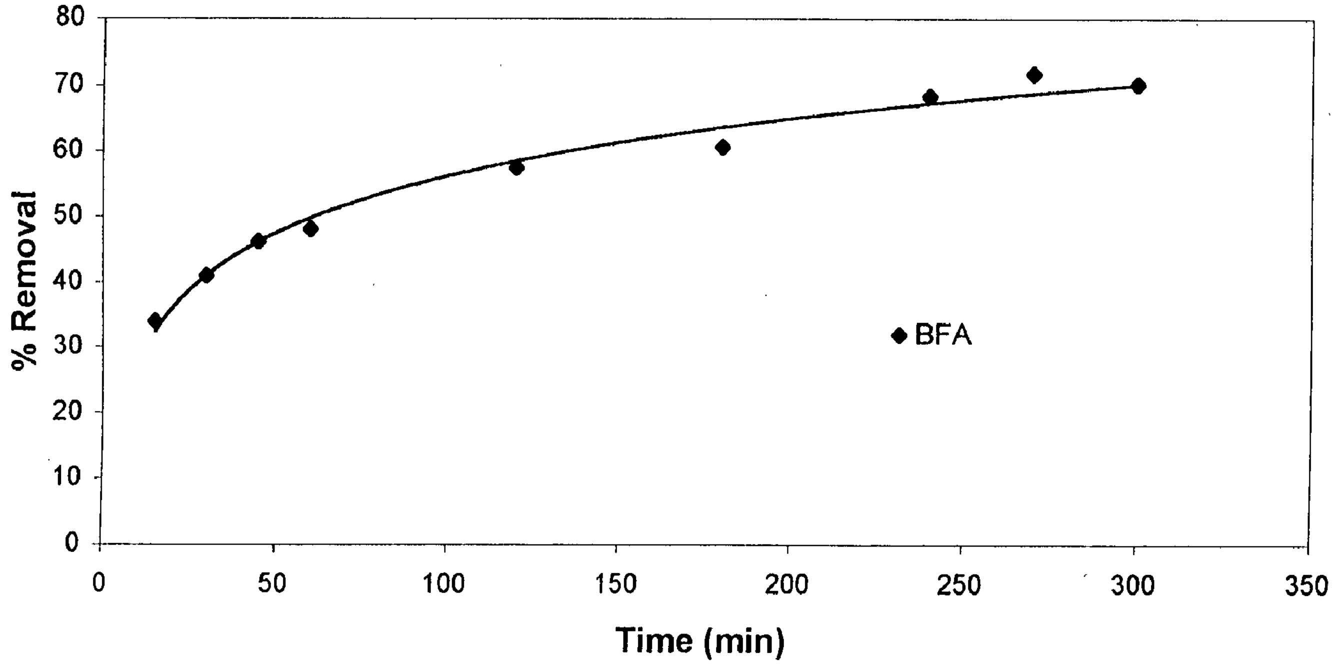
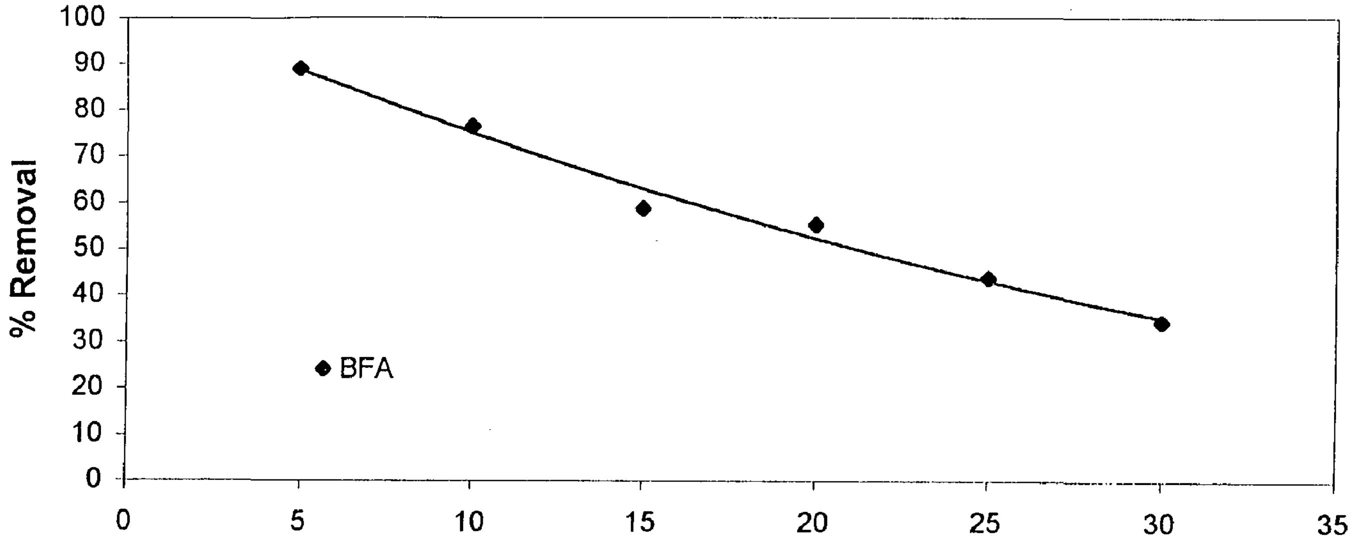


FIG 5.40 EFFECT OF CONTACT TIME ON REMOVAL OF ORANGE- G

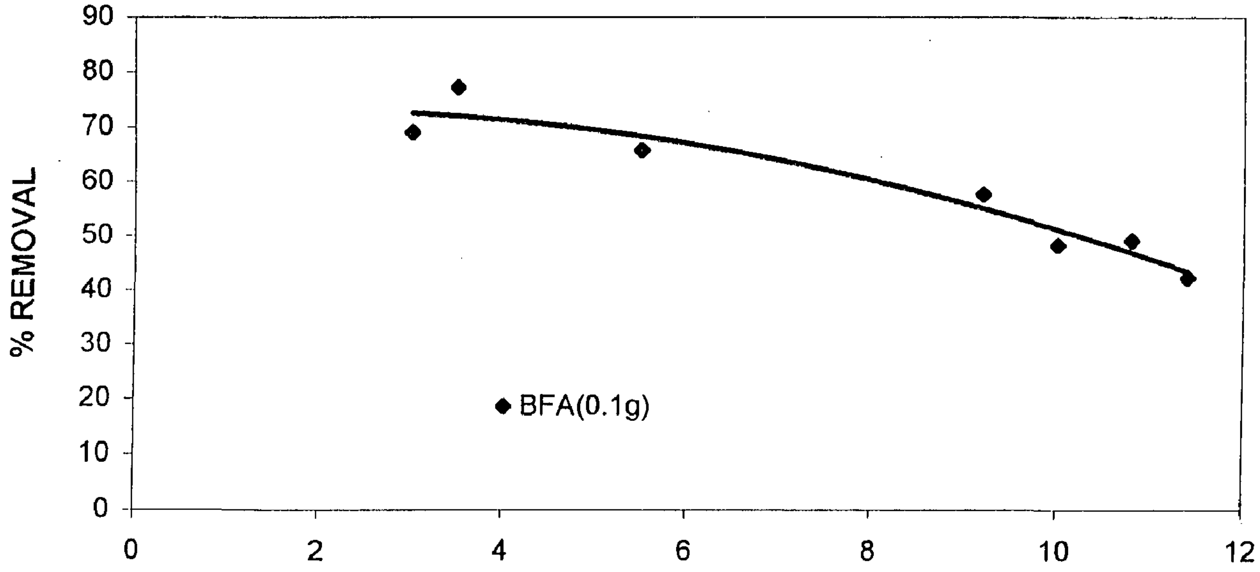
initial concentration = 10 mg/l, BFA= 0.1g



Initial concentration (mg/l)

FIG 5.41 EFFECT OF INITIAL CONCENTRATION OF ORANGE-G ON ITS REMOVAL

BFA = 0.1 g, Time 5 hr, pH = 7.7



pH

FIG 5.42 EFFECT OF pH ON REMOVAL OF ORANGE-G

Initial concentration =10 mg/l, Time=5 hr

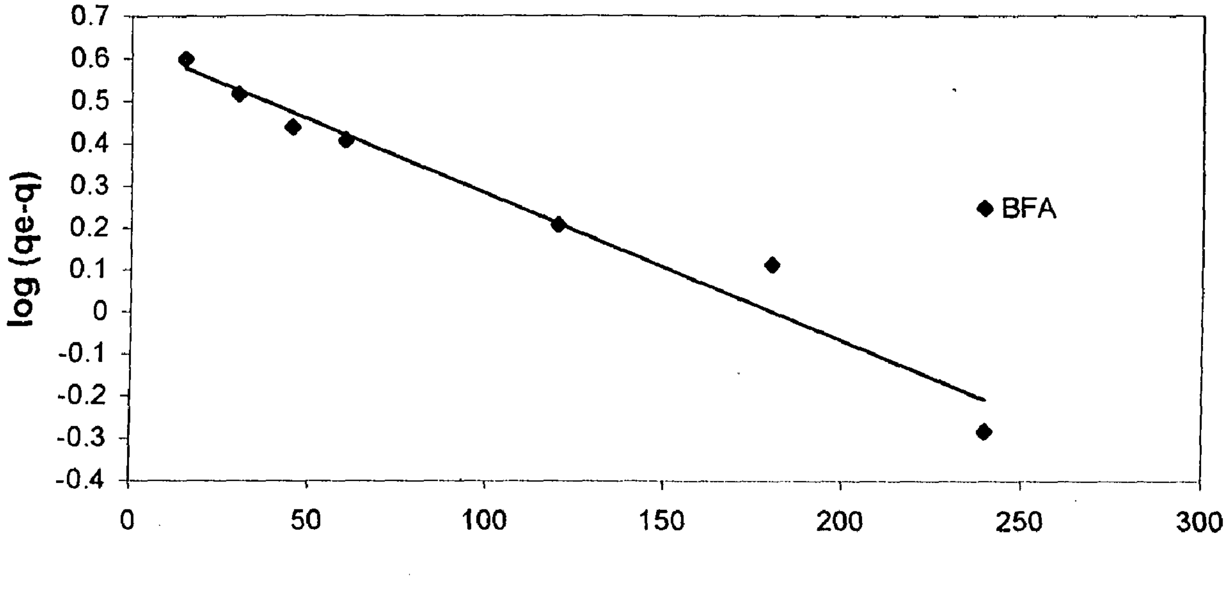


FIG 5.43 LAGREGREN PLOT FOR REMOVAL OF ORANGE - G

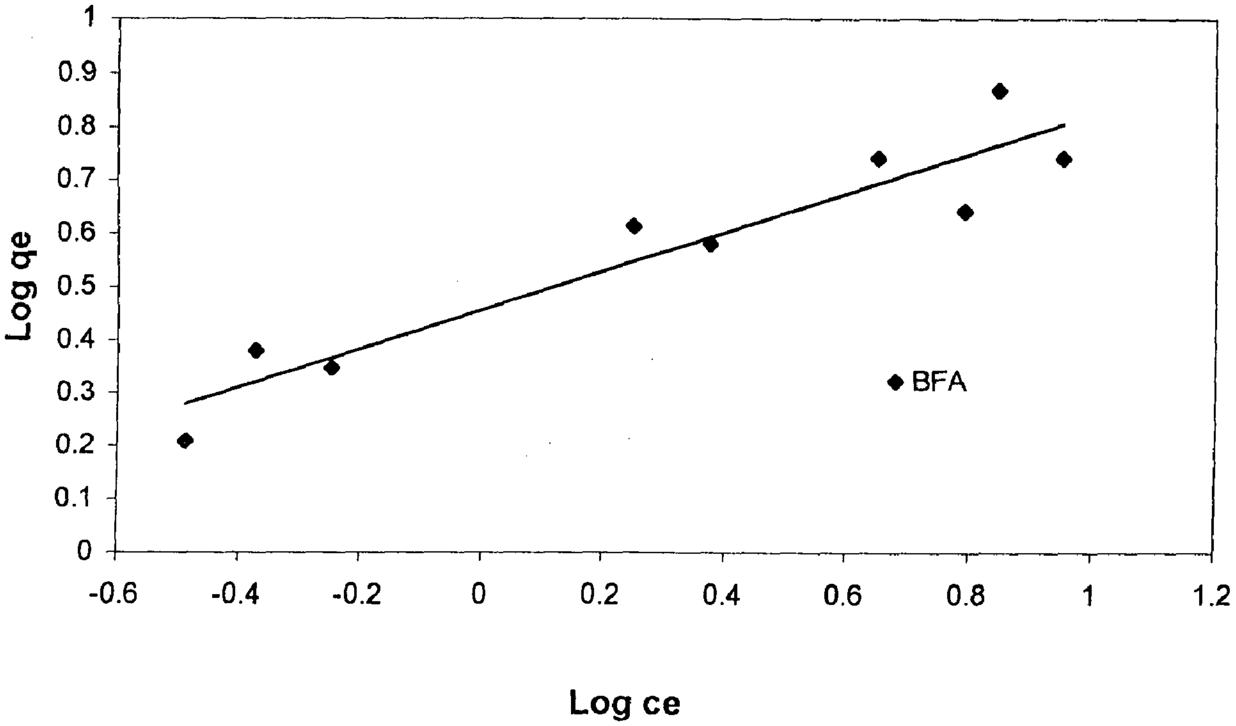


FIG 5.44 **FREUNDLICH ISOTHERM FOR REMOVAL OF ORANGE-G**

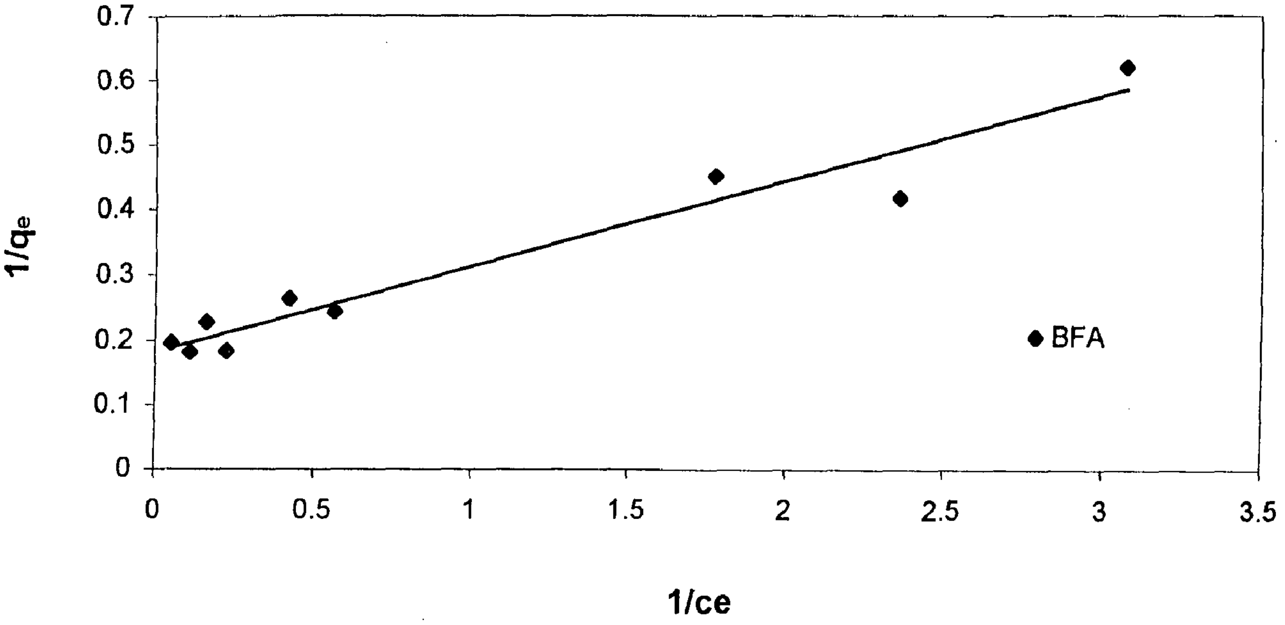


FIG 5.45 LANGMUIR ISOTHERM FOR REMOVAL OF ORANGE-G

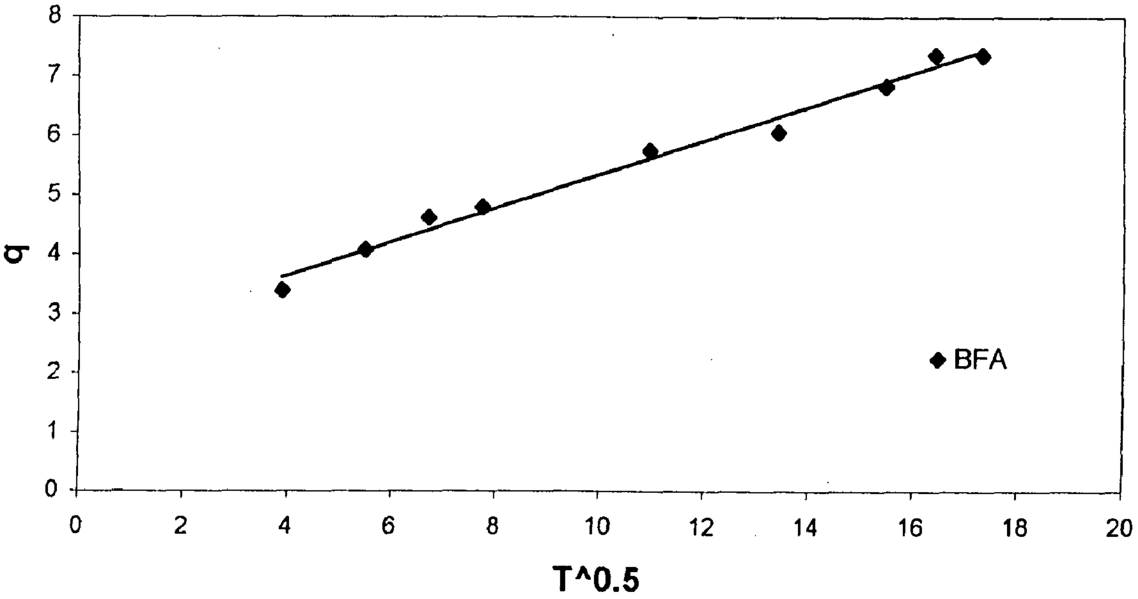


FIG 5.46 WEBER AND MORRIS INTRA PARTICLE DIFFUSION PLOT FOR REMOVAL OF ORANGE-G

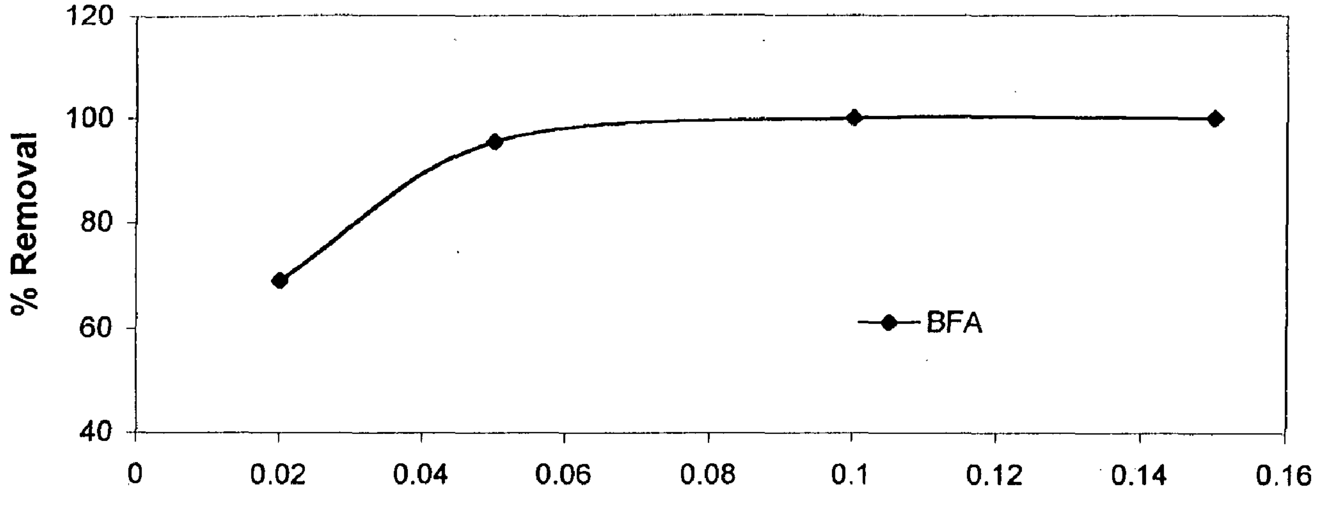


FIG 5.47 EFFECT OF ADSORBENT DOSE ON REMOVAL OF METHYL VIOLET

Initial concentration = 10 mg/l , Time = 5 hr, pH = 7.5

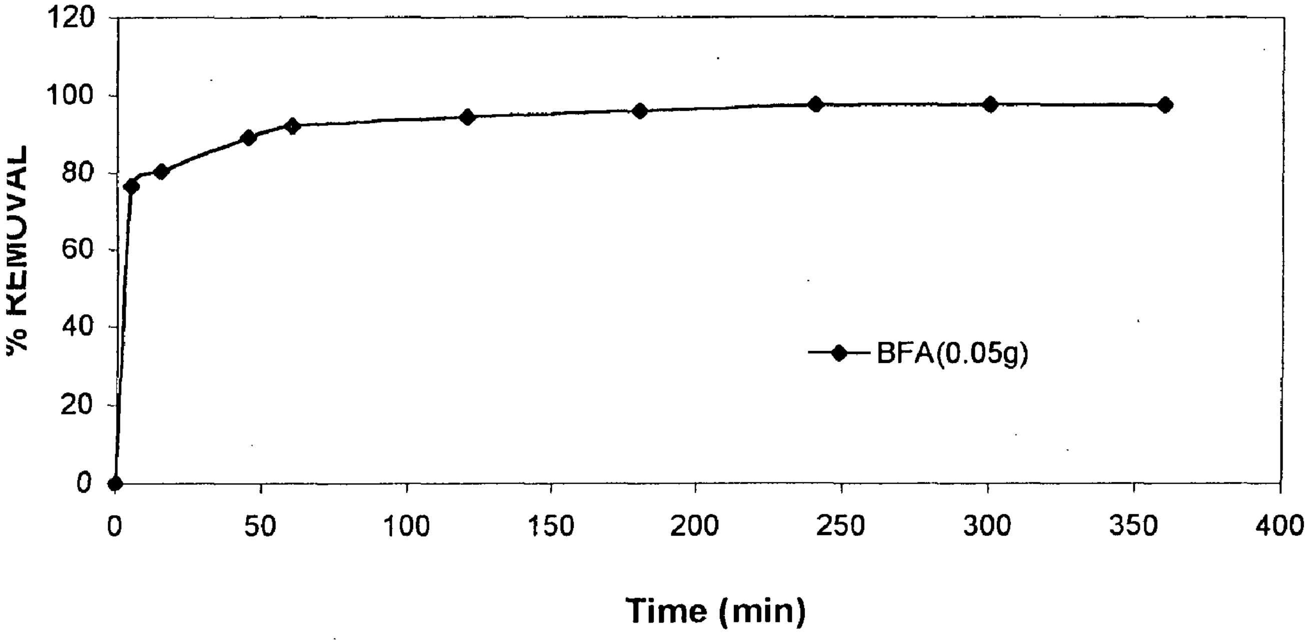


FIG 5.48 EFFECT OF CONTACT TIME ON REMOVAL OF METHYL VIOLET

Initial concentration= 10 mg/l, pH = 7.5

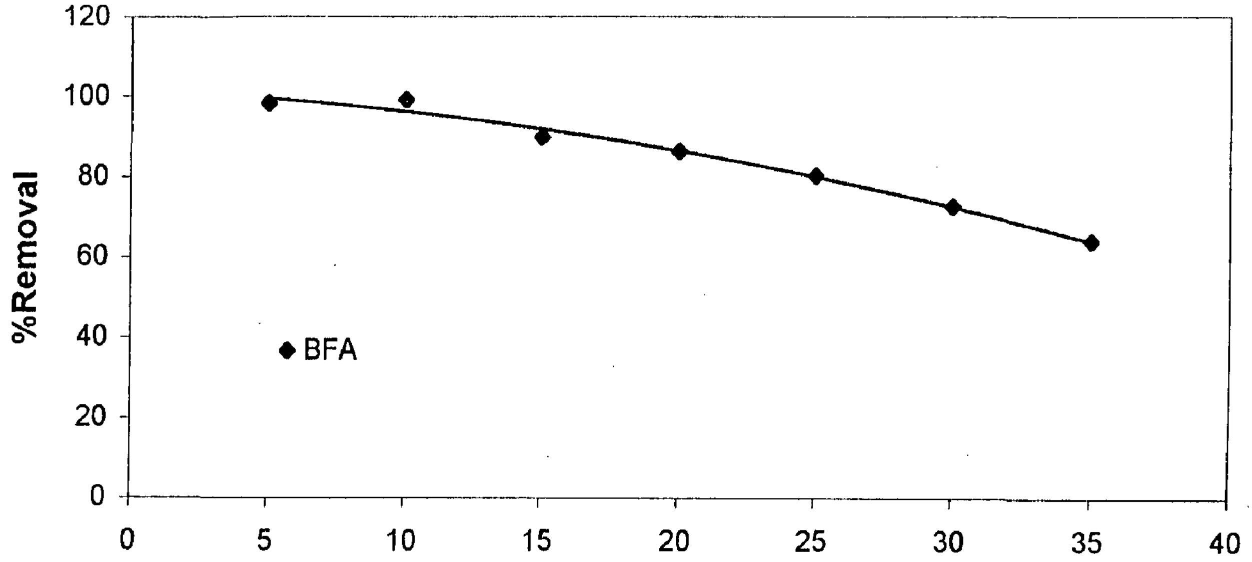


FIG 5.49 EFFECT OF INITIAL CONCENTRATION OF METHYL VIOLET ON ITS REMOVAL

BFA = 0.05 g, Time 5 hr, pH = 7.5

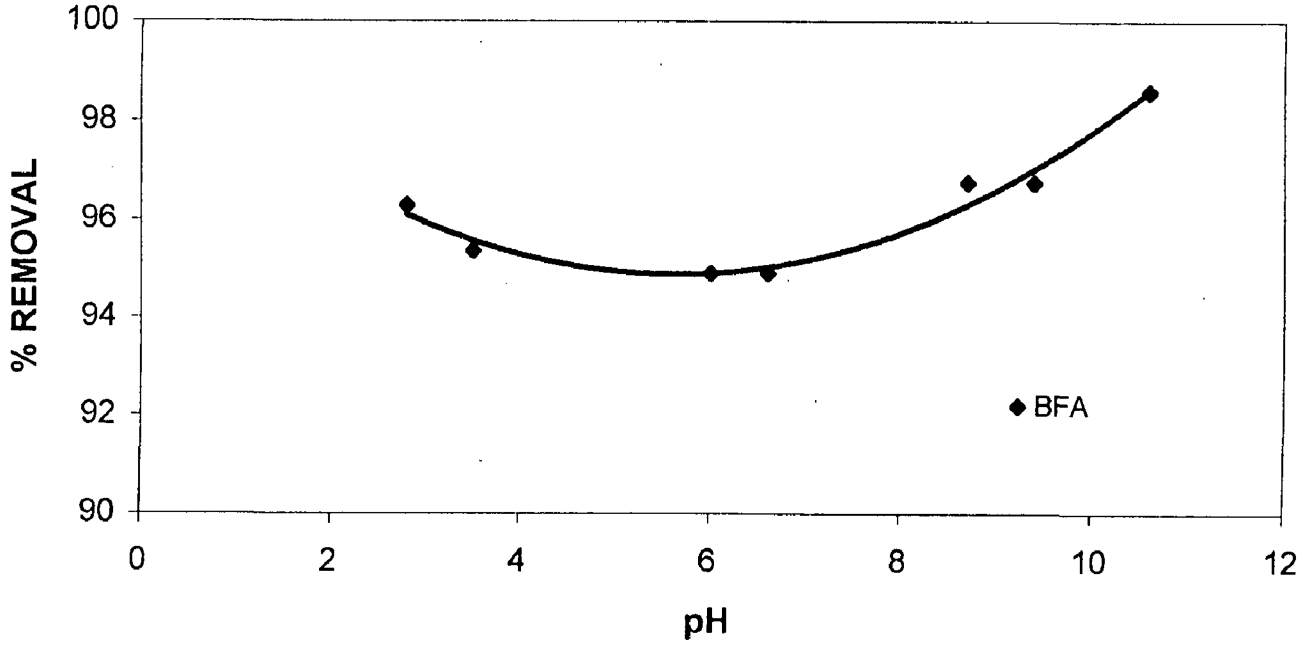


FIG 5.50 EFFECT OF pH ON REMOVAL OF METHYL VIOLET

BFA = 0.05 g, Time = 5.0 hr, initial concentration = 10 mg/l

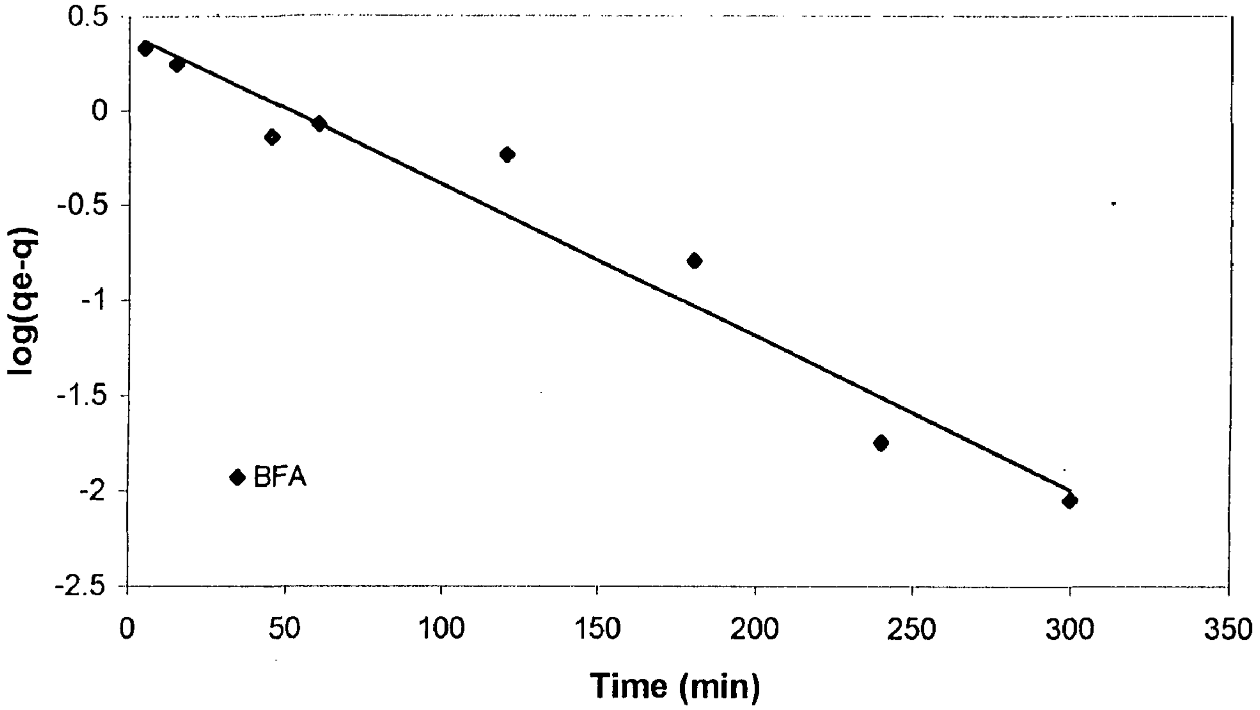


FIG 5.51 LAGERGREN PLOT FOR REMOVAL OF METHYL VIOLET

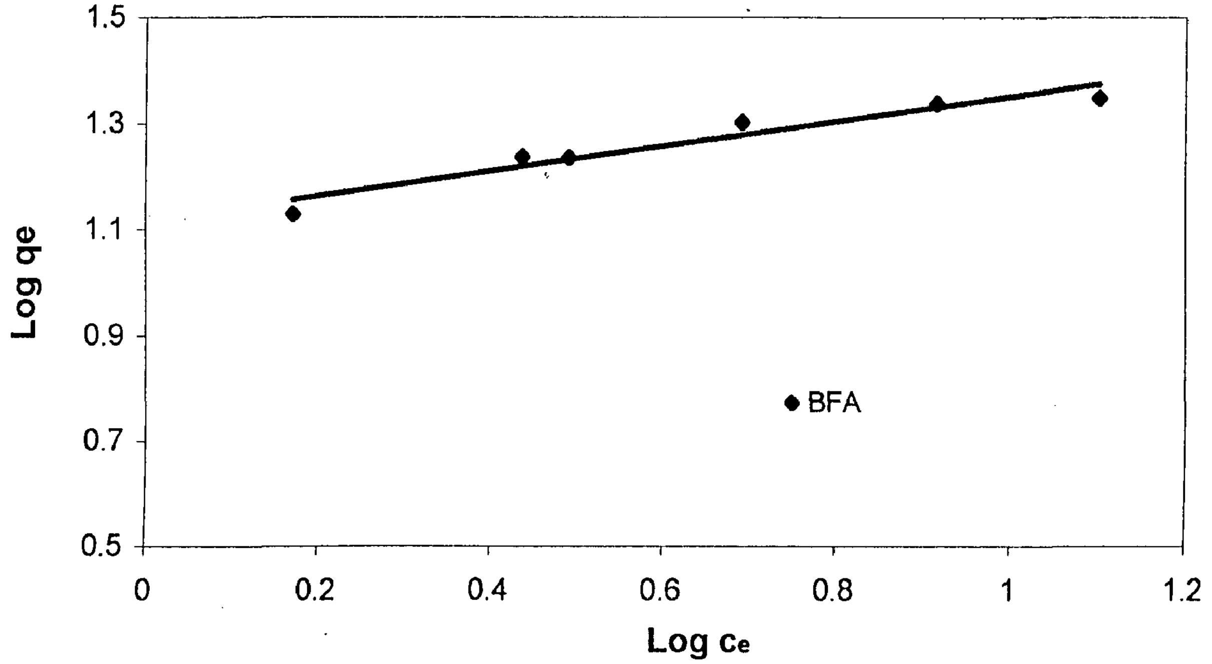


FIG 5.52 FREUNDLICH ISOTHERM FOR REMOVAL OF METHYL VIOLET

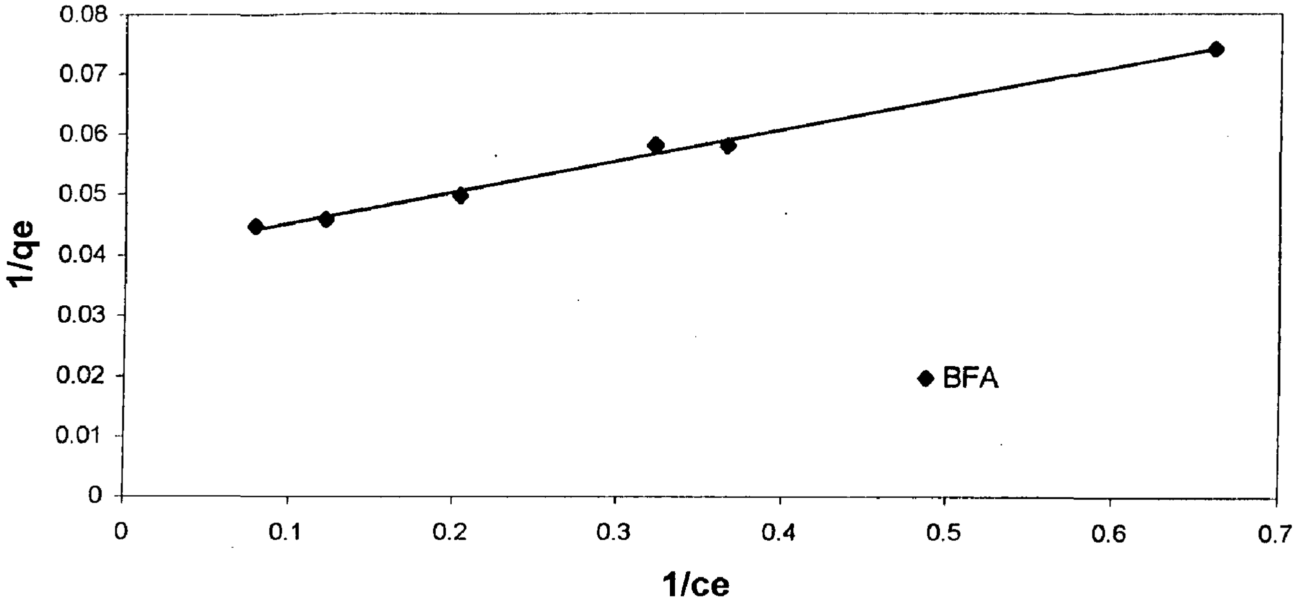
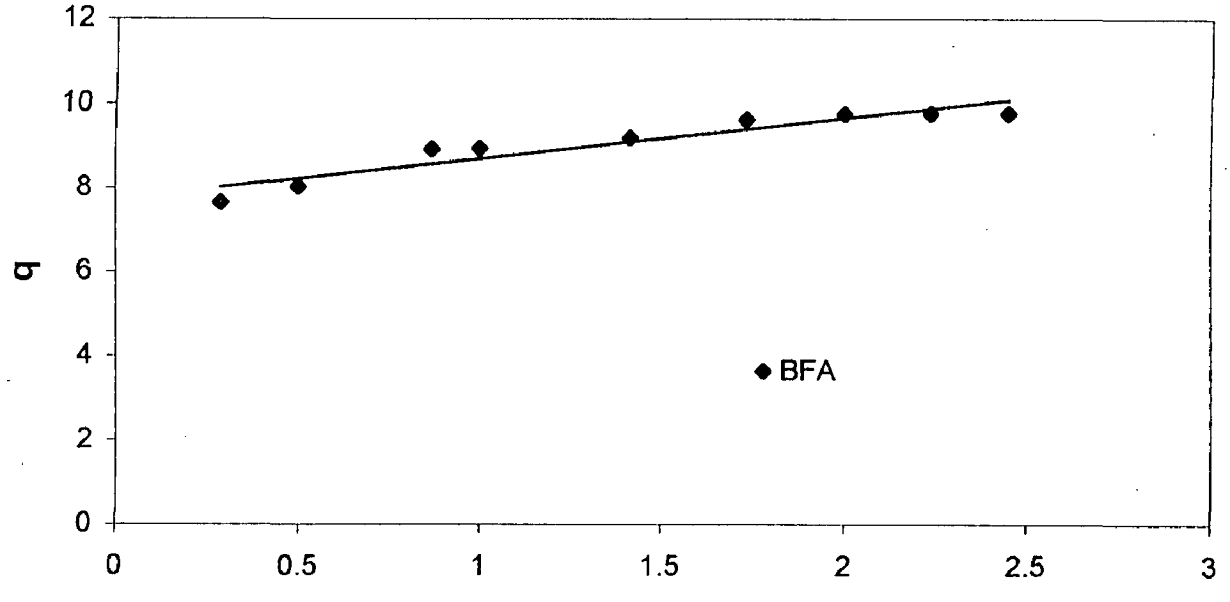


FIG 5.53 LANGMUIR ISOTHERM FOR REMOVAL OF METHYL VIOLET



T^0.5

FIG 5.54 WEBER AND MORRIS INTRA PARTICLE DIFFUSION PLOT FOR REMOVAL OF METHYL VIOLET

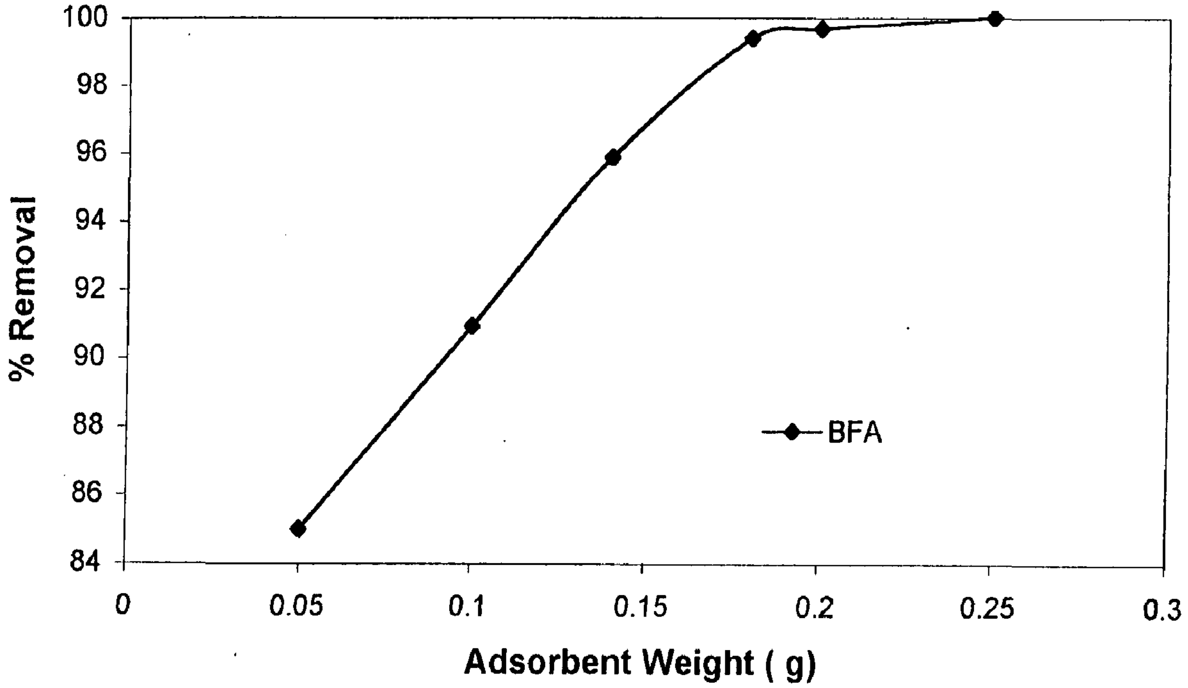


FIG 5.55 EFFECT OF ADSORBENT DOSE ON REMOVAL OF RHODAMINE-B

Initial concentration = 10 mg/l , Vol=50ml, Time = 5 hr, pH = 7.0

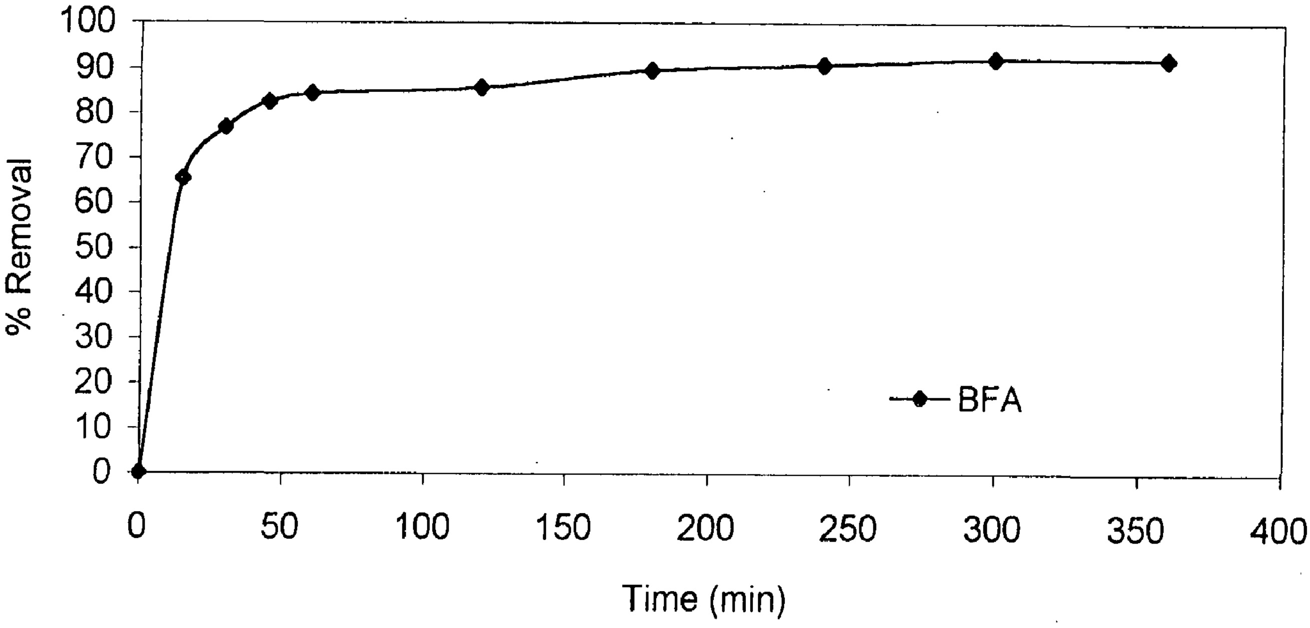


FIG 5.56 EFFECT OF CONTACT TIME ON REMOVAL OF RHODAMINE -B

initial concentration = 10 mg/l, BFA= 0.1g, pH= 7.0,Vol =50ml

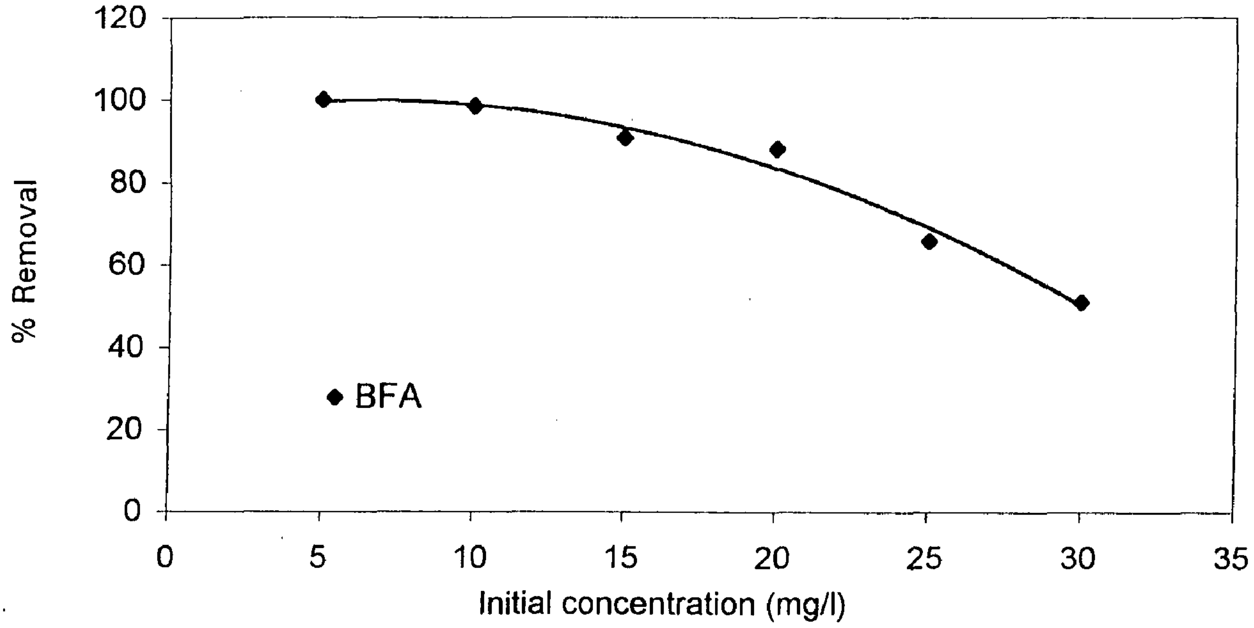


FIG 5.57 EFFECT OF INITIAL CONCENTRATION OF RHODAMINE - B ON ITS REMOVAL

BFA = 0.1 g ,Vol=50ml, Time 5 hr, pH = 7.0

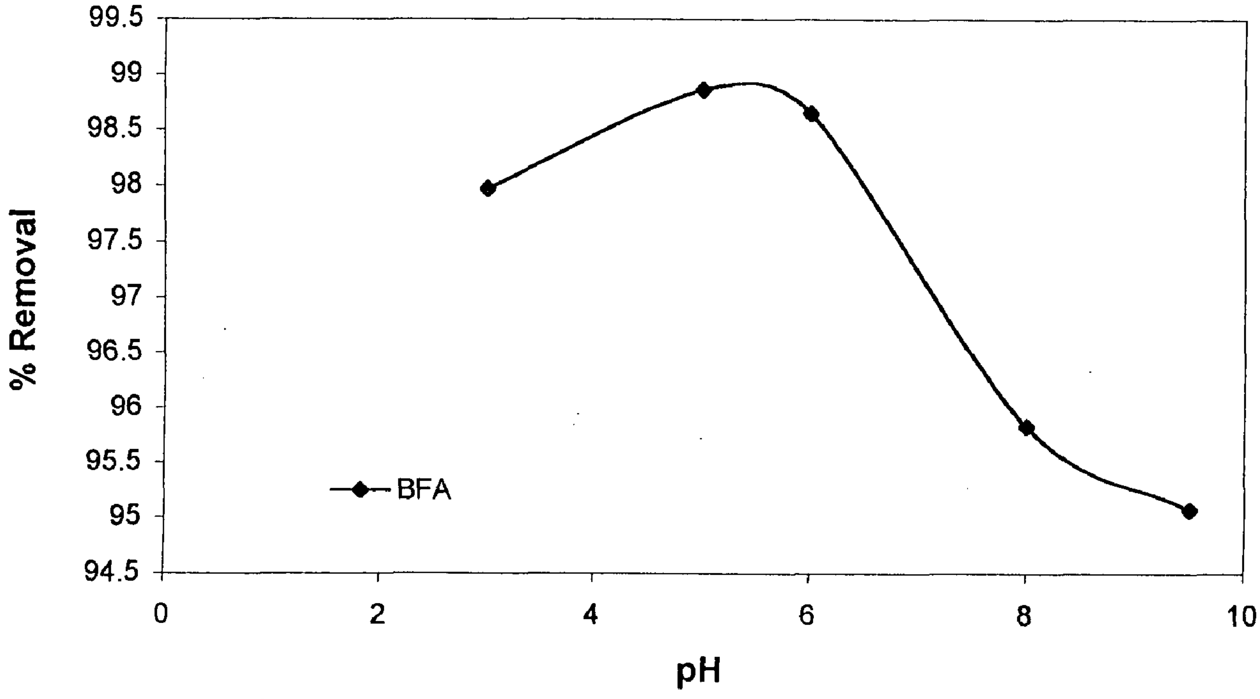


FIG 5.58 EFFECT OF pH ON REMOVAL OF RHODAMINE -B

BFA = 0.1 g,Vol=50ml Time = 5.0 hr, initial concentration = 10 mg/l

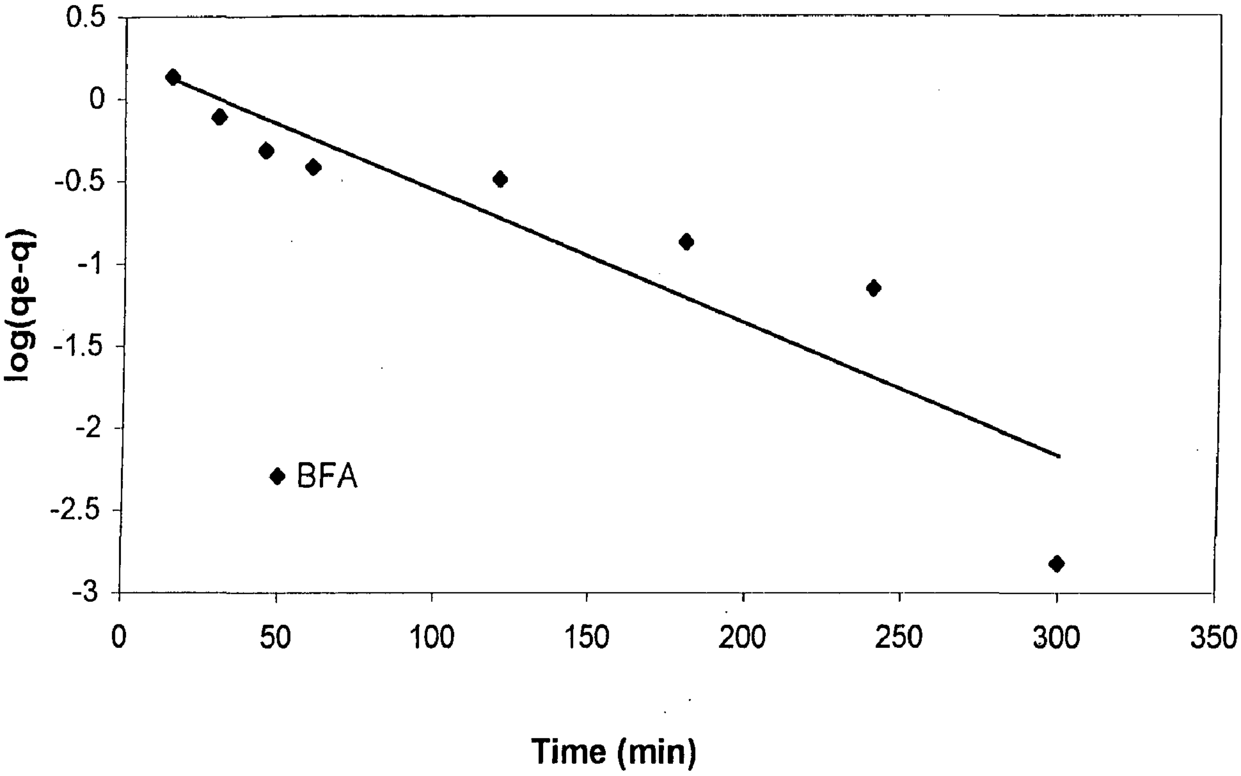


FIG 5.59 LAGERGREN PLOT FOR REMOVAL OF RHODAMINE- B

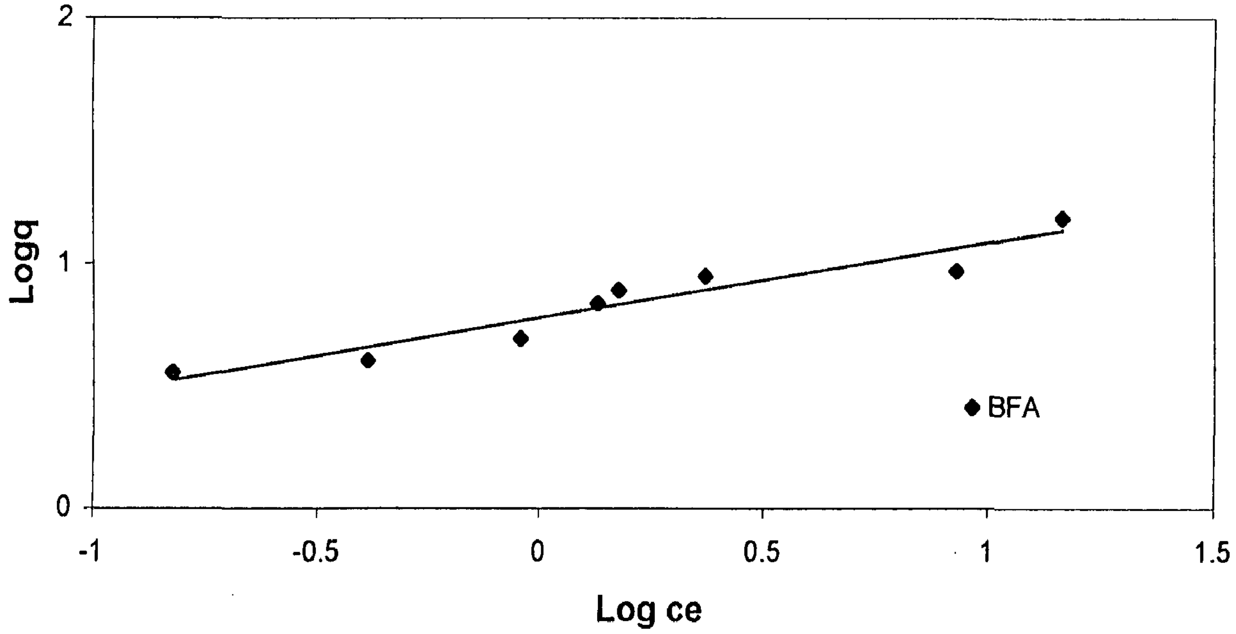


FIG 5.60 FREUNDLICH ISOTHERM FOR REMOVAL OF RHODAMINE B

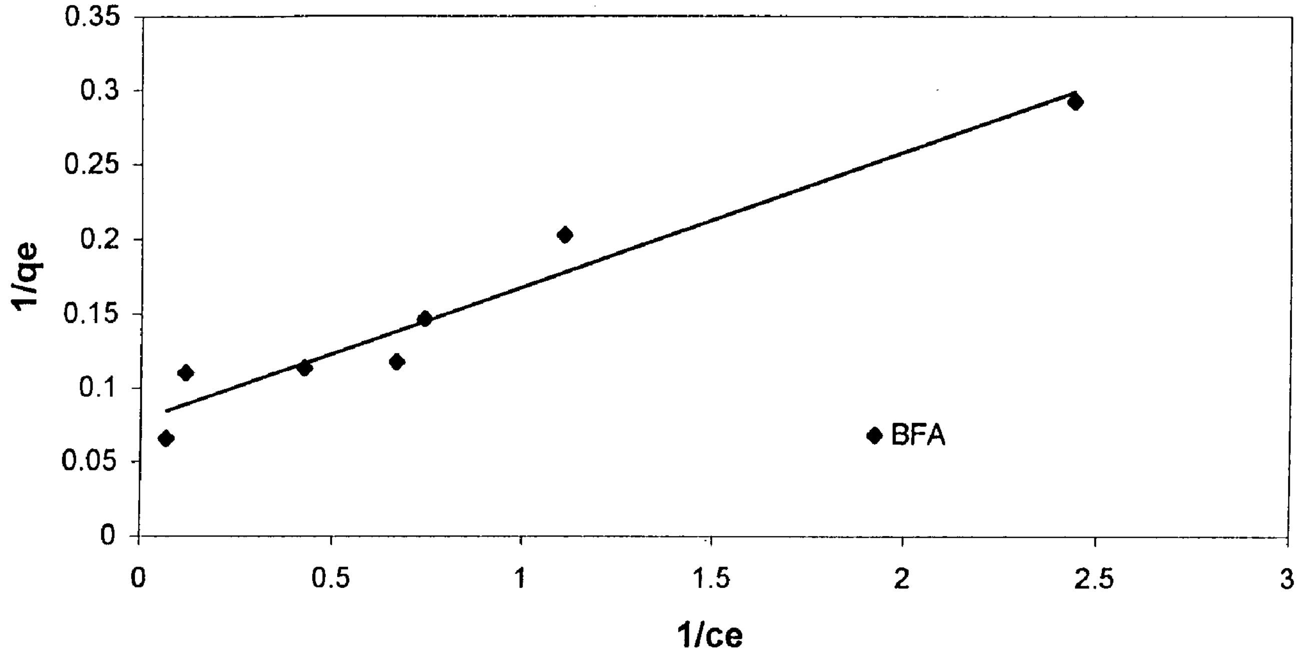


FIG 5.61 LANGMUIR ISOTHERM FOR REMOVAL OF RHODAMINE-B

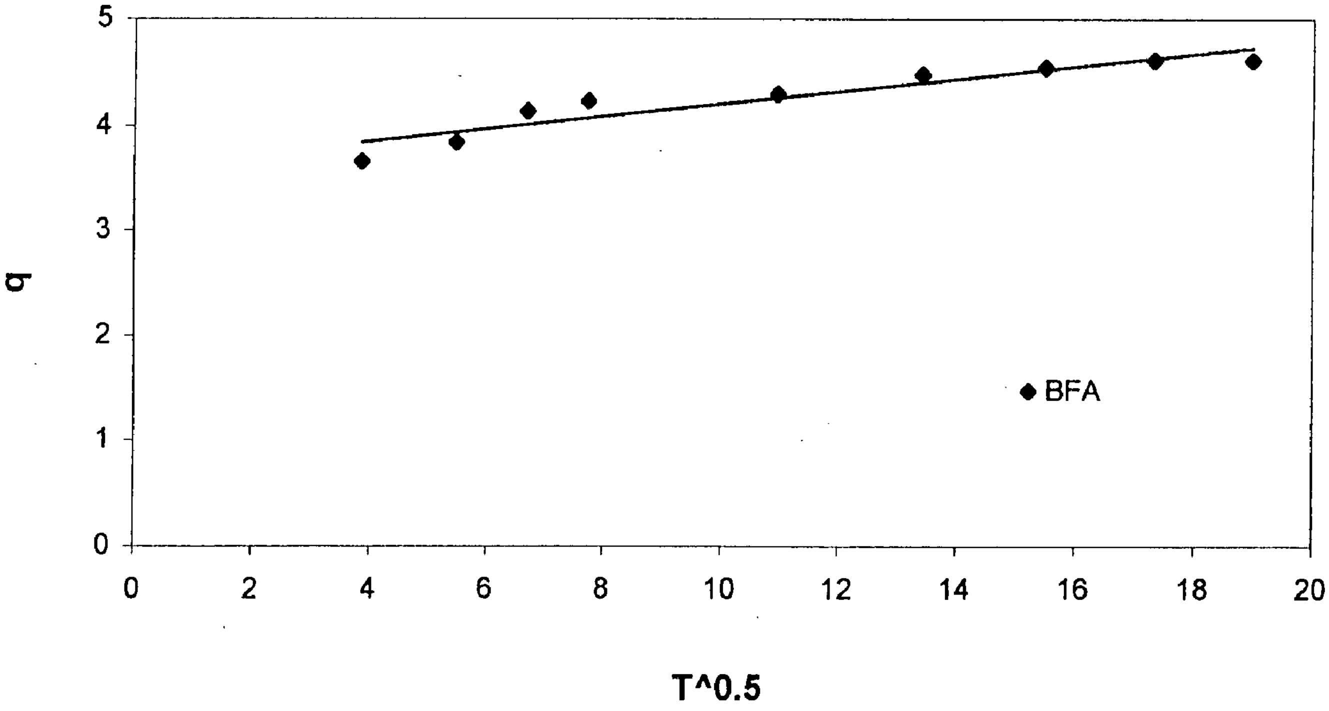


FIG 5.62 WEBER AND MORRIS INTRA PARTICLE DIFFUSION PLOT FOR REMOVAL OF RHODAMINE -B

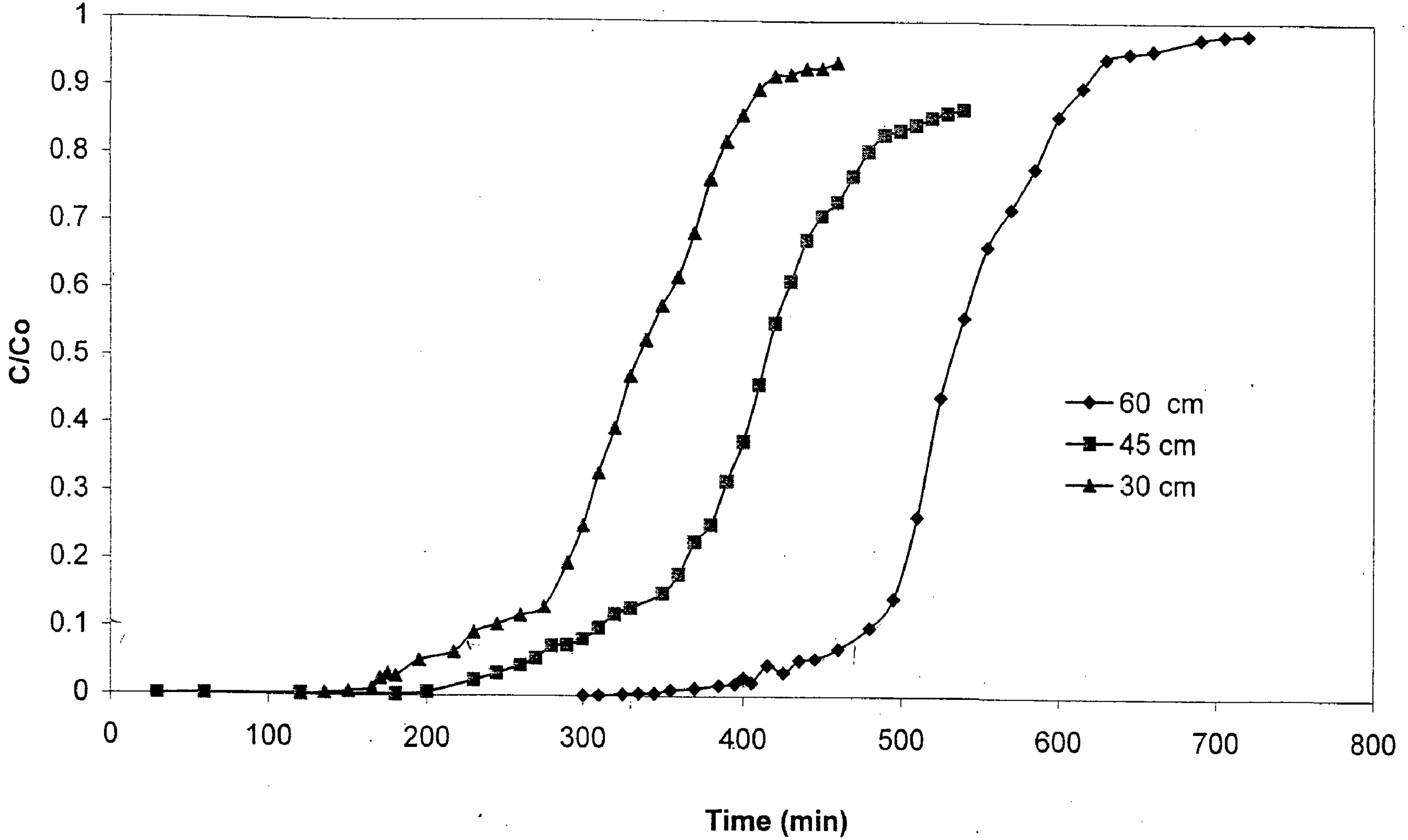


FIG 5.63 : Break through curve for removal of Methyl Violet for different bed heights of Bagasse Flyash

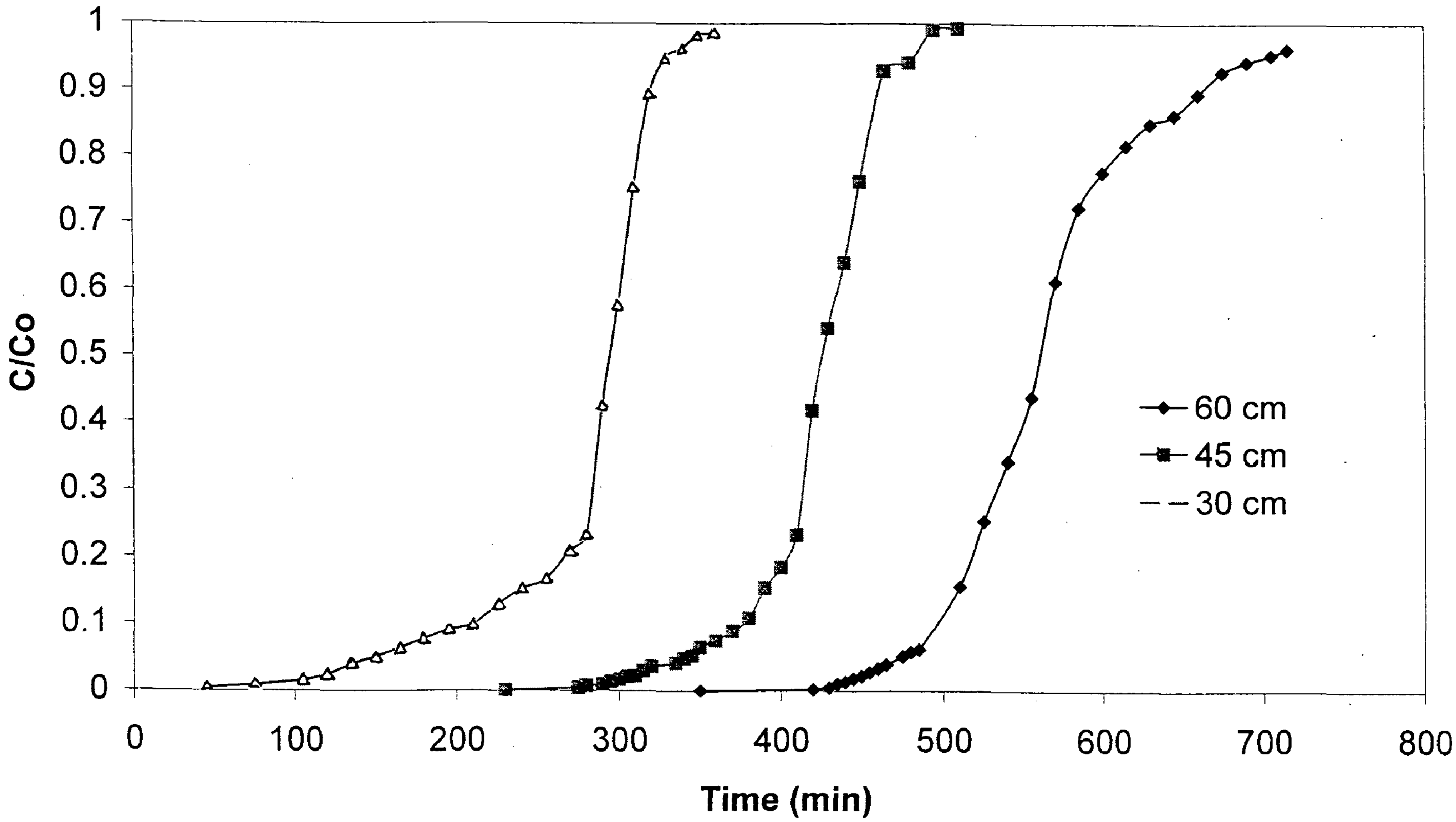


FIG 5.64 : Break through curve for removal of Rhodamine -B for different bed heights of Bagasse Fly ash

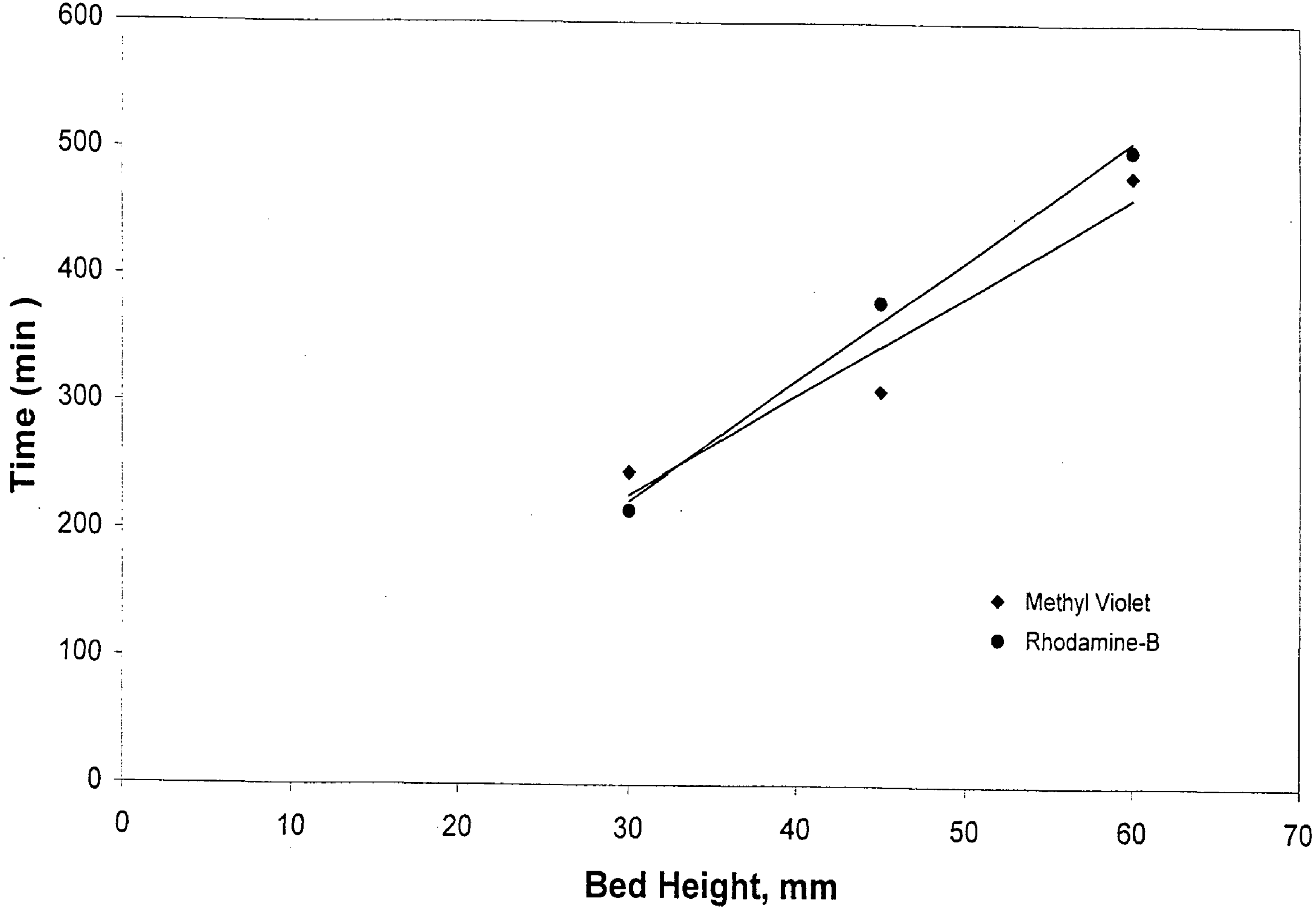


FIG 5.65 BDST PLOT FOR BAGASSE FLY ASH

Chapter - 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

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

- Bagasse fly ash is found to be very good adsorbent for the removal of dyes. Adsorptive capacity of bagasse fly ash and coal fly ash was higher than the commercial activated carbon.
- Percentage removal of dyes (Auramine, Congo-Red, Malachite Green, Orange-G, Methyl Violet, Rhodamine-B) increases with adsorbent dose till it attains equilibrium.
- Orange-G dye was strongest among the other dyes and removal per unit weight of the adsorbent was less.
- Removal of dyes was found to be rapid in initial stages of adsorption followed by slow adsorption, upto saturation.
- Percentage removal of dyes decreases with increase 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 pore diffusion is the rate-controlling step.
- Adsorber column study shows that Rhodamine-B adsorption wavefront moves faster as compared to those for Methyl Violet.
- Adsorption capacity of the adsorbents was in the following order
  BFA > CFA > ACL > ACC

- Removal per unit weight of the adsorbent for various dyes was in the following order

  Orange-G > Rhodamine-B > Congo-Red > Methyl Violet > Auramine > Malachite Green
- Removal of the basic dyes was higher in basic range whereas removal of direct dyes was higher in acidic range.
- Economic evaluation of the process reveals that use of Bagasse fly ash will be quite economical.
- The straight line between break through time and bed height plot verifies the Bohart-Adams Equation.

6.2 RECOMMENDATIONS

- Column studies of other dyes can be done to see the effect of bed height of adsorbent, flow rate and inlet concentration of adsorbate.
- Bagasse fly ash from different sugar mills should be characterised for physico-chemical parameters and surface characteristics to use its availability so that it may be utilised in effluent treatment.
- Costing of the adsorption based industrial scale treatment system be carried out to popularise the adsorption technique with Bagasse fly ash.

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APPENDIX –A

Table A- 1: Effect of adsorbent dose on removal of Auramine using different adsorbents

S. No.	Bagasse Flyash			Activated Carbon (commercial)			Activated Carbon (Lab)		
	Wt (gm)	% Removal	Amount Adsorbed /Amount Adsorbent (mg/g)	Wt (gm)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	Wt (gm)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	0.050	97.44	9.745	0.10	77.20	3.860	0.20	91.51	2.288
2	0.075	98.51	6.568	0.50	93.32	0.933	0.50	97.88	0.979
3	0.100	98.83	4.942	1.00	98.62	0.493	0.75	99.79	0.665
4	0.200	99.68	2.492	1.50	99.58	0.332	1.00	100.00	0.500
5	0.500	100.00	1.000	2.00	99.47	0.249	-	-	-

Table A-2: Effect of contact time on removal of Auramine using different adsorbents

S. No.	Time (min)	Bagasse Flyash (0.05gm)		Activated Carbon (Commercial) (1.0gm)		Activated Carbon (Lab) (0.10 gm)	
		% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	5	76.878	7.688	70.51	0.353	69.67	3.483
2	15	92.151	9.215	79.00	0.395	76.45	3.823
3	30	98.576	9.258	81.86	0.409	76.98	3.849
4	60	98.197	9.820	90.14	0.451	80.06	4.003
5	90	99.197	9.820	95.02	0.475	87.06	4.353
6	120	99.576	9.958	97.03	0.485	90.67	4.533
7	180	99.578	9.958	98.30	0.492	91.94	4.597
8	240	100.00	10.000	98.09	0.491	92.15	4.608

Table A-3: Effect of initial concentration on removal of Auramine using different adsorbents

S. No.	Initial Concentration of Dye (mg/l)	Bagasse Flyash (0.05gm)		Activated Carbon (Commercial) (1.0gm)		Activated Carbon (Lab) (0.10 gm)	
		% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	5	100.00	5.000	99.76	0.249	97.24	2.431
2	10	100.00	10.000	99.68	0.498	98.09	4.905
3	15	99.72	14.958	99.36	0.745	95.05	7.129
4	20	98.73	19.745	97.98	0.980	91.04	9.104
5	25	95.76	23.939	97.03	1.213	85.28	10.660
6	30	89.15	26.744	96.32	1.445	78.79	11.818

Table A-4: Effect of pH on removal of Auramine using Bagasse flyash (0.05g) as adsorbent

S. No.	pH	% Removal	Amount Adsorbed/Amount Adsorbent (mg/g)
1	3	99.06	9.906
2	6.5	99.26	9.926
3	10.0	99.58	9.958
4	12.5	98.94	9.894
5	7.2	97.45	9.745

Table A-5: Lagegren plot for removal of Auramine using different adsorbents

S. No.	Time (Min)	$\log(q_e-q)$		
		Bagasse Flyash	Activated Carbon (Commercial)	Activated Carbon (Lab)
1	5	0.3640	-0.8601	0.0511
2	15	-0.1051	-1.0177	-0.1051
3	30	-0.1296	-1.0862	-0.1198
4	60	-0.7447	-1.3979	-0.2182
5	90	-0.7447	-1.7959	-0.5934
6	120	-1.3767	-2.2218	-1.1249
7	180	-1.3767	-	-1.9586

Table: A-6: Freundlich isotherm for adsorption of Auramine using different adsorbents

S. No.	Bagasse Flyash		Activated Carbon (Commercial)		Activated Carbon (Lab)	
	$\log c_e$	$\log q_e$	$\log c_e$	$\log q_e$	$\log c_e$	$\log q_e$
1	0.0256	1.3791	-1.6726	-0.6039	-0.7192	0.6906
2	0.5127	1.4272	-1.4973	-0.3024	-0.1293	0.8530
3	-0.5942	0.9888	-1.0200	-0.1277	0.2534	0.9592
4	-0.8283	0.8174	-0.3946	-0.0088	0.5659	1.0277
5	-0.9330	0.6938	-0.1293	0.0838	0.8037	1.0725
6	-1.4973	0.3966	0.0426	0.1614	-	-

Table A-7: Langmuir Isotherm for adsorption of Auramine using different adsorbents

S. No.	Bagasse Flyash		Activated Carbon (Commercial)		Activated Carbon (Lab)	
	1/c	1/q	1/c	1/q	1/c	1/q
1	3.9284	0.0506	47.0580	4.0171	7.2525	0.4113
2	0.9428	0.0418	31.4276	2.0060	5.2379	0.2039
3	0.3071	0.0374	10.4758	1.3418	1.3469	0.1403
4	3.9285	0.1026	2.4811	1.0205	0.5579	0.1098
5	6.7345	0.1523	1.3469	0.8244	0.2717	0.0938
6	8.5712	0.2023	1.4965	1.0716	0.1571	0.0846

Table A-8: Weber and Morris intraparticle diffusion plot for removal of Auramine using different adsorbents

S. No.	$\sqrt{\text{Time}}$ ($\text{min}^{0.5}$)	Amount adsorbed per unit weight of adsorbent (mg/g)		
		Bagasse flyash	Activated Carbon (Commercial)	Activated Carbon (Lab)
1	2.236	7.688	0.353	3.483
2	3.873	9.215	0.395	3.823
3	5.477	9.258	0.409	3.849
4	7.746	9.820	0.451	4.003
5	9.4868	9.820	0.475	4.353
6	10.954	9.958	0.485	4.533
7	13.416	9.958	0.492	4.597
8	15.492	10.000	0.491	4.608

Table A- 9: Effect of adsorbent dose on removal of Congo Red using different adsorbents.

S. No.	Bagasse Fly Ash			Activated Carbon (Commercial)			Activated Carbon (LAB)		
	Wt (gm)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	Wt (gm)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	Wt (gm)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	0.020	46.34	11.586	0.10	40.00	2.000	0.10	43.40	2.151
2	0.050	79.28	7.930	0.50	52.23	0.522	0.30	66.94	1.115
3	0.075	95.02	6.333	0.75	75.32	0.502	0.40	89.35	1.117
4	0.100	96.15	4.807	1.00	94.56	0.473	0.50	92.30	0.923
5	0.200	96.04	2.400	2.00	98.07	0.245	0.75	100.00	0.667
6	0.500	99.43	0.990	2.50	100.00	0.245	1.00	100.00	0.500

Table A-10: Effect of contact time on removal of Congo Red using different adsorbents

S. No.	Time (min)	Bagasse Fly Ash (0.1gm)		Activated Carbon (Commercial) (2.0g)		Activated Carbon (LAB) (0.75g)	
		% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	5	71.02	3.551	48.95	2.447	63.10	3.135
2	15	81.21	4.061	64.45	3.223	76.12	3.806
3	30	94.00	4.700	78.95	3.948	83.70	4.185
4	60	94.68	4.734	84.61	4.231	92.64	4.632
5	120	96.15	4.807	89.47	4.474	91.39	4.5695
6	180	97.15	4.857	95.25	4.763	95.92	4.796
7	240	98.53	4.926	98.98	4.949	96.38	4.819
8	300	98.30	4.915	99.20	4.960	96.38	4.819

Table A- 11: Effect of initial concentration on removal of Congo Red using different adsorbents.

S. No.	Initial Concentration of Dye	Bagasse Fly Ash (0.1gm)		Activated Carbon (Commercial) (2.0g)		Activated Carbon (LAB) (0.75g)	
		% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	5	100.00	2.500	100.00	0.125	98.64	0.328
2	10	98.53	4.927	98.980	0.248	96.37	0.643
3	15	98.11	7.360	95.690	0.359	93.00	0.930
4	20	95.07	9.510	92.020	0.460	90.10	1.201
5	25	90.40	11.300	87.770	0.548	86.60	1.443
6	30	86.94	13.040	80.100	0.601	81.30	1.626

Table A- 12: Effect of pH variation on removal of Malachite green using Bagasse fly ash (0.05g) as adsorbent.

S. No.	pH	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	3	83.59	8.359
2	4	84.04	8.404
3	6	84.00	8.400
4	9	79.96	7.997
5	10	78.49	7.849
6	11.5	59.50	5.950

Table A- 13: Lagergren plot for the removal of Congo Red using different adsorbents.

S. No.	Time (min)	Bagasse Fly Ash (0.1gm) log (q_e-q)	Activated Carbon (Commercial) (2.0g) log (q_e-q)	Activated Carbon (Lab) (0.75g) log(q_e-q)
1	5	0.1348	0.4001	0.2236
2	15	-0.0683	0.2393	0.0056
3	30	-0.6676	0.0054	-0.1979
4	60	-0.7423	-0.1370	-0.7282
5	120	-0.9606	-0.3129	-0.6029
6	180	-1.2403	-0.7044	-1.6383
7	240	-	-1.9586	-

Table: A – 14: Freundlich isotherm for the removal of malachite green using different adsorbents.

S. No.	Bagasse Fly Ash		Activated Carbon (Commercial)		Activated Carbon (Lab)	
	log c_e	log q_e	log c_e	log q_e	log c_e	log q_e
1	-0.8327	0.6926	-0.1894	-0.4451	-0.4401	-0.1918
2	-0.5474	0.8668	0.2030	-0.3371	0.0212	-0.0315
3	-0.4451	0.9780	0.4854	-0.2608	0.2967	0.0795
4	-0.3371	1.0531	0.7760	-0.2213	0.5250	0.1593
5	-0.2608	1.1153	0.6792	-0.2821	0.7490	0.2111
6	-0.2213	1.0639	0.3923	-0.2992	0.7528	0.3365

Table A-15: Langmuir isotherm for adsorption of Malachite green using different adsorbents.

S. No.	Bagasse Fly Ash		Activated Carbon (Commercial)		Activated Carbon (Lab)	
	$1/c_e$	$1/q_e$	$1/c_e$	$1/q_e$	$1/c_e$	$1/q_e$
1	6.8027	0.2030	1.5468	2.7868	0.9524	1.0753
2	3.5273	0.1359	0.6266	2.1734	0.5051	0.8326
3	1.0142	0.1052	0.3271	1.8229	0.2985	0.6930
4	0.4167	0.0885	0.1675	1.6646	0.1782	0.6150
5	0.2552	0.0767	0.1667	0.5000	0.1767	0.4608
6	0.1864	0.0863	0.2093	1.9146	0.3025	0.8963
7	0.4826	0.1261	0.4052	1.9915	0.9390	0.8953
8	2.008	0.1579	-	-	1.2988	1.0834

Table A-16: Weber and Morris intraparticle diffusion plot for removal of Congo Red using different adsorbents.

S. No.	$\sqrt{time}$ ($min^{0.5}$)	Bagasse Fly Ash (0.1g) q(g/mg)	Activated Carbon (Commercial) (1.0g) q(g/mg)	Activated Carbon (Lab) (0.2g) q(g/mg)
1	2.236	3.551	2.447	3.135
2	3.873	4.061	3.223	3.806
3	5.477	4.700	3.948	4.185
4	7.746	4.734	4.231	4.632
5	10.954	4.807	4.474	4.570
6	13.416	4.858	4.763	4.796
7	15.492	4.927	4.949	4.819
8	17.320	4.915	4.960	4.819

Table A-17: Effect of adsorbent dose on removal of Malachite green using different adsorbents.

S. No.	Bagasse Flyash			Activated Carbon (commercial)			Activated Carbon (Lab)		
	Wt (g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	Wt (gm)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	Wt (gm)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	0.02	93.17	23.291	0.10	89.43	4.471	0.05	92.29	9.229
2	0.03	97.20	16.199	0.50	96.26	0.963	0.075	93.87	6.258
3	0.05	97.96	9.796	1.00	98.54	0.493	0.10	96.26	4.813
4	0.07	99.30	7.093	1.50	99.12	0.330	0.15	96.67	3.222
5	0.10	99.30	4.965	2.00	100.00	-	0.20	98.42	2.460
6	0.15	100.00	-				0.50	100.00	-

Table A-18: Effect of contact time on removal of Malachite green using different adsorbents.

S. No.	Time (min)	Bagasse Fly ash (0.1gm)		Activated Carbon (Commercial) (1.0gm)		Activated Carbon (Lab) (0.2 gm)	
		% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	5	96.73	4.836	87.33	0.437	83.23	2.081
2	15	98.07	4.904	90.60	0.453	91.71	2.293
3	30	98.95	4.947	93.34	0.467	92.76	2.319
4	60	99.12	4.956	97.14	0.486	95.85	2.396
5	90	99.47	4.974	99.24	0.496	97.49	2.437
6	120	99.47	4.974	99.36	0.497	98.36	2.459
7	180	99.53	4.977	99.88	0.499	98.25	2.456
8	240	99.71	4.985	100.00	0.500	99.88	2.497
9	270	99.71	4.985	100.00	0.500	100.00	2.500

Table A-19: Effect of initial concentration on removal of Malachite green using different adsorbents.

S. No.	Initial Concentration of Dye	Bagasse Fly ash (0.1gm)		Activated Carbon (Commercial) (1.0gm)		Activated Carbon (Lab) (0.2 gm)	
		% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)	% Removal	Amount Adsorbed/ Amount Adsorbent (mg/g)
1	10	99.82	4.991	99.18	0.496	97.96	2.449
2	15	98.52	7.389	98.52	0.739	97.12	3.642
3	20	96.58	9.658	96.06	0.960	95.41	4.771
4	25	95.79	11.974	95.23	1.190	95.37	5.961
5	30	94.90	14.235	94.35	1.415	94.67	7.100
6	35	94.48	16.533	93.89	1.643	94.73	8.289

Table A-20: Effect of pH variation on removal of Malachite green using Bagasse fly ash as adsorbent.

S. No.	pH	% Removal	Amount Adsorbed/Amount Adsorbent (mg/g)
1	4	96.7289	4.836445
2	6	99.182	4.9591
3	7	99.5327	4.976635
4	9	99.883	4.99415

Table A-21: Lagergren plot for the removal of Malachite green using different adsorbents.

S. No.	Time (min)	Bagasse Fly Ash (0.1gm) log (q_e-q)	Activated Carbon (Commercial) (1.0g) log (q_e-q)	Activated Carbon (Lab) (0.2g) log(q_e-q)
1	5	-0.8268	-1.1979	-0.3776
2	15	-1.0874	-1.3276	-0.6832
3	30	-1.4202	-1.4776	-0.7421
4	60	-1.5345	-1.8441	-0.9842
5	90	-1.9318	-2.4202	-1.2020
6	120	-1.9318	-2.4921	-1.3883
7	180	-2.0555	-3.2218	-1.3595
8	240	-	-	-2.5376

Table: A- 22: Freundlich isotherm for the removal of malachite green using different adsorbents.

S. No.	Bagasse Fly Ash		Activated Carbon (Commercial)		Activated Carbon (Lab)	
	log c_e	log q_e	log c_e	log q_e	log c_e	log q_e
1	-1.7564	0.6982	-1.0874	-0.3046	-0.6894	0.3890
2	-0.6537	0.8686	-0.6537	-0.1314	-0.3643	0.5613
3	-0.1653	0.9849	-0.1032	-0.0175	-0.0376	0.6786
4	0.0218	1.0783	0.0761	0.0757	0.0632	0.7753
5	0.1848	1.1534	0.2289	0.1508	0.2042	0.8512
6	0.2863	1.2184	0.3300	0.2157	0.2662	0.9185
7	-0.6894	0.9910	-0.4273	-0.0165	-0.4776	0.5082
8	-1.1543	0.8509	-0.8356	-0.3074		

Table A-23: Langmuir isothern for adsorption of Malachite green using different adsorbents.

S. No.	Bagasse Fly Ash		Activated Carbon (Commercial)		Activated Carbon (Lab)	
	$1/c_e$	$1/q_e$	$1/c_e$	$1/q_e$	$1/c_e$	$1/q_e$
1	4.5052	0.1353	4.5053	1.3533	4.8914	0.4083
2	1.4632	0.1035	1.2681	1.0410	2.3135	0.2746
3	0.9511	0.0835	0.8392	0.8400	1.0905	0.2096
4	0.6534	0.0702	0.5903	0.7066	0.8647	0.1678
5	0.5172	0.0605	0.4677	0.6086	0.6248	0.1409

Table A-24: Weber and Morris intraparticle diffusion plot for removal of Malachite green using different adsorbents.

S. No.	$\sqrt{\text{time}}$ ($\text{min}^{0.5}$)	Bagasse Fly Ash (0.1g) q(g/mg)	Activated Carbon (Commercial) (1.0g) q(g/mg)	Activated Carbon (Lab) (0.2g) q(g/mg)
1	2.236	4.8800	0.4366	2.1808
2	3.873	4.90362	0.45297	2.2926
3	5.477	4.9474	0.4667	2.3189
4	7.746	4.9562	0.4660	2.3963
5	9.4868	4.9737	0.4740	2.4372
6	10.954	4.9737	0.49678	2.4591
7	13.416	4.9766	0.4994	2.4562
8	15.492	4.9854	0.5000	2.4971
9	16.43167	4.9854	0.5000	2.5000

Table A-25: Effect of adsorbent dose on removal of Orange-G using Bagasse Fly ash as adsorbent.

S. No.	Weight (g)	%Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	0.02	29.57	7.3925
2	0.05	55.26	5.5260
3	0.10	82.22	4.1110
4	0.20	95.76	2.3940
5	0.30	96.75	1.6125
6	0.50	100.00	1.0000

Table A- 26: Effect of contact time on removal of Orange –G using Bagasse Fly Ash as adsorbent.

S. No.	Time (min)	%Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	15	33.95	3.3951
2	30	40.87	4.0866
3	45	46.23	4.6229
4	60	48.06	4.8064
5	120	57.52	5.7519
6	180	60.62	6.0624
7	240	68.39	6.8387
8	270	73.61	7.3608
9	300	73.62	7.3620

Table: A- 27: Effect of initial concentration on removal of Orange-G using Bagasse Fly Ash (0.1g) as adsorbent.

S. No.	Initial Concentration of Dye (mg/l)	% Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	5	88.71	2.2177
2	10	76.29	3.8145
3	15	58.60	4.3950
4	20	55.19	5.5190
5	25	43.66	5.4575
6	30	34.23	5.1345

Table A- 28: Effect of pH on removal of Orange-G using Bagasse fly Ash as adsorbent.

S. No.	pH	% Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	3.0	68.95	3.4475
2	3.5	77.14	3.8570
3	5.5	65.71	3.2852
4	9.2	57.66	2.8830
5	10.0	48.21	2.4102
6	10.8	49.19	2.4595
7	11.4	42.28	2.1138

Table A- 29: Lagergren plot for the removal of Orange-G using Bagasse Fly Ash as adsorbent.

S. No.	Time (min)	log(q_e-q)
1	15	0.5984
2	30	0.5153
3	45	0.4376
4	60	0.4075
5	120	0.2069
6	180	0.1138
7	240	-0.2813

Table A- 30: Freundlich isotherm for removal of Orange – G using Bagasse Fly ash as adsorbent.

S. No.	log c	log q
1	-0.2483	0.3459
2	0.3750	0.5814
3	0.7931	0.6429
4	0.9524	0.7419
5	0.8478	0.8688
6	0.6507	0.7424
7	0.2499	0.6139
8	-0.3726	0.3791
9	-0.4881	0.2075

Table A- 31: Langmuir Isotherm for adsorption of Orange – G using Bagasse fly Ash as adsorbent.

S. No.	1/c_e	1/q_e
1	1.7714	0.4509
2	0.4218	0.2622
3	0.1610	0.2275
4	0.1116	0.1812
5	0.0507	0.1948
6	0.2235	0.1820
7	0.5624	0.2432
8	2.3585	0.4177
9	3.0769	0.6202

Table A- 32: Weber and Morris intraparticle diffusion plot for removal of Orange-G using Bagasse Fly ash as adsorbent.

S. No.	$(Time)^{0.5}$ ($min^{0.5}$)	Amount adsorbed / gm of adsorbent (mg/g)
1	3.8730	3.3951
2	5.4772	4.0866
3	6.7082	4.6229
4	7.7460	4.8064
5	10.9545	5.7519
6	13.4164	6.0624
7	15.4919	6.8387
8	16.4317	7.3608
9	17.3205	7.3620

Table A- 33: Effect of adsorbent dose on removal of Methyl Violet using Bagasse Fly ash as adsorbent.

S. No.	Wt (gm)	%Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	0.02	68.96	17.240
2	0.05	95.42	9.542
3	0.10	100.00	5.000
4	0.15	100.00	3.330

Table A- 34: Effect of contact time on removal of Methyl Violet using Bagasse Fly Ash as adsorbent.

S. No.	Time (min)	% Removal	Wt. of Adsorbate/ Wt. of Adsorbent (mg/g)
1	5	76.51	7.651
2	15	80.29	8.029
3	45	89.17	8.917
4	60	89.36	8.936
5	120	91.95	9.195
6	180	96.16	9.616
7	240	97.59	9.759
8	300	97.68	9.768
9	360	97.77	9.777

Table A- 35: Effect of initial concentration on removal of Methyl Violet using Bagasse Fly Ash as adsorbent.

S. No.	Initial concentration of dye (mg/l)	%Removal	Wt. of Adsorbate/ Wt. of Adsorbent (mg/g)
1	5	98.33	4.917
2	10	99.17	9.917
3	15	89.91	13.486
4	20	86.33	17.266
5	25	80.38	20.095
6	30	72.56	21.768
7	35	63.87	22.354

Table A- 36: Effect of pH on removal of Methyl Violet using Bagasse fly Ash as adsorbent.

S. No.	pH	%Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	2.8	96.30	9.630
2	3.5	95.37	9.537
3	6.0	94.91	9.491
4	6.6	94.91	9.491
5	8.7	96.76	9.676
6	9.4	96.76	9.676
7	10.6	98.6	9.860

Table A- 37: Lagergren plot for the removal of Methyl Violet using Bagasse Fly Ash as adsorbent.

S. No.	Time (min)	$\log(q_e\text{-}q)$
1	5	0.3275
2	15	0.2424
3	45	-0.14
4	60	-0.0752
5	120	-0.2351
6	180	-0.7932
7	240	-1.7447
8	300	-2.0458
9	360	-

Table A- 38: Freundlich Isotherm for adsorption of Methyl Violet using Bagasse fly Ash as adsorbent.

S. No.	log C_e	log Q_e
1	0.1700	1.1299
2	0.4368	1.2372
3	0.6906	1.3031
4	0.9155	1.3378
5	1.1019	1.3494
6	0.4919	1.2365

Table A- 39: Langmuir Isotherm for the adsorption of Methyl Violet using Bagasse Fly ash as adsorbent.

S. No.	$1/C_e$	$1/Q_e$
1	0.6607	0.0741
2	0.3658	0.0579
3	0.2039	0.0498
4	0.1215	0.0459
5	0.0791	0.0447
6	0.3222	0.0580

Table A- 40: Weber and Morris intraparticle diffusion plot for removal of Methyl Violet using Bagasse Fly ash as adsorbent.

S. No.	$(\text{Time})^{0.5}$ ($\text{min}^{0.5}$)	Amount adsorbed / gm of adsorbent (mg/g)
1	0.2886	7.651
2	0.5000	8.029
3	0.8660	8.917
4	1.0000	8.936
5	1.4140	9.195
6	1.7320	9.616
7	2.0000	9.759
8	2.2360	9.768
9	2.4490	9.777

Table A- 41: Effect of adsorbent dose on removal of Rhodamine-B using Bagasse Fly ash as adsorbent.

S. No.	Wt (gm)	% Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	0.05	85.00	8.5000
2	0.10	90.95	4.5475
3	0.14	95.90	3.4250
4	0.18	99.40	2.7680
5	0.20	99.68	2.4920
6	0.25	100.00	2.0000

Table A- 42: Effect of contact time on removal of Rhodamine –B using Bagasse Fly Ash as adsorbent.

S. No.	Time (min)	% Removal of Dye	Amount adsorbed / gm of adsorbent (mg/g)
1	15	65.42	3.2709
2	30	76.88	3.8438
3	45	82.58	4.1289
4	60	84.52	4.2261
5	120	85.82	4.2910
6	180	89.55	4.4777
7	240	90.82	4.5412
8	300	92.20	4.6099
9	360	92.22	4.6110

Table A- 43: Effect of initial concentration on removal of Rhodamine-B using Bagasse Fly Ash as adsorbent.

S. No.	Initial concentration of dye (mg/l)	% Removal of Dye	Amount adsorbed / gm of adsorbent (mg/g)
1	5	100.00	2.500
2	10	98.50	4.925
3	15	91.00	6.825
4	20	88.26	8.826
5	25	65.88	8.236
6	30	51.09	7.664

Table A- 44: Effect of pH on removal of Rhodamine –B using Bagasse fly Ash as adsorbent.

S. No.	pH	% Removal	Amount adsorbed / gm of adsorbent (mg/g)
1	3	97.97	4.8985
2	5	98.86	4.9430
3	6	98.65	4.9325
4	8	95.83	4.7913
5	9.5	95.07	4.7535

Table A- 45: Lagergren plot for the removal of Rhodamine – B using Bagasse Fly Ash as adsorbent.

S. No.	Time (min)	log (q_e-q)
1	15	0.1273
2	30	-0.1149
3	45	-0.3165
4	60	-0.4145
5	120	-0.4942
6	180	-0.8732
7	240	-1.1549
8	300	-2.8239

Table A- 46: Freundlich Isotherm for the adsorption of Rhodamine – B using Bagasse Fly ash as adsorbent.

S. No.	log C_e	log Q_e
1	-0.8228	0.5500
2	0.1305	0.8341
3	0.3708	0.9457
4	0.9309	0.9700
5	1.1665	1.1855
6	0.1761	0.8900
7	-0.0435	0.6900
8	-0.3876	0.6000

Table A- 47: Langmuir Isotherm for adsorption of Rhodamine – B using Bagasse fly Ash as adsorbent.

S. No.	$1/C_e$	$1/Q_e$
1	0.7404	0.1465
2	0.4257	0.1133
3	0.1172	0.1100
4	0.0682	0.0652
5	0.6667	0.1176
6	1.1053	0.2030
7	2.4414	0.2920

Table A- 48: Weber and Morris intraparticle diffusion plot for removal of Rhodamine –B using Bagasse Fly ash as adsorbent.

S. No.	$(\text{Time})^{0.5}$ ($\text{min}^{0.5}$)	Amount adsorbed / gm of adsorbent (mg/g)
1	3.8730	3.6600
2	5.4772	3.8438
3	6.7082	4.1289
4	7.7460	4.2262
5	10.9545	4.2910
6	13.4164	4.4777
7	15.4919	4.5412
8	17.3205	4.6099
9	18.9737	4.6110

APPENDIX – B

Table B-1: Effect of bed height of Bagasse Flyash on removal of Methyl Violet.

S. No.	Time (min)	C/Co (2.0 ft)	Time (min)	C/Co (1.5 ft)	Time (min)	C/Co (1.0 ft)
1	300	0	30	0	60	0.00023
2	310	0.00035	60	0.00116	120	0.00093
3	325	0.00197	120	0.0022	135	0.00428
4	335	0.00335	180	0.0022	150	0.00648
5	345	0.00439	200	0.00497	165	0.01064
6	355	0.00914	230	0.0222	170	0.02579
7	370	0.01168	245	0.03261	175	0.03249
8	385	0.01584	260	0.04429	180	0.0362
9	395	0.01839	270	0.05435	195	0.05197
10	400	0.02752	280	0.07285	205	0.07401
11	405	0.03388	290	0.07401	230	0.09251
12	415	0.04591	300	0.08326	245	0.10408
13	425	0.04938	310	0.09945	260	0.11795
14	435	0.05331	320	0.12026	275	0.13067
15	445	0.05516	330	0.15264	290	0.19543
16	460	0.05539	340	0.17346	300	0.25094
17	480	0.10107	350	0.17924	310	0.32841
18	495	0.14478	360	0.17924	320	0.39433
19	510	0.26551	370	0.22781	330	0.47181
20	525	0.4422	380	0.25325	340	0.52616
21	540	0.56085	390	0.31685	350	0.57704
22	555	0.66724	400	0.37583	360	0.61983
23	570	0.72274	410	0.46024	370	0.68574
24	585	0.78288	420	0.5516	380	0.76553
25	600	0.86035	430	0.61404	390	0.82104
26	615	0.90314	440	0.67533	400	0.86035
27	630	0.94593	450	0.71118	410	0.89852
28	645	0.95402	460	0.732	420	0.91817
29	660	0.95865	470	0.77016	430	0.92039
30	690	0.97599	480	0.80716	440	0.92917
31	705	0.98062	490	0.83144	450	0.93008
32	720	0.98178	500	0.83723	460	0.93847
33			510	0.84648		
34			520	0.85689		
35			530	0.86385		
36			540	0.86949		

Table B-2: Effect of bed height of Bagasse Flyash on removal of Rhodamine –B.

S. No.	Time (min)	C/Co (2.0 ft)	Time (min)	C/Co (1.5 ft)	Time (min)	C/Co (1.0 ft)
1	350	0	230	0.00026	45	0.00414
2	420	0.00181	275	0.00467	75	0.0083
3	430	0.00493	280	0.00778	105	0.01555
4	435	0.01011	290	0.00985	120	0.02437
5	440	0.01296	295	0.014	135	0.0394
6	445	0.01763	300	0.01685	150	0.05107
7	450	0.02178	305	0.02126	165	0.06403
8	455	0.02748	310	0.02255	180	0.07751
9	460	0.03318	315	0.02955	195	0.09073
10	465	0.03914	320	0.03655	210	0.09877
11	475	0.05081	335	0.04122	225	0.12806
12	480	0.05755	340	0.04848	240	0.15217
13	485	0.06144	345	0.05211	255	0.16669
14	510	0.15639	350	0.06481	270	0.21024
15	525	0.25386	360	0.07466	280	0.23331
16	540	0.34213	370	0.08918	290	0.42515
17	555	0.43867	380	0.1081	300	0.57809
18	570	0.61286	390	0.15399	310	0.75437
19	585	0.72359	400	0.18483	320	0.89436
20	600	0.77683	410	0.23253	330	0.9488
21	615	0.81672	420	0.41737	340	0.96176
22	630	0.84863	430	0.5418	350	0.9825
23	645	0.86179	440	0.64031	360	0.98509
24	660	0.89324	450	0.76215		
25	675	0.92687	465	0.92806		
26	690	0.94214	480	0.94102		
27	705	0.95236	495	0.99028		
28	715	0.9612	510	0.99287		

Table B-3: Relation between bed height of Bagasse flyash and service time for Methyl violet and Rhodamine-B. (Break through concentration 0.1 Co).

S. No.	BED HEIGHT(cm)	TIME(min) (Methyl Violet)	TIME(min) (Rhodamine-B)
1	30	245	215
2	45	310	380
3	60	480	500

APPENDIX-C

Table c- 1: Correlation coefficient (r) for fitting experimental data to straight line for Lagregren plot, Freundlich Isotherm, Langmuir Isotherm and Weber and Morris plot.

DYE	ADSORBENT	CORRELATION COEFFICIENT(r)			
		LAGREGREN PLOT	FREUNDLICH ISOTHERM	LANGMUIR ISOTHERM	WEBER AND MORRIS PLOT
AURAMINE	BFA	0.9325	0.9801	0.9439	0.8023
	ACC	0.9943	0.9502	0.9531	0.9399
	ACL	0.9750	0.9976	0.9403	0.9621
CONGO RED	BFA	0.8925	0.9817	0.8952	0.9975
	ACC	0.9473	0.9595	0.9780	0.9994
	ACL	0.9385	0.9757	0.8488	0.9883
MALACHITE GREEN	BFA	0.9081	0.9539	0.9382	0.8967
	ACC	0.9921	0.9704	0.9219	0.9512
	ACL	0.9458	0.9919	0.9622	0.9414
ORANGE -G	BFA	0.9815	0.9440	0.9717	0.9932
METHYL VIOLET	BFA	0.9771	0.9644	0.9967	0.9452
RHODAMINE - B	BFA	0.9172	0.9131	0.9714	0.9431