Detoxification of bleach plant effluent using low cost adsorbents : Removal of 2, 4 dichlorophenol

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ABSTRACT

Adsorption of 2,4-dichlorophenol by bagasse fly ash (BFA), rice husk fly ash (RHFA) and activated carbon (AC) has been investigated. The practical applicability of these adsorbents in batch operations and various parameters such as effect of contact time, adsorbent dose, pH of the solutions have been investigated. The removal kinetics of 2,4-dichlorophenol shows first order rate expression and equilibrium adsorption data suited well for both Langmuir and Freundlich isotherms. Economic evaluation of the adsorbents BFA and RHFA with the AC shows that use of BFA and RHFA will be viable.

INTRODUCTION

Bleach plant effluent presents the highest pollution load responsible for the generation of large amount of wastewater containing high toxicity and colour. Chlorinated and non-chlorinated compounds in pulp mill effluents contribute to the toxic nature of these effluents. The seriousness of the effluents depends on the extension of effects in time and space (1). The content of chlorinated organic matter present in the bleach plant varies depending on types of raw material, bleaching chemicals, bleaching conditions and extent of bleaching. Virtually all of the chlorinated organics produced at bleached kraft pulp mills originated in the bleaching process with the initial chlorinated and extraction stage contributing largest quantities (2). The bleach plant effluent contains a broad range of chlorinated organics starting from low molecular weight compounds, such as chloroform to complex high molecular weight lignin derivative materials. About 4-5 kg AOX are produced per tonne of pulp in case of wood (1). Various toxic compounds present includes chlorinated resin acids, chlorinated fatty acids, adsorbable organohalogens, gentoxic and other carcinogenic compounds (3) which are shown in Fig 1. Various adsorbable organohalogen consists of chlorophenols, di-chlorophenols, tri-chlorophenols, tetra-chlorophenols, chlorocatechol, dichloroguaiacol, tri-chloroguaiacol and tetra-chloroguaiacol. These chlorinated organic compounds are considered to be toxic and hazardous to various target organisms including human being and it is necessary to reduce their concentrations to safe values (2). Majority of organic chemicals is non-biodegradable and requires tertiary treatment for safe disposal to environment. 2, 4 di-chlorophenol is present in appreciable quantity in bleach plant effluent. Chlorophenols impart disagreeable taste to water and toxic to aquatic life and human being. Chlorinated phenols are one of the environmentally harmful compounds, having been proved to be toxic to many water organisms even at 0.1 ppm level. Furthermore, 0.01 ppm level of chlorophenols suffice to impact an extremely disagreeable taste and odour to water (4). Therefore treatment of 2, 4-dichlorophenol containing wastewater

Table-1 Characteristics of adsorbents

Characteristics	Activated carbon	Bagasse fly ash	Ricehusk flyash
Bulk density (kg/m^3)	617.5	118.6	224.2
Volatile matter (%)	36.61	30.49	7.8
Ash (%)	28.2	50.4	72.9
Chemical analysis			
Loss on ignition (%)	71.7	49.7	9.0
SiO_2 (%)	0.54	39.98	74.0
Al_2O_3 (%)	0.30	2.75	6.2
Fe_2O_3 (%)	0.20	0.70	4.0
CaO (%)	0.40	1.60	2.3
MgO (%)	0.50	1.40	0.6

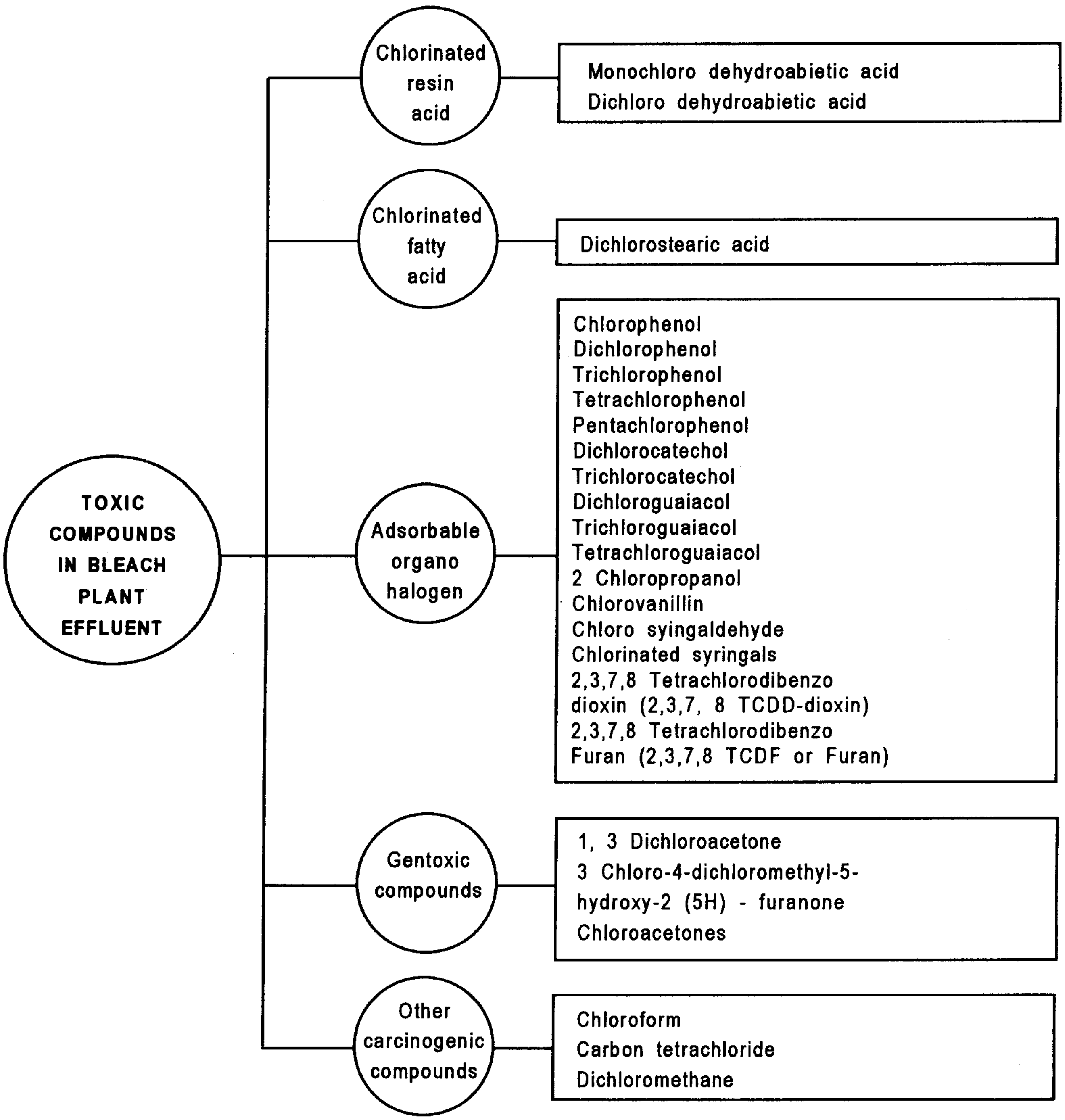

Fig. 1 : Toxic Compounds in Bleach Plant Effluent

is of vital importance. Characteristics of the 2, 4-dichlorophenol are presented in the Table-5.

Biodegradation of halophenol to halide ion appears to be very slow process. Reverse osmosis, hyper-filtration, radio chemical degradation, photo-oxidation destruction and oxidation by hydrogen peroxide and sodium hypochlorite etc. has been investigated for removal of phenolic compound (5). Among the several currently known physical, chemical and biological methods which are used in wastewater treatment, adsorption still continues to be most widely used process for removal of nonbiodegradable matter like heavy metals, phenols, colour and other refractory organics. Although activated carbon is most widely used adsorbent its high cost and about 10-15% loss on regeneration there has been continuous search for low cost adsorbents (6). A critical review of economical treatment of wastewaters and effluent by adsorption

Table-2 Particle size analysis of activated carbon

Particle size (mm/μm)	Weight (%)
>2.0 mm	11.1
1.4 mm-2.0 mm	42.5
1.18mm-1.4 mm	9.2
1.0 mm-1.18 mm	20.2
710 μm-1.0 mm	13.1
< 710 μm	3.9

Table-3 Particle size analysis of bagasse flyash

Particle size (μm)	Weight (%)
>710	3.8
500-600	2.5
400-500	13.2
300-400	17.3
212-300	28.2
100-212	24.7
<100	10.3

Table 4 Particle size analysis of rice husk flyash

Particle size (μm)	Weight (%)
>710	10.1
500-600	2.9
400-500	9.7
300-400	20.3
212-300	13.2
100-212	34.5
<100	9.3

has been reported (7). The present study deals with the adsorption of 2,4-dichlorophenol from wastewater onto BFA, RHFA and AC. The adsorbents bagasse fly ash and rice husk fly ash are produced in large amount by the sugar mills and rice mills respectively. Due to its cheapness, easy handling and no disposal problem draw the attention of researchers for its utilization in treatment of wastewater.

EXPERIMENTAL

Adsorbent bagasse fly ash and rice husk fly ash were collected from nearby sugar and rice mills and used after washing thorughly by distilled water for removing water soluble impurities and dried in oven at 80°C for 8 hours. Analytical grade of activated carbon was used for the adsorption studies and economic evaluation. Stock solution of 2,4-dichlorophenol was prepared in distilled water. The experimental solutions of the desired concentrations were obtained by successive dilution. Batch experiments were conducted

Table-5 Characteristics of 2,4-dichlophenol

Parameter	2,4-Dichlorophenol
Formula	C_6H_3 OH Cl_2-2,4
Description	Colourless crystals
Mol. wt.	163
m.p.	45°C
b.p.	210°C
Flash pt.	237°F (113°C)
Sp. gr.	1.383 at 60°C/25°C
Solubility	4,500 mg/l at 25°C, 46 mg/l 20°C
Odour	Strong medicinal Cancer
Toxicity	suspect agent toxic moderately toxic by skin absorption Causes burns
Acute Oral LD_{50} mg/kg	
Male Mice	1276
Female Mice	1352
Odour Threshold	Av. 0.21 mg/lt Range 0.02-1.35 mg/lt
Taste threshold	0.008-0.02 mg/lt
Conc. Causing taste in fish	0.005 mg/lt
TOC	0.002 mg/lt
Water Pollution	May be dangerous if it enters water intake
Aquatic toxicity	5 ppm/3h/rainbow trot/killed/fresh water
Toxicity by ingestion	LD_{50} = 0.5-5 g/kg rat

with known amount of adsorbent and 50 ml of 2,4-dichlorophenol solution in 100 ml of conical flask at different initial concentrations, adsorbent dose and pH in a shaking water incubator at constant speed. The supernatant liquid was obtained from the suspension solution by filtering from the Whatman no. 42 filter paper. The amount and percentage adsorption were determined using double-beam UV-visible spectrophotometer make [Shimadzv Seisak Avso ltd. Ktoyo, Japan]. Adsorbents BFA, RHFA and activated carbon were characterized for proximate, sieve and chemical analysis and presented in Table 1-4. X-ray diffraction analysis of rice husk fly ash, bagasse fly ash 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 A. Goniometer and chart speed were maintained at 1^0 min^{-1} and 1cm min^{-1} respectively (Fig. 2-4) and SEM analysis were carried out by using LEO 435 VP (Fig. 5-7). In activated carbon the major peaks indicate the presence of silica in form of tridymite and alpha cristobalite. The major peaks of

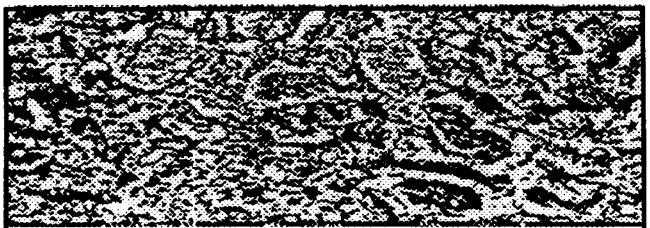

Fig. 2: Scanning electron micrograph of activated carbon

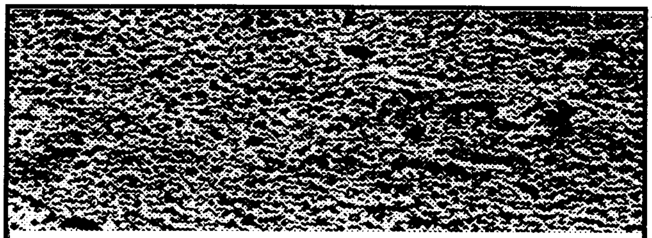

Fig. 3: Scanning electron micrograph of rice fly husk

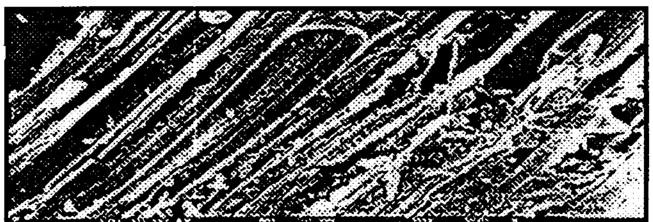

Fig. 4: Scanning electron micrograph of bagasse flyash

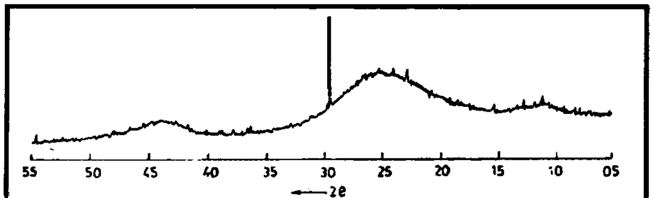

Fig. 5: X-ray diffraction pattern of activated carbon

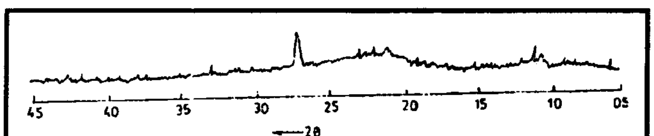

Fig. 6: X-ray diffraction pattern of rice ash husk

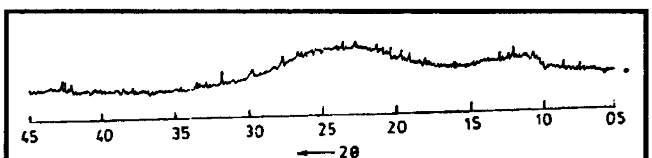

Fig. 7: X-ray diffraction pattern of bagasse fly ash

bagasse fly ash exhibits the presence of silica in the form of tridymite, alpha cristobalite and keatite. In case of rice husk fly ash the major peak indicated the presence of silica in the form of alpha quartz. Besides these, other peaks indicated also the presence of Fe_2O_3, Al_2O_3, MgO and CaO etc.

RESULTS AND DISCUSSION

Effect of adsorbent dose

The effect of adsorbent dose on removal of 2,4-dichlorophenol by the adsorbents is presented in Fig. 8. It may be observed that on increasing of adsorbent dose, the precentage removal of 2,4-dichlorophenol increases at certain range but further increasing of adsorbent dose there was no increase in the percentage removal. Initially the percentage removal increases with increase in adsorbent dose, as more surface area is available for adsorption. The plot of unit adsorption versus dose reveals that the unit adsorption was high at low doses than at high doses. As the adsorbent dose was increased, there was less commensurate increase in adsorption resulting from lower adorption capacity utilization of adsorbent. Unit adsorption decreases significantly with decreasing mass of adsorbent per unit volume. This effect has been termed as "solid concentration effect" meaning overcrowding of particles (8).

Effect of pH

Fig. 9 shows the effect of pH on removal of 2,4-dichlorophenol. It is clear from the figure that the percentage removal of 2,4-dichlorophenol is higher at the pH 4 for the adsorbents. The ionic nature of the 2,4-dichlorophenol depends on the pH of aqueous solution. The hydrophilic interaction between solution media effects its interaction with the adsorbent surface at this range and adsorption becomes maximum.

Effect of contact time of 2,4-dichlorophenol

The effect of contact time on removal of 2,4-dichlorophenol is shown in Fig. 10. It may be observed that the amount of 2,4-dichlorophenol adsorbed is very rapid during the initial period of time and maximum adsorption taking place in first 120 miuntes. The attaining of equilibrium takes longer time. However, the percentage removal of 2,4-dichlorophenol decreases with increasing initial concentrations and the amount adsorbed increases with increasing initial concentrations (7). This is because at lower concentration, the ratio of initial number of moles of 2,4-dichlorophenol to the available surface area is low and subsequently the fractional adsorption becomes independent of initial concentration (9-10). However, at higher concentration, the available sites of adsorption becomes less and hence percentage removal of 2,4-dichlorophenol is dependent upon the initial concentration. The equilibrium time is independent of initial concentration of 2,4-dichlorophenol.

Kinetics of removal of 2,4-dichlorophenol

The rate constants of 2,4-dichlorophenol have been determined using the Lagergren first order rate expression (11)

$$\text{Log}\,(qe - q) = \text{Log}\,qe - \frac{K_{ad}}{2.303}\,t$$

where q and qe are the amounts of 2,4-dichlorophenol adsorbed at time t and at equilibrium on the unit weight of adsorbents and k_{ad} is the adsorption rate constant. The plot of log (qe-q) vs t gives straight line showing validity of the equation (Fig 11). The values of rate constant have been presented in Table-6.

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 (9). The values of intraparticle diffusion rate parameters are given in Table-7.

Adsorption Isotherm

For better understanding and evaluating of the process, determination of feasibility of adsorbing system, selection of adsorbents and evaluation of dose of adsorbents, etc. is necessary to study the modelling of equilibrium data. Langmuir and Freundlich isotherms have been commonly used for these studies and presented in the following equation.

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

Freundhlich Isotherm

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

where C_e and q_e are the equilibrium concentration mg/L and amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium respectively. K_A and Q_m are the Langmuir constants and K_F and n are Freundlich constants. The plot of log q_e vs log C_e and $1/C_e$ at different temperatures have been given in Fig. 12-13. Straight line of these plots shows the applicability of Langmuir and Freundlich isotherms. The values of n found less more than 1 shows favourable adsorption, The value of Q_m decreases with increasing temperature further shows the exothermic nature of the process. The values of Langmuir and Freundlich constants have been recorded in Table-8.

Table 6 Lagergren adsorption rate constant k of 2,4 dichlorophenol for the different adsorbents

Adsorbent	k (min^{-1})
Activated carbon	0.01863
Bagasse flyash	0.02254
Rice husk flyash	0.02047

Table 7 Intraparticle diffusion rate parameter k' from Weber-Morris plot

Adsorbent	k' ($mg\ g^{-1}\ min^{-0.5}$)
Activated carbon	0.06500
Bagasse flyash	0.0622
Rice husk flyash	0.0574

Table 8 Isotherm parameters for different 2,4dichlorophenol - adsorbent

Isotherm equation Paramters	Activated carbon	Bagasse flyash	Rice husk flyash
Freundlich isotherm			
K_F ($(mg1^{-1})^{-1/n}$ $x10^{-3}$)	0.78886	0.52747	0.32337
n	2.74725	2.45942	1.91718
Langmuir isotherm			
q_m ($mg\ g^{-1}$)	1.83117	1.44676	1.54392
K_A ($1\ mg^{-1}$)	0.717999	0.54649	0.22350

Table 9 Economic evaluation of various adsorbents

Adsorbents	Cost of adsorbent (Rs/Ton)
Activated carbon	60,000-70,000
Bagasse fly ash	5,000*
Rice husk fly ash	5,000*

* *Handling charges*

Economic Evaluation

The economic evaluation of the treatment process using activated carbon, bagasse flyash and rice husk fly ash is presented in Table-9. Though the percentage removal by activated carbon is higher than that of rice husk fly ash and bagasse fly ash, the overall cost of treatment with bagasse fly ash and rice husk fly ash is lower, as these adsorbents are available almost free of cost involving only handling charges. Removal efficiency of bagasse fly ash was found higher than that of rice husk fly ash.

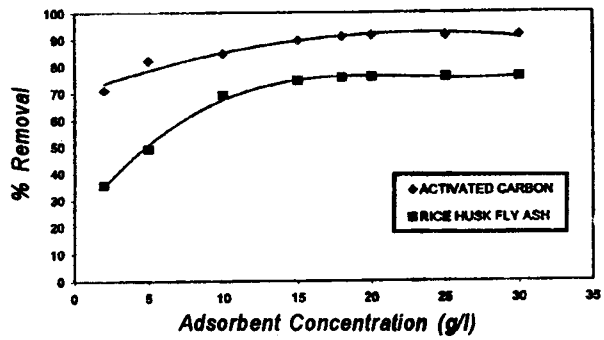

Fig. 8: Effect of adsorbent dose on removal of 2,4-dichlorophenol

Initial concentration = 20 mg/l, Contact time = 4h, Temperature 30°C

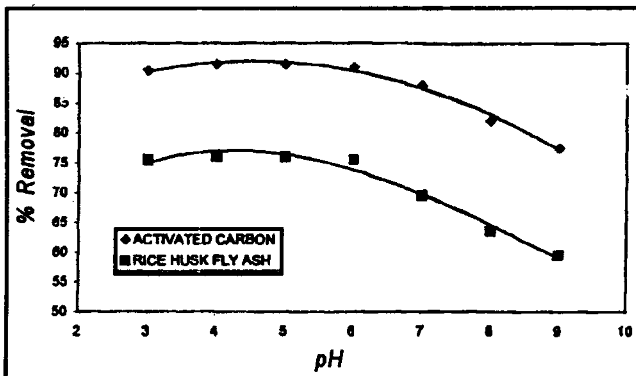

Fig. 9: Effect of pH on removal of 2,4-dichlorophenol Initial concentration =20 mg/l, Adsorbent concentration=20g/l

Contact time = 4h, Temperature 30°C

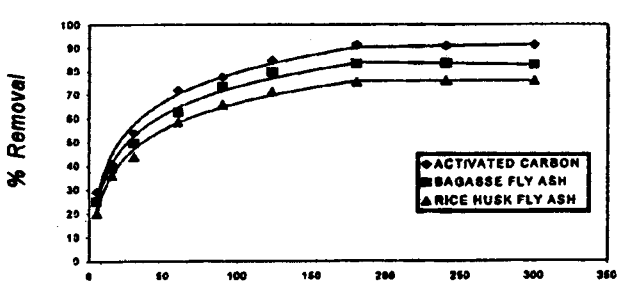

Fig. 10: Effect of contact time on removal of 2,4-dichlorophenol

Initial concentration=20 mg/l, Adsorbent concentration=20g/l

Contact time=4h, Temperature 30°C

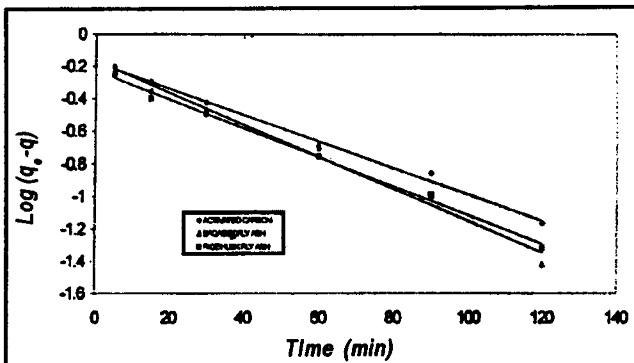

Fig. 11: Lagergen plot for removal of 2,4 dichlorophenol

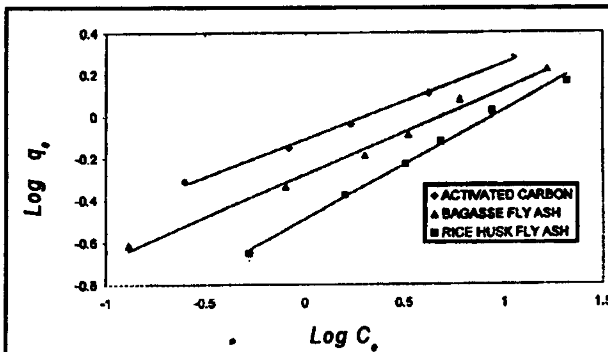

Fig. 12: Freundlich Isotherm for removal of 2,4 dichlorophenol by different adsorbents

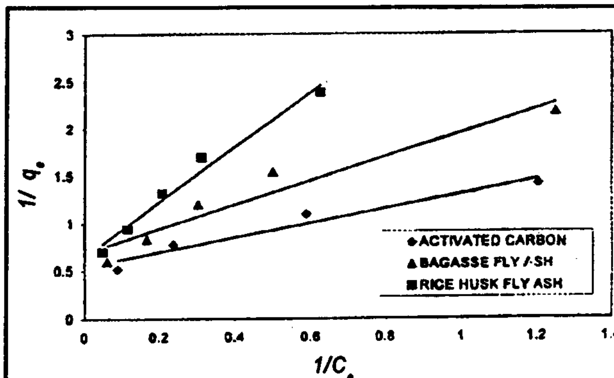

Fig. 13: Langmuir Isotherm for the removal of 2,4 dichlorophenol by different adsorbents

CONCLUSIONS

Removal of 2,4-dichlorophenol was observed higher in acidic ranges. Kinetics of removal follow first order rate expression. Equilibrium data confirms applicability of Langmuir and Freundlich adsorption isotherms. Economic evaluation of the entire process shows that use of bagasse fly ash for treatment of 2,4-dichlorophenol will be viable.

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