Studies on Treatment of Rhodamine Bearing Wastewater from Paper Mill Effluent by Adsorption: Batch and Column Studies

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ABSTRACT

Adsorption of rhodamine a red basic dye, on coal fly ash have been studied. Removal of dye has been found to increase with increase in dye concentration, speed of agitation, carbon content of ash and decrease in pH. Removal has been found to be higher by fly ash having higher carbon content. Kinetic modelling of adsorption process has been done using Lagergren first order expression. Equilibrium data at various temperatures fitted well with Freundlich and Langmuir isotherms for both the fly ashes. Breakthrough time has been found to increase with increase in bed height and decrease in flow rate and BDST model has been found to be applicable.

INTRODUCTION

Adsorption is a proven and reliable pollution control technology for the removal of various non biodegradable materials like colour, dyes, odour, phenol, heavy metals etc. and it has the added benefit of recovering valuable products. Importance of adsorption can be realised from the fact that the world wide sale of adsorbents is more than $ 500 million (1). High cost is the major deterrent towards the utilisation of activated carbon one of the commonly used adsorbent by smaller units. During recent years low cost adsorbents have received much attention as possible substitute for the costly activated carbon-the most commonly used adsorbent for the removal of these pollutants. A critical review of the economical treatment of wastewater by low cost adsorbents has been presented by Mall et al. (2).

The dyes discharged into water streams not only imparts colour but also affect the aquatic life. Dyes have a tendency to sequester metal ions causing micro toxicity to fish and other organisms (3). A number of dyes are suspected to be human carcinogens (4). The various sources of dye bearing wastes are textile, pulp and paper, carpet industries and textile industries. Removal of dyes and colour from the wastewater of these industries has been the cause of major concern during recent years as these dyes can be removed by conventional biological processes.

Rhodamine is a basic dye commonly used in textile, paper and carpet industriers. Though not used in large amounts (1-2 kg per tonne of paper) as compared to other dyes, however, its presence in wastewater from paper mills is a cause of great

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TABLE 1 Characteristics of Rhodamine

Name of the dye	Consumption kg/Tonne of pulp	Colour	Type of dye	χ max	Characteristics of 20 mg/l dye solution		
					pH	COD mg/l	Conductivity mho
Rhodamine	1.5	Red	Basic	555	5.10	16.0	0.009

concern due to its very nature. Rhodamine is one of the brightest dyes and have high tinctorial value. Presence of even 1 ppm dye produces appreciable colour in the wastewater stream and makes the recycling of water difficult.

Some typical data pertaining to rhodamine dye is given in Table 1. Form this table it is amply clear that considerable amount of this dye is used in paper mills and even a concentration as low as 10 mg/l imparts significant COD to the water and affects the light penetration depth adversely.

The present study has been carried out for evaluating the suitability of fly ash from two different type of boilers for removal of rhodamine. In particular the effects of various operating parameters like initial dye concentration, contact time, pH, temperature, speed of agitation, particle size and carbon content in ash on the removal of rhodamine have been studied. Equilibrium data and kinetic of removal have been also reported. Suitability of larger size fractions of fly ash in down flow packed column adsorber for the removal of rhodamine have also been evaluated.

EXPERIMENTAL

Fly ash samples used in this study as adsorbents were collected from Orient Paper Mills, Brajrajnagar, Orissa (Fly ash I) which is using unpulverised coal in boiler and cyclone separator to trap the ash and Obra Thermal Power Station, Sonbhadra, U.P. which is using pulverised coal and electrostatic precipitator to trap the fly ash (Fly ash II). Fly ash I sample had a higher carbon content than Fly ash II. Both the fly ash samples were used without any pre-treatment except in the runs made for the study of effect of particle size where Fly ash I was ground and fly ash of different sized were used. The proximate and chemical analyses of flyash was done as per standard methods (5). The particle size analysis of Fly ash I (coarse sample) was done by sieve shaking whereas that of Fly ash II (fine sample) was determined using a laser particle size analyser (Model: Malvern 3600E). Surface area was determined using surface area analyser (Flowsorb II Model, 2300). Bulk density was determined using Densitometer. The X-ray diffraction and scanning electron microscopic studies were carried out for knowing the surface morphology. The dye solutions were characterised for COD, conductivity and pH. Batch experiments were carried out by shaking 1 g of fly ash samples with 50 ml of rhodamine bearing water in a constant temperature shaking bath at 150 rpm. Temperature and pH were maintained

TABLE 2 Characteristics of Fly Ash Used in the Present Investigation

| Characteristics	Fly Ash I	Fly Ash II
Bulk density, kg/m³	976.00	1023.60
Surface area, m²/g	6.70	5.10
Average particle diameter, um	201.75	18.00
Proximate Analysis :		
% Ash	92.50	98.02
% Volatile Matter	1.93	0.44
% Fixed carbon	5.57	1.54
Chemical Analysis : (% Composition)		
Loss on Ignition	7.50	1.98
Silica (SiO₂)	58.20	61.25
Alumina (Al₂O₃)	26.27	29.78
Fe₂O₃	5.60	3.29
CaO	1.90	3.01
MgO	0.47	0.54
Others	0.06	0.05
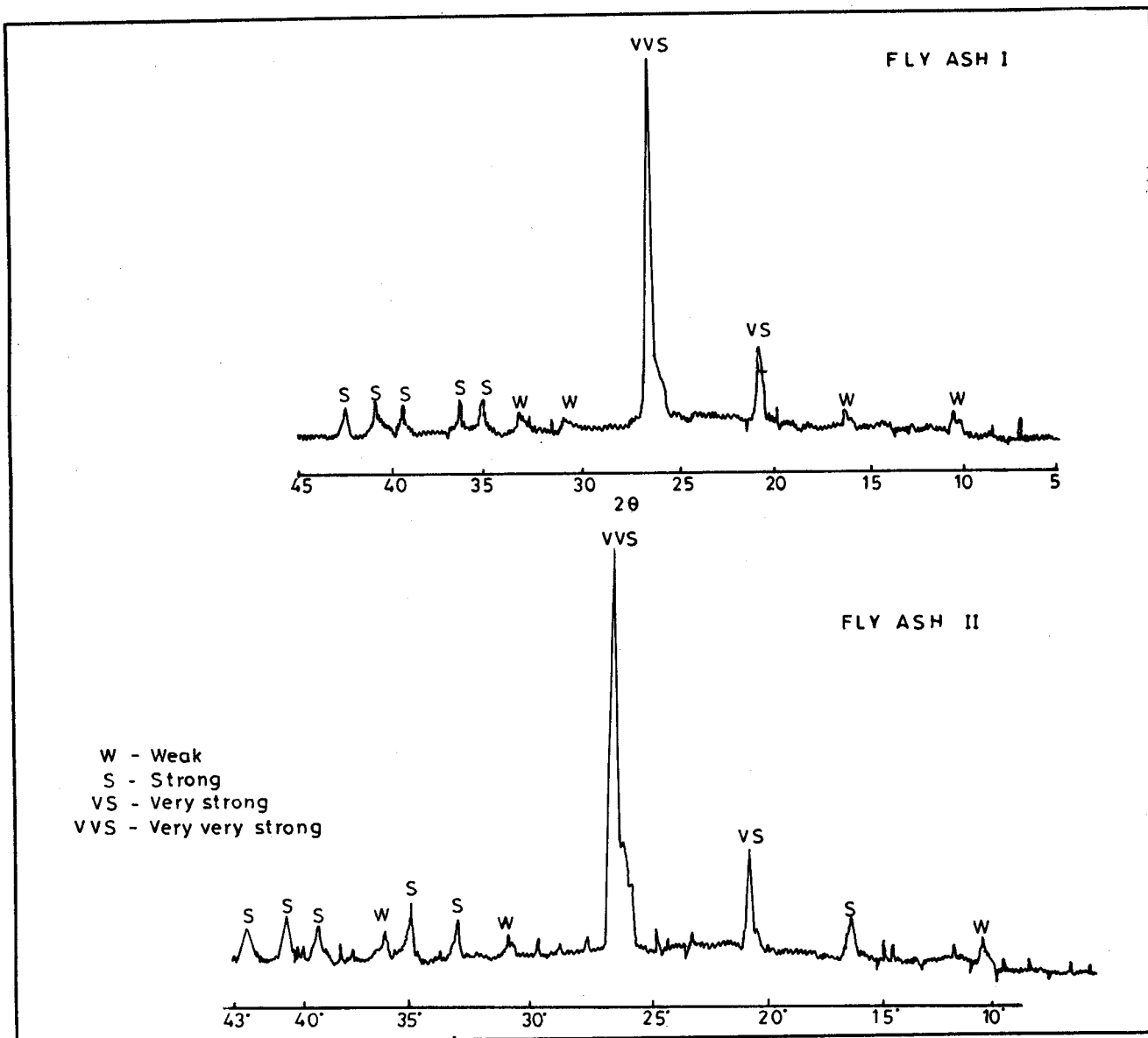
Fig 1: I Ray Diffraction pattern of fly ash

30 0.5 °C and 8.0 respectively throughout the experiments. Adsorption studies in a down flow fixed bed mode were conducted in a 20 mm diameter persplex column using fly ash of 441.0 m particle size obtained from the sieving of Fly ash I. Concentration of dye in the treated effluents was determined spectrophoto-metrically after centrifuging the aqueous solution aliquots.

RESULTS AND DISCUSSION

Characteristics of Fly ash

A summary of the main physico-chemical characteristics of fly ash samples used in the present study is given in Table 2. Difference in particle size of the two fly ashes is due to the difference in the size of coal fed to boiler and fly ash trapping methods used in the units. Cyclones normally capture relatively coarse particles than electrostatic precipitators. Inspite of smaller particle size the surface area of Fly ash I is lower than that of Fly ash II. The high operating temperature in pulverised coal combustors is likely to cause fusion of ash particles and reduce the surface area of Fly ash II. Further, this fly ash has been found to have less unburnt carbon than Fly ash I which has been produced in boiler fed with unpulverised coal and has more unburnt coal and smooth fused pieces of combined coal and ash. Chemical analysis of fly ash show presence of silica and alumina as main
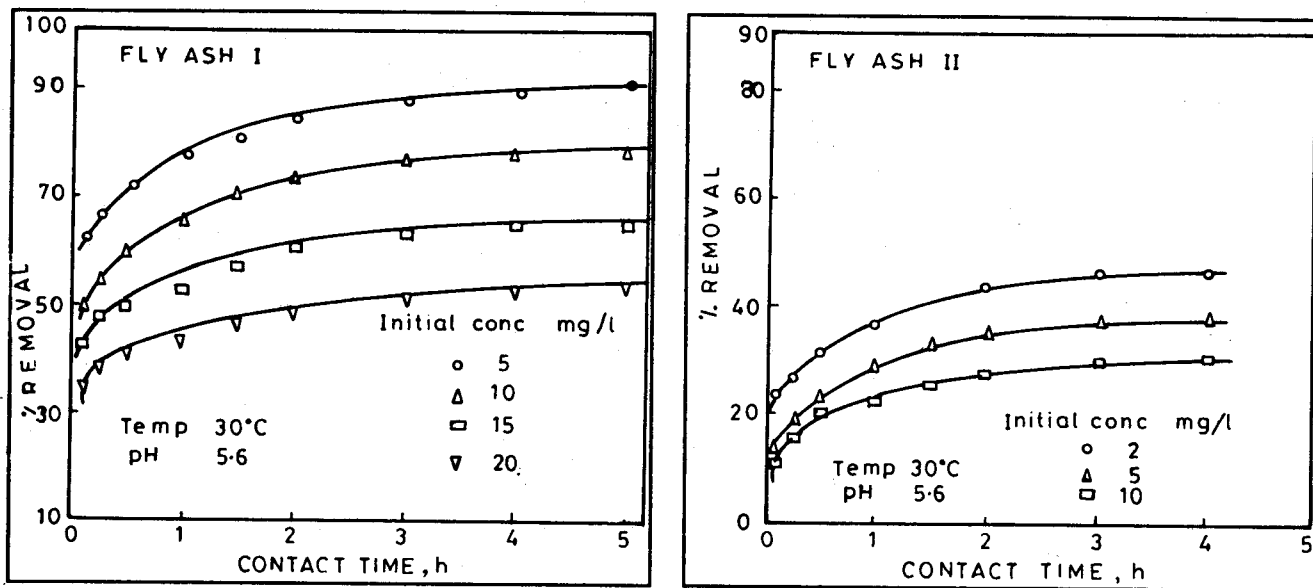
Fig 2: Effect of initial concentration and contact time on removal of Rhodamine.

constituents alongwith oxides of calcium, magnesium etc. The carbon content of the ash samples varied widely and in fly ash from coal fired boiler it was very low as compared to other ash sample. X-ray diffractogram and SEM reveal the presence of crystalline structure and presence of quartz, crystoballite, illite, magnetite etc. (6, 7). The X-ray diffraction pattern of Fly ash I is given in Fig. 1 similar X-ray diffraction pattern for Fly ash II was also observed fig. 1). The carbon present in fly ash samples did not show any diffraction peaks corresponding to any crystalline form of carbon. The SEM of Fly ash I and Fly ash II show similar morphology and presence of alumino silicate as a onporous continuous phase with spheres attached to it.

Effect of Initial Dye Concentration and Contact Time

The initial concetration of adsorbents plays an important role and in higher adsorbate concentration the resistance to the up take of solute from the solution decreases with the increasing solute concentration (8). The effects of initial dye concentration and contact time on the removal of rhodamine by fly ash is in Fig. 2. Percentage removal of dyes is found to increase with increase in dye concentration. From contact time data (Fig. 2), it may be inferred that the adsorption process. comprises mainly of two phases: initial steep and staight part of the curve with high adsorption and almost 80% of removal occurs in the initial 20-30 minutes and

the remaining in the next phase where the adsorption rate gradually decreases and level off as the equilibrium is attained. The removal of rhodamine was found to increase from 54% to 90% and 38% to 47% with decrease in concentration from 20 to 5 mg/1 for Fly ash I and from 5 to 2 mg/1 for Fly ash II respectively. However up take of dye ie mg per init weight of the adsorbent increases with increase in dye concentration. Similar observations have been reported by other investigators. (9-13).

Effect of pH:

The hydrogen ion concentration affects the adsorption process through dissociation of functional groups on the adsorbate and adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the sorption process. The effect of pH and contact time on the removal of rhodamine by two fly ash is shown in Fig. 3. No appreciable effect of pH on percentage removal is observed. For a pH change of 2-9 the percentage removal drops by only about 5% for both the adsorbents. Although it is common observation in case of adsorbent having metallic oxides that the particle surface adsorbs cations more favourably at higher pH (14-15), however increase in rhodamine removal was observed with decrease in pH. This might be due to chemical reaction between functional groups on the adsorbent particles and the rhodamine, which might be taking place simultaneously with adsorption. During study of removal of rhodamine on sulfonated coal, Mittal and
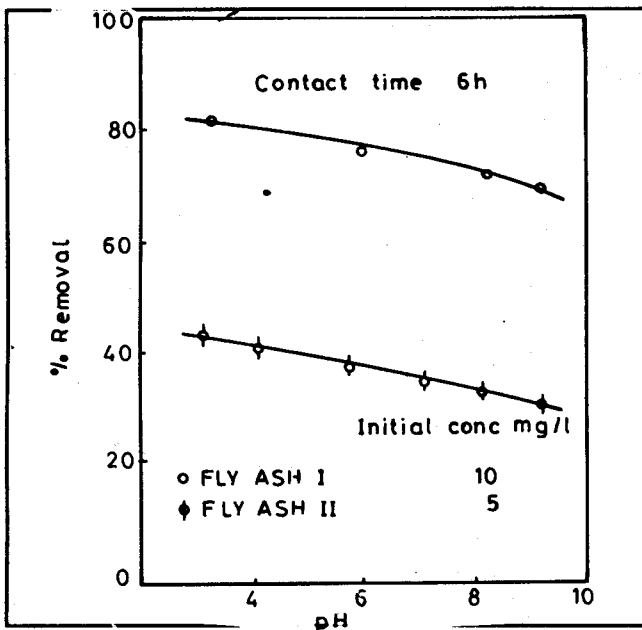
Fig 3: Effect of pH on removal of Rhodamine.

Venkobachar (15) has also reported chemisorption responsible fór sorption of rhodamine over and above physical adsorption.

Effect of Agitation Speed

Agitation speed influences the adsorption rate as increasing agitation speed decrease the film resistance to mass transfer surrounding the adsorbent particles (16). Effect of the agitation speed on the removal of rhodamine is shown in Fig. 4. It may be seen that the removal of dye is markedly poor at the lower agitation speed, however, after an agitation
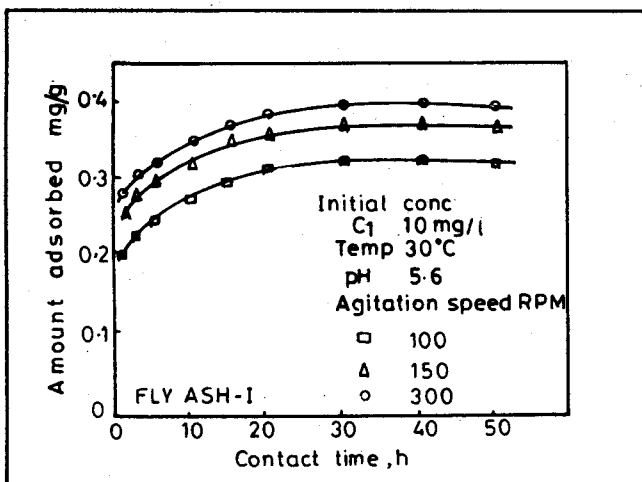

Fig 4: Effect of speed of agitation on uptake of Rhodamine.

speed of 150 rpm, there is no appreciable increase in uptake of the dye. Higher speed of agitation causes decrease in the external film resistance surrounding the adsorbent and allows the dye to reach the adsorbent surface more rapidly. This in turn provides a greater driving force for intraparticle diffusion (17).

Effect of particle size

Adsorbent particle size has significant influence on the adsorption. The effect of particle size has been investigated using Fly ash I of particles 202.0, 28.0 and 15.0 micron size. The removal of rhodamine at different particle sizes reveals that the percentage removal of rhodamine increases with decrease in particle diameter (Fig. 5). The presence of larger number of small particles provides the sorption system with a greater surface area available for dye removal and it also reduces the external mass transfer resistance.
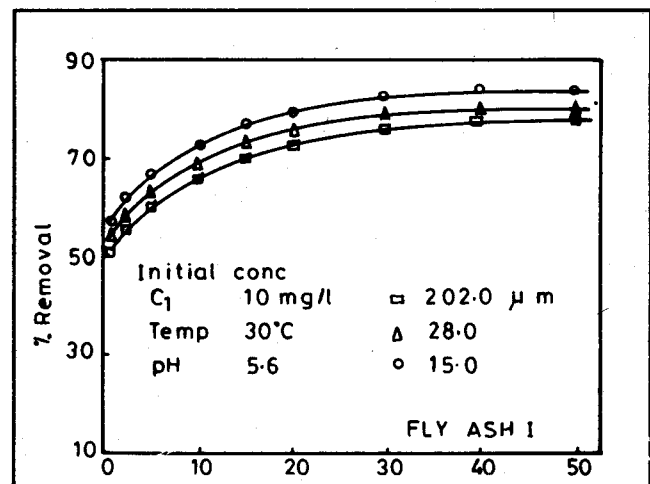

Fig 5: Effect of particle size of removal of Rhodamine.

Adsorption Isotherms

Several models have been used for representing the adsorption equilibrium data. In the present study equilibrium data for the adsorption of rhodamine on fly ash were analysed using Freundlich and Langmuir isotherms:

and $\quad q_e = a_F C_e^{1/n}$

$Ce/qe = Ce/Qo + (1/Q_o b)$

where C_e is equilibrium concentration of dyes mg/1, q_e amount of dye adsorbed per unit weight of fly ash, a_F and n are Freundlich constants and indicate
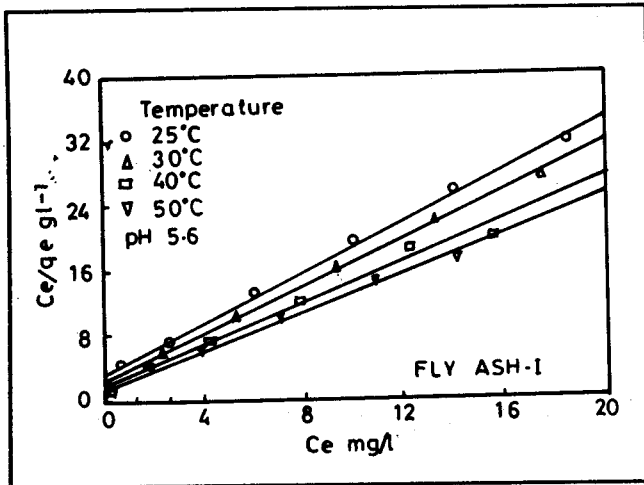
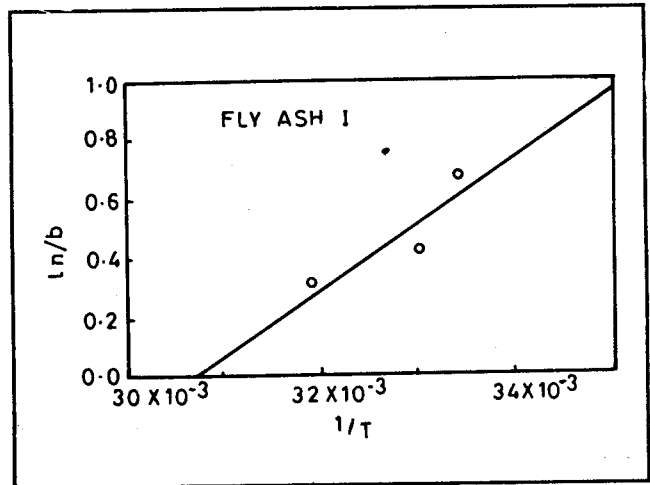Fig 6: Langmuir Isotherm for removal of Rhodamine.

Fig 8: Plot of ln/b Vs T for removal of Rhodamine.

adsorption capacity and intensity, respectively, Q_0 and b are Langmuir constants and indicate adsorption capacity and adsorption equilibrium constant.

The plots of C_e versus q_e and C_e/q_e versus C_e for the adsorption of rhodamine show linear relationship which confirm the applicability of both Langmuir and Freundlich isotherms. Langmuir and Freundlich plots for removal of rhodamine are given in Fig. 6 and 8. The value of Freundlich and Langmuir isotherm constants are listed in Table 3. It is gererally stated that the value of Freundlich constant, n in the range 2-10 represents good adsorption (18). The value of Freundlich constant n in the present investigation for both the dyes investigated is in the range 2.595-7.155 for both the flyash adn represent good adsorption potential of the adsorbent.

The essential characteristics of Langmuir

isotherm have been described by term separation factor or equilibrium constant R_L which is defined as R_L = $1/1+b$ C_i (where C_i is initial concentration and b is Langmuir constant indicates the nature of adsorption as (18).

R_L	$>$	1	Unfavourable
R_L	$=$	1	Linear
O $<$ R_L $<$		1	Favourable
R_L	$=$	0	Irreversible

The values of R_L in the present investigation has been found to be below 1.0 for rhodamine removal showing that the adsorption of rhodamine is very favourable (18). The values of Freundlich isotherm constants 1/n were also below 1 showing that the adsorption is favourable (19).

TABLE 3 Langmuir and Freundlich Isotherm Constants for Adsorption of Rhodamine

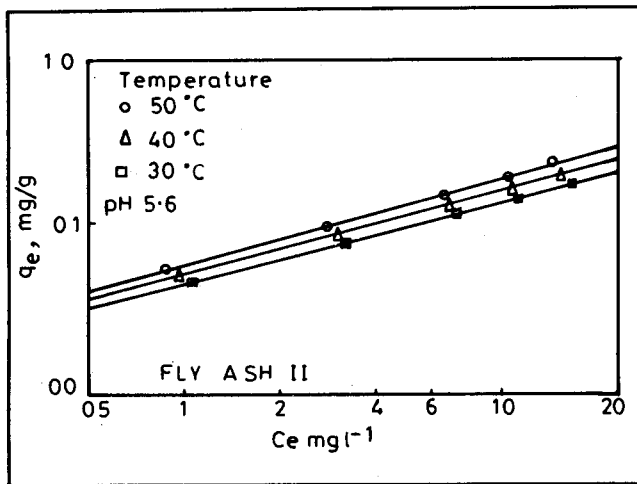| Dyes and Adsorbents	Temp. °C	Langmuir constants		Freundlich constants	
		Qo, mg/g	b, 1/mg	n	a_r mg/g
Fly ash I	25	0.320	1.942	3.219	0.242
	30	0.436	1.520	3.532	0.290
	40	0.552	1.376	4.357	0.379
	50	0.779	1.028	4.808	0.432
Fly Ash II	30	0.045	7.816	1.669	0.047
	40	0.052	7.778	1.640	0.054
	50	0.0.059	6.917	1.612	0.062

Fig 7: Freundlich isotherm for removal of Rhodamine.

Effect of Temperature on Removal of Rhodamine

The net enthalpy H of adsorption is related to the Langmuir constant b and should follow the Van't Hoff equation (19)

$$b = b_0 \, e^{-\Delta H/RT}$$

$$\text{In } b = \text{In } b_0 - \Delta H/RT$$

The plot of ln b versus 1/T should yield a straight line (Fig. 8). The decreasing value of b with increasing temperature (Table 3) negative value of ΔH shows that the adsorption is exothermic. The values of H calculated from the slope of the plot ln b vs. 1/T is given in Table 3. The higher removal of rhodamine with increasing temperature was contradictory to the findings obtained from the Vant Hoff equation. This might be because of the chemical reractions taking place between the functional groups of the coal ash and adsorbents. Similar observation has been also reported by Mittal and Venkobachar (3) during study of the removal of rhodamine on sulfonated coal.

Adsorption dynamics

Kinetic modelling of the removal of dyes by fly ash has been carried out using Lagergren model (9)

$$\text{Log } (q_e - q) = \log q_e - (k_d / 2.303) \, t$$

where q and q_e are the amounts of dye adsorbed at time t and at equilibrium respectively and k_d is the adsorption rate constant. The linear plot of log (q_e-q) vs. t (Fig. 9) for adsorption of rhodamine show the applicability of Lagergren model. The value of rate constant k_d calculated from above linear plot is given in Table 4.
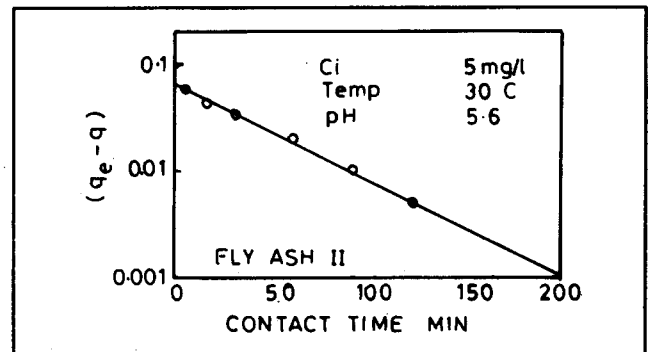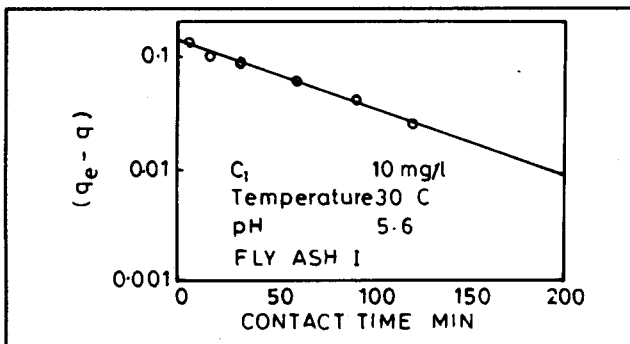

Fig 9 : Kinetics of removal of Rhodamine.

TABLE 4 Adsorption Rate Constant kad' Intraparticle Diffusion Rate Constant Ki, Pore Diffusion Coefficient D
Initial Concentration : 10 mg/l; Temperature : 30 °C; pH : 5.6;
Speed of Agitation : 150 rpm

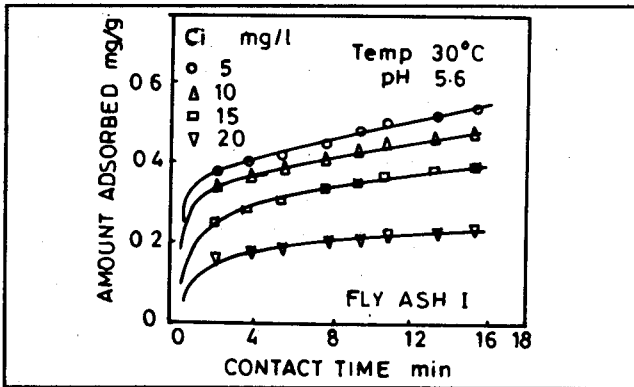| Adsorbate/ Adsorbent	Adsorption rate constant Kad min^{-1} X10^{-3}	Pore Diffusion constant D cm^2/sec	Intrapar particle diffusion constant K_I mg/l	ΔH k cal/mol
Fly Ash I	13.84	10.16x10^{-10}	0.004	- 4.457
Fly Ash II	21.12	12.34x10^{-12}	0.007	- 11.367

Fig 10: Intraparticle diffusion plot for removal of Rhodamine by fly ash.

The pore diffusion coefficient, D, for the removal of rhodamine by different fly ashes have also been calculated using following equation assuming spherical shape geometry for the adsorbent particles (20, 21).

$$t_{1/2} = 0.03 \ r^2/D$$

where $t_{1/2}$ is time for half adsorption, r_o is diameter of the particle and D is the pore diffusion constant, cm^2/sec. The values of pore diffusion coefficients are shown in Table 4. The values of pore diffusion rate constant were found in the order of 10^{-10} to 10^{-12} cm^2/sec for both fly ash samples, indicating that the process is controlled by pore diffusion (22).

The Weber and Morris plot of amount of dye adsorbed per unit weight of adsorbent versus square root of time have been commonly used to determine the intraparticle diffusion rate constant k_i and is defined as the linear gradient of the Webber Morris plot (23, 24). The plot of q vs t is linear for wide range of contact time for the removal of rhodamine (Fig. 10). The initial curved portion of the plot at initial stages may be due to external mass transfer.

The value of the intraparticle rate constant is given in Table 4.

Effect of unburnt carbon

The presence of carbon is found to have significant effect on removal of rhodamine. The removal of rhodamine in case of Fly Ash II, having low carbon inspite of its smaller particle size is low in comparison of Fly ash. Fly ash I was reburnt to remove the carbon present and used for adsorption of rhodamine. The effect of carbon present in fly ash on adsorption of rhodamine is shown in Table 5. The removal of dye is higher in case of fly ash when used as received than the after burning the carbon.

Column Experiment for Adsorption of Rhodamine in Fixed Beds of Fly Ash

Column studies for treatment of rhodamine in a down flow fixed beds of Fly ash I having particles of size 441.0 micron obtained by sieving the Fly Ash I were carried out at different bed heights (10-40 cm) and flow rates (0.6-2 1/h). The effect of bed height on break through curve for removal of rhodamine is shown in Fig. 11. Break through time was found to increase with increase in bed height and decrease flow rates. The liner plot of break through time versus bed height shows the applicability of Bohart Adam Model (19).

$$\ln (C_o/C_B - 1) = \ln \{\exp (K \ N_o \ H/V) - 1 \} - k_B \ C_o \ t_B$$

$$t_B = (N_o/C_o \ V) \ H - (V/K_B N_o) \ \ln (C_o/C_B) - 1)$$

where C_B is breakthrough concentration mg/1; C_o is the initial concentration of rhodamine mg/1; H_o is critical bed depth cm; v is linear flow rate cm/min, K_B is the rate constant, $cm^3/g/min$; t_B is the breakthrough time, min and N^o is the adsorptive capacity, mg/cm.

TABLE 5 Effect of Carbon Present in Coal Ash on Removal of Rhodamine

Initial Concentration : 10 mg/1 Temperature 30 °C
Adsorbent dose : 20 kg/m³

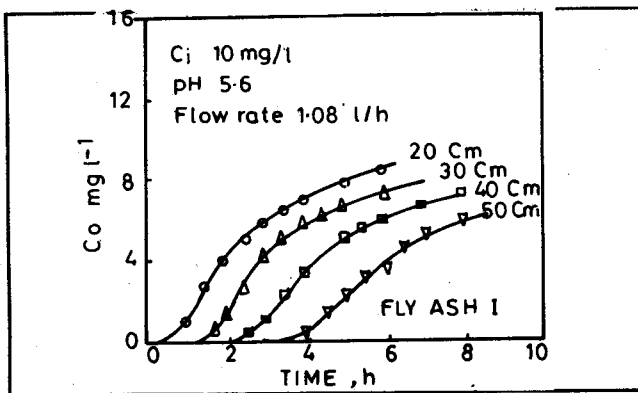| Adsorbent	% Carbon	Amount adsorbed mg/g	% Removal
Fly ash I	5.57	0.390	78.00
Fly ash I after reburning	Nil	0.225	45.00
Fly ash II	1.54	0.155	31.00

Fig 11: Break through curve at different bed heights for removal of Rhodamine.

The theoretical depth of absorbent which is sufficient to prevent the effluent solute concentration to exceed C_B zero time is called critical bed depth and may be calculated from equation (19).

$$H_0 = (V/K_B \ N_0) \ \ln (C_0/C_B - 1)$$

The adsorptive capacity of system N_0 and the rate constant K_B can be evaluated from the slope and intercept of t versus H, which yields a straight line. The rate constant is in true calculated from the intercept by using equation (19).

$$b = (1 / C_0 \ K_B) \ \ln \ (C_0 / C_B - 1)$$

The value of adsorptive capacity, N_0 rate constant, K_B and critical depth, H_0 are 0.38 mg/cm, 30.88 cm³/g/min and 1.068 cm, respectively. These calculations are based on inlet concentration of 10 mg/1 and 90% removal i.e. at breakthrough concentration of 1.0 mg/1.

CONCLUSIONS

Based on above findings it may be concluded that flyash having higher carbon content have very good potential as substitute for activated carbon for treatment of rhodamine bearing wastewater from paper mills and other industries. However, fly ash of low carbon content may not be a good choice. About 95-100% removal can be achieved in the lower concentration range. Removal of rhodamine is found to increase with increase in initial dye concentration, particle size, carbon content, agitation speed and decrease with decreasing pH. The equilibrium data show the applicability of both Freundlich and Langmuir isotherms. The contact time data show the applicability of Lagergren first order model. The break through time was found to increase with increase in

bed height and decrease in flow rate.

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