

Adsorption of Chrysoidine R by using fly ash in batch process

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Abstract

This investigation deals with effective utilization of fly ash as adsorbent for the removal of Chrysoidine R from the aqueous solution. The fly ash is a major byproduct generated in coal-based thermal power plants and has good potential for use as an adsorbent. A series of experiments were carried out in a batch adsorption technique to obtain the effect of process variables viz. contact time, pH (2, 4, 6 and 8) initial concentration of the dye (400, 600, 800 and 1000 mg L⁻¹), amount of the adsorbent (125, 250, 375 and 500 mg L⁻¹), and temperature (303, 313, 323 and 333 K) on adsorption. The concentration of dye was determined by spectrophotometer. The results showed that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly; higher adsorption percentage was observed at lower concentration of chrysoidine. The adsorption data were analyzed using Langmuir and Freundlich isotherms. The adsorption was found to obey pseudo-first order kinetics. An intra particle diffusion model was used to fit the experimental data. The thermodynamic parameters such as standard change in free energy, enthalpy and entropy of adsorption have been calculated. Adsorption of Chrysoidine R on fly ash was found to be an exothermic reaction. © 2006 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Fly ash; Chrysoidine R; Azo dye; Adsorption kinetics

1. Introduction

The environmental pollution is increasing in recent decades due to rapid industrialization and population growth throughout the world. Most of the areas situated near various industries are polluted continuously because of the disposal of industrial wastes. Water quality is continuously deteriorating due to addition of toxic as well as colored effluents from textile, paper, carpet, leather, distillery, and printing industries and poses severe health hazard problems [1]. Many textile and leather industries use large quantities of water and chemicals for dyeing and finishing processes [2]. The wastewater from the textile industries contains intense colored, high-suspended solids and dissolved organics matter [3].

Azo dyes are used for producing majority of textile dyestuffs and also synthetic formulations in many industries [4,5]. Azo dye containing effluent poses a severe threat to the aquatic life and also damaging the aesthetic nature of the environment. Therefore removal of the dye from the effluent to the desired level as recommended by statutory regulatory bodies is required in an

economical way before they are discharged into large bodies of water.

The removal of dyes by various techniques likes coagulation [6], ozonation [7], membrane process [8], filtration with coagulation [9], ozonation with coagulation [10], adsorption [11,12] and aerobic and anaerobic microbial degradation [5] was proposed under the various conditions. Nevertheless, all methods have some limitations for the removal of color of wastewater [1,13]. Among these processes, adsorption is widely used method for the separation and purification of organic and inorganic pollutants from aqueous phase since its first introduction in the 1940s [14,15]. The advantages of this process are low cost (compared to other separation processes), ease of operation and the systems was least affected by the toxic substances [16,17]. Activated carbon is the most widely used adsorbent in the industrial applications [18,19]. However the high cost and tedious procedure for the preparation and regeneration of activated carbons force us to search for low cost potential adsorbents.

At present, various low cost materials are used as adsorbents such as wood [20], phenolic resin [21], bagasse peat [1], coal [22], activated slag [23], lignite [24], maize cob [25], clays [26], zeolites [16], MgCO₃ [27], perlite [28], wool [29], silica [30], wood meal [31], shale oil ash [14], activated carbon prepared

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from bamboo [32], recycled alum sludge [2], biomaterial [33] and fly ash [1,15].

In the present work, fly ash from thermal power waste is used as an adsorbent for the removal of azo dyes. The focal theme of this work was to obtain the kinetic and thermodynamic parameters on the adsorption of the azo dyes from synthetic effluents. The effect of system variables such as contact time, pH, initial dye concentration, temperature and the adsorbent loading were investigated under the equilibrium conditions. The data were fitted to Langmuir and Freundlich adsorption isotherms.

2. Experimental

2.1. Dye and fly ash properties

Chrysoidine R (C.I. No. 11320) has the structure as shown in Fig. 1, was used as the adsorbate molecule. The fly ash sample was obtained from thermal power station of Neyveli Lignite Corporation, Tamilnadu, India. The fly ash was sieved to the desired mesh size range –16 to +30 meshes. After sieving the fly ash sample was washed with distilled water for removing the dissolved matter and dried at 373 K for 24 h and then kept in vacuum desiccators. The chemical compositions of fly ash derived from lignite coal were shown in Table 1. The surface area is $1260 \text{ m}^2 \text{ g}^{-1}$ and the specific gravity is 1.33 g cm^{-3} as characterized previously [34].

2.2. Analysis of the samples

The concentrations of the dye in the sample solution were measured in a Genesys-2 spectrophotometer (Thermo Spectronic, USA). All measurements were performed at the wavelength of 660 nm using distilled water as the blank.

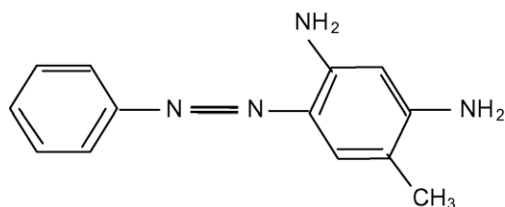


Fig. 1. Structure of Chrysoidine R.

Table 1
Chemical composition of fly ash derived from lignite coal

Component	%
SiO ₂	41.7
CaO	22.5
Al ₂ O ₃	17.1
Fe ₂ O ₃	6.63
MgO	4.91
P ₂ O ₅	3.83
Na ₂ O	1.38
SO ₃	0.42
K ₂ O	0.4
LOI ^a	1.13

^a Loss on ignition indicates the carbon content.

2.3. Adsorption experiments

Adsorption experiments were conducted in a batch mode using aqueous solution of Chrysoidine R. The various process parameters like pH, contact time, initial concentration of dye, adsorbent dosage, and temperature were investigated. A stock solution of the dye with a concentration of 1000 mg L^{-1} was prepared in distilled water. From the stock solution, various concentrations were prepared by dilution. Measured quantities of fly ash (125–500 mg) were placed in a 250 mL conical flask to which a measured 100 mL solution of the dye with concentration of 200–1000 mg L^{-1} was added. The samples were shaken in a thermostatic mechanical shaker for a specific period of time at a constant temperature, pH and shaking speed (200 strokes/min). The samples were separated from the adsorbent by centrifugation. The residual concentration of the dye was determined using a UV–Vis spectrophotometer. All the measurements were carried out at room temperature. Adsorption isotherms were obtained by shaking fly ash ($125\text{--}500 \text{ mg L}^{-1}$) with dye solutions (600 mg L^{-1} to 100 mL) at different temperatures (303–333 K), at constant shaker speed (200 strokes/min) up to equilibrium time of 150 min.

The dye concentration retained in the adsorbent phase was calculated according to

$$q_e = \left(\frac{C_0 - C_e}{W} \right) V$$

where C_0 and C_e are, respectively, the initial and equilibrium concentrations (mg L^{-1}) of dye in aqueous solution, V the volume (L), and W is the weight (mg) of the adsorbent.

2.4. Kinetic studies

The adsorption of dyes from liquid to solid phase can be considered as a reversible reaction with equilibrium established between the two phases. The kinetics of adsorption processes were evaluated following pseudo first order Lagergren Eq. (1) [35,36]. The differential rate equation is of the form:

$$\frac{dq}{dt} = k_{ad}(q_e - q_t) \quad (1)$$

where q_e and q_t are the amount of the dye adsorbed (mg g^{-1}) at time t (min) at equilibrium and k_{ad} is the pseudo first order rate constant (min^{-1}).

After integrating Eq. (1) with initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303} \quad (2)$$

A plot of $\log(q_e/(q_e - q_t))$ versus t is drawn. The slope of the straight line yields the value of the adsorption rate constant.

2.5. Intra-particle diffusion

Adsorption rate of the dye onto the particle depend on the rate of mass transport processes of the dye within the pores of solid particulates by diffusion. The intra particle diffusion rate of the

dye molecule in particle, k_i can be calculated by the following equation [37].

The intra particle diffusion rate k_i can be calculated from the following equation:

$$k_i = \frac{q_t}{t^{0.5}} \quad (3)$$

The linear form of Eq. (3) is

$$q_t = k_i t^{0.5} \quad (4)$$

where k_i is the intra particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$). From the slope of the plot between q_t versus $t^{0.5}$ the value of k_i was calculated.

2.6. Adsorption isotherms

The equilibrium isotherm is very important for the design of adsorption system. The adsorption characteristics of an adsorbent were studied from the constructed isotherm of the adsorbent. The Langmuir adsorption isotherm can be represented in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (5)$$

where C_e (mg L^{-1}) is the equilibrium concentration of the dye, q_e (mg g^{-1} , i.e. the amount of dye adsorbed at equilibrium), Q_0 and b are the Langmuir constants related to the capacity and energy of adsorption, respectively. The Freundlich isotherm equation can also be used for the adsorption of dyes [38,39]

$$q_e = k_f C_e^{1/n} \quad (6)$$

where k_f and n are constants for the adsorption capacity and intensity of adsorption, respectively, incorporating all influencing factors. The linear Freundlich and Langmuir plots were obtained by plotting (a) $\log q_e$ versus $\log C_e$ and (b) C_e/q_e versus C_e . From the slope and intercept adsorption coefficients were calculated. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant (separation factor or equilibrium parameter, R_L) defined as follows:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where C_0 is the initial dye concentration (mg L^{-1}). Also the range of R_L value is significant in defining the nature of adsorption, $0 < R_L > 1$ shows favorable adsorption, $R_L = 1$ for linear adsorption, $R_L = 0$ for irreversible adsorption and $R_L > 1$ for unfavorable adsorption [40].

2.7. Thermodynamic parameters

The changes in standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) of the adsorption processes were determined from the data obtained at different

temperatures using the following equations [41,42]:

$$K_c = \frac{C_{Ae}}{C_e} \quad (8)$$

where K_c is the equilibrium constant C_{Ae} is the amount of dye (mg) adsorbed on the adsorbent per litre of the solution at equilibrium and C_e is the equilibrium concentration of the dye in the solution (mg L^{-1}).

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

where T is temperature in Kelvin and R is the gas constant.

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (10)$$

The values of ΔH° and ΔS° were determined from the slope and intercepts of the Van't Hoff plot of $\log K_c$ against $1/T$.

3. Results and discussion

3.1. Effect of contact time

Fig. 2 shows the effect of contact time with respect to different temperatures under fixed initial concentration, pH and adsorbent. The removal of dye was rapid in the initial stages up to 90 min and reaches the equilibrium gradually. Therefore, the equilibrium time was set ideally at 150 min for further experiments. The rate of removal of dye was decreased with time may be due to the decrease in the diffusion layer thickness surrounding the adsorbent particle. Under the equilibrium condition, the percentage removal of dye was decreased with respect temperature. However, the removal curves are single, smooth and continuous, suggesting the formation of monolayer coverage on the outer interface of the fly ash adsorbent. A similar trend was reported for the adsorption of Direct red 12 B [38].

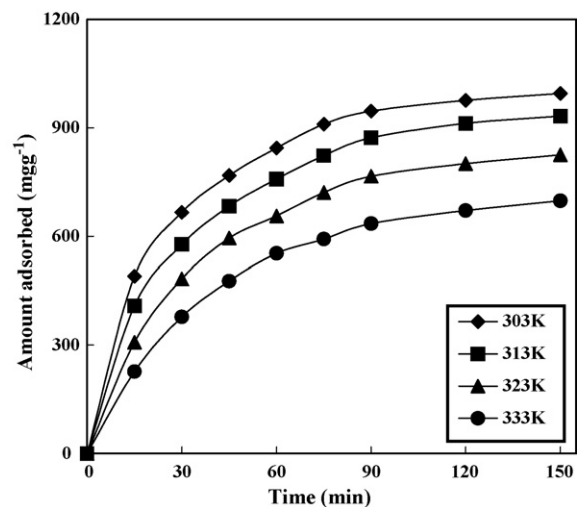


Fig. 2. Effect of contact time on the removal of Chrysoidine R by fly ash (conditions—concentration of dye: 500 mg L^{-1} ; adsorbent dosage: 250 mg L^{-1} ; pH 4).

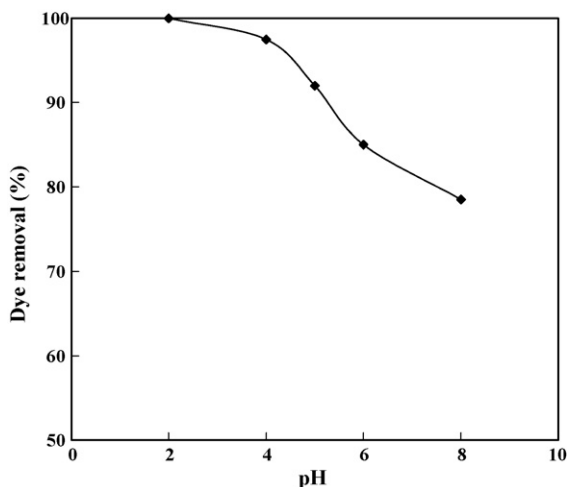


Fig. 3. Effect of pH on the adsorption of Chrysoidine R by fly ash (conditions—adsorbent dosage: 250 mg L^{-1} ; concentration of dye: 500 mg L^{-1} ; temperature: 303 K ; t : 150 min).

3.2. Effect of pH

The pH is one of the most important factors controlling the adsorption of dye onto suspended particles. When the pH was increased from 2 to 8, the percentage removal was decreased as shown in Fig. 3. The magnitudes of electrostatic charges imparted by the ionized dye molecules are primarily controlled by the pH of the medium [43,44]. From Fig. 3 pH 4 was considered as the optimum pH for the adsorption of Chrysoidine R and therefore rest of the studies were carried out on this pH.

3.3. Effect of initial dye concentration

The effect of initial dye concentration on the removal of Chrysoidine R by the adsorbent at optimum dosage of 250 mg/L is shown in Fig. 4. From the figure, it is evident that the Chrysoidine R removal decreased with increased initial concentration,

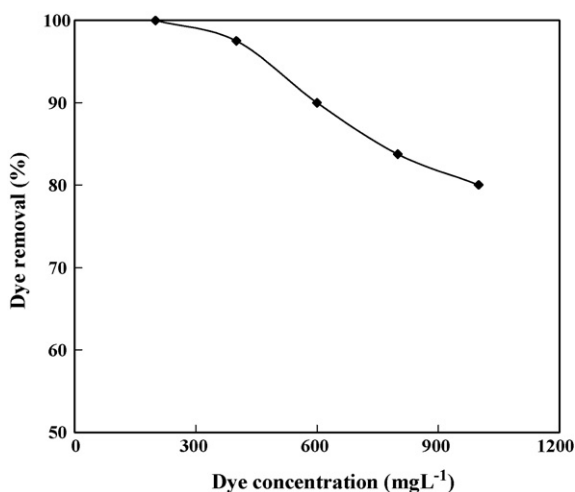


Fig. 4. Effect of initial dye concentration on the adsorption of Chrysoidine R by fly ash (conditions—adsorbent dosage: 250 mg L^{-1} ; pH: 4; temperature: 303 K ; t : 150 min).

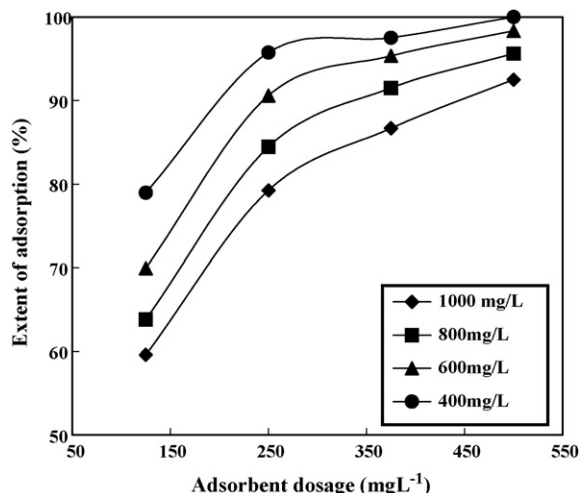


Fig. 5. Effect of adsorbent dosage on the removal of Chrysoidine R (conditions—temperature: 303 K ; pH: 4; t : 150 min).

although the actual amount of the dye adsorbed per unit mass of adsorbent increased with the increase in initial concentration. The rate of adsorption also increased with increase in initial concentration due to the increase in the mass transfer driving force.

3.4. Effect of adsorbent dosage

The effect of adsorbent load with different initial concentrations was studied under the constant temperature 303 K and pH 4. The experiments were carried out up to the equilibrium condition. The percentage removal of dye was shown in Fig. 5. The results show that the percentage removal of the dye was increased with increasing the amount of adsorbent loading. This was due to the increase in total surface area of fly ash. The concentration of the dye in solution was increasing the percentage of adsorption decreasing.

3.5. Kinetics of adsorption

The kinetics of Chrysoidine R adsorption on fly ash was studied at different temperatures for the initial concentration of 500 mg L^{-1} . The equilibrium was attained after 150 min .

The rate constant of adsorption was determined from Eq. (2). A plot of $\log(q_e/(q_e - q_t))$ versus t yielded a straight line, as can be seen in Fig. 6, confirming the applicability of pseudo-first order rate expression of Lagergren. The adsorption parameter for the dye, k_{ad} , was calculated from the slope of the plot. The correlation coefficients for the plots were in the range of 0.95–0.99. The first order rate constants evaluated from these plots were between 1.46×10^{-2} and $1.22 \times 10^{-2} \text{ min}^{-1}$ for different temperatures at optimum loading of the adsorbent. The k_{ad} values are shown in Table 2. The value of k_{ad} was found to decrease with increasing temperature.

3.6. Intra particle diffusion

During the adsorption process, adsorption occurs at the outer surface of the adsorbent; the dye diffuses from the bulk of the

Table 2
Effect of temperature on the rate constants and intra particle parameters for Chrysoidine R adsorption on fly ash

Temperature (K)	q_e (mg g ⁻¹)	Dye removal (%)	k_{ad} ($\times 10^2$ min ⁻¹)	k_{i1} (mg g ⁻¹ min ^{-0.5})	k_{i2} (mg g ⁻¹ min ^{-0.5})
303	995	99.50	1.46	105.7	17.81
313	952	95.20	1.31	95.44	21.12
323	863	86.30	1.23	85.23	21.52
333	728	72.80	1.22	71.13	22.86

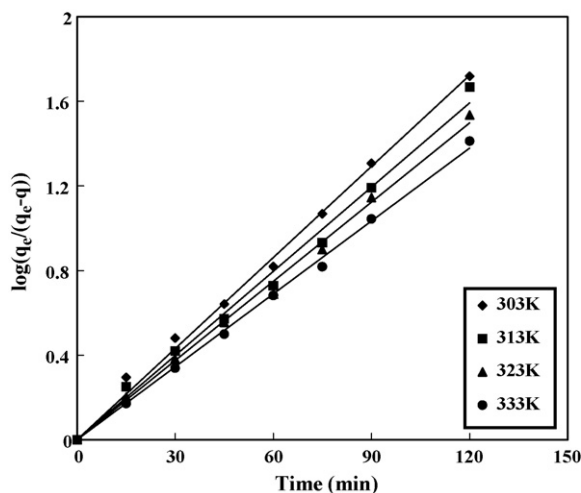


Fig. 6. Lagergren plots for the adsorption of Chrysoidine R by fly ash at different temperatures (conditions—concentration of dye: 500 mg L⁻¹; adsorbent dosage: 250 mg L⁻¹; pH: 4; t : 150 min).

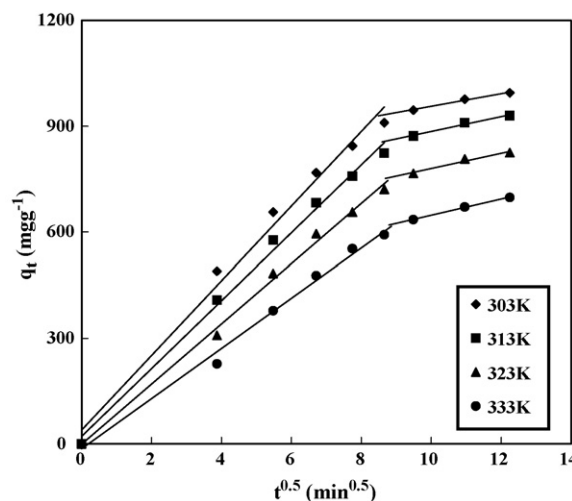


Fig. 7. Plots of amount of dye adsorbed (q_t) vs. $t^{1/2}$ for evaluating intra particle diffusion of Chrysoidine R by fly ash at different temperatures (conditions—concentration of dye: 500 mg L⁻¹; adsorbent dosage: 250 mg L⁻¹; pH: 4; t : 150 min).

solution into the pores of the adsorbent and condenses on the wall [45,46]. The adsorption process of the dye on the adsorbent, involved the external surface and also diffusion into the interior as system approached the steady state. The initial curved portion is attributed to the bulk diffusion effect; the linear portion represents intra-particle diffusion effect and the plateau region to the equilibrium. A plot of q_t versus $t^{0.5}$ according to Eq. (4) was shown in Fig. 7. The k_i values were obtained from the slope of the linear portions of the curve of different temperatures and shown in Table 2. The intra-particle diffusion rate constant values were decreasing with increasing temperature. A similar trend was observed in the removal of diazo and triphenylmethane dyes on rice bran based activated carbon [46].

3.7. Effect of temperature and thermodynamic parameters

The effect of temperature on different initial concentrations of the dye was shown in Fig. 8. In the adsorption process the temperature was varied over the range of 303–333 K. Fig. 8 shows the extent of adsorption of the dye on fly ash decreased with increasing the temperature. Therefore the adsorption process was exothermic in nature.

The thermodynamic parameters such as the standard changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined from the plot of $\log(q_e/C_e)$ versus $1/T$ (Fig. 9) for the constant amount of adsorbent loading (250 mg L⁻¹). The slope and intercept of the plot gives the values of ΔH° and ΔS° . The

thermodynamic parameter values were shown in Table 3. The negative value of ΔH° confirms that the adsorption process of Chrysoidine R on fly ash was exothermic in nature and physical nature of the adsorption. Similar trend was observed for diazo and triphenylmethane dyes on rice bran-based activated carbon [46]. The negative value of ΔG° indicates that the adsorption was spontaneous with a high affinity of fly ash towards Chrysoidine R dye.

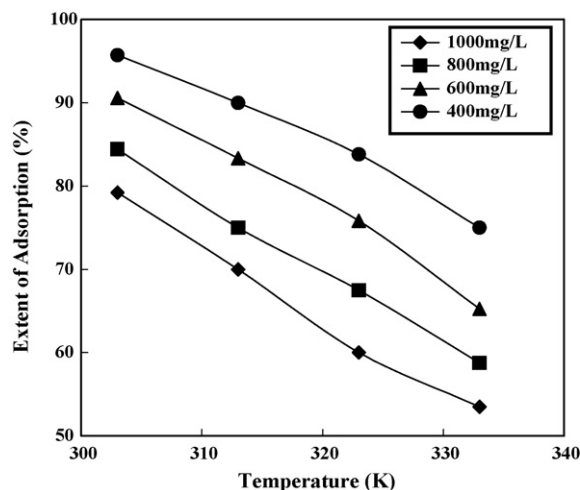


Fig. 8. Effect of temperature on the removal of Chrysoidine R by fly ash (conditions—adsorbent dosage: 250 mg L⁻¹; pH: 4; t : 150 min).

Table 3
Thermodynamic parameters for adsorption of Chrysoidine R on fly ash

[Chrysoidine R] (mg L ⁻¹)	-ΔG° (kJ mol ⁻¹)				-ΔH° (kJ mol ⁻¹)	-ΔS° (J mol ⁻¹ K ⁻¹)
	303 K	313 K	323 K	333 K		
400	9.63	8.03	6.43	4.83	58.09	160.0
600	7.30	5.94	4.59	3.24	48.35	135.5
800	5.78	4.80	3.82	2.84	35.52	98.13
1000	5.11	4.12	3.13	2.13	35.19	99.27

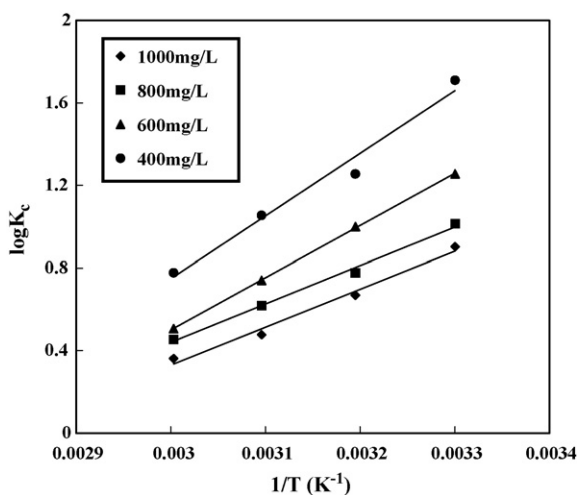


Fig. 9. The plots of $\log K_c$ vs. $1/T$ for the adsorption of Chrysoidine R at different temperatures (conditions—adsorbent dosage: 250 mg; pH: 4; t : 150 min).

3.8. Adsorption isotherm

Langmuir and Freundlich adsorption models were analyzed for the equilibrium data of dye removal from aqueous solution by fly ash at 303, 313, 323 and 333 K. Figs. 10 and 11 show the applicability of both models for the various amount of adsorbent loading at different temperatures. A detailed analysis of the

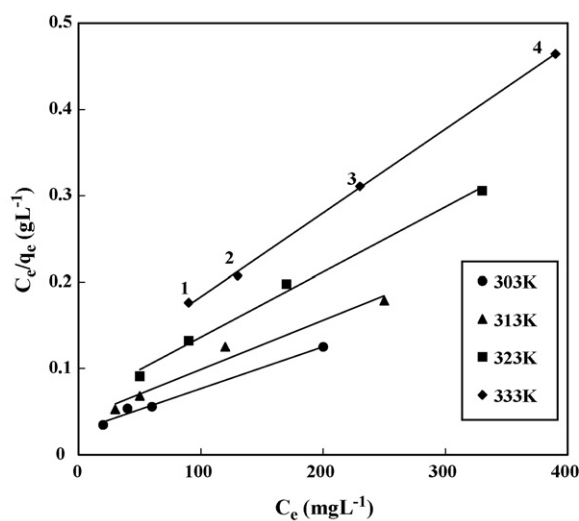


Fig. 10. Langmuir plots for adsorption of Chrysoidine R on fly ash (conditions—concentration of dye: 600 mg L⁻¹; adsorbent dosage: points from left to right in the graph show, respectively (1) 500 mg L⁻¹, (2) 375 mg L⁻¹, (3) 250 mg L⁻¹ and (4) 125 mg L⁻¹; pH: 4; t : 150 min).

regression coefficients indicated that both the isotherm models adequately described the adsorption data at different temperatures.

In Fig. 10 the linear plot between C_e/q_e versus C_e conforms to the Langmuir model of adsorption of dye on the fly ash. The value of Langmuir constants Q_0 and b at different temperatures were determined from slope and intercept of the respective plots. The Q_0 and b values were shown in Table 4. The good regression correlation coefficients (>0.97) were obtained for all the temperatures studied, suggesting that Langmuir isotherm model was applicable to describe the Chrysoidine R adsorption equilibrium by fly ash. The Langmuir monolayer adsorption capacity b was in the range 1.76×10^{-2} and 1.16×10^{-2} L mg⁻¹. The Langmuir adsorption intensity Q_0 , value lies in between 2000 and 1000 mg g⁻¹. The values of Q_0 found decreasing with increasing the temperature and confirm the exothermic nature of adsorption process.

The feasibility of adsorption isotherm was evaluated from the separation factor, R_L (dimensionless constant). The R_L value calculated from Eq. (7) varied between 0 and 1 and confirms the favorability of the adsorption processes. It was also observed that R_L value was increasing with temperature, indicating better adsorption at lower temperatures.

The Freundlich isotherm also applied for the adsorption of Chrysoidine R on fly ash. The linearized Freundlich adsorption isotherms obtained at different temperatures are shown in

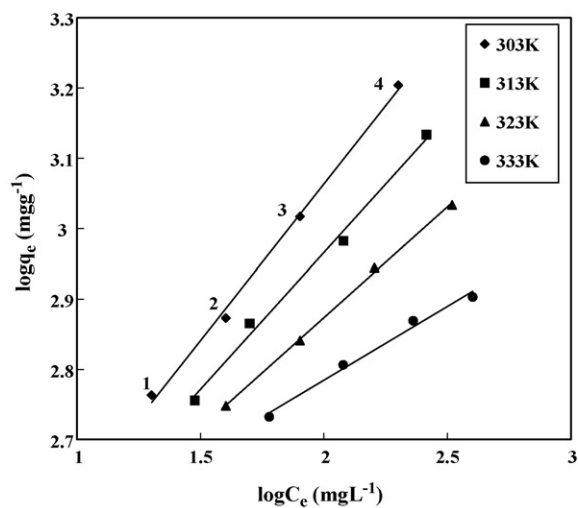


Fig. 11. Freundlich plots for adsorption of Chrysoidine on fly ash (conditions—concentration of dye: 600 mg L⁻¹; adsorbent dosage: points from left to right in the graph show, respectively (1) 500 mg L⁻¹, (2) 375 mg L⁻¹, (3) 250 mg L⁻¹ and (4) 125 mg L⁻¹; pH: 4; t : 150 min).

Table 4
Langmuir and Freundlich adsorption parameters for Chrysoidine R on fly ash

Temperature (K)	Freundlich parameters			Langmuir parameters			R_L
	k_f (mg g^{-1}) (L mg^{-1}) ^(1/n)	1/n	R^2	Q_0 (mg g^{-1})	b ($\times 10^2 \text{ L mg}^{-1}$)	R^2	
303	149.0	0.445	0.988	2000	1.76	0.989	0.09
313	154.2	0.389	0.993	1666	1.43	0.970	0.10
323	175.8	0.314	0.998	1250	1.31	0.997	0.11
333	232.1	0.209	0.929	1000	1.16	0.999	0.13

Fig. 11. The regression correlation coefficients of Freundlich model were around 0.98. The k_f and $1/n$ were determined from the intercept and slope of the plot $\log q_e$ versus $\log C_e$. The k_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. The k_f and $1/n$ values were shown in Table 4. The adsorption capacity k_f was in the range of 152.16–177.582 (mg g^{-1}) (L mg^{-1})^(1/n). Table 4 also shows range of $0 < (1/n) < 1$, indicating that Chrysoidine was adsorbed favorably by fly ash at all the temperatures studied.

4. Conclusions

The fly ash generated from thermal power plant was used as an effective adsorbent for the removal of color from wastewaters. Chrysoidine R was successfully removed from aqueous solution by using the fly ash. The adsorption of the dye on fly ash followed pseudo first order kinetics. The kinetics data may be useful for designing treatment plant for removal of Chrysoidine R. The results obtained were well fitted in the linear forms of Langmuir and Freundlich adsorption isotherms and the adsorption process was feasible, spontaneous and exothermic in nature. The adsorption equilibrium constants at various temperatures were used to determine the thermodynamic parameters viz. ΔG° , ΔH° and ΔS° . The ΔG° values were found to be negative signifying the spontaneous nature of adsorption. The negative value of ΔH° shows that adsorption was favorable at lower temperatures. The studies revealed that fly ash could be fruitfully employed as an adsorbent for dye removal.

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