Original Research Paper

Equilibrium and Kinetic Studies on Adsorption of Congo-Red Dye from Aqueous Solution onto Rice Husk Carbon

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ABSTRACT

Equilibrium and kinetic data for the adsorption of Congo-red dye from aqueous solution onto activated rice husk carbon have been reported. The effects of dye initial concentration, adsorbent-adsorbate contact time, temperature, adsorbent's amount and particle size on the percent adsorption of the dye on the adsorbent have been investigated. Kinetics of adsorption of Congo-red onto the adsorbent in aqueous solution was monitored spectrophotometrically. At the specified dye initial concentration, percent adsorption of dye increases with increase in temperature as well as the adsorbate-adsorbent contact period. However, at the given temperature, % adsorption of Congo-red decreases with the increase in dye initial concentration. The observed adsorption data were analysed in light of Langmuir and Freundlich adsorption isotherms. Dye adsorption rate constant (k_{ad}) follows the first order kinetics. Activation energy (E_a) of adsorption, intra-particle diffusion rate constant and thermodynamic parameters of Congo-red adsorption on the rice-husk carbon have been evaluated and interpreted.

INTRODUCTION

Wastewater contaminated with various dyes discharged from tanneries, distilleries, textile, paper and pulp mills, electroplating and food processing industries is one of the serious causes of water pollution. The coloured effluents from these sources, on mixing with surface and groundwaters, also contaminate the drinking water. The water contaminated with dyes is not only unfit for drinking but also becomes unsuitable for agriculture due to its inhibitory action on photosynthesis in plants. Disposal of rice husk solids, accumulated in and around rice processing units, is a big challenge for solid waste management. Using rice husk for the synthesis of carbon may not only provide a solution for its disposal but also provides a low cost adsorbent for the effective removal of water pollutants such as organic dyes. Congored dye is used in paper and textile industries and its presence in the industrial discharges contributes to severe environmental pollution.

Adsorption method may be one of the environment friendly, economic and efficient techniques with considerable potential for the removal of dyes from contaminated waters (Grabowska & Gryglewicz 2007). Adsorbents that have earlier been used for dye removal from contaminated water include: wood powder (Ozacar & Sengil 2005), fly ash (Acemioglu 2004), coconut husk (coir pith) (Tan et al. 2008), lignin (Cotoruelo et al. 2009), pomegranate peel (Amin 2009), banana stalks (Salman & Hameed 2010), rice husk ash (Lakshmi et al. 2009), sugar beet (Demiral & Gunduzool 2010) and cotton stalk (Deng et al. 2010).

There has been a wide use of activated carbon as adsorbent for the removal of dyes and biologically resistant organic pollutants from polluted waters (Arivoli et al. 2008). The studies on the adsorption of dyes on adsorbent surfaces in aqueous system may not only provide valuable information regarding the nature of intermolecular interaction involved at solid-liquid interface but it may also help in designing the technique for effective removal of colour from the contaminated water.

MATERIALS AND METHODS

Materials

Preparation of rice husk carbon: Rice husk was thoroughly washed with non-ionized water and dried at 75°C for 24 hours. The dried material was immersed in equal volume of conc. H_2SO_4. After 24 hours excess acid was removed by washing the solid residue with distilled water till the residue was free of acid and then the product was dried at room temperature. The carbon, thus, prepared was kept in hot air oven at 120°C for 10 hours and then transferred to a muffle furnace at 500°C for an hour. The activated carbon, thus, obtained was ground to yield a fine powder. It was then fractionated into different mesh sizes and analysed for physico-chemical characteristics. The characteristic parameters of the rice husk carbon are presented in Table 1.

Table 1: Characteristic parameters of activated rice husk carbon.

Property	Value
Particle size (mm)	0.12-0.17
Density (g/cc)	0.489
Water soluble matter (%)	0.17
pH (dispersed in water)	6.4
Moisture content (%)	0.26

Congo-red dye: Congo-red is a water soluble, anionic secondary azo-dye. It has the molecular formula: $(C_{32}H_{22}N_6S_2O_6Na_2)$ with molecular mass of 696.66. It is used in medicines and textile. It has molar extinction coefficient of 2.7×10^5 litre.mol^{-1}cm^{-1}with l_{max} = 499 nm.

Methods

Characterization of rice husk carbon: XRD spectra: XRD spectra of activated rice husk carbon was obtained using X-ray diffractometer (Model: XRDML) (X-ray wave length: 1.54060°A., 2θ range: 5-7°., step size: 2θ = 0.0170°., step time: 30.368 seconds).

TEM analysis: Transmission Electron Microscopic (TEM) analysis of the activated rice husk carbon was obtained in imaging mode using HV = 80 KV at magnification of 3×10^5.

Specific surface area of carbon: Surface area per g of the activated rice husk carbon was obtained using Sears method (Sear 1956). 1.5 g of carbon was mixed with 100 mL of water and 30 g of NaCl. The mixture was stirred for five minutes. To this was added 0.1 N HCl to make final volume 150 mL and pH = 4.0. It was then titrated against 0.1N NaOH. The volume (V mL) of 0.1N NaOH required to raise the pH from 4.0 to 9.0 was noted. The specific area (i.e., area per g) was obtained using the formula:

A = 32V-25

Where, A = Surface area of carbon per g (m²/g); V = volume of 0.1 N NaOH required to raise the pH from 4.0 to 9.0.

Kinetics of the adsorption study: A known amount (0.5 or 1.0 g) of the adsorbent (rice husk carbon) was thoroughly mixed with 100 mL of 100 mg/L dye solution in a conical flask. The reaction flask, kept in a water-thermostat, was maintained at the desired constant temperature ± 0.1°C. Concentration of Congo-red dye solution, free of suspended carbon, was determined at a regular interval of time using a UV-Visible digital spectrophotometer (SIC Model 301).

RESULTS AND DISCUSSION

Characterization of rice husk carbon: XRD spectra: XRD spectra of activated rice husk carbon (Fig. 1) show a single hump ranging from 2θ = 16° to 29° indicating amorphous disordered structure. It indicates that the X-ray diffraction is

Table 2: Values of % Congo-red dye adsorbed as a function of time and temperature (dye initial concentration: 10 mg/dm³; Adsorbent: rice husk carbon; Amount: 1.0 g/100mL; Mesh No. 60).

Time (min)	298.15K	308.15K	318.15K
15	51.5	58.1	64.8
30	61.8	67.2	71.4
45	66.4	72	76.4
60	71.1	76.2	80.7
75	75.7	81.4	88.1
90	85.1	88.4	92.7
105	87.4	90.7	97.4
120	87.7	91.4	97.7

Table 3: Equilibrium dye concentration (Ce) (mg/L) and the amount of dye adsorbed at equilibrium, Qe, (mg/g) as a function of dye initial concentration (C_0) for Congo-red. Adsorbent: rice husk carbon; Amount: 1.0 g/ 100mL; Mesh No. 60.

	Ce (mg/L)			Qe (mg/g)		
C_0	298.15	308.15	318.15	298.15	308.15	318.15
(mg/L)	K	K	K	K	K	K
10	0.93	0.46	0.23	9.07	9.54	9.77
30	5.58	3.72	2.79	24.42	26.28	27.21
50	12.1	8.35	6.05	37.9	41.65	43.95
75	21.9	13.05	10.2	53.1	61.95	64.8

Table 4: Parameters of Langmuir and Freundlich adsorption isotherms for Congo-red dye on rice husk carbon. Adsorbent: rice husk carbon; Amount: 1.0 g/100mL; Mesh No. 60.

	Langmuir isotherm parameters			Freundlich Isotherm parameters		
Tempra-ture(K)	S.D	Q_0 (mg/g)	b (dm³/g)	S.D	K_f	n
298.15	0.027	86.95	0.0676	0.025	10.00	1.867
308.15	0.013	110.85	0.0592	0.027	14.13	2.125
318.15	0.016	131.58	0.0950	0.039	19.95	2.225

Table 5: Values of adsorption rate constant ($k_{ad} \times 10^2$) at varying initial dye concentration (C_0) and temperature (K) for Congo-red. Adsorbent: rice husk carbon; Amount: 1.0 g/100mL; Mesh No. 60.

	Adsorption rate constant ($k_{ad} \times 10^2$)			
Temper-ature (K)	C_0=10 mgdm^{-3}	C_0=30 mgdm^{-3}	C_0=50 mgdm^{-3}	C_0=75 mgdm^{-3}
298.15	1.1497	0.7215	0.6375	0.6246
308.15	1.3802	1.0442	0.8645	0.8178
318.15	1.4941	1.1899	1.0345	0.9650

mainly due to amorphous silica particles. As the atomic scattering factor of carbon is very small, intervening carbon atoms seem to contribute little with respect to scattering from silica.

TEM analysis: Transmission Electron Microscopic (TEM) analysis of activated rice husk carbon adsorbent has been presented in Fig. 2. The observed TEM image suggests the
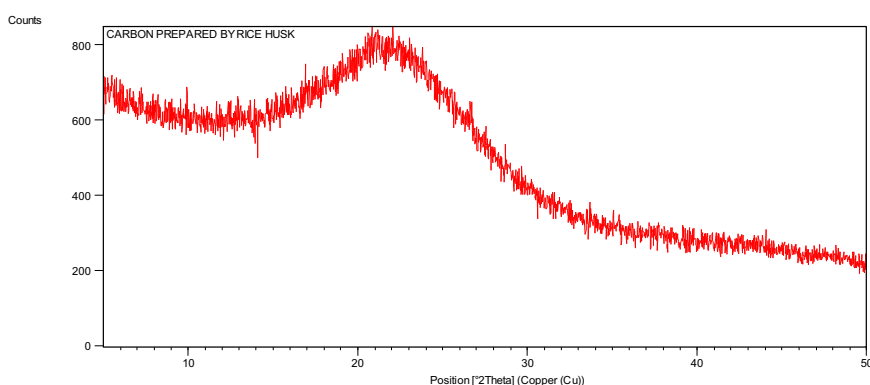
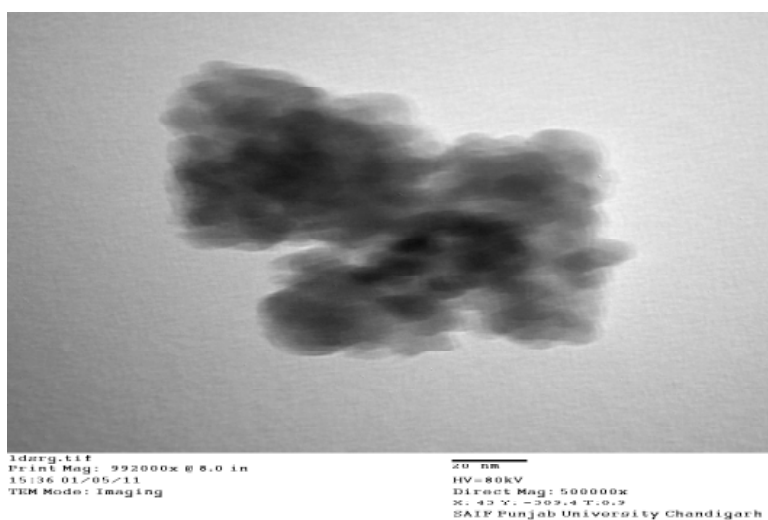Fig. 1: XRD spectra of activated rice husk carbon.

Fig. 2: Transmission Electron Microscopic (TEM) image of activated rice husk carbon adsorbent.

presence of aggregates of carbon nanoparticles of 10-20 nm.

Specific surface area of rice husk carbon: Specific surface area of carbon, was found to be 615 m²/g.

Effects of dye initial concentration, contact time, and temperature on percent adsorption of dye: Percentage values of Congo-red adsorbed on the adsorbate, as a function of time as well temperature, for the given dye initial concentration (10 mg/dm³) are recorded in Table 2. Plots of percent adsorption of dye as a function of dye initial concentration at different temperatures are given in Figs. 3-5. It is evident that at the specified initial dye concentration, % adsorption of dye increases with increase in temperature as well as with the increase in adsorbate-adsorbent contact period, and the adsorption equilibrium state reached at 120 minutes. Further, the curves are single and continuous leading to saturation, suggesting monolayer coverage of the dye on the adsorbent surface. At the given temperature, the percentage

adsorption of Congo-red decreases with the increase in dye initial concentration. It may be because at higher initial concentration of the adsorbate (dye), the number of available active sites per adsorbate molecule at the adsorbent surface become fewer, resulting in a decrease in the adsorption of dye (Gopal & Elango 2007). However, net amount of the dye adsorbed per unit mass of the adsorbent, increases with the increase in the dye initial concentration.

Adsorption isotherms: Equilibrium dye concentration, C_e, (mg/L) and the amount of dye adsorbed at equilibrium, Q_e, (mg/g) at different temperatures are given in Tables 3, and the adsorption isotherm plots of Q_e versus C_e, are presented in Fig. 6. Adsorption isotherms show the trend of levelling at higher adsorbate concentrations (at 298.15 K) suggesting that these are of the Langmuir type and there is flat position of the adsorbate molecules at the adsorbent surface inferring monolayer coverage (Grabowska & Gryglewicz 2007) of ad-

sorbent surface with the adsorbate molecules. The observed data were analysed using the linear form of Langmuir and Freundlich isotherms.

Langmuir adsorption isotherm: The Langmuir adsorption isotherm is represented by the equation (Langmuir 1918):

$$C_e/Q_e = 1/(Q_0 b) + C_e/Q_0$$

Where, C_e is the adsorbate (dye) equilibrium concentration (mg/L) in the bulk; Q_e is the amount of adsorbate (mg/g) adsorbed at equilibrium. Q_0 and 'b' are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. Linear plots of C_e/Q_e as a function of C_e for Congo-red dye (Fig. 7) at different temperatures suggest applicability of the Langmuir isotherms in the present adsorbate-adsorbent system.

Freundlich adsorption isotherm: The Freundlich adsorption isotherm is given by the relation (Freundlich 1906):

$$\log Q_e = \log K_f + 1/n \log C_e$$

Where, Q_e and C_e have their usual meanings and the constants 'K_f' and 'n' are measures of adsorption capacity and intensity of adsorption, respectively. Plots of $\log Q_e$ as a function of $\log C_e$ at the studied temperatures are linear (Fig. 8) suggesting that adsorption of the dye on the adsorbent (rice husk carbon) follows the Freundlich isotherm. The parameters 'K_f' and 'n' were obtained from the intercept and slope respectively in the above linear plots and their values are also recorded in Table 4. The value of 'K_f', a measure of adsorption capacity of the adsorbate on the adsorbent surface, increases with increasing temperature. This may be attributed to the enhanced rate of transfer of dye molecules from bulk to the adsorbent surface at higher temperature. Also, higher temperature may produce a swelling effect within the internal structure of the adsorbent enabling more number of dye molecules to penetrate further (Dogan & Alkan 2003). The values of 'n', a measure of intensity of adsorption, also increases with the rise of temperature. The observed values of 'n', greater than unity, suggest the feasibility of the process of adsorption in present adsorbate-adsorbent systems. Values of Q_0 and 'b' are obtained from the slope and intercept of the plot respectively, and these are presented in Table 4. The observed Q_0 values, an index of adsorption efficiency of the adsorbate (dye) on the adsorbent are positive. The observed positive values of Langmuir parameter 'b', that increases with increase of temperature, indicates: (i) the endothermic nature of the adsorption process, and (ii) absence of any chemical interaction in the adsorbate-adsorbent system.

Kinetics of adsorption: The rate constant (k_{ad}) of adsorption was determined using the following first order kinetic equation.

$$\log (C_0/C_t) = (k_{ad}/2.303).t$$

Where, C_0 is the dye initial concentration and C_t is its concentration at time 't'. The plots of $\log (C_0/C_t)$ as a function of time, t (minutes) at different temperatures are presented in Figs. 9-11. Adsorption rate constant, k_{ad} at varying dye initial concentrations and temperatures for the studied dye systems are given in Table 5. At the given temperature, the adsorption rate constant (k_{ad}) decreases with the increase in initial dye concentration. This may be because at higher dye initial concentration, the number of available binding sites per adsorbate molecule at the adsorbent surface decrease. However, at a constant initial dye concentration, k_{ad} value increases on increasing the temperature. This may be attributed to the enhanced intra-particle diffusion as well as larger pore size at the adsorbent surface at higher temperatures.

Activation energy (E_a) of adsorption: Activation energy (E_a) of adsorption as a function of dye initial concentration (C_0) was obtained from the observed adsorption rate constant (k_{ad}) values at different temperatures using Arrhenius equation:

$$k_{ad} = A. e^{(-E_a/RT)}$$

$$\text{or } \log k_{ad} = -E_a/(2.303RT) + \log A$$

Where, A = Arrhenius factor; R = gas constant (8.314 J/K/mol); T = temperature in Kelvin.

Activation energy (E_a) of adsorption was obtained from the slope of the linear plot between $\log k_{ad}$ and 1/T (Fig. 12). The values of the activation energy (E_a) as a function of dye initial concentration (C_0) are given in Table 6. The magnitude of E_a increases with the increase of initial dye concentration. It may be due to the involvement of stronger solute-solute as well as solute-solvent interactions at higher solute (dye) concentrations, which obstruct closer approach of adsorbate (dye) molecules to the adsorbent surface. Further, the values of activation energy are low suggesting that adsorption process may be controlled by intra-particle diffusion (Sismanoglu & Pura 2001).

Intra-particle diffusion: Possibility of intra-particle diffusion was explored by using the relation:

$$Q_t = k_{dif}(t)^{0.5} + C$$

Where, Q_t (molg^{-1}) is the amount of dye adsorbed at time 't'. Intra-particle diffusion rate constant k_{dif} (mol.min$^{-0.5}$.g^{-1}) is obtained from the slope of plot between Q_t and $(t)^{0.5}$. The magnitude of the intercept C is a measure of the thickness of adsorbed layer. Larger the intercept greater is the boundary layer effect (Kannan & Sundaram 2001). The values of Q_t versus $(t)^{0.5}$ at 298.15K at different Congo-red initial concentration are presented in Fig. 13. The values of intra-particle diffusion rate constant k_{dif} and intercept C as a function
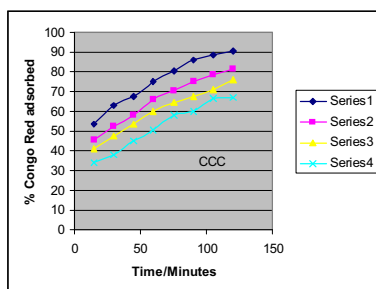
Fig. 3: Plot of % Congo-red dye adsorbed as a function of time using various initial dye concentrations (Series-1: 10 mg/dm³; Series-2: 30 mg/dm³; Series-3: 50 mg/dm³; Series-4: 75 mg/dm³) at 298.15K. Adsorbent (rice husk carbon); Amount: 1.0 g/100 mL; Mesh No. 60.
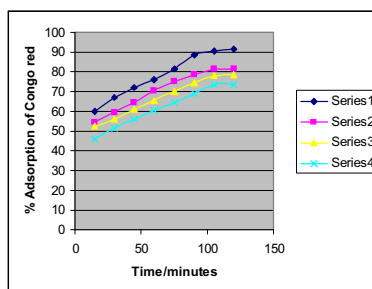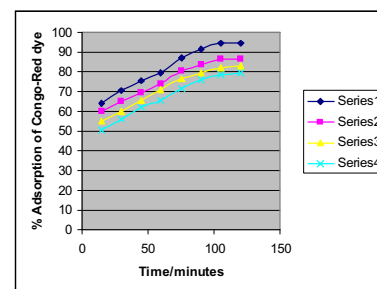
Fig. 4: Plot of % Congo-red dye adsorbed as a function of time using various initial dye concentrations (Series-1: 10 mg/dm³; Series-2: 30 mg/dm³; Series-3: 50 mg/dm³; Series-4: 75 mg/dm³) at 308.15K. Adsorbent (rice husk carbon), Amount:1.0 g/100 mL; Mesh size: 60.

Fig. 5: Plot of % Congo-red dye adsorbed as a function of time using various initial dye concentrations (Series-1: 10 mg/dm³; Series-2: 30 mg/dm³; Series-3: 50 mg/dm³; Series-4: 75 mg/dm³) at 318.15K. Adsorbent (rice husk carbon), Amount: 1.0 g/100 mL; Mesh No. 60.

of dye initial concentration (C_0) and temperature for the studied dye systems are given in Table 7. It was found that at the given temperature diffusion rate constant k_{dif} as well as intercept C increase with the increase of dye initial concentration. The increase in diffusion rate constant at higher dye initial concentration may be attributed to larger adsorbent (dye) concentration gradient between the adsorbent surface and the bulk solution. An increase in the intercept (C), a measure of thickness of the adsorbate layer, at higher dye initial concentration, is obvious as the amount of dye adsorbed then would be more. It is also seen (Table 7) that at the given dye initial concentration, on increasing the temperature, the diffusion rate falls. It is because at higher temperature, due to more thermal agitation, the concentration gradient of the adsorbate between adsorbent surface and the bulk diminishes resulting in the lowering of the diffusion rate. Further, the observed higher value of the intercept (an indicator of more adsorbate thickness at the adsorbent surface) at higher temperature, may be due to enhanced adsorption at higher temperature as described earlier.

Equilibrium constant and thermodynamic parameters of adsorption: Equilibrium constant, K_0, for the adsorption of adsorbate (dye) at the adsorbent surface was calculated using the relation:

$$K_0 = C_{ad}/C_{sol}$$

Where, C_{ad} and C_{sol} represent concentrations of the adsorbate on the solid adsorbent and in solution phase, respectively. Gibbs free energy of adsorption (ΔG_0) values were obtained using the relation:

$$\Delta G_0 = -RT. \ln K_0$$

Where, R = 8.314 JK⁻¹mol⁻¹ and T = temperature in Kelvin. Entropy of adsorption (ΔS_0) was obtained from the relation:
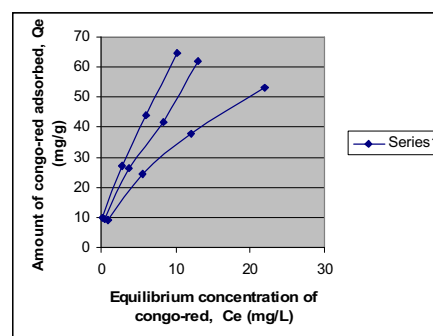

Fig. 6: Plot of amount of dye adsorbed at equilibrium, Qe (mg/g) as a function of equilibrium concentration Ce (mg/L) of Congo-red dye at different temperatures (upper curve: 318.15K; middle curve: 308.15K; lower curve: 298.15K). Adsorbent (rice husk carbon) Amount: 1.0 g/100 mL; Mesh No. 60.
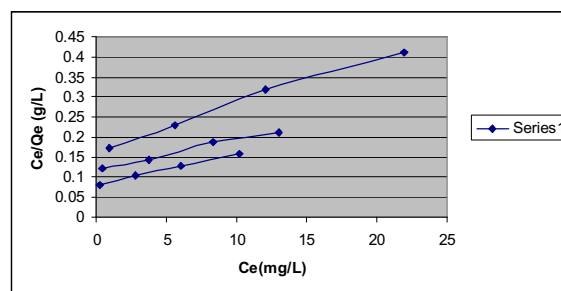

Fig. 7: Plot of Ce/Qe (g/L) as a function of Ce (mg/L) at different temperatures for Congo-red (upper curve: 298.15K; middle curve: 308.15K: lower curve: 318.15K. Adsorbent (rice husk carbon); Amount: 1.0 g/100 mL; Mesh No. 60.

$$\Delta S_0 = -d(\Delta G_0)/dT$$

Enthalpy of adsorption (ΔH_0) was obtained using Gibbs Helmholtz equation:
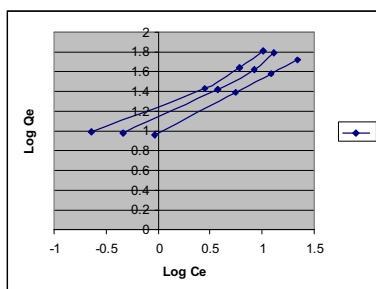
$$\Delta H_0 = \Delta G_0 + T. \Delta S_0$$

Fig. 8: Plot of logQe as a function of logCe for Congo-red dye (lower curve: 298.15K; middle curve: 308.15K; upper curve: 318.15K); Adsorbent (rice husk carbon); Amount: 1.0 g/100 mL; Mesh No. 60.
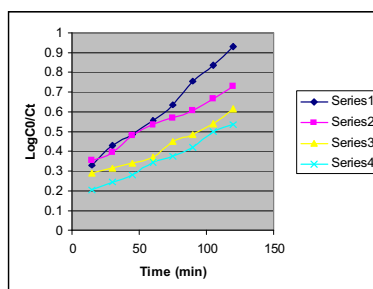

Fig. 9: Plots of log (C_0/C_t) as a function of time of contact 't' (minutes) at 298.15K for Congo-red dye (dye initial concentrations: Series-1: 10 mg/L; Series-2: 30 mg/L; Series-3: 50 mg/L; Series-4: 75 mg/L.); Adsorbent (rice husk carbon); Amount: 1.0 g/100 mL; Mesh No. 60.

Fig.10: Plots of log (C_0/C_t) as a function of time of contact 't' (minutes) at 308.15K for Congo-red dye (dye initial concentrations: Series-1: 10 mg/L; Series-2: 30 mg/L; Series-3: 50 mg/L; Series-4: 75 mg/L); Adsorbent (rice husk carbon); Amount: 1.0 g/100mL; Mesh No. 60.

Fig. 11: Plots of log (C_0/C_t) as a function of time of contact 't' (minutes) at 318.15K for Congo-red dye (dye initial concentrations: Series-1: 10 mg/L; Series-2: 30 mg/L; Series-3: 50 mg/L; Series-4: 75 mg/L); Adsorbent (rice husk carbon); Amount: 1.0 g/100mL; Mesh No. 60.
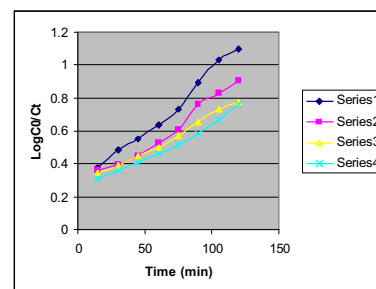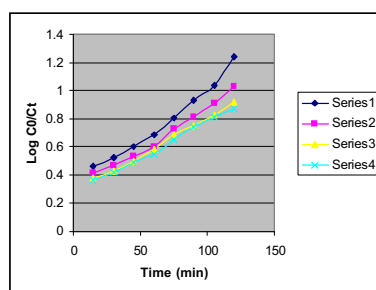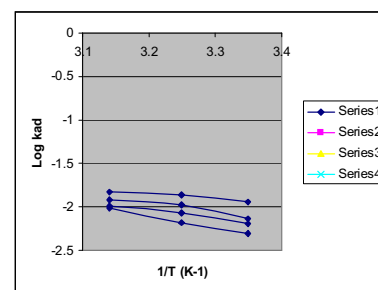

Fig. 12: Plots of log k_{ad} as a function of 1/T for Congo-red (from top to bottom: C_0 = 10, 30, 50, 75 mg/L); Adsorbent (rice husk carbon); Amount: 1.0 g/100 mL; Mesh No. 60.
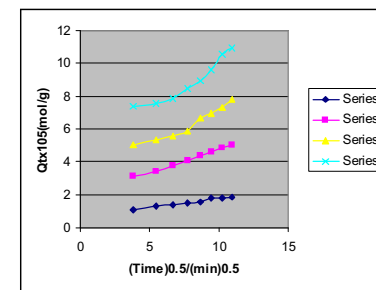

Fig. 13: Amount of Congo-red dye adsorbed $(Qt) \times 10^5$ $(molg^{-1})$ as a function of $t^{0.5}$ $(min)^{0.5}$ at 298.15K; Initial dye concentration C_0 are: Series-1: $10 mg/dm^3$; Series-2: $30 mg/dm^3$; Series-3: $50 mg/dm^3$; Series-4: $75 mg/dm^3$); Adsorbent (rice husk carbon); Amount: 1.0 g/100mL; Mesh No. 60.

The values of equilibrium constant (K_0) and thermodynamic parameters $(\Delta G_0, \Delta H_0$ and $\Delta S_0)$ are given in Table 8. Equilibrium constant (K_0) values decrease at higher dye initial concentration but increase at higher temperature. The observed negative values of ΔG_0 for the studied adsorbate-adsorbent systems, indicate that adsorption process is spontaneous irrespective of initial dye concentrations as well as temperatures. At the given temperature, ΔG_0 values increase (becomes less negative) with the increase of initial dye concentration. This may be due to decrease in intra-particle diffusion rate at higher concentrations of the dye. However, at a fixed initial dye concentration, ΔG_0 decreases (becomes more negative) with the increase of temperature. It may be attributed to (a) the enhanced diffusion rate of the adsorbate molecules, which facilitates their approach to the adsorbent's surface active sites, and (b) the larger pore-size of the adsorbent at higher temperature. The observed positive ΔH_0 suggests that adsorption process is of endothermic nature, and uptake of the adsorbate by the adsorbent may be through

Table 6: Values of energy of activation $(E_a/KJmole^{-1})$ of adsorption at varying Congo-red initial concentrations; Adsorbent (rice husk carbon); Amount: 1.0 g/100 mL; Mesh No. 60.

C_0 (mg/L)→	10	30	50	75
$E_a/KJmole^{-1}$	10.32	15.27	17.26	19.14

Table 7: The values of intra-particle diffusion constant (k_{dif}) and C for Congo-red dye as a function of initial dye concentration (C_0) at 298.15K; Adsorbent (rice husk carbon); Amount: 1.0 g/100 mL; Mesh No. 60.

T(K)	C_0 (mg/dm³)	$k_{dif} \times 10^6$ (mol.min⁻⁰·⁵.g⁻¹)	Intercept, C
298.15	10	1.08	0.63
298.15	30	2.71	2.16
298.15	50	3.92	4.01
298.15	75	5.01	5.87
308.15	10	0.82	1.21
318.15	10	0.64	1.93

Table 8: Equilibrium constants (K_0) and thermodynamic parameters (DG_0, DH_0 and TS_0) for adsorption of dye (Congo-red) onto activated carbon (Amount of adsorbent: 1.0 g/100 mL; Mesh size: 60).

Dye mg/dm³	K_0			$-\Delta G_0$ (KJ/mol)			ΔH_0 (KJ/mol)			$T \Delta S_0$ (KJ/mol)		
	25⁰C	35⁰C	45⁰C	25⁰C	35⁰C	45⁰C	25⁰C	35⁰C	45⁰C	25⁰C	35⁰C	45⁰C
10	9.75	20.74	42.48	5.64	7.76	9.92	58.16	58.18	58.16	63.8	65.94	68.08
30	4.38	7.06	9.75	3.66	5.01	6.02	31.52	31.35	31.52	35.18	36.36	37.54
50	3.13	4.99	7.26	2.83	4.12	5.24	32.95	32.86	32.94	35.78	36.98	38.18
75	2.42	4.75	6.35	2.19	3.99	4.89	38.06	37.61	38.06	40.25	41.6	42.95

Table 9: Effects of temperature, particle size (Mesh No.) and amount of adsorbent on % adsorption and thermodynamic parameters for adsorption (Initial concentration, C_0 of Congo-red dye: 10mg/L).

Temp. (K)	Mesh No. of adsorbent	Amount of Adsorbent) (g/100mL	% adsorption	$-\Delta Go$ (KJ/mol)	$\Delta Ho/$ (KJ/mol)	$T\Delta So$ (KJ/mol)
298.15	30	0.50	71.98	3.48	22.31	25.79
298.15	60	0.50	78.85	4.25	36.45	40.70
298.15	30	1.00	83.01	4.94	43.81	48.75
298.15	60	1.00	87,50	5.64	58.17	63.81
308.15	30	0.50	74.54	4.23	22.42	26.65
308.15	60	0.50	82.61	5.08	36.98	42.06
308.15	30	1.00	85.78	6.49	43.89	50.38
308.15	60	1.00	91.42	7.76	58.18	65.94
318.15	30	0.50	77.56	5.21	22.30	27.51
318.15	60	0.50	85.90	6.98	36.44	43.42
318.15	30	1.00	92.68	8.21	43.80	52.01
318.15	60	1.00	97.73	9.92	58.16	68.08

physi-sorption (Gopal & Elango 2007). The observed positive ΔS_0 of adsorption indicates the increase of disorder and randomness at the adsorbent-adsorbate interface. This may be due the displacement of larger number of water molecules by the adsorbate species from the adsorbent surface during the adsorption process, resulting in a net gain of translational entropy than that lost due to the adsorption of adsorbate molecules (Elango & Gopal 2007). At the given concentration, ΔG_0 values decrease on raising the temperature. This may be attributed to enhanced adsorption of adsorbate due to a cumulative effect of higher adsorbate diffusion rate, the enlargement of adsorbent pore size and more activation of the adsorbent surface at higher temperature (Gopal & Elango 2007).

Effects of size and amount of the adsorbent on adsorption: Effects of the size and the amount of the adsorbent (Congo-red) on % adsorption at equilibrium and thermodynamic parameters of adsorption are given in Table 9. At the given temperature, percent adsorption of dye increases and Gibb's free energy of adsorption (ΔG_0) decreases with the increase in the amount as well as the mesh number of the adsorbent particles. These observations may be explained in terms of the fact that on increasing the amount as well as mesh number of the adsorbent, the number of available ac-

tive binding sites per adsorbate (dye) molecule at the adsorbent surface are raised, therefore, the adsorption becomes more feasible. The magnitudes of endothermic enthalpy and entropy of adsorption increases on increasing amount as well as the adsorbent particle mesh number. This is because at higher load of adsorbent and with finer adsorbent particles the release of adsorbed water molecules replaced by the adsorbing dye molecules will be much higher leading to enhanced endothermicity and randomness of system.

CONCLUSIONS

The present work reports the kinetic and equilibrium studies on adsorption of Congo-red dye from aqueous solution onto activated rice husk carbon. The effect of parameters such as contact time, dye initial concentration, temperature, adsorbent particle size and amount of adsorbent on % adsorption of Congo-red on the rice husk carbon have been investigated. At the specified initial dye concentration, percent adsorption increases with increase in temperature as well as with the increase in the adsorbate-adsorbent contact period. At the given temperature the percent adsorption of dye decreases with increase in dye initial concentration. However, the total amount of the dye adsorbed per unit mass of the adsorbent, increases with the increase in the dye initial con-

centration. The observed adsorption data were analysed in light of Langmuir and Freundlich adsorption isotherms. From the evaluated thermodynamic parameters of adsorption, it is inferred that the adsorption of Congo-red at rice husk carbon is endothermic and predominately controlled by entropy gain. The observed positive entropy of adsorption may be due to a net gain of more translational entropy due to the desorption of water molecules than that lost by the adsorption of dye molecules at the adsorbent surface. At the given temperature, percent adsorption of dye increases and Gibb's free energy of adsorption (ΔG_0) decreases with the increase in the amount as well as the mesh number of the adsorbent particles. These observations may be explained in terms of the fact that on increasing the amount and decreasing the particle size of adsorbent, the number of available active binding sites per adsorbate (dye) molecule at the adsorbent surface are raised, therefore, the adsorption becomes more feasible.

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