Preparation and Characterization of Elephant Dung Activated Carbon and its Application for Rhodamine B Adsorption

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ABSTRACT

Low cost activated carbon prepared from elephant dung was used as an eco-friendly adsorbent for the removal of the textile dye Rhodamine B from an aqueous solution. The adsorbent was characterized by Scanning Electron Microscope (SEM), X-Ray Diffraction(XRD), Thermo gravimetric(TG) and Fourier Transform Infra red (FT-IR)analysis. Batch adsorption experiments were carried out by varying the initial dye concentration, adsorbent dosage, pH and temperature. Zeta potential (pH_{ZPC}) was found to be 3.2. The optimum dosage of the adsorbent was found to be 100 mg. The adsorption process reached equilibrium within 240 minutes. Maximum amount of dye was adsorbed at pH 3. The percentage removal of the dye was increased with increase in temperature. The adsorption followed pseudo second order kinetic model. The experimental data can be best fitted with Langmuir isotherm compared to Freundlich isotherm. The thermodynamic parameters like Gibb's Free energy change (ΔG), Entropy change (ΔS) and enthalpy change (ΔH) were calculated which indicated that Rhodamine B adsorption process was endothermic and spontaneous.

Key words: Elephant dung, Rhodamine B, Adsorption, kinetics, Isotherm, Thermodynamics.

INTRODUCTION

Textile and dyeing industry effluent can create serious environmental pollution problems when they are discharged into water bodies. The untreated effluents possess toxic dyes and pigments which impart colour even at low concentration. These hazardous materials affect photosynthetic activity[1] because of reduced light penetration. So it is important to adopt some treatment methods before discharging the effluents into water to reduce the harmful effects. The methods employed for the removal of dyes from wastewaters include anaerobic decolourisation[2] chemical oxidation[3] reverse osmosis[4] ion exchange[5] adsorption[6] and biological treatment methods[7]. These physico chemical methods are less efficient, expensive and produce wastes which are difficult to dispose. Among these methods, adsorption onto activated carbon has been proven to be the most effective method for the colour removal in terms of initial cost, simplicity of design, easy operation and insensitivity to toxic substances[8]. Adsorption is more than advantageous than the other conventional methods due to its

sludge free clean process and high adsorption capacity for the coloured particles. However, usage commercial activated carbon for adsorption has some limitations like high cost and regeneration problems. This has necessitated the exploration of some effective, cheaper and easily available alternatives. Such alternatives include low cost activated carbons prepared from natural products like date pits[9],bagasse[10], fruit stones and nutshells[11], Jute fiber[12], rice husks[13],plum kernels[14] and coconut shells[15]. Activated carbons prepared from various products are widely used as adsorbents due to their high adsorption capacity, large surface area and microporous structure. The wide usefulness of activated carbon as adsorbent is a result of their chemical and thermal stability. In this paper, an attempt has been made to use activated carbon prepared from elephant dung for the removal of Rhodamine B from aqueous solution. Elephant dung is available in large quantities throughout the year in the western districts of Tamil Nadu and Kerala, a nearby state. Elephant dung is used to manufacture biogas, paper, paper products and to make briquettes. Still a considerable amount of elephant dung goes unused. Elephant dung is disposed by dumping in landfills or by burning which causes environmental pollution problems. Therefore, use of elephant dung as a biosorbent will prove to be an effective application of the product. Further, the zero or negligible cost of elephant dung makes this project feasible and cost effective for the removal of Rhodamine B, a basic dye from aqueous solution. Among various classes of dyes basic dyes are the brightest class of soluble dyes. Rhodamine B is a cationic dye used in textile, printing and paint industries. Rhodamine B is found to be toxic to human and animals even in trace quantities. The main objectives of the study are: Evaluating the possibility of using elephant dung as a low cost activated carbon and studying its application to remove Rhodamine B from wastewater through batch adsorption experiments; Studying the adsorption mechanism through kinetic and equilibrium data; Determining the thermodynamic and adsorption isotherm parameters.

MATERIAL AND METHODS

Adsorbate

Rhodamine B was procured from Sigma Aldrich and it was used as received without further purification. A stock solution of the dye (1000 mg/L) was prepared using distilled water and dilutions were made to the required concentrations. The characteristics and chemical structure of the dye are listed in Table 1 and Fig.1.

Adsorbent preparation and characterization

Elephant dung was collected and dried well. The lumps were crushed and the resulting material was activated using concentrated sulphuric acid (1:2) in an oven at 120°C for 3 hours. The acid was then removed by repeated washings with a large quantity of distilled water. It was then dried in a hot air oven for 6 hours. The carbon was then ground, sieved (< 150 µm) and used as Elephant Dung Activated Carbon (EDAC) for batch adsorption experiments. It was then characterized by Scanning electron microscopic technique (Joel JSM 6360 model microscope),Thermo gravimetric analysis (Perkin Elmer, Diamond TG/DTA analyzer in air atmosphere at a heating rate of 10^0C min^{-1}), X-ray diffraction method(Shimadzu XRD 6000 model X-ray diffractometer using Co-Kα radiation with a nickel filter) and Fourier transform Infra red spectroscopy(Schimadzu FT-IR-8400 S spectrophotometer). For the FT-IR analysis 2-4 mg of the adsorbent was finely ground and encapsulated in 20 mg of KBr in order to prepare translucent sample disk. The physico chemical properties of EDAC were determined by various standard procedure including Drift method and Boehm titration studies are listed in Table 2.

Batch adsorption experiments

Batch adsorption experiments were carried out by taking different dye concentrations (10 mg/L to 40 mg/L). 50 ml of the samples were shaken using Labline shaking incubator at a constant agitation speed (120 rpm) with a required dose of adsorbent. The experiments were conducted till the equilibrium state was attained (240 minutes). Experiments were also carried out to study the influence of pH and temperature (308 K to 338 K) on adsorption. The pH of the solutions was adjusted from 2 to 11 by adding 0.1M HCl and 0.1M NaOH solutions. Dye concentrations were estimated spectrophotometrically at the wavelength corresponding to maximum absorbance (554 nm) using a Shimadzu UV-1700 PharmaSpec UV visible

spectrophotometer. The samples were withdrawn from the shaker at predetermined time intervals and the supernatant liquid portions were centrifuged using R-8C laboratory centrifuge (Remi make) at 2500 rpm for 20 minutes and analyzed for remaining dye concentration spectrophotometrically. The amount of dye adsorbed onto activated carbon was calculated as follows.

$$q_e = (C_0 - C_e)v/w \qquad \qquad ...(1)$$

Where, C_0 and C_e are the initial and equilibrium concentrations (mg/l) of the dye respectively. v is the volume of the solution and w is the weight of the adsorbent used.

RESULTS AND DISCUSSION

Scanning Electron Microscope

Scanning electron microscopic technique has been used as a tool to understand the surface morphology of the adsorbent. The scanning electron microscopic examination results of EDAC are given in Fig.2. From the images, it is clear that the adsorbent possesses irregular, fibrous and porous surface with the particle size ranging from 50-100 microns. This porous surface easily facilitates the adsorption of dye molecules into the pores of the adsorbent.

Thermo gravimetric analysis

Thermo gravimetric analysis is useful to study the thermal stability of the adsorbent. The Thermo Gravimetric analysis of EDAC is shown in Fig.3. The adsorbent is thermally stable up to 230⁰C . At higher temperature decomposition of the carbon takes place leaving behind the ash as residue. The initial weight loss at 100⁰C is found to be 5.6 % due to moisture. The decomposition of carbon takes place between 230⁰C -570⁰ C. The residue present in carbon as ash is found to be 14.0 %. The results obtained from thermo gravimetric analysis are complementary with proximate analysis results.

X-ray Diffraction method

X- Ray Diffraction technique is helpful to find out whether the adsorbent is crystalline or amorphous in nature. The XRD pattern of EDAC is shown in Fig.4. The XRD studies revealed that the EDAC is amorphous in nature.

Fourier Transform Infra red spectroscopy

The FT-IR spectrum of EDAC was recorded in the range of 4000- 400 cm⁻¹. FT-IR spectroscopy was used to characterize the functional groups present in the adsorbent. FT-IR spectrum of EDAC is shown in Fig.5. A peak at 1600 cm⁻¹ was observed due to the presence of C=O stretching of carboxyl group. The phenolic O-H stretching and N-H stretching frequencies are merged in the region of 3200-3400 cm⁻¹. A band in the region of 3200-3600 cm⁻¹ is observed due to the presence of C-H stretching frequency.

Effect of contact time and initial dye concentration

The effect of initial dye concentration and contact time for the removal of Rhodamine B by EDAC were investigated in the concentration range

Table 1: Physical and chemical characteristics of Rhodamine B

CAS Number:	81-88-9
Empirical formula:	$C_{28}H_{31}ClN_2O_3$
Molecular weight:	479.01
Colour Index Number:	45170
Beilstein Registry Number:	4091619
EC Number:	201-383-9

Table 2: Characteristics of adsorbent

Bulk density, g/ml	0.5814
Specific gravity	0.9737
Porosity %	40.28
Methylene blue decolourisation, mg/g	31.2
Phenol adsorption capacity	54.54
Water soluble matter %	0.93
Acid soluble matter %	3.75
Moisture content %	11.08
Ash content %	17.1
Ion exchange capacity ,meq	0.959
pH	3.0
pH_{ZPC}	3.2
Surface area (BET) m²/g	23.13
Functional groups	
Carboxylic groups , meq/g	0.299
Phenolic groups, meq/g	0.30
Lactonic groups, meq/g	1.60
Basic groups , meq/g	0.08

10 mg/L – 40 mg/L ,at pH 3, at room temperature with 100 mg adsorbent dose. The adsorption of the dye onto EDAC increased with increase in time and then attained equilibrium at a time of 240 minutes. As the initial dye concentration was increased from 10 mg/L to 40 mg/L , the percentage removal of the dye decreased and the amount adsorbed increased. At high concentration the available sites for adsorption become fewer and hence the amount of dye adsorbed is dependent on initial concentration (16). The data shown in Fig.6, reveals that the curves are single, smooth and continuous leading to saturation suggesting the monolayer coverage of the dyes (17).

Effect of adsorbent dosage
        The effect of adsorbent dosage on the

percentage removal of the dye is shown in Fig.7. The effect of adsorbent dosage on the adsorption of Rhodamine B was studied by varying the adsorbent dose (10 mg -150 mg) for the initial dye concentrations ranging from 10 mg/L – 40 mg/L, at natural pH and at room temperature for 240 minutes. It is evident from the data that the amount of dye adsorbed increased as the dosage of the adsorbent increased. This is due to the increased available surface area and increased number of active sites for adsorption[18].

Effect of Temperature
        The effect of temperature on percentage removal of the dye is shown in Fig.8. The effect of temperature on the adsorption of Rhodamine B was studied by carrying out experiments at , 308 K, 318

Table 3: Thermo dynamic parameters

Temperature (Kelvin)	308	318	328	338
$-\Delta G$ (kJ/mol)	36.744	37.938	39.132	40.326
ΔH (kJ /mol) = 26.838	ΔS (J mol^{-1}K^{-1}) = 119.389			

Table 4: Kinetic parameters

C_0 (mg/l)	$q_{e.exp}$ (mg/g)	Pseudo I order model			Pseudo II order model			Intra particle diffusion model		
		$q_{e.cal}$ (mg/g)	$K_1 \times 10^{-2}$ (min^{-1})	r^2	$q_{e.cal}$ (mg/g)	$K_{1x} 10^{-2}$ (g mg^{-1} min^{-1})	r^2	$q_{e.cal}$ (mg/g)	K_{id} (g mg^{-1} min$^{-1/2}$)	r^2
10	4.977	1.749	- 6.218	0.954	5.155	7.349	0.999	0.823	0.087	0.949
20	9.922	4.831	- 4.606	0.987	10.417	1.888	0.999	5.901	0.539	0.922
30	15.0 0	11.168	- 3.224	0.995	16.393	0.482	0.997	15.237	1.138	0.900
40	18.576	3.552	- 2.533	0.997	20.000	0.331	0.999	22.566	1.457	0.933

Table 5: Langmuir and Freundlich isotherm parameters

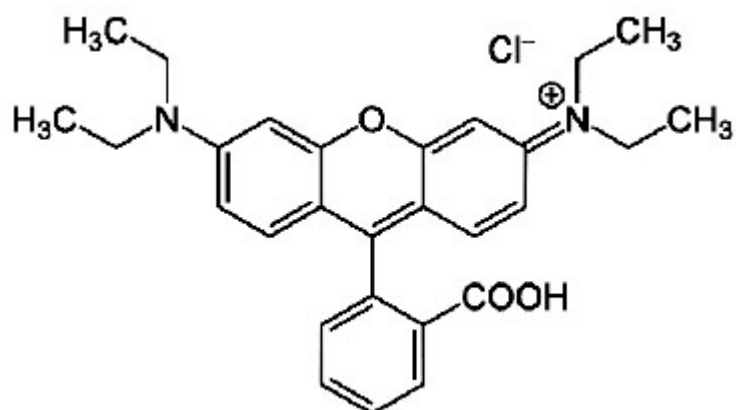| Langmuir isotherm $b = 0.0777$			Q_m (mg/g) = 34.483			$r^2 = 0.996$	
C_o (mg/l)	60	80	100	120	140	160	180
R_L	0.176	0.138	0.114	0.096	0.084	0.074	0.066
Freundlich isotherm							
$K_F = 7.493$	$1/n$ = 0.333	r^2= 0.935					

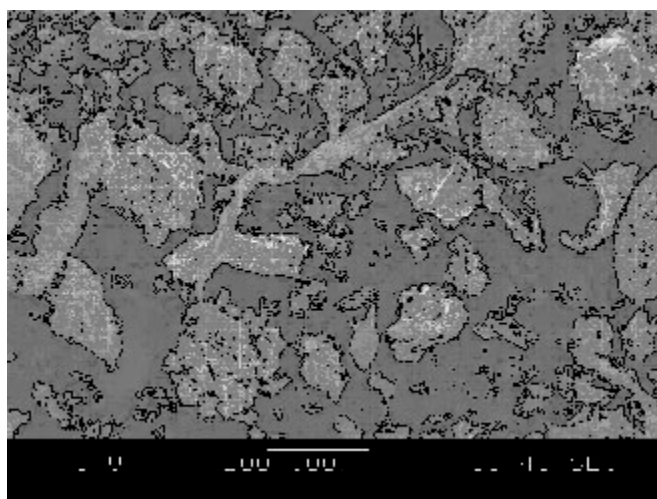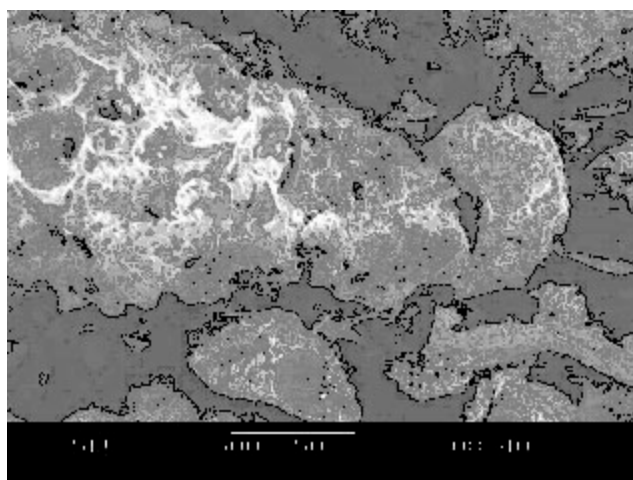**Fig. 1: Sructure of Rhodamine B**

Fig. 2: Scanning electron microscope images of EDAC

K, 328 K and 338 K, keeping all the other factors constant. From the results it was observed that the percentage removal of the dye increased as the temperature was increased. When the temperature was increased, the mobility of the dye molecules increased and the retarding forces on the diffusing ions decreased, thereby increasing the sorption capacity of the adsorbent[19]. The enhancement of adsorption capacity of the adsorbent at high temperatures was also attributed to the enlargement of pore size and activation of the adsorbent surface[20].

Thermodynamics

The thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH) and entropy change (ΔS) play an important role in determining the feasibility, spontaneity and heat change for adsorption process. These parameters are calculated using the following equation (21).

$$\Delta G = - RT \ln K_c \qquad ...(2)$$

Where, R is the Universal gas constant (8.314 $J\ K^{-1}mol^{-1}$) ;T is the temperature (Kelvin); K_c is the distribution coefficient. The value of K_c is
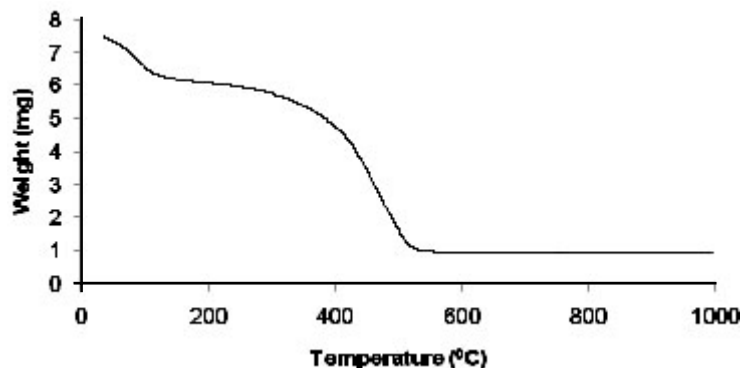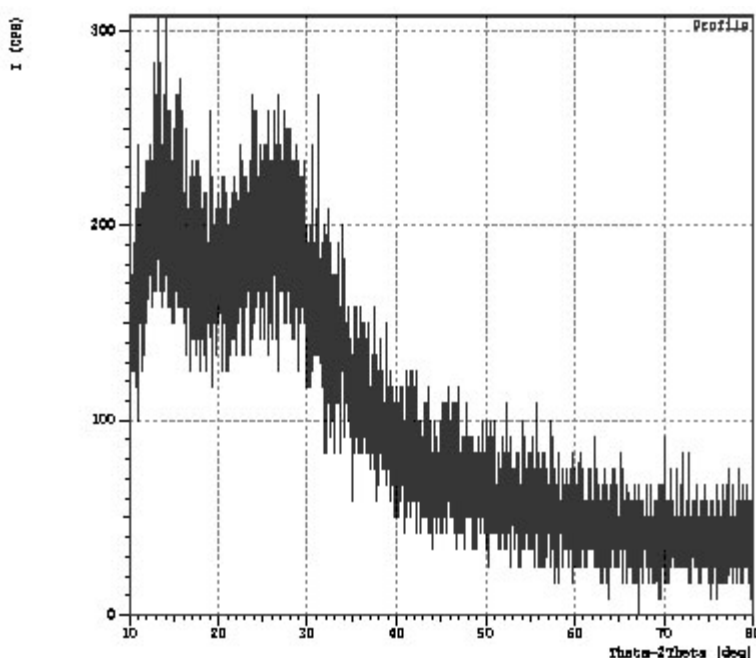

Fig. 3: Thermo gravimetric analysis of EDAC

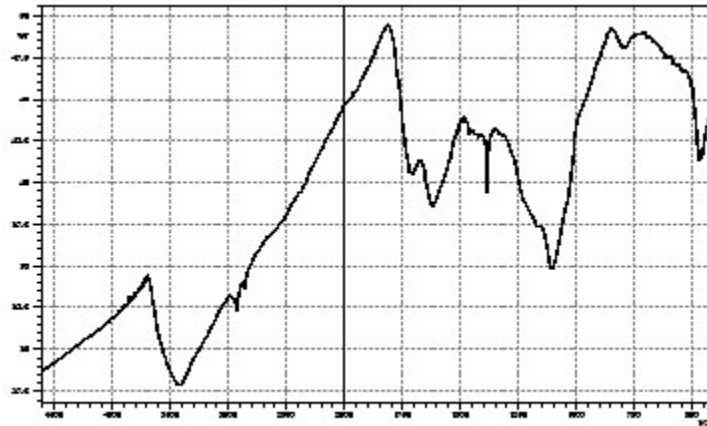**Fig. 4: X-ray diffraction of EDAC**
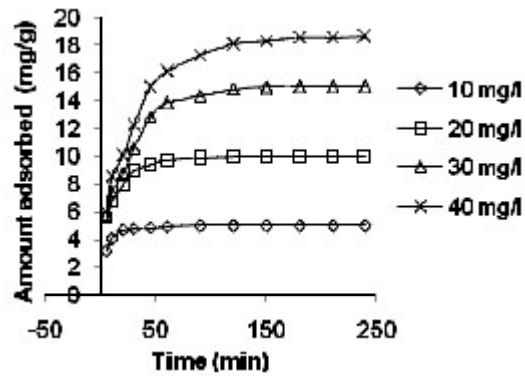
Fig. 5: FTIR spectrum of EDAC

Fig. 6 : Effect of contact time Vs amount of dye adsorbed (T = 301 K ; w =100 mg; v = 50 ml ; pH = 3 ; Agitation Time = 240 minutes)
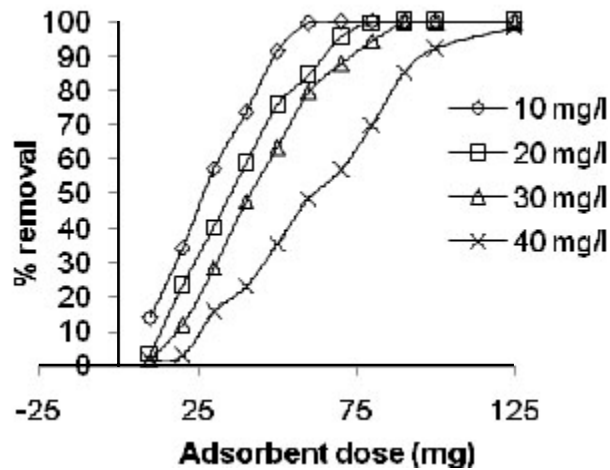

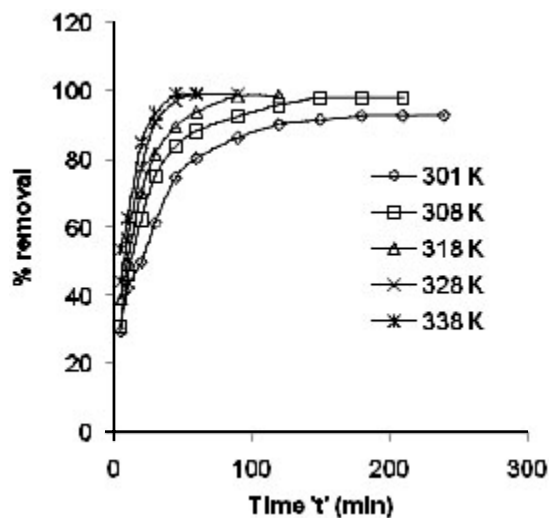**Fig. 7: Effect of adsorbent dosage Vs % removal (T = 301 K ; v = 50 ml ; pH = 3 ; Agitation Time = 240 minutes)**

**Fig. 8: Effect of temperature Vs % removal (C_0 = 40 mg/l;
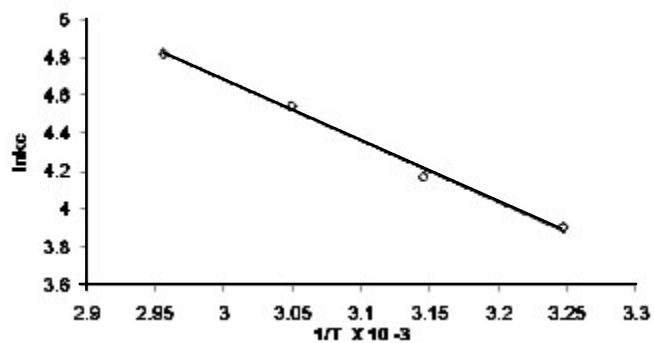w = 100 mg ; v = 50 ml ; pH = 3 ; Agitation Time = 240 minutes)**

**Fig. 9: Vont Hoff's plot (C_0 = 40 mg/l ; w = 100 mg ; v = 50 ml ; T =
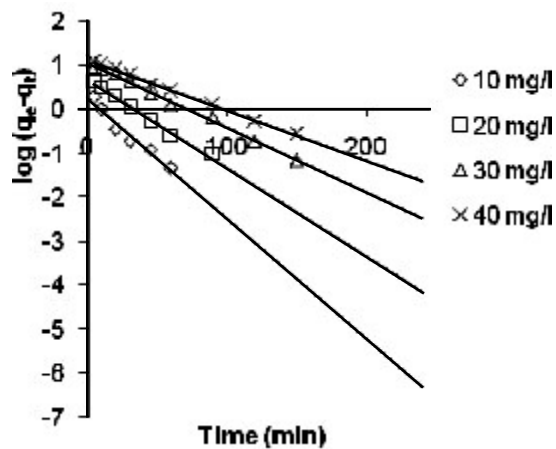301 K, 308 K, 318, 328 K and 338 K ; Agitation Time = 240 minutes)**

**Fig. 10: Pseudo first order kinetic model (T = 301 K ;
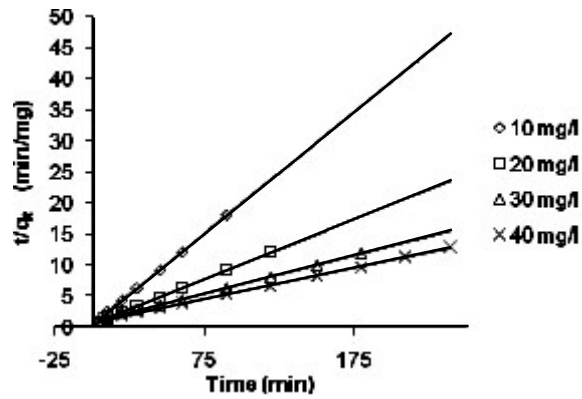w = 100 mg; v = 50 ml ; Agitation Time = 240 minutes)**

**Fig. 11: Pseudo second order kinetic model (T = 301 K ;
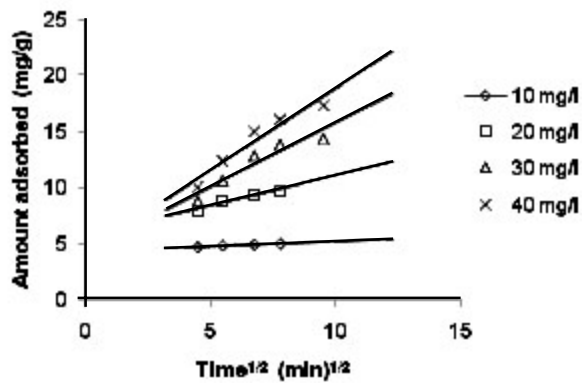w = 100 mg ; v = 50 ml ; Agitation Time = 240 minutes)**

**Fig. 12: Intra particle diffusion model (T = 301 K ;
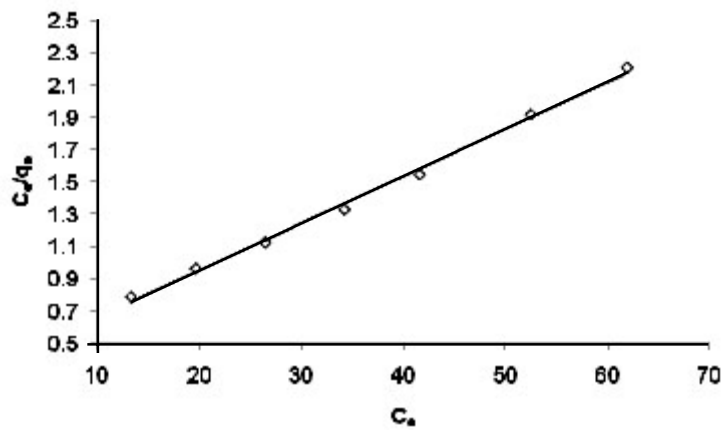w = 100 mg ; v = 50 ml ; Agitation Time = 240 minutes)**

**Fig. 13: Langmuir adsorption isotherm (C_0= 60 mg/l , 80 mg/l , 100 mg/l,120 mg/l,140 mg/l ,
160 mg/l and 180 mg/l ;T = 301 K ; w = 150 mg ; v = 50 ml ; Agitation Time = 7 hours)**

obtained from the following equation (22).

$$K_c = q_e / C_e \qquad ...(3)$$

Where, q_e is the concentration of the dye in the solid phase and C_e is the concentration of the dye in solution phase. The Gibb's free energy change is calculated from the following equation.

$$\Delta G = \Delta H - T \Delta S \qquad ...(4)$$

The equation can also be written as

$$\ln K_c = \Delta S / R - \Delta H / RT \qquad ...(5)$$

The thermodynamic parameters ΔH and ΔS are obtained from the slope and intercept of the plot $\ln K_c$ versus $1/T$ respectively. The values are presented in Table 3. The linear plot of $\ln K_c$ versus

$1/T$ is shown in Fig.9. As the temperature was increased from 301K to 338K, ΔG values decreased from -36.744 kJ/mol to - 40.326 kJ mol^{-1}. This confirmed that the adsorption of Rhodamine B onto EDAC was enhanced at higher temperatures. Negative ΔG values at different temperatures indicated that the adsorption process was feasible and spontaneous. The positive value of ΔH suggested that the sorption process was endothermic. Positive ΔS value was due to the increased randomness at the solid solution interface.

Kinetics of adsorption

In order to correlate the experimental data to explain the adsorption kinetics , pseudo first order, pseudo second order and intraparticle diffusion models were used. The kinetic parameters are presented in Table 4.
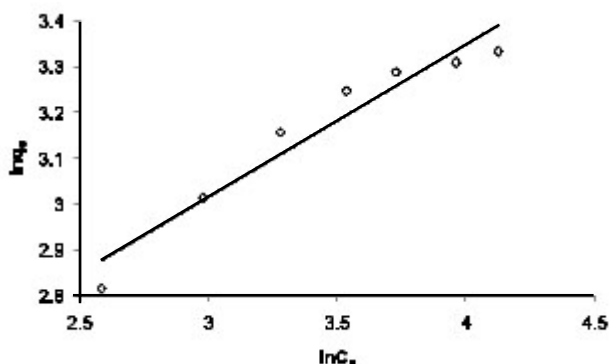

Fig. 14: Freundlich adsorption isotherm (C$_0$= 60 mg/l , 80 mg/l ,100 mg/l ,120 mg/l ,140 mg/l, 160 mg/l and 180 mg/l ;T = 301K ; w = 150 mg ; v = 50 ml ; Agitation Time = 7 hours)
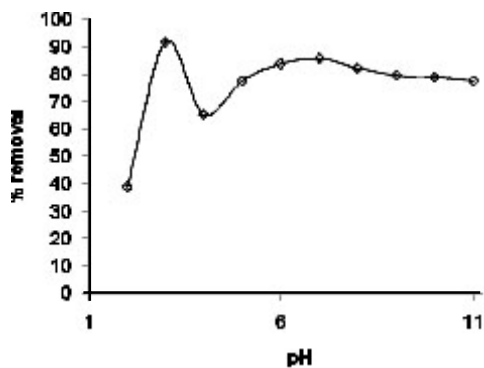

Fig. 15: Effect of pH Vs % removal (C$_0$ = 40 mg/l ; T = 301 K ; w = 100 mg; v = 50 ml ; Agitation Time = 240 minutes)

Pseudo first order kinetic model

The pseudo first order kinetic model has been used to explain the sorption kinetics . A linear first order model was described by Lagergren[23].

$$\text{Log } (q_e - q_t) = \log q_e - K_1 \, t/2.303 \qquad ...(6)$$

Where, q_t (mg/g) is the amount adsorbed at time t ; q_e (mg/g) is the amount adsorbed at equilibrium ; K_1 is the rate constant of adsorption (min^{-1}). From the slope and intercept of the plot of log $(q_e - q_t)$ versus t, the rate constants K_1 and equilibrium adsorption capacity q_e were calculated. The correlation coefficients for the first order kinetic model obtained for all initial dye concentrations were relatively lower. Pseudo first order kinetic model is shown in Fig.10. From the results it was found that pseudo first order kinetic model is not well suited with the experimental data.

Pseudo second order kinetic model

Pseudo second order kinetic model can be represented as follows (24).

$$t / q_t = 1 / K_2 \, q_e^2 + 1 / q_e \; t \qquad ...(7)$$

Where, K_2 is the pseudo second order rate constant (g/mg min), q_e is the equilibrium adsorption capacity. q_e and K_2 can be obtained from the slope and intercept of the plot of t/q_t versus t. From the results it can be observed that the calculated q_e values obtained from Pseudo second order kinetic model are closer to experimental q_e values than Pseudo first order kinetic model and the correlation coefficients for all the initial dye concentrations are >0.99 . From the values of r^2 it can be concluded that pseudo second order kinetic model shows good agreement with the experimental data. Pseudo second order kinetic model is represented in Fig.11.

Intraparticle diffusion model

The possibility of intraparticle diffusion was explored by using intraparticle diffusion model. According to Weber and Morris[25], an intraparticle diffusion coefficient K_{id} is defined by the following equation.

$$q_t = K_{id} \, t^{1/2} + C \qquad ...(8)$$

Where, Kid is the intraparticle diffusion rate constant (mg/g min[1/2]); q_t (mg/g) is the amount of dye adsorbed at time t (min) and C is the intercept. K_{id} is obtained from the slope of the linear plot of q_t versus $t^{1/2}$. It is understood that, the initial sharp portion is due to surface adsorption, the second linear portion is due to the intraparticle diffusion into the pores and the third portion is due to equilibrium stage where intraparticle diffusion starts to slow down due to the reduced number of dye molecules in the solution. The slope of the second linear portion of the plot (Fig.12) has been defined as the intraparticle diffusion parameter. However, in this case, the lines do not pass through the origin indicating that intraparticle diffusion mechanism is not the only rate limiting step, but surface adsorption also contributes to the rate controlling step[26].

Adsorption isotherms

The adsorption isotherm models show the distribution of molecules between the liquid and solid phases when the sorption process attains equilibrium stage. A suitable isotherm model is selected by fitting the data to different isotherm models for designing purpose. The most widely used isotherm are Langmuir (Fig.13) and Freundlich (Fig.14) models.

Langmuir isotherm

The experimental data have been analysed by correlating with Langmuir adsorption isotherm. Langmuir adsorption assumes the uptake of dye molecules on a homogeneous surface by monolayer adsorption.

The linear form of Langmuir equation is represented as follows (27) .

$$C_e/q_e = 1/Q_m b + (1/Q_m)C_e \qquad ...(9)$$

Where, C_e is the equilibrium concentration of the adsorbate (mg/l) ; q_e is the amount of adsorbate adsorbed per unit mass of the adsorbate (mg/g); Q_m and b are Langmuir constants related to monolayer adsorption capacity and rate of adsorption respectively. The linear plot of C_e / q_e versus C_e indicates the applicability of Langmuir model . The values of Q_m and b are obtained from the slope and intercept of the plot respectively. The results are presented in Table 5. In order to determine if the adsorption process favorable or

unfavorable, a dimensionless separation factor R_L is calculated using the following equation.

$$R_L = 1/1+bC_0 \qquad ...(10)$$

Where, C_0 is the initial dye concentration (mg/l); b is the Langmuir constant. The R_L value indicates the type of isotherm to be either favorable ($0<R_L<1$), unfavorable ($R_L>1$), linear ($R_L= 1$) or irreversible ($R_L=0$). From the results the values of R_L is found to be less than 1 showing that the adsorption process is favorable.

Freundlich isotherm

Freundlich isotherm model attempts to describe the heterogeneity of the surface of the adsorbent[28]. The adsorption isotherm data were correlated with Freundlich equation and the Freundlich constants K_f (mg/g) and n (intensity of adsorption) were calculated using the following equations.

$$q_{e =} K_F . C_e^{1/n} \qquad ...(11)$$

$$\log q_e = \log K_F + (1/n) \log C_e \qquad ...(12)$$

Where q_e is the amount of dye adsorbed (mg/g). Freundlich constants, K_F are the adsorption capacity of the adsorbent and n giving an indication of how favorable is the adsorption process. Freundlich isotherm parameters K_F, n and the correlation coefficient r^2 are given in table 4. From the results it is found that the correlation coefficient of Langmuir isotherm is higher than Freundlich isotherm. It can be concluded that Langmuir adsorption isotherm is suitable for better description of the adsorption data.

Effect of pH

pH is one of the most important factors controlling the adsorption process. The effect of pH on the adsorption of Rhodamine B onto the EDAC was examined over a range of pH 2-11 and the results are shown in Fig.15. The pH of the solution was adjusted by the addition of 0.1M HCl and 0.1M NaOH solutions. As the pH was increased from 2 to 11, the percentage removal of the dye increased from 38.77 % to 77.54 % and it was maximum at pH 3. (91.84%). It appears that a change in pH of the solution results in the formation of different ionic species and different carbon surface charges. At pH values lower than 4, Rhodamine B ions are in cationic and monomeric molecular form[29]. Thus the dye molecules can easily enter into the pores of the adsorbent. Due to this reason, the percentage removal of the dye is maximum at pH 3. At a pH value higher than 3, the zwitterionic form of the dye molecules in aqueous medium increases the aggregation of Rhodamine B to form dimer which makes it difficult for the dye to enter into the pores resulting in the lowering of dye uptake. As the pH is increased further, OH^- ions create a competition between $-N^+$ and $-COO^-$ which decreases the aggregation of the dye molecules resulting in higher adsorption of Rhodamine B on the carbon surface[30].

CONCLUSION

Sulphuric acid treated EDAC was prepared and characterized by various physical and chemical methods. From the experiments, it is concluded that EDAC can be used as an effective adsorbent for the removal of Rhodamine B from aqueous solution due to its easy availability, negligible cost and dye uptake capacity. From the batch adsorption studies, the percent removal of dye was dependent on contact time, initial dye concentration, pH, adsorbent dosage and temperature. The equilibrium time was found to be 240 minutes. Maximum adsorption takes place at pH 3. The optimum adsorbent dosage was found to be 100 mg. The kinetics of adsorption process was investigated using pseudo first order, pseudo second order kinetic model, and intraparticle diffusion model. The data show that the sorption process follows pseudo second order kinetic model. The thermodynamic parameters indicated that the adsorption of Rhodamine B onto EDAC was exothermic and spontaneous. The experimental data show better fits with Langmuir adsorption isotherm model compared to Freundlich isotherm model.

ACKNOWLEDGEMENTS

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