

Removal of basic dyes from aqueous solutions by activated carbon prepared from *Tamarindus indica* fruit shells

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ABSTRACT

Activated carbon prepared from *Tamarindus Indica* fruit shells has been used for the removal of two basic dyes, namely, rhodamine B and malachite green from aqueous solutions. Freundlich, Langmuir and Redlich-Peterson isotherm equations were used to fit the equilibrium adsorption data and the isotherm parameters were evaluated. The Langmuir monolayer adsorption capacity was found to be 3.1 mg/g for rhodamine B and 68.7 mg/g for malachite green at 30°C. The sorption processes were rapid and appear to follow pseudo-second order kinetics. Amounts of dyes adsorbed increased with increase in solution pH. Thermodynamic studies reveal that the sorption processes are endothermic and thermodynamic parameters like, ΔG , ΔH and ΔS were evaluated. Results of desorption studies point that the dyes are chemisorbed onto the surface of the carbon sorbent.

Key words: Adsorption, activated carbon, rhodamine B, malachite green, kinetic study.

INTRODUCTION

Discharge of coloured wastewaters into natural water bodies is not desirable, as they are aesthetically displeasing and prevent reoxygenation in receiving waters by cutting off penetration of sunlight. The colour also upsets the biological activities in water bodies. In addition most of the dyes used as colouring materials are toxic to aquatic organisms¹. Contamination of water bodies with dyeing industry effluents has caused great environmental problems, for example, in Coimbatore district of Tamil Nadu². Wastewater emerging from dyeing industries contains a wide spectrum of dyes and chemicals and the removal of such contaminants is very difficult and expensive. This has initiated a search for effective and economic treatment techniques to offer significant reduction

in cost than other such methods as electrolysis, membrane filtration, chemical coagulation, oxidation, etc.

Adsorption is one of the most effective and widely used techniques for the removal of dyes from aqueous solutions. In recent years several investigators have concentrated their work on low-cost and non-conventional adsorbent materials to achieve the economically feasible and effective treatment of wastewaters containing dyes.

Tamarindus Indica (tamarind tree) is one of the common and most important trees of India. The tree is widely planted especially on the roadside for shade. A full-grown tree yields 180-225 Kg of fruit per season. On the average the pod is composed of 55% pulp, 34% seed and 11% shell

and fibre³. India is the chief producer of this fruit in the world with an estimated production of approximately 250,000 tones per annum.

The present study is undertaken to evaluate the efficiency of activated carbon prepared from *Tamarindus Indica* fruit shells for the removal of two basic dyes – Rhodamine B (RB) and Malachite Green (MG) from aqueous solutions. Malachite green is a common basic dyestuff of triphenyl methane series used for dyeing silk and wool. Rhodamine B is also widely used in dyeing industries. The structures of these dyes are shown in figure 1.

EXPERIMENTAL

Adsorbent preparation

Carbonization of agricultural materials can be performed with sulphuric acid⁴. This can be achieved at low relatively low temperatures (less than 300°C) and produces carbons, which have the capability of decolourising dye solutions and possess ion exchange properties. Tamarind fruit shell carbon (TFSC) was prepared by charring the shells with concentrated sulphuric acid⁵. The shells were mixed with concentrated sulphuric acid in a weight ratio of 1:1.5 and the resulting black product was kept in an air oven maintained at 120°C for 2 hours. The carbon was then cooled, washed with large quantities of water to remove excess acid and finally dried at 120°C before use. Carbon particles of size 150-250 µm were used for study.

Analysis of dyes

The dyes were analyzed by monitoring their absorption in the visible region (with Spectronic 20D+ spectrophotometer, USA), 555nm for RB and 620nm for MG. Calibration graphs were prepared (1- 6mg/L for RB and 1-8mg/L for MG) and concentrations of sample aliquots were established by referring to the respective calibration graph.

Adsorption experiments

Each equilibrium adsorption experiment comprised three replicate 100mL glass-stoppered bottles containing appropriate amount of adsorbent and 50mL of dye solutions of selected concentrations. Control flasks without the adsorbents also prepared simultaneously. Mixtures

were maintained in a rotary shaker (Orbitek, Chennai, India) at constant temperature (30, 45 or 60°C). After the attainment of equilibrium the contents of each flask were filtered through a Whatmann No. 41 filter paper. The filtered samples were then analyzed for unadsorbed solutes.

For kinetic studies, a series of bottles with fixed amounts of carbon and dye solutions were taken. One bottle was taken out for the determination of unadsorbed dye at time intervals of 5, 10, 15, 20, 25, 30, 45, 60, 120 and 180 minutes. For determining the effect of pH on adsorption, dye solutions adjusted to different pH values using dilute NaOH or HCl solutions were taken with the chosen carbon dose. For desorption experiments, the carbon materials previously equilibrated with dyes were separated by filtration and shaken with 50 mL of desorbing medium (dil. HCl, dil. Acetic acid or water).

RESULTS AND DISCUSSION

Equilibrium adsorption studies-isotherm analysis

The adsorption process is a mass transfer operation, which can be described mathematically by an equilibrium process and a rate process. The equilibrium is established between the concentration of the material dissolved in water and that bound to the adsorbent. To facilitate the description of an adsorption process in terms of a batch equilibrium process, a finite amount of adsorbent is brought into contact with various concentrations of the adsorbate. Batch equilibrium studies yield information as to the total capacity of an adsorbent for a particular material in single component systems. Additionally, isotherm constants, necessary in the mathematical modeling of sorption systems may be obtained from representation of the equilibrium data as isotherm plots. These data are mathematically represented by the following isotherms, Freundlich, Langmuir and Redlich-Peterson:

$$\text{Freundlich} \quad q_e = K_F C_e^{(1/n)} \quad \dots(1)$$

$$\text{Langmuir} \quad q_e = K_L C_e / (1 + b C_e) = q_m b C_e / (1 + b C_e) \quad \dots(2)$$

$$\text{Redlich- Peterson} \quad q_e = K_R C_e / (1 + b_R C_e^\beta) \quad \dots(3)$$

where q_e is the adsorption capacity (mg/

Table 1: Isotherm parameters for the adsorption of RB and MG at 30°C

System	Model	Model parameters			
		K_F	$1/n$	n	r^2
TFSC- RB	<i>Freundlich</i>	0.7897	0.1543	6.4802	0.9501
TFSC- MG		18.5099	0.0974	10.2711	0.8658
	<i>Langmuir</i>	Model parameters			
		K_L	b	q_m	r^2
TFSC- RB		0.6066	0.1979	3.0654	0.9933
TFSC- MG		222.4104	3.2384	68.6791	0.9644
	<i>Redlich-Peterson</i>	Model parameters			
		K_R	b_R	β	r^2
TFSC- RB		0.7504	0.2935	0.9622	0.9945
TFSC- MG		222.2438	3.2345	1.0001	0.9644

Table 2: R_L values for adsorptions of RB and MG

Dye	C_i , mg/L	R_L value
RB	10	0.9785
	20	0.9579
	30	0.9381
	40	0.9191
	50	0.9009
	60	0.8834
MG	20	0.2432
	40	0.1384
	50	0.1139
	60	0.0967
	80	0.0744
	100	0.0604

g); C_e , equilibrium concentration of the adsorbate (mg/L or mmole/L); K_F (mg/g) and n , Freundlich constants; K_L and b (L/mg), Langmuir constants; q_m , Langmuir monolayer adsorption capacity (mg/g) and K_R , b_R and β are Redlich-Peterson isotherm constants. The isotherm parameters evaluated are listed in table 1. It is to be noted that the Langmuir monolayer adsorption capacity of the adsorbent towards MG is far greater than that of RB. This could be due to the larger molecular size the RB dye molecules, which will restrict the entry of them into micro and mesopores present in the carbon surface. The Langmuir b values determined are further used to calculate the dimensionless separation factor, R_L ,⁶ defined as

$$R_L = 1/(1 + bC_i) \quad \dots(4)$$

Table 3: Pseudo-first order parameters for adsorption of dyes on TFSC at 30°C

Dye	C_i mg/L	Equilibrium uptake, mg/g		First order rate constant, k_t , min ⁻¹	r^2
		$q_{e(1)}$	$q_{e(exp)}$		
RB	25	1.6218	1.222	0.0171	0.9669
	100	0.9703	1.437	0.0099	0.9970
MG	50	7.8127	23.163	0.0021	0.9550
	100	11.1661	25.535	0.0107	0.9874

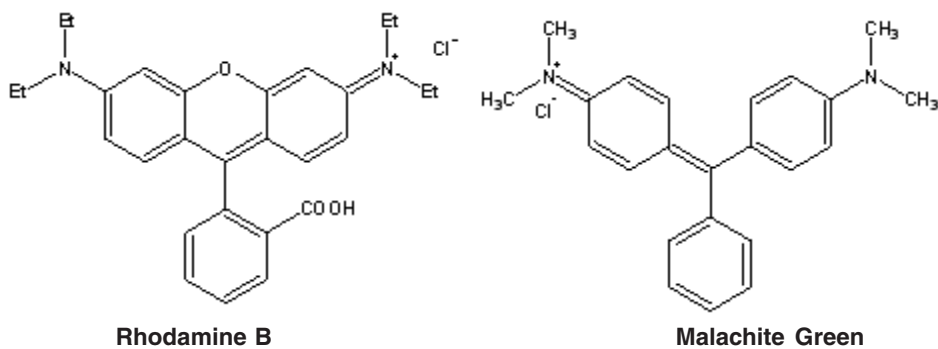


Fig. 1: Structure of rhodamine B and malachite green

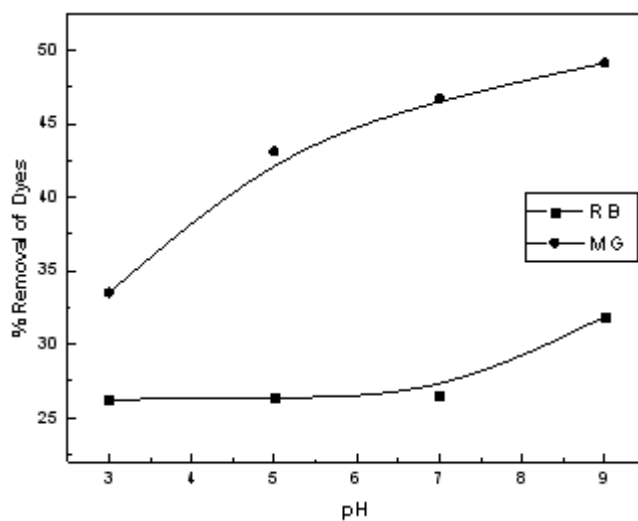


Fig. 2: Effect of pH on the adsorption of dyes

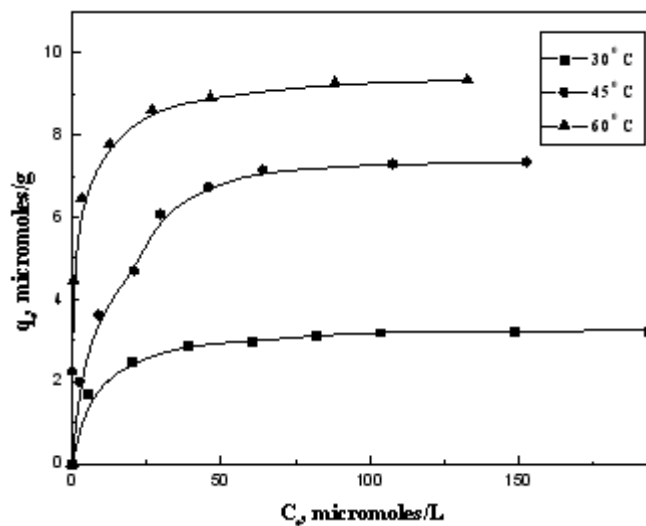


Fig. 3: Effect of temperature on the adsorption of RB on TFSC

where C_i is the initial solute concentration. The magnitude of R_L value gives an idea about the nature of adsorption equilibrium:

$R_L > 1$	non spontaneous
$1 > R_L > 0$	favourable
$R_L = 0$	irreversible

The R_L values calculated for all the adsorption processes in this study are in between 0 and 1 indicating favourable adsorption of all the dyes on TFSC. The R_L values calculated for the various dyes concentrations are listed in table 2.

Effect of pH

The effect of pH of dye solutions on adsorption is shown in figure 2. The results indicate that increase in solution pH leads to greater retention of both the dyes on the adsorbent. This is in accord with the charge on the dyes and the change in the surface charge of the carbon with

respect to the change in pH. The carbon surface becomes more and more negatively charged with increase in solution pH, and as a result will have greater affinity towards the positively charged dye molecules.

Adsorption kinetics

Adsorption isotherms are useful quantitative tools when representing the adsorption capacity of an adsorbent for a given solute. However, isotherms are obtained under equilibrium conditions, whereas in most adsorption treatment applications the retention time is too short for equilibrium to be attained. For this reason, we must obtain information on the time dependence of adsorption processes by carrying out process oriented kinetic studies.

To describe the adsorption kinetics, the pseudo-first order model proposed by Lagergren⁷

Table 4: Pseudo-second order parameters for adsorption of dyes on TFSC at 30°C

Dye	C_i mg/L	Equilibrium uptake, mg/g		Second order rate constant, k_2 , gmg ⁻¹ min ⁻¹	Initial sorption rate, h mgg ⁻¹ min ⁻¹	r^2
		$q_{e(2)}$	$q_{e(exp)}$			
RB	25	1.6008	1.222	0.0176	0.0451	0.9960
	100	1.6345	1.437	0.0302	0.0807	0.9963
MG	50	23.3645	23.163	2.8361	1.5482	0.9999
	100	25.6410	25.535	5.6648	3.7288	1.0000

Table 5: Thermodynamic parameters for adsorption of dyes on TFSC

Dye	C_i mg/L	-ΔG kJ mol ⁻¹			ΔH kJ mol ⁻¹	ΔS JK ⁻¹ mol ⁻¹
		30°C	45°C	60°C		
RB	10	2.9135	5.4475	17.2000	139.6709	466.0414
	20	0.5463	3.6983	11.9105	113.4118	373.5607
	30	0.7477	2.1402	8.3356	91.9566	299.4613
	40	1.7812	1.8903	5.0430	70.8046	228.0425
	50	2.4269	1.0148	3.2159	59.6365	189.3652
	60	2.9500	0.2876	1.8017	51.2379	160.2616
	80	3.4813	1.0335	0.8341	51.2276	156.8151
	100	4.4964	1.9336	0.9768	40.3185	119.0952
MG	40	12.7201	15.7892	18.5033	45.7577	193.1947
	50	6.3361	10.5733	15.2754	83.8885	297.5466
	60	3.6094	6.1602	8.2808	43.6517	156.1928

and the pseudo-second order model proposed by Ho and McKay⁸ were used in the following forms:

$$\text{First order rate equation} \\ \log(q_e - q_t) = \log q_{e(1)} - k_1 t \quad \dots(5)$$

$$\text{Second order rate equation} \\ t/q_t = (1/h) + (1/q_{e(2)})t \quad \dots(6)$$

where, q_t (mg/g) is the amount adsorbed at time t (min); q_e , amount adsorbed at equilibrium (mg/g); $q_{e(1)}$, adsorption capacity predicted by the I order model (mg/g); k_1 , first order rate constant (min^{-1}); $h (=k_2/q_{e(2)}^2)$, initial sorption rate ($\text{mgg}^{-1}\text{min}^{-1}$); and $q_{e(2)}$, adsorption capacity predicted by the II order model (mg/g).

The results of kinetic fitting and the parameters associated with each model along with the correlation coefficients are shown in tables 3 and 4.

The correlation coefficients in tables 3 and 4 indicate that the second order kinetic model is far better than the corresponding first order model. The comparison between experimental adsorption capacity values ($q_{e(\text{exp})}$) and those predicted by the two models ($q_{e(1)}$ and $q_{e(2)}$) also strongly support this view.

Effect of temperature and thermodynamics

Apart from room temperature studies, the

adsorption experiments were repeated at two more temperatures, namely 45 and 60°C. The general observation is that increase in reaction temperature resulted in greater adsorption. For example, the results for the adsorption of RB on TFSC are shown in figure 3. The increased adsorptions at higher temperatures could be due to increase in the number of activation sites on the adsorbent's surface or decrease in the size of the cationic dyes by desolvation of water molecules

Thermodynamic parameters such as Gibbs's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated using the following expressions:

$$K_c = C_{ae} / C_e \quad \dots(7)$$

$$DG = - RT \ln K_c \quad \dots(8)$$

$$\log K_c = [DS / 2.303 R] - [DH / 2.303 RT] \quad \dots(9)$$

where, K_c is the equilibrium constant for the distribution of dyes between the liquid and solid

Table 6: Desorption of dyes

Dye	% Desorption with		
	Water	0.1M AcOH	0.1M HCl
RB	42.25	89.27	62.58
MG	52.19	93.41	67.29

Table 7: Comparison of adsorption capacities of TFSC with adsorbents already reported in the literature

Dye	Adsorbent	q_m	Reference
RB	Waste banana pith	8.5mg/g	10
	Activated carbon	536 mg/g	11
	Natural biopolymer poly(α -glutamic acid)	390.25 mg/g	12
	TFSC	1.47mg/g	Present work
MG	Jack fruit peel carbon	166.37 mg/g	9
	Fly ash-GAC blend	25 mg/g	13
	Rubber wood (<i>Hevea brasiliensis</i>) sawdust	36.5 mg/g	14
	Jute fibre carbon	136.58 mg/g	15
	TFSC	25.06 mg/g	Present work

phases; C_{ae} , solid phase dye concentration (mg/L); C_e , liquid phase dye concentration (mg/L); T, absolute temperature ($^{\circ}$ K) and R is the gas constant. Equation (9) was used to construct Van't Hoff plots and ΔH and ΔS were calculated from the slope and intercept of the Van't Hoff plot respectively. The thermodynamic parameters evaluated are listed in table 5.

The negative values of ΔG obtained for the adsorptions reflect the spontaneity. The positive values of ΔH indicate the endothermic nature and the positive values of ΔS indicate increased randomness at the interface. The magnitudes of ΔS for the adsorption of dyes are much higher and this could be due to the large sizes of the dye molecules. As the dyes are large in size a single dye molecule displaces a lot of water molecules from the adsorbent surface.

Desorption studies

The results of desorption studies are presented in table 6. The results indicate that desorption is maximum with acetic acid as the desorbing medium. This strongly points that the dyes are chemisorbed on the adsorbent.⁹

Comparison of removal efficiency of TFSC with other adsorbents

Finally, an attempt has been made to compare the removal efficiency of TFSC with those already reported in the literature for the removal of the selected dyes (table 7).

CONCLUSIONS

The present study shows that the carbon sorbent prepared from tamarind fruit shells by charring with sulphuric acid can be successfully used for the removal basic dyes from aqueous solutions. The adsorption capacities of the adsorbent towards rhodamine and malachite green are comparable to those sorbents already studied. The equilibrium adsorption data were better represented by the Redlich-Peterson isotherm equation. Kinetic batch adsorption studies performed indicate that the sorption dynamics are better represented by the pseudo-second order kinetic model. The q_e values predicted by this model are in close agreement with the experimental values. Increase of operating temperature resulted in increased adsorptions. The endothermic nature was confirmed by negative free energy changes and positive enthalpy changes. Acetic acid was found to be the best desorbing agent among those tried in this work.

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