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REMOVAL OF CONGO RED DYE BY ADSORPTION USING ACTIVATED IPOMOEA CARNEA

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ABSTRACT

Industrial discharges containing dyes are hazardous to all living organisms. In the present study, the activated carbonized form of natural plant material, *ipomoea carnea* leaves was used as an adsorbent for the removal of the Congo red dye from aqueous solution. Batch experiments were carried out using initial concentration, dosage, pH, contact time and temperature as operating variables. Equilibrium data were fitted to the Langmuir and Freundlich isotherms. Kinetic studies were conducted and the parameters were correlated with pseudo second-order kinetic model, Elovich model and intra-particle diffusion model. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° were evaluated to prove the adsorption behaviour of Congo red dye onto acid activated *ipomoea carnea*. The results clearly suggest that this activated carbon can be used for the removal of Congo red dye from aqueous solution.

Key Words: Ipomoea carnea, Congo red dye, adsorption isotherm, equilibrium, thermodynamics, intra-particle diffusion.

INTRODUCTION

Dyes are intensely coloured complex organic compounds used to colour the textiles, plastics, paper, leather, food stuffs, printing inks and other materials. In the process of washing and finishing the coloured products, waste water contaminated with dyes is

generated. Pollution of water bodies by dyes leads to various health problems in human, animals, plants and aquatic biota.¹⁻³ Therefore, their presence in the environment, in particular in water, should be controlled. Waste water containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light. A synthetic dye in waste water cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye waste water at large scale in textile and paper industries.^{4,5} Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants.^{6,7} Adsorption also does not result in the formation of harmful substances. For the removal of toxic dyes from contaminated water by adsorption, a suitable adsorbent is needed. Activated carbon is one of the most popular adsorbents used for the removal of toxic dyes from waste water. The present study is focusing the feasibility of activated carbon prepared from *ipomoea carnea* leaves (AAIC) for the removal of Congo red dye (CR dye) from aqueous solution.

EXPERIMENTAL METHODS

Preparation of adsorbent

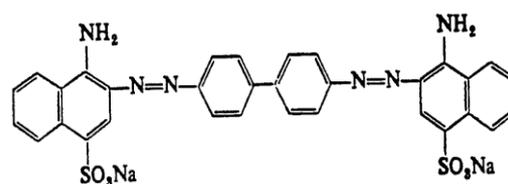
The *ipomoea carnea* leaves were collected from Tiruchirappalli district, the middle part of Tamil Nadu State, India. The leaves were carbonized with concentrated sulphuric acid in weight/volume ratio of 1:1 for 24 hours, filtered and then washed with distilled water. The residual mass was dried at 110°C for 1hour and activated in a muffle furnace at 400°C for 5 hours. It was ground well to a fine powder and sieved to obtain the desirable size. This was used for the batch experiments.

Preparation of adsorbate

A known weight of 1000 mg of commercially available high purity Congo red dye was dissolved in one liter of distilled water to get the stock solution. The solutions of various concentrations were prepared by diluting the stock solution



Ipomoea carnea



Congo red

Batch equilibrium method

The adsorption experiments were carried out in a batch process⁸ at 30, 40, 50 and 60°C. A known weight of AAIC was added to 50 ml of the CR dye solutions with initial concentrations of 25 mg/L to 125 mg/L. The contents were shaken thoroughly using a mechanical shaker with a speed of 150 rpm. The solution was then filtered at pre-set time intervals and the residual dye concentration was measured using UV-Visible spectrophotometer with the $\lambda_{\max}=500$ nm. The amount of adsorption at equilibrium, Q_e (mg/g) was calculated by the following mass balance equation

$$Q_e = (C_0 - C_e)V/W \quad \dots (1)$$

Where, C_0 and C_e (mg/L) are the liquid phase concentrations of CR dye at initial and equilibrium stages respectively. V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used. The percentage removal of CR dye can be calculated as follows:

$$\text{Percentage removal} = (C_0 - C_e) 100/C_0 \quad \dots (2)$$

RESULT AND DISCUSSIONS

Effect of contact time and initial dye concentration

The removal of CR dye by AAIC at various time intervals is graphically represented in fig. 1. It was observed that the maximum removal was taken place at 50 minutes. After this, there was no appreciable change in the removal of CR dye. The figure revealed that the curve is single, smooth and continuous leading to saturation, suggesting the possibility of monolayer coverage of the CR dye on the AAIC adsorbent surface. The effect of contact time on the amount of CR dye adsorbed on the adsorbent surface at various concentrations viz., 25, 50, 75, 100 and 125 mg/L of CR dye was investigated to study the rate of CR dye removal. It was observed from the study that the equilibrium has been established at 50 minutes for all concentrations. The equilibrium data obtained are presented in table 1. From the table, it is seen that the percentage of adsorption decreased with increase in initial CR dye concentrations. But, the actual amount of CR dye adsorbed per unit mass of AAIC increased with increase of CR dye concentration.⁹ This indicates that the adsorption is highly dependent on the initial concentration of CR dye. At lower concentration, the ratio of initial number of CR dye to the available surface area is low. Hence, the fractional adsorption becomes independent of initial concentration of CR dye. However at higher concentrations, the available sites of adsorption become fewer and hence the percentage removal is dependent on the initial concentration. Optimum removal of CR dye was observed at 50mg/L of initial CR dye concentration.

Table:1. Equilibrium parameters for the adsorption CR dye onto AAIC

C ₀ (mg/L)	C _e (mg/L)				Q _e (mg/g)				% Removal of CR dye			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	2.312	1.734	1.156	0.983	15.20	15.59	15.98	16.09	90.75	93.06	95.38	96.07
50	5.202	4.624	3.468	2.312	30.01	30.40	31.18	31.95	89.59	90.75	93.06	95.38
75	10.98	8.671	6.358	4.624	42.89	44.44	45.99	47.15	85.36	88.44	91.52	93.83
100	16.19	13.29	10.98	5.780	56.16	58.09	59.64	63.13	83.82	86.71	89.02	94.22
125	22.54	20.81	17.92	12.14	68.65	69.81	71.74	75.62	81.97	83.35	85.66	90.29

Effect of adsorbent dose

The effect of different doses viz., 10, 25, 50, 75, 100, 125 and 150mg of AAIC adsorbent for 50ml of 50mg/L of CR dye concentration was studied to optimize the dosage of adsorbent for the study. The data are presented in the fig. 2. It was observed that the percentage of adsorption was increased with increase in AAIC dose due to the increase of surface area and the availability of more adsorption sites.^{10,11} The optimum CR dye removal was obtained at the carbon dose of 75 mg/50ml for 50mg/L of CR dye concentration. Hence, the remaining parts of the experiments were carried out with 75 mg of adsorbent for 50 ml of adsorbate solution.

Effect of solution pH

The removal of CR dye by AAIC was studied at wide range of pH of the solution, 2-10 since pH is one of the most important parameters controlling the adsorption process. A change in pH of the solution results in the formation of different ionic species and different charges on the surface of the adsorbent. Therefore, the removal of CR dye is affected by the pH of the medium. The results obtained are graphically presented in fig. 3. It was observed that the percentage removal of CR dye in the acidic pH was relatively higher, and maximum uptake was obtained at pH 6.5 (zero point charge of the adsorbent). At these lower pH values, the CR dye can enter into the pore structure.¹² At pH greater than 6.5, the zwitter ionic form in water may increase the aggregation of CR dye to form a bigger molecular dimer and become unable to enter the pore structure of the AAIC surface.

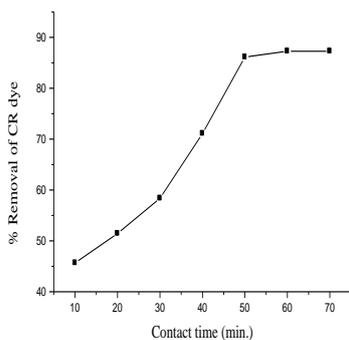


Fig.1 - Effect of Contact time on the removal of CR dye
[CR]=50mg/L;[AAIC]=75mg/50ml;Temp.=30°C

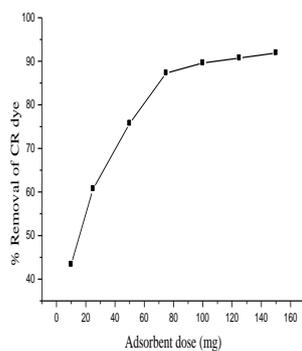


Fig.2 - Effect of adsorbent dose on the removal of CR dye
[CR]=50mg/L; contact time=50min; Temp.=30°C

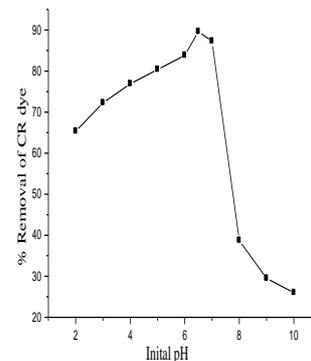


Fig.3 - Effect of initial pH on the removal of CR dye
[CR]=50mg/L; [AAIC]=75mg/50ml; contact time=50min.; Temp.=30°C

Adsorption isotherms

Langmuir isotherm

The theoretical Langmuir isotherm is used for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Therefore, the Langmuir isotherm model¹³ was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as follows:

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \dots \dots \dots (3)$$

Where C_e is the equilibrium concentration of adsorbate in the solution (mg/L), Q_e is the amount adsorbed at equilibrium (mg/g), Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The values of Q_m and b were calculated from slope and intercepts of the plot of C_e/Q_e vs. C_e and the values are given in table 2. From the results, it is obvious that the value of adsorption efficiency Q_m and adsorption energy b of the AAIC increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with endothermic nature of adsorption. To confirm the favorability of the adsorption process, the separation factor (R_L) was determined from the equation $R_L = 1/(1 + bC_0)$ and the values are given in table 3. These values lying between 0 and 1 confirm that the ongoing adsorption process is favourable.¹⁴

Freundlich isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. The Freundlich equation was employed for the adsorption of Congo red dye on the adsorbent. The Freundlich isotherm¹⁵ was represented by the following equation.

$$\log Q_e = \log K_f + (1/n) \log C_e \dots \dots \dots (4)$$

Where Q_e is the amount of CR dye adsorbed per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of CR dye in solution (mg/L), and K_f and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. The values of K_f and n were calculated from the intercept and the slope of the plot $\log Q_e$ versus $\log C_e$ and the values are given in Table 3. The values of n lying between 0 and 1, indicating the physisorption is much more favorable.

Table: 2. Langmuir and Freundlich isotherm parameters for adsorption of CR onto AAIC

Temp. (°C)	Langmuir parameters		Freundlich parameters	
	Q_m	b	K_f	n
30	110.79	0.0662	9.3776	1.5522
40	105.34	0.0915	11.525	1.6331
50	97.566	0.1477	15.322	1.7922
60	113.59	0.1718	17.735	1.5763

Table : 3. Dimensionless separation factor (R_L) for the adsorption of CR dye onto AAIC

C_0 (mg/L)	Temperature (°C)			
	30	40	50	60
25	0.3766	0.3043	0.2131	0.1888
50	0.2320	0.1794	0.1193	0.1042
75	0.1676	0.1272	0.0828	0.0720
100	0.1312	0.0986	0.0634	0.0550
125	0.1078	0.0804	0.0514	0.0445

Thermodynamic studies

To study the effect of temperature on the adsorption of CR dye by AAIC, the experiments were performed at various temperatures of 30, 40, 50, 60°C. Thermodynamic parameters such as change in free energy (ΔG°) (kJ/mol), enthalpy (ΔH°) (kJ/mol) and entropy (ΔS°) (J/K/mol) were determined using the following equations.

$$K_0 = C_{\text{solid}}/C_{\text{liquid}} \dots\dots\dots (5)$$

$$\Delta G^\circ = -RT \ln K_0 \dots\dots\dots (6)$$

$$\ln K_0 = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \dots\dots\dots (7)$$

Where K_0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The ΔH° and ΔS° values were obtained from the slope and intercept of Van't Hoff plot $\ln K_0$ vs $1/T$ and the calculated values are given in Table 4. It is observed that the ΔG° values were negative at all temperatures. This indicates that the adsorption of CR dye onto AAIC was taken place through physisorption and the adsorption was highly favourable and spontaneous. The positive values of ΔH° indicate the endothermic nature of adsorption, and it governs the possibility of physical adsorption. The low ΔH° values (below 40 kJ/mol) also confirmed the adsorption of CR dye onto AAIC adsorbent taken place via physisorption. The increase of temperature of the system resulted in the increase of adsorption of CR dye. This enhancement of adsorption

capacity of the AAIC at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface.¹⁶ The positive values of ΔS° indicate the increased disorder and randomness at the solid-solution interface of CR dye with AAIC adsorbent.

Table: 4. Thermodynamic parameters for adsorption of CR onto AAIC

(C ₀)	ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (J/K/mol)
	30°C	40°C	50°C	60°C		
25	-5.7528	-6.7568	-8.1274	-8.8491	-26.632	106.93
50	-5.4238	-5.9427	-6.9727	-8.3791	-24.433	97.837
75	-4.4408	-5.2949	-6.3890	-7.5375	-26.987	103.47
100	-4.1428	-4.8797	-5.6193	-7.7275	-30.417	113.24
125	-3.8140	-4.1918	-4.8008	-6.1732	-19.304	75.625

Adsorption kinetics

The study of adsorption dynamics describes the solute up take rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface .The kinetics of CR dye adsorption on the AAIC were analyzed using pseudo second-order, Elovich and intra-particle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation co- efficient (r^2).

The pseudo second- order equation

The pseudo second-order adsorption kinetic rate equation¹⁷ is expressed as

$$dq_t/dt = k_2(q_e - q_t)^2 \dots\dots\dots(8)$$

Where k_2 is the rate constant of pseudo second- order adsorption (g/mg/min). Integrating this equation by applying the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, and rearranging to the linear form:

$$t/q_t = (1/k_2 q_e^2) + ((1/q_e)t) \dots\dots\dots(9)$$

If the initial adsorption rate, h ($\text{mg g}^{-1} \text{min}^{-1}$) is given as $k_2 q_e^2$: then the equation (9) becomes

$$t / q_t = (1/h) + (1/q_e) t \dots\dots\dots (10)$$

The plot of (t/q_t) and t of Eq. (10) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The calculated values are summarized in table 5. The correlation coefficients (r^2) are closer to 1 indicate that the adsorption process followed pseudo-second order.

The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / dt = \alpha \exp (-\beta q_t) \dots\dots\dots(11)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g/mg). To simplify the Elovich equation, Chien and Clayton¹⁸ assumed $\alpha\beta t \gg t$ by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$. Hence, Eq.(11) becomes

$$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \dots\dots\dots (12)$$

If CR dye adsorption fits with the Elovich model, a plot of q_t vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The Elovich model parameters α , β , and correlation coefficients (r^2) were calculated from the plot, and the values are summarized in table 5. The correlation co-efficient (r^2) values appeared closer to 1 indicate the fitness of the model.

The intra particle diffusion model

The intra-particle diffusion model proposed by Weber and Morris¹⁹ is

$$q_t = K_{id} t^{(1/2)} + C \dots\dots\dots(13)$$

where, K_{id} is the intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$) and C is constant. The intra-particle diffusion coefficient, K_{id} was obtained for the plot of q_t versus $t^{1/2}$. The calculated K_{id} , the intercept C and the corresponding correlation coefficient (r^2) values are presented in table 5. The obtained values indicate the fitness of this model towards CR dye adsorption. The intercept, C indicates that the curve is not passing through the origin, and this gives the thickness of formed CR dye layer on the boundary. So, the intra-particle diffusion alone is not the rate controlling step but some others were also involved during percolation of CR dye onto AAIC adsorbent.²⁰

Table: 5. The kinetic parameters for the adsorption of CR onto AAIC

C_0	Temp. ($^{\circ}\text{C}$)	Pseudo second order				Elovich model			Intra-particle diffusion		
		q_e	k_2 (10^{-3})	h	r^2	β	α	r^2	K_{id}	C	r^2
25	30	21.1212	2.42	1.0776	0.9691	0.2121	2.3192	0.9508	1.9842	1.5061	0.9690
	40	19.7177	3.47	1.3483	0.9908	0.2392	3.1830	0.9801	1.7517	3.2032	0.9944
	50	19.4129	3.66	1.3798	0.9794	0.2581	3.7372	0.9529	1.6465	3.7610	0.9808
	60	19.2983	4.31	1.6058	0.9871	0.2724	4.9352	0.9591	1.5574	4.7987	0.9852
50	30	34.0906	3.23	3.7552	0.9894	0.1791	18.797	0.9450	2.3836	12.343	0.9769
	40	34.5018	3.37	4.0129	0.9923	0.1768	20.053	0.9661	2.3987	12.883	0.9868
	50	35.8066	3.06	3.9187	0.9932	0.1618	16.310	0.9712	2.6076	12.318	0.9924
	60	35.7589	3.69	4.7123	0.9949	0.1777	27.652	0.9733	2.3720	14.728	0.9935
75	30	45.4057	5.97	12.309	0.9987	0.2206	1020.0	0.9792	1.9043	29.233	0.9962
	40	46.9809	5.52	12.188	0.9980	0.2148	1070.2	0.9647	1.9695	30.049	0.9883

	50	48.6067	4.97	11.751	0.9974	0.1999	769.91	0.9587	2.1214	30.251	0.9846
	60	50.0146	5.09	12.737	0.9984	0.1931	798.72	0.9765	2.1783	31.421	0.9949
100	30	59.1583	4.76	16.650	0.9986	0.1777	2041.3	0.9733	2.3720	38.934	0.9935
	40	61.0791	4.82	17.967	0.9988	0.1726	2257.7	0.9831	2.4256	40.586	0.9968
	50	62.7156	4.71	18.529	0.9988	0.1707	2655.7	0.9798	2.4595	41.878	0.9964
	60	66.0377	4.91	21.424	0.9989	0.1777	7045.8	0.9733	2.3720	45.905	0.9935
125	30	72.2618	3.80	19.827	0.9981	0.1481	2825.1	0.9580	2.8664	47.563	0.9851
	40	73.5290	3.78	20.419	0.9985	0.1426	2443.4	0.9703	2.9610	48.223	0.9919
	50	75.3120	4.46	25.305	0.9995	0.1483	5227.4	0.9928	2.8048	51.995	0.9996
	60	79.2569	3.82	23.988	0.9985	0.1433	5776.8	0.9653	2.9539	53.993	0.9892

CONCLUSION

Equilibrium, thermodynamic and kinetic studies were carried out under batch mode to evaluate the AAIC adsorbent for the removal of Congo red dye from aqueous solution. The adsorption of Congo red was dependent on adsorbent dose, Congo red concentration, time of contact, pH and temperature. The adsorption process was faster and the rate was mainly controlled by intra-particle diffusion, and also the process followed pseudo-second order kinetics. The equilibrium data conformed well to the Langmuir and Freundlich isotherms models. The temperature variation study to evaluate ΔG° , ΔH° , and ΔS° , showed that the Congo red dye adsorption was endothermic and spontaneous with increased randomness at the solid solution interface, and the process was taken place through physisorption mechanism. Significant effect on the adsorption was observed on varying the pH of Congo red solution. The present study has proved the effectiveness of using activated carbon prepared from *ipomoea carnea* leaves (AAIC) in the removal of Congo red dye from aqueous solution.

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