# Kinetic and Equilibrium Studies of Crystal Violet, A Basic Dye Using Activated Prosopis Spicigera

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Abstract: The efficiency of acid activated fruits of Prosopis Spicigera (SAPS) was tested in removing the basic dye, Crystal violet, from aqueous solution. The batch adsorption experiments were conducted to understand the effects of various operating parameters like initial dye concentration, contact time, adsorbent dose, pH, particle size and temperature. The adsorbent was characterized by SEM. Kinetic studies indicate that the adsorption was pseudo second order process which was supported by Elovich equation indicating possible chemisorption. The equilibrium adsorption data were analyzed using Langmuir and Freundlich isotherm and intraparticle diffusion models. The maximum monolayer adsorption capacity was 78.98 mg/g at  $25^{\circ}C$  (at room temperature). Thermodynamic parameters indicate that adsorption process to be endothermic and spontaneous with randomness at the solute-solution interface. It can be concluded that this low cost and effective adsorbent may provide an alternative to commercial activated carbon for the removal of Crystal violet from wastewaters.

Keywords: Adsorption, Prosopis Spicigera, Activated carbon, Crystal violet, Langmuir and Freundlich isotherms.

# 1. Introduction

The removal of dyes from wastewater is a matter of great interest in the field of water pollution. Several physical, chemical and biological decolorization methods (1-3) such as coagulation/flocculation, biodegradation, oxidation, membrane filtration and adsorption have been reported and attempted for the removal of dyes from plastics, dyestuffs, pulp and paper and textile effluents. Among these numerous techniques of dye removal, it is now recognized that adsorption using solid adsorbents was an effective and useful process(4-6). There are numerous materials such as coal, fly ash, wood, silica, shale oil ash, Fuller's earths, zeolite, perlite, alunite, clay materials (bentonite, montmorillonite, etc.) activated slag and agricultural wastes (bagasse pith, maize cob, coconut shell, rice husk, waste fruit residues etc (Mall et al., 2005, Dogan et al., 2000 and Parimaladevi et al., 2011) for removal of dyes<sup>(7)</sup> <sup>10)</sup>. Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use in dyeing wool and silk (11).Crystal violet, a basic dye, is most widely used for the dyeing of cotton, wool, silk, nylon, paper, leather etc., among all other dyes of its category. In fact, basic dyes, are the brightest class of soluble dyes with very high tinctorial values; less than 1 mg/L of the dye produces an obvious coloration.

# 2. Materials and Methods

## 2.1 Preparation of Activated Carbon (SAPS)

Fruits of Prosopis Spicigera are collected from various areas in and around Pollachi. Sun dried fruits are cut into small pieces and ground well. The powder (100 g) is treated with 40 ml of 40%  $H_2SO_4$  for 2 hours, then carbonised and digested in an oven at 120°C for 12 h. The carbonized material is then impregnated in 50% solution of NaHCO<sub>3</sub>, washed with distilled water to remove the free acid until the pH of the activated carbon reached 6.6–6.8 and finally dried at 105°C. After that, the impregnated

samples were again activated by carbonization in a furnace at 500°C for 60 min under nitrogen atmosphere. The clean biomass obtained is mechanically ground and finally sieved to get particles of different sizes.

# 3. Results and Discussion

## 3.1 Batch Adsorption Experiments

Batch experiments for the removal of crystal violet were carried out in a thermostatic shaker to study the effects of parameters, contact time, initial dye concentration, adsorbent dosage, pH, particle size and temperature. Before mixing with the adsorbent, pH of the adsorbate solution was adjusted by adding 0.1N HCI or 0.1N NaOH. Dye samples were prepared by dissolving a known quantity of the dye in double-distilled water and used as a stock solution (1000 mg/L) and diluted to require concentration.

## 3.2 SEM Analysis



Figure 1: SEM images of SAPS

The surface morphology of SAPS was determined using scanning electron microscope (SEM). The SEM image (Fig.1) showed a heterogeneous morphology.

# **3.3** Effect of agitation time and initial dye concentration

The adsorption of dye was studied as a function of time in order to find out the equilibrium time required for maximum adsorption of dye. Figure 2 shows the adsorption of dye adsorbed using SAPS. It was observed that percent adsorption increased with increase in initial dye concentration and attains equilibrium in 180 minutes.



#### 3.4 Effect of Adsorbent Dose

One of the parameters that strongly affect sorption capacity is the quantity of the contacting sorbent in the liquid phase because it determines the capacity of adsorbent to adsorb for a given initial concentration of dye solution. The effect of adsorbent dosage on basic dye removal was studied by keeping all other experimental conditions constant except the adsorption dosage. The effect of **SAPS** dose on the removal of CV at two different initial concentrations of the dye solutions viz, 20 and 40 mg.L<sup>-1</sup> (Figure 3) was studied. Increase in the percent removal with increase in carbon concentration was noticed which can be attributed to increased surface area and hence availability of more adsorption sites.



## 3.5 Effect of pH

The pH of the aqueous solution is an important parameter in the adsorption of both cations and anions at the liquidsolid interface as it plays an important role in the whole adsorption process and on the adsorption capacity. To determine the influence of pH, experiments were performed at various initial pH, ranging between 2 -10. The dye uptake was found to increase with increase in pH (Figure4).



**3.6 Effect of particle size** 

The particle size has a significant influence on dye adsorption. Figure 5 shows the dye adsorption on SAPS of different particle sizes. The relatively higher adsorption rate as the particle size decreases is due to the increase in surface area.



Figure 5: Effect of Particle size

## 4. Adsorption Isotherm

The study of adsorption isotherm is essential in selecting an adsorbent for the removal of dyes. Adsorption equilibrium isotherms are useful for the estimation of the amount of adsorbent needed for sorbing a required amount of sorbate from solution. The most widely used isotherm to analyse the adsorption data as that of Langmuir and Freundlich.

#### 4.1 Langmuir isotherm

Langmuir isotherm has been used by many workers for studying the sorption of a variety of compounds. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. Langmuir isotherm is represented by the following equation

#### C./q.=1/bq\_+Ce/q\_

where  $C_e$  is the equilibrium concentration of the dye solution (mg.L<sup>-1</sup>) at equilibrium,  $q_e$  is the amount of dye adsorbed at equilibrium (mg.g<sup>-1</sup>) and Qo and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plot of Ce/qe vs. Ce (Figure 6) shows that the adsorption obeys Langmuir isotherm model with  $R^2 > 0.95$ . The adsorption capacity, Qo was found to be 165.83 mg.g<sup>-1</sup> for CV onto SAPS. The applicability of the Langmuir isotherm suggests the monolayer coverage of the AO dye on the surface of **SAPS**. The values of Langmuir constant  $R_L$ ,  $b.Q^0$  and  $R^2$  are listed in Table1. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor  $R_L$ .

 $R_{L} = 1 / (1 + bC_{O})$ 

where  $C_o$  is the initial dye concentration (mg.L<sup>-1</sup>) and  $R_L$  values indicate the shape of the isotherm. The  $R_L$  values were found between 0 and 1 for this adsorption of CV on SAPS confirm the ongoing adsorption process is favorable.



Figure 6: Langmuir adsorption isotherm

Table 1: Data for Langmuir adsorption isotherm

Conc. of dye(mg/L)	$R_L$	b	Q <sup>0</sup> (mg/g)	$\mathbf{R}^2$
20	0.0456			
40	0.0233			
60	0.0156			
80	0.0118			
100	0.0094	1.0454	78.98	0.9815
120	0.0079			

#### 4.2 Freundlich Isotherm

The Freundlich sorption isotherm (12), one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The adsorption data of SAPS were fitted into the linear form of Freundlich equation.

$$\log q_{\bullet} = \log K_{r} + 1/n \log C_{\bullet}$$

where  $K_f (mg^{1-1/n} L^{1/n} g^{-1})$ , and 1/n (g/L) are Freundlich constants. The plot of ln q<sub>e</sub> versus ln C<sub>e</sub> is linear (Figure 7) with a regression coefficient of 0.9 showing the data fit well with Freundlich isotherm also. The value of n was evaluated as 1.31, indicating that the favorable adsorption conditions (13). The value of Kf was evaluated as 42.66  $mg^{1-1/n}L^{1/n}g^{-1}$ )



Figure 7: Freundlich adsorption isotherm

# 5. Adsorption Kinetics

In order to investigate the mechanism of adsorption of Crystal violet by SAPS the following three kinetic models were considered.

#### 5.1 Pseudo first order kinetic model

The Lagergren's rate equation (14) is one of the most widely used rate equation to describe the adsorption of an adsorbate from the liquid phase. The linear form of pseudo first-order kinetic equation is given as:

 $Log (q_e-q_t) = log q_e- (k_1 / 2.303) t$ 

where  $q_e$  and qt are the amounts of CV adsorbed at equilibrium and at time t(min) respectively; k1 is the first order rate constant(min<sup>-1</sup>).The data of this study does not give a straight line as expected. The data given in Table 2 have a poor regression coefficient suggesting adsorption of CV on activated carbon does not follow the pseudo first-order kinetics.

#### 5.2 Pseudo second order kinetic model

The linear form of pseudo second order model is given by equation (14)

 $t/q_t = 1/_{K2}qe^2 + 1/q_et$ 

where  $k_2$  is the pseudo – second order rate constant. The data of this study shows good compliance with the pseudo second order equation. A plot of  $t/q_t vs. t$  is shown in Figure 8. The linearity of the plots and data in Table 2 clearly indicate that the adsorption process followed Pseudo second order kinetics.



Figure 8: Pseudo-second order kinetics

### **5.3 Intraparticle Diffusion**

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, eg., film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. Adsorption rate of the dye onto the particle depends on the rate of the dye within the pores of solid particulates by diffusion. The intraparticle diffusion rate of the dye molecule in particle,  $K_{id}$  can be calculated from the following equation:

$$q_{t} = K_{td}t_{1/2} + C$$

Where  $K_{id}$  is the intraparticle diffusion rate constant and C is the intercept. A plot between amount of dye adsorbed per unit mass of adsorbent  $q_t$  and  $t^{1/2}$  was shown in Figure 9 and data given in Table 2. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through the origin suggesting that pore diffusion is the only controlling step and not the film diffusion. This deviation may be due to the variation of mass transfer in the initial and final stages of adsorption.



Figure 9: Intraparticle diffusion

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## 5.4 Elovich Model

The Elovich model is usually represented as (15)

 $Qt=1/b \ln(ab)+1/b \ln t$ 

Where a is the initial sorption rate and b is the (mg.g-1min) and b is related to the extent of surface coverage and activation energy for chemisorptions (g.mg-1). The values of a and b calculated from the intercept and slope of the plot of ln t versus  $q_t$  and the results were listed in Table 2 along with correlation coefficient values(16). a and b parameters derived from Elovich equation to estimate reaction rates. It was suggested that an increase in a value and/or decrease in b value would increase the rate of adsorption process. The obtained  $R^2$  values for SAPS for all the concentrations were high suggesting that Elovich model best described this adsorption system. The plot of qt versus ln t is shown in Figure 10.



Table 2: Results of kinetic plots for the adsorption of CV onto SAPS

Conc. of CV in mg/L	q <sub>e</sub> exp mg/g	Pseudo First order		Pseudo Second order			Elovich			Intraparticle		
		q cal mg/g	K <sub>1</sub> min	$\mathbf{R}^2$	q cal -1 mg g	k <sub>2</sub> X10 <sup>-3</sup> (g/mg/min)	$\mathbf{R}^2$	a	b	$\mathbf{R}^2$	k	$\mathbf{R}^2$
10	4.738	4.1985	2.87	0.8869	5.7012	4.611	0.9866	0.3860	0.8322	0.9233	0.3054	0.7811
20	9.347	9.6738	2.35	0.7766	12.2399	1.342	0.9816	0.5609	0.4022	0.9686	0.6594	0.8920
30	12.944	14.5545	2.51	0.7841	16.9952	0.958	0.9837	0.7642	0.2893	0.9757	0.9193	0.9036
40	17.240	22.3769	2.20	0.8758	23.0627	0.579	0.9839	0.9094	0.2249	0.9836	1.2049	0.9461

# 6. Effect of Temperature

Adsorption studies were also carried out at different temperatures i.e., 33<sup>o</sup>C, 38<sup>o</sup>C, 43<sup>o</sup>C and 48<sup>o</sup>C with a fixed dose of adsorbent and the results are presented in the Figure 11. The rate of the uptake of dye increases with increasing temperature indicating the endothermic nature of the process.



## 6.1 Thermodynamic of Adsorption

Thermodynamic parameters like  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were evaluated using Van't Hoff's equation:

 $ln \ K_c = \Delta S^{\circ} / R \ \text{-} \Delta H^{\circ} / \ R$ 

Where  $K_c$  is the Langmuir equilibrium constant,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are the standard enthalpy and entropy changes of adsorption respectively and their values are calculated from the slopes and intercepts respectively of the linear plot of ln Kc Vs 1/T. The free energy change for the adsorption process  $\Delta G^{\circ}$  is derived using the relation

 $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ 

Negative free energy and positive entropy change of adsorption indicate that the adsorption process is favorable and spontaneous in nature. The endothermic nature of adsorption is confirmed by the positive  $\Delta H^{\circ}$  value.

# 7. Conclusion

The present study showed that SAPS can be used as an effective adsorbent for the removal of Crystal violet from aqueous solution. The study of the influence of various parameters (contact time, initial dye concentration, adsorbent dosage, particle size, pH and temperature) has led to the conclusion that the dye is quickly adsorbed by the SAPS. Adsorption process obeys both Langmuir and Freundlich isotherm and also follows pseudo second order kinetics, with intraparticle diffusion as one of the rate determining steps.

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