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# Kinetic and Thermodynamic Studies of Adsorption of Crystal Violet Dye Using a Low Cost Activated Carbon Prepared from *Bauhenia racemosa* Seed

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**In this study the efficiency of low cost eco-friendly carbon adsorbent prepared from *Bauhenia racemosa* seed (BRSC) was analysed for the removal of crystal violet (CV) dye from aqueous solution. Kinetics and thermodynamic parameters of the adsorption of crystal violet dye were evaluated. Adsorption kinetics is an important parameter as it provides significant details, such as reaction pathways and mechanism of the reactions. The adsorption kinetics of crystal violet dye onto *Bauhenia racemosa* seed followed Pseudo second order reaction model. The intraparticle diffusion study shows that the rate constant for intraparticle diffusion ($K_p$) increased with increase in initial concentration of crystal violet dye solution. The results of the thermodynamic studies revealed that the adsorption of crystal violet dye onto *Bauhenia racemosa* seed was spontaneous and endothermic in nature. The positive value of entropy change showed increased randomness during adsorption.**

**KEYWORD**

*Bauhenia racemosa* seed, Kinetic modelling, Lagergren pseudo first order, Pseudo second order, Intraparticle diffusion, Enthalpy change, Entropy change, Free energy change.

## INTRODUCTION

Industries, such as textile, paper, plastic, paint, printing, leather, cosmetic, drug and carpet consume enormous amount of water to colour their products. The effluents discharged from these industries are highly coloured with large amounts of suspended organic solid. Most of the dyes are stable to biological degradation and reduce photo synthetic action by inhibiting sunlight penetration. Untreated disposal of this coloured water into the receiving water bodies causes damage to aquatic life and human beings by their mutagenic and carcinogenic effect (McKay *et al.,* 1985). Activated carbon is a most efficient widely used adsorbent in the effluent treatment. However, high cost in the procurement of activated carbon restricts its use in the developing countries, like India. This has led to the development of many non-conventional low-cost adsorbents for the removal of dyes from industrial effluents. Hence the present study is aimed at utilising a low-cost, eco-friendly adsorbent *Bauhenia racemosa* seed carbon for the removal of crystal violet dye from aqueous solution. Crystal violet plays a major role in textile dyeing and paper printing. It is used as a dermatological agent and as a veterinary medicine. It can act as an additive to poultry feed to restrain the propagation of mould, intestinal parasites and fungus. In human beings, crystal violet causes eye irritation and permanent injury to the cornea (Ho and McKay, 1998). Crystal violet dye causes mutagenic and mitotic poisoning in humans and cause cancer (Jain and Jayaram, 2010). In water it gets readily absorbed into the fish tissues and affects the respiratory system and cause kidney failure and also it is highly toxic to mammalian cells (Ho and McKay, 1998). Hence the present study is focussed on the use of a low cost activated carbon prepared from the seeds of *Bauhenia*

*racemosa* using conc.sulphuric acid in the removal of crystal violet dye from aqueous solution. Kinetic and thermodynamic parameters have been investigated and presented in this paper.

## MATERIAL AND METHOD

The activated carbon was prepared from the seeds of *Bauhenia racemosa* by treatment with conc. sulphuric acid. The *Bauhenia racemosa* belonging to the family *Caesalpiniaceae* and is abundantly found in Tamil Nadu, Kerala and Karnataka. The tree *Bauhenia racemosa* is a road side shade tree available plenty in number in Udumalpet and Pollachi areas of Tamil Nadu.

### Preparation of the adsorbent

The seeds of *Bauhenia racemosa* were collected and cut into small pieces, dried in sunlight for 10 days and further dried in hot air oven at 60°C for 24 hr. The completely dried material was powdered well and chemically activated by treating it with concentrated sulphuric acid with constant stirring and kept for 24 hr. It is then activated at 110°C in the hot air oven for 12 hr. The carbonised material thus obtained was washed well with plenty of distilled water several times to remove the excess acid present and then dried at 100°C to 120°C in a hot air oven for 24 hr. The adsorbent thus obtained was ground well and sieved through a 125-250 mesh and kept in air tight containers for further use.

### Preparation of adsorbate

Stock solution (1000 mg/L) of crystal violet dye was prepared by dissolving 1 g of crystal violet dye in 1000 mL of double distilled water. All the test solutions were prepared by diluting the stock solution with double distilled water.

### Equipment's used

Elico pH meter was used to measure pH. Digital Systronic model 104 spectrophotometer was used for measuring the concentration of the dye solution. Lab line mechanical shaker with temperature control was used to for the shaking of solution containing adsorbent and adsorbate.

### Adsorption studies

Batch mode experiments were performed to study the effect of contact time, concentration of the adsorbate and temperature. In the adsorption experiments 50 mL of the dye solutions of the desired concentration and pH were taken in Pyrex bottles containing pre-determined weighed amounts of adsorbents. The Pyrex bottles containing adsorbent and adsorbate were equilibrated by shaking the contents at room temperature using thermostated rotary shaker (200 rpm) for different time intervals (10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160 and 0 min). Then the solutions were filtered using Whatmann 40 filter paper and the filtrates were analysed for the residual crystal violet dye concentration spectrophotometrically at a wavelength of 570 nm against a reagent blank.

## RESULT AND DISCUSSION

### Effect of initial dye concentration of crystal violet dye solution on crystal violet dye removal

The initial concentration of crystal violet dye solution was varied (20, 30, 40 and 50 mg/L) and batch experiments were carried out by taking 50 mL of the crystal violet solution with fixed adsorbent dosage of 100 mg of the adsorbent at pH 6.8. The system was equilibrated by shaking the contents of the flask at 32°C. The results obtained reveal that the percentage removal of crystal violet dye decreases with increase in initial dye concentration and this may be due to the saturation of adsorption sites on the adsorbent surface (Jayarajan *et al.*, 2011; Mane and Vijay Babu, 2011). The amount of dye adsorbed $q_e$ (mg/g) increases with increase in contact time at all initial dye concentrations used in this study (Table 1) is on par with the results by various researchers (Marius *et al.*, 2011; Mittal *et al.*, 2010). This is so because the initial dye concen-

**Table 1.** *Adsorption of crystal violet dye with variation of initial concentration of crystal violet dye solution*

Condition : Adsorbent dose: 100 mg, pH : 6.8 ± 0.02, Temperature : 32°C

| Contact time, min | q, mg/g | | | |
|---|---|---|---|---|
| | 20 ppm | 30 ppm | 40 ppm | 50 ppm |
| 10 | 4.28 | 6.02 | 7.42 | 8.63 |
| 20 | 5.86 | 8.21 | 10.00 | 12.14 |
| 30 | 7.26 | 10.12 | 12.34 | 14.99 |
| 40 | 8.52 | 11.71 | 14.29 | 16.47 |
| 50 | 9.13 | 12.88 | 15.99 | 17.43 |
| 60 | 9.69 | 13.24 | 17.02 | 19.4 |
| 80 | 9.69 | 13.65 | 17.62 | 21.23 |
| 00 | 9.69 | 13.65 | 17.62 | 21.44 |
| 120 | 9.69 | 13.65 | 17.62 | 21.44 |
| 140 | 9.69 | 13.65 | 17.62 | 21.44 |
| 160 | 9.69 | 13.65 | 17.62 | 21.44 |
| 180 | 9.69 | 13.65 | 17.62 | 21.44 |

**Table 2.** *Kinetic modelling for crystal violet adsorption using Lagergren's pseudo first order equation*

Condition : Adsorbent dose : 100 mg, pH : 6.8 ± 0.02, Temperature : 35°C

| Time, min | log ($q_e$-$q_t$) | | | |
|---|---|---|---|---|
| | 20 ppm | 30 ppm | 40 ppm | 50 ppm |
| 10 | 0.7332 | 0.8822 | 1.008 | 1.1076 |
| 20 | 0.5832 | 0.7352 | 0.8816 | 0.9685 |
| 30 | 0.3856 | 0.5471 | 0.7221 | 0.8095 |
| 40 | 0.0682 | 0.286 | 0.5221 | 0.6963 |
| 50 | -0.2518 | -0.1169 | 0.2095 | 0.6031 |
| 60 | - | -0.3958 | -0.2247 | 0.3096 |
| 80 | - | - | - | -0.6778 |
| 100 | - | - | - | - |
| Slope | -0.0248 | -0.0263 | -0.0239 | -0.0232 |
| Intercept | 1.0492 | 1.2437 | 1.3577 | 1.5084 |
| $R^2$ | 0.9874 | 0.9865 | 0.9724 | 0.9376 |

**Table 3.** *Kinetic modelling for crystal violet adsorption using pseudo second order equation*

Condition : Adsorbent dose : 100 mg, pH : 6.8 ± 0.02, Temperature : 32°C

| t, min | $t/q_t$ | | | |
|---|---|---|---|---|
| | 20 ppm | 30 ppm | 40 ppm | 50 ppm |
| 10 | 2.33 | 1.66 | 1.35 | 1.16 |
| 20 | 3.41 | 2.43 | 1.99 | 1.65 |
| 30 | 4.13 | 2.96 | 2.43 | 2 |
| 40 | 4.69 | 3.41 | 2.79 | 2.43 |
| 50 | 5.48 | 3.88 | 3.13 | 2.87 |
| 60 | 6.19 | 4.53 | 3.52 | 3.09 |
| 80 | 8.25 | 5.86 | 4.54 | 3.77 |
| 100 | 10.32 | 7.33 | 5.68 | 4.66 |
| 120 | 12.38 | 8.79 | 6.81 | 5.6 |
| 140 | 14.45 | 10.26 | 7.94 | 6.57 |
| 160 | 16.63 | 11.73 | 9.08 | 7.46 |
| 180 | 18.71 | 13.19 | 10.21 | 8.39 |
| Slope | 0.0964 | 0.0678 | 0.0521 | 0.0418 |
| Intercept | 0.9633 | 0.7451 | 0,6251 | 0.6883 |
| $R^2$ | 0.9978 | 0.9982 | 0.9978 | 0.9983 |

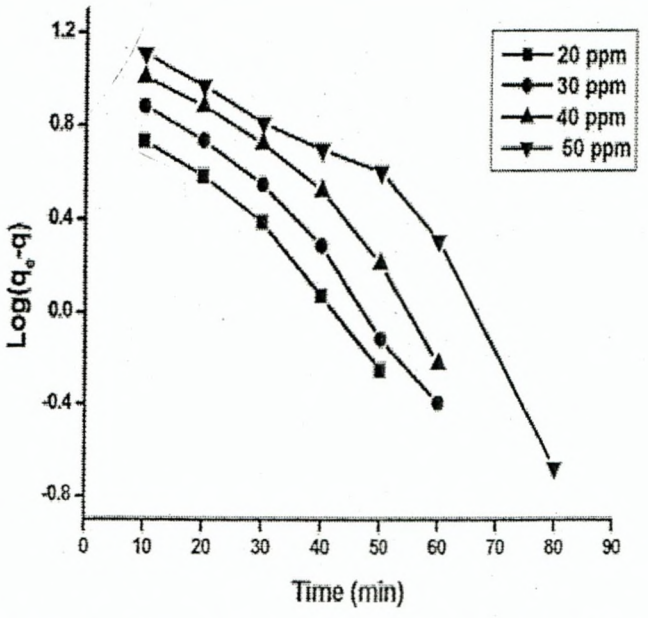


Figure1. *Lagergren's plots for crystal violet adsorption*

tration provides the driving force to overcome the resistance to the mass transfer of

**Table 4.** *Comparison of pseudo first and second order adsorption rate constant and calculated and experimental $q_e$ values for different initial dye concentration*

| Dye conc., mg/L | First order kinetic model | | | | Second order kinetic model | | |
|---|---|---|---|---|---|---|---|
| | $q_e$ (exp), mg/g | $k_1 x10^{-2}$, 1/min | $q_e$ (cal), mg/g | $R^2$ | $k_2 x10^{-3}$, g/mg/min | $q_e$ (cal), mg/g | $R^2$ |
| 20 | 9.69 | 5.711 | 11.20 | 0.9874 | 9.65 | 10.37 | 0.9978 |
| 30 | 13.65 | 6.057 | 17.53 | 0.9865 | 6.17 | 14.75 | 0.9982 |
| 40 | 17.62 | 5.504 | 22.79 | 0.9724 | 4.34 | 19.19 | 0.9978 |
| 50 | 21.44 | 5.343 | 32.34 | 0.9376 | 2.54 | 23.92 | 0.9983 |

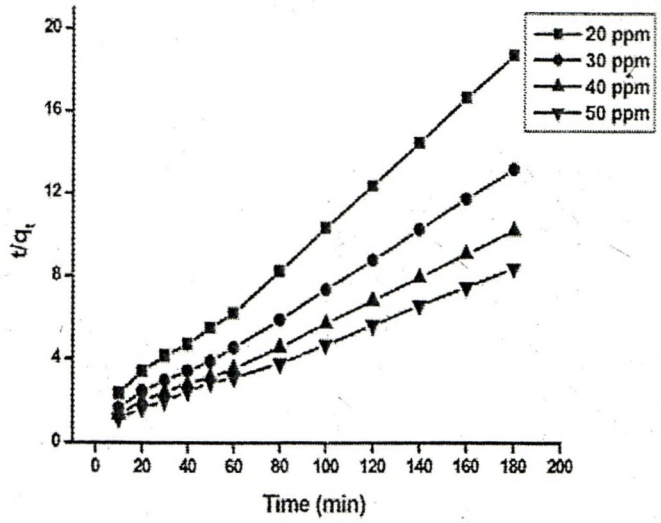


**Figure 2.** *Pseudo second order adsorption*

dye between the aqueous and the solid phase.

**Adsorption kinetics**

Lagergren's pseudo first order, pseudo second order and intraparticle diffusion models were applied to the experimental data obtained in this study. Lagergren's first order rate equation is given as follows (Ho and McKay,1998) :

$$\log q_e - q_t = \log q_e - k_1 t / 2.303 \quad ...(1)$$

Where $q_e$ and $q_t$ (mg/g) are the amount of dye adsorbed at equilibrium and at time t and $k_1$ (1/min) is the rate constant of the pseudo first order adsorption (Table 2). The plot of values of log ($q_e$-$q_t$) vs t gives a linear relationship (Figure 1). The values of $k_1$ and $q_e$ were calculated from the slope and intercept of the plots, respectively.

The second order Lagergren's equation was given (Ho and McKay,1999) as follows :

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad ...(2)$$

Where $k_2$ (g/mg/min) is the rate constant of pseudo second order adsorption.

From table 3 and figure 2 ($t/q_t$ vs t), $q_e$ and $k_2$ were calculated from the slope and intercept of the plot, respectively.

The first and second order adsorption rate constants with experimental and calculated $q_e$ values for different initial crystal violet dye solution concentrations are tabulated in table 4.

The values of $R^2$ are close to unity in pseudo second order (0.998) than that of pseudo first order. The values of $q_e$ calculated from pseudo second order are in good agreement with $q_e$ experimental values. This indicates that crystal violet adsorption system obeys the pseudo second order kinetic rate equation.

**Intraparticle diffusion**

The intraparticle diffusion model was proposed by Weber and Morris (1963). The intraparticle diffusion rate equation is expressed as :

$$q_t = K_p t^{0.5} + C \quad ...(3)$$

Where C is the intercept and $K_p$ is the intraparticle diffusion rate constant (mg/g $min^{0.5}$) which can be calculated from the slope of the linear plot of $q_t$ vs $t^{1/2}$ given in table 5. Figure 3 shows the plot of intraparticle diffusion of crystal violet onto *Bauhenia racemosa* seed. The experimental data showed a multi linear plot which indi-

**Table 5.** Intraparticle diffusion rate equation for adsorption crystal violet dye

Condition : Adsorbent dose : 100 mg, pH : 6.8 ± 0.02, Temperature : 32°C

| $t^{1/2}$, min | q, mg/g | | | |
|---|---|---|---|---|
| | 20 ppm | 30 ppm | 40 ppm | 50 ppm |
| 3.162 | 4.28 | 6.02 | 7.42 | 8.63 |
| 4.472 | 5.86 | 8.21 | 10.00 | 12.14 |
| 5.477 | 7.26 | 10.12 | 12.34 | 14.99 |
| 6.324 | 8.52 | 11.71 | 14.29 | 16.47 |
| 7.071 | 9.13 | 12.88 | 15.99 | 17.43 |
| 7.745 | 9.69 | 13.24 | 17.02 | 19.40 |
| 8.944 | 9.69 | 13.65 | 17.62 | 21.23 |
| 10.000 | 9.69 | 13.65 | 17.62 | 21.44 |
| 0.954 | 9.69 | 13.65 | 17.62 | 21.44 |
| 11.832 | 9.69 | 13.65 | 17.62 | 21.44 |
| 12.649 | 9.69 | 13.65 | 17.62 | 21.44 |
| 13.416 | 9.69 | 13.65 | 17.62 | 21.44 |
| Slope | 0.4506 | 0.6461 | 0.9099 | 1.1747 |
| Intercept | 4.7409 | 6.5121 | 7.4929 | 8.1339 |
| $R^2$ | 0.8237 | 0.8398 | 0.8639 | 0.9061 |

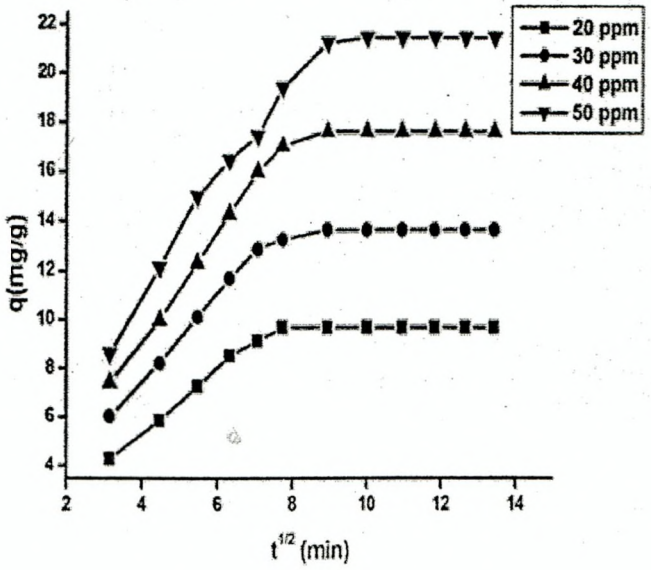


**Figure 3.** *Intraparticle diffusion plots for crystal violet dye adsorption*

cates that two or more steps influence the adsorption process. The first linear portion is due to the diffusion of adsorbate through the solution to the external surface or boundary layer diffusion of solute molecules. The second linear portion showed the gradual reach of equilibrium stage and the third linear portion is due to low adsorbate concentration left in the solution (Mane and Vijay babu, 2011).

**Table 6.** CV dye adsorption with the temperature variation

| Time, min | % Adsorption of CV dye | | |
|---|---|---|---|
| | 300 K | 308K | 313K |
| 10 | 35.1 | 38.0 | 42.5 |
| 20 | 42.4 | 48.5 | 57.2 |
| 30 | 53.0 | 60.0 | 65.4 |
| 40 | 61.0 | 68.2 | 73.0 |
| 50 | 69.0 | 75.3 | 80.6 |
| 60 | 75.0 | 80.3 | 84.4 |
| 90 | 83.3 | 86.6 | 89.0 |
| 120 | 87.0 | 89.0 | 90.9 |
| 150 | 89.0 | 90.5 | 91.2 |

The slope of the first linear plot gives the intraparticle rate constant ($k_p$) and intercept of this portion is proportional to the thickness of the boundary layer (Weng *et al.*, 2009). The lines lies obtained by plotting q vs $t^{1/2}$ are not passing through the origin and, therefore, the intraparticle diffusion alone is not the rate determining step and boundary layer control may also be involved in the process. From table 5, it was observed that the values of C increased with increase in concentration of crystal violet dye solution which showed an increase in the thickness and the effect of boundary thickness.

**Adsorption thermodynamic**

Adsorption of crystal violet dye was carried out using 50 mL of crystal violet dye solution containing 50 mg/L of crystal violet dye with 100 mg of adsorbent at pH 6.8 ± 0.02 by varying the temperature. The change in standard free energy, enthalpy and entropy of adsorption were calculated using the following equation :

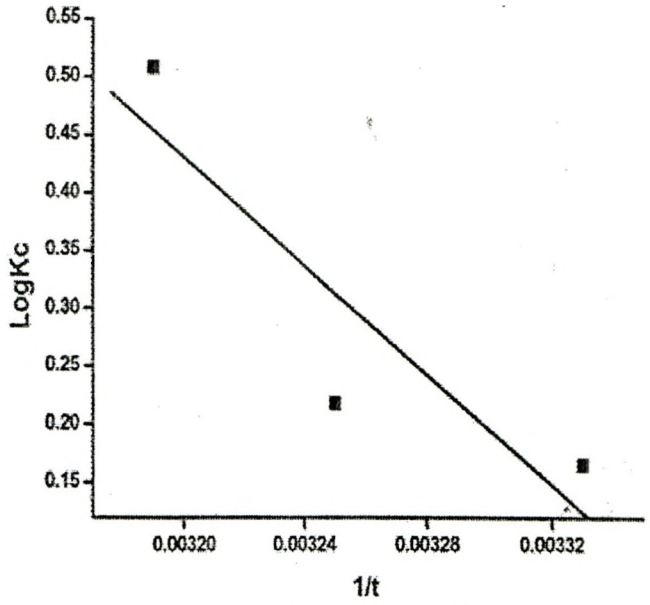


**Figure 4.** *Vant Hoff plot for crystal violet adsorption*

**Table 7.** *Thermodynamic parameter*

| T (K) | $\Delta G^0$ | $\Delta H^0$ | $\Delta S^0$ |
|---|---|---|---|
| 300 | -0.9474 | 45.05 | 152.43 |
| 308 | -1.9579 | — | — |
| 313 | -3.2214 | — | — |

$$\Delta G^0 = -RT \ln K_c \quad ...(4)$$

Where R is gas constant, $K_c$ is equilibrium constant and T is temperature in 'K'.

According to the Vant Hoff equation :

$$\log_{10} K_c = \Delta S^0/2.303R - \Delta H^0/2.303\ RT \quad ...(5)$$

Where $\Delta S^0$ and $\Delta H^0$ are change in entropy and enthalpy of adsorption, respectively. Plot of log $K_c$ vs 1/T is linear (Figure 4). The value of $\Delta S^0$ and $\Delta H^0$ were evaluated from the slope and intercept of Vant Hoff plots (Table 7).

The negative values of $\Delta G^0$ obtained in this study indicate that the adsorption process is spontaneous. The values of $\Delta H^0$ and $\Delta S^0$ calculated are 45.05 kJ/mol and 152.43 J/mole/K, respectively. The positive values of $\Delta H^0$ and $\Delta S^0$ indicate that the adsorption process is of endothermic and entropy controlled process.

## CONCLUSION

The kinetic study of crystal violet dye adsorption onto *Bauhenia racemosa* seed carbon has revealed that the pseudo second order rate equation is more suitable than pseudo first order rate equation. The intraparticle diffusion study shows that the rate constants for intraparticle diffusion ($K_p$) increased with increase in initial concentration of crystal violet dye solution and this is due to concentration diffusion. The adsorption process is endothermic and spontaneous in nature and the evaluated thermodynamic parameters, such as negative value of standard enthalpy change ($\Delta H^0$) and negative value of standard free energy change ($\Delta G^0$) supports the favourable adsorption. The positive standard entr change ($\Delta S^0$) indicate increased randomn during the adsorption process.

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