SPECTROSCOPIC ANALYSIS OF CRYSTAL VIOLET DYE REMOVAL BY SIDA RHOMBIFOLIA: KINETIC, EQUILIBRIUM, THERMODYNAMIC STUDIES

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ABSTRACT
The kinetics, adsorption isotherms, thermodynamics and spectroscopic analysis of the removal of the crystal violet dye by adsorption onto Sida Rhombifolia were studied. The surface area of Sida Rhombifolia activated carbon (SRAC) was found to be 18.14 m²/g. Batch adsorption experiments were conducted using dye solution and the effects of initial dye concentration and contact time, adsorbent dose and temperature were investigated. The Sida Rhombifolia adsorbent was characterized using FTIR, SEM with EDAX, BET and XRD. The equilibrium adsorption data fitted very well with the Langmuir, Temkin and D-R isotherm model. The kinetic process followed the pseudo second order kinetic model Positive ΔH° and negative ΔG° were indicative of the endothermic and spontaneous nature respectively of Crystal violet removal by adsorption onto Sida Rhombifolia.

Keywords: Crystal violet, Sida rhombifolia, Langmuir, kinetic, adsorption.

INTRODUCTION
Recently, environmental contaminations by synthetic dyes have become a serious problem due to their negative ecotoxicological effects and bioaccumulation in wildlife. Most of these dyes are toxic, mutagenic, and carcinogenic. They are extensively used in industries such as textile, paint, acrylic, cosmetics, leather and pharmaceutical, which generate a considerable
amount of colored wastewater. It is difficult to degrade dyes because they have complex structure and most of them contain aromatic rings, which make them mutagenic and carcinogenic \cite{1-3}. The color in water bodies reduces light penetration and photosynthesis, therefore, affects the aquatic life. Moreover, dyes are one of esthetic pollution and eutrophication sources. So it is highly desirable to remove dyes from water/wastewater before discharging.

Various techniques such as chemical precipitation \cite{4}, coagulation \cite{5}, biochemical degradation \cite{6}, solvent extraction \cite{7}, sonochemical degradation \cite{8}, photo catalytic degradation \cite{9}, micellar enhanced ultra filtration \cite{10}, electrochemical degradation \cite{11}, ozone oxidation \cite{12-13}, ion exchange \cite{14-16} and adsorption \cite{17-20} etc., are used to remove dyes from wastewater. Among them, adsorption has been recognized as a reliable alternative due to its ease of operation, simplicity of design, high efficiency, insensitivity of toxic substances and comparable low cost of application.

In as much as cost of these methods is quite high, adsorption has a superior for the treatment of wastewaters compared to the above mentioned processes \cite{21}. There is a need to produce low cost and effective carbons that can be applied to water pollution control. A wide variety of low cost materials has been exploited for the removal of dyes from aqueous solutions, including lemon peel \cite{22}, sugarcane dust \cite{23}, orange peel \cite{24}, ground nut shell \cite{25}, coconut tree \cite{26}, etc.

In the present study, SRAC prepared from waste kurumthotti (Sida Rhombifolia) by chemical activation with con.\text{H}_2\text{SO}_4 was used as an adsorbent to removal of basic Crystal violet dye (CV) from aqueous solution. The objective of the work is to examine the applicability of the prepared activated carbon in removing basic dyes from aqueous solutions. The effects of different parameters including initial concentration of dye solution and contact time, adsorbent dose and temperature were investigated. The adsorption kinetics, isotherms and thermodynamic properties were also explored.

**MATERIALS AND METHODS**

**Dye Solution Preparation**

The dye crystal violet [C.I name = Basic violet 4, chemical formula weight = 407.9, \( \lambda_{\text{max}} = 617\text{nm} \)] is supplied by S.D fine Chemicals, Mumbai, India was used as such without further
purification. An accurately weighed quantity of dye was dissolved in double distilled water to prepare the stock solutions.

**Adsorbent**

Kurumthotti (*Sida Rhombifolia*) was used as an adsorbent, was collectively obtained from Nedunkulam, Sivagangai (India) washed with tap water and finally with double distilled water to remove the suspended impurities, dust, and soil and then dried in oven. About 500g of powdered kurumthotti was mixed with 100ml of con. sulfuric acid and kept at room temperature for 24h. and was then dried in a hot air oven at 80°C. The dried material was washed with distilled water for removing excess of acid. Finally charcoal was dried in 110°C for 12 h to remove moisture and kept in an airtight bottle[27].

**Adsorption Experiments**

Batch mode adsorption studies were carried out by adding certain amount of adsorbent and 50ml of dye solutions of certain concentrations, dose, contact time and temperatures in a thermo stated water bath shaker with a shaking of 200 rpm. The samples were withdrawn from the shaker at predetermined time intervals and solutions were separated from the adsorbent by centrifugation at 4000 rpm for 5 min. To determine the residual dye concentration, the absorbance of the supernatant solution was measured before and after treatment with double beam spectrophotometer (JASCO V530 Spectrophotometer). Experiments were carried out twice and the concentrations given were average values. The initial dye concentrations in the test solution and the contact time were changed to investigate their effect on the adsorption kinetics. The pH of the dye solution was adjusted by using NaOH or HCl solution. The adsorption studies were carried out at different temperatures (308K, 318K and 328K). This is used to determine the effect of temperature on the thermodynamic parameters.

The amount of adsorption in batch experiments, \( q \) (mg g\(^{-1}\)) (1) and adsorption efficiency (2) were calculated as follows

\[
q = \frac{(C_o - C_e)}{m} \times V \quad (1)
\]

Efficiency (%) = \( \frac{(C_o - C_e)}{C_o} \times 100 \quad (2) \)

Where, \( C_o \) is the initial concentration (mg.L\(^{-1}\))
\( C_e \) is the equilibrium concentration (mg.L\(^{-1}\))
\( V \) is the volume of solution (mL)
\( M \) is the mass of adsorbent (g)
\( q \) is the amount of adsorbed (mg/g)
Surface Characteristic of the Adsorbent

Surface area and porous size distribution of SRAC sample were measured by nitrogen adsorption analysis (Quantachrome V5.02). Crystal structure of sample was determined by performing X-ray diffraction (XRD) on SHIMADZU 6000 X-ray diffraction spectrometer. Surface morphologies were examined by a scanning electron microscope (SEM, JEOL (JSM 6390) with the working distance of 9.9 mm and an accelerating voltage of 30 keV. The SEM was equipped with an energy dispersion spectrometer (EDS) and it was used to perform the analysis of chemical constituents of the adsorbent. Infrared absorption spectroscopy (IR) spectra were measured at room temperature on a Fourier transform infrared (FTIR) spectroscopy (8400s SHIMADZU spectrometer) using the KBr pellet technique.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

BET

The surface area of SRAC was found to be 18.14 m²/g. Total pore volume is 10.00 cm³/g and pore size is 408.3Å. SRAC has a relatively promising surface area although it was obtained from kurumthotti only by carbonization process as shown in “Fig. 1”.

![Adsorption-desorption isotherms of nitrogen at 77 K on SRAC](image)

Fig. 1. Adsorption-desorption isotherms of nitrogen at 77 K on SRAC
FTIR

FTIR spectra of the raw material, SRAC, SRAC-CV, MAC-CR were shown in “Fig. 2”, FTIR data of raw material showed that characteristic band at 3285.1, 1624.5, 1238.0 and 1032.5 cm\(^{-1}\) correspond to the free OH, aliphatic, C=C stretching and C-O-C stretching vibrations respectively “Fig. 2”, (a).

The FTIR spectrum of chemical activated carbon (SRAC) was exhibited in “Fig. 2”, (b) After modification Free OH group disappeared. The new band appeared at 1601.6 cm\(^{-1}\) and 1013.7 was assigned to C=O stretching vibration and C-O-C vibrations respectively. The band observed at 755.6 cm\(^{-1}\) was due to the CH=CH stretching vibrations.

“Fig. 2”, (c) indicated that mostly the bonded C=O stretching, C-H bending vibrations, C-O-C vibrations and –CH=CH- were involved in CV adsorption. A new band was observed in the after adsorption at 1438.44. There were clear band shifts and intensity decrease in “Fig. 2”, (c) These findings suggest that there is attachment of CV on the SRAC.

![Fig. 2. FTIR spectra of: (a) Raw material (b) SRAC (c) SRAC-CV](image)

XRD

The XRD patterns as shown in “Fig. 3”, were performed to analyze the crystalline nature. The characteristic 20-30° peaks of SRAC were discernible in carbon, the diffraction spectrum of SRAC did not show any obvious crystalline peak at the scan range 10-60° thereby indicating the amorphous phase of SRAC.
SEM

“Fig. 4”, showed the SEMs of SRAC and SRAC adsorbed CV dye. The particles (“Fig. 2”, (a) appeared obviously diverse. Clearly, there were particle fragments and irregular structure on the surface. Such cracks and irregularities are beneficial for the dye removal to diffuse to the inner adsorption sites located in the interior portion of the adsorbent. “Fig. 2”, (b) showed micrographs of the SRAC surface after adsorbed CV dye, which is covered with some small particulates on the surface, suggesting CV dye has been adsorbed.

EDX

Further confirmation of the adsorption of CV on SRAC carbon was done by energy dispersive X-ray analysis (EDX). “Fig. 5”, (a) for the unloaded SRAC showed four characteristic signals for C, O, S and Ca composition as 82.93%, 16.11%, 0.78% and 0.18%
respectively. The EDS spectrum “Fig. 5”, (b) of after adsorption of SRAC-CV presented the same element but C atomic percentage was decreased from 82.93 to 61.98% and oxygen percentage was increased from 16.11 to 36.76%. The Ca atom also increased from 0.18 to 0.91%. The S atom also decreased from 0.78 to 0.35%. It provided an evidence for CV adsorption onto SRAC surface.

**Fig. 5.** Energy dispersive spectra of (a) SRAC (b) SRAC-CV

**UV-Visible**

“Fig. 6”, (a) indicates that before the adsorption of CV dye a high intensity peak is observed but after the adsorption of CV dye onto SRAC the peak intensity decreased due to dye adsorption shown in “Fig. 6”, (b)

**Fig.6.** UV-Vis spectra of (a) Before adsorption of CV dye (b) After adsorption of CV dye
The effect of initial CV concentration on the percentage removal of the dye is shown in Table.1. The initial CV concentration was varied from 50 to 90 mg/L. A rapid initial adsorption of CV took place within the first 20 min, after which the adsorption slowed down and then almost reached at 50 min. The percentage of CV removal evidently decreased with increasing initial dye concentration. The percentage of removal was 87% for 50 mg/L initial concentration and only 26.2% for 90 mg/L after 50 min of adsorption. This was caused by an increase in the mass gradient pressure between the solution and adsorbent. The gradient acted as the force that drove the transfer of the dye molecules from the bulk solution to the particle surface.

**Effect of Adsorbent Mass**

The effect of adsorbent dosage varied from 0.010 to 0.050 g/L on the percentage removal of 50 mg/L CV solution is shown in Table.2. The percentage of removal of CV from the solution increased from 35.10% to 70.21% as the adsorbent dosage increased from 0.010 to 0.050 g/L. This result is expected because of the increased adsorbent surface area and availability of more adsorption sites caused by increasing adsorbent dosage.

### Table.1. Effect of dye concentrations

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Crystal violet dye concentrations (ppm)</th>
<th>Adsorption Efficiency (%)</th>
<th>Amount of adsorbed (q) mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
<td>60</td>
<td>70</td>
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<tr>
<td>10</td>
<td>59.2</td>
<td>54.8</td>
<td>12.2</td>
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<tr>
<td>20</td>
<td>68.5</td>
<td>67.7</td>
<td>20.0</td>
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<td>30</td>
<td>81.4</td>
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<td>27.7</td>
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<tr>
<td>40</td>
<td>83.3</td>
<td>77.4</td>
<td>30.0</td>
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<tr>
<td>50</td>
<td>87.0</td>
<td>82.7</td>
<td>36.6</td>
</tr>
</tbody>
</table>

### Table.2. Effect of Adsorbent mass (g)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Adsorption mass (g)</th>
<th>Adsorption Efficiency (%)</th>
<th>Amount of adsorbed (q) mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.010</td>
<td>0.020</td>
<td>0.030</td>
</tr>
<tr>
<td>10</td>
<td>6.3</td>
<td>8.5</td>
<td>29.7</td>
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<td>20</td>
<td>15.9</td>
<td>18.0</td>
<td>35.1</td>
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<td>21.2</td>
<td>26.5</td>
<td>37.2</td>
</tr>
<tr>
<td>40</td>
<td>27.6</td>
<td>38.2</td>
<td>43.6</td>
</tr>
<tr>
<td>50</td>
<td>35.1</td>
<td>44.6</td>
<td>50.0</td>
</tr>
</tbody>
</table>
Adsorption Isotherms: The experimental data collected at 298 K and the initial concentration of 50 mg/L were fitted on the standard models used in waste water treatment application: Langmuir, Freundlich, Temkin, Jovanoic and D-R isotherm respectively.

A Langmuir isotherm assumes monolayer onto a surface containing a finite number of adsorption with no transmigration of the adsorbate in the plane of the surface. The linear form of the Langmuir isotherm equation is given as

\[
\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m}
\]

(3)

Where \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), \( q_e \) is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), \( K_L \) the Langmuir adsorption constant (L/mg), and \( q_m \) is the theoretical maximum adsorption capacity (mg/g). Plotting \( C_e/q_e \) “Fig. 7”, gives a straight line with slope and intercept equal to \( q_e \) and \( K_L \), respectively.

![Fig. 7. Langmuir isotherm plots for the adsorption of CV onto SRAC](image)

In order to determine if the adsorption process is favorable or unfavorable, a dimensionless constant separation factor or equilibrium parameter \( R_L \) is defined according to the following equation [28]

\[
R_L = \frac{1}{1 + K_L C_o}
\]

(4)

Where, \( K_L \) is the Langmuir isotherm constant (L/mg) and \( C_o \) is the initial dye concentration (mg/L). The \( R_L \) value indicates the type of the isotherm to be either unfavorable \((R_L>1)\), linear \((R_L=1)\), favorable \((0<R_L<1)\), irreversible \((R_L=0)\).
The Freundlich isotherm, on the other hand, assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [29]. The well known logarithmic form of the Freundlich isotherm is given by the following equation

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (5)

where, $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), $K_F$ and $n$ are Freundlich constants with $n$ giving an indication of how favorable the adsorption process is and $K_F$ (mg/g) is the adsorption capacity of the adsorbent. Plotting $\ln q_e$ against $\ln C_e$ gives a straight line with slope and intercept equal to $1/n$ and $\ln K_F$, respectively. The Freundlich constant $1/n$ is smaller than 1, indicates a more heterogeneous surface whereas a value closer to or equal to one indicates that the adsorbent has relatively more homogeneous binding sites.

In order to determine the type of adsorption, D-R isotherm has also been tested for the sorption of CV onto SRAC. The D-R equation can be defined by the following equation [30].

$$\ln q_e = \ln q_{m} - \beta \varepsilon^2$$  \hspace{1cm} (6)

In this equation, $\beta$ a constant related to the adsorption energy (mol$^2$/kJ$^2$), $q_m$ is a constant that indicates the sorption degree characterizing the sorbent (mg/g) and $\varepsilon$ is the Polanyi potential shown in Eq.7:

$$\varepsilon = RT \ln (1+1/C_e)$$  \hspace{1cm} (7)

Where, $T$ is the absolute temperature (K) and $R$ is the ideal gas constant ($R=8.314$ J/mol K).

By plotting $\ln q_e$ vs $\varepsilon^2$, it is possible to determine the value of $\beta$ from the slope and the value of $q_m$ from the intercept, which is $\ln q_m$.

The mean free energy $E$ (kJ/mol) of sorption can be estimated by using $\beta$ values as expressed in the following equation [31].

$$E = 1/ (2\beta)^{1/2}$$  \hspace{1cm} (8)

The magnitude of $E$ may characterize the type of the adsorption as chemical ion exchange ($E=8-16$ kJ/mol), or physical adsorption ($E<8$ kJ/mol). The mean free energy of adsorption for the present study was found to be CV has 0$s$ KJ/mol. This implies that, the adsorption of CV dye on SRAC may be considered as physical adsorption process.
The linearized form of Temkin isotherm is given as

\[ q_e = B_1 \ln K_T + B_1 \ln C_e \tag{9} \]

Temkin isotherm contains a factor that explicitly takes into account adsorbing species and adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by uniform distribution of binding energies, up to some maximum binding energy \(^{[32]}\). A plot of \( q_e \) versus \( \ln C_e \) enables the determination of the isotherm constants \( B_1 \) and \( K_T \) from the slope and the intercept, respectively. As shown in Fig 8, \( K_T \) is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and constant \( B_1 \) is related to the heat of adsorption.

![Fig. 8. Temkin isotherm plots for the adsorption of CV onto SRAC](image)

The Jovanovic isotherm \(^{[33]}\), which is based on the same assumptions of the Langmuir isotherm, also considers the possibility of some mechanical contacts between the adsorbing and desorbing molecules on the homogeneous surface and can be represented in a linear form as follows

\[ \ln q_e = \ln q_m + K_J C_e \tag{10} \]

where, \( q_m \) is the maximum amount adsorbed (in mg/g) and \( K_J \) (in L/mg) is the constant related to the energy of adsorption. The \( q_m \) and \( K_J \) can be calculated from the intercept and slope of the linear plot of \( \ln q_e \) against \( C_e \) “Fig. 9”,
Fig. 9. Jovanoic isotherm plots for the adsorption of CV onto SRAC

The $R^2$, $q_m$, $K_L$, $R_L$, $R^2$ (correlation coefficient for Langmuir isotherm), $K_F$, $n$, $R^2$ (correlation coefficient for Freundlich isotherm), $B_1$, $K_T$, $R^2$ (correlation coefficient for Temkin isotherm), $\beta$, $q_m$, $E$, $R^2$ (correlation coefficient for D-R isotherm), $R^2$, $K_j$, $q_m$ (correlation coefficient for Jovanoic isotherm), are given in Table 4. The data of Table 3 indicate that the Langmuir, Jovanoic and Temkin isotherms are the most appropriate for adsorption of CV on SRAC.

Table 3. Different adsorption isotherm model parameters for the adsorption of CV on SRAC.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Constants</th>
<th>Crystal violet dye Concentrations (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$R^2$</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>$q_m$ (mg/g) × 10^{-2}</td>
<td>2.79</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (l/mg) × 10^{-2}</td>
<td>29.85</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.060</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$R^2$</td>
<td>0.968</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>2.985</td>
</tr>
<tr>
<td></td>
<td>$K_F$ × 10^{-3}</td>
<td>195.8</td>
</tr>
<tr>
<td>Temkin</td>
<td>$R^2$</td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td>$B_1$</td>
<td>131.6</td>
</tr>
<tr>
<td></td>
<td>$K_T$</td>
<td>129.3</td>
</tr>
<tr>
<td>Jovanoic</td>
<td>$R^2$</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>$q_m$</td>
<td>6.338</td>
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<tr>
<td></td>
<td>$K_J$</td>
<td>2.559</td>
</tr>
<tr>
<td>D-R</td>
<td>$R^2$</td>
<td>0.964</td>
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<tr>
<td></td>
<td>$q_m$ (mg/g) × 10^{-5}</td>
<td>21.77</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$E$ (kJ/mol)</td>
<td>-</td>
</tr>
</tbody>
</table>
Kinetic Studies

Kinetic models have been proposed to determine the mechanism of the adsorption process which provides useful data to improve the efficiency of the adsorption and feasibility of process scale-up. The rate constants were calculated by using pseudo-first-order and pseudo-second-order kinetic models and the rate controlling step was determined by intra-particle diffusion model.

Pseudo-First-Order Model

The Lagergren pseudo first-order model is given by the following equation \[^{[34]}\].

\[
\ln (q_e - q_t) = \ln q_e - k_1 t 
\] (11)

where, \( q_e \) and \( q_t \) are the sorption capacities at equilibrium and time \( t \) respectively and \( k_1 \) represents the rate constant of the pseudo first-order kinetic model. The data obtained for sorption of CV on activated carbon based on the pseudo first–order kinetic model showed that the adsorption kinetics were not in good agreement with the pseudo first-order model. The inapplicability of the Lagergren model to describe the kinetics of CV adsorption was also reported by Lata et al \[^{[35]}\].

Pseudo-Second-Order Model

The linearized form of the pseudo second-order kinetic model is represented as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} 
\] (12)

Where, \( k_2 \) (g/mg/min) is the second-order rate constant of adsorption. The plot of \( t/q_t \) versus \( t \) shows a linear relationship. Values of \( k_2 \) and equilibrium adsorption capacity \( q_e \) were calculated from the intercept and slope of the plot shown in “Fig. 10”,

Intra-Particle Diffusion Model

For a solid-liquid adsorption process, the solute transfer is usually characterized by external mass transfer or intra-particle diffusion or both. The intra-particle diffusion model proposed by Weber and Morris \cite{36} was used to identify the mechanism involved in the adsorption process

\[ q_t = k_{id} t^{0.5} + C \]  \hspace{1cm} (13)

Where, \( k_{id} \) (mg/g/min\(^{0.5}\)) is the rate constant of the intra-particle diffusion model and C (mg/g) reflects the boundary layer effect. The \( k_{id} \) and C can be determined from the slope and intercept of the linear plot of \( q_t \) against \( t^{0.5} \) shown in “Fig. 11”,

![Fig. 10. Pseudo-second-order kinetic plots for adsorption of CV onto SRAC](image1)

![Fig. 11. Intra particle diffusion plots for adsorption of CV onto SRAC](image2)
The kinetic model parameters at different initial concentrations were determined. Table 4 summarizes the parameters and coefficients of the pseudo first-order and pseudo second-order kinetic and intra-particle diffusion model. Among the tested models, the correlation coefficient ($R^2$) for the pseudo-second-order adsorption model and intraparticle diffusion model has high value (> 98). These facts suggested that the pseudo-second-order adsorption mechanism was predominant, and that the overall rate of the CV adsorption process appeared to be controlled by the chemisorptions process.

Table 4. Kinetic parameters for the adsorption of CV dye onto SRAC

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>First-order model</th>
<th>Second-order model</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$q_e$ mg/g $\times 10^{-4}$</td>
<td>$k_1$ min$^{-1}$</td>
</tr>
<tr>
<td>50</td>
<td>0.842</td>
<td>50.46</td>
<td>0.007</td>
</tr>
<tr>
<td>60</td>
<td>0.888</td>
<td>15.5</td>
<td>0.008</td>
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<td>70</td>
<td>0.904</td>
<td>3.176</td>
<td>0.024</td>
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<tr>
<td>80</td>
<td>0.943</td>
<td>4.315</td>
<td>0.022</td>
</tr>
<tr>
<td>90</td>
<td>0.933</td>
<td>0.254</td>
<td>0.042</td>
</tr>
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</table>

Effect of Temperature and Thermodynamic Data

The effect of temperature on the adsorption of CV on SRAC particles has been studied in the range of 308-328K, keeping all the other parameters constant at their optimum value, that is the sorbent mass (0.050g), the target dye concentration (50 mg/L) and the contact time (50 min). The results show that the adsorption of CV dye is favored by an increase in temperature.

Table 5. Effect of Temperature

<table>
<thead>
<tr>
<th>Adsorption Efficiency (%)</th>
<th>Amount of Adsorbed (q) mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>308 K</td>
<td>318 K</td>
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<tr>
<td>71.7</td>
<td>79.3</td>
</tr>
<tr>
<td>660</td>
<td>730</td>
</tr>
</tbody>
</table>

The thermodynamic parameters, namely the enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) associated with the adsorption process were calculated from the slope and intercept of the linear plot of $\ln K_L$ versus 1/T “Fig. 12”, using the following equation

$$\ln K_L = \Delta S^\circ - \frac{\Delta H^\circ}{R} - \frac{RT}{\Delta H^\circ}$$ (13)
where, $K_L$ is the distribution coefficient. The correlation coefficient for the linear plot was $R^2=0.975$ for CV dye.

![Graph](image)

**Fig. 12. van’t Hoff plots of ln $K_L$ versus 1/T for the adsorption of CV onto SRAC**

The Gibbs free energy of specific adsorption ($\Delta G^*$) was calculated using the equation:

$$\Delta G^* = \Delta H^* - T \Delta S^*$$  \hspace{1cm} (14)

The estimated thermodynamic parameters are presented in Table 6. The positive $\Delta H^*$ values mean a chemical endothermic process. A positive value of $\Delta S^*$ showed a change in biomass structure during the sorption process, causing an increase in the disorderness of the system [37]. The negative value of $\Delta G^*$ at all temperatures indicated the spontaneous nature of the adsorption of CV dyes on the SRAC adsorbent.

**Table 6. Thermodynamic parameters for the adsorption of Crystal violet dye on SRAC**

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^*$</th>
<th>$\Delta S^*$</th>
<th>$-\Delta G^*$ (kJ/mol) ×10^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>J/mol</td>
<td>J/mol K</td>
<td>308K</td>
</tr>
<tr>
<td>0.999</td>
<td>33.01</td>
<td>114.8</td>
<td>23.85</td>
</tr>
</tbody>
</table>

**CONCLUSION**

*Sida Rhombifolia* activated carbon (SRAC) prepared by chemical activation with $\text{H}_2\text{SO}_4$ was an efficient adsorbent with relatively large surface area of 18.14 m$^2$/g and total pore volume of 10.0 cm$^3$/g.
The present study showed that SRAC could be used as an adsorbent for the removal of crystal violet dye from aqueous solutions. From batch experiments, the adsorption amount was highly dependent on operating variables such as initial concentration of dye, contact time, adsorbent dose and temperature. The equilibrium time was found to be 50min SRAC-CV system. The optimum adsorbent dose was found to be 0.050 g/L for CV dye. The adsorption kinetics was investigated using the pseudo-first-order and pseudo-second-order model.

The kinetic studies showed that the adsorption process followed the pseudo-second-order model. The equilibrium data were better represented by the Langmuir, Temkin and Jovanoic isotherm. The negative ΔG˚ and the positive ΔH˚ indicated the spontaneous and endothermic nature of the adsorption.

REFERENCE


