Removal of Victoria Blue using Prosopis juliflora bark carbon: Kinetics and Thermodynamic modeling Studies

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Abstract
This research article presents the feasibility for the removal of Victoria blue dye using adsorption process. Victoria blue have used as medicine in several mammalian cells, shows antitumour activity in animal systems. The activated carbon used as adsorbent in this study and prepared from prosopis juliflora bark using acid digestion method. The parameters used for the adsorption process are effect of pH, initial concentration, adsorbent dose, contact time and temperature. The feasibility of adsorption process evaluated in the pH range of 2 to 10, concentration range from 4 to 20 mg/L, temperature varied from 303 K to 343 K, variation of contact time from10 to 90 minutes and dose of the adsorbent from 0.05g to 1.0 g. The prediction of isotherm parameters like Freundlich and Langmuir isotherm equations were tested and the feasibility of adsorption found out with the equation of dimension less separation factor (Rl). The kinetic parameters were determined by using Lagergren's pseudo-first order and pseudo-second order kinetic models. The intra particle diffusion model was investigated for the determination of diffusion mechanism. The thermodynamic parameters of change in free energy (ΔG°), change in Enthalpy (ΔH°) and change in entropy (ΔS°) were determined by using Vant Hoff plot. The adsorbent surface functional groups identified with Fourier Transform Infrared (FTIR) spectroscopy and the morphology of the surface identified with Scanning Electron Microscope (SEM).

Key words: prosopis juliflora, bark carbon, adsorption, Victoria blue, kinetics and thermodynamics

1. Introduction
Effluents often contain large quantities of organic materials that causes a major environmental problem in large-scale production and huge amount utilization of synthetic materials produce environmental pollution [1]. Various types of contaminants like dyes and pharmaceuticals in water are not easily decomposable in nature. Therefore, there are enormous research works going on for the identification of the best suitable decomposable agent. The dyes and pigments are widely used in textile, leather, dyeing, paper, printing, pharmaceutical and cosmetic industries, and enormous amount of pharmaceuticals used by humans as well as in veterinary for curing diseases. The disposal of dyes, pharmaceuticals and their derivate products to the aquatic system by many industries causes extremely toxic effects to aquatic life even at very low concentrations [2]. Textile dyes are the most dangerous chemical pollutants in the environment, there are more than 100,000 types of commercially available dyes with over 70x10^5 tones of dyes are produced annually [3]. The effluent released in these industries often contains large quantities of dyes, that are diverted through streams may cause severe environmental problems in the aquatic environment. The unprocessed effluent cause cytotoxicity [4], genotoxicity and reduce light penetration in aquatic systems that produce carcinogenic aromatic amines [5] in water matrices, they contribute to organic load and toxicity of the wastewater [6].

Basic dyes have used in the dyeing of silk, cotton, wool, acrylic fibers and other fibers that contain anionic sites, which attract and interact with cationic molecules. These dyes have the highest tinctorial value and less than 1 ppm of the dye produces an obvious coloration in water [7].The removal of chemical dyes using various methods from effluents has examined, the adsorption process found to be the most effective method for the removal of dyes. The activated carbon as an adsorbent has yielded excellent results. However, taking into account the high costs involved in the preparation and regeneration process of activated carbon [8], the searching of alternate adsorbents has done recently by scientists. These include industrial as well as agricultural products, namely coir pith, seed shell, corncob and tree bark etc…
Cationic dyes are especially important for staining of microorganisms [9]. Moreover, Victoria blue is a photosensitizer, which induce a cytotoxic response in several mammalian cell lines, though some dark toxicity observed [10]. The phenylamino analogue of Victoria blue B (VBB) has shown antitumour activity in animal systems [11] and the derivatives of Victoria blue have specific cellular sites action, and their combination with sufficient lipophilicity that ensure high level uptake of intracellular phototoxic behaviour activity that governed by photosensitizing efficiency [12]. The mode of action of VBBO reported recently has Type I photosensitization [13]. The site of action of VBBO in cultured tumor cell lines has the photosensitizer inhibition of respiratory complex-I in mitochondria [14].

Recent studies have shown that municipal effluents mimic a physiological state close to inflammation in mussels, in addition to their endocrine-disrupting activity [15]. It thus appeared justified to examine the influence that PPCPs and dyes commonly found in municipal wastewaters that might have on the immune function of endemic mussels exposed to municipal effluent outfalls [16]. Wastewaters are the major source of pharmaceutical and textile dye products to the aquatic environment, thereby exposing biota to unknown chronic effects in humans. The importance of reducing the adverse effect of the environmental impact of dyes and pharmaceuticals, this study has investigated the ability of the activated carbon to decolorize Victoria blue. The objectives of the present study are i) The adsorbent material used in this study as an activated carbon, prepared from prosopis juliflora bark, ii) The parameters are used for the adsorption process are the effect of pH, initial concentration, adsorbent dose, contact time and temperature, iii) The parameters are evaluated in the pH range of 2 to 10, concentration range from 4 to 20 mg/L, temperature varied from 303 K to 343 K, variation of contact time from 10 to 90 minutes and dose of the adsorbent from 50 mg to 250 mg, iv) The isotherm parameters like Freundlich and Langmuir isotherm equations were tested and the feasibility of the adsorption was found out with the equation of dimension less separation factor (Rd), v) The kinetic parameters were determined by using Lagergren’s pseudo-first order and pseudo-second order kinetic models, vi) The intra particle diffusion model was investigated for the determination of diffusion mechanism, vii) The thermodynamic parameters like change in free energy (ΔG°), change in Enthalpy (ΔH°) and change in entropy (ΔS°) were determined by using Vant Hoff plot, viii) The adsorbent surface functional groups were identified with Fourier Transform Infrared (FTIR) spectroscopy and the morphology was identified with Scanning Electron Microscope (SEM).

2. Materials and Methods
2.1. Preparation of adsorbent
The activated carbon preparation method has described in our previous work [17-19].

2.2. Adsorbate
A stock solution of the Victoria blue dye was prepared by dissolving the exact and calculated quantity of Victoria blue (4-[(4-Anilino-1-naphthyl][4(dimethylamino)-phenyl]-methylene)cyclohexa-2,5-dienylidene )dimethylammonium chloride) molecular formula - C35H32ClN5, Formula weight- 506.10 in doubly distilled water which was used throughout the experiments. Fig. 1 shows the structure of Victoria blue. Commercially available analytical grade other reagents (Merck, India and SD-fine, India) were used for this study.

![Figure 1: Structure of Victoria blue.](image)

2.3. Experimental Methods
25 mL of a known concentration of Victoria blue solution and 100 mg of the adsorbent taken in a 100 mL glass stoppered flask at 30 ± 0.5 °C and the mixture stirred on a mechanical shaker for 50 min. The samples were withdrawn during stirring at preset time intervals and the adsorbent was separated from the solution by centrifugation process at speed of 4500/min for 5 min. The absorbance of the supernatant solution estimated to determine the residual dye concentration and measured before and after treatment with double beam spectrophotometer. All experiments has carried out in twice, and the concentrations
given are average values. The initial dye concentration in the test solution and the adsorbent dosage varied to investigate their effect on the adsorption kinetics. The effect of pH was observed by studying the adsorption of dye over the pH range from 2 to 10. The pH of the dye solution adjusted by using NaOH or HCl solution and determined by using a pH meter. The sorption studies carried out at different temperatures (303, 313, 323, 333 and 343 K). This used to determine the effect of temperature on the thermodynamic parameters. The amount of sorption at time t, \( q_t \) (mg/g), calculated using the following equation:

\[
q_t = \frac{(C_0 - C_t)V}{M}
\]

where, \( C_0 \) is the initial concentration of dye, \( C_t \) is the concentration at a given time \( t \), \( V \) is the volume of the dye solution in L and \( M \) are the weight of activated carbon in g.

The percentage of dye removal in solution was calculated using the following equation,

\[
\text{Removal} \% = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]

Where, \( C_i \) and \( C_f \) are initial and final concentration of dye, before and after of the sorption process.

2.4. Characterization of bark Activated Carbon

The purpose of using activation of carbon is to enhance the efficiency of adsorption without the evolution of huge amounts of fumes while carbonizing the bark material. Excess moisture can removed inside the pores of the adsorbent material then the carbonized material kept in an oven for 12 h at a temperature of 373 to 383 K. Morphology of the adsorbent material performed using Scanning electron micrograph (SEM) analysis. The surface functional groups of the activated carbon studied by Fourier transform infrared (FTIR) spectroscopy in before and after adsorption. The FTIR spectrum recorded in the frequency range from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\).

3. Results and Discussion

3.1. Characteristic studies of activated carbon

3.1.1. FT-IR study

The characteristic pattern for the adsorption of Victoria blue onto PJBC was investigated by using FTIR spectroscopic analysis. The characteristic FTIR spectra of activated carbon (A.C) provide the presence of preliminary functional groups present in them. The VB dye (D) adsorbed activated (D+A.C) carbon characteristic FTIR spectra give the information with which functional groups are involved for the adsorption process. The adsorption pattern of FTIR of A.C (dotted line) and Dye+A.C (line) shown in Fig. 2. Peaks of preliminary functional groups of A.C are a sharp peak at 3432.81 cm\(^{-1}\), broad peak at 2161 cm\(^{-1}\), a sharp peak at 1591 cm\(^{-1}\), small peak at 1359 cm\(^{-1}\) and a presence of sharp peak at 1146 cm\(^{-1}\) intimates that there is a presence of intermolecular bond [20], aromatic primary group, aromatic C=C group, aromatic conjugation and free OH groups respectively. After the adsorption of dye the A.C+D shows there was reduction in the peak heights and disappearance of some peak heights and there some changes in the peak positions of the FTIR spectrum. The peaks expected in the positions of 3432.81 cm\(^{-1}\), 2161 cm\(^{-1}\), 1591 cm\(^{-1}\), 1359 cm\(^{-1}\) and 1146 cm\(^{-1}\) but the peaks obtained at slightly shifted positions at 3420 cm\(^{-1}\), 2426.0 cm\(^{-1}\), 2193.5 cm\(^{-1}\), 1592.2 cm\(^{-1}\) and 1232.3 cm\(^{-1}\). This peak reduction reveals that there was a strong characteristic adsorption of dye onto the surface of the activated carbon.

![Figure 2. The FTIR spectrum for the adsorption of VB dye](image-url)
3.1.2 SEM Studies

The Scanning Electron Microscope (SEM) provides the information about the surface morphology of the adsorbent material. The SEM images of before and after adsorption presented in the Fig. 3a and 3b. The Fig. 3a shows that there was porous structure of the surface with distorted layers but in the case of after adsorption (Fig. 3b), the porous and distorted layer structure was wholly occupied with the VB dye molecules. Hence, there was a completely occupied site of the surface of the adsorbent material shows almost flatten surface image. These variation in image structure concluded that the VB dye strongly adsorbed on the surface of the activated carbon.

![SEM image of activated carbon](image1)

![SEM image of activated carbon + VB dye](image2)

**Figure 3.** a) SEM image of activated carbon b) SEM image of activated carbon + VB dye

3.2. Parameters study

3.2.1. Effect of pH

The adsorption of dye molecules onto an adsorbent is highly dependent on the pH. The pH of the system effects the nature of the surface charge of the adsorbent, which are responsible for interaction between dye molecules and adsorbent, which can be protonated or deprotonated to produce different surface charges in solution at different pH values [21]. Generally, in aqueous medium on ionization, basic dyes acquire a net positive charge and adsorbents containing organic functional groups on their surfaces have shown to develop charges on their surface, which are pH dependent. The adsorptive removal of victoria blue dye reaction rate have affected by the initial of pH of the solution. The adsorption capacity of PJBC was found to be decreased in the PH>5. Since in the range of pH-2 to 5 (Fig. 4), there is an enhancement for the removal capacity of PJBC. Hence, the optimum pH for the removal of Victoria blue has selected using PJBC as pH-5.

![Effect of pH for the adsorption of VB dye](image3)

**Figure 4.** Effect of pH for the adsorption of VB dye

3.2.2. Effect of Dose

The effect of the dose of the adsorbent has evaluated using various quantity of adsorbent ranging 0.5-1.0 g. With various quantities, 0.1g of adsorbent gives 93.12% removal of dye (Fig. 5).

![Effect of adsorbent dose for the adsorption of VB dye](image4)

**Figure 5.** Effect of adsorbent dose for the adsorption of VB dye
3.2.3. Effect of initial concentration

The effects of initial dye concentration of Victoria blue onto PJBC adsorption process identified by varying the initial dye concentrations in the range of 4-20mg/L (Fig. 6) with the 4mg/L variation. The various concentrations range 12mg/L of the dye gives best adsorption removal in 90.21%.

![Figure 6. Effect of time for the adsorption of VB dye](image)

3.2.4. Effect of temperature

The effect of temperature plays a vital role for the adsorption of Victoria blue has studied by carrying out a series of experimental temperatures at 30-70 °C. Increasing the temperature has slight decreases the rate of adsorption of the adsorbate molecules in the external boundary layer and in the internal pores of the adsorbent particle. This increased temperature decreases the viscosity of the solution. Furthermore, changing the temperature will change the equilibrium capacity of the adsorbent at the adsorption process [22] and the enhanced rate of intraparticle diffusion of the sorbate. In Fig. 7 shows that the adsorption of Victoria blue slightly decreases with increasing temperature this indicates that the adsorption is endothermic adsorption. A decreased adsorption capacity of the Victoria blue with increasing temperature could attributed to the slight screen for the mobility of the dye molecules with temperature and is an indication of a physiochemical mechanism. Similar observations have reported for adsorption of basic and reactive dyes. The removal of Victoria blue for the adsorption on PJBC decreases from 90.57 to 89.27%.

3.3. Equilibrium Modeling

The adsorption equilibrium was evaluated by using the Freundlich isotherm and Langmuir isotherm equations. The Freundlich isotherm used for an assumption of the ratio of the amount of solute adsorbed on a given mass of sorbent to the concentration of the solute in the solution that is not a constant at different concentrations [23]. Non-linear form of Freundlich equation

\[ q_e = K_F C_e^{1/n_F} \]  

(3)

The linearized form Freundlich equation

\[ \log q_e = \log (K_F) + \frac{1}{n_F} \log (C_e) \]  

(4)

where \( q_e \) is the amount of adsorbate adsorbed at equilibrium (mg/g), \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), \( K_F \) is the Freundlich adsorption constant related to adsorption capacity of the adsorbent ((mg/g)/(L/mg)^1/n) and 1/n is the adsorption intensity. The values of \( K_F \) and 1/n were calculated from the intercept and slope of the plot of \( C_e/q_e \) vs. \( C_e \) (Fig. 8).

The Langmuir isotherm is used for the monolayer sorption processes and the adsorption takes place on a surface containing a finite number of binding sites. It is an assumption of uniform distribution energies of sorption on the surface and there is no transmigration of sorbate particles in the plane of the surface of the adsorbent [24, 25]. Non-linear form of Langmuir equation

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

(5)

The linearized form of Langmuir equation

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

(6)
where $q_e$ (mg/g) and $C_e$ (mg/L) are the amount of dye adsorbed per unit mass of sorbent and unabsorbed dye concentration in solution, $q_m$ is the maximum amount of dye adsorbed per unit mass of sorbent at complete monolayer on surface bound, and $K_a$(L/mg) is a constant related to the affinity of the binding sites. Linear regression is the most common method to evaluate the adsorption process, so the adsorption constants were obtained by using linear least square method (Fig. 9).

Figure 7. Effect of temperature for the adsorption of VB dye

Figure 8. Freundlich isotherm for the adsorption of VB dye

Figure 9. Langmuir isotherm for the adsorption of VB dye

The experimentally calculated values of Freundlich and Langmuir isotherm parameters are presented in Table 1.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Temperature (K)</th>
<th>303</th>
<th>313</th>
<th>323</th>
<th>333</th>
<th>343</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>$q_m$(mg/g)</td>
<td>0.3693</td>
<td>0.5867</td>
<td>1.4465</td>
<td>2.0219</td>
<td>2.9678</td>
</tr>
<tr>
<td></td>
<td>$K_a$(L/mg)</td>
<td>2.3709</td>
<td>1.2766</td>
<td>2.3034</td>
<td>1.2030</td>
<td>1.3524</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9931</td>
<td>0.9629</td>
<td>0.9951</td>
<td>0.9811</td>
<td>0.9825</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$1/n$</td>
<td>0.6897</td>
<td>0.5001</td>
<td>0.3101</td>
<td>0.2987</td>
<td>0.2220</td>
</tr>
<tr>
<td></td>
<td>$K_F$(mg/g)(L/g)</td>
<td>1.5685</td>
<td>1.3838</td>
<td>0.8294</td>
<td>0.4740</td>
<td>0.3335</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.8702</td>
<td>0.8963</td>
<td>0.8850</td>
<td>0.9238</td>
<td>0.9091</td>
</tr>
</tbody>
</table>
From the table, the Freundlich isotherm shows the correlation coefficient value ($r^2$) is 0.9238 and the Langmuir isotherm shows the correlation coefficient value ($r^2$) is 0.9951. These values tell that the Langmuir isotherm was the most suited isotherm rather than the Freundlich isotherm for the removal of VB dye. Moreover, the Freundlich isotherm shows the $r^2$ value 0.9238, this indicates that there was a involvement of the Freundlich isotherm in small manner. Hence, the monolayer (Langmuir) sorption process was the dominant one as compared with the multilayer process (Freundlich).

The feasibility of the adsorption isotherm was checked by using the dimensionless separation factor ($R_L$) equation:

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (7)

In this study, the $R_L$ value lies between 0 to 1 (Fig. 10) and the low value of $R_L$ indicates that there was strong interaction between the adsorbate and adsorbent material for the adsorption of VB dye.

**Figure 10.** Dimensionless separation factor ($R_L$) for the adsorption of VB dye

### 3.4. Kinetic studies

Adsorption equilibrium of kinetic profiles were characterized in order to determine the rate limiting steps involved in the process of sorption of VB dye onto PJBC. Lagergren pseudo first order (Eq. (8)) and pseudo second order (Eq. (9)) kinetic models were applied [26,27]:

$$\log (q_e - q) = \log (q_e) - \frac{K_1 t}{2.303}$$  \hspace{1cm} (8)

Where, $K_1$ is the pseudo first order adsorption rate constant, $q_e$ is the amount of dye adsorbed on the PJBC at equilibrium (mg/g), $q_t$ is the amount of VB dye adsorbed on the PJBC at any time $t$ (mg/g):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}$$  \hspace{1cm} (9)

Where, $K_2$ is the pseudo-second order adsorption rate constant, $q_e$ amount of dye adsorbed on the PJBC at equilibrium (mg/g), $q_e^2$ is the pseudo second order adsorption rate constant (g/mg/min).

The calculated value of pseudo-first order rate constant ($K_1$), pseudo-second order rate constant ($K_2$), equilibrium uptake capacity ($q_e$) and their corresponding regression coefficient ($r^2$) were presented in Table 2. From the table the coefficient values of pseudo-first order rate constant and the obtained $q_e$ values are very low.

On the other hand the obtained values of pseudo-second order kinetics (Figure. 12) showed the correlation coefficient value of 0.9904 and the Pseudo-first order (Figure. 11) showed the correlation coefficient value 0.7140, this result shows that the sorption process follows second order rate reaction. That is the rate of the process not depend only on the concentration factor (Pseudo-first order) and the rate of the process depends on both concentration as well as time (Pseudo-second order).

The kinetic parameters are not able to provide the enough information about the diffusion mechanism of the adsorption process. So, researchers are tending to produce a new method that provides the information about the diffusion mechanism. From various methods the intraparticle diffusion model is the widely used and suited model for the prediction of the mechanism of diffusion process [28]. The mathematical expression for the intraparticle diffusion equation is:
\begin{equation}
q_t = K_{id} t^{1/2} + C
\end{equation}

(10)

Where, \(k_{id}\) is the intraparticle diffusion rate constant (mg/g/min\(^{1/2}\)) and \(C\) is the intercept. The experimentally predicted values of intraparticle parameters are presented in the Table 3.

**Table 2. Kinetic parameters for the adsorption of VB dye**

<table>
<thead>
<tr>
<th>(C_0) (mg/g)</th>
<th>(K_1)</th>
<th>(q_e)</th>
<th>(r^2)</th>
<th>(q_{e,\exp})</th>
<th>(K_2)</th>
<th>(q_{e,\cal})</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0227</td>
<td>0.0510</td>
<td>0.7140</td>
<td>0.85</td>
<td>0.3066</td>
<td>0.2201</td>
<td>0.9827</td>
</tr>
<tr>
<td>8</td>
<td>0.0400</td>
<td>0.0047</td>
<td>0.6648</td>
<td>1.75</td>
<td>0.2998</td>
<td>0.2415</td>
<td>0.9845</td>
</tr>
<tr>
<td>12</td>
<td>0.0394</td>
<td>0.1416</td>
<td>0.5340</td>
<td>2.82</td>
<td>0.2455</td>
<td>0.2827</td>
<td>0.9787</td>
</tr>
<tr>
<td>16</td>
<td>0.0277</td>
<td>0.5392</td>
<td>0.5664</td>
<td>3.74</td>
<td>0.2172</td>
<td>0.4134</td>
<td>0.9917</td>
</tr>
<tr>
<td>20</td>
<td>0.0277</td>
<td>0.5392</td>
<td>0.5664</td>
<td>4.67</td>
<td>0.1721</td>
<td>0.4348</td>
<td>0.9805</td>
</tr>
</tbody>
</table>

**Table 3. Intraparticle diffusion parameters for the adsorption of VB dye**

<table>
<thead>
<tr>
<th>(C_0) (mg/g)</th>
<th>(k_{id}) (mg/g.s(^{1/2}))</th>
<th>(C) (mg/g)</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0062</td>
<td>0.3743</td>
<td>0.6974</td>
</tr>
<tr>
<td>8</td>
<td>0.0102</td>
<td>0.5936</td>
<td>0.7722</td>
</tr>
<tr>
<td>12</td>
<td>0.0173</td>
<td>0.7223</td>
<td>0.6399</td>
</tr>
<tr>
<td>16</td>
<td>0.0199</td>
<td>0.9146</td>
<td>0.6404</td>
</tr>
<tr>
<td>20</td>
<td>0.0221</td>
<td>1.0868</td>
<td>0.6776</td>
</tr>
</tbody>
</table>

The graph using \(q_e\) vs. \(t^{1/2}\) provides a straight line; the adsorption process proceeds with the intraparticle diffusion mechanism and parameters \(k_{id}\) and \(C\) are determined from the linear regression analysis of the slope and intercept. The obtained graph was present in the Fig. 13. From the Fig. 13, the plot was not provide a straight line at various time intervals but it shows two segments of straight line. This reveals that the adsorption of victoria blue dye on activated carbon may involve several modes of sorption, rather than a single mode. From the Table 3, the correlation coefficient value provides the value of 0.7722 and it intimated that the process was not involved in a linear single linear mode of sorption. Hence, the results were confirmed that the adsorption process involved in a multi mode of diffusion process rather than a single mode of diffusion process.

3.5. Adsorption Thermodynamics

The thermodynamic parameters helps to predict the inherent energetic changes of the process and that are associated with adsorption. The thermodynamic parameters, such as standard Gibbs energy (\(\Delta G^0\)), enthalpy (\(\Delta H^0\)), and entropy (\(\Delta S^0\)), were determined by using the following equations [29].
\[ K_d = \frac{q_e}{C_e} \]  
(11)

\[ \Delta G^0 = -RT \ln K_d \]  
(12)

\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  
(13)

where, \( K_d \) is the distribution coefficient, \( T \) is the temperature, and \( R \) is the gas constant (8.3145 J/mol/K), respectively. \( \Delta G^0 \), \( \Delta S^0 \) and \( \Delta H^0 \) were calculate from the slope and intercept of Van’t Hoff plot of \( \ln K_d \) vs. \( 1/T \) (Fig. 14).

The calculated values of thermodynamic parameters presented in Table 4. The negative \( \Delta G^0 \) values at different temperatures indicate the spontaneous nature of the adsorption of VB dye onto the PJBC. The more negative value shows that the amount adsorbed at equilibrium must increase, the value of \( \Delta H^0 \) found to be positive in the temperature range of 303 to 343 K. This indicates that the endothermic nature of adsorption was involved during the adsorption process. The positive value of entropy (\( \Delta S^0 \)) shown that the increased randomness between the VB dye and PJBC activated carbon interface and significant affinity of VB dye toward the PJBC activated carbon [30].

**Table 4. Thermodynamic parameters for the adsorption of VB dye**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( \Delta G^0 ) (KJ/mol)</th>
<th>( \Delta H^0 ) (KJ/mol)</th>
<th>( \Delta S^0 ) (J/K/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-0.25</td>
<td>3.06</td>
<td>54</td>
</tr>
<tr>
<td>313</td>
<td>-0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>-0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>-0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>-0.50</td>
<td></td>
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</tr>
</tbody>
</table>

These experimental results were concluding that the adsorption of VB dye onto PJBC was favor and shows good affinity between VB dye and PJBC activated carbon.

**Conclusion**

The experimentally predicted results are shows that the removal of Victoria blue on PJBC carbon shows good affinity of adsorption process. The optimum pH of the process found to be pH-5, dye concentration 12 mg/L and 50 minutes of contact time shows the effective removal of the VB dye. 100 mg of adsorbent dose and 303 K temperature shows higher removal of VB dye. The Langmuir isotherm equation shows the correlation coefficient value (\( r^2 \)) while the Freundlich isotherm shows the correlation coefficient lower than Langmuir isotherm. Hence, the monolayer (Langmuir) sorption process was the dominant one as compared with the multilayer process (Freundlich). The dimension less factor (\( R_L \)) value lye between 0 to 1,
which confirming that the isotherm process was favorable. The sorption process follows second order rate reaction shows that the rate of the process not depend only on the concentration factor (Pseudo-first order) and the rate of the process depends on both concentration as well as time (Pseudo-second order). The intra particle diffusion model indicates the adsorption process involved in a multi mode of diffusion process rather than a single mode of diffusion process. The thermodynamic investigation gave negative $\Delta G^o$ values indicate the process was spontaneous. The positive value of $\Delta S^o$ and $\Delta H^o$ shows that the increased randomness between the VB dye and PJBC activated carbon. The Fourier Transform Infrared (FTIR) scope shows well peak reduction and changed positions reveals that there was a strong characteristic adsorption of dye onto the surface of the activated carbon and the morphology images provides good variation in images that concluded that the VB dye strongly adsorbed on the surface of the activated carbon.

References


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