Kinetic and Thermodynamic Studies of the Adsorption of Crystal Violet onto Used Black Tea Leaves

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Abstract: This study presents the kinetic and thermodynamic investigations of the adsorption of crystal violet (CV) on used black tea leaves (UBTL) from aqueous solution to evaluate the feasibility of the process. The effects of concentration, solution pH and temperature on adsorption kinetics were carried out in batch process. Kinetic studies have shown that the adsorption data partially follow simple first order, second order and pseudo second order kinetic equations for different initial concentrations at pH 2.0. The equilibrium amount adsorbed, equilibrium concentration and rate constant were calculated from better fitted pseudo second order kinetic plots for different initial concentrations. The equilibrium amount adsorbed (200 mg/g at 30 °C) increased with the increase of temperature, indicated endothermic nature of the adsorption. The apparent activation energy of adsorption was determined from Arrhenius plot using pseudo second order rate constant and the value, $E_a = 83.1$ kJ/mol, revealed the process is chemisorption. Thermodynamic parameters: $\Delta H^o$, $\Delta G^o$ and $\Delta S^o$, were determined from the equilibrium adsorption constant and the results obtained confirmed that the adsorption process was feasible, less spontaneous and endothermic. The equilibrium amount adsorbed was found to be increased with increase of solution pH from 2.0 to 6.0 indicating electrostatic interaction between cationic CV with anionic surface of UBTL dominated at higher pH due to the low zero point charge pH of UBTL.

Keywords: adsorption kinetics; crystal violet; used black tea leaves; adsorption thermodynamics

1. INTRODUCTION

Environmental pollution by industrial effluents is an important issue in recent years. Different types of dyes are common pollutants usually found in textile industries effluents in many developing countries. Moreover, rapid industrialization has led to disposal of synthetic dyes which are mostly used in relevant industries such as textile, leather, paper, plastic etc. to color their final products [1]. Most of dyes are toxic and carcinogenic compounds posing a serious threat to human and animal health which is not only limited to themselves but may be passed onto further generations [2]. Dyes from the wastewater of these factories must be removed before discharging into water. Crystal violet (CV) is one of the most useful dye uses in textile and paper dyeing, and 15% of such dyes produced worldwide are released to environment in wastewater. Crystal violet destroys cells and can be used as a disinfectant. Compounds related to CV are potential carcinogens [3]. Crystal violet binds to DNA which causes replication errors in living tissue, possibly leading to mutations and cancer [3]. Thus crystal violet is a mutagen and mitotic poison; therefore concerns exist regarding the ecological impact of the release of CV into the environment. Numerous methods have been developed to treat CV pollution. The most common methods are chemical bleaching [4], biodegradation [5-6], photodegradation [7], photocatalytic degradation [8-10], electrochemical degradation [11-12], cation exchange membrane [13], micellar enhanced ultra filtration [14], fenton-biological treatment [15] and adsorption [16] onto various solids such as activated charcoal. Among the above methods, adsorption has proven to be more versatile and efficient for the removal of dyes from aqueous system. Among them, adsorption is a cost effective method for treatment of wastewater. Activated carbon has been recognized as a highly effective adsorbent for the treatment of heavy metals in wastewater [17]. However, high cost of activated carbon and regeneration difficulties has deterrent in the utilization of activated carbon in the developing countries [18].

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Therefore, there is increasing research interest in using alternative low cost adsorbents. Recently, used black tea leaves (UBTL) are interested due to their high adsorption capacity, low cost and easy to recover the adsorbate from adsorbed UBTL [19]. Crystal violet was selected as a common basic dye available in textile effluent for its removal study. Main focus of the present study was to investigate the kinetics and thermodynamics of adsorption of CV onto UBTL under various operational conditions.

2. MATERIAL AND METHODS

2.1. Adsorbent

The used black tea leaves (UBTL) was prepared by using same method described Alam [20]. In this process, tea liquor was completely removed from fresh black tea leaves collected from local market in Dhaka, Bangladesh. Leaves were dried at room temperature and then dried in oven at 105 °C for 8 h. Dried leaves were sieved through the sieves of mesh size 212-300 µm and the particles in the size range of 212-300 µm in diameter were stored in a desiccator for adsorption experiments. Figure 1 shows the heterogeneous surface morphology of prepared UBTL observed by scanning electron microscope (SEM) (JSM-6490LA, JEOL, Japan).

![Figure 1. SEM micrograph of prepared UBTLx500.](image1)

2.2. Adsorbate

All chemicals used in the study were analytical grade. Crystal violet (CV) is a basic dye which exists as cationic form in acidic to neutral media. It is used as a pH indicator, with a range between 0 and 1.6. The protonated form (found in acidic conditions) is yellow, turning blue-violet above pH levels of 1.6. IUPAC name of CV is tris(4-(dimethylamino)phenyl)methylmethyl chloride. Synonyms of crystal violet are methyl violet 10B, methyl violet 10BNS, aniline violet, baszol violet 57L, brilliant violet 58, gentian violet, pyoktanin, methylrosanilide chloride and hexamethyl-p-rosaniline chloride. Molecular formula of crystal violet is \( C_{25}H_{30}N_3Cl \) and the structural formula is given in Figure 2. C.I. number and CAS number of crystal violet are basic violet 3 and 548-62-9, respectively. Molecular weight of crystal violet is 407.98 g.

A stock solution of 1000 mg/L was prepared by dissolving CV (Analytical grade) in distilled water from which different concentrated solutions were prepared. Concentration of CV in different solutions was determined by a computerized UV-visible spectrophotometer (UV-1650A, Shimadzu, Japan) using \( \lambda_{\text{max}} = 582 \text{ nm} \) and solution pH was at 6.0 as an optimum pH for CV solution to analyze [21]. According to Beer-Lambert law, the calibration limit of CV was determined which was in the range of 0.1 to 20.0 mg/L at optimum pH 6.0 and the absorption coefficient was 0.109 L/mg.cm.

![Figure 2. Molecular structure of crystal violet (CV).](image2)
solution at pH 6.0 with proper dilution was also measured by UV-vis spectrophotometer at $\lambda_{\text{max}}$ 582 nm to determine the initial concentration of the solution. Similar kinetic experiments were performed using different initial concentrations of crystal violet solutions. The amount adsorbed at different contact times for different initial concentration was calculated from the following equation (1).

$$q_t = \left( C_o - C_t \right) \times \frac{V}{W}$$  \hspace{1cm} (1)

where, $C_o$ is the initial concentration of CV (mg/L), $C_t$ is the concentration of CV at time $t$ (mg/L), $q_t$ is the amount adsorbed at time $t$ (mg/g), $V$ is the volume of solution in liter and $W$ is the mass of adsorbent in g.

2.4. Effect of temperature on adsorption kinetics

To investigate the effect of temperature on the adsorption kinetics, kinetic experiments were conducted at three different temperatures using same initial concentration of about 100.2 mg/L of CV solution at pH 2.0, keeping other parameters constant. The change of amount adsorbed of CV with different contact time for different temperatures were recorded.

2.5. Effect of pH on adsorption kinetics

To observe the effect of solution pH on adsorption of CV, a series of adsorption kinetic experiments were conducted at three different pH values using initial concentration of about 51.6 mg/L of CV solution, keeping other parameters constant. The change of amount adsorbed with different contact time for different initial pH values were calculated.

3. RESULTS AND DISCUSSION

3.1. Effect of concentration on adsorption kinetics

Kinetic of adsorption is one of the important characteristics defining the efficiency of an adsorbent. To investigate the effect of CV concentration on adsorption kinetics, a series of kinetic experiments, change of concentration with contact time, were performed at different initial concentrations of CV for a constant temperature, solution pH, adsorbent dose and agitation rate. As the time passes, the CV adsorbed on the UBTL surface resultant the decreased of CV concentration in solution. Figure 3 (a-b) shows the variation of amount adsorbed of CV with contact time for a fixed amount of adsorbent. The adsorption of CV onto UBTL are quite rapid initially, however the adsorption rate becomes slower with progress of time. The initial faster rate of adsorption may be due to the availability of the uncovered surface sites of UBTL. Again, the amount of CV adsorbed per unit mass of UBTL increased with increase in CV concentration as shown in Figure 3 (a-b) which indicated that the extent of adsorption is highly dependent on the concentration of CV. This is because at low concentration, the ratio of the initial number of CV molecules to the available sites is low, resultant the finished of CV in solution before reach the saturation of UBTL surface; subsequently, the fractional adsorption becomes independent of the initial concentration. However, at high concentration of CV the available surface sites of adsorption become fewer, and hence the percent adsorption as well as adsorption amount depends on the initial concentration of CV up to a certain limit.

![Figure 3](image.png)

Figure 3. (a) and (b): Variation of the amount adsorbed of CV on UBTL with time for different initial concentrations of CV where solution pH 2.0, particle size: 212-300 $\mu$m and temperature: 30.0 ± 0.2 °C.
The adsorption mechanism depends on the physicochemical characteristics of adsorbent and adsorbate and as well as on the mass transfer process. With the maximum agitation speed of 150 rpm, it was assumed to offer no mass transfer (both external and internal) resistance to the overall adsorption process. Therefore the adsorption kinetics can be studied through the residual adsorbate concentration in the solution. The kinetic experimental results obtained for different initial concentration of CV were analyzed using simple first order, second order and pseudo second order kinetic equations. Linear regression ($R^2$) value was used to determine the best fitting kinetic model for experimental data.

### 3.2. First order kinetics

To evaluate the feasibility of the adsorption of CV on UBTL, simple first order kinetic model was verified using the following equation (2) [21-22]

$$\ln C_t = k_1 t + \ln C_o$$  \hspace{1cm} (2)

where, $C_t$ is the concentration of dye at time $t$ (mg/L), $C_o$ is the initial concentration of dye (mg/L) and $k_1$ is first order rate constant. Applicability of the first order kinetic equation (2) was examined by plotting $\ln C_t$ vs $t$ as shown in Fig. 4 (a-b) which shows that the adsorption of CV on UBTL partially follow the simple first order kinetic equation for different initial concentrations of CV and regression values are given in Table 1.

![Figure 4](image)

**Figure 4.** (a) and (b): First order kinetics CV adsorption onto UBTL at various initial concentrations pH 2.0 and temperature 30.0 ± 0.2 °C.

### Table 1. A comparison of the data fitness to the first, second and pseudo second order kinetic equations.

<table>
<thead>
<tr>
<th>Initial concentration $C_o$ (mg/L)</th>
<th>$R^2$ (-)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>22.66</td>
<td>0.862</td>
<td>0.837</td>
<td>0.892</td>
<td></td>
</tr>
<tr>
<td>49.27</td>
<td>0.928</td>
<td>0.939</td>
<td>0.916</td>
<td></td>
</tr>
<tr>
<td>86.97</td>
<td>0.913</td>
<td>0.929</td>
<td>0.873</td>
<td></td>
</tr>
<tr>
<td>200.92</td>
<td>0.970</td>
<td>0.918</td>
<td>0.932</td>
<td></td>
</tr>
<tr>
<td>275.23</td>
<td>0.946</td>
<td>0.944</td>
<td>0.967</td>
<td></td>
</tr>
<tr>
<td>679.82</td>
<td>0.855</td>
<td>0.832</td>
<td>0.979</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3. Second order kinetics

Second order kinetic equation (3) was applied to evaluate the feasibility of the adsorption of CV on UBTL [21].

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_o}$$ \hspace{1cm} (3)

where, $C_t$ is the concentration of dye at time $t$ (mg/L), $C_o$ is the initial concentration of dye (mg/L) and $k_2$ is second order rate constant (g/mg.min). The experimental results of the adsorption of CV on UBTL was investigated by plotting $1/C_t$ versus $t$. Figure 5 (a-b) shows the adsorption of CV on UBTL partially follow the simple second order kinetic
equation for different initial concentration of CV and the regression factors are presented in Table 1. The values of average regression factor ($R^2$) for simple first order and second order kinetic equations are 0.912 and 0.899, respectively, which indicated that both kinetic models prediction deviated considerably from experimentally obtained data.

3.4. Pseudo second order kinetics

Pseudo second order kinetic equation based on solid phase adsorption was applied to the experimental data obtained for different initial concentrations to investigate the feasibility of adsorption of CV on UBTL [24]. The linearized form of the Ho and McKay’s pseudo second order rate equation (4) was verified by plotting $t/q_t$ vs. $t$ as shown in Figure 6 (a-b).

$$\frac{t}{q_t} = \frac{1}{kq_e} + \frac{t}{q_e}$$  \hspace{1cm} (4)

where, $q_t$ is the amount adsorbed at time, $t$ (mg/g), $q_e$ is equilibrium amount adsorbed (mg/g) and $k$ is pseudo second order rate constant (g/mg.min). Figure 6 (a-b) shows that each plot does not gives straight line with the whole range of concentration but the average value of regression factor ($R^2 = 0.933$) for different concentrations of CV is better than that of both simple first order and second order kinetic equations. A comparison of the regression factor for the fitness of simple first order, second order and pseudo second order kinetic equations to the adsorption kinetics of CV on UBTL at pH 2.0 is given in Table 1.
3.5 Effect of temperature on adsorption kinetics

To investigate the effect of temperature on the adsorption kinetics, kinetic experiments were performed at different temperatures using same concentration of CV solution at pH 2.0. Figure 7 shows the variation of amount adsorbed with time for different temperatures. Pseudo second order kinetic equation was also applied for the system at different temperatures (Figure not shown). From the slope of the each straight line, equilibrium amounts adsorbed were calculated (200 mg/g at 30 °C). Again, the equilibrium amount adsorbed was plotted against temperature as shown in Figure 8 which shows that the equilibrium amount adsorbed increases with temperature i.e. the process is endothermic indicating chemical interaction of the process.

3.6. Adsorption thermodynamics

Activation energy of adsorption

The effect of temperature on the reaction rate is well known and important in understanding reaction mechanism. The apparent activation energy of adsorption was calculated from the pseudo second order rate constant obtained at different temperatures using the following (6) Arrhenius equation [25]

\[ \ln k = -\frac{E_a}{RT} + \ln A \]  

where, \( E_a \) is the apparent activation energy (kJ/mol ), \( A \) is the Arrhenius temperature independent factor and \( k \) is the pseudo second order rate constant (g/mol·s). \( E_a \) was calculated from the slope of the plot of lnk values at different temperatures against the reciprocal of absolute temperatures as shown in Figure 9. The calculated value of apparent activation energy was 83.10 kJ/mol, implying that adsorption occurs comparatively slowly by like as chemical reaction in which \( E_a \) is in the range 65–250 kJ/mol [26].

Thermodynamic equilibrium constant

The value of the equilibrium adsorption (\( K_C \)) at different temperatures was calculated according to the following equation (7) [27-30] to estimate the thermodynamic parameters of adsorption.

\[ K_C = \frac{C_a}{C_e} \]  

\( C_a \) is the dye concentration on the adsorbent at equilibrium (mg/L) and \( C_e \) is the dye concentration in solution at equilibrium (mg/L).

To determine the apparent activation energy.
Standard enthalpy, entropy and free energy change were calculated by using equation (8) and (9), respectively [27-32].

\[
\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)
\]

\[
\Delta G^0 = -RT \ln K_C \quad (9)
\]

where $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ are the change of standard free energy (kJ/mol), enthalpy (kJ/mol) and entropy (kJ/mol·K), respectively. $K_C$ is the equilibrium adsorption constant (-) and $T$ is the absolute temperature (K). The values of $\Delta H^0$ and $\Delta S^0$ were calculated from the slope and intercept of the linear plot of $\ln K_C$ vs $1/T$ as shown in Figure 10.

![Figure 10](image)

**Figure 10.** A plot of $\ln K_C$ vs $1/T$ for determination of enthalpy of the adsorption of CV on UBTL.

The value of $\Delta G^0$ was calculated from equation (9) and presented in Table 2 as well as the values of $\Delta H^0$ and $\Delta S^0$. The results indicated that the adsorption of CV on UBTL was endothermic and chemical in nature. The calculated values of $\Delta H^0$ and $\Delta S^0$ were 8.32 kJ/mol and 0.0174 kJ/mol·K, respectively indicated that the adsorption of CV on UBTL was endothermic and less spontaneous. The positive value of $\Delta G^0$ which decreased with increasing temperature indicated the process is slow and less feasible [33]. The positive value of entropy predicted the increased randomness through the fragmentation of CV molecules during the adsorption on the UBTL surface.

**Effect of pH on Adsorption Kinetics**

The pH of solution is one of the most important parameters in the adsorption of solid/liquid interface. Basically, the pH of solution affects the adsorbent surface charge through the protonation/deprotonation process based on adsorbent’s zero point charge pH (pH_{ZPC}). In case of cationic CV as an adsorbate, solution pH has a large effect on its molecular structure through the protonation of the amino groups located at the aromatic rings. The number of positive charge decreases from 3 to 1 with the increase of solution pH. For the solution pH>5 the CV has a blue-violet color whereas at solution pH <2, the CV is green. The different colors are results of the different charged states of CV molecule. Therefore, to investigate the effect of solution pH on the adsorption kinetics as well as the adsorption capacity of CV on UBTL, a series of adsorption kinetic experiments were carried out at a fixed concentrated CV solution with different initial pH values from 2.0 to 6.0. All the solutions before and after adsorption were analyzed at a constant pH 6.0. The change of amount adsorbed with time at different initial pH is shown in Figure 11. Pseudo second order rate equation was verified for different initial pH values and respective parameters were determined. The variation of equilibrium amount adsorbed with pH is shown in Figure 12 which indicated the increase of equilibrium amount adsorbed with increase of solution pH from 2.0 to 6.0.

![Figure 11](image)

**Figure 11.** Variation of equilibrium amount adsorbed of CV with time for different initial pH with initial concentration of 51.6 mg/L at 30.0 ± 0.2 °C.

![Figure 12](image)

**Figure 12.** Change of the amount adsorbed with pH for adsorption of CV on UBTL at 30.0 ± 0.2 °C.
The observation can be explained by the pH\textsubscript{ZPC} on UBTL (pH\textsubscript{ZPC}= 4.2) [34]. The cationic species of CV are expected to be adsorbed more at higher pH values of solution than the pH\textsubscript{ZPC} of UBTL surface which leads to negative surface. The result of investigation agreed with the expectation of electrostatic interaction between the positively charged cationic CV molecules and adsorbent, which is enhanced considering the negatively charged UBTL surface (i.e. gradual deprotonation as the solution pH increases) [35]. The same trend has also been reported in the adsorption of CV by other adsorbent materials such as Peel of Cucumis sativa Fruit [36], Chaetophora elegans algae [37], Coconut coir pith (CCP) [38], Jackfruit plant (Artocarpus heterophyllus) leaf powder (JPLP) [38], Pineapple (Ananas comosus) peel powder (PPP) [38], Teak tree (Tectona grandis) leaf powder (TTLP) [38], Chiku (Manikara zopota) leaf powder (CLP) [38] and Cinnamon Plant (Cinnamomum zeylanicum) leaf powder (CPLP) [38].

### Table 2. Adsorption constant and thermodynamic parameters for CV adsorption on UBTL at different temperatures.

<table>
<thead>
<tr>
<th>Equilibrium concentration on adsorbent ( C_a ) (mg/L)</th>
<th>Equilibrium concentration in solution ( C_e ) (mg/L)</th>
<th>Equilibrium adsorption constant ( K_C ) (-)</th>
<th>( \ln K_C )</th>
<th>( \Delta G^o ) (kJ/mol)</th>
<th>( \Delta H^o ) (kJ/mol)</th>
<th>( \Delta S^o ) (kJ/K.mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.00</td>
<td>66.97</td>
<td>0.2986</td>
<td>-1.208</td>
<td>3.04</td>
<td>0.0174</td>
<td></td>
</tr>
<tr>
<td>22.33</td>
<td>66.68</td>
<td>0.3348</td>
<td>-1.090</td>
<td>2.85</td>
<td>8.32</td>
<td>0.0174</td>
</tr>
<tr>
<td>24.21</td>
<td>66.43</td>
<td>0.3644</td>
<td>-1.009</td>
<td>2.71</td>
<td>0.0174</td>
<td></td>
</tr>
</tbody>
</table>

3.7. Comparison studies

The adsorption kinetics as well as adsorption capacity and enthalpy of CV onto UBTL were compared with other biosorbents reported in literature and presented in Table 3. All the biosorbents given in Table 3 shows that the adsorption of CV follows pseudo second order kinetic equation and the process is favorable at neutral media and endothermic in nature. The adsorption capacity vary due to the properties of each adsorbent such as surface area, structure and functional groups, etc.

### Table 3. A comparison of the adsorption kinetics, capacity and enthalpy of CV onto UBTL with different biosorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>pH</th>
<th>( q_e ) (mg/g)</th>
<th>Kinetics</th>
<th>( \Delta H ) (kJ/mole)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>peel of Cucumis sativa fruit</td>
<td>7.0</td>
<td>34.2</td>
<td>Pseudo second order</td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>Chaetophora elegans algae</td>
<td>6.5</td>
<td>158.7</td>
<td>Pseudo second order</td>
<td>21.080</td>
<td>[37]</td>
</tr>
<tr>
<td>Coconut coir pith (CCP)</td>
<td>6.0</td>
<td>182.0</td>
<td>Pseudo second order</td>
<td>27.112</td>
<td>[38]</td>
</tr>
<tr>
<td>Jackfruit plant leaf powder</td>
<td>6.0</td>
<td>169.0</td>
<td>Pseudo second order</td>
<td>10.160</td>
<td>[38]</td>
</tr>
<tr>
<td>Pineapple peel powder (PPP)</td>
<td>6.0</td>
<td>153.5</td>
<td>Pseudo second order</td>
<td>10.999</td>
<td>[38]</td>
</tr>
<tr>
<td>Teak tree leaf powder (TTLP)</td>
<td>6.0</td>
<td>77.0</td>
<td>Pseudo second order</td>
<td>7.335</td>
<td>[38]</td>
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<tr>
<td>Chiku leaf powder (CLP)</td>
<td>6.0</td>
<td>73.5</td>
<td>Pseudo second order</td>
<td>5.326</td>
<td>[38]</td>
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<tr>
<td>Cinnamon Plant leaf powder (CPLP)</td>
<td>6.0</td>
<td>72.0</td>
<td>Pseudo second order</td>
<td>5.129</td>
<td>[38]</td>
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<tr>
<td>Used black tea leaves (UBTL)</td>
<td>2.0</td>
<td>200.0</td>
<td>Pseudo second order</td>
<td>8.314</td>
<td>Present Study</td>
</tr>
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</table>

4. CONCLUSION

Kinetic study on the adsorption of CV on UBTL has shown that the adsorption kinetics partially follows simple first order or second order kinetic equation but mostly follows pseudo second order rate equation for different initial concentrations of CV at pH 2.0. Pseudo second order kinetic was used to calculate the equilibrium amount adsorbed, equilibrium concentration and pseudo second order rate constant for different initial concentrations. The equilibrium amount adsorbed obtained (200 mg/g at 30 °C) from pseudo second order kinetics were found to be increased with increase in temperature i.e. the process is endothermic and chemical in nature. Pseudo second order rate constant was used to determine the apparent activation energy of adsorption. The calculated apparent activation energy and standard enthalpy were 83.1 kJ/mol and 8.27 kJ/mol, respectively. The value of apparent activation energy supported the chemical nature of the
Acknowledgments

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6. REFERENCES AND NOTES

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