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Adsorption of Crystal Violet on Used Black Tea Leaves from Acidic Solution: Equilibrium, Thermodynamic and Mechanism Studies

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Abstract: The present study investigates the potential use of used black tea leaves (UBTL) for the removal of Crystal Violet (CV) from acidic solution in batch process. The influences of different adsorption parameters such as contact time, concentration, processing temperatures and ionic strength were investigated. UV-visible spectrophotometer was used to analysis CV at a specific pH (6.0) of solution. Several model isotherms were depicted at different processing temperatures using acidic solution of pH 2.0. Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich (D-R) and Florry-Huggins model equation were subjected to analyze the equilibrium adsorption data. The experimental data reveals Langmuir and D-R models comparatively better fitted than Freundlich, Tempkin and Florry-Huggins models. The equilibrium adsorption capacity (q_m) computed from Langmuir equation is 184.1 mg/g at 30°C which is increased with increase of processing temperature. The adsorption energy (E) calculated from D-R model indicates physical adsorption which plays cardinal role in this adsorption process. The value of separation factor informs that the adsorption process is favorable in nature. The effect of electrolytes (NaCl and $NaNO_3$) suggests a possible adsorption mechanism of CV onto UBTL. The values of thermodynamic variables such as Gibbs free energy (ΔG_{ads}), enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) suggests the adsorption process is non-spontaneous, physisorption with negligible amount of fragmentation of dye molecules.

Keywords: Crystal Violet, used black tea leaves, adsorption isotherm models, thermodynamics

1. Introduction

Synthetic dyes are used extensively at this recent period in many industries including dye houses, paper printers and textile dyers. A significant proportion of synthetic dyes are lost annually to waste streams during textile processing, which eventually enters into the environment. Use of variety of dyes and chemicals in the dyeing processes causes considerable variation in the wastewater characteristics like pH, color and chemical oxygen demand (COD). Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes are used for dying wool cotton nylon, silk and modified acrylics. Textile dyes are potentially toxic because of their low removal rate [1, 2] and if untreated dyes would cause long-term health concerns. Crystal Violet (CV) is one the most useful dye uses in textile and paper dyeing and 15% of such dyes produced worldwide are released to environment in wastewater [3]. Crystal violet's common side effect is the staining of skin and cloths. However, in large quantities, CV may causes ulceration of a baby's mouth and throat and is linked with mouth cancer. CV has also been linked to cancer in the digestive tract of other animals. Therefore, concerns exist regarding the ecological impact of the discard of CV into the environment. So, it is necessary to remove this dye from wastewater stream before it is release into environment. Several possible treatment process have been developed to remove CV from wastewater stream include physiochemical, chemical and biological treatment process, such as coagulation and flocculation [4] fungal decolonization [5], ozonation [6], photodegradation [7], adsorption [8], electrochemical techniques [9], chemical bleaching [10] and micellar enhanced ultrafiltration [11]. Among the above mentioned techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [12, 13, 14]. The major advantage of adsorption technique is simple design, easy operation, cost affective and versatile. Commercial activated carbon is highly recognized adsorbent for adsorption

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process but its widespread use is restricted due to its high cost [15]. To overcome this problem, nonconventional adsorbents have been investigated. Numerous biomasses had been used as a low cost adsorbent for removal of dyes from wastewater stream including banana pith [16], coir pith [17], pine sawdust [18], rice husk [19] and neem leaf powder [20]. Out of them, used black tea leaves (UBTL), a biomass material are getting interest to researchers due to their high adsorption capacity, low cost and easy to recover the adsorbate from adsorbed UBTL [21]. In this present work, batch adsorption experiments were performed on UBTL for the removal of CV from acidic aqueous stream. The main concentration of this present work is to test the effect of initial dye concentration, temperature and salt ion in acidic aqueous stream.

2. Materials and methods

2.1 Adsorbent

Fresh black tea leaves (FBTL) were collected from local market of Dhaka city in Bangladesh. The used black tea leaves (UBTL) was prepared from FBTL by following same method as described previously [22]. In this process, about 700g of FBTL were soaked about 8 hours in boiling distilled water to remove almost all color materials. Then, leaves were dried at room temperature and also dried in oven at 105ºC for about 12 hours. Afterwards, leaves are grounded and sieved through a metallic sieve of mesh size 425-500 µm. The particles in the size range of 425-500 µm in diameter were stored in an air tight bottle and kept 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).

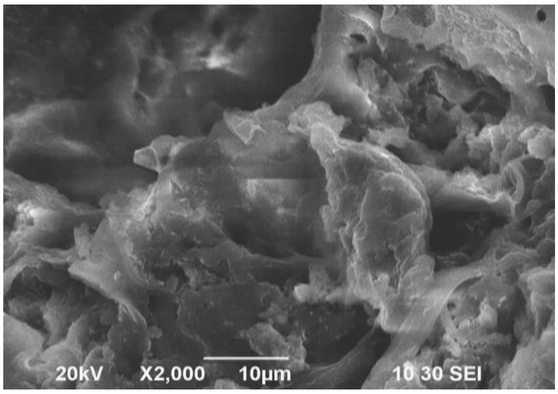


Figure 1 SEM micrograph of prepared UBTL×2000.

2.2 Adsorbate

Crystal violet (CV), a monovalent basic dye, which exist as cationic form in acidic to neutral media with molecular formula $C_{25}H_{30}N_3Cl$ and molecular weight of 407.98 g/mol used in the present study. IUPAC name of CV is tris (4-(dimethylamino) phenyl) methylium chloride. In dye classification, it is classified as C.I. 42555 and basic dye 3 [23]. All chemicals used throughout this study were analytical grade. The structural formula of CV is given in Figure 2.

A stock solution of 1000 mg/L CV was prepared in distilled water and the required different concentrated working solutions were obtained from its successive dilution. Concentration of CV in different solutions was measured by a computerized UV-visible spectrophotometer (UV-1650A, Shimadzu, Japan) at λ_{max} = 582 nm and solution pH was at 6.0 as an optimum pH for CV solution to analyze. According to Beer-Lambert law, the calibration limit of CV was evaluated 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.

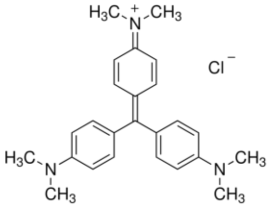


Figure 2 Molecular structure of Crystal Violet (CV)

2.3 Estimation of equilibrium time

To estimate the equilibrium time, 0.05 g of UBTL was taken in 25 mL of about 100 mg/L CV solution in each of a series of adsorption bottles. Before addition of UBTL, pH of CV solution was adjusted at optimum pH 2.0 by drop-wise addition of 0.05 mol/L HNO_3 or 0.05 mol/L NaOH solutions. All bottles were shaken in a thermostatic mechanical shaker (NTS-4000 EYELA, Japan) at 30ºC. The bottles were individually taken out from the shaker after different time of interval such 15, 45, 60, 120, 240 and 360 minutes of shaking. After adsorption, the UBTL was separated from solutions and the separated solutions were diluted as required concentration in calibration limit and pH of the diluted solutions were adjusted at 6.0 before measuring their absorbance at 582.0 nm, due to the construction of calibration curve at pH 6.0 as an optimum value. Similarly, the concentration of CV in solution, before adsorption, was also determined. The amounts of CV adsorbed on to UBTL at different contact times were calculated using the following relationship of Equation 1.

$$q_t = \frac{(C_o - C_t)V}{W} \qquad (1)$$

where C_o and C_t (mg/L) are the liquid phase concentration of CV at initial and time t, respectively. V is the volume of the solution (L) and W is the weight of the UBTL (g). The amount adsorbed is plotted against the contact time as shown in Figure 3.

2.4 Effect of temperature on adsorption isotherm

Using estimated equilibrium time of 6 hours, equilibrium adsorption experiments were performed with 25 mL of 7 different concentrated CV solutions at 25^{o}C. Other experimental parameters such as shaking time, mesh size, shaking speed and solution pH were kept constant described previously. Similar equilibrium adsorption experiments were performed at 30, 40 and 50^{o}C to investigate the effect of on adsorption and presented in Figure 4.

2.5 Effect of electrolytes

To evaluate the effect of electrolytes on CV adsorption, equilibrium adsorption experiments were performed using approximately 100 mg/L of CV solution at 30^{o}C and pH 2.0, in presence of different concentrated NaCl as reference electrolyte. Variation of amount adsorbed of CV with electrolyte concentration investigated. Similar experiments were also performed using $NaNO_3$ as reference electrolyte.

3. Results and discussion

3.1 Characteristics of adsorbent

Used black tea leaves (UBTL) are considered as a low cost adsorbent. The composition of black tea leaves are polyphones, flavones, polysaccharides, cellulose and hemicelluloses, protein, lipids, lignin, caffeine, etc [25, 26]. The continuous treatment of black tea leaves by boiling water brings a considerable change in composition while preparing UBTL. Cellulose, hemicelluloses and lignin are the main composition of prepared UBTL. The SEM microgram of UBTL shows in Figure 1 which is a heterogeneous surface indicating the possibility to adsorb CV on different parts of UBTL surface.

3.2 Estimation of equilibrium time

Equilibrium time is the most important parameter for adsorption study which is indicated the adsorption and desorption became steady. For the estimation of equilibrium time, the adsorption kinetic experiment was conducted at 30^{o}C. Figure 3 shows the change of amount adsorbed with time. The figure shows that after six hours of contact time the change of concentration with time is small which indicates most of adsorption taken place. Thus for the present system six hours of contact time was considered as equilibrium time.

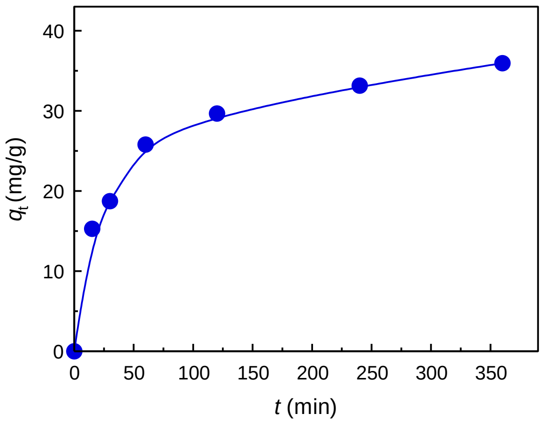


Figure 3 Change of amount adsorbed of CV on UBTL with time for the initial concentration of 100 mg/L at pH 2.0 and 30^{o}C.

3.3 Adsorption isotherms at different temperatures

To evaluate the effect of temperature on adsorption isotherm, equilibrium adsorption experiments were performed at four different temperatures and other parameters were kept constant. Adsorption isotherm is the variation of amounts adsorbed (q_e) on the surface of adsorbent with equilibrium concentration (C_e) of adsorbate at constant temperature. The changes of CV adsorbed at equilibrium with respect to equilibrium concentration of CV on UBTL at different processing temperatures are presented in Figure 4. Adsorption isotherm data is important to monitor the adsorption behavior and exploit the isotherm data for design purpose. Numerous adsorption isotherm models such as Langmuir, Freundlich, Tempkin, Dubinin-Reaudiskvich and Flory-Huggins isotherms were used to analyze the relationship between q_e and C_e in our experiments. The parameters obtained from these different models provide substantial information of adsorptive capacity of UBTL as well as its surface property and adsorption mechanism. Separation factor (R_b) values are also computed using Langmuir constant values which provide information about the formation of monolayer on adsorbent surface. The rationality of these different isotherm models are compared by determining and comparing the correlation coefficient. The change of enthalpy (ΔH_{ads}), entropy (ΔS_{ads}) and free energy (ΔG_{ads}) are also calculated from isotherms data which provide thermodynamic information about the adsorption system.

3.3.1 Langmuir isotherm

The Langmuir isotherm is a well established isotherm model assumes monolayer surface coverage on

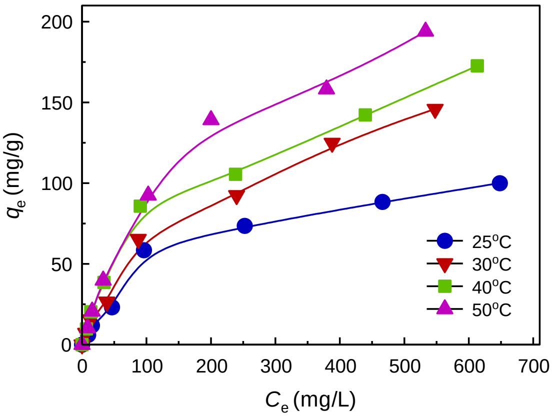


Figure 4 Adsorption isotherms of CV on UBTL for different temperature at pH 2.0.

equivalent sites [27]. The Langmuir isotherm model has been successfully applied to many adsorbate for adsorption processes. Langmuir isotherm model also assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of surface [28]. The linear form of Langmuir equation is expressed as followed:

$$\frac{C_e}{q_e}=\frac{1}{q_m b}+\frac{C_e}{q_m} \qquad (2)$$

where, C_e (mg/L) is the equilibrium concentration of CV, q_e (mg/g) is the equilibrium amount adsorbed of CV, q_m (mg/g) is the maximum adsorption capacity for complete monolayer and b (L/mg) is the Langmuir constant related to adsorption equilibrium constant. The value of q_m and b obtained from a linear plot of C_e/q_e against C_e at different temperatures (Figure 5) is presented in Table 1. The values of q_m is increased with the increase of temperatures that is indicated that the adsorption process is endothermic in nature.

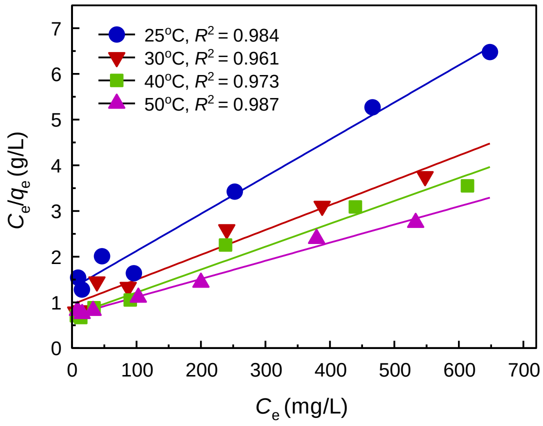


Figure 5 Langmuir isotherm for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

3.3.2 Freundlich isotherm

The Freundlich isotherm equation assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available [29]. The linear form of Freundlich equation is mathematically given by,

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \qquad (3)$$

where, k_F is the proportionality constant and n is considered as heterogeneity constant in literature which are presented in Table 1 and the others parameters is previously described in Langmuir equation. The values of n and k_F for different temperatures were calculated from the slope and the intercept of lnq_e vs lnC_e plots, respectively as shown in Figure 6. The values of n and k_F means the adsorption process is favorable and the adsorption capacity of UBTL for CV is increased with temperature [16].

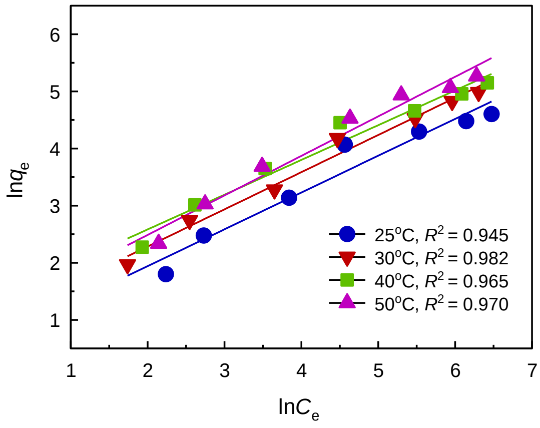


Figure 6 Freundlich isotherm for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

3.3.3 Temkin isotherm

Tempkin and Pyzhev studied the heat of adsorption and the adsorbent-adsorbate interaction on surfaces using an equation known as Temkin isotherm [30]. The linear form of Temkin isotherm equation is given by the following equation (4),

$$q_e = B\ln A + B\ln C_e \qquad (4)$$

where, A (L/g) is the equilibrium binding constant corresponding to the maximum binding energy, B is a factor related to the heat of adsorption. This model was obtained with consideration of adsorption interaction which was attained from the plot of q_e vs lnC_e as shown in Figure 7. The calculated values of B and k_T from the slope and intercept of the plots at different temperatures are presented in Table 1 which increased with increase in temperature.

3.3.4 Dubinin-Radushkevich (D-R) isotherm

Dubinin-Radushkevich (D-R) isotherm is a temperature dependant adsorption isotherm. The linear form of D-R equation [31] can be expressed by equation (5)

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \qquad (5)$$

where, q_m (mol/g) is denoted as maximum adsorption capacity, β is the D-R isotherm constant (mol^2/kJ^2) and ε is Polanyi potential which is computed from equation (6)

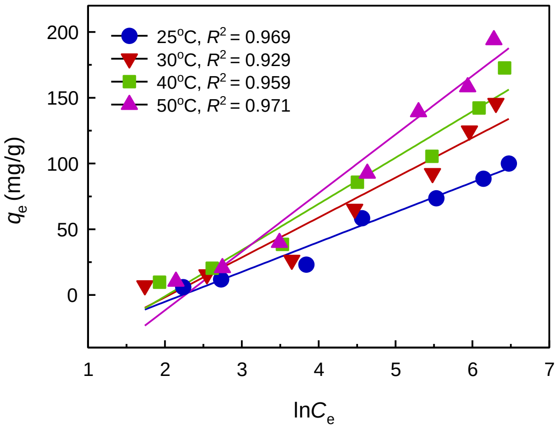


Figure 7 Temkin isotherm for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{6}$$

The mean free energy of adsorption, *E* (kJ/mol) can be calculated from equation (7)

$$E = \frac{1}{\sqrt{2\beta}} \tag{7}$$

The mean free energy (*E*) value which lies in the range of 8–16 kJ/mol indicates chemisorption and *E* < 8 kJ/mol informs physisorption [32] play a vital role in the adsorption process. The calculated values from the plot of lnq_e versus ε^2 presented in Figure 7 are given in Table 1. The correlation coefficient values inform that this isotherm model comparatively better fitted than other isotherm model. The experimental values of *E* (0.09 kJ/mol) for the adsorption of CV on UBTL suggested that the process is physisorption.

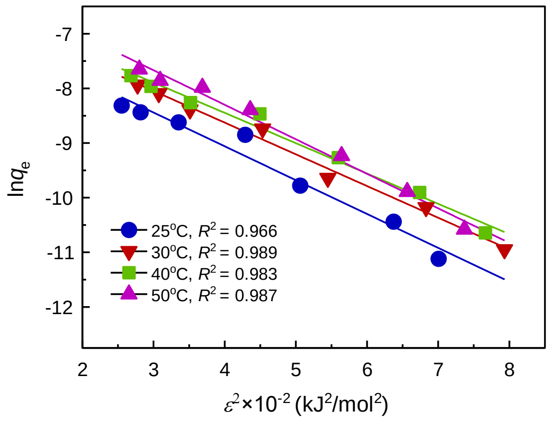


Figure 8 D-R isotherm for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

3.3.5 Flory-Huggins isotherm

Flory-Huggins isotherm model is used to describe the adsorption of adsorbate onto adsorbent surface [33]. The linear form of Flory-Huggins equation can be described by equation (8),

$$\log\frac{\theta}{C_e} = \log K_{FH} + \alpha_{FH}\log(1-\theta) \tag{8}$$

where, θ is the surface coverage of the adsorbent by the adsorbate, C_o and C_e are the initial and equilibrium CV concentrations, respectively. K_{FH} and α_{FH} are Flory-Huggins model equilibrium constant and Flory-Huggins model exponent, respectively. K_{FH} and α_{FH} values are obtained from the intercept and slope value of the linear plot of log (θ /C_e) vs log (1-θ) as shown in Figure 9 and these values are presented in Table 1. The correlation co-efficient data reflect this isotherm model does not fitted very well. One of the cardinal characteristic of this isotherm model is that provides information of degree of surface coverage of adsorbate on adsorbent surface and the degree of surface coverage helps to understand adsorption studies is related to sticking probability of the adsorbate on the adsorbent by the following relationship (9)

$$S^* = (1-\theta)\exp\left(-\frac{E_a}{RT}\right) \tag{9}$$

where, S^* is denoted as the sticking probability, E_a is energy of activation. The sticking probability is a function of adsorbate/adsorbent system gives the potential of an adsorbate to remain on the adsorbent indefinitely [33].

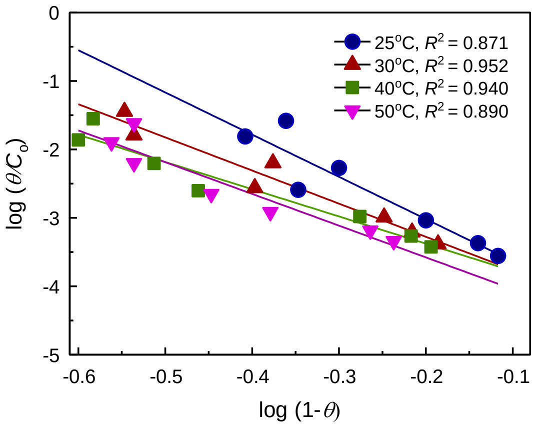


Figure 9 Flory-Huggins model for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

Table 1: Calculated different parameters from different isotherms for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

Isotherm Model	**Parameters**	**Temperatures (ºC)**			
		25	**30**	**40**	**50**
Langmuir	q_m (mg/g)	123.5	184.1	200.0	250.0
	$b\times10^3$ (L/mg)	6.17	5.649	6.966	5.554
	R^2 (-)	0.984	0.962	0.968	0.987
Freundlich	K_f (L/mg)	1.921	2.672	3.920	3.013
	$1/n$ (-)	0.644	0.650	0.608	0.692
	R^2 (-)	0.945	0.982	0.965	0.970
Temkin	B (-)	22.69	30.33	35.14	44.56
	A (-)	0.108	0.128	0.132	0.104
	R^2 (-)	0.969	0.929	0.959	0.971
Dubinin-Radushkevich	$q_\mathrm{m}\times10^3$ (mol/g)	1.386	1.829	1.975	3.114
	β (mol^2/kJ^2)	61.90	58.00	55.40	63.10
	E (kJ/mol)	0.090	0.093	0.095	0.089
	R^2 (-)	0.966	0.989	0.983	0.987
Flory-Huggins	$K_\mathrm{FH}\times10^5$ (mg/g)	5.60	5.68	6.71	3.12
	α_FH (-)	-6.17	-4.84	-3.98	-4.64
	R^2 (-)	0.871	0.952	0.940	0.890

3.4 Separation factor (R_b)

Separation factor is an important criterion which provides information of adsorption process is favorable or unfavorable. Separation factor is computed from following equation,

$$R_b = \frac{1}{1+bC_\mathrm{o}} \qquad (10)$$

where C_o (mg/L) is initial CV concentration and b is refer to Langmuir constant. If the R_b values lies in between ($0 < R_\mathrm{b} < 1$) that reflects the adsorption process is more favorable, unfavorable ($R_\mathrm{b} > 1$), linear ($R_\mathrm{b} = 1$) or irreversible ($R_\mathrm{b} = 0$) [34]. The calculated values of R_b for different initial concentrations and at different temperatures were found to be in the range of 0.07 to 0.9 which is in the favorable range (0-1) of adsorption. Figure 10 shows the variation of separation factor with initial concentration and processing temperature. The gradual decreasing of separation factor with the increase of initial concenration indicating the favorable adsorption at low concentration of CV, and the nature changed from reversible to irreversible with the increasing of dye concentration. Again, the increased of R_b values with increase of temperature suggesting the less favorable adsorption at high temperature [35].

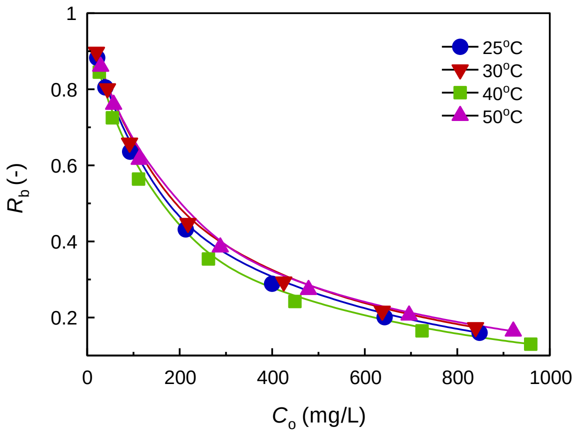


Figure 10 Separation factor for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

3.5 Thermodynamics of adsorption

Thermodynamic parameters such as change in free energy (ΔG_ads), enthalpy (ΔH_ads) and entropy (ΔS_ads) of adsorption can be determined by using the following equations:

$$\ln b = \frac{\Delta S_{\text{ads}}}{R} - \frac{\Delta H_{\text{ads}}}{RT} \qquad (11)$$

$$\Delta G_{\text{ads}} = -RT \ln b \qquad (12)$$

where, R is the molar gas constant (8.314 J/mol·K), T is the absolute temperature (K) and b is the Langmuir constant (L/mol). The values ΔH_{ads} and ΔS_{ads} were estimated from the slopes and intercepts of the plot of ln*b* versus *1/T*. Again, ΔG^o value is computed by using above mentioned Equation 12 [36]. The values of ΔG_{ads}, ΔH_{ads} and ΔS_{ads} of CV adsorption on UBTL at different temperatures are presented in Table 2. The positive values of ΔG_{ads} attribute that the adsorption process is non-spontaneous in nature. The negative ΔH_{ads} value indicates physical adsorption plays major role in this removal process. The negative ΔS_{ads} value implies favorable adsorption of CV molecule on UBTL surface.

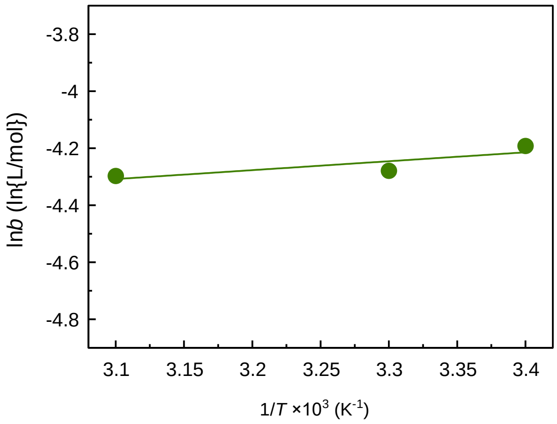


Figure 11 A plot of ln*b* vs 1/*T*

Table 2: Different thermodynamics parameters for the adsorption of CV onto UBTL at pH 2.0 and different temperatures.

Temperature (K)	***b*×10³ (L/mg)**	**ln*b* (ln{L/mol})**	**Δ*H*ᵒ (kJ/mol)**	**Δ*G*ᵒ (kJ/mol)**	**Δ*S*ᵒ (kJ/{mol·K})**
298	6.170	-4.192	-2.603	+10.384	-0.044
303	5.649	-4.279		+10.779	
323	5.554	-4.297		+11.539	

3.6 Effect of electrolytes and adsorption mechanism

Aquatic environment is mostly contaminated by industrial effluents contain dye as well as various additives such as inorganic salt. Therefore it is necessary to study the effect of electrolytes on dye adsorption onto adsorbent [37]. The mechanism of adsorption is also assumed from the effect of electrolytes. Figure 12 shows the effect of NaCl and $NaNO_3$ on adsorption of CV solution onto UBTL surface at pH 2.0, where the amount adsorbed increased with increase an increase of electrolytes concentration. Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions are attractive, an increase of electrolyte concentration will reduce the adsorption capacity. On the contrary, when the electrostatic forces are repulsive, an increase of electrolyte concentration will enhance the adsorption capacity [38, 39, 40]. Since the zero point charge pH of UBTL is 4.2 [41], due to protonation process UBTL surface became positively charged at pH 2.0. Again, the CV molecules are positively charged at this pH but due to the presence of three aromatic rings in each CV molecules became attracted by positively charged UBTL surface. Such attractive phenomenon is suggested by comparing the effects of Cl^- and NO_3^- ions on this adsorption. Figure 12 shows that in presence of highly electronegative Cl^- ions, the amount adsorbed of CV is lower than that in presence of less electronegative NO_3^- ions. This mechanism can be presented in Figure 13.

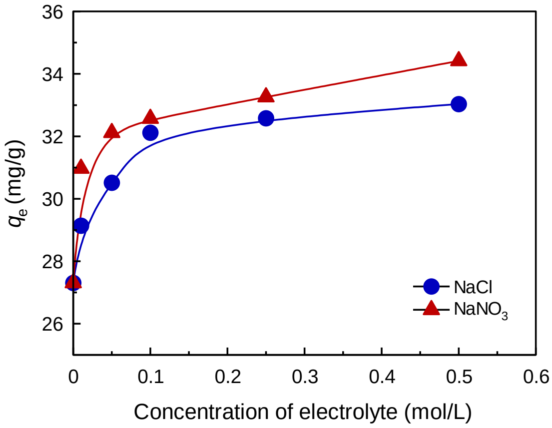
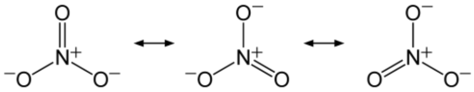


Figure 12 A plot of amount adsorbed with different electrolyte concentrations for the adsorption of CV onto UBTL at pH 2.0.

At pH 2.0, in absence of electrolytes, positively charged CV ions contained aromatic rings are slowly attracted by the protonated UBTL surface to adsorb. In presence of NaCl, highly electronegative and small size Cl^- ions are fast adsorbed on positively charged UBTL surface and neutralized the surface. Then the positively charged CV ions contained aromatic ring attracted by the UBTL surface and increased the amount adsorb. Again, in presence of $NaNO_3$, due to resonance structure, nitrate ions (NO_3^-) are fast attach with protonated UBTL surface by its negatively charged oxygen (O^-) and the positively charged CV molecules then electrostatically attracted with another negative charged oxygen (O^-) of nitrate ions, resultant the amount adsorbed increases in addition of normal adsorption of CV on UBTL.



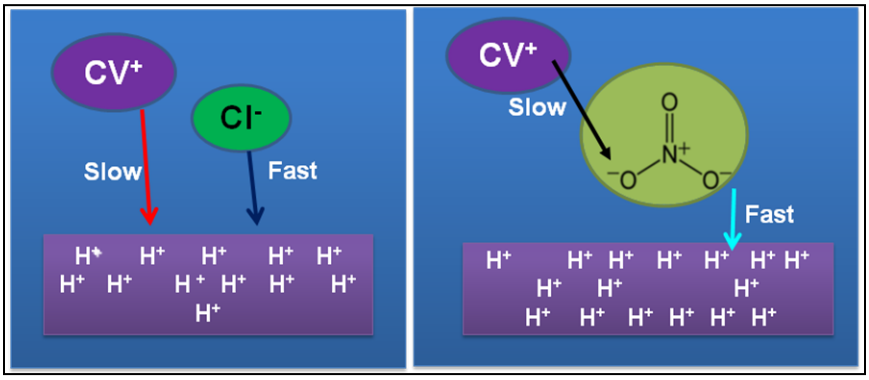


Figure 13 Proposed mechanism for the adsorption of CV onto UBTL at pH 2.0.

4. Conclusion

- The outcome obtained from the present study reveals used black tea leaves (UBTL) is a potential adsorbent.
- The contact time considered as six hours for this removal process when maximum number of dye molecule consumed on the UBTL surface.
- Equilibrium adsorption studies showed that the adsorption isotherms of Crystal Violet (CV) on UBTL at different processing temperatures follow Langmuir and D-R equations better than Freundhich, Temkin and Florry-Huggins equations.
- The adsorption of CV on UBTL is an endothermic process. Separation factor implies that the adsorption process is favorable at low concentration.
- The effect of electrolytes on the adsorption informed that the adsorption of CV on UBTL is due to the attractive force between CV molecules and UBTL surface in acidic aqueous media (pH 2.0).
- Standard enthalpy and free energy value implied that this adsorption process is physical in nature and less-spontaneous.

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