

ADSORPTION OF BASIC DYE ON LOW COST TYPHA LATIFOLIA BIOREMEDIATOR STEM CARBON: ISOTHERM, KINETIC AND EQUILIBRIUM STUDIES

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ABSTRACT

To remove the toxic cationic dyes like crystal violet a low-cost abundant adsorbents was investigated. Crystal violet is harmful by inhalation, ingestion and skin contact, and has also been found to cause cancer and severe eye irritation to human beings. *Typha latifolia*, a variety of broad leaf cattail type bioremediator, stem and leaves are used to prepare the activated carbon which was used as a novel adsorbent. The influence of pH, adsorbent dose and contact time, adsorbent nature and concentration on the selectivity and sensitivity of the removal process was investigated. The kinetics of adsorption process was studied by Lagergren's pseudo-first order. The feasibility of the sorption was studied using Freundlich and Langmuir isotherms. Various thermodynamic parameters such as the standard Gibbs free energy (ΔG°), standard entropy (ΔS°), and standard enthalpy (ΔH°) were calculated. This readily available low-cost adsorbent could be an excellent alternative for the removal of Basic dyes and organic matter from water and wastewater.

Key Words: Adsorption, Dye Crystal Violet, Kinetics, Thermodynamics, *Typha Latifolia*

I INTRODUCTION

Dyes are important chemicals widely used in industries such as paints, rubbers, pharmaceuticals and pesticides etc. Trace dyes in water may cause allergic dermatitis or skin irritation may be carcinogenic and mutagenic to humans and aquatic organism [1]. Organic dyes with intense color are highly toxic, stable to oxidizing agents because of their complex chemical structure [2]. On the other hand, dyes by reducing oxygen levels in water lead to suffocation of aquatic flora and fauna [3]. Treatment of wastewater becomes a difficult task due to dyes stability in the presence of light and heat, oxidizing agents and in addition to their resistance to aerobic digestion [4]. As to dye Crystal Violet (CV) it is described as an irritant causing harmfulness by inhalation, ingestion and skin contact, and also been found to cause cancer and severe eye irritation to human beings [5, 6]. Therefore, from an environmental point of view, the removal of organic dyes from waste water is of great significance.

Several treatment technologies have been developed to remove dye from water and wastewater which include physical, chemical, and biological methods. Amongst these methods adsorption process is superior to other waste water treatment due to its initial cost, design simplicity, easy operation and insensitivity to toxic pollutants [7].

Activated carbon is a versatile adsorbent used regularly for adsorption process but it is expensive. Consequently, many researchers focused to study the feasibility of producing various types of low cost and abundantly available adsorbent. There are various activated carbons from different bio-waste, industrial waste and agricultural waste materials. These waste materials have no economical value and still cause environmental disposal problem [8]. Although there are a number of reports on the adsorption of basic dye onto different types of adsorbents, it is necessary to investigate any potential local resources that would possess the required adsorption characteristics. Therefore, there is a need to produce a low cost, easily and abundantly available adsorbent which can be employed in waste water environment to remove dye organic and investigate adsorption properties [9, 10].

In this work, we study the synthesis of activated carbon prepared from *Typha latifolia*, a variety of broad leaf cattail type bioremediator, stem and leaves (TLAC) by chemical activation with acid and the removal of Crystal violet from aqueous solution by adsorption onto TLAC. The influence of several important operating parameters, such as TLAC dosage, initial pH and temperature, were studied by batch experiments. Furthermore, the adsorption kinetics, isotherms and thermodynamics of CV on TLAC were also investigated. The surface functional group characterization of the adsorbent material was done using Fourier Transform Infrared Spectroscopy (FTIR).

II MATERIALS AND METHODS

2.1. Preparation of activated carbon

Typha latifolia activated Carbon (TLAC) was prepared from *Typha latifolia* stem and leaves. It was collected in Dr. Ambedkar Government Arts College, Chennai, premises and the stem was dried without sunlight for 10 days and carbonized with 1:1 sulfuric acid. Carbon was washed with distilled water to attain neutral pH and dried in hot air oven at 423 K for 24 h then kept in a muffle furnace at 773 K for complete carbonization. Carbon was powdered in a ball mill to get the desired size of an activated carbon.

2.2. Preparation of metal solution

Crystal violet Tris(4-(dimethylamino)phenyl)methylium chloride its molecular formula $C_{25}N_3H_{30}Cl$. Crystal Violet obtained from Merck, India limited (analytical grade (assay 99.8%)) was used. For spectrophotometric measurements a number of standard solutions were prepared in the concentration range of 0.1-100 mg l^{-1} by successive dilutions in order to obtain the calibration curve for the determination of solution concentration.

2.3. Sorption studies

Batch adsorption studies of CV onto TLAC were determined by various parameters such as pH, metal concentration, adsorbent dose, contact time and temperature. The optimum concentration of dye solution was evaluated using 10 to

80 mg L⁻¹ with 10 mg L⁻¹ variation using 40 mL of dye solution. The pH values were adjusted from 2 to 10 using 0.1M NaOH and 0.1 M HCl using Elico pH meter. The adsorbent dosage was varied from 0.1 g to 1 g with 0.1 g variation. The effect of temperature of sorption process was estimated by using various temperatures as 303 K, 313 K, 323 K and 333 K. The contact time of the process was predicted by varying the contact time as 10–80 min with 10 min variation. The CV concentration of supernatant liquids was determined by using UV–Vis Spectrophotometer (λ max: 590 nm) model Elico Double Beam SL191 UV-Spectrophotometer. The percentage removal of CV was calculated using the following relationship

$$\% \text{ CV removal} = (C_o - C_t) / C_o \times 100 \quad (1)$$

where C_o (mg/l) and C_t (mg/l) are the dye concentration at initial and at time respectively.

2.4. Isotherm and kinetic studies

The isotherm equations used in this study are Freundlich and Langmuir isotherm equations of linear regression methods. In Langmuir isotherm various forms of linearized equations were examined. The amount of sorption at equilibrium q_e (mg g⁻¹), calculated by the following equation,

$$q_e = (C_o - C_e) \times V / W \quad (2)$$

where, C_o and C_e (mg L⁻¹) are the liquid phase concentration of CV at initial and equilibrium respectively. In order to obtain kinetic data of the adsorption process Lagergren's pseudo-first order and pseudo-second order kinetic equations were used.

2.5. Characterization of the adsorbent

The Typha latifolia stem carbon was characterized by using FTIR Spectroscopy. The FTIR provides the information about the type of functional groups present on the surface of the adsorbent material. FTIR shows that changes occur on the surface of the adsorbent before and after adsorption of the adsorbate molecule.

III RESULTS AND DISCUSSION

3.1 FTIR studies

FTIR studies are used for prediction of different types of functional groups present in the adsorbent material. The FTIR spectrum of carbon and CV loaded carbon is presented in Fig.2. The carbon spectrum shows the peaks in the positions of 3732 cm⁻¹, 3452 cm⁻¹, 2534 cm⁻¹, 2018 cm⁻¹, 1707cm⁻¹, 1618cm⁻¹, 1359 cm⁻¹ and 1146 cm⁻¹. The peak position of 3452 cm⁻¹ indicates that the presence of stretching vibration of the OH group involves in the intermolecular or intra-molecular hydrogen bonding or moisture present either in carbon or KBr. The peak positions at 2018 cm⁻¹, 1618cm⁻¹, 1193 cm⁻¹ and 1035 cm⁻¹ shows that the presence of alkyl group or due to the presence of tannin, C-C bond in aromatic conjugation, C–N peptide bond and S, O interaction respectively [11,12]. The CV loaded spectrum of FTIR shows that there is no change in their position of the peaks but there is a reduction in peak

heights and intensity of the peaks. This confirms that CV was strongly adsorbed onto the Typha latifolia Carbon (TLAC).

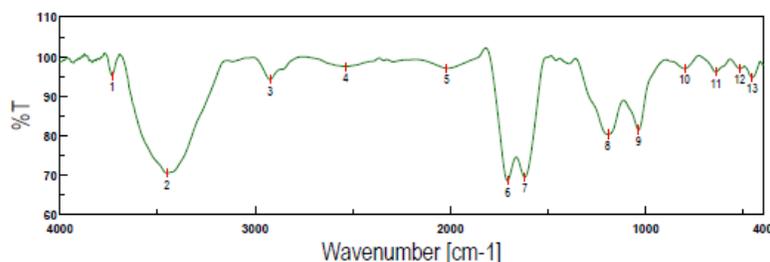


Figure 2: FTIR spectrum of TLAC

3.2. Sorption studies

Initial dye concentration is an important factor that affects the adsorption process. The increase of initial concentration of CV results in the increased uptake capacity, further enhancement leads to a decreased percent removal since number of molecules of dye available on surface area of the adsorbent is high at higher concentrations [13]. Adsorption of dye was studied at different concentrations from 10 mg L^{-1} to 80 mg L^{-1} with 10 mg L^{-1} variation.

3.2.1 Effect of pH

The pH of the solution is an important parameter which controls the adsorption process. The effect of pH on the percent removal of CV by TLAC was evaluated with the pH range of 2-10 at initial dye concentration of 50 mg L^{-1} . Fig 3 shows the variations of dye removal from wastewater at different pH, it is evident from the figure a maximum removal is observed at pH of 8. At low pH, an increase in H^+ concentration in the solution and acquires positive charge on the surface of TLAC by absorbing H^+ ions. On the other hand, at higher pH values, a significantly strong electrostatic attraction occurs between the negatively charged surface of the TLAC and cationic dye molecule leading to maximum adsorption of CV [14]. The lowest adsorption occurred at low pH and the highest adsorption at pH 8. Adsorbent surface would be positively charge up to pH 4 and thereafter, becomes negatively charged increasing the adsorption of CV.

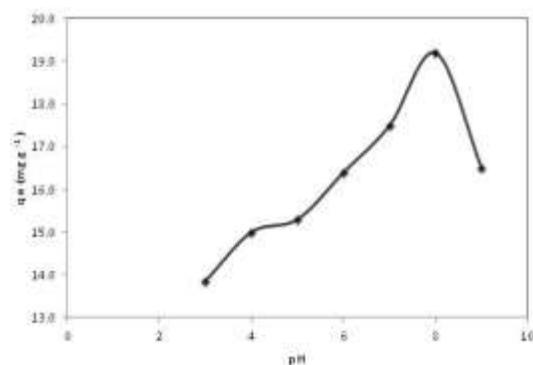


Figure 3: Effect of pH

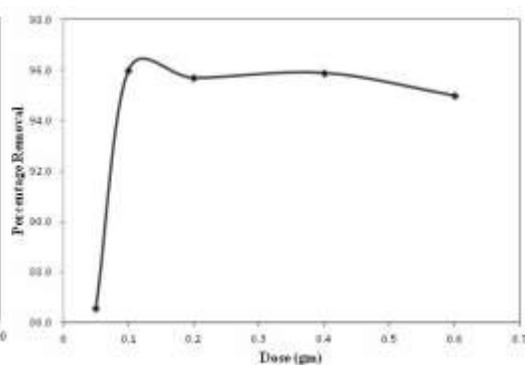


Figure 4: Effect of Adsorbent dose

3.2.2 Effect of dosage rate

The effect of adsorption capacity of CV was found with the variation of dosage of adsorbent material. The dose of adsorbent varied from 0.05 g to 1.0 g L⁻¹. From Fig. 4, the effect of adsorbent dose on percentage adsorption of CV was found with a dose of 0.3 g adsorbent showing higher CV removal when compared with other dosages. As the adsorbent dose increased, the percentage removal of CV slightly increased due to the availability of more binding sites for adsorption [15]. No considerable increment in adsorption with increasing dosage can be attributed to the change in the concentration gradient of dye molecules between the bulk solution and adsorbent [16].

3.2.3 Effect of Temperature

The adsorption test was carried out with different temperatures at 303 K, 313 K, 323 K and 333 K to study the effect of temperature on adsorption. These experiments were carried out in the pH 8 with 100 mg L⁻¹ of dye solution on TLAC. The amount of adsorbed CV dye was decreased with increasing temperature. This can be explained by the fact that the mobility of CV dye molecules increases with increase in temperature. Fig 5. indicates the decrease in percentage removal could be due to the reduction of the physical forces of attraction between CV dye and TLAC. The experimental results showed that the removal of dye is reduced with increase in temperature onto the adsorbent TLAC which is a kinetically controlled exothermic process [17]. Fig.6 shows the effect of contact time of dye on to TLAC with increase in time the amount of dye adsorbed per unit mass of sorbent slightly increases and attain constant.

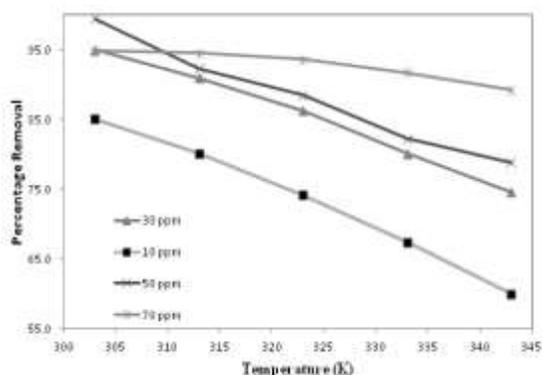


Figure 5: Effect of Temperature

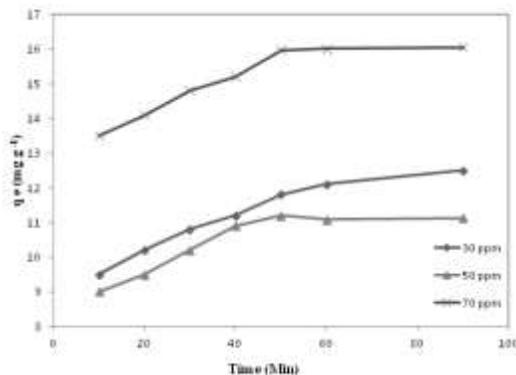


Figure 6: Effect of contact time

3.3. Isotherm studies

The adsorption data were analyzed with two adsorption isotherm models, namely Freundlich and Langmuir. Various forms of Langmuir and Freundlich were tested in their linear and non-linear forms [18,19]. The Langmuir isotherm is expressed as

$$q_e = q_m K_a C_e / 1 + K_a C_e \quad (3)$$

The term q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of CV dye adsorbed per unit mass of sorbent and unadsorbed dye concentration in solution. Where q_m is the maximum amount of CV dye adsorbed per unit mass of sorbent at complete monolayer on surface bound, and K_a (L mg^{-1}) is a constant related to the affinity of the binding sites. The formula of Langmuir and Freundlich isotherms of linear and non-linear are presented in Table 1.

Table 1 : Isotherm Formulae

Isotherms	Non-Linear	Linear	Plot	Reference
Freundlich	$q_e = K C_e^{1/n}$	$\log q_e = \log K + \frac{1}{n} \log C_e$	$\log q_e$ Vs. $\log C_e$	Freundlich (1906)
Langmuir	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e	Langmuir (1916)

The Freundlich isotherm equation is expressed as

$$q_e = K C_e^{1/n} \tag{4}$$

where K (mg g^{-1}) (L g^{-1}) is an indicator of the adsorption capacity, $1/n$ is the adsorption intensity.

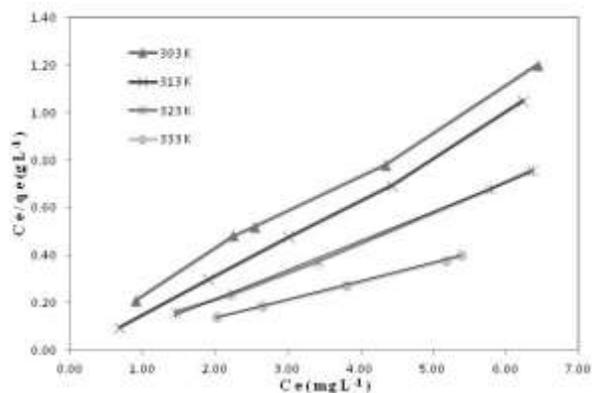


Figure 7: Langmuir adsorption isotherms

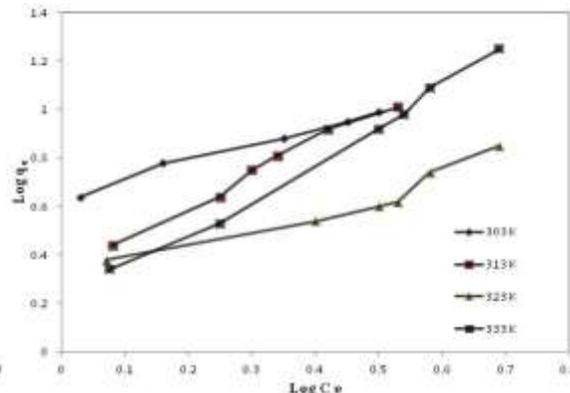


Figure 8: Freundlich adsorption isotherms

Table 2: Isotherm Parameters obtained from Linear Method

Isotherm	Parameters	Temperature (K)			
		303	313	323	333
Freundlich	1/n	0.7047	1.3194	0.7185	1.500
	K (mg g^{-1}) (L g^{-1})	4.3	2.18	1.9498	1.557
	r^2	0.984	0.985	0.8996	0.992
Langmuir	q_m (mg g^{-1})	5.76	5.89	8.16	12.97
	K_a (L mg^{-1})	2.60	5.79	3.95	4.17
	r^2	0.994	0.9974	0.998	0.9902

The magnitude of the exponent $1/n$, shows the favorability of adsorption, $1/n$ value when $n < 1$ represents favorable adsorption condition. The best suited isotherm model of Freundlich and Langmuir isotherms is used to calculate q_m , K_a and coefficient of determination r^2 are presented in Table 2. The q_m and K_a values predicted using the parameters of $1/q_e$ vs. $1/C_e$, q_e vs. q_e/C_e and q_e/C_e vs. q_e by plotting graphs. Various forms of Langmuir constants are varied with different forms of linear equations and that depends on the way isotherm equations has linearized [20]. Langmuir isotherm shows a better correlation coefficient (r^2) value compared to Freundlich isotherm. The higher q_m value of Langmuir confirms that the maximum quantity of adsorption at 303 K. The equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set of experimental data, by plotting $\log(q_e)$ vs. $\log(C_e)$. It was observed that at all the temperatures; the r^2 values were found to be relatively suggests that the Langmuir isotherm is the most appropriate isotherm than Freundlich isotherm for the present system. Fig. 7 and Fig.8 shows experimental data and the predicted equilibrium curve using linear method given in Table 2, for the two-equilibrium isotherms Freundlich and Langmuir at 303 K, 313 K, 323 K, and 333 K respectively. It was observed that at different temperatures, 303 K was found to be more suitable condition. But in the case of other temperatures there was a deviation.

Table 3: Pseudo - first order and second order rate equations and their formulae

Type	Non-Linear	Linear	Plot
Pseudo – first order	$q = q_e (1 - e^{-K_1 t})$	$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303}$	$\log(q_e - q) vs. t$
Pseudo – second order	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$t/q = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	$t/q vs. t$

Table 4: Pseudo – first order and second order rate constant for the sorption of CV onto TLAC

C_o	Pseudo – First order kinetics			Pseudo – second order kinetics			r^2
	K_1	q_e	r^2	q_e (Experimental)	K_2	q_e (Calculated)	
30	0.0016	8.600	0.8243	0.75	3.44	0.3261	0.996
50	0.0029	6.61	0.9697	2.17	0.04	2.1460	0.9941
70	0.003	9.4	0.816	1.45	0.089	1.4511	0.9963

3.4. Kinetic studies

The equilibrium kinetic profiles were characterized to determine the rate limiting steps involved in the process of sorption of CV dye onto TLAC. Lagergren's Pseudo first order equation (5) and Pseudo second order equation (6) kinetic models were applied [21]. The linearized form of the pseudo-first order equation is

$$\log(q_e - q) = \log(q_e) - K_1 t / 2.303 \quad (5)$$

where, K_1 is the pseudo first order adsorption rate constant, q_e is the amount of dye adsorbed onto TLAC at equilibrium (mg g^{-1}), q_t amount of dye adsorbed onto TLAC at any time t (mg g^{-1}). The linearized form of the pseudo-second order form is

$$T/q = 1 / K_2 q_e^2 + (1/q_e) t \quad (6)$$

where, K_2 is the pseudo second order adsorption rate constant, q_e is the amount of dye adsorbed onto TLAC at equilibrium (mg g^{-1}); q_e^2 is the pseudo second order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). Various forms of pseudo-first order and pseudo-second order kinetic equations are presented in the Table 3. From the experiments Fig. 9 and Fig. 10, the calculated value of pseudo-first order rate constant (K_1), pseudo-second order rate constant (K_2), equilibrium uptake capacity (q_e) and regression coefficient (r^2) are presented in Table 4. From table the coefficient values of pseudo-first order rate constant are very low when compared with pseudo-second order kinetic values. On the other hand the obtained values of pseudo-second order kinetics have shown the correlation coefficient value 0.995 while pseudo-first order shows 0.866. Hence, the results intimate that the sorption process follows second order rate equation throughout the process. Moreover, the rate of the reaction process does not depend on the concentration factor (Pseudo-first order) but depends on both concentration as well as time (Pseudo-second order).

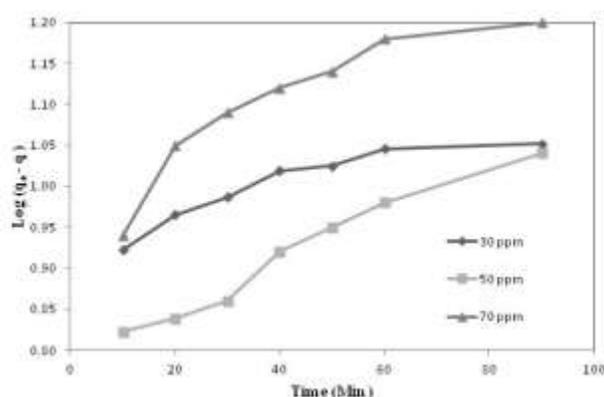


Figure 9: Pseudo first order kinetic model

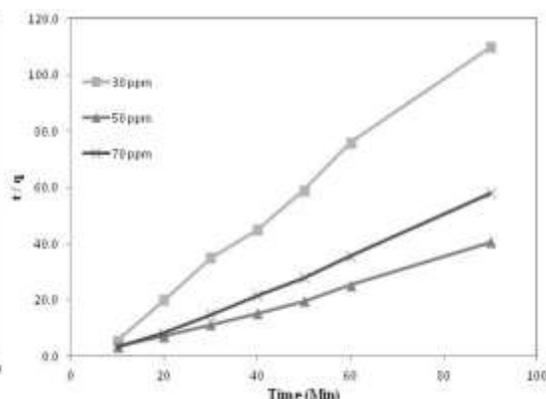


Figure 10: Pseudo second order kinetic model

3.5. Thermodynamic studies

The effect of heat of adsorption of the adsorbate onto the adsorbent material was determined using the thermodynamic parameters like free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0), were calculated from the Van Hoff's equation using the following equations [22, 23]

$$K_d = q_e / C_e \quad (7)$$

$$\Delta G = -RT \ln K_d \quad (8)$$

$$\ln K_d = \Delta S^0 / R - \Delta H^0 / RT \quad (9)$$

where, K_d is the distribution coefficient, T is the temperature and R is a gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). From Fig. 11, the thermodynamic parameters ΔS^0 and ΔH^0 are calculated using the linear regression analysis of Van't Hoff plot using the parameters $\ln K_d$ vs. $1/T$. The positive value of the enthalpy change of ΔH^0 value shows that the endothermic nature of the reaction involved during the adsorption process. The entropy (ΔS^0) shows positive value, this indicates that there was a increased randomness between the solid-solution interfaces during the adsorption

process Table 5. The Gibbs free energy change (ΔG^0) shows a negative value which reveals that the adsorption process is spontaneous in nature for the adsorption of CV dye onto TLAC.

Table 5: Thermodynamic parameters for the sorption of CV onto TLAC

T (K)	ΔG^0 (KJmol ⁻¹)	ΔH^0 (KJmol ⁻¹)	ΔS^0 (KJmol ⁻¹ K ⁻¹)
303	-3.22	0.09	70.86
313	-2.12		
323	-1.98		
333	-1.68		
343	-1.32		

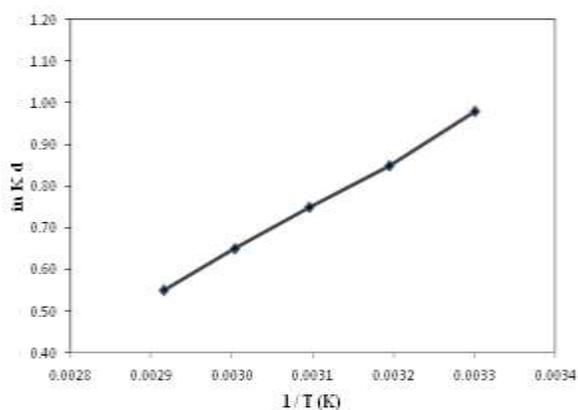


Figure 11: Van't Hoff plot

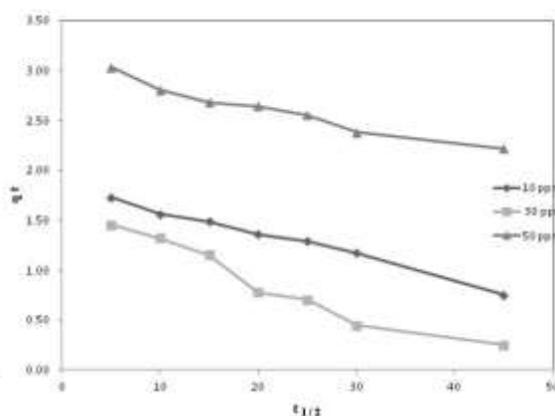


Figure 12: Intra-particle diffusion model

The kinetic models do not provide enough information of an exact diffusion mechanism that is involved during the process and the rate controlling steps, which affect the nature of the adsorption process [24]. The new method to provide the diffusion mechanism is intra particle diffusion model developed by the theory of Weber and Morris. This method shows all the adsorption process with the dye uptake capacity varying almost proportional with $t^{1/2}$ rather than with the contact time t . The intra particle diffusion equation is given by

$$q_t = K_d t^{1/2} + C$$

where K_d is intra particle diffusion rate constant and C is intercept.

The plot between q_t vs. $t^{1/2}$ shows a straight line and the parameters of K_d and C are calculated from the linear regression analysis of the slope and intercept. The experimental values are depicted in the Fig. 12 which shows the quantity of CV adsorbed vs $t^{1/2}$ for various dye concentrations. The predicted plot shows linearity at different time intervals. This demonstrated that intraparticle diffusion played a significant role in the uptake of dye on to TLAC. The results of r^2 (0.999) and k_d values indicated that the adsorption and intra particle diffusion mechanism are occurring concurrently.

IV CONCLUSION

From the experimental results, the linear regression analysis shows better result for both Langmuir and Freundlich equations. Langmuir isotherm was the most favorable method for the adsorption of basic Crystal Violet dye. So the

adsorption process was favorable for the adsorption of dye onto TLAC. The kinetic result shows that the adsorption process follows pseudo-second order kinetics, which implies that the adsorption process depends on both time and concentration. The thermodynamic parameter change in enthalpy (ΔH^0) shows positive value intimating that the adsorption process was endothermic in nature and the magnitude of adsorption supports the formation of partial chemical process that is involved during the removal process. The change in entropy (ΔS^0) shows a positive value suggests good affinity of CV towards TLAC and increase randomness at the solid-solution interface during adsorption. The Gibbs free energy change (ΔG^0) shows a negative value revealing that the adsorption process is spontaneous in nature. The FTIR spectrum shows a well characterized variation before and after adsorption with reduction in peak height and intensity. All the studies clearly indicate that TLAC is a low cost best alternative adsorbent for the removal of toxic dyes from industrial effluent and waste water. Further, removal of Crystal Violet dye through adsorption process is effective and eco-friendly.

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