

## Utilization of Waste Biomass for the Removal of Basic Dye from Water

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**Abstract:** In this study we used the *Delonix regia* tree pods' as a raw material to produce activated carbon. The common name of the tree is Flame tree. Batch experiments were conducted to assess the potential for the removal of Crystal violet dye from aqueous solution using the activated carbon. Equilibrium isotherm and kinetic studies have been done by varying the parameters such initial concentration of Crystal violet dye solution, adsorbent dose, pH of the dye solution, temperature of the system and varying the contact time between the carbon and the dye. Non-linear forms of equations were used for comparing the best-fitting of isotherms. The equilibrium data obtained were fitted to Langmuir, Freundlich and Redlich-Peterson isotherms models. The kinetic data were fitted to pseudo first order and pseudo second order kinetics model. The experimental data were well explained by the Redlich-Peterson isotherm model and the pseudo second order kinetic model compared to other models. The pH of the dye solution played an important role in the uptake of Crystal violet dye by the activated carbon from aqueous solution. Increase in the pH of the solution leads to the surface modification and the adsorption capacity increased from 13.0mg/g to 19.3mg/g. Increased in temperature of the adsorption system increased the adsorption of capacity of the activated carbon confirmed the endothermic nature of the reaction. The adsorption capacity of the activated carbon derived from *Delonix regia* pods' depends on the factors like pH of the solution, temperature of the system, structure of the dye molecule and the nature of pores present on the structure of activated carbon.

**Key words:** Crystal violet • Adsorption • Redlich-Peterson isotherm • Pseudo second order kinetics

### INTRODUCTION

Water pollution due to toxic metals and organic compounds remains a serious environmental and public problem. Heavy metal ions, aromatic compounds including phenolic derivatives, polycyclic aromatic compounds and dyes are often found in the environment as a result of their wide industrial uses. They are common contaminants in wastewater and many of them are known to be toxic. Today more than 3000 dyes are in use worldwide [1]. Presence of colour in the wastewater is one of the main problems in textile industries. Colours are easily visible to human eyes even at very low concentration. From an environmental point of view, the removal of synthetic dyes is of great concern, because some dyes and their degradation products are carcinogenic and toxic [2]. It is very difficult to remove these chemicals by conventional biological treatment methods. Amongst all the treatments proposed, adsorption using sorbents is one of the most popular methods since proper design of the adsorption process

will produce high-quality treated effluents [3-5]. It is now recognized as an effective, efficient and economic method for water decontamination applications and for separation analytical purposes. Since commercially available activated carbon is very expensive, now the research is focused on the use of low cost adsorbents derived from agricultural and wood wastes, such as bagasse [6], coir pith [7], wood apple shell [8], tree fern [9], rice husk [10] etc., have been used for dye removal from wastewater. Crystal violet dye is one of the frequently used dyes in all industries. In this work, we used Flame tree pods' (*Delonix regia* tree pods') as a raw material to produce activated carbon to remove the Crystal violet dye from water.

### MATERIALS AND METHOD

The pods' were crushed into smaller pieces and soaked with concentrated  $H_2SO_4$  at 1:1 ratio (wt of raw material/ volume of acid) for 48 hours and activated at 160°C for 6 hours. The activated carbon was repeatedly

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washed with distilled water until the pH of the wash water becomes the pH of the distilled water. The carbon obtained from the Flame tree pods (FTPC) was dried at  $105 \pm 1^\circ\text{C}$  for 2 hours. All the chemicals used are of analytical grade. The stock solution of 1000 mg/L Crystal violet (CV) was prepared using double distilled water. Solutions of desired concentration were prepared by diluting the stock solution. A calibration graph of absorbance verses concentration of CV was obtained using systronics photometer (model 104) at  $\lambda_{\text{max}}$  595 nm. Batch experiments were conducted using screw cap closed containers using ORBITEK shaker at 300 rpm. For isotherm studies 100 mg of FTPC and 50 mL of different concentrations of CV dye solution in the range of 20 to 100 mg/L were taken in the closed containers after having adjusted for required pH and shaken for 2 hours. The required initial pH of the dye solution was obtained by using HCl (0.1 N, 0.01 N and 0.001 N) and NaOH (0.1 N, 0.01 N and 0.001 N). Effect of carbon dose was studied by using 50 mL of 50 mg/L dye solution with varying the carbon dose ( $\text{pH} = 7 \pm 0.05$ ) for 2 hours shaking. Effect of contact time was carried out by using 50 mL of different initial concentrations of dye solution (5, 10, 15 and 20 mg/L) with 100 mg of carbon after adjusting the pH ( $7 \pm 0.05$ ). After equilibrium time, the residual concentration of the dye and the activated carbon was separated by using micro filters was analyzed using spectrophotometer at a wavelength of 595 nm. All the experiments were carried out at  $25^\circ\text{C}$ . Non-linear forms of equations were used throughout the study. In order to study the influence of temperatures on the adsorption of dye on FTPC, the experiments were carried out at two higher temperatures 323 and 333 K apart from one at room temperature (313 K) in an orbital shaker equipped with incubation facility for regulating temperature. For temperature study 50 mL of dye solutions were shaken with 0.1 g of each adsorbent separately for different initial concentrations, after adjusting the pH of the solution to  $7 \pm 0.1$ , for 2 h. Calculations were done using Microsoft Excel spreadsheet software.

## RESULTS AND DISCUSSION

**Adsorption Isotherm Models:** Adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. The equilibrium adsorption isotherm is very important one to design the adsorption systems. For solid-liquid systems, several isotherms equations are available. The Langmuir

isotherm takes an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent [11], the equation is

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

The Freundlich isotherm is an empirical equation [12] employed to describe the heterogeneous system. The equation is given below:

$$q_e = K_f C_e^{1/n} \quad (2)$$

The Redlich-Peterson isotherm model [13] combines both Langmuir isotherm and Freundlich isotherm equation and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. The equation is

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (3)$$

In the above equation, 'g' is the exponent, which lies between 0 and 1. If g is equal to one, the equation modifies to Langmuir model, if g is equal to zero then the equation changes to Henry's law equation.

**Effect of Initial Concentration of the Dye Solution:** The most important factor, which controls the sorption of dyes on the sorbent material, is the pH of the solution. In the present study, the removal of CV increased with increase of pH of the dye solution from 5 to 9. And there is a decrease in the pH of the dye solution after the removal of dye from the solution by FTPC. This shows there is protons release from the surface of the carbon due to cation exchange between the FTPC and the dye molecules [9]. This reveals that the increase of pH deprotonate the acidic groups on the surface of the carbon and provides more negative sites for the sorption of cationic form of the dye molecules [14]. Whereas at low pH, there would be more number of hydrogen ions in the solution that prevents the negative charge formation on the carbon surface and reduces the uptake of the dye. The aggregation of cationic dyes sorbed on the carbon surface is mainly due to ion exchange mechanism [15]. Similar type of results was reported by other authors [16]. The pH of the CV dye loaded carbon was found to be 4.53 (before adsorption  $\text{pH} = 3.91$ ), which shows the strong attachment of dye molecules on the surface of the carbon. The non linear form of isotherms at different initial

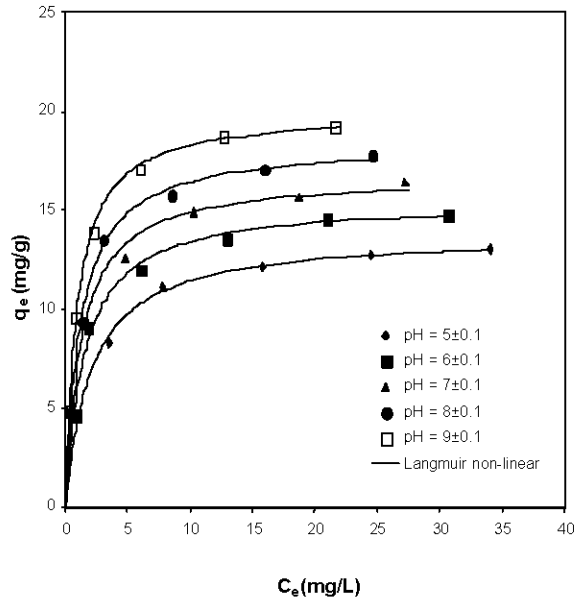


Fig. 1: Langmuir Isotherms for FTFC-CV at various pH

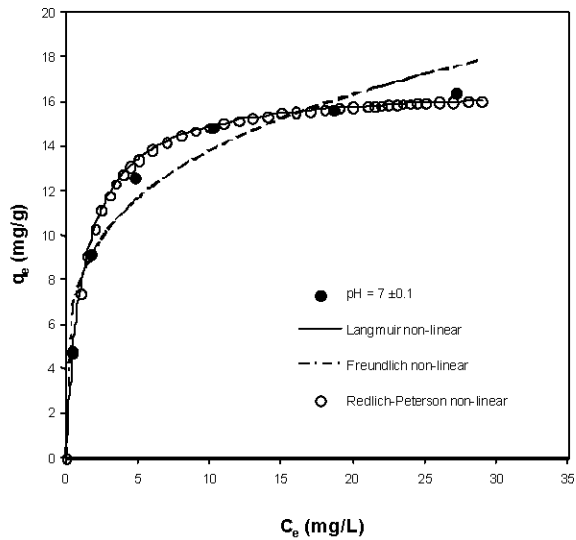


Fig. 2: Fitted isotherm models for FTFC-CV for varying the  $C_0$

pH is shown in Fig. 1. At lower  $C_e$ , there is no significant difference in the adsorption of dye. But at higher  $C_e$  there is an appreciable difference in the adsorption of dye molecules. The  $q_m$  is the maximum sorption and is found to be increased from 13.0 to 19.3 mg/g by increasing the pH from 5 to 9 and is given in Fig.1.

The Langmuir parameters obtained for this FTFC-CV system at different pH of the dye solution were given in Table 1. The three isotherm models fitted with the

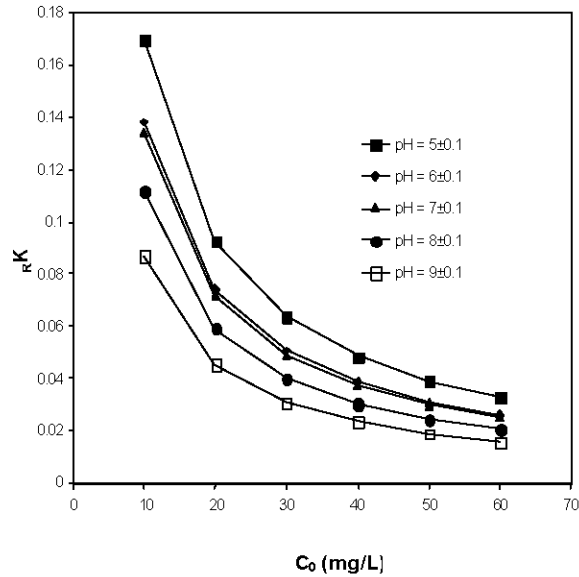


Fig. 3: Relation between  $C_0$  and  $K_R$  for FTFC-CV system various pH

Table 1: Fitted isotherm parameters for FTFC-CV system at pH 7

Isotherm model	Parameters	Units	FTFC-CV
Langmuir	$q_m$	mg/g	16.700
	$K_a$	L/mg	0.796
	$r^2$		0.991
Freundlich	$K_F$	g/L	7.900
	$1/n$		0.244
	$r^2$		0.923
Redlich-Peterson	$g$		1.000
	$B$	L/mg	0.796
	$A$	L/g	13.300
	$r^2$		0.991

experimental data are shown in Fig. 2. In this Figure, there is a steep rise of the Langmuir isotherm curve shows that there is strong affinity between FTFC and CV dye. In this adsorption system the 'g' value becomes 1 which shows the overlap of Redlich-Peterson isotherm on Langmuir isotherm (8). The  $r^2$  (0.991) value also same for both the models. The relation between the initial concentration and the  $K_R$  values [17,18] are given in Fig. 3, which shows the increase of concentration reduces the  $K_R$  value (speed up the reaction) due to the increase in the number of dye molecules and the increase of pH also lowers the value due to the increase of more negative sites on FTFC. This leads to the electrostatic attraction between the dye molecules and the negative sites on the surface of the carbon. The Langmuir rate constants  $K_a$  increases with increase of the pH of the solution.

Table 2: Fitted kinetic parameters for FTPC-CV system

Pseudo 1st order				Pseudo 2nd order			
$C_0$	$q_i$	$k_1$	$r^2$	$q_e$	$k$	$h$	$r^2$
mg/L	mg/g	1/min		mg/g	g/mg min	mg/g min	
5	2.3	0.047	0.952	3.0	0.01584	0.1	0.966
10	4.3	0.032	0.944	5.0	0.00572	0.2	0.960
15	6.4	0.039	0.938	7.8	0.00568	0.3	0.975
20	8.5	0.0365	0.971	11	0.00295	0.4	0.974

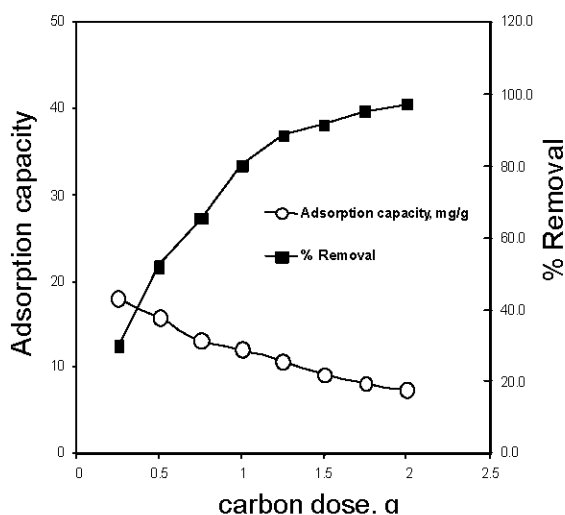


Fig. 4: Dose effect of FTPC-CV

**Effect of Carbon Dose:** The effect of carbon dose for the uptake of CV by FTPC was found to be increased by increasing the adsorbent dose, due to the increase of the activated site available for adsorption. From Fig. 4, a minimum carbon dose of 100 mg of FTPC was required for the maximum removal of dye from 50mg /L of CV dye from solution. The  $q_m$  value was found to be 15.0 mg/g.

**Effect of Contact Time:** It is necessary to identify the step that governs the overall removal rate in the above sorption process. The pseudo-first order and pseudo-second order kinetic models were tested to fit the experimental data obtained for CV dye uptake by FTPC. The kinetic study results were given in Table 2.

**Pseudo-First Order Kinetic Model:** A simple kinetic model which describes the process of sorption is the pseudo-first order equation suggested by Lagergren [19,20].

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (4)$$

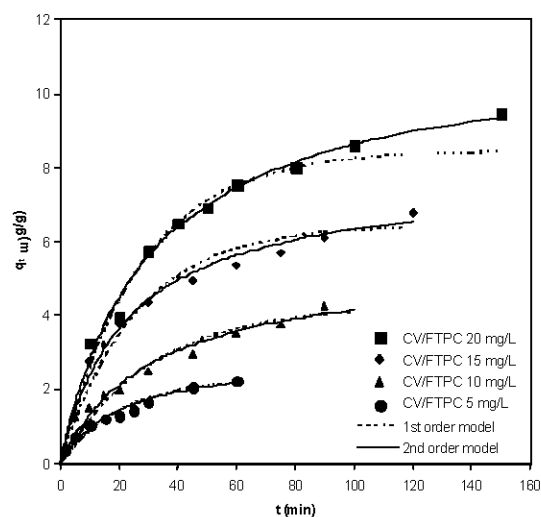


Fig. 5: Fitted kinetic models for CV-FTPC system

But this first order equation is applicable only for the initial 20 to 30 min of the sorption process. The  $q_e$  value obtained using the above equation is lower than the experimental one. The removal of CV dye using FTPC does not follow the pseudo-first order equation.

**Pseudo-Second Order Kinetic Model:** The pseudo-second order kinetic equation was developed for the sorption process [21]. The equations are given below:

$$q_t = q_e \left( \frac{q_e k_2 t}{1 + q_e k_2 t} \right) \quad (5)$$

The plots of time vs.  $q_t$  are shown in Fig. 5. The correlation coefficients ( $r^2$ ) for the non-linear plots of pseudo-second order plots are higher than the pseudo-first order reaction plots (Table:2). This shows that the pseudo-second order kinetic model explains the sorption in a better way. The pseudo-second order model is based on the assumption that the rate determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate [22]. Increase in the initial dye concentration from 5 to 20 mg/L increased the sorption capacity from 3 to 11 mg/g. The plot of rate constant values versus the  $C_0$  (Fig.6) shows that intraparticle/pore diffusion is involved in the overall rate of CV sorption on FTPC. When pore diffusion limits the rate of sorption process, the relation between initial concentration of the dye solution and the rate of the reaction will not be linear [23]. Increase of initial dye concentration from 5 to 20 mg/L increased the initial

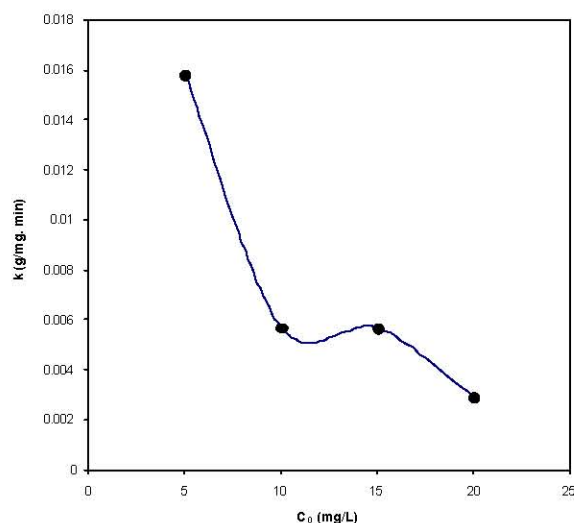
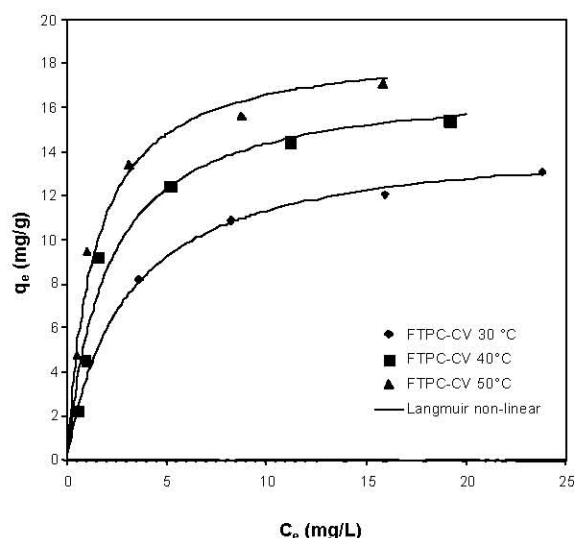
Fig. 6: Relation between  $C_0$  and  $k$  for FTPC-CV system

Fig. 7: Effect of temperature on FTPC-CV system

rate constant ' $h$ ' from 0.1 to 0.4 mg/g.min due to the increased in randomness of the molecules. But the pseudo second order rate constant value  $k_2$  decreases from 0.01584 to 0.00295 g/mg.min This is due to the decrease in the readily available vacant adsorption sites as the dye concentration is increased. In other words, once the easily available sites are occupied the excess dye molecules in solution find remote adsorption sites inside the pores of the carbon with difficulty.

**Effect of Temperature:** The adsorption capacity of FTPC-CV system increased from 14.6mg/g to 18.8mg/g while increasing the temperature (Fig.7) of the system at pH equal to  $7.0 \pm 0.1$ . The enhancement of adsorption capacity

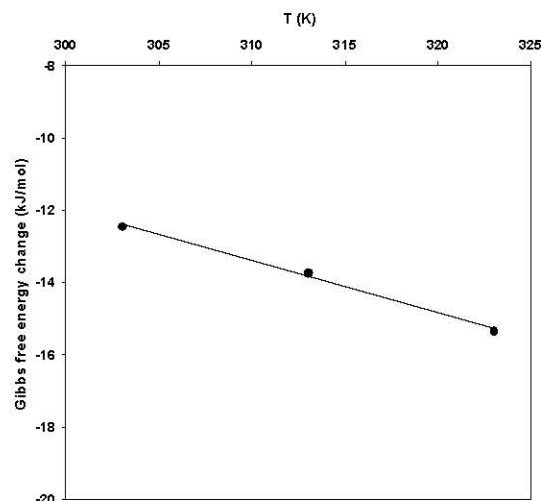


Fig. 8: Van't Hoff plot for FTPC-CV system

Table 3: Thermodynamic parameters for FTPC-CV system

System	$\Delta G^\circ$ kJ/mol	$\Delta H^\circ$ k J/mol	$\Delta S^\circ$ J/mol /K
FTPC-CV	-12.39	31.43	0.1446
	-13.83		
	-15.28		

on increasing the temperature may be due to increase in the mobility of dye molecules and enlargement of pore size due to "activated diffusion" which causes pores to widen and deepen ("pore burrowing") [24] thereby creating more surface for adsorption. Since diffusion is an endothermic process it would be expected that an increased solution temperature would result in increased adsorption capacity. The decrease in  $\Delta G^\circ$  values while increasing the temperature indicates that the adsorption process becomes more spontaneous at higher temperatures. The  $\Delta H^\circ$  and  $\Delta S^\circ$  [24-26] values were calculated (Table: 3) from the slope and intercept of the Van't Hoff plots obtained by plotting Gibbs Free Energy Vs temperature (Fig. 8). The positive value of  $\Delta S^\circ$  shows increased randomness at the solid-solution interface during adsorption and indicates affinity [27] of the dye onto adsorbents.

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (6)$$

## CONCLUSION

The sorption kinetics and isotherm of CV removal using FTPC was carried out in batch experimental system. The following conclusions were drawn based on the above study:

The waste biomass from Flame tree pods' is converted into activated carbon using concentrated sulphuric acid. The sorption was found to be dependent on initial CV dye concentration, pH, temperature and the contact time. The rate of sorption follows pseudo-second order rate equation. The above experimental data were well fitted with the Langmuir model and Redlich-Peterson model and the increased in pH of the initial concentration of dye solution and carbon dose increased the rate of the reaction. The present study has demonstrated that the carbon derived from flame tree pods' can be employed for the removal of CV from water. The experimental results obtained by the batch experiments can be useful for the environmental engineers in designing the batch experimental set up for removal of CV from water using FTFC.

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