

# **Research Journal of Pharmaceutical, Biological and Chemical**

# Sciences

# Spectral and Cyclic Voltammetric Monitoring of the Removal of Crystal Violet Using *Carica Papaya* Seeds.

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#### ABSTRACT

An effective and low cost adsorbent was prepared from the seeds of Carica Papaya for the removal of crystal violet from aqueous solutions. Adsorption studies were carried out using batch experiments. The dependence of initial dye concentration, pH, contact time, adsorbent dose, particle size and temperature on the adsorption process was studied. The crystal violet was found to be electroactive and hence cyclic voltammetric studies were also performed. The study showed that the equilibrium states were achieved within 60 min. The equilibrium adsorption data were analyzed using various isotherm models and they were found to fit Langmuir, Freundlich, Tempkin and Harkins-Jura isotherm models in varying orders of magnitude. The maximum dye adsorption capacity was found to be 166.67 mg/g (spectral studies) and 6.38 x  $10^{-4}$  A/g ( cyclic voltammetic studies) at 30°C. The Adsorption kinetics was best represented by pseudo-second order kinetic model. The thermodynamic parameters including  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the adsorption process have been evaluated using which it was concluded that the process of adsorption was spontaneous and endothermic. The various results conclude that both spectral and cyclic voltammetric methods could be used as monitoring techniques for the removal of crystal violet dye from aqueous solutions.

Keywords: Adsorption, Crystal Violet, Carica Papaya, Cyclic voltammetric.

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## INTRODUCTION

The major problem that exists in most of the developing countries like India is pollution which could be due to large population growth and industrial growth. Many industries use toxic and hazardous chemicals for manufacturing their finished products. The waste products (effluents) discharged by those industries contain toxic heavy metals, dyes, hazardous chemicals that may affect our environment even if they are present at low concentrations [1]. The use of various dyes has become popular among many industries such as paper, textile, leather, food, cosmetics and pharmaceuticals [2]. These industries generate coloured effluents which are directly discharged into the natural water sources like river, lakes etc. They cause adverse effects to the aquatic plants by reducing the light penetration through the water and thereby inhibiting photosynthetic process [3].

Crystal violet, a well-known basic dye, belonging to triphenylmethane group, is used as biological stain, veterinary medicine, additive to poultry feed to inhibit propagation of mould, intestinal parasites and fungus, textile dying and paper printing [4]. It is harmful upon inhalation, ingestion and skin contact and also has been found to cause cancer and severe eye irritation [5]. Basic dyes have high brilliance, intense colours and are highly visible even in very low concentration [6]. Such dyes are poorly degraded by microbial enzyme and can persist in a variety of environment. The treatment of the dye effluents before being discharged into water sources is therefore a concern environmental protection. Among the various effluent treatment processes, adsorption is found to be the most economical and efficient process [7]. Several adsorbents have been used for the removal of crystal violet such as grapefruit peel [8], tamarind seed powder[9], coniferous pinus bark powder[10], treated ginger waste [11], Spent TeaLeaves (STL)[12], male flowers of coconut tree [13], Pumpkin seed hull[14], coconut bunch waste[15], agricultural waste[16], Citric Acid Modified Rice Straw[17], Date Palm Fiber [18], leaf biomass of *Calotropis procera* [19], *Ricinus Communis* Pericarp carbon[20] Citrullus Lanatus Rind[21].

Papaya seeds have been evaluated as a low cost adsorbent for the removal of methylene blue [22]. However, it has not been used for the removal of crystal violet dye. Moreover, electrochemical studies on the adsorption of crystal violet dye from aqueous solutions have not yet been reported. Our studies were aimed at the removal of crystal violet dye from aqueous solutions under different experimental conditions using papaya seeds along with the exploration of adsorption kinetics and isotherms using both spectral and electrochemical techniques.

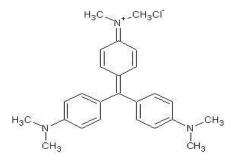


Figure 1: Structure of crystal violet



#### MATERIALS AND METHODS

## Adsorbent

Papaya seeds collected were thoroughly washed with distilled water to remove the dirt adhering to the surface. It was then dried, powdered and sieved to a size of 250 -300  $\mu$ m and stored in an air tight container till further use. No other physical or chemical treatment was done prior to adsorption experiment.

## Adsorbate solution

Crystal violet (CV) used for this study was received from Sigma Aldrich (CI-42555, molecular formula –  $C_{25}H_{30}N_3CI$ , molecular weight – 408 gmol<sup>-1</sup>,  $\lambda_{max}$  – 584 nm) and used without further purification. A stock of 1000 mg/L dye solution was prepared using deionized water. Different concentrations of dye solution were prepared by apprpriate dilution from the stock solution.

#### Instruments used

The absorbance of dye solutions at the desired wavelength was determined using Thermo Scientific Helious Alpha UV-Visible spectrophotometer. The surface morphology of powdered *Carica Papaya* Seeds (*CPS*) before and after adsorption was determined using JSM- 5610LV JEOL Scanning Electron Microscope. Cyclic voltammetric studies were carried out using CHI 6063C – Electrochemical analyzer.

#### EXPERIMENTAL

## **Electrochemical measurements**

All voltammetric experiments were performed in the single compartment cell with a volume of 5 ml at 30°C. The working electrode was glassy carbon. Ag/AgCl electrode was used as a reference electrode and a platinum wire served as the counter electrode.

## **Batch adsorption studies**

Adsorption of CV dye solution was carried out using batch experiments and the effect of various parameters like contact time (10-80 min), adsorbent dose (0.05-0.3 g), pH (2-12), initial dye concentration (10-30mg/L), particle size (200 - 250  $\mu$ m, 250-300  $\mu$ m and 300-500  $\mu$ m) and temperature (30-50°C) on the removal of CV were studied.

The adsorption studies were carried out by adding varying amounts of adsorbent to 50 ml of dye solution of known concentrations. The solutions were agitated at 160 rpm using shaker to attain equilibrium at predetermined time intervals. The samples were taken and the supernatant solution was separated from the adsorbent by centrifugation for 5 minutes. The absorbance values of the supernatant solutions were measured using UV-Visible spectrophotometer. The same solutions were used to obtain reduction peak current ( $i_p$ ) values as a function of the concentration of CV dye remaining after adsorption, using electrochemical analyzer. Amount of dye adsorbed at equilibrium was given by,



ISSN: 0975-8585

$$q_e = \frac{(C_0 - C_e)V}{W}$$
(1)

where  $C_o$  is the initial concentration of the dye (mg/L),  $C_e$  is the concentration of dye at equilibrium (mg/L), V is the volume of the solution (L), W is the weight of adsorbent (g)

The percentage dye removal was calculated using

Percentage removal=
$$\frac{(C_o-C_e)}{C_o} \times 100$$
 (2)

For cyclic voltammetric studies, amount adsorbed at equilibrium can be calculated as

$$q_e = \frac{(i_{po} - i_{pe})V}{W}$$
(3)

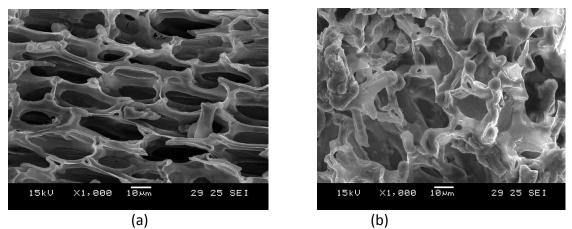
where  $i_{Po}$  is the initial reduction peak current of the dye solution ( $\mu A$ ), and  $i_{Pe}$  is the reduction peak current of the dye solution at equilibrium ( $\mu A$ ).

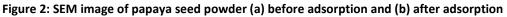
The percentage dye removal was calculated using

Percentage removal= 
$$\frac{(i_{po}-i_{pe})}{i_{po}} \times 100$$
 (4)

#### **RESULTS AND DISCUSSION**

## Surface characterization of CPS





The surface morphology of the *CPS* before and after dye adsorption has been studied by scanning electron microscopy (Fig. 2). The SEM analyses showed that the adsorbent has considerable number of pores (Fig.2a) which was occupied by the dye molecule (Fig.2b)



## Effect of pH on adsorption of CV

The pH of dye solution is an important parameter in adsorption process which affects the surface binding sites of the adsorbent and the degree of ionization of the dye in solution. In order to understand the effect of pH, the equilibrium adsorption studies were carried out at a concentration of 10mg/L dye solutions at pH ranging from 2 to 12. The percentage removal of dye was found to be marginally greater at pH 8 (Fig.3), which is indeed the pH of the dye solution itself. Hence further studies were carried out without adjusting the pH of the dye solution.

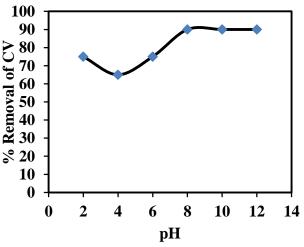


Figure 3: Effect of pH on adsorption of CV onto CPS

# Effect of adsorbent dose

The adsorption of CV onto CPS was studied by varying the adsorbent dose from 0.3g to 0.5g, keeping all other parameters constant. The data suggested that the percentage removal of dye increased with increase in adsorbent dose which is not surprising given that the increase in the amount of adsorbent effectively increases the number of active sites available for adsorption [21], thereby increasing the percentage removal of dye. The equilibrium state was achieved beyond 0.2g as shown in Fig.4.

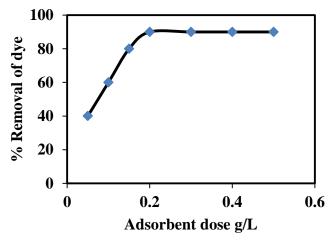


Figure 4: Effect of CPS dose on adsorption of CV



# Cyclic Voltammetric studies on CV

The electrochemical behaviour of CV dye was examined over a potential range from -1.5V to +1.5V (vs. Ag/AgCl) with a scan rate of 100 mVs<sup>-1</sup>. The cyclic voltammogram of CV dye was shown in Fig.5. A reduction peak was observed at -0.756V which indicated that the CV dye was electroactive [23].

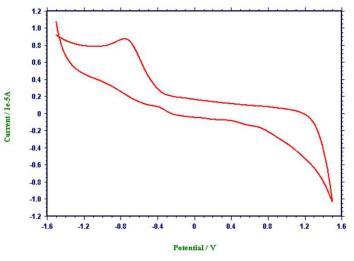


Figure 5: Cyclic voltammogram of CV dye.

# Effect of contact time and initial dye concentration

The effect of initial dye concentration onto adsorption of CV by *CPS* was studied at different initial concentrations (10 - 30 mg/L) at 30° C and the results were shown in Fig.6. As the initial concentration of CV increased, the percentage removal increased from 90 to 93%. This is due the fact that increase in concentration enhances the interaction between the dye and the adsorbent despite the necessary driving force to overcome the resistance to mass transfer of dye [19]. The uptake of CV increased rapidly during initial stages and reached a constant value beyond 60 min for all the initial concentrations studied.

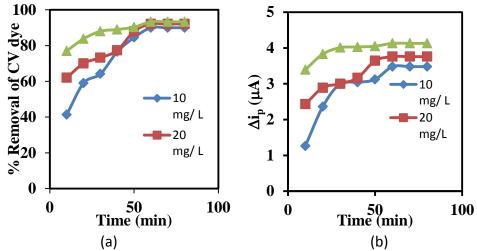


Figure 6: Effect of contact time on adsorption of CV onto *CP*S at different initial concentrations (adsorbent dose= 0.2 g; particle size=200-250 µm; agitation speed=160 rpm; temperature=30°C) (a) Spectral studies (b) Cyclic Voltammetric studies

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Similar results were also observed in cyclic voltammetric studies. The reduction peak current  $(i_p)$  values at various time intervals for different initial concentrations of CV dye solutions were noted. It was found that the  $i_p$  values decreased as the time of contact between the CV dye solution and CPS increased and reached a constant value indicating an increase in the percentage removal of CV.

The  $\Delta i_p = (i_{Po} - i_{Pe})$  values were found to increase as the initial concentrations of CV increased. This indicated that the percentage removal of dye also increased (from 90% to 93 %) with increasing concentrations.

# **Adsorption Kinetics**

The mechanism of adsorption and the potential rate controlling steps involved in the process of adsorption had been investigated using kinetic models such as pseudo-first-order, pseudo-second-order and intraparticle diffusion model [19]. The linear form of these models is given by equations (5), (6) and (7), respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$
(5)

$$\frac{t}{q_{e}} = \frac{1}{k_{2}q_{e}^{2}} + \frac{1}{q_{e}} t$$
(6)

$$q_{t} = k_{id} t^{\frac{1}{2}} + C$$
(7)

where  $q_t$  and  $q_e$  (mg/g) are the adsorption capacities at time t and at equilibrium, respectively  $k_1$  (min<sup>-1</sup>) and  $k_2$  (mg/ (g min)) are pseudo-first and pseudo-second order rate constants;  $k_{id}$  is the intraparticle diffusion rate constants (mg/ (g min<sup>0.5</sup>)) and C is the intercept which gives an idea about the boundary layer thickness.

The effect of contact time and initial dye concentration was investigated to find the best kinetic model. The pseudo-first order rate equation did not fit well to the range of concentrations studied as indicated by poor correlation coefficients (R<sup>2</sup>). Both spectral and cyclic voltammetric studies yielded similar results. The results were summarized in Table 1 and 2. These results suggested that the adsorption of CV onto *CPS* was not preceded by diffusion through a boundary. This was confirmed by the results obtained with the intraparticle diffusion. The plot shown in Fig.8 was not linear over the whole time range. Hence it could be concluded that more than one process had affected adsorption. The initial linear dependence can be attributed to the boundary layer diffusion whereas the latter linear dependence was due to attributed to intraparticle diffusion [5, 21].

The pseudo second-order model was developed based on the assumption that the rate-controlling step is chemisorption involving valence force due to sharing or exchange of electrons between adsorbent and adsorbate molecules [5]. The higher  $R^2$  (>0.98) for the pseudo-second order kinetics (Fig.7), indicated the fitness of this model and it was suggested that chemisorption might be a rate-controlling step[5]. Moreover the  $q_e$  values calculated using pseudo second-order equation agreed well with the experimental  $q_e$  indicating that the adsorption of CV onto *CPS* could be well represented using the pseudo



second order kinetic model. These results were in accordance with those obtained using cyclic voltammetric studies.

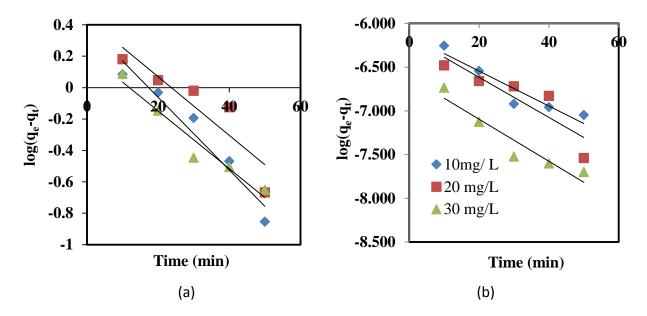


Figure 7: Pseudo-first order kinetic plot for adsorption of CV onto CPS at different initial concentrations (particle size 200-250 μm, agitation speed=160 rpm, temperature 30<sup>°</sup>C) (a) Spectral studies (b) Cyclic Voltammetric studies

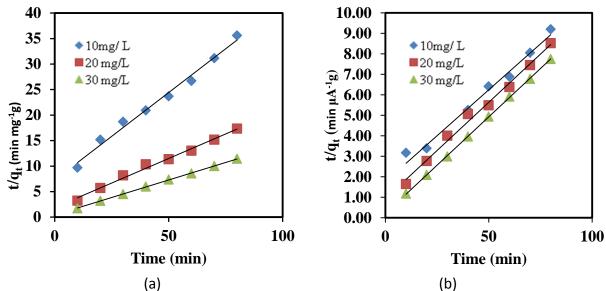


Figure 7. Pseudo-second-order kinetic plots for adsorption of CV onto *CP*S at different initial concentrations (particle size 200-250 μm, agitation speed=160 rpm, temperature 30°C) (a) Spectral studies (b) Cyclic Voltammetric studies



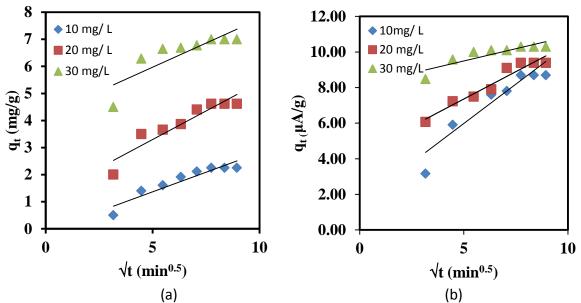


Figure 8.Intra particle diffusion plot for adsorption of CV onto CPS at different initial concentrations (particle size 200-250 μm, agitation speed=160 rpm, temperature 30°C)
 (a) Spectral studies (b) Cyclic Voltammetric studies

Table 1: Adsorption kinetic model parameters obta	ained using spectral studies
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C <sub>o</sub> (mg/ L)	q <sub>e</sub> (exp) (mg/ g)	Pseudo First- order Kinetic model			Pseudo Second- order Kinetic model			Intra-particle diffusion Model		
		q <sub>e</sub> (cal ) mg/g	k <sub>1</sub> (min- <sup>1</sup> )	R <sup>2</sup>	q <sub>e</sub> (cal ) mg/g	k₂ (mg/ (g min)	R <sup>2</sup>	k <sub>id</sub>	С	R <sup>2</sup>
10	2.25	2.51	0.041	0.945	2.42	0.016	0.987	0.231	0.347	0.714
20	4.62	2.77	0.052	0.815	4.50	0.026	0.990	0.327	1.900	0.877
30	6.99	1.65	0.041	0.948	7.09	0.046	0.999	0.205	5.322	0.889

C <sub>o</sub> (mg/ L)	q <sub>e</sub> (exp) μΑ/ g	Pseudo First- order Kinetic model			Pseudo Second- order Kinetic model			Intra-particle diffusion Model		
		q <sub>e</sub> (cal) μΑ/g	$k_1$ (min- <sup>1</sup> )	R <sup>2</sup>	q <sub>e</sub> (cal) µA/g	k₂ 10 <sup>5</sup> A/ (g min)	R <sup>2</sup>	k <sub>id</sub> 10 <sup>-8</sup>	C 10 <sup>-7</sup>	R <sup>2</sup>
10	0.87	0.72	0.046	0.891	0.81	0.762	0.980	9.0	2	0.852
20	0.94	0.24	0.051	0.898	0.96	11.6	0.991	6.2	4	0.941
30	1.33	0.693	0.050	0.787	1.06	44 .0	0.999	3.0	8	0.783

## **Adsorption Isotherms**

The adsorption isotherm establishes a relationship between the amount of dye molecules adsorbed onto the adsorbent and the equilibrium concentration of the dye molecules in solution at a given temperature. The fitness of the equilibrium data obtained for the adsorption of CV onto *CP*S was analyzed using various models viz., Langmuir, Freundlich, Tempkin and Harkins-Jura adsorption isotherm models.

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## Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption process. The linear form of it can be expressed as

$$\frac{1}{X/M} = \frac{1}{q_{max}} + \frac{1}{q_{max}} \frac{1}{b} \frac{1}{C_e}$$
(8)

where  $q_{max}$  is the maximum monolayer dye concentration in the solid phase (mg/g),  $C_e$  is the equilibrium dye concentration in the aqueous phase (mg/L), X/M=  $q_e$  is the equilibrium dye concentration in the solid phase (mg/g) and b is the Langmuir equilibrium constant (L/mg).

Langmuir plots for the adsorption of CV onto *CPS* using spectral and cyclic voltammetric studies were shown in Fig.9(a) and Fig.10(a), respectively. The constants q<sub>max</sub> and b obtained from spectral and cyclic voltammetric studies for three different concentrations (10-30 mg/L) were presented in Table 3 and 4, respectively. The dimensionless constant separation factor ( $R_L$ ) which indicates whether the adsorption process is unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) can be calculated as

$$R_{L} = \frac{1}{1 + bC_{o}}$$
(9)

The  $R_L$  values were found to be less than 1 indicating that the adsorption process was favourable [21]. The  $R^2$  values were 0.991 and 0.998 for spectral and cyclic voltammetric studies respectively, indicating the fitness of the Langmuir model with the equilibrium data.

## Freundlich isotherm

The Freundlich isotherm is suitable for heterogenous surface [21] and its logarithmic form can be expressed as

$$\log q_e = \log K + \frac{1}{n} \log C_e$$
(10)

where K and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Freundlich plots for the adsorption of CV onto *CPS* using spectral and cyclic voltammetric studies were shown in Fig.9(b) and Fig.10(b), respectively. The constants  $K_F$  and n values were determined from the intercept and slope of the plots, respectively. The values of n were found to be less than 1 which indicated favourability of the adsorption process. The R<sup>2</sup> values were 0.999 and 0.998 for spectral and cyclic voltammetric studies respectively, indicating the fitness of the Freundlich model with the equilibrium data.



# Temkin isotherm

Temkin isotherm suggests that sorption energy decreases as the degree of completion of the sorptional centers of an adsorbent is increased [21].

$$q_e = B_T (\ln A_T + \ln C_e)$$
(11)

where,  $B_T = RT/b$  is the absolute temperature (K), R is the gas constant (8.314Jmol<sup>-1</sup>K<sup>-1</sup>),  $A_T$  is the equilibrium binding constants (Lmg<sup>-1</sup>) and  $B_T$  is related to the heat of adsorption (Jmol<sup>-1</sup>).

Temkin plots for the adsorption of CV onto *CPS* using spectral and cyclic voltammetric studies were shown in Fig.9(c) and Fig.10(c), respectively. The constants  $A_T$  and  $B_T$  values were determined from the intercept and slope of the plots, respectively. The  $R^2$  values were 0.981 and 0.982 for spectral and cyclic voltammetric studies respectively, indicating the fitness of the model with the equilibrium data.

# Harkin-Jura isotherm

Harkins-Jura adsorption isotherm accounts for multilayer adsorption and can be explained with the existence of heterogenous pore distribution. It can be expressed as

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e$$
(12)

where B and A are the isotherm constants.

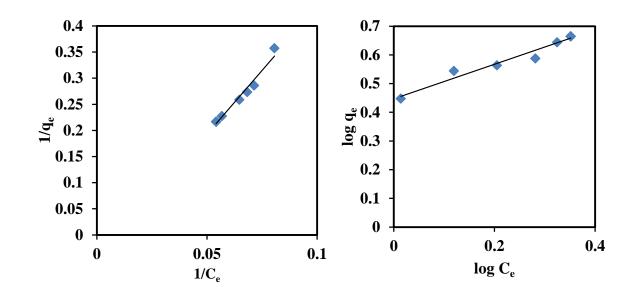
Harkins-Jura plots for the adsorption of CV onto *CPS* using spectral and cyclic voltammetric studies were shown in Fig.9(d) and Fig.10(d), respectively. The constants A and B values were determined from the slope and intercept of the plots, respectively. The  $R^2$  values were 0.938 and 0.991 for spectral and electrochemical studies respectively, indicating the fitness of the model with the equilibrium data. Hence there could be a possibility of multilayer adsorption to occur [21].

	Langn isotherm			Freundlich isotherm model		Tempkin isotherm model			Harkins- Jura isotherm model			
q <sub>max</sub> (mg/g)	b (L/mg)	R <sup>2</sup>	R <sub>L</sub>	k (mg/g)	n	R <sup>2</sup>	A <sub>T</sub> (L/mg)	Β <sub>τ</sub> (J/mg)	R <sup>2</sup>	A	В	R <sup>2</sup>
166.67	0.02	0.991	0.625	2.23	0.60	0.999	1.35	6.82	0.981	1.62	0.31	0.938



	Langi	muir		F	reundlic	:h		Tempkin		н	arkins- Ju	ura
	isotherm	n model		isotherm model		isotherm model			isotherm model			
q <sub>max</sub>	b	R <sup>2</sup>	RL	k	n	R <sup>2</sup>	A <sub>T</sub>	B <sub>T</sub> (10 <sup>-6</sup>	R <sup>2</sup>	Α	В	R <sup>2</sup>
q <sub>max</sub> (10 <sup>-4</sup>	(L/		10 <sup>-6</sup>	(A/g)			(L/µA)	J/A)		10 <sup>-13</sup>		
A/g)	μA)											
6.38	392.5	0.998	0.849	3.74	0.99	0.998	0.135	0.937	0.982	0.3	0.9	0.991
	8											

#### Table 4: Adsorption isotherm model parameters based on cyclic voltammetric studies at 30°C







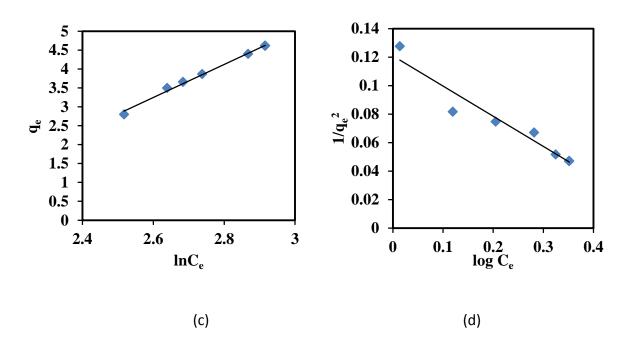


Figure 9: (a) Langmuir (b) Freundlich (c) Tempkin (d) Harkin-Jura adsorption isotherm plots for the adsorption of CV by *CP*S using Spectral studies

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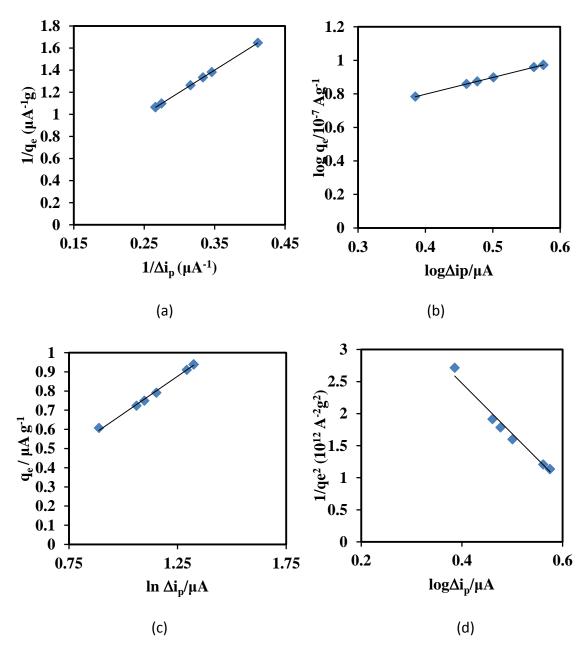


Figure 10: (a) Langmuir (b) Freundlich (c) Tempkin (d) Harkin-Jura adsorption isotherm plots for the adsorption of CV by *CP*S using cyclic voltammetric studies

## Effect of particle size

Adsorption of CV onto *CPS* of three different particle sizes (200-250, 250-300, 300-500  $\mu$ m) was studied by keeping all other parameters constant. The variation of particle size on the adsorption process based on spectral and cyclic voltammetric studies were shown in Fig.11 and Fig.12, respectively. As particle size was decreased, the adsorption efficiency of CPS increased. This could be due to increase in the total surface area with decrease in particle size leading to increase in the adsorption efficiency of the adsorbent [21].



From the Cyclic voltammetric studies, it was found that in the presence of adsorbent the cathodic peak potential ( $E_{pc}$ ) was shifted towards more positive side (from -1.2 V to -1.05V). This might be due to weak electrostatic force of attraction between *CP*S and CV [23].

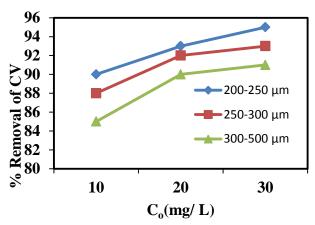


Figure 11: Effect of particle size on adsorption of CV onto CPS (adsorbent dose= 0.2 g; contact time = 60 min; agitation speed=160 rpm; temperature=30°C) using spectral studies

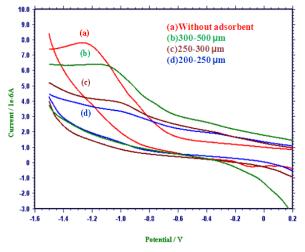


Figure 12: Cyclic voltammograms showing the effect of particle size on adsorption of CV onto CPS

## **Effect of Temperature**

Temperature has a significant effect on the process of adsorption. Adsorption of CV onto *CPS* was studied at three different temperatures (30°C to 40°C) for 10 mg/ L initial concentration of CV. From the Fig.13, it was found that the percentage removal of dye increased from 90% to 95% with increase in temperature. This may be due to the fact that increase in temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent owing to decrease in the viscosity of the solution[21]. Thermodynamic parameters such as change in free energy change ( $\Delta$ G), enthalpy change ( $\Delta$ H) and entropy change ( $\Delta$ S) were determined using the following equations



 $K_o = \frac{C_{Solid}}{C_{Iiquid}}$ 

(13)

where  $K_o$  is the equilibrium constant, C <sub>solid</sub> is the solid phase concentration (mg/ L), C <sub>liquid</sub> is the liquid phase concentration (mg/ L).

$$\Delta G = -RT \ln K_{o}$$
(14)  

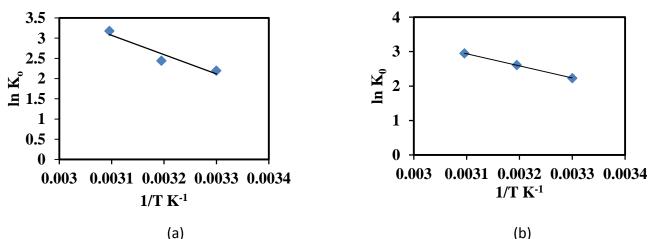
$$\ln K_{o} = \frac{-\Delta G}{RT}$$
(15)  

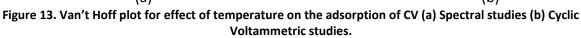
$$\Delta G = \Delta H - T\Delta S$$
(16)  

$$\ln K_{o} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(17)

A plot of ln K<sub>o</sub> vs. 1/T gives a straight line with slope is equal to  $\Delta$ H/ R and intercept is equal to  $\Delta$ S/ R. Knowing the value of R,  $\Delta$ H and  $\Delta$ S can be evaluated. From the values of  $\Delta$ H and  $\Delta$ S,  $\Delta$ G can be determined using the equation (16). The results are presented in table 5.

The negative values of  $\Delta G$  indicated that the adsorption of CV onto PS is a favourable and a spontaneous process. The positive values of  $\Delta H$  indicated the endothermic nature of the adsorption process and positive values of  $\Delta S$  indicated increased randomness of the CV at the solid solution interface. The increase in the capacity of the adsorbent to remove CV at higher temperatures may be due to activation of the adsorbent surface thereby enlarging the size of the pores [21,24].





Studies		∆G (kJ mol <sup>-1</sup> )	ΔH	ΔS	
	303 K	313 K	323 K	kJ mol⁻¹	kJ K <sup>-1</sup> mol <sup>-1</sup>
Spectral	-5.68	-7.18	-8.68	39.77	0.150
Cyclic voltammetric	-5.24	-6.71	-8.18	39.3	0.147

Table 5: Thermodynamic parameters for	the adsorption of CV.
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## Statistical analysis of the two methods

Statistical analysis of the respective sets of data for the percentage removal of the dye solution at various time intervals obtained by spectral and voltammetric studies was carried out by student's t-test. The analysis indicated that the calculated t-value ( $t_{calc} = 1.943$ ) < tabulated-value ( $t_{tab} = 2.447$ ) at 95 percentage confidence level and hence it could be concluded that there is no significant difference between the two methods.

## Comparison of Adsorption capacity of CPS with other adsorbents

The adsorption capacity of *CPS* was compared with that of the other adsorbents based on the literature search (Table 5). It was found that *CPS* could be used as an effective adsorbent for the removal of CV from aqueous solutions.

Adsorbent	Adsorption capacity (mg/g)	Reference
Grapefruit peel	77	[8]
Treated ginger waste	19.8	[11]
Spent tealeaves	114.94	[12]
Male flowers of coconut tree	60.42	[13]
Agricultural waste cocoa shell	43.5	[16]
Leaf biomass of Calotropis procera	4.14	[19]
Ricinus Communis Pericarp carbon	48.0	[20]
Citrullus lanatus rind	11.99	[21]
Waste apricot	57.80	[25]
Carica Papaya Seeds	166.67	Present work

#### Table 6: Adsorption capacities of the various adsorbents for the removal of crystal violet dye

## CONCLUSIONS

The adsorption of CV onto *CPS* was found to be an efficient process. The parameters such as pH, adsorbent dose, initial dye concentration, contact time, particle size and temperature have shown significant effect on the removal of CV from aqueous solutions. The maximum uptake of CV by *CPS* occurred at pH 8 and the equilibrium adsorption was attained after 60 min. The equilibrium adsorption data fitted the various models viz., Langmuir, Freundlich, Tempkin, Harkins-Jura isotherm models. The Adsorption process followed pseudo second-order kinetics. Evaluation of thermodynamic parameters indicated that the adsorption process was endothermic and there occurs increased disorder at the solid-solution interface. Both spectral and cyclic voltammetric monitoring methods yielded similar results as revealed by statistical analysis. The various results obtained indicated that the adsorbent chosen for the study was efficient and could be used for the removal of industrial dye effluents.

## ACKNOWLEDGEMENT

The authors greatly acknowledge the Management and the Department of Chemistry, Lady Doak College, for providing the necessary facilities to carry out the study.



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