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A Novel Approach to Investigate Adsorption of Crystal Violet from Aqueous Solutions Using Peels of *Annona squamosa*

K. Mahalakshmi, S.K. Suja, K. Yazhini, S. Mathiya and G. Jayanthi Kalaivani

Department of Chemistry, Lady Doak College, Madurai, Tamilnadu, India

Abstract: An effective and economical adsorbent was prepared from the peels of *Annonasquamosa*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, particle size and temperature on the adsorption process was studied. The crystal violet was found to be electroactive and hence electrochemical studies were also performed. The study showed that the equilibrium was achieved within 60 min for the different initial concentrations (10 to 30 mg.l^{-1}). The equilibrium adsorption data were analyzed using various isotherm models and they were found to fit Langmuir, Freundlich, Temkin and Harkins-Jura isotherm models in varying orders of magnitude. The maximum dye adsorption capacitiesfor cyclic voltammetry and spectral studiesat 303 K were found to be 5.6818×10^{-4} A.g^{-1}(in terms of current)and 5×10^4 mg.g^{-1}(in terms of weight),respectively. The data suggested that the adsorption kinetics was best represented by pseudo-second order kinetic model. The thermodynamic parameters including ΔG, ΔH and ΔS for the adsorption process have also been evaluated using which it was concluded that the process of adsorption was spontaneous and endothermic. The cyclic voltammetricand spectral studies yielded similar results. Furthermore, statistical analysis also showed the absence of any significant difference between the two methods.

Key words: Adsorption · Crystal Violet · *Annonasquamosa* · Cyclic voltammetry

INTRODUCTION

At present, most of the developing countries like India are facing a major problem viz. pollution. This may be due to the population outburst 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

Corresponding Author: S.K. Suja, Department of Chemistry, Lady Doak College, Madurai, Tamilnadu, India.
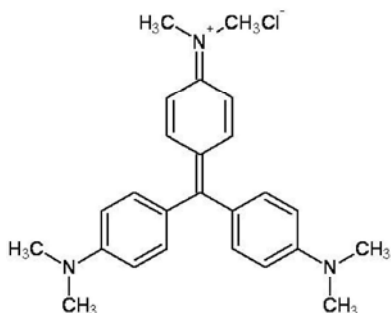E-mail senthija2007@gmail.com.

Fig. 1: Structure of crystal violet

powder [9], coniferous pinus bark powder [10], treated ginger waste [11], spent tea leaves (STL) [12], male flowers of coconut tree [13], coconut bunch waste [14], pumpkinseed hull [4], agricultural waste [16], citric acid modified rice straw [17], date palm fiber [18], leaf biomass of *Calotropisprocera* [19] , *Ricinus Communis* pericarpcarbon [20], citrulluslanatus rind [21], bottom ash [22], pretreated walnut shell [23].

Watermelon shell [24], cassava peels [25], polyanilinenanocomposite coated on rice husk [26], chitosan [27], etc., had been evaluated as effective adsorbent for the removal of metal ions.

Annonasquamosa peels have been evaluated as a low cost adsorbent for the removal of lead and cadmium ions from water [28]. 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 *Annonasquamosa*peels along with the exploration of adsorption kinetics and isotherms using both electrochemical and spectral studies. Fig. 1 shows aromatic structure of crystal violet.

MATERIALS AND METHODS

Adsorbent: Peels of *Annonasquamosa*(*PAS*) 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 μm 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 – $C_{25}H_{30}N_3Cl$, molecular weight – 408

gmol^{-1}, λ_{max}– 584 nm) and used without further purification. A stock of 1000 mg.l^{-1} dye solution was prepared using deionized water. Different concentrations of dye solution were prepared by appropriate 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. Cyclic voltammetric studies were carried out using CHI 6063C – Electrochemical analyzer.The FT-IR spectra of *PAS* before and after adsorption were recorded using FT-IR spectrophotometer (Thermofisher) using KBr pellet method.

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 (10-60 min), pH (2-12), initial dye concentration (10-30mg.l^{-1}), particle size (150μm, 250μm and 300μm) 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 supernatant solutions wereused to obtain reduction peak current (i$_p$) values as a function of the concentration of CV dye remaining after adsorption, using electrochemical analyzer. The same solutions were used to measure the absorbance of the solutions, using UV-Visible spectrophotometer.

For cyclic voltammetric studies, amount adsorbed at equil um e calculated as:

$$q_e = \frac{(i_{po} - i_{pe})V}{W} \tag{1}$$

where i$_{Po}$ is the initial reduction peak current of the dye solution (μA), and i$_{Pe}$ is the reduction peak current of the dye solution at equilibrium (μA).

The percentage dye removal was calculated using

$$\% \text{ removal} = \frac{(i_{po} - i_{pe})}{i_{po}} \times 100 \quad (2)$$

For spectral studies, amount of dye adsorbed at equilibrium was given by,

$$q_e = \frac{(C_o - C_e)V}{W} \quad (3)$$

where C_o is the initial concentration of the dye (mg.l^{-1}), C_e is the concentration of dye at equilibrium (mg.l^{-1}), V is the volume of the solution (l), W is the weight of adsorbent (g)

The percentage dye removal was calculated using

$$\% \text{ removal} = \frac{(C_o - C_e)}{Co} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Spectral Characterization of the Adsorbent: The FTIR spectra of *PAS* before and after adsorption were studiedin order to explore the surface porosity of the adsorbent in the range of 400-4000 cm^{-1}. The FTIR spectrum of *PAS* shows peaks at 614.8cm^{-1}, 771.1cm^{-1}, 823.8cm^{-1}, 1059.0cm^{-1}, 1446.3cm^{-1}, 1618.7cm^{-1}, 3418.3 cm^{-1}. Since the adsorbent shows a large number of peaks, it is evident that the adsorbent is complex in nature. Comparing Figs. 2a and 2b, it can be noted that some of the above mentioned peaks are shifted (1446.3cm^{-1} and 1618.7cm^{-1}) or disappeared (614.8cm^{-1} and 771.1 cm^{-1}) and some new peaks (456.7cm^{-1} and 466.6 cm^{-1}) are also formed. Hence

from the spectrum it is obvious that there is possible involvement of those functional groups on the surface of *PAS* in the adsorption process [21].

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^{-1} 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.

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^{-1}. The cyclic voltammogram of CV dye was shown in Fig. 4. A reduction peak was observed at -0.756V which indicated that the CV dye was electroactive [28].

Effect of Contact Time and Initial Dye Concentration: The effect of initial dye concentration onto adsorption of CV by *PAS* was studied at different initial concentrations (10 - 30 mg.l^{-1}) at 303 K and the results were shown in Fig. 5.

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 PAS increased and reached a constant value indicating an increase in the percentage removal of CV.
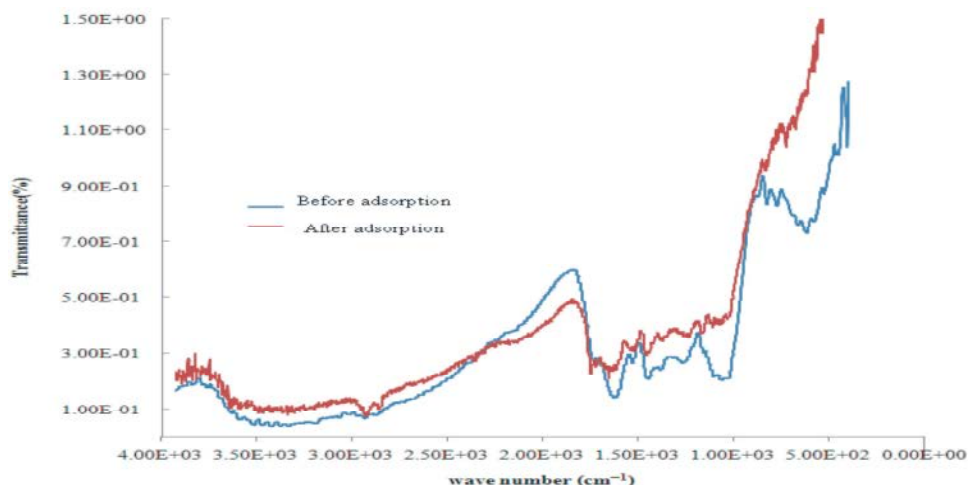

Fig. 2: FTIR spectrum of *PAS* adsorbent before (a) and after (b) adsorption.
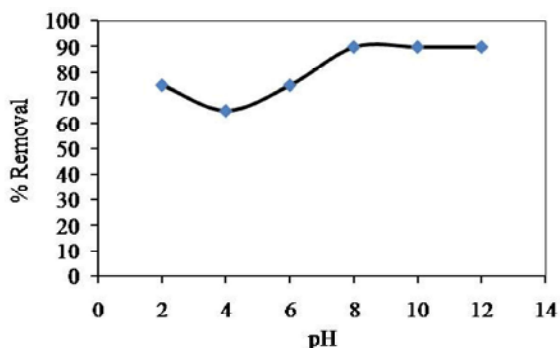
Fig. 3: Effect of pH on adsorption of CV onto *PAS* (Concentration of CV: 10mg.l⁻¹, adsorbent dose: 0.2g; particle size:200-250 μm; agitation speed:160 rpm; temperature:30°C)
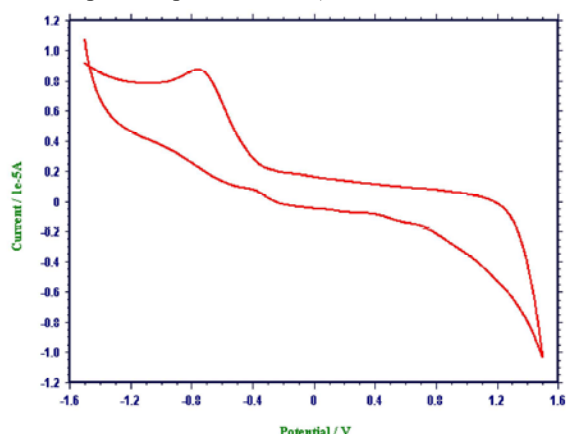

Fig. 4: Cyclic voltammogram of CV dye.

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 92 to 98 %) with increasing concentrations.Similar results were also observed in spectral studies.

As the initial concentration of CV increased, the percentage removal increased from 92 to 98 %. 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 40 min for all the initial concentrations studied.

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 andintraparticle diffusion model [19]. The linear form of these models is given by equations (5), (6) and (7), respectively.

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

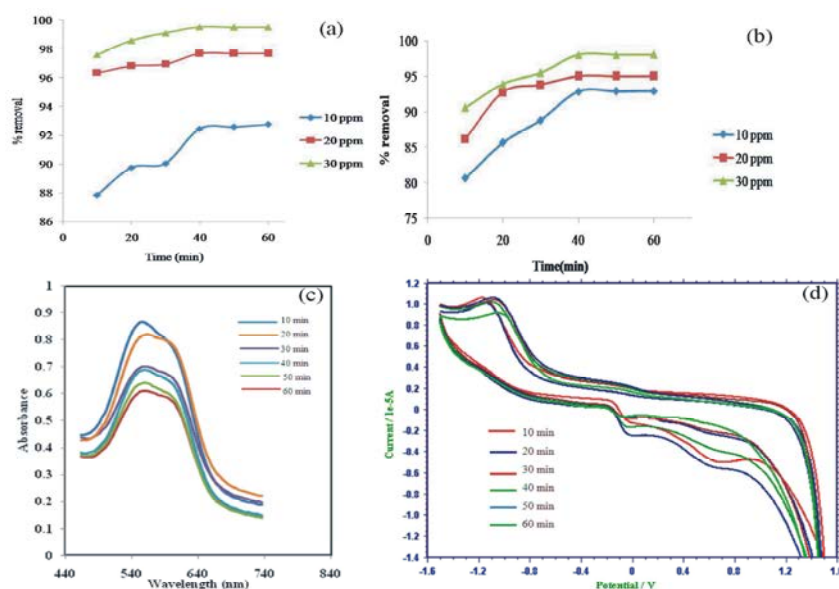$$q_t = k_{id} t^{\frac{1}{2}} + C \tag{7}$$

Fig. 5: Effect of contact time on adsorption of CV onto *PAS* at different initial concentrations (adsorbent dose: 0.2 g; particle size: 200-250 μm; agitation speed: 160 rpm; temperature: 30°C) (a) and (c) Spectral studies (b) & (d) Cyclic Voltammetric studies
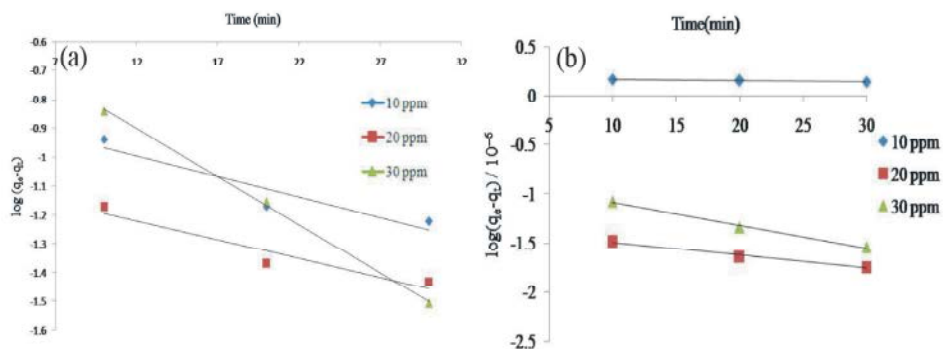
Fig. 6: Pseudo-first order kinetic plot for adsorption of CV onto PAS at different initial concentrations (particle size: 200-250 µm, agitation speed: 160 rpm, temperature: 30°C) (a) Spectral studies (b) Cyclic Voltammetric studies

Fig. 7: Pseudo-second-order kinetic plots for adsorption of CV onto *PAS* at different initial concentrations (particle size: 200-250 µm, agitation speed: 160 rpm, temperature: 30°C) (a) Spectral studies (b) Cyclic Voltammetricstudies
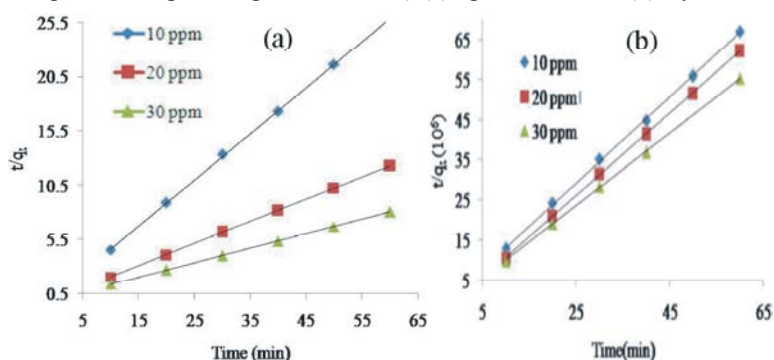
where q_t and q_e (mg.g^{-1}) are the adsorption capacities at time t and at equilibrium, respectively k_1 (min^{-1}) and k_2 (mg. (g.min)$^{-1}$) are pseudo-first and pseudo-second order rate constants; k_{id} is the intraparticle diffusion rate constants (mg.g^{-1} min$^{-0.5}$) and C is the intercept which gives an idea about the boundary layer thickness.

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]. Fig. 6 presents the pseudo-first order kinetic plot for adsorption of CV onto PAS at different initial concentrations. 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 $q_e$valuescalculated using pseudo second-order equation agreed well with the experimental q_e indicating that the adsorption of CV onto *PAS* could be well represented using the pseudo second order kinetic model. These results were in accordance with those obtained using cyclic voltammetric studies.

Intraparticle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase. In a well stirred batch adsorption system, the intraparticle diffusion model has been used to describe the adsorption process occurring on a porous adsorbent. Accordingto intraparticle diffusion model, a plot of q_t versus $\sqrt{t}$ should give a straight line with a slope k_p and an intercept of zero if the adsorption limited by an internal diffusion process. The relationship between qt and $\sqrt{t}$ at different concentrations was studied (Figs. 8a and 8b).

The plot in this analysis revealed a linear step,corresponding to fast uptake of sorbate. The line inthe initial stage does not pass through the origin. This revealed that the uptake is dominated by film diffusion than it does for the intraparticle diffusionprocess. Tables 1 and 2 summarizedadsorption kinetic model parameters using spectral and cyclic voltammetric studies, respectively.

Adsorption Isotherms: The adsorption isotherm establishes a relationship between the amount of dye molecules adsorbed onto the adsorbent and the
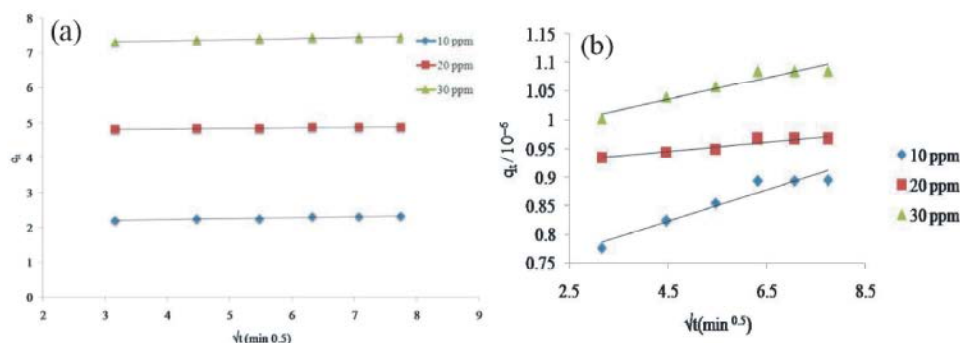
Fig. 8: Intra particle diffusion plot for adsorption of CV onto *PAS* at different initial concentrations (particle size: 200-250 µm, agitation speed: 160 rpm, temperature: 30°C) (a) Spectral studies (b) Cyclic Voltammetric studies

Table 1: Adsorption kinetic model parameters obtained using spectral studies

C_o mg/L	q_e(exp) mg/g	Pseudo First- order Kinetic model			Pseudo Second- order Kinetic model			Intra particle diffusion Model		
		q_e(cal) mg/g	k_1 (min^{-1})	R^2	q_e(cal) mg/g	k_2 (mg /(g min)	R^2	k_{id}	C	R^2
10	2.4596	1.9275	0.1059	0.946	2.3474	0.4985	0.999	0.027	2.240	0.881
20	2.4611	15.922	0.3224	0.839	2.4096	0.8401	0.999	0.016	2.267	0.910
30	2.4249	6.8706	0.3155	0.787	2.5063	0.4990	1.0	0.031	2.116	0.909

Table 2: Adsorption kinetic model parameters obtained using cyclic voltammetric studies

C_o mg/L	q_e(exp) µA/g	Pseudo First- order Kinetic model			Pseudo Second- order Kinetic model			Intra particle diffusion Model		
		q_e(cal) µA/g	k_1 (min^{-1})	R^2	q_e(cal) µA/g	k_2 (10^6A/(g min)	R^2	k_{id} 10^{-8}	C 10^{-7}	R^2
10	0.89575	1.0544	0.1519	0.886	1.000	0.5	0.999	3	7	0.926
20	0.96725	0.37932	0.1358	0.928	1.000	1	0.999	2	8	0.760
30	1.0862	0.88511	0.1635	0.877	1.1100	0.008	0.999	2	10	0.921

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 *PAS* was analyzed using various models viz.,Freundlich, Langmuir, Temkin and Harkins-Jura adsorption isotherm models.

Freundlich Isotherm: The Freundlich isotherm is suitable for heterogenous surface [16] and its logarithmic form can be expressed as

$$\log q_e = \log k + \frac{1}{n}\log C_e \qquad (8)$$

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

Freundlich plots for the adsorption of CV onto *PAS* using spectral and cyclic voltammetric studies were shown in Fig. 9 (a) and Fig. 10 (a), respectively.

The constants k and n values were determined from the intercept and slope of the plots, respectively. If n value was found to be 1, it indicates that the partition between the two phases were independent of the concentration of the dye [29]. The R^2 values were found to be 1 indicating the fitness of the Freundlich model with the equilibrium data.

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

$$\frac{1}{X/M} = \frac{1}{q_{max}} + \frac{1}{q_{max} b}\frac{1}{C_e} \qquad (9)$$

where q_{max} is the maximum monolayer dye concentration in the solid phase (mg.g^{-1}), C_e is the equilibrium dye concentration in the aqueous phase (mg.l^{-1}), X/M= q_e is

Fig 9: (a) Freundlich(b) Langmuir (c) Temkin (d) Harkin-Jura adsorption isotherm plots for the adsorption of CV by *PAS* (Concentration of CV: 20 mg.l^{-1}; adsorbent dose: 0.2g ; particle size: 200-250 µm; agitation speed: 160 rpm; temperature: 30°C) using Spectral studies
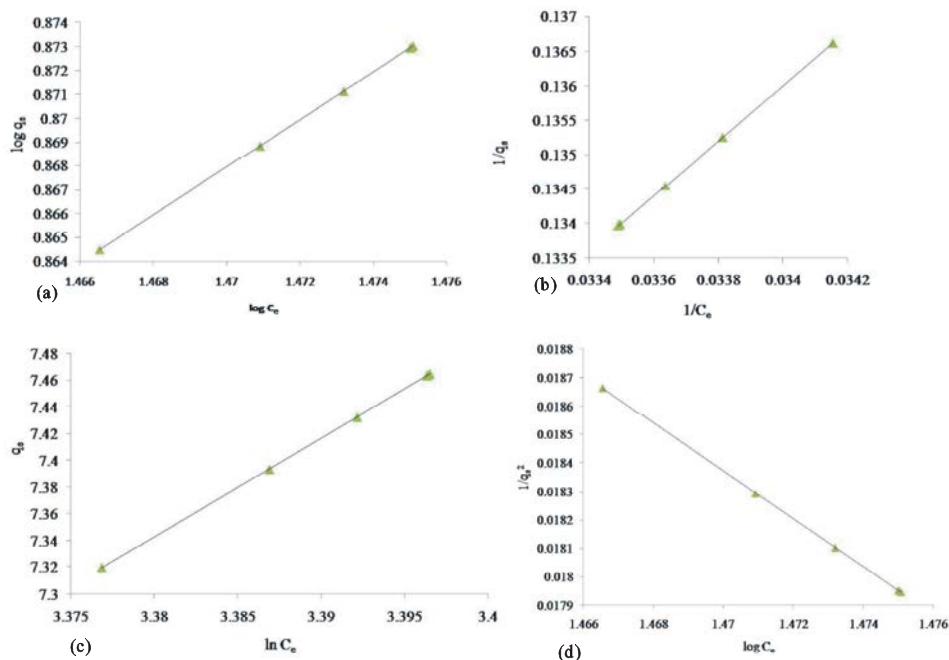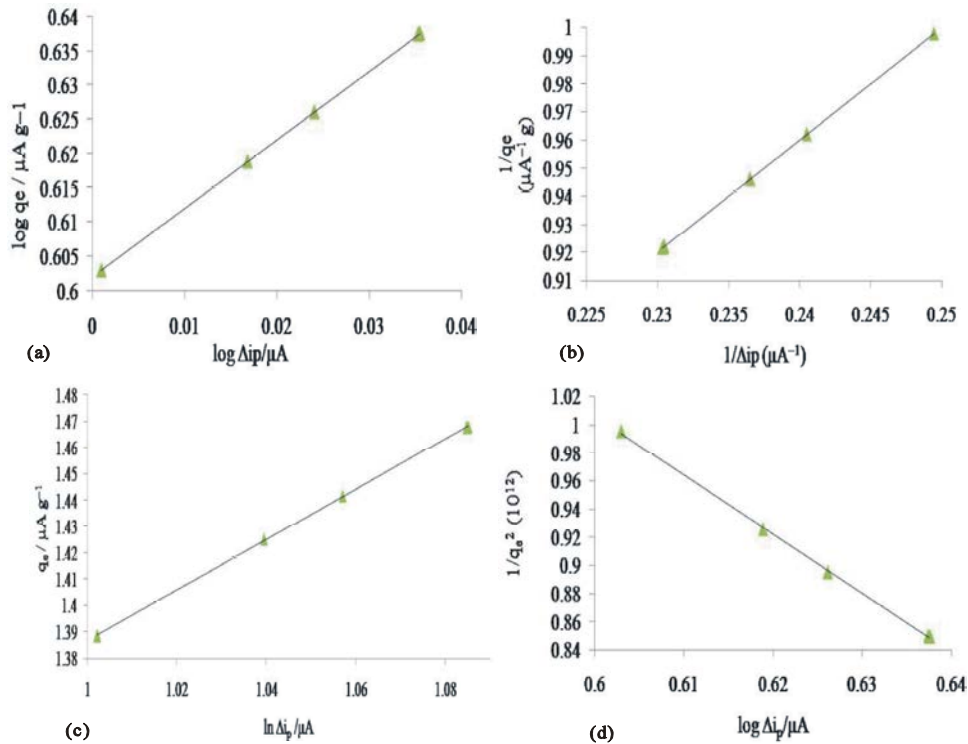

Fig 10: (a) Freundlich(b) Langmuir (c) Temkin (d) Harkin-Jura adsorption isotherm plots for the adsorption of CV by *PAS* (Concentration of CV: 20 mg.l^{-1}; adsorbent dose: 0.2g ; particle size: 200-250 µm; agitation speed: 160 rpm; temperature: 30°C) using cyclic voltammetric studies

Table 3: Adsorption isotherm model parameters based on spectral studies

T (K)	Langmuir isotherm model			Freundlich isotherm model			Temkin isotherm Model			Harkin Jura isotherm model		
	q_{max} (mg/g)	b (L/mg)	R^2	k (mg/g)	n	R^2	A_T (L/mg)	B_T (J/mg)	R^2	A	B	R^2
303	5×10^4	2×10^5	1	3.9994	1	1	2248.59	0.227	0.974	2.8985	1.4840	0.946

Table 4: Adsorption isotherm model parameters based on cyclic voltammetric studies

T (K)	Langmuir isotherm model			Freundlich isotherm model			Temkin isotherm Model			Harkin Jura isotherm model		
	q_{max} ($\mu A/g$)	b (L/μA)	R^2	k ($\mu A/g$)	n	R^2	A_T (L/μA)	B_T (J/μA)	R^2	A	B	R^2
303	5.6818×10^{-4}	2.275×10^{-3}	0.999	3.8815	0.9980	0.999	1.0000	1×10^6	0.998	2×10^{-13}	4.0	0.997

the equilibrium dye concentration in the solid phase ($mg.g^{-1}$) and b is the Langmuir equilibrium constant ($l.mg^{-1}$).

Langmuir plots for the adsorption of CV onto *PAS* using spectral and cyclic voltammetric studies were shown in Fig. 9(b) and Fig. 10 (b), respectively. The constants q_{max} and b obtained from spectral and cyclic voltammetric studies for three different concentrations (10-30 ppm) were presented in Tables 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

$$R_L = \frac{1}{1 + bC_o} \tag{10}$$

The R_L values were found to be less than 1 indicating that the adsorption process was favourable [21]. The R^2 values were to be 1 indicating the fitness of the Langmuir 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].

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

where, $B_T = RT/b$ is the absolute temperature (K), R is the gas constant ($8.314 J.mol^{-1}K^{-1}$), A_T is the equilibrium binding constants ($l.mg^{-1}$) and B_T is related to the heat of adsorption ($J.mol^{-1}$).

Temkin plots for the adsorption of CV onto *PAS* 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 in the range 0.999 to 1.0 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 heterogeneous pore distribution. It can be expressed as

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

where B and A are the isotherm constants.

Harkins-Jura plots for the adsorption of CV onto *PAS* 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 in the range 0.999 to 1.0 indicating the fitness of the model with the equilibrium data. Hence there could be a possibility of multilayer adsorption to occur [21].

Effect of Particle Size: Adsorption of CV onto *PAS* of three different particle sizes (200-250, 250-300, 300-500 µm) was studied by keeping all other parameters constant. The variation of particle size on the adsorption process monitored by spectral technique was shown in Fig.11. As particle size was decreased, the adsorption efficiency of *PAS* 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].

In Cyclic voltammetric studies, a drastic change in the peak potential was observed on changing the mesh size of the adsorbent. This may be due to the involvement of H^+ ions during the electro-oxidation process. Negative shift in the peak potential which may be due to intercalative mode of interaction between the adsorbent and the dye was observed.

Effect of Temperature: Temperature has a significant effect on the process of adsorption. Adsorption of CV onto *PAS* was studied at three different temperatures (303 K, 313 K and 323 K) for 10 $mg.l^{-1}$ initial concentration
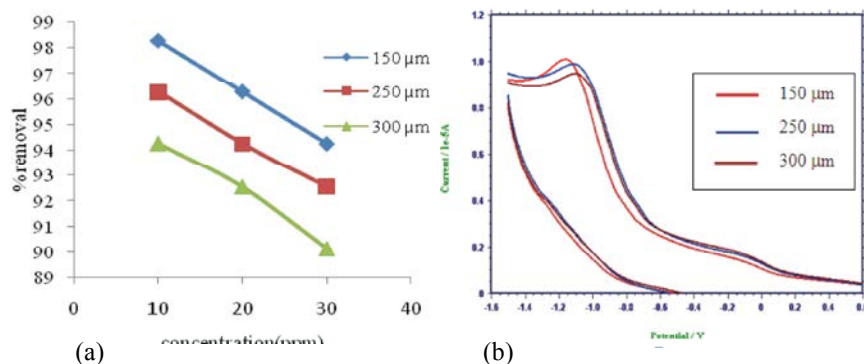
(a)　　　　　　　　　　　　　　　　(b)

Fig. 11: Effect of particle size on adsorption of CV onto PAS (adsorbent dose: 0.2 g; contact time: 60 min; agitation speed: 160 rpm; temperature: 30°C) (a) spectral studies (b) cyclicvoltammetric studies.
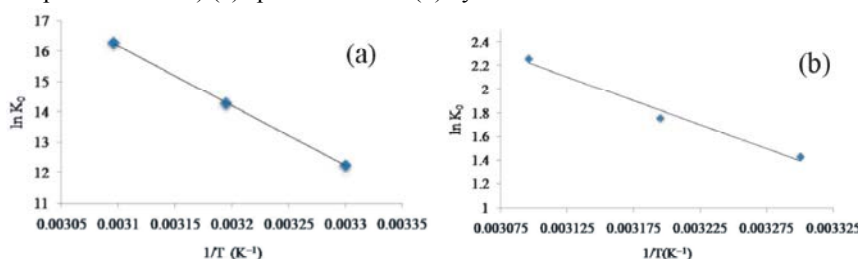

Fig. 12: Van't Hoff plot for effect of temperature on the adsorption of CV (a) Spectral studies (b) Cyclic Voltammetric studies

Table 5: Thermodynamic parameters for the adsorption of CV.

Studies	ΔG (kJ mol^{-1})			ΔH	ΔS
	303 K	313 K	323 K	kJ mol^{-1}	kJ K^{-1} mol^{-1}
Spectral	−30.7381	−37.1651	−43.5921	164	0.6427
Cyclic voltammetric	−3.4963	−4.7183	−5.9403	33.5303	0.1222

of CV. From the Fig.12, it was found that the percentage removal of dye increased from 92 to 99% 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].

Evaluation of Thermodynamic Parameters: Thermodynamic parameters such as change in free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were determined using the following equations

$$K_o = \frac{C_{Solid}}{C_{liquid}} \tag{13}$$

where K_o is the equilibrium constant, C_{Solid} is the solid phase concentration (mg.l^{-1}), C_{liquid} is the liquid phase concentration (mg.l^{-1}).

$$\Delta G = -RT \ln K_o \tag{14}$$

$$\ln K_o = \frac{-\Delta G}{RT} \tag{15}$$

$$\Delta G = \Delta H - T\Delta S \tag{16}$$

$$\ln K_o = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{17}$$

A plot of $\ln K_o$ 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, ΔH and ΔS can be evaluated. From the values of ΔH and ΔS, ΔG can be determined using the equation (16). The results are presented in Table 5.

The negative values of ΔG indicated that the adsorption of CV onto PAS is a favourable and a spontaneous process. The positive values of ΔH indicated the endothermic nature of the adsorption process and positive values of ΔS 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, 30].

Statistical Analysis of the Two Methods: Statistical analysis of the respective sets of data obtained by spectral and voltammetric studies was carried out by

student's t-test. The analysis indicated that the calculated t-value (t_{calc} = 2.571) < tabulated-value (t_{tab} =3.365) at 99 % confidence level and hence it could be concluded that there is no significant difference between the two methods.

CONCLUSION

The adsorption of CV onto *PAS* was found to be an efficient process. The parameters such as pH, 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 *PAS* occurred at pH 8 and the equilibrium adsorption was attained after 40 min. The equilibrium adsorption data were found to fitFreundlich, Langmuir, Temkin, 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. 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.

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Persian Abstract

چکیده

جاذب سطحی موثر و مقرون به صرفه از پوست گیاه *Annona squamosal* برای حذف کریستال ویوله از فاز آبی ساخته و آماده شد. مطالعات جذب در فرآیند ناپیوسته انجام پذیرفت. در حین فرآیند، وابستگی فرآیند جذب به غلظت اولیه رنگ محلول، pH، زمان تماس ،اندازه ی ذره و دما مطالعه و بررسی گردید. در طول فرایند مشخص شد که کریستال ویوله مورد آزمایش، الکترواکتیو بوده و از این رو مطالعات الکتروشیمیایی نیز انجام گرفت. این مطالعات نشان داده است که برای غلظت های اولیه (mg/L ۱۰-۳۰) فرآیند جذب در مدت زمان ۶۰ دقیقه به تعادل رسیده است. داده های جذب تعادلی به کمک مدل های مختلف ایزوترم آنالیز و بررسی گردید و مشخص گردید که این داده ها در میزان دقت های مختلف به کمک مدل های لانگمیر، فرندلیچ، تمکین و Harkins-Jura برازش می‌شود. بیشترین میزان ظرفیت ها در جذب رنگ در حالات ولتامتری چرخه ای و مطالعات طیفی در دمای ۳۰۳ درجه کلوین به ترتیب $A.g^{-1}$ ۵/۶۸۱۸×۱۰ $^{-۴}$ (برحسب جریان) و $mg.g^{-1}$ ۵×۱۰ ^{۴} (برحسب وزن) اندازه گیری شد. داده های به دست آمده نشان داده است که سینتیک جذب، در بهترین حالت با مدل سینتیکی شبه درجه دوم انطباق دارد . پارامتر های ترمودینامیکی از قبیل ΔG، ΔH و ΔS برای فرآیند جذب اندازه گیری شده و نتایج این اندازه گیری ها نشان داده است که فرآیند جذب، خودبخودی و گرماگیر است. ولتامتری چرخه ای و مطالعات طیفی نتایج مشابه ای را ارائه نمود. بعلاوه، در آنالیز های آماری تفاوت قابل ملاحظه ای بین دو روش بکاربرده شده مشاهده نشده است.