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Kinetics and Thermodynamic Studies on the Removal of Crystal Violet by Pomegranate Peel Powder

KEYWORDS: Percentage removal, dose, temperature, active sites and thermodynamic parameters.

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ABSTRACT *The present study deals with the removal of crystal violet (CV) by Pomegranate peel powder (PPP). The effect of initial concentration of dye, dose of adsorbent, contact time and temperature on the removal of crystal violet by adsorption on PPP have been studied. The percentage removal of dye was found to decrease with increase in initial concentration of dye. The percentage removal of dye increases exponentially with increase in dose of adsorbent. This was due to the availability of active sites. The percentage removal of dye was found to increases with increase in contact time. From this the kinetics of adsorption process was manipulated. The kinetic data is well fitted with second order kinetics. The percentage removal of dye was found to increases with increase in temperature. From this data the thermodynamic parameters such as H0, Go and S0 were calculated.*

INTRODUCTION

Decolorization of dye contaminated effluents generated from various industrial sources is of serious concern from environmental point of view because of their toxic effects and high biological and chemical oxygen demands. Due to their chemical structure, most of the dyes are resistant to fading on exposure to light, water and many chemicals [1]. There are many structural varieties of dyes that fall into cationic, anionic or nonionic type. Several methods are removing dyes from wastewater include flocculation, electro flotation, precipitation, electro kinetic coagulation, ion exchange membrane filtration, electrochemical destruction, irradiation and ozonation. All these methods have different color removal capability, capital costs, and operating rates. Among these methods, adsorption process is potential alternative to conventional treatment techniques for the elimination of dye contaminated effluents [2]. This process is based on the interactions between organic or inorganic pollutants and functional groups present on the biosorbent structure [3]. The efficiency of this process depends on several factors as the type of pollutant being studied to type of biosorbent used as well as other environmental parameters. Different kinds of adsorbents were used for basic dye removal from aqueous solutions such as biodegradable polymer [4], leaves [5], wood shells [6], palm kernel fiber [7], chitosan derivatives [8], natural clay [9], agricultural waste [10] and activated carbon [11].

This study aimed to examine the use of pomegranate peel powder as an agricultural waste for the efficient removal of basic dyes from aqueous solution. Batch adsorption experiments were carried out systematically in terms of process parameters such as agitation time, initial dye concentration, adsorbent dose, pH and temperature.

MATERIALS AND METHODS

The adsorbent used in this present investigation was pomegranate peel powder. It was collected from fruit market, Sivagangai, Tamilnadu. Analar grade sample of crystal violet (CV) was used in the present study. The other chemicals and reagents employed in the present work were of Analytical grade. In the present study, the experiments were carried out by employing the batch adsorption experiments.

General procedure for adsorption studies

The stock solution (500 ppm) was diluted to the required initial concentration of dye with double distilled water. 50 ml of the dye solution was taken in each 250ml leak proof corning reagent bottles. Required amount of adsorbent of fixed particle size was exactly weighed and then transferred into each one of these bottles. The bottles were placed in a mechanical shaker and shaken vigorously for a required period of contact time (15 minutes) and then taken out. After shaking for a certain period, the flask was set aside for the adsorbent to settle out and the sample taken from the flask was centrifuged. The filtrate equilibrium concentration can be obtained from the standard curve as usual.

The optical density of each solution was measured by using UV-Visible spectrophotometer (Systronic Spectrophotometer, model no: 104) at 580 nm (wave length of maximum absorption for this particular dye). A plot of optical density *versus* concentration results a straight line for this particular dye. The optical density for dye solution before and after adsorption is obtained using the spectrophotometer. The corresponding relative concentration can be had from the standard curve.

In all adsorption experiments, the extent of adsorption of dye in terms of the percentage adsorption of dye and amount adsorbent ($mg.g^{-1}$) were calculated using the following requirements.

Percentage adsorption = 100 (C_i-C_e)/C_i --------- (1)

Amount adsorbed (q_e) = (C_i-C_e)/m -----------(2)

Where C_i and C_e are the initial and final equilibrium concentration (mgL^{-1}) of dye, respectively and m is the mass of adsorbent, PPP (gL^{-1})

RESULTS AND DISCUSSION

The present work deals with the studies on the removal of crystal violet by adsorption on PPP. This is an endeavor of

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present the data for the design of economical wastewater treatment plant for the effluent discharged from the dye industries.

The experimental parameters, which affect the extent of adsorption of crystal violet dye, are reported to be initial dye concentration, dose of adsorbent and temperature. The effect of these parameters on the extent of removal of dye by adsorption on PPP has been studied. Various experiments were conducted by varying anyone of these experimental parameters like initial concentration, dose of adsorbent and temperature by keeping all the other experimental parameters constant.

Effect of initial concentration of BG

The initial concentration of crystal violet solution was varied (10-75 ppm) and batch adsorption experiments were carried out with 0.l g of adsorbent at different temperatures. The percentage removal of crystal violet decreases from 80.1 to 69.6% by increasing the initial concentration of CV with 0.1mg of the adsorbent in agitation time of 15 minutes at 30°C. The higher uptake of crystal violet at low concentration may be attributed to the availability of more active centers on the surface of the adsorbent for lesser number of adsorbate species. Crystal violet adsorption curves are single, smooth and continuous (Figure 1) suggesting the possible monolayer coverage of dye molecules on the surface of the adsorbent.

Effect of contact time

The removal of crystal violet from aqueous solution by PPP increases from 77.6 to 84.2% when the agitation time was varied from 5 to 90 minutes and attains equilibrium in 60 minutes at 30°C when the initial concentration of the crystal violet solution used was 10 ppm and the adsorbent dosage was 2 g/L. The increase in adsorption of crystal violet with increase in agitation time may be attributed to the increased intra particle diffusion occurring at long shaking time. The data obtained are graphically represented in Figure 2. It indicated that 70% of dye molecules are removed within 5 minutes.

Adsorption Kinetic studies

The adsorption kinetics is a useful parameter in the design of industrial adsorption columns. The rate constants for adsorption of CV onto PPP were evaluated using pseudo-first order and pseudo-second order kinetic models.

The linear form of pseudo-first order kinetic model [12] is given by Equation 3

$$\log (q_e - q_t) = -(k_1 t / 2.303) + \log q_e \quad (3)$$

where, q_e and q_t are the amounts of CV adsorbed (mg/g) at equilibrium and at any time, *t* respectively, and k_1 (l/min) is the pseudo-first order rate constant.

The adsorption rate constant, k_1 and q_e has been computed from the straight plot of log (*q*e − *q*t) vs. *t* (Figure 3), and are listed in Table 1.

Pseudo-second order kinetics

The pseudo-second order kinetic model [13] is given by Equation 4 .

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad \text{- - - - - - - - - - - (4)}$$

where, k_2 (g/mg/min) is the pseudo-second order rate constant.

The plot of *t/qt versus* t is shown in Figure 4. The values of q_e, k_2 and correlation coefficients are reported in Table 1. The regression correlation coefficients (0.982-0.999) and a good agreement between the calculated and experimental q_e values for pseudo-second order model indicated that the adsorption of dye onto PPP is governed by pseudo-second order rate kinetics.

Elovich model

The linear form of Elovich equation [14] is expressed as follows (Equation 5):

$$qt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad \text{- - - - - - - - - - - - - (5)}$$

where, α (mg/g/min) is the initial adsorption rate and β (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. The values of kinetic constants α and β were calculated (Figure 5) and listed in Table 1. It is found that adsorption and desorption rate increased and decreased with temperature respectively. The regression correlation coefficients (R^2) are obtained in the range of 0.924-0.985.

Intraparticle diffusion model

The experimental data was analyzed using intraparticle diffusion model with a view to elucidate the diffusion mechanism [15]. The intraparticle diffusion rate constant, *Kip* (mg/g $min^{0.5}$) can be obtained from the slope of the plot of *qt* (mg/g) versus $t^{0.5}$ according to the following equation:

$$q_t = K_{ip}\ t^{0.5} - Cip \quad \text{- - - - - - - - - - - - -(6)}$$

where *Cip* (mg/g) is a constant, which gives idea about the thickness of the boundary layer and can be calculated from the intercept of the plot. The larger the *Cip*, greater is the contribution of surface adsorption in the rate limiting step.

According to this model, a linear plot of q_t versus $t^{0.5}$ indicated that the uptake process was controlled by intraparticle diffusion. On the other hand, plot showed multi-linearity; indicating adsorption process as controlled by two or more steps. In the present study, the plot of *qt versus* $t^{0.5}$ gives a straight line (Figure 6), which passes from the origin, indicating that the adsorption process tends to be intraparticle diffusion controlled. The values of *Kip* and *Cip* along with the regression correlation coefficients are listed in Table 1. The liquid film diffusion model may be applied. The plot of *1/(1-qt/qe) vs. t* gives a straight line (Figure 8), with slope equal to K_{fd}.

Effect of temperature

In order to study the effect of temperature on the rate of adsorption of CV on PPP, the adsorption experiments were repeated at optimum parameter conditions at different temperatures. The temperature was varied from 303K, 313K, 323K, 333K and 343K at different concentration (10, 20, 30, 40, 50 and 75 ppm), agitation time (15minutes) and dose of adsorbent (0.1mg). The uptake of crystal violet by PPP increases from 80.1 to 91.9 %. The experimental values indicate that the rate of removal of dye increases with increase in temperature. This effect is graphically represented in Figure 7. This is due to the availability of active sites at high temperature.

Calculation of thermodynamic parameters

Thermodynamic parameters are calculated from the variations of the thermodynamic distribution co-efficient (K_C) with change in temperature. K_C for the CV adsorption is determined by plotting log Kc *vs* 1/T and extrapolating to zero. The variation of K_c is given in table 6. The standard

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free energy change ΔG° for the interaction of the PPP with CV has been calculated using $\Delta G° = -RT \ln K_c$. From the variation of log K_c with inverse of temperature (figure 8) the standard enthalpy (ΔH°) and entropy change (ΔS°) were computed using the equation $\ln K_c = \Delta S°/R - \Delta H°/RT$.

The positive value of ΔH° indicates that CV interaction with PPP is endothermic. Similar endothermic adsorption of methylene blue was observed earlier on Guava leaves [16]. The positive value of ΔS° indicates that CV interaction with the PPP is spontaneous reaction and also reflects the affinity of the adsorbent material. As the dye concentration increases (10-75 ppm), the entropy of the system decreases from 112.6 to 36.97J/K/mol.

Conclusion

The kinetics and thermodynamics for the removal of Crystal violet dye by Pomegranate peel powder from aqueous solution were studied. The kinetics data agreed well with pseudo-second order kinetics. The negative values of *ΔG°* and positive values of *ΔH°* and *ΔS°* indicated adsorption process as spontaneous, endothermic and favorable.

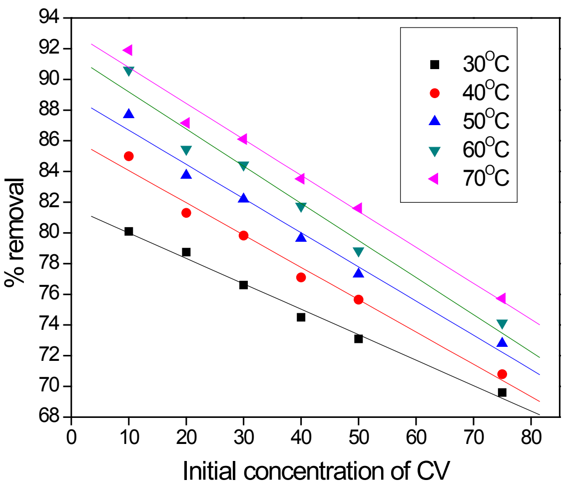

Figure 1: Effect of initial concentration of CV on the percentage removal of CV by PPP.

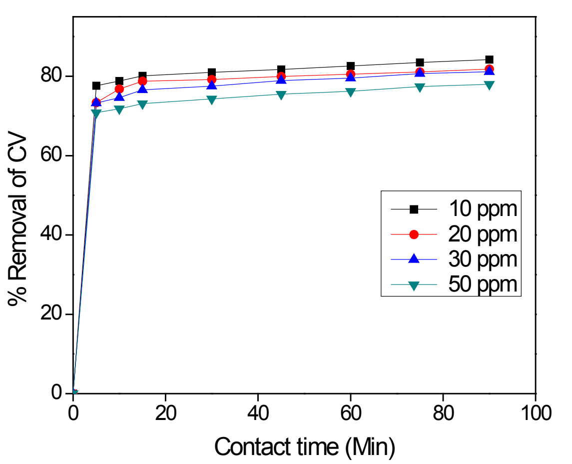

Figure 2: Effect of contact time for the removal of CV using PPP

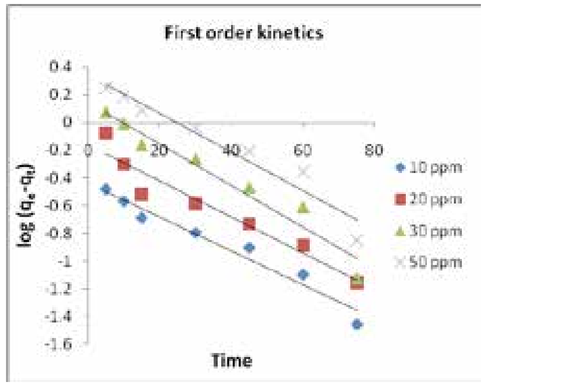

Figure 3: Pseudo first order kinetics for CV adsorption onto PPP.

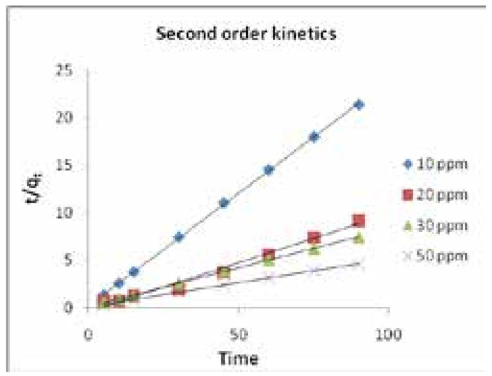

Figure 4 : Pseudo second order kinetics for CV adsorption onto PPP

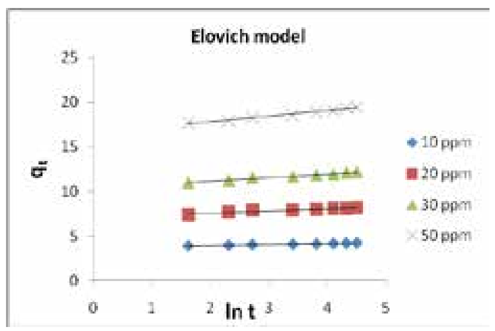

Figure 5: Elovich model plot for the adsorption of CV onto PPP.

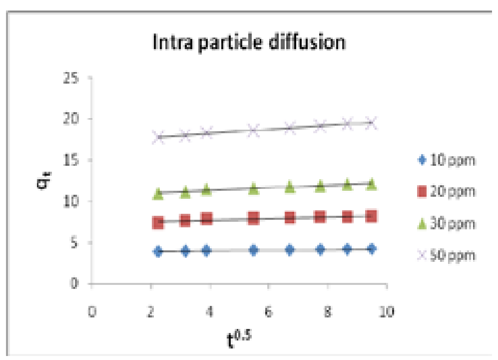

Figure 6: Intraparticle diffusion plot for the removal of CV by PPP.

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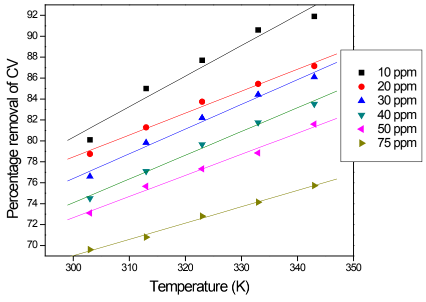

Figure 7: Effect of temperature on the removal of CV by PPP

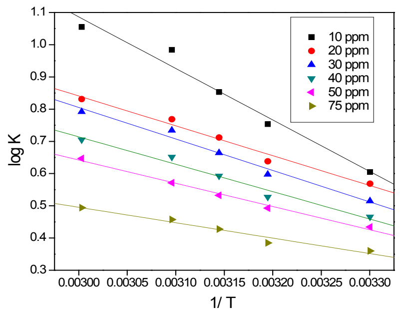

Figure 8: van't Hoff plots for the removal of CV by PPP at different concentration of dye.

Table 1 : Kinetic parameters for the removal of CV by PPP.

Kinetic model	10 ppm	20 ppm	30 ppm	50 ppm
qe Experimetal	4.21	8.18	12.16	19.50
Lagergren model				
K_1	0.0276	0.0299	0.0345	0.0299
R^2	0.958	0.931	0.946	0.941
q_e calculated	0.3689	0.6934	1.406	2.213
Pseudo second order model				
q_e calculated	4.237	9.804	12.34	19.6
K_2	0.258	0.0245	0.0738	0.0449
R_2	0.999	0.982	0.999	0.999
Elovich Model				
α	7.814×10^{13}	3.548×10^{11}	4.786×10^{10}	3.078×10^{11}
β	9.259	3.968	2.475	1.623
R^2	0.977	0.924	0.985	0.977
Intra particle diffusion				
K_{ip}	0.042	0.093	0.156	0.242
$-C_{ip}$	3.808	7.339	10.74	17.23
R^2	0.980	0.933	0.969	0.992
Film diffusion				
K_{fd}	0.028	0.030	0.034	0.032
R^2	0.958	0.931	0.946	0.941

Table: 2 Thermodynamic parameters for the removal of CV by PPP.

[CV] ppm	ΔH kJ/mol	ΔS J/K/mol	-ΔG J/mol				
			303K	313K	323K	333K	343K
10	9270.9	112.6	3508.7	4514.7	5276.0	6274.0	6927.6
20	5375.2	69.30	3300.5	3825.1	4404.2	4902.2	5459.9
30	5669.8	71.55	2987.9	3581.2	4109.3	4682.0	5201.4
40	4929.6	62.48	2701.3	3159.6	3665.1	4152.2	4630.0
50	4184.7	53.48	2518.8	2951.9	3294.2	364.2	4248.3
75	2776.6	36.97	2087.0	2305.2	2644.3	2915.6	3244.1

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