Equilibrium and Kinetics Study of Adsorption of Crystal Violet onto the Peel of *Cucumis sativa* Fruit from Aqueous Solution

T. SMITHA^A, S. THIRUMALISAMY^{A*}, and S. MANONMANI^B

^aDepartment of Chemistry, Karpagam University,
Coimbatore-641021, India.

^bDepartment of Chemistry, PSG College of Arts and Science,
Coimbatore-641014, India

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Abstract: The use of low-cost, locally available, high efficiency and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. This study investigates the potential use of the peel of *Cucumis sativa* fruit for the removal of crystal violet (CV) dye from simulated wastewater. The effects of different system variables, adsorbent dosage, initial dye concentration, pH and contact time were investigated and optimal experimental conditions were ascertained. The results showed that as the amount of the adsorbent increased, the percentage of dye removal increased accordingly. Optimum pH value for dye adsorption was determined as 7.0. The adsorption of crystal violet followed pseudo-second –order rate equation and fit well Langmuir and Freundlich equations. The maximum removal of CV was obtained at pH 7 as 92.15% for adsorbent dose of 0.2 g/ 50 mL and 25 mg L⁻¹ initial dye concentration at room temperature. The maximum adsorption capacity obtained from Langmuir equation was 34.24 mg g⁻¹. Furthermore, adsorption kinetics of (CV) was studied and the rate of adsorption was found to conform to pseudo-second –order kinetics with a good correlation ($R^2 > 0.9739$). The peel of *Cucumis sativa* fruit can be attractive options for dye removal from diluted industrial effluents since test reaction made on simulated dyeing wastewater show better removal percentage of (CV).

Keywords: *Cucumis sativa*; Adsorption; Wastewater; Crystal Violet; Kinetics; Activated carbon.

Introduction

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid¹. Untreated disposal of this colored water into the receiving water body either causes damage to aquatic life or to human beings by mutagenic and carcinogenic effect. As a matter of fact, the discharge of such effluents is worrying for both toxicological and environmental reasons^{2,3}.

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation⁴, adsorption⁵, ozonation⁶, electrochemical techniques⁷, and fungal decolonization⁸. Among these methods adsorption has gained favour in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above treatment methods¹. Activated carbon, as an adsorbent has been widely investigated for the adsorption of dyes⁹, but its high cost limits its commercial application. In recent years, there has been growing interest in finding inexpensive and effective alternatives to carbon, such as clay minerals¹⁰, fly ash¹¹, peat¹², wood powder¹³, coir pith^{14,15} and lignin¹⁶.

Cucumis sativa is a local fruit available in abundance throughout the year. The peel of *Cucumis sativa* fruit, which is removed before consumption is a waste product which is usually discarded. Local vendors at a railway level cross (Near Eachnari, Coimbatore, Tamil Nadu) sell about 600 to 700 kg of the fruit everyday, at this one locale, about 3% of this accounts as waste. Since the peel of *Cucumis sativa* fruit is available free of cost, Therefore the main objective of this study was to evaluate the possibility of using dried peel of *Cucumis sativa* to remove crystal violet from simulated wastewater. Peel of *Cucumis sativa* fruit was previously investigated to adsorb cationic dyes¹⁷. Systematic evaluation of the parameters involved, such as pH, adsorbent dose, adsorbent particle size, initial dye concentration and time.

Experimental

Preparation of the peel of Cucumis sativa fruit (CCS)

The peel of *Cucumis sativa* fruit was obtained from local vendors, Eachnari railway Gate, Coimbatore District (Tamil Nadu). Then the material was washed with distilled water and dried at $110 \pm 2^\circ\text{C}$. It was air-dried and powdered in a grinder. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators for use.

Preparation of synthetic solutions

A stock solution of 500 mg L⁻¹ was prepared by dissolving the appropriate amount of CV (obtained from s.d. Fine Chemicals, Mumbai, India) in 100 mL and completed to 1000 mL with distilled water. Different concentrations ranged between 25 and 200 mg L⁻¹ of (CV) were prepared from the stock solution. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH is adjusted with 0.1 M HCl or 0.1 M NaOH. All the adsorption experiments were carried out at room temperature ($27 \pm 20^\circ\text{C}$).

Batch adsorption studies

Effect of pH on CV adsorption

The effect of pH on the equilibrium uptake of dyes was investigated by employing initial concentration of CV (100 mg/L) and 0.2 g/50 mL of CS. The initial pH values were adjusted with 0.1 M HCl or NaOH to form a series of pH from 2 to 10. The suspensions were shaken at room temperature ($27 \pm 20^\circ\text{C}$) using agitation speed 150 rpm for the minimum contact time required to reach the equilibrium 90 min and the amount of (CV) adsorbed determined.

Effect of CCS dose on CV adsorption

The effect of adsorbents dose on the equilibrium uptake of CV (100 mg L⁻¹) was investigated with CCS concentrations of 0.2, 0.4 and 0.6 g/ 50mL. The experiments were performed by shaking known (CV) concentration with the above different CCS

concentrations to the equilibrium uptake 90 min and the amount of (CV) adsorbed determined.

Kinetics studies

Adsorption studies were conducted in 250-mL shaking flasks at solution pH 7.0. CCS (0.2g/50mL) was thoroughly mixed individually with 50mL of (CV) solution 100 mg/L and the suspensions were shaken at room temperature. Samples of 1.0 mL were collected from the duplicate flasks at required time intervals viz. 10, 20, 30, 40, 50, 60, 70, 80, and 90 min and were centrifuged for 5 min. The clear solutions were analyzed for residual (CV) concentration in the solutions.

Adsorption isotherm

Batch adsorption experiments were carried out in a rotary shaker at 150 rpm using 250ml-shaking flasks at room temperature for 90 min. The CCS (0.2 g) was thoroughly mixed with 50 mL of (CV) solutions. The isotherm studies were performed by varying the initial (CV) concentrations from 25 to 200 mg/L at pH 7.0, which was adjusted using 0.1 M HCl or 0.1 M NaOH before addition of CCS and maintained throughout the experiment. After shaking the flasks for 90 min, the reaction mixture was analyzed for the residual (CV) concentration.

The concentration of (CV) in solution was measured by using a direct UV-vis spectrophotometric method using Systronic Spectrophotometer-104 at wavelength 480 nm. All the experiments are duplicated and only the mean values are reported. The maximum deviation observed was less than $\pm 4\%$.

Adsorption of (CV) from simulated wastewater was studied using 0.2g / 50 mL of CCS and (CV) concentrations 100 mg /L at initial pH 7.0. The amount of dye adsorbed at equilibrium onto carbon, q_e (mg/g), was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e) V/W \quad (1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium liquid –phase concentration of (CV), respectively, V the volume of the solution(L), and W is the weight of the CCS used(g).

Results and Discussion

Adsorbent characterization

Characteristics of activated carbon prepared from the peel of Cucumis sativa fruit are presented in Table 1. The moisture content of the carbon was found to be 1.62% (Table 1). This would not influence the adsorptive power of activated carbon, It was then observed from the literature that if the moisture content of the adsorbent is more, it will dilute the action of activated carbon and it necessitates utilizing some extra load of carbon¹⁸. The decolorizing power was 47.0 mg/g which indicates that the carbon prepared by acid activation method has good adsorption capacity and it can be considered for adsorption of organic dyes.

Effect of system pH on CV Uptake

The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecule presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Figure 1, shows the variations in the removal of dye from wastewater at various system pH. From the figure, it is evident that the maximum removal of (CV) color is observed at pH 7. That may be attributed to the hydrophobic nature of the developed carbon which led to absorb hydrogen ions (H^+) onto

the surface of the carbon when immersed in water and make it positively charged. Low pH value (1.0 to 3.0) leads to an increase in H^+ ion concentration in the system and the surface of the activated carbon acquires positive charge by absorbing H^+ ions. On the other hand, increase of the pH value (7) led to increase of the number of negatively charged sites. As the CRC surface is negatively charged at high pH, a significantly strong electrostatic attraction appears between the negatively charged carbon surface and cationic dye molecule leading to maximum adsorption of (CV) 19 from waste water. The lowest adsorption occurred at pH 2.0 and the greatest adsorption occurred at pH $\approx$ 7.0. Adsorbents surface would be positively charged up to pH < 4, and heterogeneous in the pH range 4–6. Thereafter, it should be negatively charged. Moreover, the increasing in the adsorption of (CV) with increasing of pH value is also due to the attraction between cationic dye and excess OH^- ions in the solution.

Table 1. Characteristics of CCS.

Parameter	Value
pH of 1% solution	6.5
Moisture content(%)	1.62
Water soluble matter(%)	10.12
Acid soluble matter(%)	8.07
Decolorizing power (mg/g)	47.0
Conductivity	0.92
pH _{ZPC}	4.0

Figure 1. Effect of system pH on adsorption of CV (100 mg L^{-1}) onto CS (0.2 g/50 mL) at room temperature ($27 \pm 2^\circ \text{C}$), agitation speed 150 rpm for the minimum contact time required to reach the equilibrium (90 min).

Effect of adsorbent mass on CV adsorption

The adsorption of CV on CS was studied by changing the quantity of adsorbent (0.2, 0.3, 0.4, 0.5 and 0.6 g/50 mL) in the test solution while keeping the initial (CV) concentration 100 mg L^{-1} temperature ($27 \pm 2^\circ \text{C}$) and pH 7.0 constant at contact times for 90 min Figure.2. The adsorption increased from 78.07% to 80.86%, as the CCS dose increased from 0.2 g to 0.6 g/50 mL at equilibrium time 90 min. Maximum (CV) removal was achieved within 10–50 min after which (CV) concentration in the reaction solution was almost constant. Increase in the adsorption with adsorbent dose can be attributed to increased (CV) surface area and availability of more adsorption sites, while the unit adsorbed of (CV) decreased with increase in CCS dose.

Figure 2. Effect of adsorbent concentration on CV removals (C_0 : 100 mg L⁻¹, pH 7.0, agitation speed: 150 rpm, temperature: 27 ± 2 °C).

Isotherm data analysis

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir, and Freundlich isotherm equations. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

Langmuir isotherm

The theoretical Langmuir isotherm²⁰ is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface²¹. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as followed:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

In Eq. (2), C_e and q_e are as defined before in Eq.(1), Q_m is a constant reflect a complete monolayer (mg g⁻¹); K_a is adsorption equilibrium constant (L mg⁻¹) that is related to the apparent energy of sorption. The Langmuir isotherm Eq. (2) can be linearized into the following form^{22,23}.

Langmuir-1

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \quad (3)$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_a Q_m)$.

The results obtained from the Langmuir model for the removal of (CV) onto CCS are shown in Table 2. The correlation coefficients reported in Table 2 showed strong positive evidence on the adsorption of (CV) onto CCS follows the Langmuir isotherm. The applicability of the linear form of Langmuir model to CCS was proved by the high correlation coefficients $R^2 > 0.998$. This suggests that the Langmuir isotherm provides a good model of the sorption system. The maximum monolayer capacity Q_m obtained from the Langmuir is 34.24 mg g^{-1} .

Table 2. Comparison of the coefficients isotherm parameters for CV adsorption onto CS.

Isotherm model Cucumis sativa activated carbon concentrations (g /50mL)	
0.2	
Langmuir	
$Q_m (\text{mg g}^{-1})$	34.24
$K_a (\text{L mg}^{-1})$	0.066
R^2	0.9979
Freundlich	
$1/n$	0.3775
$K_F (\text{mg g}^{-1})$	5.851
R^2	0.9854

The Freundlich isotherm

The Freundlich isotherm model²⁴ is the earliest known equation describing the adsorption process. It is an empirical equation can be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. $1/n$ is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Langmuir isotherm while $1/n$ above 1 is indicative of cooperative adsorption. Eq. (4) can be linearized in the logarithmic form (Eq.(5)) and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting $\log(q_e)$ versus $\log(C_e)$. The data obtained from linear Freundlich isotherm plot for the adsorption of the (CV) onto CCS is presented in Table 2. The correlation coefficients (>0.985) showed that the Freundlich model is comparable to the Langmuir model. The $1/n$ is lower than 1.0, indicating that (CV) is favorably adsorbed by CCS.

Kinetic models applied to the adsorption of (CV) onto CCS

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of (CV) onto CCS. The kinetics of (CV) adsorption onto CCS is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of (CV) adsorption onto CCS were analyzed using pseudo-first-order²⁴, pseudo-second-order²⁵ kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of (CV) adsorption onto CCS.

Pseudo-first-order equation

The adsorption kinetic data were described by the Lagergren pseudo-first-order model²⁵, which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expresses a follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (12)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg g^{-1}), k_1 is the rate constant of pseudo-first-order adsorption (L min^{-1}). Integrating Eq. (12) for the boundary conditions $t = 0 \rightarrow t$ and $q_t = 0 \rightarrow q_t$ gives

$$\log \left(\frac{q_e}{q_e - q_t} \right) = \frac{k_1}{2.303} t \quad (13)$$

Eq. (13) can be rearranged to obtain the following linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (14)$$

In order to obtain the rate constants, the values of $\log(q_e - q_t)$ were linearly correlated with t by plot of $\log(q_e - q_t)$ versus t to give a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively Figure3. The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. Figure4

shows that the pseudo-first-order equation fits well for the first 50 min and thereafter the data deviate from theory. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Furthermore, the correlation coefficient R^2 are relatively low for most adsorption data Table 3. This shows that the adsorption of (CV) onto CCS cannot be applied and the reaction mechanism is not a first-order reaction.

Figure 3. Pseudo-first-order kinetics for CV adsorption onto CS. Conditions: adsorbent dosage 0.2 g/50 mL, pH 7.0, temperature 27 ± 2 °C.

Figure 4. Plot of the pseudo-second-order model at different initial CV concentrations, CS 0.2 g/mL, pH 7.0, temperature 27 ± 2 °C.

Table 3. Comparison of the first- and second-order adsorption rate constants and calculated and experimental q_e values for 100 mg/ L initial CV and CS (0.2g /50mL).

Parameter			First-order kinetic model			Second-order kinetic model		
CS concentration (g /50mL)	Cv (mg L ⁻¹)	q_e (experimental)	k_1	q_e (calculated)	R^2	k_2	q_e (calculated)	R^2
0.2	100	15.25	0.04	23.85	0.8154	0.001	25.31	0.9739

k_1 (min⁻¹), k_2 (g (mg min)⁻¹), q_e (mg g⁻¹).

Pseudo-second-order equation

The adsorption kinetic may be described by the pseudo-second-order model²⁵. The differential equation is generally given as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (15)$$

where k_2 (g (mg min)⁻¹) is the second-order rate constant of adsorption. Integrating Eq. (15) for the boundary conditions $q_t = 0$ – q_t at $t = 0$ – t is simplified as can be rearranged and linearized to obtain:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (16)$$

If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots of t/q_t versus t Figure 4. The linear plots of t/q_t versus t show good agreement between experimental and calculated q_e values at different initial (CV) and adsorbent concentrations Table 3 .The correlation coefficients for the second-order kinetic model are greater than 0.974, which led to believe that the pseudo-second-order kinetic model provided good correlation for the bioadsorption of different initial of (CV) onto CCS.

Conclusion

The results of this investigation show that the Cucumis sativa has a suitable adsorption capacity for the removal of (CV) from aqueous solutions. The equilibrium adsorption is practically achieved in 90 min. The experimental results were analyzed by using Langmuir and Freundlich isotherm models and the correlation coefficients for Langmuir and Freundlich equations are well fitted. Adsorption behavior is described by a monolayer Langmuir-type isotherm. The kinetic study of (CV) on CCS was performed based on pseudo-first-order and pseudo-second-order equations. The data indicate that the adsorption kinetics follow the pseudo-second-order rate. The present study concludes that the CCS could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of color and dyes from water and wastewater.

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