Adsorption Studies of Crystal Violet from Aqueous Solution Using Low Cost Material: Equilibrium and Kinetics Studies

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Abstract:

Crystal violet (CV), one of the toxic dyes which are extensively used for dyestuffs, textile, paper and plastics industries. CV does not easily biodegrades in aqueous medium and show harmful effect on aquatic as well as human life. In the present work adsorption studies of CV onto husk powder of Red gram crop (*Cajanuscajan*) seed was examined in aqueous solution at 27.8°C. The effects of initial concentration, adsorbent dose, temperature, and contact time etc were determined. Highest 81.49% adsorption efficiency recorded was for 50 mg/L solution concentration onto 2.5g of husk powder of Red gram crop seed. The applicability of Langmuir and Freundlich isotherm model was investigated, and the Langmuir adsorption isotherm model exhibited the best fit than Freundlich isotherm model with the experimental data. The adsorption follows pseudo-second-order kinetics.

Keywords: Crystal Violet; Red gram crop seed husk; Isotherm; Thermodynamics; Kinetics.

Introduction:

In recent years, environmental contamination by synthetic dyes is a serious problem due to rising existence of dyes in the aqueous bodies and their negative eco-toxicological effects and bioaccumulation in wildlife[1].Usually the industrial wastewater contains important group of chemicals and toxic substances which are harmful to fish and other aquatic life. Synthetic dyes are extensively used in paper, textile, food, leather, paint, acrylic, cosmetics, plastics, and pharmaceutical industries. About 40,000–50,000 tons of dyes are continuously entering the water systems due to improper processing and dying methods from industries [2]. It has been investigated that the decolourisation of dyes is an important aspect of wastewater treatment before discharge. The color removal was extensively studied with various techniques such as coagulation, chemical precipitation, membrane filtration, solvent extraction, reverse osmosis, photo catalytic degradation, cation exchange membranes,

Electro-chemical degradation, integrated chemical–biological degradation, solar photo-Fenton and biological processes, and adsorption have been checked and evaluated for the treatment of dye bearing effluents. Out of these several techniques employed for dye removal, the most experimental technique was found to be the use of adsorption to adsorb the dye from waste water [3]. Several agricultural by-products have been used as adsorbents for the removal of different organic compounds. The major advantage of adsorption techniques for water pollution control is low investment for terms of cost, simple design, easy and cheap operation.Many low cost adsorbents (agricultural, domestic or plant biomass waste) have been used for removal of CV dye such from waste water BaelBark [4], rice husk [5], jackfruit leaf powder [6], ginger waste [7], black gram seed husk [8] etc. In the present work a waste material like husk powder of red gram crop seed was appliedas an adsorbent for the removal of Crystal Violet (CV) dye, from aqueous solutions. The main cause of the research is to investigate the adsorption efficiency of red gram crop seed husk powder (RGSH) for Crystal Violet (CV). Red gram crop seed husk is a low cost adsorbent, easily available and biodegradable. The effects of initial solution, effect of adsorbent dose, effect of contact time and effect of temperature on CV adsorption rate have been investigated. Adsorption kinetics, adsorption isothermsand thermodynamics were also evaluated and reported.

Materials and methods:

Preparation of adsorbent:

The mature and fresh seeds of red gram crop were purchased from local market and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, seeds of red gram crop are soaked into distilled water up to 24 hours. Then their skin was removed and washed with distilled water. It was dried in shadow. After complete drying the seed husk was ground by grinder. The homogeneous powder was obtained by passing through mesh of desired particles size(micron) of red gram seed husk (RGSH). The dried fine powder of RGSH adsorbent was stored in an air tight glass bottle ready for further experimental process.

Preparation of adsorbate:

Crystal violet (CI: 4255, FW: 407.99, dye content: 88%,) dye supplied by Loba Chemicals Pvt. Ltd., Mumbai (India). Crystal violet dye (Fig.1) was used as adsorbate in experimental process. The stock solution of CV dye was prepared by dissolving the desired amount of Crystal violet powder in double distilled water and suitable diluted to require initial concentrations.

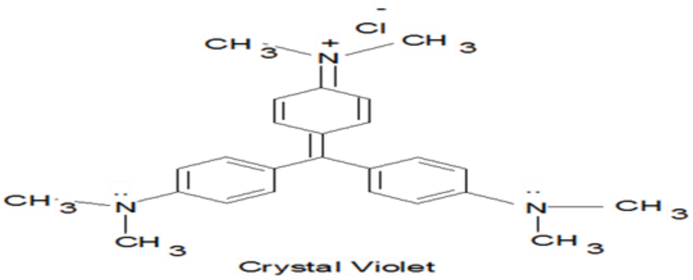

Fig:1. Chemical structure of crystal violet dye.

Batch Adsorption Experiments:

Adsorption experimental techniques were carried out at room temperature (303.6 K). Stock solution of CV dye of concentration 1000 mg/L. in double distilled water was used. Standard technique was followed to determine the adsorption of CV dye concentration using UV-Vis Spectrophotometer. Different initial concentrations of CV dye like 25, 50, 75 and 100 mg/L were used. To observe the effect of adsorbent dose on CV dye adsorption, adsorbent dose varies from 10 gm/L to50 gm/L. was used with 100 mg/L CV dye solution. Effect of temperature has been studied using different temperatures. The operating parameters for each set of experiment are summarized in Table: 1.

Table 1: Variation of experimental operating parameters

Parameters	Values Investigated
Contact time in min.	5, 10, 15, 20, 25, 30, 35 and 24hrs.
Amount of RGSH adsorbent gm/50ml	0.5, 1.00, 1.50, 2.00, 2.50.
Initial concentration of CV dye solution (mg/L)	25, 50, 75, 100
Adsorption temperature (K)	304.2, 309.2. 314.2, 319.2, 324.2
pH	2, 3, 4, 5, 6, 7, 8, 9, 10, 11

A series of required CV dye concentrations and a fixed 50 ml. volume placed in a conical flask where they brought in to contact with RGSH powder at various temperatures. The CV dye solution corresponding to different adsorption time was then analyzed using UV-Vis. Spectrophotometer. The amount of CV dye adsorbed per unite weight of RGSH adsorbent

q_t(mg/g) at time ('t') and percentage adsorption capacity was calculated as

$$q_t = \frac{V(Co-Ct)}{M} \quad (1)$$

$$\% \text{ adsorption capacity} = \frac{(Co-Ct)}{C_0} * 100 \quad (2)$$

Where, C_0 is the initial CV dye concentration (mg/L), C_t is the concentration of CV dye at any time t, V is the volume of CV dye solution (ml) and M is the mass of red gram crop seed husk in gm.

Results and Discussion:

Effect of contact time and initial concentration:

The effect of contact time is an important parameter; the doses of adsorbent were kept constant in all bottles. The effect of contact time was studied at different initial concentration of CV dye with time. The time is varies in parameter for the adsorption of CV dye on red gram seed husk (RGSH) is shown in Fig.2. The experimental results of adsorptions of CV dye on RGSH investigates that the percentage adsorption capacity increased with increasein contact time due to availability of more number of active sites on the surface of the RGSH adsorbent. As increase the initial concentration of CV dye, increase the percentage adsorption capacity due to higher probabilities of collusion between CV dye and RGSH adsorbent. Similar observation was

reported in literature [9].

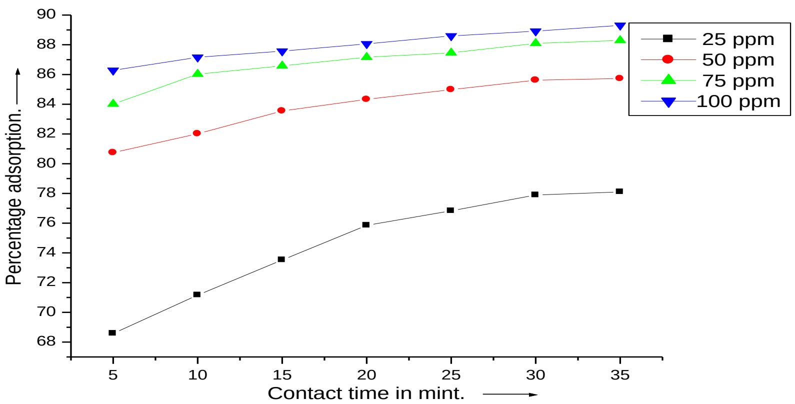

Fig.2:Effect of contact time and initial concentration of CV dye on adsorption of RGSH adsorbent.
[Adsorbent dose=1.0 gm.,Volume=50 ml.,Temp.=300.8 K,pH=7.2]

Effect of adsorbent dose

It is an important parameter that strongly influences the adsorption technique by affecting adsorption capacity of the adsorbent. The experiments were carried out following general procedure for adsorption studies at the various contact time for each adsorbent. The effect of dose of RGSH adsorbent the initial concentration of the dye solution in all the bottles are kept constant and the dose of adsorbent of fixed particle size was varied. The plots of percentage adsorptionof CV dye versus contact time of various dose of adsorbent. The results are shown in Fig. 3.

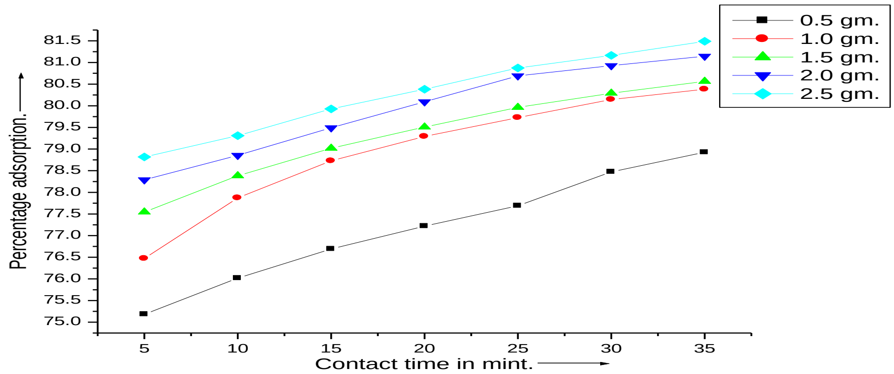

Fig.3:Effect of adsorbent dose of RGSH on adsorption of CV dye.
[Initial conc.= 50 ppm,Volume of adsorbate=50 ml,Temp.=300.8K, pH=7.2]

The influence of adsorbent dose on CV adsorption by RGSH was investigated in the range of 0.5–2.5 gm. The adsorption efficiency increased from 73.93% to 81.49% as the adsorbent dose increased from 0.5 to 2.5 gm. The increase in the percentage adsorption of the Crystal Violet dye adsorption with an adsorbent dose could be attributed to an increase in adsorbent surface area augmenting the large number of adsorbent sites available for adsorption as already reported [10].

Effect of temperature

It is one of the important parameters affecting separation in most of the adsorption processes. In order to examine the effect of temperature on CV dye adsorption five different temperatures were selected. Experiments were carried out at 306.2, 311.2, 316.2, 321.2, and 326.2 K. In the present work percentage removal of CV dye decreases from 87.16 % to 79.76 % by increase in temperature from 304.2 to 326.2 k. The percentage adsorption of CV dye was found to decreases with increasein temperature as shown in Fig.4. It reveals that the adsorbate-adsorbent system is exothermic in nature for which the evaluation of thermodynamic parameters was carried out. Thus, the removal of CV dyes is leading to a decrease in the residual forces on the surface of the RGSH adsorbent and hence causing a decrease in the surface energy of the adsorbent [11].

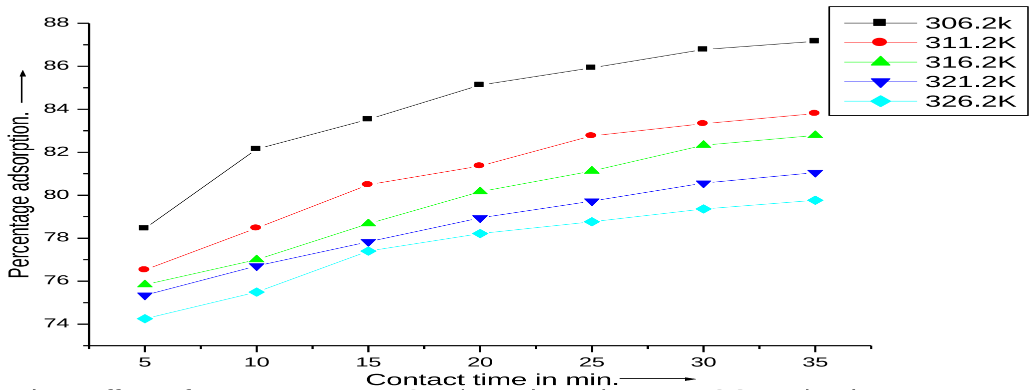

Fig.4:Effect of temperature on CV dye adsorption on RGSH adsorbent.
[adsorbent dose=1 gm.,Int.conc.=50 ppm.,Volume=50 ml,pH=7.2.]

Thermodynamic study was performed to find the nature of adsorption process. Thermodynamic parameters such as Gibb's free energy change ΔG^0enthalpy change of $\Delta H^0$and entropy change of ΔS^0were calculated by using Van't Hoff's equation.

Table: 2. Thermodynamic parameter values of RGSH adsorbent with CV solution at different temperatures.

Temperature (K)	−(ΔG°) KJ/mole	−(ΔH°) KJ/mole	−(ΔS°) J/mole
306.2	-4.046	20.813	54.723
311.2	-3.773		
316.2	-3.499		
321.2	-3.225		
326.2	-2.952		

The ΔG^0values obtained in this study for the CV are < -10 KJ /mole, it indicates that physical adsorption was the predominant mechanism in the adsorption process. The Gibb's free energy indicates the degree of spontaneity of the adsorption process, where more negative value reflects a more energetically favourable adsorption process. The negative value of ΔG^0(Table: 2.) indicates that the adsorption is favourable and spontaneous [12, 13]. The negative value of ΔS^0 and ΔH^0suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption [14, 15].

Adsorption isotherm:

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence Langmuir and Freundlich isotherms were selected in the present study.

Langmuir isotherm: Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites. The linear form of the equation is given by,

$$\frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0C_e} \quad (3)$$

Where, C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e(mg/gm) is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, Q_0 (mg/gm) and b (L/mg) are Langmuir constants related to maximum monolayer adsorption capacity and energy of adsorption respectively. The values of Q_0 and b are calculated from the slope and intercept of plot of $1/q_e$ against $1/C_e$ respectively. The essential features of the Langmuir isotherm may be expressed in termsof equilibrium parameter R_L. Equilibrium parameter R_L is a dimensionless constant referred to as separation factor.

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

Where, C_0 is initial concentration in ppm and b is Langmuir constant related to the energy of adsorption. R_L Value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if, $R_L = 0$ [16].

Freundlich isotherm

Freundlich presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is also expressed as

$$\frac{x}{m} = K_f {C_e}^{1/n} \quad (5)$$

Where, x is the quantity adsorbed, m is the mass of the adsorbent, C_e is the equilibrium concentration of adsorbate (mg/L), The constants $K_f$and n can be obtained by taking log on both sides of equation (5) as follows,

$$\log\frac{x}{m} = \frac{1}{n}\log C_e + \log K_f \quad (6)$$

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. If n=1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one, it indicates a normal adsorption; on the other hand, 1/n being above one indicates co-operative adsorption. A plot of logx/m against $\log C_e$ gives a straight line with an intercept on the ordinate axis. Thevalue of n and $K_f$can be obtained from the slope and the intercept of the linear plot.

Table: 3. Isotherm parameter values of RGSH with CV dye solution.

Concentration of CV (mg/L)	***Langmuir constants***				***Freundlich constants***		
	Q_0 (mg/gm.)	***b*10^{-5} (L/gm.)***	R_L	R^2	***n***	***K_f (mg/gm.(L/gm.))$^{1/n}$***	R^2
50	526.352	0.786	0.999	0.999	1.004	4.879	0.999

The $K_f$value was found to be between 0 and 1 for CV studies, it is confirm that the on-going adsorption of CV is favourable. The data reveal that the Langmuir model yields better fit than the Freundlich model. The value of n suggests that deviation from linearity, if n = 1 the adsorption is homogenous and there is no interaction between adsorbed species. The value of n is greater than unity, (1< n <10), that means favourable adsorption [17]. If value of 1/n > 1 indicates the adsorption is favoured and new adsorption sites are generated [18-21]. The value of n presented in Table: 3. the value of n was found to be between 1 and 10, this indicates favourable adsorption.

Kinetic model of adsorption:

Kinetic studies are significant for any kind of adsorption process. Lager Gren pseudo-first and pseudo-second order kinetic models can be suggested for an adsorption. Pseudo-first order kinetics is present to describe the rate of adsorption process in liquid-solid phase. The Lager Gren pseudo-first order rate equation is given as,

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (7)$$

After definite integration by applications of the conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ Equation (5) becomes,

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (8)$$

Where, q_e (mg/gm) is the amount of adsorption at equilibrium, q_t (mg/gm) denotes the amount of adsorption at time t (min.) and K_1 (min-1) is the rate constant of the pseudo-first order model. Based on experimental results, linear graphs were plotted between log (q_e-q_t)

versus t, to calculate K_1, q_e and R^2.

The pseudo-second order equation can be written as

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (9)$$

Where, K_2 (gm.mg-1min-1) is the rate constant of the pseudo-second order.

The linear form of equation is

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{1}{q_e}t \quad (10)$$

K_2 and q_e can be obtained from the intercept and slope of plotting t/q_t against t

Table: 4. Kinetic parameter values of RGSH adsorbent with CV

Conc. of CV (mg/L)	***Pseudo-First order***			***Second order***		
	K_1 (min^{-1})	***q_e (mg/gm)***	***R^2***	***K_2 (gm./mg.min)***	***q_e (mg/gm)***	***R^2***
50	$14.693*10^{-3}$	165.261	0.928	$1.980*10^{-3}$	751.880	0.999

The value of R^2 with first order kinetics was 0.949, while for second order is 0.999 for RGSH adsorbent. The best correlation for the system provided by the pseudo second order kinetic model suggests that chemical adsorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate might be significant [22]. It is clear that the adsorption of CV on RGSH adsorbent was better represented by pseudo second order kinetics.

Conclusion:

The following conclusions can be drawn based on the investigation of CV dye adsorption by BGSH adsorbents.

1. The percentage adsorption of CV dye on RGSH increased with increasing in adsorption dose of RGSH.
2. The percentage adsorption of CV dye on RGSH adsorbent increased with increase in initial concentration of CV dye solution.
3. Higher percentage adsorption capacity of CV dye on RGSH was observed at lower temperature.
4. The negative value of ΔG^0 confirms that the feasibility of the reaction and spontaneous nature of the adsorption.
5. The negative value of ΔS^0 andΔH^0 suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption.
6. The experimental data for the adsorption of CV dye on RGSH fits well for the Langmuir adsorption isotherm model than Freundlich isotherm model.
7. The investigation showed that RGSH adsorbent was agricultural waste, abundant, cheap, readily available and environment-friendly effective adsorbent, which could be used as potential adsorbent for removal of CV dye from aqueous solution and polluted water.

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