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Kinetics and Isotherm Studies on Crystal Violet Dye Adsorption onto Black Gram Seed Husk

D. B. Jirekar[1] Ghumare Pramila[1] Mazahar Farooqui[2]*

[1,] Anandrao Dhonde Alias Babaji College, Kada. (India)
[2] Dr. Rafiq Zakaria College for Women, Aurangabad. (India)

Abstract: In this work, batch adsorption experiments were carried out to study the adsorption of crystal violet (CV) dye from aqueous solutions using Black gran seed husk (BGSH). The effects of major variables governing the efficiency of the process such as contact time, initial CV concentration. BGSH dose, pH and temperature were investigated.. The adsorption kinetic data were analyzed using pseudo-first order and pseudo-second order models. It was found that pseudo-first order kinetic model was the most appropriate model, describing the adsorption kinetics. Adsorption isotherm of CV dye onto the BGSH was determined at 306.2, 311.2, 316.2, 321.2, and 326.2 K with 50 mg/L as initial concentration of CV . Adsorption equilibrium was attained within 24 hours. Equilibrium data was fitted to the Langmuir and Freundlich adsorption isotherm models and isotherm constants were determined. The equilibrium data were best fitted by the Langmuir isotherm model than Freundlich model. Thermodynamic parameters such as Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated. The negative values of ΔH^0 and ΔG^0 indicates that the CV adsorption process is exothermic and spontaneous in nature. Experimental results have shown that, the amount of CV adsorption increased with increasing the initial concentration of the dye and BGSH dose, while the amount of CV adsorption decreased with increasing the temperature.
Key words: Crystal violet dye, black gram seed husk, adsorption, adsorption isotherms models, equilibrium, kinetics, thermodynamics.

Introduction:

Environmental pollution has recently become a severe problem worldwide[1]A large number of dyes are discharged into waste stream by the many industries. Dyes are widely used in industries such as textiles, plastics, paper rubber, tanning, cosmetics, pharmaceutical and food stuff.[2]. In industrial effluents dyes are one of the most hazardous chemical compound found and need to be treated since their presence in water bodies reduces light penetration, producing the photosynthesis of aqueous flora[3]. Crystal violet is a well-known dye for various purposes like biological stain, dermatological agent, veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus etc.[4,5]. It is a mutagen and mitotic poison and may cause cancer. It is known to be a severe eye irritation, ingestion or through skin contact.

Nowaday various physic-chemical techniques have been studied to assess their applicability for the treatment of this type of industrial discharge. Among these processes may be included coagulation[6], nano-filtration and ozonalysis[7], flocculation[8], ultrasound oxidation process[9], adsorption[10] etc., in which adsorption process is one of the effective technique that have been successfully employed for dye removal from wastewater. Although, activated carbon adsorption appears to be one of the most widely used techniques for dye removal, but in view of the high cost and regeneration problems, there has been a constant search for alternative low-cost adsorbents[11-18]

In present study black gram seed husk powder was tested as adsorbent for adsorption of CV from aqueous solution.

Materials and methods:

Preparation of adsorbent:

The mature and fresh black gram crop seeds were purchased from local market and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, the black gram cropseeds 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 drying the husk was ground by grinder to constant size of 60 μm fine powders of black gram seed husk (BGSH). The dried fine powder adsorbent was kept in an air tight glass bottle ready for further experiments.

Preparation of adsorbate:

Crystal violet (CI: 4255, FW: 407.99, dye content: 88%, supplied by Loba Chemicals Pvt. Ltd., Mumbai (India)) dye(fig 1) was used as adsorbate without purification. The stock solution of 1000 mg/L CV dye was prepared by dissolving the desired amount of Crystal violet in double distilled water and suitable diluted to require initial concentrations.

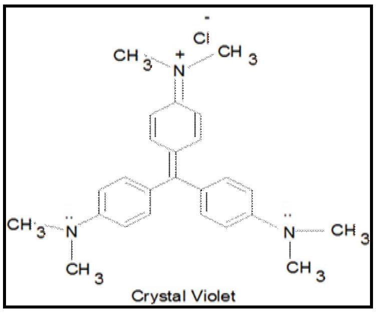

Figure 1: Chemical structure of Crystal violet.

Adsorption experiments:

All adsorption experiments were carried out by batch adsorption techniques at room temperature. The effect of pH on CV removal was studied by shaking 25 ml, 50 mg/L. of CV dye solution concentration with 0.5 gm. adsorbent dose in conical flasks. The effect of contact time and initial concentration were studied by shaking 50 ml 50 mg/L CV solutions concentration with 1.0 gm. adsorbent in a 100 ml conical flask. After definite time intervals, a sample were withdrawn from the flask, the supernatant solution was analyzed for residual dye concentration. Adsorbent dose effect was studied using 50 mg/L CV solution concentration. The optical density was analyzed using a UV-Visible single beam Spectrophotometer (BioEra: Cal No.BI/CI/SP/SB-S-03), at λ max = 540 nm.The pH of the CV solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution and measurement was done by digital pH-meter (Elico: LI 615). The amount of CV dye adsorbed per unit weight of BGSH adsorbent at time 't', q_t(mg/L) and percentage CV dye 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 solution (ml) and M is the mass of BGSH (gm).

Results and Discussion:

Effect of contact time:

The time-dependent behavior of CV dye adsorption was examined by varying the contact time between adsorbent and adsorbate in the range of 5 – 35 min. The results are shown in **Fig. 2**.

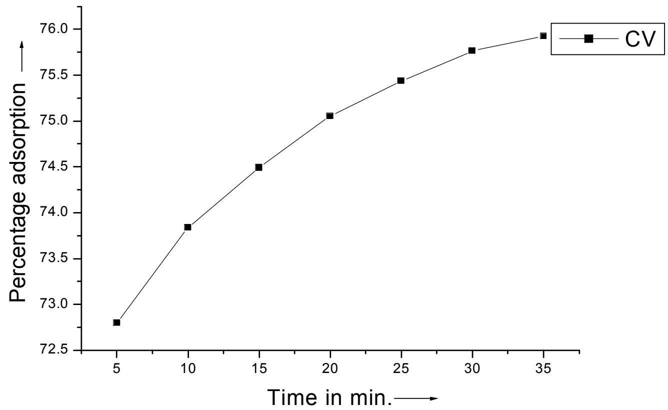

Fig. 2. Effect of contact time on percentage adsorption of CV [Initial conc.=50 mg/L, Adsorbent dose=1.0 gm., Temp=303.6k,pH=6.618]

The removal of CR dye increased with increasing contact time due to large surface area available of the GSH adsorbent. The percentage adsorption increases upto 75.6 in 35 minutes and then becomes constant

Effect of adsorbent dose:

Adsorbent dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of adsorbate. The effect of adsorbent dose was studied with CV dye removal keeping all the experimental conditions constant. The adsorption of CV by BGSH at different adsorbent doses from 0.5 gm. to 2.5.gm. for 50 mg/L of CV dye concentration at pH 7.094 was studied.The results are shown in **Fig. 3**.

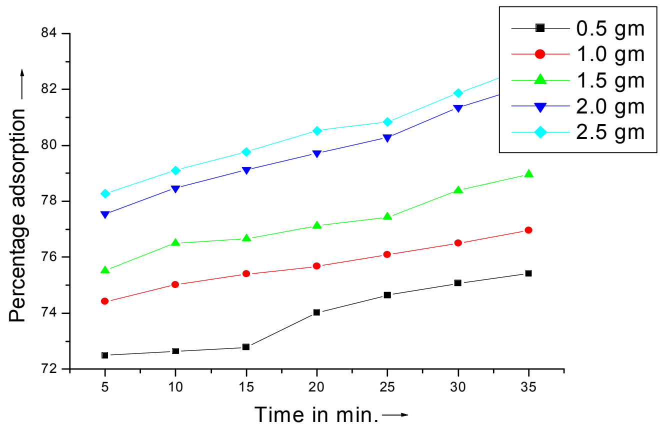

Fig. 3. Effect of adsorbent dose on percentage adsorption of CV [Initial conc.=50 mg/L, Temp=300.0k,pH=7.094]

The results (Fig. 3.) shows that as the adsorbent mass increases from 0.5 to 2.5 gm., the percent CV adsorption increase from 75.42 to 82.80 %. This may be due to increase in total number of exchange sites with dosage.

Effect of initial dye concentration:

The concentration range of dye varied from 25 to 100 mg/L keeping other parameters constant. The result revealed that percentage adsorption of CV dye was increases with increase in initial concentration. The maximum percentage adsorption efficiency was 86.43 at 100 mg/L.CV concentration. The results are shown graphically given in **Fig. 4.**

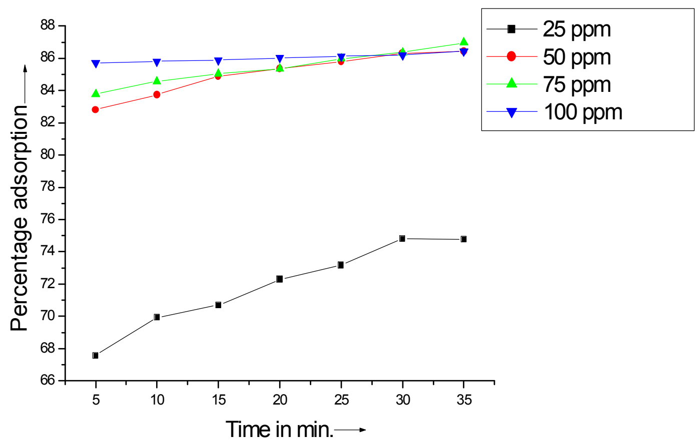

Fig. 4. Effect of initial concentration of CV on percentage adsorption of CV
[Adsorbent dose=1.0 gm, Temp=300.7k, pH=7.0]

Effect of pH:

The pH of the adsorbate solution is considered one of the most important factors affecting the adsorption process. The dye solution below pH 2 changed colour from red to dark blue and the original red colour was different above pH 11. Hence the effect pH of solution was studied between 2.0 to 11.0 shown in **Fig. 5**.

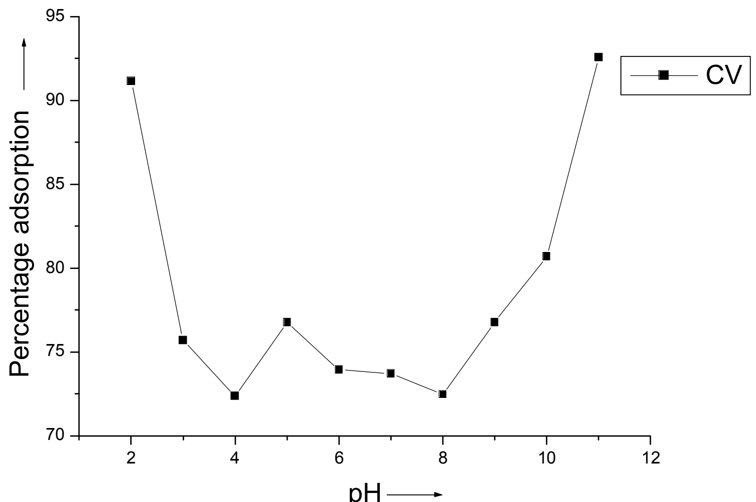

Fig. 5. Effect of pH on percentage adsorption of CV on BGSH.
[Adsorbent dose=0.5 gm, Temp=300.7k, Initial conc.=50 ppm.]

The result show that as pH increases from 2 to 8 the percentage adsorption of CV dye decreases from 91.16 to 72.45 %, after pH 8 percentage adsorption increases up to 92.58.

Effect of temperature:

Temperature has a pronounced effect on the adsorption capacity of various adsorbents. The temperature effect was investigated for temperatures ranging from 306.2 to 326.2 K. The results are shown in **Fig.6.**

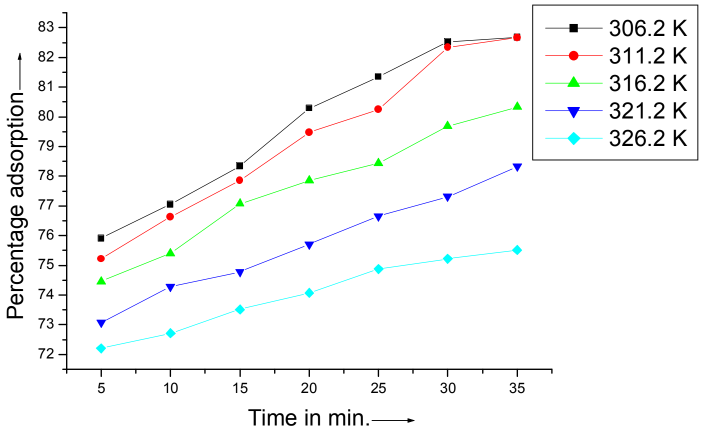

Fig. 6. Effect of temperature on percentage adsorption of CV on BGSH. [Adsorbent dose=1.0 gm, Initial conc.=50 ppm. pH=6.618.]

The maximum percentage CV dye adsorption decreases with increase in temperature. Since adsorption is an exothermic process. Thus the removal of CV dyes is leading to a decrease in the residual forces on the surface of the BGSH adsorbent and hence causing a decrease in the surface energy of the adsorbent[19].

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

Table: 1. Thermodynamic parameter values of BGSH adsorbent with CV solution at different temperatures.

Temperature (K)	$-(\Delta G^0)$ KJ/mole	$-(\Delta H^0)$ KJ/mole	$-(\Delta S^0)$ J/mole
306.2	3.377	18.328	48.796
311.2	3.133		
316.2	2.889		
321.2	2.645		
326.2	2.401		

The ΔG^0 values 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 favorable adsorption process. The negative value of ΔG^0 (Table:1.) indicates that the adsorption is favorable and spontaneous[20-21].The negative value of ΔS^0 and ΔH^0 suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption.

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,

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

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 $\frac{1}{q_e}$ against $\frac{1}{C_e}$ respectively. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameterR_L. Which is a dimensionless constant referred to as separation factor or equilibrium parameter[22].

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

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 unfavorable if R_L> 1, linear if R_L= 1, favorable if 0 <R_L< 1 and irreversible if, R_L= 0 .

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

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

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,

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

The constant K_f is an approximate indicator of adsorption capacity, while $\frac{1}{n}$ 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 $\frac{1}{n}$ is below one, it indicates a normal adsorption, on the other hand $\frac{1}{n}$ being above one indicates co-operative adsorption. A plot of $\log\frac{x}{m}$ against $\log C_e$ gives a straight line with an intercept on the ordinate axis. The value of *n* and K_f can be obtained from the slope and the intercept of the linear plot.

Table: 2. Isotherm parameter values of BGSH with CV dye solution.

Concentration of CR (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	526.316	0.840	0.929	0.999	1.001	4.553	0.951

The R_L value was found to be between 0 and 1 for CV studies, it is confirm that the ongoing adsorption of CV is favorable. 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 favorable adsorption. If value of $\frac{1}{n}$> *1* indicates the adsorption is favored and new adsorption sites are generated. The value of *n* presented in **Table: 2**. The value of *n* was found to be between 1 and 10, this indicates favorable adsorption.

Kinetic model of adsorption:

Kinetic studies are significant for any kind of adsorption process.Lagergren 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 Lagergren 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 is developed by Ho can be written as

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

Where, K_2 (*gm.mg*$^{-1}$*min*$^{-1}$) 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: 3. Kinetic parameter values of BGSH adsorbent with CV

Conc. of CR (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	16.140*10^{-3}	144.937	0.949	2.056*10^{-3}	671.141	0.999

The value of R^2 with first order kinetics was 0.949, while for second order is 0.999 for BGSH adsorbent. It is clear that the adsorption of CV on BGSH adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second order kinetic model.

Conclusion:

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

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

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