

Comparative Study of Adsorption of Red Gram Seed Husk for the Adsorption of Congo Red, Crystal Violet, and Methylene Blue from Aqueous Solution

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Abstract: Many industries such as paper, food, cosmetics, textiles etc. use dyes in order to color their products. The presence of Congo red, Crystal violet and Methylene blue dyes in water even at very low concentration is highly visible and undesirable. The degradation by-products of organic dyes have dangerous impacts on the environment. The ability of the low-cost materials viz. red gram seed husk (RGS) powder to remove Methylene Blue (MB), Congo Red (CR), and Crystal Violet (CV), dyes in aqueous solution was studied by using batch adsorption process. Effect of contact time, adsorbent dosage (g/L), pH, and effect of temperature were studied in batch technique and results showed that amount of the dye adsorbed increases with increase in contact time and adsorbent dosage studied. The extent of adsorption was strongly depending on pH of solution, free energy of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were calculated. Equilibrium adsorption isotherms and kinetic were investigated. The experimental data were analyzed by the Langmuir and Freundlich models and the isotherm data fitted well to both Langmuir Freundlich isotherm. The kinetic data obtained were analyzed using a pseudo-first order and pseudo-second-order equation. The experimental data fitted very well the pseudo second-order kinetic model.

Key Word: Adsorption, red gram seedhusk, Dyes, Adsorption isotherm, Equilibrium kinetics, etc.

I. Introduction

Pollution caused by the textile wastewater is a common problem faced by many countries. The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution. Wastewaters from dyeing and finishing operations in the textile industry are generally high in both color and organic content. Color removal from textile effluents has been the target of great attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems. Recent estimates indicate that approximately 12% of synthetic textile dyes used each year is lost during manufacture and processing operations and 20% of these lost dyes enter the environment through effluents that result from the treatment of industrial wastewaters. Many dyes and their break down products may be toxic for living organisms [1]. Dyes may be carcinogenic, mutagenic or teratogenic. Additionally, it may also cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver brain and central nervous system. The dyes are generally resistant to environmental conditions like light, effect of pH and microbial attack. The removal of dyes from industrial effluents in an economical way is a growing concern these days. There are various methods for the removal of dyes including sedimentation and flotation, membrane separation, coagulation, ion exchange and adsorption. The cost of operation is the main drawback of these techniques [2]. Among these methods, adsorption is a widely used for dye removal from wastewaters [3, 4]. Generally biological aerobic wastewater systems are not successful for decolorization of majority of dyes. Thus, the use of several low-cost adsorbents has been tested and used for the

removal of dyes from polluted water by many researchers. They have studied the feasibility of using low-cost materials, such as waste black gram seed husk [5]; banana bith [6]; cotton waste, rice husk [7]; neem leaves [9], treated guava seeds [10], palm kernal coat [11], Gram Seed Husk [12]; duck weed [13], almond tree bark powder [14], cucumber peel [15], have been employed for the removal of CR, CV and MB dyes via adsorption. In the present study, the potential of red gram seed husk (RGSH) powder low-cost bio-sorbent for the removal hazardous of Congo red, crystal violet and methylene blue from the aqueous solution is studied.

II. Material And Methods

The mature and fresh red 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 seeds are soaked into distilled water up to 24 hours. Then their skin was removing from their pulses and washed with distilled water. It is dried in shadow. After drying the husk was ground by grinder to constant size of 60 μm fine powders of seed husk. The dried fine powder adsorbent was kept in an air tight glass bottle ready for further experiments.

Organic dyes (Congo Red, Crystal Violet and Methylene Blue) are purchased from different chemical laboratories such as methylene blue were purchased from Qualigens, Fine Chemicals, Mumbai (India), crystal violet and Congo red were purchased from Loba Chemicals Pvt. Ltd. Mumbai (India). All solutions were prepared in double distilled water. The concentration of dye solutions was determined by using UV-Visible single beam Spectrophotometer, (BioEra: Cal No.BI/CI/SP/SB-S-03). Stock solutions (500 ppm) were prepared by dissolving weighed quantities of these organic compounds (500 mg) in double distilled water (1000 ml). The experimental solutions were prepared by successive dilution using double distilled water. The solutions were carried out from the stock solution to prepare solutions in different concentrations. The concentration of solution was determined from calibration curve spectrophotometrically at their λ_{max} that is Congo Red ($\lambda_{\text{max}} = 510 \text{ nm}$), Crystal Violet ($\lambda_{\text{max}} = 540 \text{ nm}$) and for Methylene Blue ($\lambda_{\text{max}} = 570 \text{ nm}$). The structures of dyes are shown in Fig. 1.

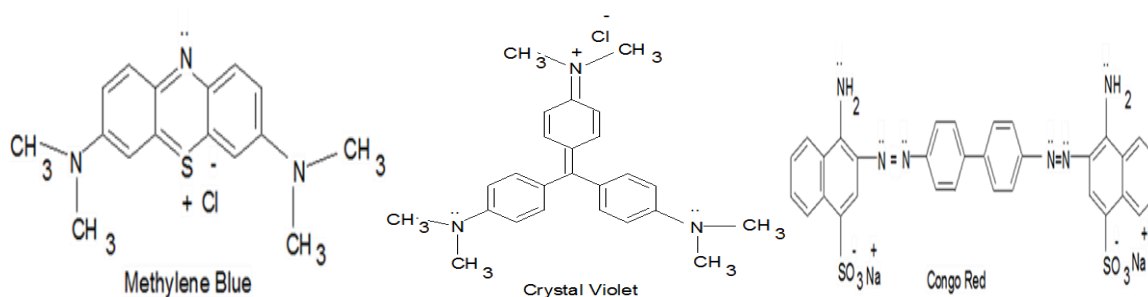


Fig:1. Chemical structures of Congo red, Crystal Violet and Methylene blue dye.

Adsorption experiment was carried out by batch adsorption techniques at room temperature ($306.2 \pm 3^0 \text{ k}$). The effect of pH on CR, CV and MB removal were studied by shaking 50 ml, 20 mg/L. of CR, CV and MB solution concentration with 0.5 g adsorbent dose in conical flasks. The effect of contact time and initial concentration were studied. After definite time intervals, a sample were withdrawn from the flask, the supernatant solution was analyzed for residual dye concentration. The optical density was analyzed using a UV-Visible single beam Spectrophotometer. The pH of the 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 dye adsorbed per unite weight of husk adsorbent at time, 't', q_t (mg/L) and percentage dye adsorption capacity was calculated as

$$q_t = \frac{V(C_0 - C_t)}{M} \quad (1)$$

$$\% \text{ Percentage adsorption efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

Where, C_0 is the initial concentration of dye (mg/L), C_t is the concentration of dye at any time t, 'V' is the volume of dye solution (mL) and M is the mass of red gram seed husk (g).

III. Result and Discussion

Comparative study was conducted using red gram seed husk powder surface as adsorbent for the adsorptive removal of Congo red, Crystal violet and Methylene blue dyes from its aqueous solution. Operational conditions such as contact time, adsorbent dose, pH, and temperature were optimized for the dyes.

Effect of contact time:

The time-dependent behavior of MB, CR, and CV adsorption on red gram seed husk (RGSH) powder were examined by varying the contact time between adsorbent and adsorbate in the range of 5 to 35 min. The results are shown in Fig. 2.

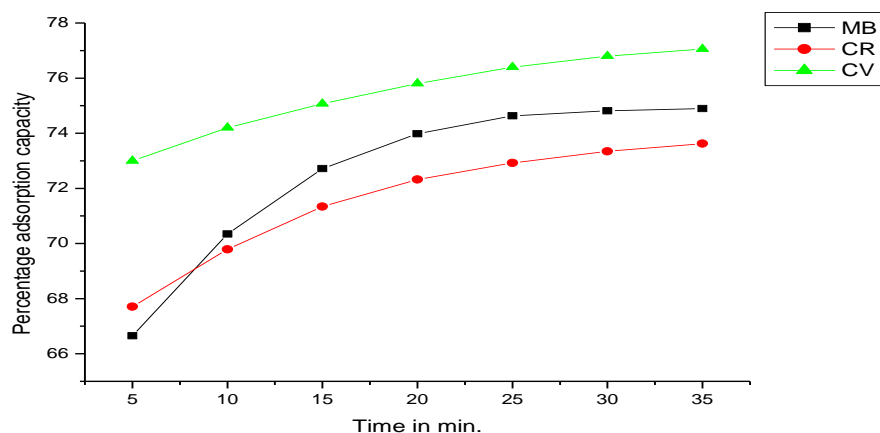


Fig.2: Effect of contact time on adsorption of MB, CR & CV on RGSH adsorbent.

The percentage adsorption of MB, CR, and CV dyes were increased with increasing contact time due to larger surface area available of the adsorbent. The maximum adsorption efficiency was 77.05 % for CV, 74.89 % for MB, and 73.62 % for CR at 35 min. The CV dye has higher percentage adsorption capacity than MB and CR dyes due to the boundary layer resistance will be affected by the rate of adsorption and increase in contact time, which will reduce the resistance and increase the mobility of dye during adsorption [16].

Effect of adsorbent dose:

The study of adsorbent dose for the removal of the MB, CR, and CV dyes from aqueous solution was carried out using red gram seed husk with their amount varying from 0.5 to 2.5 g.

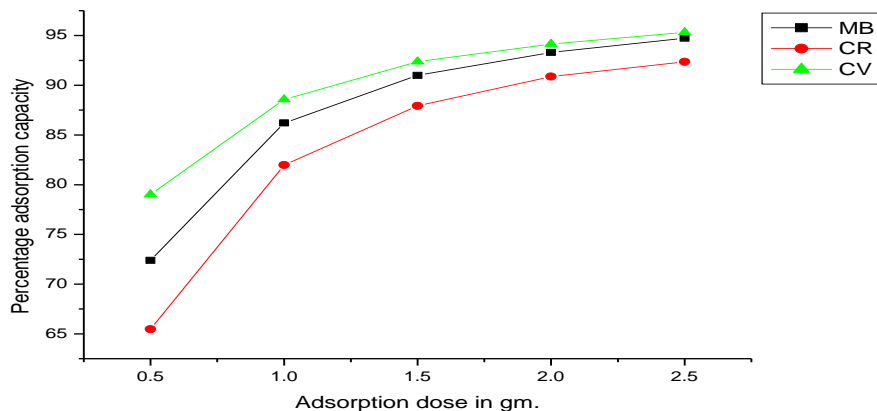


Fig.3: Effect of adsorption dose on adsorption of MB, CR & CV on RGSH adsorbent.

The maximum adsorptions of dyes were 95.33 % of CV, 94.73 % of MB and 92.35 % of CR attained for adsorbent dose at 2.5 g. as shown in **Fig. 3**. The percentages adsorption of the dyes increases with increase in adsorbent dose due to increase in total number of exchange sites. The percentages adsorption capacity of CV dye has more than the percentages adsorption capacity CR and MB.

Effect of pH:

Fig: 4 clearly showed the influence of the initial solution pH on the adsorption extent of MB, CR, and CV on to red gram seed husk powder.

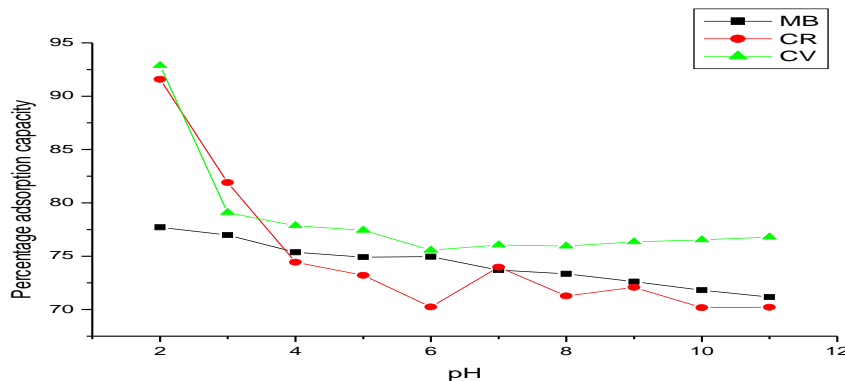


Fig.4: Effect of pH on adsorption of MB, CR & CV on RGS adsorbent.

The maximum adsorption of CV dye was 93.63 %, CR dye was 70.21 % and MB dye was 71.16 % at pH 2 respectively. It can be seen from the figure that as the solution pH increases, the percentage adsorption capacity decreases. At higher pH the high negatively charged adsorbents surface sites did not favor the adsorption of deprotonated dyes due to electrostatic repulsion [17]. At higher pH, the percentage adsorption was found to decrease because the surface area of the adsorbent was more protonated and competitive adsorption occurred between H+ and free MB ions and their OH- towards the fixation sites. Therefore, H+ ions react with anionic functional groups on the surface of the adsorbent and results in restriction of the number of binding sites favorable for the adsorption of MB ions.

Effect of Temperature:

Temperature has a pronounced effect on the adsorption capacity of various adsorbents. The temperature effect was investigated for temperatures ranging 306.2 to 326.2 k. The results are shown in **Fig. 5**.

The maximum adsorption efficiency of adsorbent was 78.12 %, 83.48 % and 89.96 % for MB, CR and CV respectively at 306.2 k. Since adsorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate-adsorbent system would result in decreased adsorption capacity. Thus, the adsorption of dyes was leading to a decrease in the residual forces on the surface of the adsorbent and hence causing a decrease in the surface energy of the adsorbent [18].

The Gibb's free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes for the adsorption were determined by using equation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{3}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \tag{4}$$

For the adsorbent concentration is unity ($m = 1.0$ g) equation (4) becomes

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \tag{5}$$

q_e is the amount of dye adsorbed per unite mass of husk (mg/g), C_e is the equilibrium concentration (mg/L) and T is the temperature in °k. $\frac{q_e}{C_e}$ is called adsorption affinity. The values of Gibb's free energy (ΔG°) has been calculated by knowing the enthalpy of adsorption (ΔH°) and entropy of adsorption (ΔS°) and (ΔH°) was obtained from a plot of $\log\left(\frac{q_e}{C_e}\right)$ versus $1/T$ from equation (4) and (5). Once these two parameters were obtained, (ΔG°) is determined from equation (3). The calculated values are given in **Table:1**

Table: 1. Comparison of thermodynamic parameter values of MB, CR, and CV dyes.

Thermodynamic parameters of CR, CV and MB Dyes								
(-ΔG°) KJ/mole			(-ΔH°) KJ/mole			(-ΔS°) J/mole. k		
MB	CR	CV	MB	CR	CV	MB	CR	CV
-3.226	-4.046	-5.559	16.389	20.813	23.929	43.146	54.723	59.991
-3.042	-3.772	-5.259						
-2.807	-3.499	-4.959						
-2.579	-3.225	-4.659						
-2.378	-2.951	-4.359						

The ΔG^0 values obtained in present study for the CR, CV and MB dyes 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 indicates that the adsorption is favorable and spontaneous [19, 20]. The negative value of ΔS^0 and ΔH^0 suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption [21, 22].

Adsorption Kinetic Models:

Pseudo first order kinetic model assumed that the rate of solute up take with time was directly proportional to difference in saturation concentration and the adsorbed amount.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (6)$$

Where, q_t and q_e are the amount of dye adsorbed (mg/g) at contact time t (min) and at equilibrium k_1 is the pseudo first order rate constant (min^{-1})

After integrating with the boundary conditions at $t = 0, q_t = 0$ and at $t = t, q_t = q_t$ and rearranging equation (6), the rate law for a pseudo first order reaction become.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303R} t \quad (7)$$

The plot of $\log(q_e - q_t)$ versus t gave a straight line with slope $-\frac{k_1}{2.303R}$ and intercept $\log q_e$. Adsorption rate were calculated from the slope and results are given in table (6)

Pseudo second order kinetic model was

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

k_2 is equilibrium rate constant for pseudo second order adsorption (g/mg min).

After integrating with the boundary conditions at $t = 0, q_t = 0$ and at $t = t, q_t = q_t$ and rearranging equation (8), the rate law for a pseudo second order reaction become.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

The plot of $\frac{t}{q_t}$ versus t gave a straight line with slope $\frac{1}{q_e}$ and intercepts $\frac{1}{k_2 q_e^2}$ the calculated values of k_2, q_e values are given in **Table: 2**.

Table: 2. Comparison of the experiments and the kinetic model of MB, CR, and CV dyes on RGSH adsorbent.

Dyes	Pseudo-First order			Second order		
	K_1, min^{-1}	q_e (mg/g)	R^2	$K_2, \text{g/mg.min}$	q_e (mg/g)	R^2
MB	36.364×10^{-3}	616.311	0.882	0.321×10^{-3}	3839.391	0.999
CR	14.693×10^{-3}	165.261	0.928	1.980×10^{-3}	751.880	0.999
CV	26.047×10^{-3}	206.001	0.985	1.080×10^{-3}	1948.429	0.999

The R^2 values of MB, CR and CV with first order were 0.882, 0.928 and 0.985 respectively, while for second order R^2 values of CR, CV and MB are 0.999. It is clear that the adsorption of MB, CR and CV on RGSH adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second order kinetic model.

Adsorption Equilibrium:

To study the validity of Freundlich adsorption isotherm the following equation has been used

$$\text{Log } x/m = \log K_f + (1/n) \log C_e \quad (10)$$

K_f is the Freundlich constant [$\text{mg/g (L/g)}^{1/n}$] related to bonding energy, and n is the heterogeneity factor. The plot of $\text{Log } x/m$ against $\log C_e$ gives straight line which exhibits monolayer coverage of the adsorbate on the other surface of the adsorbent. The value of n ranging in between 2-10 indicates good adsorption.

The equilibrium data was also analyzed in the light of Langmuir adsorption model.

$$\frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0C_e} \quad (11)$$

Where, C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, Q_0 (mg/g) 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 parameter R_L . Which is a dimensionless constant referred to as separation factor or equilibrium parameter [23].

$$R_L = \frac{1}{1+bC_0} \quad (12)$$

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, $R_L = 0$ [24]. The calculated values are given in **Table: 3**

Table: 3. Comparisons of Langmuir and Freundlich isotherm constants for the adsorption of MB, CR, and CV dyes on RGSH.

Dyes	Langmuir constants				Freundlich constants		
	Q_0 (mg/g)	$b * 10^{-3}$ (L/g)	R_L	R^2	n	K_f ($\text{mg/g(L/g)}^{1/n}$)	R^2
MB	429.995	7.454	0.999	0.999	1.236	10.061	0.998
CR	526.352	0.786	0.999	0.999	1.004	4.879	0.999
CV	555.555	4.844	0.999	0.953	1.016	7.686	0.905

The R_L value was found to be between 0 and 1 for MB, CR, and CV studies, it is confirmed that the ongoing adsorption of MB, CR, and CV on RGSH adsorbent is favorable. The data of MB, CR, and CV reveal that the Langmuir model and Freundlich model yields better fit. The value of n is greater than unity, ($1 < n < 10$), that means favorable adsorption. [25]. From Table: 3 value of n was found to be between 1 and 10; this indicates that adsorption is favorable.

IV. Conclusion

Adsorption of dyes like Methylene blue, Congo red and Crystal violet and were investigated using low-cost bio-waste adsorbents, viz. red gram seed husk. Conclusion from this study can be represented as follows.

1. The percentage adsorption of MB, CR, and CV dyes on RGSH increases with increasing dose of adsorbent, contact time and decreased with increasing temperature.
2. It was found that pH of dyes has a significant effect on the adsorption of dyes.
3. The negative value of ΔG^0 confirms that the feasibility of the reaction and spontaneous nature of the adsorption. Negative value of ΔS^0 and ΔH^0 suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption.
4. In case of MB, CR, and CV both Langmuir and Freundlich isotherm model fitted well for RGSH adsorbent.
5. The suitability of pseudo-first-order kinetic and pseudo-second-order kinetic models for the adsorption of MB, CR, and CV dyes on RGSH were also discussed. The kinetic modeling study has shown that the experimental data were found to follow the pseudo-second-order model suggesting a chemisorption process.
6. The values of the separation factor, R_L , indicated that the dyes were a favorable adsorption.

Since the raw material red gram seed husk abundantly in large quantities, cheap, locally available, renewable adsorbent for the removal of color of aqueous solution of MB, CR, and CV dyes as well as textile dyeing effluent.

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