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Full Paper

Evaluation of Adsorption Capacity of Low Cost Adsorbent for the Removal of Congo Red Dye from Aqueous Solution

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Abstract: *Vigna unguiculata* seed husk powder has been investigated as low cost adsorbent for the removal of hazardous chemicals like Congo Red (CR) dye from aqueous solution. Various parameters such as effect of contact time, initial CR dye concentration, adsorbent dose, effect of pH, zero-point pH were studied. Batch adsorption technique was employed to optimize the process parameter. The result indicated that, the percentage adsorption of Congo Red increased with increase in contact time, dose of adsorbent and initial concentration of Congo Red and decreased with addition of salt. The adsorption of Congo Red was 78% at the optimum pH of 6. Adsorption equilibrium was found to be reached in 24 h for 5 to 25 g/50 mL Congo red concentrations. The Langmuir and Freundlich isotherm models were found to provide an excellent fitting of the adsorption data. The adsorption of CR follows Second order rate kinetics. Thermodynamic parameter (ΔG^o) showed that it was an exothermic process. This adsorbent was found to be effective and economically attractive.

Keywords: congo red; kinetics; Langmuir-Freundlich isotherms; thermodynamic parameters; Vigna unguiculata

1. INTRODUCTION

The potable water used by every human being for cooking as well as drinking should be uncontaminated and pure. Thanks to the over pollution, India is suffering from persistent demand for safe drinking water. Discharge of effluents, bearing dyes, surfactants, salts and heavy metals, etc. from industries like textiles, paints, pulp and paper mills, carpet, electroplating, tanneries and printing, etc. not only contaminate ground water and surface water but also impart toxicity and non-visibility. A huge amount of water is necessary by these industries for the cleaning and washing purposes and the discharge highly coloured effluents containing various dyes. The degradation by-products of organic dyes such as synthetic azo-dyes have dangerous impacts on the environment since it contains toxic aromatic compounds and the removal rate of these materials during aerobic waste treatment are still low [1]. Many of the organic dyes are toxic and may affect the aquatic life and even the food chain. Additionally, the dye presence on natural water systems inhibits sunlight diffusion into the water, consequently reducing the photosynthetic process of aquatic plants [2]. Therefore, it is very important to develop new system that can be used for removing dyes from water. We have already reported the adsorptive capacity of some low cost materials towards metals and dyes earler [3-7] Literature survey reveals that various adsorbents have been tested and used for the removal of dyes from polluted water. A number of non-conventional adsorbents such as bale tree leaf powder [8], neem leaves [9], *Alternanthera bettzichiana* plant [10], gram husk [11], subabul seed pods [12], fly ash [13], coir pith carbon [14], green gram husk [15] etc., have been used for the removal of CR dye from aqueous solution.

In the present work *Vigna unguiculata* crop seed husk powder was employed for removal of hazardous CR dye and used as an effective adsorbent in the wastewater treatment. The adsorption technique was found to be very useful and cost effective for a better removal of hazardous CR dye.

2. MATERIAL AND METHODS

The mature and fresh *Vigna unguiculata* crop

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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 fine powders of seed husk. The dried fine powder adsorbent was kept in an air tight glass bottle ready for further experiments.

Congo Red (CR) (CI: 22120, MW: 696.66 g) supplied by Loba Chemicals Pvt. Ltd. Mumbai (India) were used as adsorbate without purification. The stock solution of 1000 mg/L CR dye was prepared by dissolving the desired amount of Congo Red in double distilled water and suitable diluted to require initial concentrations. The structure of this dye is shown in Fig. 1.

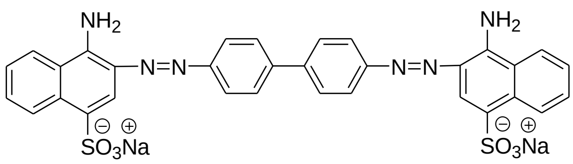

Figure 1. Chemical structure of Congo Red.

Adsorption experiment was carried out by batch adsorption techniques at room temperature. The effect of pH on CR removal were studied by shaking 25 mL, 20 mg/L. of CR dye solution concentration with 0.5 g. adsorbent dose in conical flasks. The effect of contact time and initial concentration were studied by shaking 50 mL 20 mg/L CR solution concentration with 1.0 g 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 20 mg/L CR 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 = 510 nm. The pH of the CR 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 CR dye adsorbed per unite weight of husk at time, t, (mg/L) and percentage dye adsorption capacity was calculated as:

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

$$\text{Percentage adsorption} = \frac{(C_0 - C_e)}{C_0} * 100 \qquad (2)$$

where, C_0 is the initial dye concentration (mg/L), C_t is the concentration of CR dye at time t, *V* is the volume of solution (ml) and M is the mass of husk (g).

3. RESULTS AND DISCUSSION

Effect of contact time and initial concentration

The time-dependent behavior of CR dye adsorption was 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.

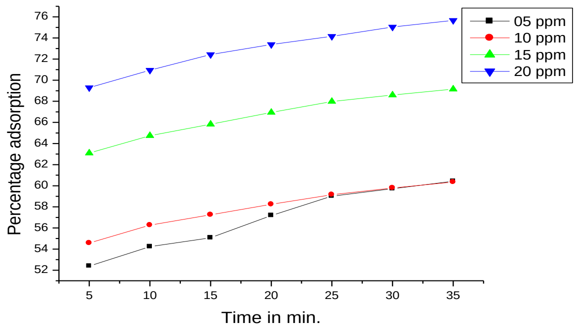

Figure 2. Effect of contact on adsorption f CR on CSH (Adsorbent dose: 1 g/50 mL, pH: 6.17, Temp.: 297.4 K).

The extent of adsorption of CR on husk was found to increase, reach a maximum percentage adsorption value with increase in contact time shown in Fig.2. The CR dye concentration increased from 5 to 20 ppm, the adsorption increased from 60.42 to 75.67%. Higher concentration resulted in higher driving force of the concentration gradient. This driving force accelerates the diffusion of dye from the solution into the adsorbent [16]. It is cleared that the efficiency of CR adsorption depends on the initial concentration of CR dye. The percentage adsorption of CR dye increased with increase in CR dye concentration and remained constant after equilibrium time.

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 on CR dye removal keeping all the experimental conditions constant. The removal of CR by husk at different adsorbent doses from 0.5 gm. to 2.5.gm. for 20 mg/L of CR dye concentration at pH 6.28 was studied. The results are shown in Fig. 3.

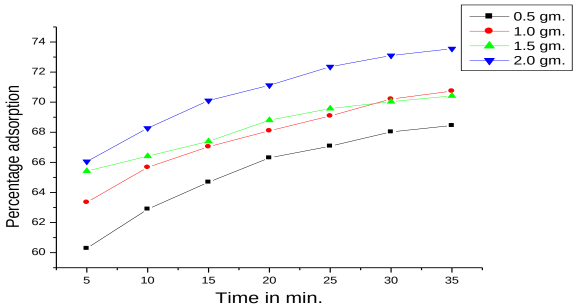

Figure 3. Effect of adsorbent dose on CR adsorption on CSH (CR conc.: 20 mg/L, pH: 6.15, Temp.: 302.2 K).

The effect of adsorbent dose was studied with on CR dye adsorption keeping all the experimental conditions. The adsorption of CR on husk at different adsorbent dose from 0.5 to 2.0 g/50mL for 20 mg/L of CR dye concentration at pH 6.15 was studied. The results (Fig.3) show that the percent adsorption of CR dyes increases with increase in the adsorbent dose due to increase in total number of exchange sites.

Effect of pH

Congo Red is an example of diazo dye, and the initial pH influences the molecular form of Congo Red in the aqueous solution. The effect pH of solution was studied between 2.0 to 11.0 shown in Fig. 4.

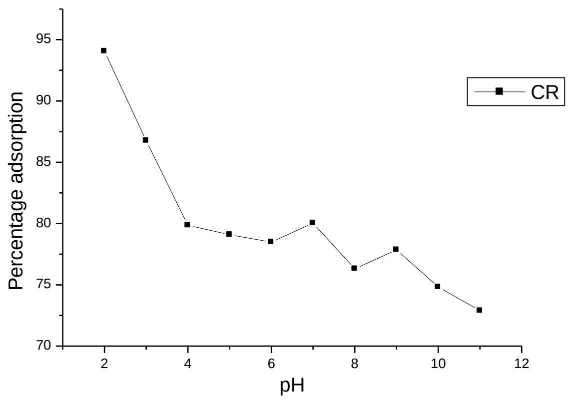

Figure 4. Effect of pH on adsorption of CR on CSH (CR concentration: 20 mg/L, adsorbent dose: 0.5 g/25 mL, contact time: 30 min).

The CR dye solution below pH 2 changed colour from red to dark blue and the original red colour was different above pH 11. Fig. 4 shows that the pH increases from 2 to 11 the percentage removal of CR dye decreases from 99.05 to 72.88%. The maximum CR dye adsorption takes place at pH 2.

Zero-point pH

The pH point of zero charge (pH_{pzc}) of the adsorbent is determined by powder addition method. 0.02g adsorbent was added to 50 mL of conical flask containing 20 mL of CR solution containing 0.1 M NaCl solution. Several batches were carried out for, 2.00 to 11.00 initial solution pH, called pH. The pH was adjusted using 0.1 M HCl and 0.1 M NaCl solution. The electrolyte solution with adsorbent was equilibrated for 24 h. After equilibrium, the final pH, pH_f was recorded. Both positive and negative ΔpH (pH_i - pH_f) values recorded for the adsorbent are plotted against the initial pH values. The pH at which ΔpH becomes zero is called pH_{pzc}. The 6.0 zero-point charge was found in adsorbents used in present work. Cationic adsorption on CSH adsorbent will be favorable at pH > $pH_{pzc.}$ The surface of the adsorbent gets negatively charged and favors uptake of cationic dyes to increased electrostatic force of attraction. Thus, CR adsorption favored at higher pH (pH > 6.0). At lower pH (pH < pH_{pzc}), adsorbent surface is positively charged, concentrations of H^+ were high and they complete with positively charged CR cations for vacant adsorption sites causing a decrease in dye uptake.

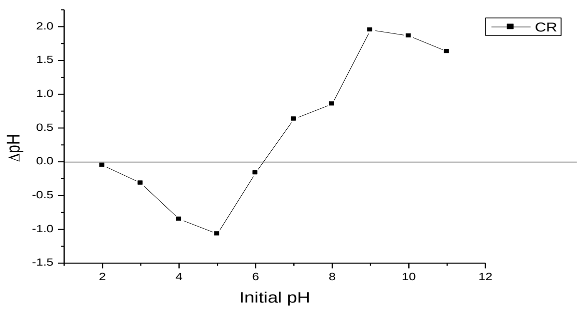

Figure 5. Effect of zero-point pH.

Effect of temperature

Temperature is one of the important parameter affecting separation in most of the processes. In the present work adsorption of CR dye decreased from 74.01 % to 68.66 %, by increasing temperature from 306.4k to 321.4 k. The trend of decrease confirms that process of adsorption of CR dye to be exothermic. It is shown in Fig. 6.

The Gibb's free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes for the adsorption were determined by using equation.

$$\Delta G° = \Delta H° - T\Delta S° \quad (3)$$

$$\log\left(\frac{q_e m}{Ce}\right) = \frac{\Delta S°}{2.303R} + \frac{-\Delta H°}{2.303RT} \quad (4)$$

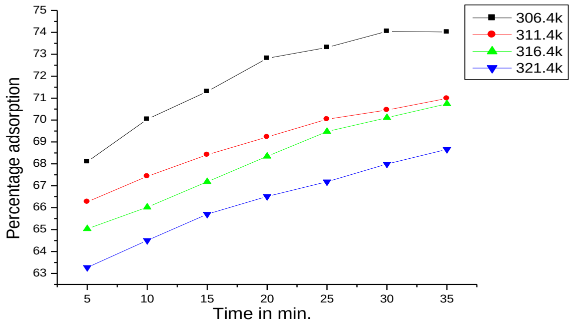

Figure 5. Effect of temperature adsorption of CR on CSH (Initial conc.: 20 mg/L, adsorbent dose: 1g/50 mL, pH: 6.05).

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

$$\log\left(\frac{q_e}{Ce}\right) = \frac{\Delta S°}{2.303R} + \frac{-\Delta H°}{2.303RT} \quad (5)$$

q_e is the amount of CR dye adsorbed per unite mass of husk (mg/g), *Ce* is the equilibrium concentration (mg/L) and T is the temperature in °K. $\frac{q_e}{Ce}$ is called adsorption affinity. The values of ($\Delta G°$) has been calculated by knowing the enthalpy of adsorption ($\Delta H°$) and entropy of adsorption ($\Delta S°$). The enthalpy of adsorption ($\Delta H°$) was obtained from a plot of $\log(\frac{q_e}{Ce})$ versus 1/T. Once these two parameters were obtained, ($\Delta G°$) is determined.

Table 1. Thermodynamic parameter values of CR.

Thermodynamic parameters of Congo Red Dye			
Temp (K)	**(ΔG°) KJ/mol**	**(ΔH°) KJ/mol**	**(ΔS°) J/mol.K**
306.4	-3.570		
311.4	-3.426		
316.4	-3.282	-12.372	-28.729
321.4	-3.139		

The ΔG^0 values obtained in present work for the CR are < -10 KJ /mol, 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 [17, 18], the negative value of ΔH^0 suggests that the adsorption is exothermic [19, 20] and the negative value of ΔS^0 suggests that the decreased disorder and randomness at the solid solution interface with adsorption.

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.

The value of R^2 with first order was 0.964 while for second order R^2 value was 0.999 for husk adsorbent. It is clear that the adsorption of CR on *Vigna unguiculata* seed husk adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second order kinetic model similar phenomenon were observed in the previous work [21, 22].

Adsorption equilibrium

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

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

K_f is the Freundlich constant [mg/g $(L/g)^{1/n}$] related to bonding energy, and n is the heterogeneity factor. The plot of *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 between 2-10 indicates good adsorption.

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

$$\frac{x}{m} = \frac{Q_0 b\ C_e}{1 + bC_e} \quad (11)$$

where, *x/m* is the amount of dye removed per unit mass of adsorbent, C_e is the equilibrium concentration. Plot of $\frac{Ce}{qe}$ versus C_e, gives a straight line. The values of Q_0 and b were determined from graph.

Table 2. Kinetic parameter values of adsorbent with Congo red dye solution.

Dyes	**Pseudo-First order**			**Second order**		
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg. min)	q_e (mg/g)	R^2
CR	$15.080*10^{-3}$	171.791	0.964	$1.791*10^{-3}$	709.220	0.999

Table 3. Langmuir and Freundlich isotherm constants for the adsorption of Congo red dye.

Dyes	**Langmuir constants**				**Freundlich constants**		
	Q_0 (mg/g)	b $*10^{-3}$ (L/g)	R_L	R^2	n	K_f $(mg/g(L/g))^{1/n}$	R^2
CR	714.286	0.600	0.999	0.969	1.010	4.725	0.977

The R_L value was found to be between 0 and 1 for CR studies, it is confirming that the ongoing adsorption of CR is favorable. The data reveal that the Langmuir model yields better fit than the Freundlich model. The value of n is greater than unity, $(1 < n < 10)$, that means favorable adsorption. The value of n was found to be between 1 and 10, this indicates favorable adsorption.

4. CONCLUSION

Adsorption of CR is dependent on pH, initial concentration, adsorption time and contact time. From the result, it was concluded that maximum removal of hazardous CR dye from aqueous solution occurred at pH 2. The percentage adsorption of CR dye on *Vigna unguiculata* seed husk increases with increasing dose of adsorbent, contact time and initial concentration and decreased with increasing temperature. The negative value of confirms that the feasibility of the reaction and spontaneous nature of the adsorption. Negative value of and suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption. The experimental data for the adsorption capacity of CR dye on *Vigna unguiculata* seed husk fits well for the Langmuir adsorption isotherm model than Freundlich isotherm model. The investigation showed that *Vigna unguiculata* seed husk adsorbent was agricultural waste, abundant, cheap, readily available and environment-friendly effective adsorbent, which can be successfully, used for the removal of hazardous Congo Red dye from aqueous solution.

5. REFERENCES AND NOTES

[1] Khedr, M. R.; Halim, K. S. A.; Soliman. N. K. *Mater. Lett*. **2009**, 63, 598. [CrossRef]

[2] Sharma, J.; Janveja, B. *Rasayan J. Chem*. **2008**, *1*, 936.

[3] Jirekar, D, B.; Ghumare, P.; Farooqui, M. *Journal of Industrial Pollution control*, **2015,** *31*, 129.

[4] Jirekar, D, B.; Ghumare, P.; Fatema, S.; Farooqui, M. *Arab. J. Phy Chem*. **2015**, *2*, 79.

[5] Jirekar, D, B.; Farooqui, M. *Arab. J. Phy. Chem*. **2015**, *2*, 1**.**

[6] Jirekar, D, B.; Pathan, A. A.; Farooqui, M. *Orient. J. Chem.* **2014**, *30*, 1.

[7] Jirekar, D, B.; Ghumare, P.; Farooqui, M. *Inter. J. Chem. Tech. Res*. **2015**, *7*, 427.

[8] Kumar, P. S.; Kirthik, K. *J. Engi. Sci. Tech.* **2009**, *4*, 351.

[9] Singh, S.; Kauushik, C. P. *Asian J. chem*. **2008**, *20*, 4994.

[10] Patil, A. K.; Shrivastava, V. S. *Inter. J. Chem. Tech. Res*. **2010**, *2*, 842.

[11] Jirekar, D. B.; Dar, B. A,; Farooqui, M. *J. Environ. Sci. Water Resour.* **2013**, *2*, 226.

[12] Shrivastava, V. S. *Inter. J. Chem. Tech. Res*. **2012**, *4*, 1038.

[13] Mall, I. D.; Srivastava, V. C.; Agarwal, N. K.; Mishra, I. M. *Chemosphere* **2005**, *61*, 492. [CrossRef]

[14] Namasivayam, C.; Kavitha, D. *Dyes Pigm.* **2002**, *54*, 47. [CrossRef]

[15] Jirekar**,** D. B.; Pathan, A. A.; Farooqui, M. *Orient. J. Chem.* **2014**, *30*, 1263. [CrossRef]

[16] Mehment, D.; Ysemin, O.; Viahir, A. *Dyes Pigm.* **2006**, *1*, 1.

[17] Sharma, Y. C.; Kaul, S. N.; Weng, C. H. *Eng. Poll*. **2007**, *150*, 251. [CrossRef]

[18] Vimala, T.; Mary, S. A. P.; Thamizharasan, V.; Arivoli, S. *Ind. J. Env. Prot*. **2007**, *12*, 1090.

[19] Sivkukmar, P.; Palanisamy, P. N. *Rasayan J. Chem.* **2008,** *4*, 872.

[20] Zheng, Z.; Xiong, C.; Yow, C. *Asian J. Chem*. **2010**, *22*, 2003.

[21] Wang, L.; Wang, A. *J. Haz. Mat*. **2008**, *160*, 173. [CrossRef]

[22] Kannan, N.; Sarojini, P. *Ind. Env. Prot*. **2010**, *30*, 404.