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Adsorption of Congo Red Dye from Aqueous solution using Eco-Friendly low cost material prepared from *Cicerarientinum*

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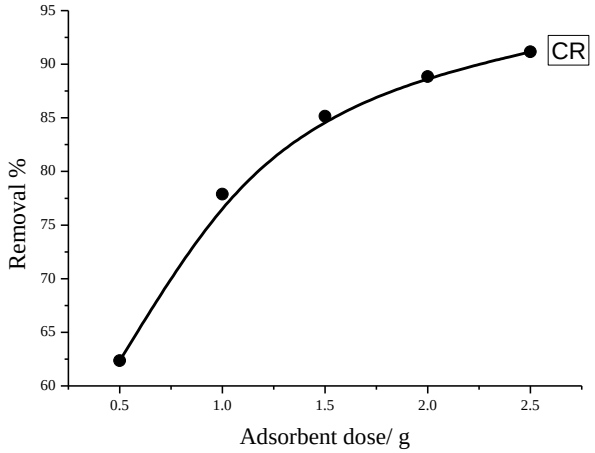
- **Novelty and Highlights:**

1 –Adsorbent was agricultural waste, abundant, cheap, readily available and environment-friendly.
2 –Effective adsorbent, which could be used as potential adsorbent for removal of CR dye from aqueous solution and polluted water.

- **Graphical Abstract:**
- An adsorption study of Congo red dye was carried out on Gram Seed Husk. Higher percentage removal capacity of CR dye on GSH was observed at lower temperature, high adsorbent dose and high initial concentration.



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Abstract: A low cost adsorbent prepared from *Cicerarientinum* crop seeds for the removal of Congo Red dye from aqueous solution has been studied. Experiments in batch technique were carried out to study the removal efficiency of seed husk of *Cicerarientinum* crop towards the adsorption of Congo red dye by stirring it with *Cicerarientinum*crop seed husk powder. Kinetic study of adsorption and equilibrium studies were carried out by varying different parameters like contact time, initial concentration of CongoRedsolution, adsorbent dose, initial pH of Congo Red solution and temperature. An adsorption rate model has been developed. The experimental data have also been studied in light of Langmuir and Freundlich adsorption isotherm. Adsorption equilibrium data fit most satisfactorily to Langmuir adsorption isotherm model.

Keywords: Congo Red Dye; Adsorption; Cicerarientinum crop seeds.

Introduction

Out of all contaminants contained in industrial sewage, dyes are the most undesired ones, as the direct discharge of dye effluents can cause serious problems to the environment due to contribution of high organic loading, toxicity and aesthetic pollution related to colour[1]. Dyes are used in various industries such as paper and plastics, leather, pharmaceutical, food, cosmetics, dyestuffs, textiles, etc. to colour the products. As a result, considerable amount of coloured wastewater is generated. The presence of these dyes in water even at very low concentration is highly visible and undesirable[2]. 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[3]. Congo Red [1-naphthalene sulfonic acid, 3, 30-(4, 40-biphenylenebis (azo)) bis (4-amino-) disodium salt, CR] is a benzidine-based anionic disazo dye, i.e. a dye with two azo groups. It is toxic to many organisms and is a suspected carcinogenic and mutagen. Benzidine, a human carcinogen, and CR, are however, banned in many countries because of health concerns. But, it is still widely used in several countries. Synthetic dyes, such as CR, are difficult to biodegrade due to their complex aromatic structures, which provide them physic-chemical, thermal and optical stability[4]. Therefore, there is an urgent requirement for development of innovative, but low-cost processes, by which dye molecules can be removed. Adsorption technique is quite popular due to simplicity and high efficiency, as well as the availability of a wide range of adsorbents[5, 6].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[7], neem leaves[8], Alternantherabettzichiana plant[9], Rice hull ash[10], subabul seed pods[11], flyash[12], coir pith carbon[13], etc. have been used for the removal of CR dyes from aqueous solutions.

In the present paper *Cicerarientinum*crop seed husk powder was employed for removal of CR and used as an effective adsorbent in the wastewater treatment. The technique was found to be very useful and cost effective for a better removal of dye. This adsorbent showed the highest adsorption capacity of CR compared to many other adsorbents.

Experimental

Preparation of adsorbent The mature and fresh*Cicerarientinum*crop seeds (gram seeds) were purchased from local market and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, the gram 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 gram seed husk (GSH). The dried fine powder adsorbent was kept in an air tight glass bottle ready for further experiments.

*Preparation of adsorbate*Congo Red(CR) (CI: 22120, MW: 696.66 gm.) 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[14] of this dye is shown in **Fig. 1.**

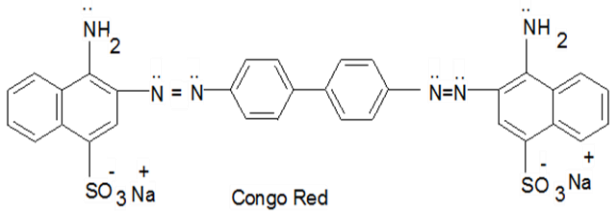

Fig. 1 Chemical structure of Congo red.

*Adsorption experiments*All adsorption experiments were 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 concentrationwith 0.5 gm. adsorbent dose in conical flasks. The effect of contact time and initial concentration were studied by shaking 50 ml 20 mg/L CR solutionsconcentration 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 analysed for residual dye concentration. Adsorbent dose effect was studied using 20 mg/L CR solutionconcentration. The optical density was analysed 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 dye removed per unite weight of husk adsorbent at time 't', q_t(mg/L) and percentage dye removal capacity was calculated as

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

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

Where,$C_0$is the initial dye concentration (mg/L), C_t is the concentration of dye at any time *t*,*V* is the volume of solution (ml) and *M* is the mass of husk (gm).

Results and Discussion

*Effect of contact time:*The time-dependent behaviour of CR 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**.

The removal of CR dye increased with increasing contact time due to large surface area available of the GSH adsorbent. The maximum percentage removal efficiency was 70.46 at 35 min. The mechanism for the removal of CR dye by adsorption may be assumed to involve:

- Migrations of CR dye from bulk of the solution to the surface of the GSH adsorbent.
- Diffusion of CR dyes through the boundary layer to the surface of the GSH adsorbent.
- Intra-particle diffusion of CR dyes into the interior pores of the GSH adsorbent particle.

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 CR dye during adsorption time[15].

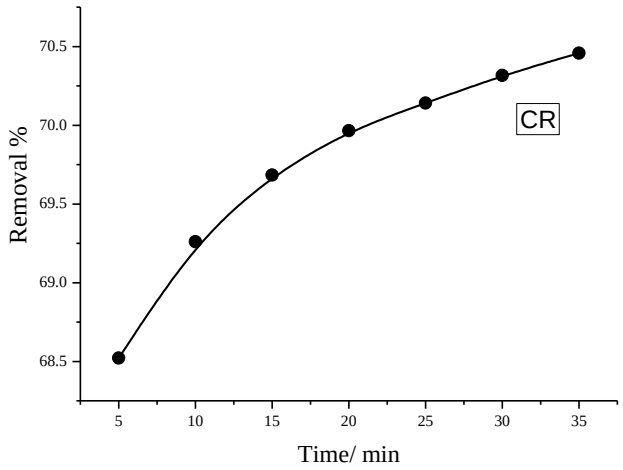

Fig. 2 Effect of contact time on percentage removal of CR, [Initial conc.= 20 mg/L, Adsorbent dose=1.0 g, temp = 298.3 k, pH = 5.87].

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

The results (Fig. 3.) shows that as the adsorbent mass increases from 0.5 to 2.5gm., the percent CR removal increase from 62.36 to 91.16 %. The percent CR removal increase as the adsorbent dose increase due to increase in total number of exchange sites.

*Effect of initial dye concentration*The adsorption studies were investigated at 298.3 K the concentration range of 5, 10, 15 and 20 mg/L. In the present investigation percentage adsorption of CR dye was increases with increase in initial concentration. The maximum percentage removal efficiency was 70.60 at 20 mg/L.CR concentration.The results are shown graphically given in **Fig. 4.**

Effect of pH Congo red is an example of diazo dye, and the initial pH influences the molecular form of CongoRed in the aqueous solution[16]. The effect pH of solution was studied between 2.0 to 11.0 shown in **Fig. 5**. The dye solution below pH 2 changed colour from red to dark blue and the original red colour was different above pH 11.

Fig.5 shows that the pH increases from 2 to 11 the percentage removal of CR dye decreases from 88.20 to 66.12 %. The maximum CR dye removal takes place at pH 2.

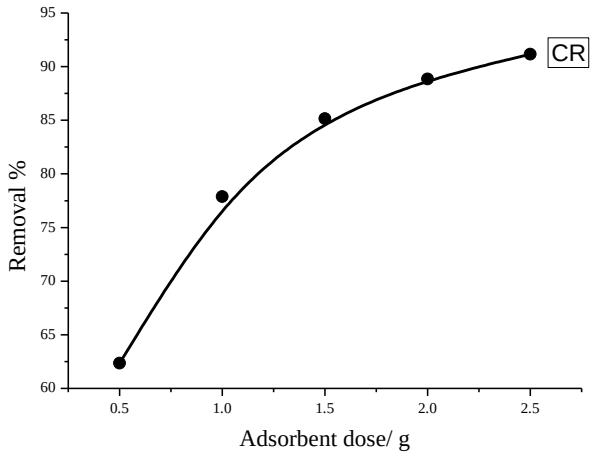

Fig. 3. Effect of adsorbent dose on percentage removal of CR[Initial conc.=20 mg/L, Time of adsorption=24 hrs., Temp=302k,pH=6.28, volume of adsorbate=50 ml].

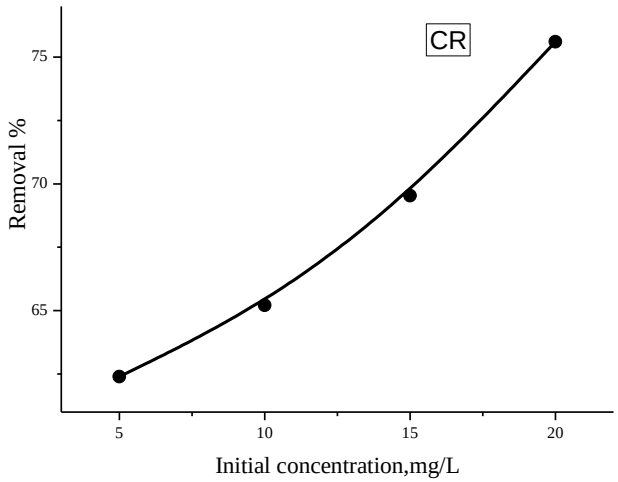

Fig. 4 Effect of initial conc.on percentage removal of CR [Adsorbent dose=1.0gm., Time of adsorption=24 hrs. Temp=298.3k,pH=6.14, volume of adsorbate=50 ml] .

*Effect of temperature*Temperature has a pronounced effect on the adsorption capacity of various adsorbents. The temperature effect was investigated for temperatures ranging from 306.4 to 326.4 K. The results are shown in **Fig.6.**

The maximum percentage CR dye removal decreases with increase in temperature. Since adsorption is an exothermic process. Thus the removal of CR dyes is leading to a decrease in the residual forces on the surface of the GSH adsorbent and hence causing a decrease in the surface energy of the adsorbent[17].

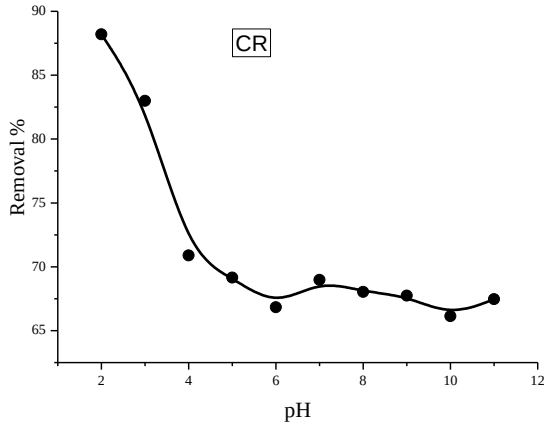

Fig. 5. Effect of pH.on percentage removal of CR [Adsorbent dose=0.5 gm, Initial Conc.=20 mg/L., Temp=301.5k,volume of adsorbate=25 ml.]

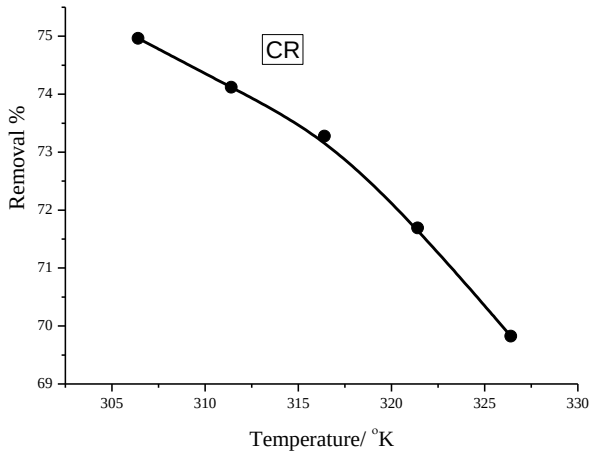

Fig. 6 Effect of temperature on percentage removal of CR [Initial conc.=20 mg/L, Adsorbent dose=1.0 g,volume=50 ml,pH=6.12, time of adsorption=24 hrs.].

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

TheΔG^0 values obtained in this study for the CR 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:1.) indicates that the adsorption is favourable and spontaneous[18, 19].The negative value ofΔS^0 andΔH^0 suggests that the decreased disorder and randomness at the solid solution interface with exothermic adsorption.

Table: 1. Thermodynamic parameter values of GSH adsorbent with CR solution at different temperatures

Temperature(K)	−(ΔG°) KJ/mole	−(ΔH°) KJ/mole	−(ΔS°) J/mole
306.4	2.839	10.587	25.286
311.4	2.713		
316.4	2.586		
321.4	2.460		
326.4	2.334		

Adsorption isotherm: Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence LangmuirandFreundlich 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[20]

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

Where, C_0 is initial concentration in ppm and b is Langmuir constant related to the energy of adsorption. R_LValue indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable[21] 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 (3) 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 [22].

Table: 2. Isotherm parameter values of GSH with CR dye solution.

Conc 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
20	99.009	6.349	0.998	0.996	1.109	3.991	0.997

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[23]. 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. The R_L valuewas found to be between 0 and 1 for CR studies, it is confirm 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* 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[24]. If value of $\frac{1}{n}$> *1* indicates the adsorption is favoured 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 favourable 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,

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

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

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

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 calculateK_1, $q_e$andR^2.

The pseudo-second order equation is developed by Ho can be written as

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

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

The linear form of equation is

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

K_2andq_e can be obtained from the intercept and slope of plotting t/q_t against$t$.

Table: 3. Kinetic parameter values of GSH adsorbent with CR

Conc. of CR (mg/L)	q_e *exp. (mg/gm)*	*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
20	754.58	$4.836*10^{-3}$	176.319	0.945	$4.533*10^{-3}$	625.000	0.999

The value of R^2 with first order kinetics was 0.945, while for second order is 0.999 for GSH adsorbent. It is clear that the adsorption of CR on GSH adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the second order kinetic model.

Conclusion:

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

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