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ADSORPTION OF CONGO RED DYE FROM AQUEOUS SOLUTION USING *LATHYRUS SATIVUS* CROP SEED HUSK

Dattatraya Babasaheb Jirekar
Assistant Professor
AnandraoDhonde Alias Babaji College, Kada. (INDIA)
e-mail Id: dattajirekar1@gmail.com
Contact:9423754837

ABSTRACT:

Adsorption of Congo Red (CR)from aqueous solutions usinglathyrussativus crop (Lakh) seed husk as low-cost adsorbent have been studied as a function of contact time, adsorbent dose, initial concentration, temperature and solution pH. The adsorption capacity increased with increasing contact time, adsorbent dose and initial concentration of CR but decreasing with increase in temperature. The maximum adsorption capacity was 72.15 at 50C, 1gm/50ml adsorbent dose and pH = 6.53. The experimental data were analyzed by Langmuir and Freundlich adsorption isotherms and found that Langmuir adsorption isotherms best fit the experimental data over the whole concentration range with R2 value 0.999. Thermodynamic parameters such as standard Gibb's free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) changes were calculated. Thermodynamic parameters of CR / LSH system indicated spontaneous and exothermic nature of the adsorption process. The adsorption of CR follows pseudo second order rate kinetics. The results investigates that lathyrussativus crop (Lakh) seed husk is effective in the adsorption of CR dye from aqueous solutions and can be used as alternative of high cost commercial adsorbents.

Keywords: Adsorption, Congo Red, lathyrussativus crop, thermodynamic parameters, adsorption isotherms, kinetics.

INTRODUCTION:

Water pollution caused by discharge of wastewater as a result of industrial activities has been considered one of the grave environmental issues in the world, especially in developing countries (YusefOmidiKhaniabadi*et al*. 2017). The discharge of many organic and inorganic pollutants into water media by different industries, as a global environmental problem, has stimulated worldwide attention because of theirharmful effects on the environment and also human health (Enenebeaku K.*et al*.2016.). One of the most important of these pollutants is dye substances.

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics andfood industries. Color stuff discharged from these industries poses certain hazards andenvironmental problems. These colored compounds are not only aesthetically displeasing butalso inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usuallyhave complex aromatic molecular structures which make them more stable and difficult tobiodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause directdestruction or inhibition of their catalytic capabilities. There are more than 100,000commercially available dyes with over 7×10^5 tons of dyestuff are produced annuallyacross the world today(Jourvand M*et al.*2015.).Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes.Most of these dyes represent acute problems to the ecological system as they considered toxicand have carcinogenic properties, which make the water inhibitory to aquatic life. Due to theirchemical structure, dyes possess a high potential to resist fading on exposure to light andwater. The main sources of wastewater generated by the textile industry originate from thewashing and bleaching of natural fibers and from the dyeing and finishing steps. Given the greatvariety of fibers, dyes and process aids, these processes generate wastewater of great chemicalcomplexity and diversity, which are not adequately treated in conventional wastewater treatmentPlant.

Congo red (CR) is an anionic dye widely used in textiles, paper, rubber and plastic industries. The present study is undertaken with a view to assess thefeasibility of abundantly available *lathyrussativus* crop seed husk powder as an adsorbent for the Congo red adsorption. The effects of various parameters such as adsorbent dose, pH, contact time and initial CR concentration on the adsorption process have been studied.

In our day 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 includednano-filtration and ozonalysis (E. Remoudaki*et al*.2003), flocculation (P. K. Baskaran*et al*. 2010.), ultrasound oxidation process (C. B. Chandran*et al*. 2002.), adsorption (Mckay G. 1982.) etc., in which adsorption process is one of the effective techniques that have been successfully employed foradsorption of dye from wastewater. Although, activated carbon adsorption appears to be one of the most widely used techniques for adsorption of dye, but in view of the high cost and regeneration problems, there has been a constant search for alternative low-cost. A number of non-conventional adsorbents such as bale tree leaf powder (P. SenthilKumaret*et al*.2009.),neem leaves (Shenu Singh *et al*.2008.), Alternantherabettzichiana plant (A. K. patil*et al*.2010.),Gram seed husk (Jirekar, D. B.*et al*.2013.), Rice hull ash (Kan-SenChau*et al* 2001.), subabulseed pods (V. S. Shrivastava 2012.), fly ash, (I. D. Mall *et al*. 2005.), Green gram seed husk(Jirekar, D. B. *et al*. 2014.), coir pith carbon (C. Namasivayam*et al*. 2002.), etc. have been used for the adsorption of CR dyes from aqueous solutions.

In the present paper *lathyrussativus*(Grass pea) cropseed husk powder was employed for adsorption of CR 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 adsorption of dye.

MATERIALS AND METHODS:

The mature and fresh *lathyrussativus* cropseeds were purchased from local market and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, the *lathyrussativus* crop seeds were soaked into distilled water up to 24 h. Then their skin was removing from their pulses 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 *lathyrussativus* cropseed husk (LSH). 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.**

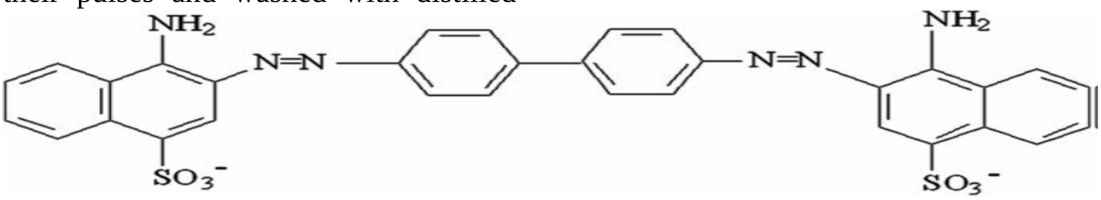

Fig. 1: Structure of Congo red

Adsorption experiment was carried out by batch adsorption techniques at room temperature. The effect of pH on CR adsorption 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 solutions 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 CR concentrations 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 dye adsorbed per unite weight of husk adsorbent at time,'t', q_t(mg/L) and percentage dye adsorption capacity was calculated as

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

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

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 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**.

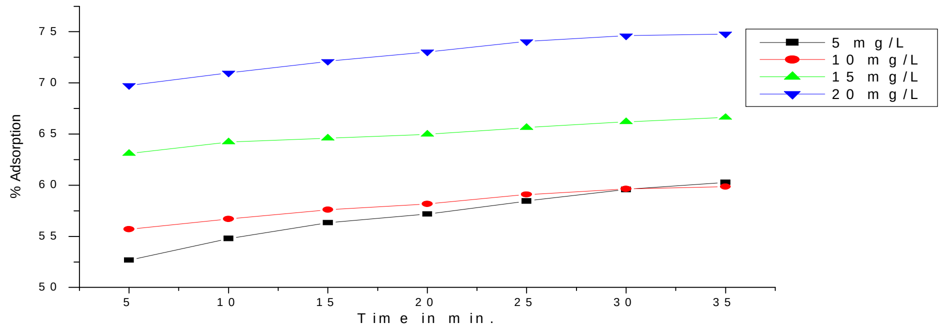

Fig:2. Effect of contact time with various concentrations of CR
[Adsorbent dose=1.0 gm, Temp.=300.5K, pH=6.52]

The extent of adsorption of CR on LSH was found to increase, reach a maximum adsorption value with increase in contact time shown in Fig.2. The CR concentration increased, the adsorption of CR dye increased from 60.28% in 5 mg/L to 74.79% in 20 mg/L solution. 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 (Mehment, D. Ysemin, O. and Viahir, A). It is cleared that the efficiency of CR adsorption depends on the initial CR dye concentration. The adsorption of CR dye increased with increase in CR dye concentration and remains 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 onadsorption of CR dye keeping all the experimental conditions constant. The adsorption of CR by LSH at different adsorbent doses from 0.5 g. to 2.5.g. for 20 mg/L of CR dye concentration at pH 6.52 was studied. The results are shown in **Fig. 3**.

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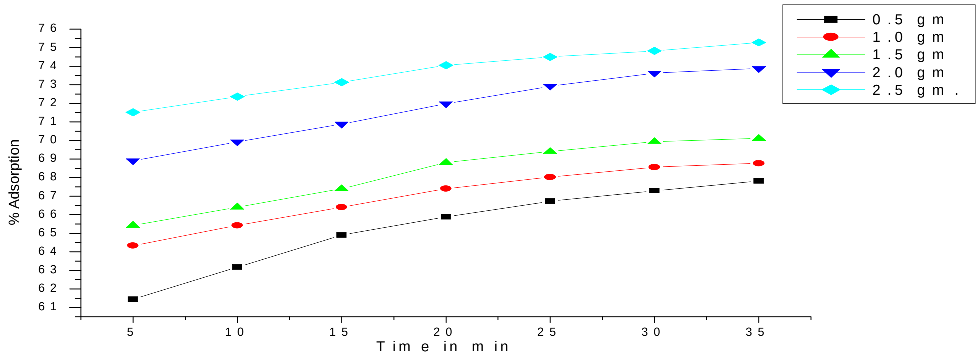

Fig:3. Effect of adsorbent dose with time.
[Initial conc.=20 mg/L., Temp.=300.5 K,pH=6.52]

The results show that the adsorption of CR dyes increases as the adsorbent dose increase 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**.

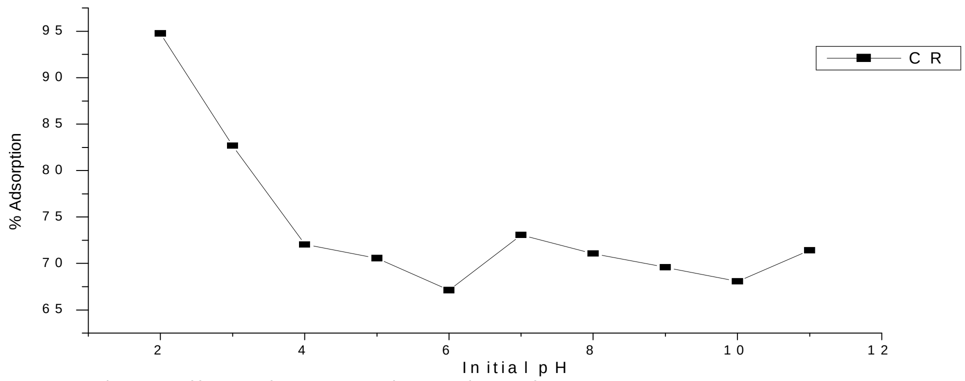

Fig:4. Effect of pH on adsorption of CR
[Adsorbent dose=0.5 gm., Initial conc.=20 mg/L., Iemp.=300.5K]

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 adsorption of CR dye decreases from 94.75 to 71.41 %. The maximum CR dye adsorption takes place at pH 2.

Effect of temperature: Temperature is one of the important parameters affecting separation in most of the processes. In the present work adsorption of CR dye decreased from 72.15 % to 66.16 %, by increasing temperature from 306.4 K to 326.4 K .

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The trend of decrease confirms that process of adsorption of CR dye to be exothermic. It is shown in Fig.7

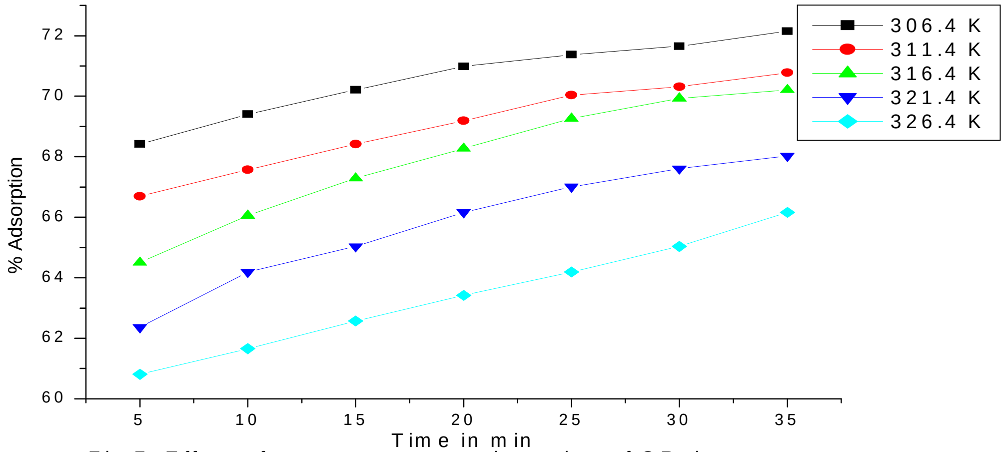

Fig:7. Effect of temperature on adsorption of CR dye.
[Adsorbent dose=1.0 gm, Initial conc.= 20 mg/L, pH=6.53]

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

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

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

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

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

$q_e$isthe amount of dye adsorbed per unite mass of husk (mg/g), $Ce$is the equilibrium concentration (mg/L) and T is the temperature in ^{o}K .$\frac{q_e}{Ce}$is called adsorption affinity. The values of Gibb's free energy ($\Delta\boldsymbol{G}°$) has been calculated by knowing the enthalpy of adsorption ($\Delta\boldsymbol{H}°$) and entropy of adsorption ($\Delta\boldsymbol{G}°$) and ($\Delta\boldsymbol{H}°$) was obtained from a plot of log ($\frac{q_e}{Ce}$)versus 1/T from equation (4) and (5). Once these two parameters were obtained, ($\Delta\boldsymbol{G}°$) is determined from equation (3) (Table:1)

Table: 1. Thermodynamic parameter values of CR.

Thermodynamic parameters of Congo Red Dye		
($\Delta G°$) KJ/mole	***($\Delta H°$) KJ/mole***	***($\Delta S°$) J/mole.K***
-2.977	-10.168	-23.472
-2.859		
-2.742		
-2.625		

The ΔG^0 values obtained in present 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 favorable adsorption process. The negative value of ΔG^0 indicates that the adsorption is favorable and spontaneous (Y. C. Sharma *et al*. 2007; T. Vimala*et al*. 2007). The negative value of ΔH^0 suggests that the adsorption is exothermic (P. Sivkukmar*et al*. 2008). The negative value of ΔS^0suggests 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 andq_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 (2)

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.

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

The plot of $\frac{t}{q_t}$versus t gave a straight line with slope$\frac{1}{q_e}$ and intercepts $\frac{1}{k_{2q_e^2}}$ 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 CR dye on LSH adsorbent.

Dyes	***Pseudo-First order***			***Pseudo Second order***		
	K_1 (min^{-1})	***q_e(mg/g)***	***R^2***	***K_2 (g/mg.min)***	***q_e (mg/g)***	***R^2***
CR	$28.060*10^{-3}$	54.688	0.953	$4.147*10^{-3}$	675.676	0.999

The value of R^2 with first order was 0.953 while for pseudo second order R^2 value was 0.999 for LSH adsorbent. It is clear that the adsorption of CR on LSH adsorbent was better represented by pseudo second order kinetics. This indicates that the adsorption system belongs to the s pseudo second order kinetic model similar phenomenon were observed in the previous work (Li Wang *et al.* 2008;C. Namasivayam*et al.* 1994).

ADSORPTION EQUILIBRIUM:

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

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

$K_f$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 Langmuiradsorption model.

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

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

Table:3. Langmuir and Freundlich isotherm constants for the adsorption of CR 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	526.316	1.111	0.999	0.941	1.004	3.477	0.876

The R_L value was 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* is greater than unity, *(1< n <10)*, that means favorable adsorption.(N. Kannan*et al* 2010). The value of *n* was found to be between 1 and 10, this indicates favorable adsorption.

CONCLUSION:

Adsorption of CR is dependent on pH, initial concentration, adsorption time and contact time. From the result, it was concluded that maximum adsorption of CR from aqueous solutions occurred at pH 2. The percentage adsorption of CR dye on LSH increases with increasing dose of adsorbent, contact time and initial concentration and decreased with increasing temperature. The adsorption of CR on LSH adsorbent was better represented by pseudo second order kinetics than first order. 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. The experimental data for the adsorption of CR dye on LSH fits well for the Langmuir adsorption isotherm model than Freundlich isotherm model. The investigation showed that LSH adsorbent was agricultural waste, abundant, cheap, readily available and environment-friendly effective adsorbent, which can be successfully, used for the adsorption of Congo Red from aqueous solutions.

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