International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.4, No.3, pp 1038-1043, July-Sept 2012

Removal of Congo red dye from aqueous solution by Leucaena leucocephala (Subabul) seed pods

V.S.Shrivastava*

Nano-Chemistry Research Laboratory, G.T.P. College, Nandurbar-425412(M.S.),India.

Corres.author: profvinodshrivastava@gmail.com

Abstract: The kinetics of adsorption of Congo red (acidic dye) on *Leucaena leucocephala* seed pods has been investigated. It has been observed from experiments that adsorbent prepared from seed pods of *Leucaena leucocephala* plant was effective, for the removal of Congo red from aqueous solutions at room temperature. Adsorption of Congo red was dependent on pH, initial concentration, adsorbent dose and contact time. The result indicated that, the adsorption of Congo red was 91 % at the optimum pH of 5. The optimum contact time was 120 minutes and the adsorbent dose was 2 g/l of *Leucaena leucocephala* seed pods.

The Freundlich and Langmuir isotherm equations were applied for the equilibrium adsorption data and the various isotherm parameters were evaluated. The Congo red adsorption on the *Leucaena leucocephala* seed pods follows pseudo second-order rate kinetics.

Key words: Congo red dye ,*Leucaena leucocephala (Subabul)* seed pods.

Introduction

Dyes are widely used in industries such as textiles, paper, paints, leather, rubber, plastics, cosmetics, food, and drug etc, to color their products. Textiles industries consumed more than 60 % dyes of the total world production. It was estimated that 10-20 % of dye was lost during the dyeing process and released as effluent [1]. Due to their chemical structures, dyes are resistant to fading on exposure to light, water and many chemicals and, therefore, are difficult to be decolorized once released into the aquatic environment [2]. Many of the organic dyes are hazardous and may affect 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 [3]. Therefore, it is very important to develop new systems that can be used for removing dyes from waters. Research is being carried out for removal dyes using physicochemical, chemical and biological treatment technologies, such as chemical coagulation–flocculation [4], different type of oxidation processes [5], membrane-based separation processes [6], adsorption [7] for the removal of colored dye from wastewater. Among these advanced treatments, at this moment, adsorption is considered more effective and less expensive then other technologies. Activated carbon is the most used material owing to its adsorption capacity, but it is very expensive and its regeneration is difficult. Research has been directed towards developing more effective and economical solutions, investigating the use of various low cost adsorbents. These materials should be low cost, easily available and disposable without regeneration. The agricultural and plant wastes could be a good way to reduce cost problems.

Materials and Methods

Preparation of Adsorbent

Leucaena leucocephala (Subabul) seeds were separated from the pods. Then the pods were ground to get desired particle size of 100 to 150 µm. It was then soaked 1-2 hours in 0.1N NaOH solution to remove the lignin content. Excess alkalinity was then removed by neutralizing with 0.1 N HCl. The *Leucaena leucocephala* (Subabul) seed pod powder (LLSPP) was again washed several times with distilled water till the wash water became colorless and then oven dried at 50 ^{0}C for 24 hrs.

Preparation of Stock Solution

Congo Red (CR) (Direct Red 28, C.I. 22120, azo dye) supplied by BDH (India) were used as adsorbate without further purification. The stock solution of 1000 mg/L dye were prepared by dissolving the desired amount of Congo red in double distilled water and suitably diluted to required initial concentration. The structure of this dye is shown in Figure 1.

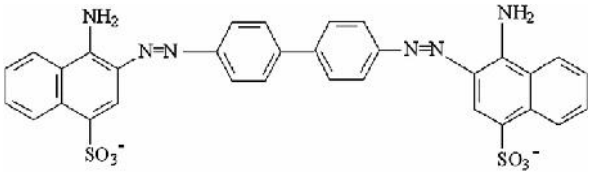

Fig. 1: Structure of Congo red

Adsorption experiments

All adsorption experiments were carried out by batch techniques at room temperature. The effect of pH on CR removal were studied by agitating 50 ml, 10 mg/l dye solution with 2 g/l adsorbent dose in 100 ml conical glass flasks. The effect of contact time and initial concentration were studied by shaking 500 ml 10 and 30 mg/l CR solutions with 1.0 gm adsorbent in a 1000 ml conical flask. After definite time intervals, a sample were withdrawn from the flask, centrifuged and supernatant solution was analyzed for residual dye concentration. Adsorbent dose effect was studied using 20 mg/l CR solution. The optimum pH 5 was used for all batch experiments. The optical density was analyzed using a UV-VIS Spectrophotometer, Systronics model-118 at λ_{max} = 500 nm.

Results and Discussion

Effects 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 [8]. The effect pH of solution was studied between 2 and 11 shown in Fig. 2. The dye solution below pH 2 changed color from red to dark blue and the original red color was different above pH 11. It was observed that as the pH increases from 2 to 5 the percent removal increases from 23 to 91.5 % and farther increase in pH from 5 to 11 the percent removal decrease from 91.5 to 29 %. The maximum color removal takes place at pH 5.

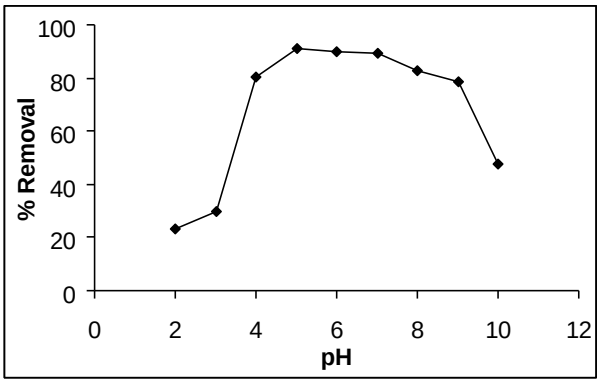

Fig.2: Effect of pH on adsorption of Congo red on LLSP
(CR conc.: 10 mg/l, Adsorbent: 2 g/l, agitation time: 120 min)

Effect of Contact Time

The effect of contact time on the amount of CR adsorbed was investigated using 10 and 30 mg/l initial concentration of CR with 2 g/l LLSPP at pH 5. The extent of removal of CR by LLSP was found to increase, reach a maximum value with increase in contact time shown in Fig. 3. The equilibrium time was found to be 120 minutes. It was observed that with increasing initial dye concentration from 10 to 30 mg/l, the amount of dye adsorbed per unit mass of adsorbent increases from 4.55 to 10.8 mg/g. Higher concentration resulted in higher driving force of the concentration gradient. This driving force accelerated the diffusion of dye from the solution into the adsorbent [9].It is cleared that the efficiency of dye removal depends on the initial dye concentration. The amount of dye adsorbed increased with increase in dye concentration and remained constant after equilibrium time.

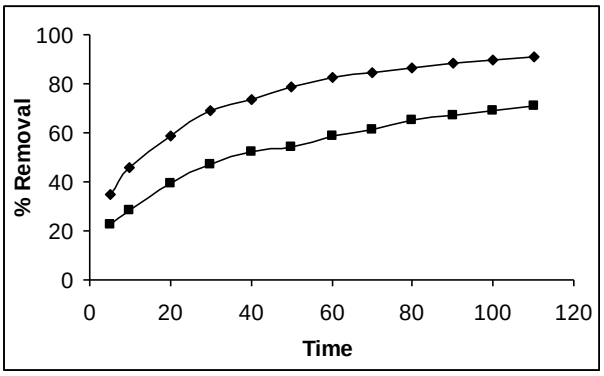

Fig. 3: Effect of contact time on adsorption of Congo red by LLSP
(Congo red concentration: 10 and 30 mg/l, adsorbent: 2 g/l, pH: 5)

Effect of Adsorbent Dose

Adsorbent dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of adsorbet. The effect of adsorbent dose was studied with on dye removal keeping all the experimental conditions constant. The removal of CR by LLSP at different adsorbent doses from 2 to 10 gm/l for 20 mg/l of dye concentration at pH 5 was studied. The results (Fig. 4) show that as the adsorbent mass increases from 2 to 10 gm/l, the percent CR removal increase from 52.5 to 94.75%, but the amount adsorbed per unit mass of adsorbent decrease from 5.25 to 1.89 mg/g. The percent CR removal increase as the adsorbent dose increase due to increase in total number of exchange sites. The decrease in unit adsorption with increase in the dose of adsorbent is basically due to adsorption sites remaining unsaturated during adsorption process [10].

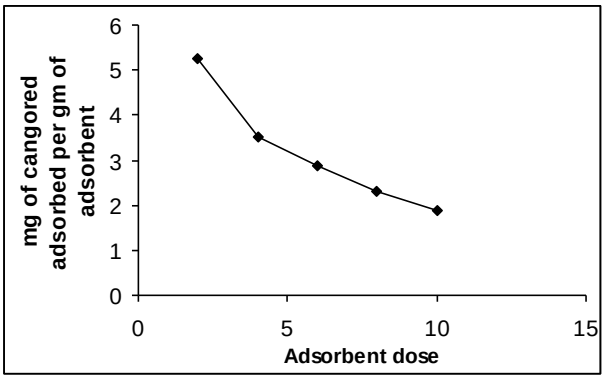

Fig. 4: Effect of adsorbent dose on Congo red adsorption by LLSP
(Congo red concentration: 20 mg/l, pH: 5, agitation time: 60 min)

Isotherm Models

Adsorptions isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence, Langmuir, and Freundlich isotherms were selected in this study.

Langmuir isotherm

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent [11].

$Ce / qe = 1/ b V_m + Ce / V_m$ (1)

Where qe is the amount of CR adsorbed per unit mass of adsorbent (mg/g) and Ce is the equilibrium concentration of CR (mg/l). The linear plot of Ce/q_e *Vs Ce* shows that adsorption follows Langmuir isotherm (Fig.5). The values V_m and *b* were calculated from slopes and intercepts of the linear plot and presented in table 1. The applicability of the Langmuir isotherm suggests monolayer coverage of the dye on the surface of LLSP.

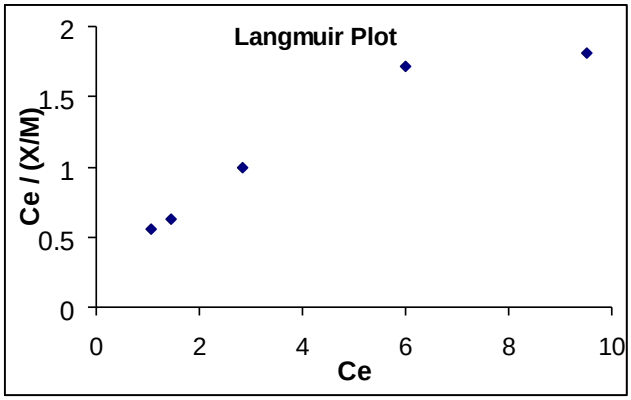

Fig. 5: Langmuir adsorption isotherm of Congo red adsorption by LLSP
(Congo red concentration: 20 mg/l, pH: 5, agitation time: 60 min)

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L that is defined by the equation-2.

$R_L = 1 / (1+ b Co)$ (2)

Where, Co is initial dye concentration (mg/l). R_L value obtain for 20 mg/l CR concentration are 0.4139. R_L values between 0 & 1 confirming that the adsorption isotherm is favorable.

Freundlich equation

Log qe = Log K + 1/n Log Ce *(3)*

Where *log K* is a measure of the adsorption capacity and n is an indicator of adsorption intensity. The linear form of the Freundlich [13] model represented by equation-3. The value *1/n* and *K* were calculated from slope and intercept of plot *ln* q_e versus *ln Ce*, respectively (Fig 6) and are given in table 1. The value Freundlich coefficient, *1/n* is 0.3, which is in the range of 0 to 1 indicates favorable adsorption.

Table 1. Langmuir and Freundlich constants

CR Concentration mg/l	Freundlich Constants			Langmuir Constants		
	K	*1/n*	R^2	V_m (mg/g)	*b* (l/mg)	R^2
20	2.042	0.3	0.9562	4.4131	0.0708	0.9670

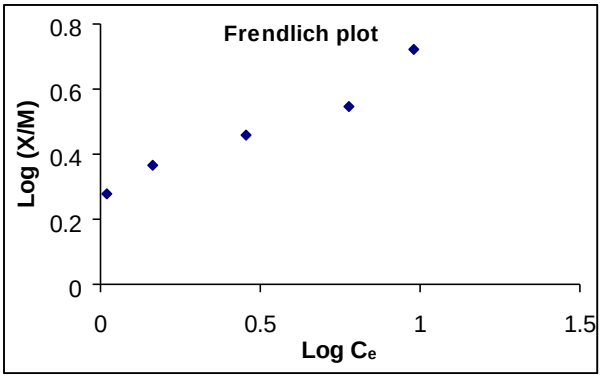

Fig. 6: Freundlich adsorption isotherm of Congo red adsorption by LLSP
(Congo red concentration: 20 mg/l, pH: 5, agitation time: 60 min)

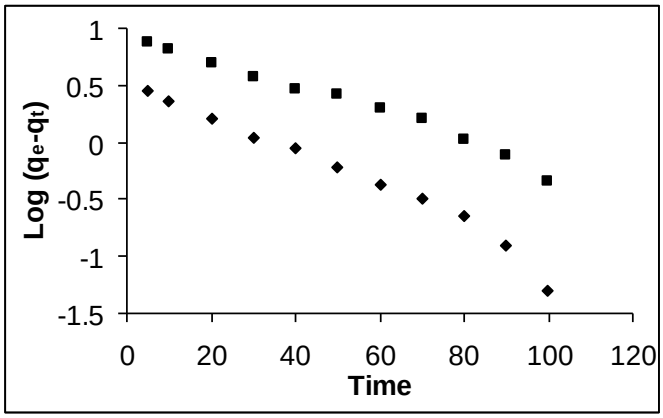

Fig. 7: Lagergren plots for the adsorption of Congo red on LLSP
(Adsorbent: 2 g/l, pH: 5)

The Langmuir, and Freundlich coefficients (R^2) are shown in table 1, both the isotherms were found to be fit well to the experimental data. The Langmuir isotherm is slightly better than Freundlich isotherm as indicated by higher R^2 value.

Adsorption Kinetics

In order to investigate the adsorption processes of CR on the LLSP adsorbent, the pseudo-first order and pseudo second- order kinetic models [14] were experimented.

Pseudo First-order Model

The pseudo-first-order kinetic model of Lagergren [15] is given by equation-4.

$$ln\ (qe - qt) = ln\ qe - K_1\ t \qquad (4)$$

Where qe and qt are the amount of CR adsorbed at equilibrium and at time t (mg g-1), respectively, and k1 is the first-order rate constant (min-1). The slopes and intercepts of plots of $ln\ (q_e - q_t)$ versus t (Fig. 7) were used to determine the pseudo-first-order rate constant K_1 and q_e. The adsorption rate constant K_1 and q_e along with correlation coefficients for the pseudo-first-order model are shown in table 2. The experimental q_e values do not agree with the calculated ones, obtained from the linear plots. The correlation coefficients (R^2) for the Lagergren equation are not very high. This shows that the adsorption of CR onto LLSP is not a pseudo first-order kinetic.

Pseudo Second order Model

The pseudo second-order kinetic model is given by equation-5.

$$t / q_t = 1 / K_2 q_e^2 + t / q_e \qquad (5)$$

Where K_2 (g/mg min) is the rates constant of second-order adsorption.

The slope and intercept of the plots t / q_t versus t are used to calculate q_e and K_2. The adsorption rate constant K_2 and q_e along with correlation coefficients for the pseudo-second-order model are shown in table 2. The linear plots of the pseudo-second-order kinetic model are shown in Fig. 8. The correlation coefficients for the second-order kinetic model are greater than 0.9922. The value of the equilibrium adsorption capacity is found to be 11 mg/g, which is close to the value of the experimental adsorption capacity (10.8 mg/g) for an initial dye concentration of 30 mg/l, confirming a very good agreement with experimental data. This shows that the adsorption process of CR onto LLSP is a pseudo second-order nature.

Table 2. Kinetic model values for adsorption of CR onto LLSP

Congo red Concentration mg/l	$q_{e,exp}$ (mg/g)	Pseudo first-order Order			Pseudo second order		
		$q_{e,cal}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg·min)	R^2
10	4.55	3.055	3.20×10^{-2}	0.9730	5.2	1.275×10^{-2}	0.9983
30	10.8	8.035	2.60×10^{-2}	0.9541	11	0.635×10^{-2}	0.9922

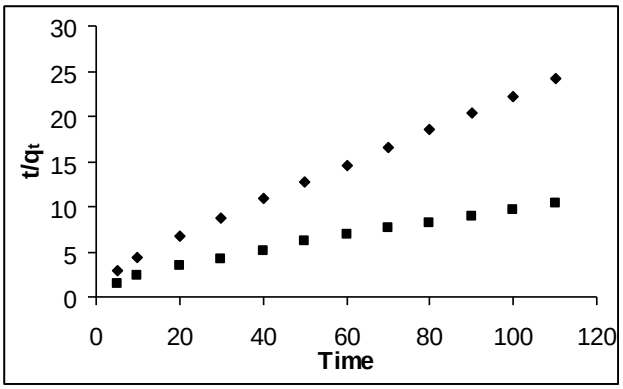

Fig. 8: Pseudo second-order adsorption of Congo red on LLSP
(Congo red concentration: 10 and 30 mg/l, adsorbent: 2 g/l, pH: 5)

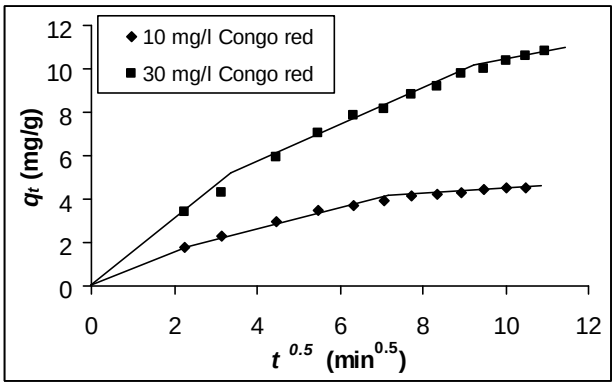

Fig. 9: Pseudo second-order plots for adsorption of Congo red.

Intra-particle diffusion:

The amount of CR adsorbed at equilibrium qt (mg/g) against $t^{0.5}$ is shown in figure-9. The intra-particle diffusion rate constant calculated from the slope of the linear portion of curves. The diffusion rate parameters K_{id1}, K_{id2} and K_{id3} as obtained were shown in table-3. Previous studies showed that such plots may present a multi-linearity, which characterizes the two or more steps involved in the adsorption process.

Adsorbent Characterization

SEM Analysis

The SEM (Scanning Electron Microscopy) micrograph of LLSP dyed by CR was visualized in figure-10. The LLSP surface shows the porosity and rough surface of the adsorbent. After CR adsorption significant change is observed in the structure of adsorbent.

Table 3. Intra-particle diffusion rate parameters for adsorption of CR

Congo red Concentration mg/l	Rate constants, intraparticle rate parameter (mg/g·$min^{0.5}$)		
	K_{id1}	K_{id2}	K_{id3}
10	1.842	1.2281	0.4276
30	3.5984	2.5908	1.3629

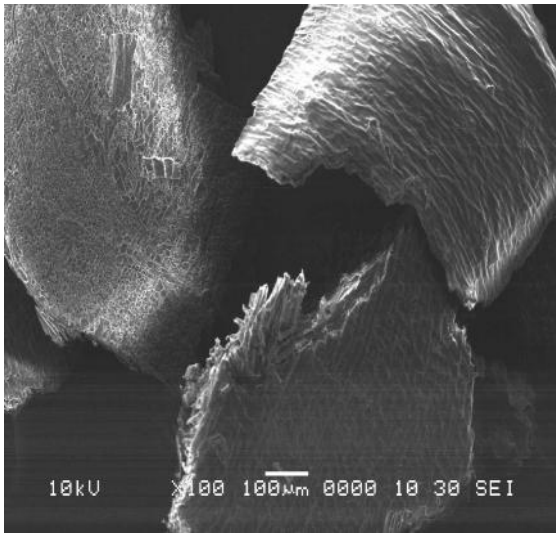

Fig. 11: SEM photograph of LLSP after adsorption.

References

1] Zhiqiao, H. Shuang, S. Huamin, Z. Haiping, Y. and Jianmeng, C., C.I.Reactive Black 5 decolorization by combined sonolysis and ozonation., Ultrasonics Sonachem., 14 (3), 298-304 (2007)..

2. Sharma, J. and Janveja, B., A study on removal of congo red dye from the effluents of textile industry using rice husk carbon activated by steam, Rasayan J. Chem., 1(4), 936-942, (2008).

3. Pavan, F. A. Dias, S. L.P. Lima, E. C. Benvenutti, E.V., Removal of Congo red from aqueous solution by anilinepropylsilica xerogel, Dyes and Pigments, 76, 64-69(2008).

4. Neelmegani, R. Baskaran, V. Dhancekar, R. and Viruthgiri, T., Decolorisation of synthetic dyes using rise straw attached pleurotus oslereths, Indian J. Chem. Techo., 11, 622-625 (2004)

6. Purkait, M.K. DasGupta, S. De, S., Micellar enhanced ultrafiltration of eosin dye using hexadecyl pyridinium chloride, J. Hazard. Mater., B 136, 972–977 (2006).

7. Purkait, M.K.. Maiti, A DasGupta, S. and De, S., Removal of congo red using activated carbon and its regeneration, J. Hazard. Mater., 145, 287–295 (2007).

8. Lian, L. Guo, L. and Guo, C., Adsorption of Congo red from aqueous solutions onto Ca-bentonite, Journal of Hazardous Materials, 161, 126–131 (2009).

9. Ozocar, M. and Sengil, A. I., Adsorption of metal complex dyes from aqueus solutions by pine sawdust. Bioresource Technology, 96, 791-795 (2005).

10. Mehment, D. Ysemin, O. and Viahir, A., Adsorption kinetics and mechanisum of cationic methyl violet and methylene blue dyes onto sepiolite, Dyes and Pigments, 1, 1-13 (2006).

11. Bouberka, Z. Khenifi, A. Benderdouche, N. Derriche, Z., Removal of Supranol Yellow 4GL by adsorption onto Cr-intercalated montmorillonite, J. Hazard. Mater., 133, 154–161 (2006).

12. Langmuir, I., The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc., 38, 2221–2295 (1916).

13. Freundlich, H., Uber die adsorption in losungen, Zeitschrift fur Physikalische Chemie, 57, 385-471 (1906).

14. DeoMall, I, Srivastava, VC, Agarwal NK. and Mishra IM., Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, Chemosphere, 61, 492-501 (2005).

*****