

Adsorption of Congo Red Dye from Aqueous Solutions using Neem Leaves as Adsorbent

SHIV PRATAP RAGHUVANSHI*, RENU SINGH† and C.P. KAUSHIK‡

Centre for Energy Studies, Indian Institute of Technology

Hauz Khas, New Delhi-110 016, India

Fax: (91)(11)26581119; E-mail: spraghuvanshi@yahoo.com

A low cost adsorbent prepared from neem leaves for the removal of congo red dye from aqueous solution has been studied. Experiments in batch reactor were carried out to study the removal efficiency of neem leaves towards the adsorption of congo red dye (adsorbate) by stirring it with neem leaves powder (adsorbent). Kinetics study of adsorption and equilibrium studies were carried out by varying different parameters like size of the adsorbent particles, initial concentration of dye and the adsorbent dosage. An adsorption rate model has been developed. The experimental data have also been studied in light of Langmuir and Freundlich. Adsorption equilibrium data fit most satisfactorily to Langmuir adsorption isotherm.

Key Words: Adsorption, Neem leaves, Congo red dye, Adsorbent, Langmuir isotherm.

INTRODUCTION

Discharge of effluents, bearing dyes, surfactants, salts and heavy metals, *etc.* from industries like paints, textile, carpet, wool, paper and pulp mills, tanneries, electroplating, food beverages and printing, *etc.* not only contaminate ground water and surface water but also impart toxicity and non-visibility, recent estimates indicate that *ca.* 12 % of synthetic dyes used each year are lost during manufacture and processing operations and that 30-35 % of these input dyes enters the environment through effluents that results from the treatment of residual industrial water¹.

In dyeing industry over, 30-60 litres of water is consumed per kg of cloth dyed and large quantities of effluent are released during the process². Presently there are over 450 mills with installed capacity of 20.2 MT with average size of 2150TPD with some units of 10000TPD and few of 5000 TPD³. Nearly 10-15 % of the synthetic textile dyes, used yearly are lost to

†Environment Sciences Division, IARI Pusa, New Delhi-110 011, India.

‡Department of Environmental Sciences & Engineering, Guru Jambheshwar University, Hissar-125 001, India.

waste streams and about 20 % of these loses enter the environment through untreated or ill-treated effluent from inefficient treatment plants³. Dyes are almost invariably a visible pollutant, so their removal from effluents, to be added to fresh water bodies, is ecologically essential. Congo red dye is used in textile industries and may cause cancer⁴.

Low cost biodegradable adsorbent have received considerable attention for colour removal from wastewaters as it offers the most economical and effective removals option. Low cost adsorbents like bagasse³, sawdust^{5,6}, rice husk⁷, coconut coir, banana pith⁸, used tea leaves and cowdung⁹ have been found to be highly effective, cheap and biologically safe adsorbents. Activated carbon is the most widely used adsorbent for removal of organic contaminants, which are biologically resistant. But activated carbon is expensive and also has problems associated with regeneration, which has necessitated the search for alternate low cost biodegradable and efficient adsorbents.

In present study, neem leaves were considered for the treatment of aqueous solution because of two significant reasons, firstly, neem tree (botanical name: *Azadirachta indica*) is globally available and thus the adsorbent can be prepared and used wherever the problem exists and secondly neem trees leaves contains volatile components for instance, azadirachtin, *etc.*, which are highly beneficial due to their properties like antibacterial, antifungal, antimalarial, antiviral, antiallergic, antidermatic, antiinflammatory, insecticidal and nematocidal in nature¹⁰. Further other useful properties of its derivatives are beneficial for water bodies in which, treated water is added.

The objective of this research communication is to present the feasibility and effectiveness of dried neem leaves for the adsorption study of congo red dye in aqueous solutions. Kinetics of adsorption has also been studied to explore the equilibrium as well as the rate of adsorption of congo red dye on neem leaves adsorbent.

Model study and assumptions:

In the present study a simple external mass transfer model for analysis of adsorption rate was considered for the removal of congo red dye in a finite batch process of suspended adsorbent in aqueous solution. Following assumptions for the study have been considered: (1) Adsorbent particles are spherical and identical, both in their physical and chemical properties. (2) The liquid phase is thoroughly mixed up so that bulk liquid-phase concentration is uniform at any instant of time. (3) The rate of disappearance of adsorbate from the solution is equal to the total rate of adsorption from the liquid phase to the outer surface of the particle. Consequently, the solid phase average concentration will rise with the progress of time.

Hence the mass balance is:

$$\frac{d(VC)}{dt} = -k_f A_s (C - C_s) \quad (1)$$

The initial condition is at $t = 0$, $C = C_0$

For spherical particles introducing

$$A_s = \frac{6m_s}{d_p \rho_p} \quad (2)$$

Now, eqn. 1 can be expressed as

$$\frac{dC}{dt} = -\frac{6k_f m_s}{d_p \rho_p V} (C - C_s) = k_a (C - C_s) \quad (3)$$

where,

$$k_a = \frac{6k_f m_s}{d_p \rho_p V} \quad (4)$$

Let us assume $f = (C_0 - C)/C_0$ = the fractional removal from the bulk solution at any time (t) and $f_s = (C_0 - C_s)/C_0$, eqn. 3 may be expressed as

$$\frac{df}{dt} = k_a (f_s - f) = k_a \left(\frac{C - C_s}{C_0} \right) \quad (5)$$

k_a can be determined from the slope $\frac{df}{dt}$ at $t = 0$ of the f vs. t curve.

EXPERIMENTAL

Dried and shed off neem leaves were collected from the neem trees available in abundance from the university campus. These were washed well with distilled water thoroughly for the removal of dirt and dust particles and were dried in sunlight. Further, it was grinded and sieved through standard sieve (Sonar GSMS, Mumbai) to obtain particle size of less than 0.33 mm. Grinded material was washed well with distilled water several times to remove the excess colour and was soaked in formaldehyde. Lastly it was dried in oven maintained at temperature range of 120-140 °C for a period of 4 h. This grinded and treated material was used as adsorbent of neem leaves throughout the study.

The purpose of formaldehyde treatment is to make an external layer around the adsorbent particles so that adsorbent does not leave its colour to the treating aqueous solutions. Some other treating agents like hot alkali impregnation, treatment with ferric nitrate, ammonium hydroxide can also be used for immobilization of the adsorbents of biological origin⁹.

Adsorbate (congo red dye): The solution of congo red dye of desired concentration was prepared by dissolving AR grade congo red dye (SD Fine Chemical Ltd., Mumbai) in normal tap water.

The concentration of congo red in water was analyzed spectrophotometrically by Elico, SL-150 (UV-Vis) spectrophotometer at wavelength of 500 nm. Spectrophotometer measured absorbance upto an accuracy of ± 0.001 units. The wavelength of instrument ranged between 200-800 nm. Spectrophotometer was calibrated using a scan of KMnO_4 solution. An electrically operated stirring system equipped with glass vessel holders was used for the kinetic and equilibrium study in the batch process.

All glass vessels were washed well with dilute nitric acid (1:15) followed by several portions of distilled water¹¹. All the experiments were carried out in triplicate and the results were reproducible with in $\pm 3\%$ error limit. The effects of various parameters on the rate of adsorption of congo red were observed *i.e.*, varying particle size of adsorbent (0.125, 0.250 and 0.300 mm), adsorbent dose (0.25, 0.50 and 0.75 g) and the initial concentration of congo red dye (50-150 mg/L).

The dye solutions of varying concentrations with adsorbents at desired proportions were taken in 250 mL stoppered flask and stirred for a period of 4 h on the electronic shaker. The temperature was maintained constant (25 °C) with a variation of ± 1 °C.

RESULTS AND DISCUSSION

Physical properties of the adsorbent prepared from neem leaves are presented in Table-1 and were determined by standard procedures^{11,12}.

TABLE-1
CHARACTERIZATION OF DRIED NEEM LEAVES ADSORBENT

| Parameters | Characteristic values |
|----------------------------------|-----------------------|
| pH | 5.62 |
| Moisture (%) | 9.38 |
| Bulk density (g/cm^3) | 0.39 |
| Matter soluble in water (%) | 1.50 |
| Matter soluble in acid (%) | 3.42 |
| Iodine number | 69.00 |
| Ion exchange capacity (meq/g) | 1.02 |

Adsorption rate study: The adsorption rate parameter (k_a) was determined for each individual kinetic study by evaluating the slope at $t = 0$ from the C versus t curve. k_f was then extracted from eqn. 4. The differential eqns. 3 and 5 have been solved numerically using fourth order Runge Kutta method with the aid of these parameters. Experimental values for all the cases have been presented in Figs. 1-3. From Figs. 1-3, it is clear that the experimental results fit satisfactorily within the simulated predictions. (*i.e.*,

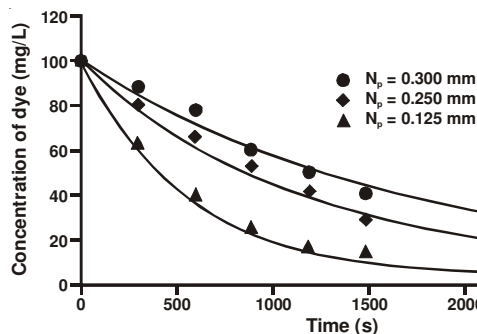


Fig. 1. Effect of particle size of adsorbent on congo red dye adsorption ($M_{\text{neem leaves}} = 0.5 \text{ g}$, $V = 0.2 \text{ L}$)

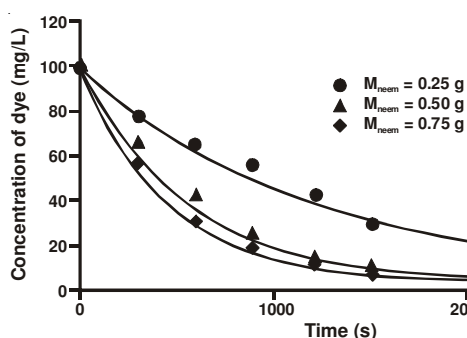


Fig. 2. Effect of adsorbent dose on congo red dye adsorption ($N_p = 0.125 \text{ mm}$, $V = 0.2 \text{ L}$)

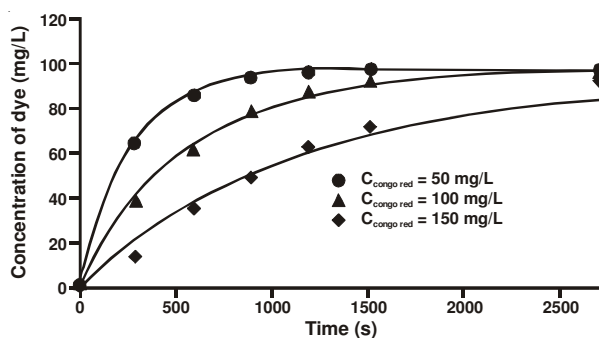


Fig. 3. Effect of initial concentration of congo red dye on adsorption ($N_p = 0.125 \text{ mm}$, $V = 0.2 \text{ L}$)

correlation coefficient varies in the range of 0.9561-0.9777). It can be therefore, concluded that proposed model holds good for whole ranges of parameters (*i.e.*, particle size, mass of adsorbent, initial concentration of adsorbate) studied. The lines in the plotted graphs represent the theoretical values of the adsorbed dye concentration, while the points in the plots indicate for the experimental values for the dye concentration.

Effect of particle size (N_p) on rate of adsorption: Dye concentration removal curves for adsorption of congo red obtained for three different particle sizes are presented in Fig. 1. It is evident from the curve that particle size greatly influences the rate of adsorption. At a certain moment of time the fractional removal of dye is low for larger particles. This is probably due to fact that the effect of adsorption and intra-particle diffusion taking place simultaneously with dominance of adsorption. The internal diffusion to mass transfer increases with increase in particle size⁵.

Satisfactory result of 97 % removal has been achieved with smallest particle size ($d_p = 0.125$ mm). Thus, using the particles of this size, the effect of intra-particle diffusion on the adsorption can be neglected.

Effect of adsorbent dose ($M_{\text{neem leaves}}$) on rate of adsorption: The effect of adsorbent dose on the rate of adsorption of dye is presented in Fig. 2. It is observed that the rate of removal of dye increases with the increase in adsorbent dosage. This may be due to the fact that an adsorption is a surface phenomenon, the surface area of contact between adsorbent and adsorbate increases with the increase in adsorbent dosage.

Effect of initial dye concentration ($C_{\text{congo red}}$) on rate of adsorption: Results of the effect of initial concentration of congo red dye on the rate of adsorption are plotted in Fig. 3, considering dye adsorption as a function of time. From Fig. 3, it can be observed that lower concentration of dye solution favours the colour removal rate and so the adsorption rate is also higher. Adsorption of the total amount of dye increase with an increase in dye concentration in solution, it shows that removal of dye is dependent upon the concentration of dye solution.

Equilibrium study: Equilibrium study for adsorption of congo red on neem leaves was carried out at 30 °C. The equilibrium data were fitted to various adsorption isotherms. The values of the parameters obtained by non-linear method of analysis for two different models (Langmuir and Freundlich) are given in Table-2. The results indicate that experimental data are fitted most satisfactorily to the Langmuir adsorption isotherm.

TABLE-2
RESULTS OF THE ANALYSIS OF DIFFERENT
ADSORPTION ISOTHERMS

| Isotherms | Values of constants |
|--|------------------------|
| Freundlich $q_e = K_c C_e^n$ | $K_c = 0.0656$ |
| | $n = 0.0656$ |
| | $\sigma = 0.3451$ |
| | $\varepsilon = 7.7504$ |
| Langmuir $q_e = \frac{K_L q^0 C_e}{1 + K_L C_e}$ | $K_L = 0.12724$ |
| | $q^0 = 67.84$ |
| | $\sigma = 0.9969$ |
| | $\varepsilon = 0.6424$ |

Conclusion

The adsorbent prepared from neem leaves can be successfully employed for the removal of congo red. Adsorption equilibrium studies show that the experimental data fits well in Langmuir equations that holds good for the representation of adsorption isotherm. It indicates a monomolecular layer type adsorption on the solid surface. Higher removal of adsorbate has been observed with smaller adsorbent particles and higher adsorbent dosage.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. Anubha Kaushik, Chairperson, Department of Environmental Sciences and Engineering, Guru Jambhaeshwar University, Hissar for providing laboratory facility and necessary research and financial support. The authors are also thankful to Dr. V.K. Garg, Reader, Department of Environmental Sciences and Engineering, Guru Jambhaeshwar University, Hissar for his guidance and support.

REFERENCES

1. S.P. Raghuvanshi, R. Singh, C.P. Kaushik and A.K. Raghav, *Int. J. Environ. Stud.*, **62**, 329 (2005).
2. S. Rajeshwari, C. Namasivayam and K. Kadirvelu, *Waste Manag.*, **21**, 105 (2001).
3. S.P. Raghuvanshi, R. Singh and C.P. Kaushik, *Appl. Ecol. Environ. Res.*, **2**, 35 (2004).
4. <http://www.chemexper.com/chemicals/supplier/cas/573-58-0.html>
5. R.P. Singh, Y. Singh, N. Gupta, A. Gautam, A. Singh, R. Suman and R.R. Kulshrestha, Proc. X National Symposium on Environment, Bhabha Atomic Research Centre, Mumbai, India pp. 143-147 (2001).
6. S.P. Raghuvanshi, R. Singh, C.P. Kaushik, A.K. Raghav and A. Chandra, Proceedings of International Conference for Water and Wastewater: Perspectives in Developing Countries (WAPDEC), International Water Association, UK, pp. 1053-1062 (2002).
7. N. Deo and M. Ali, *Indian J. Environ. Prot.*, **13**, 496 (1993).
8. C. Namasivayam and K. Kadirvelu, *Bioresource Technol.*, **62**, 123 (1997).
9. S.P. Raghuvanshi. M. Tech Thesis, Guru Jambhaeshwar University, Hissar, Haryana, India (2000).
10. <http://www.maxpages.com/neemuses/>
11. American Public Health Association (APHA), Standard Methods for Examination of Water and Wastewater, Water Pollution Control Federation, Washington, DC, edn. 19 (1995).
12. A.I. Vogel, A Text Book of Quantative Inorganic Analysis, ELBS, London, edn. 3 (1969).

(Received: 31 January 2007;

Accepted: 1 April 2008)

AJC-6492