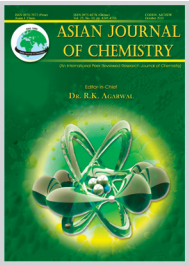
Asian Journal of Chemistry; Vol. 24, No. 7 (2012), 3070-3074

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Biosorptive Removal of Malachite Green, Methylene Blue and Methyl Orange Dyes from Aqueous Solutions by *Ficus bengalensis* (Banyan) Tree Leaves

MUHAMMAD ASLAM MALANA*, TAHIRA AMANAT, RAHEELA BEENISH QURESHI and HAFIZ BADARUDDIN AHMAD

Department of Chemistry, Bahauddin Zakariya University, Multan-60800, Pakistan

*Corresponding author: Fax: +92 61 9210085; Tel: +92 61 9210092, +92 333 6101170; E-mail: draslammalana@gmail.com

(*Received*: 7 July 2011; *Accepted*: 13 February 2012) AJC-11068

Biosorption studies of malachite green, methylene blue and methyl orange dyes were carried out on Banyan tree leaves at 298 K and 308 K. The equilibrium data for the adsorption of all the dyes were well described by Freundlich isotherm at both the temperatures. The adsorption of these dyes on the adsorbent follows pseudo second order kinetics with film diffusion and pore diffusion to be the rate limiting steps. Thermodynamic studies of the adsorption process revealed adsorption of malachite green and methylene blue to be spontaneous whereas that of methyl orange to be non-spontaneous. The value of adsorption capacity (q_m) calculated for the adsorption of malachite green, methylene blue and methyl orange at 308 K are 17.76, 12.57 and 2.56 mg/g, respectively. Keeping in view the higher values of (q_m) for malachite green and methylene blue, it is suggested that Banyan tree leaves can be effectively used for the removal of these dyes.

Key Words: Adsorption, Malchite green, Methylene blue, Methyl orange.

INTRODUCTION

Organic dyes find numerous industrial applications. Methylene blue is used as colouring agent in textile, paper, leather, food, pulp mills and plastic industries[1]. Malachite green is used as a dye in wool, silk, jute, cotton, leather and pulp industries[2]. The protozoal and fungal infections are also cured[3] by malachite green. Methyl orange is mainly used as pH indicator in laboratories and as a dye in industries[4]. Although these dyes are useful in many industries yet they have severe hazardous effects. Many of these dyes are carcinogenic[5] in nature. Methylene blue affects the eyes of both the terrestrial and aquatic animals and causes irritation to gastrointestinal tract and skin[6]. Malachite green can damage liver, gonads, intestine and skin[7]. Methyl orange is hazardous in case of skin contact, eye contact and inhalation[4] while the severe over exposure to this dye can result in death. Most of the industries discharge their waste into the nearby water bodies without paying their attention to its effect on living organisms. Therefore the treatment of effluent containing such dyes is of great interest in order to avoid their hazardous effects. Many methods have been applied for the removal of such coloured effluents from water. These include coagulation[8], reverse osmosis, photodegradation[9], ozonation, adsorption[10] *etc*. Adsorption is, however, more popular method used because of its low cost, easy operation, simple design and possibility of adsorbent recycling. Activated carbon[11] is mainly used as an adsorbent for the removal of dyes but is expensive. To minimize the cost, search for new adsorbents (alternative to carbon) are highly desirable. An adsorbent in general is considered as low cost if it requires little processing, found abundantly in nature or is a by- product or waste material from any industry. Different types of adsorbents such as rice husk, saw dust, glass fiber, silica, sun flower and bagasse have been tried by different researchers[12,13]. Banyan tree leaves, however, fulfill all the requirements of a low cost adsorbent. Leaves can be easily picked from the tree, no extra chemical processing is required and there is no shortage of leaves from giant trees spread over a wide range of the earth. This manuscript deals with the adsorptive removal of malachite green, methylene blue and methyl orange from aqueous solutions using Banyan tree leaves as adsorbent.

EXPERIMENTAL

Activation of adsorbent: Banyan leaves were collected from local trees. The leaves were washed with deionized water and dried in the sun. The dried leaves were grinded to fine particles and treated with hot deionized water to remove the pigments. The biomass was then dried in oven at 333 K for 3 h. This biomass was sieved to get particles of the same size (149 micron) and was used in further investigations.

Adsorption studies: Methyl orange, methylene blue (82 %, Fluka) and malachite green (90 %, Merck) were used

as adsorbate and the processed Banyan tree leaves as adsorbent. A stock solution of 1000 mg/L was prepared for each dye in deionized water and the solutions of different concentrations ranging from 20-38.0 mg/L were prepared by their successive dilutions with the same solvent. In a typical measurement, a weighed amount (0.1 g) of the biomass was added in a flask containing 25 mL dye solution of known concentration. The solution was shaken in a thermostat shaker at the shaking rate of 120 strokes/minute for 20 min at the desired temperature. The residue was separated by filtration and equilibrium concentration C_e of each dye in the solution was asseyed at their respective λ_{max} values (λ_{MG} 616 nm, λ_{MB}, 665 nm and λ_{MO} 430 nm) using UV visible spectrophotometer (Analytika JENA SECORD200). The amount of dye adsorbed (q_e) was calculated using eqn. (1).

$$q_e = (C_i - C_e)\frac{V}{m} \quad (1)$$

where, C_i is the initial dye concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solution volume (L) and m is the mass (g) of the adsorbent.

RESULTS AND DISCUSSION

SEM characterization of the adsorbent: Surface morphology of the adsorbent (Banyan tree leaves) before and after adsorption of the dyes was examined by using Scanning electron microscope (JEOL-JSM-6700F). SEM images of the Banyan tree leaves before and after adsorption of malachite green, methylene blue and methyl orange are shown in Fig. 1 (a-d). It is clear from the pictures that surface of the adsorbent before adsorption (Fig. 1a) is rough containing a large number of uniformly distributed pores of regular shapes and size. After adsorption, the surface is saturated and looks smooth. In case of malachite green (Fig. 1b), the surface of the adsorbent is more saturated showing greater adsorption of malachite green as compared to that in case of methylene blue (Fig. 1c). After adsorption of methyl orange on the adsorbent (Fig. 1d), the surface is sparingly filled indicating least adsorption of this dye on the surface of the adsorbent.

Adsorption isotherms: Different equilibrium isotherms applied to the experimental data and the results thus obtained are discussed below:

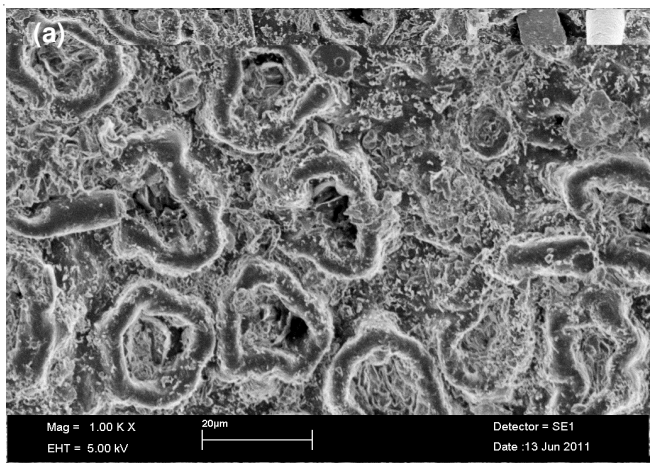


Fig. 1(a). SEM Micrograph of Banyan tree leaves before adsorption

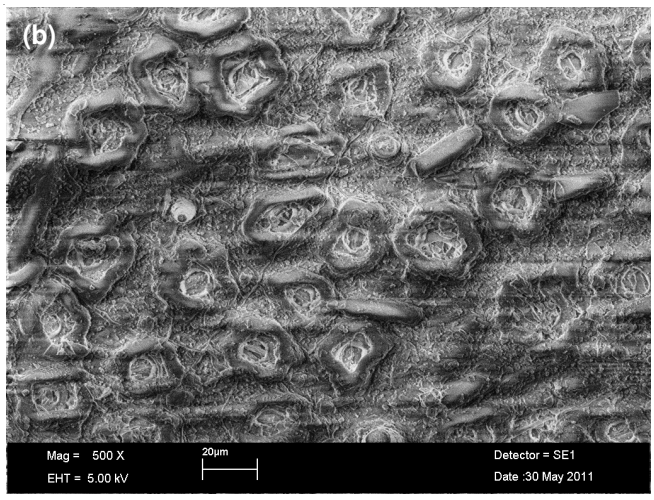


Fig. 1(b). SEM Micrograph of Banyan tree leaves after adsorption of malachite green

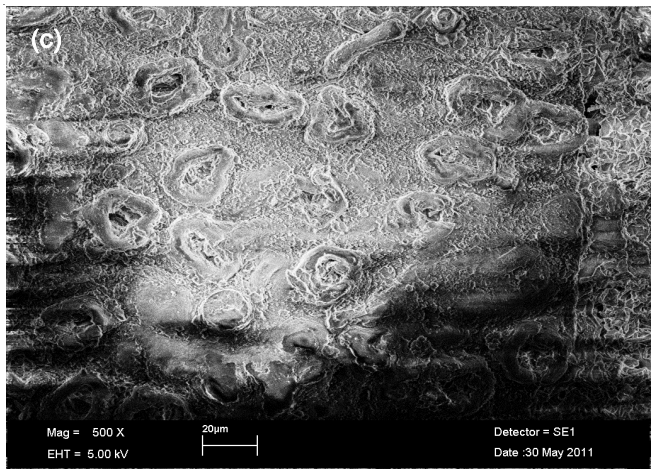


Fig. 1(c). SEM Micrograph of Banyan tree leaves after adsorption of methylene Blue

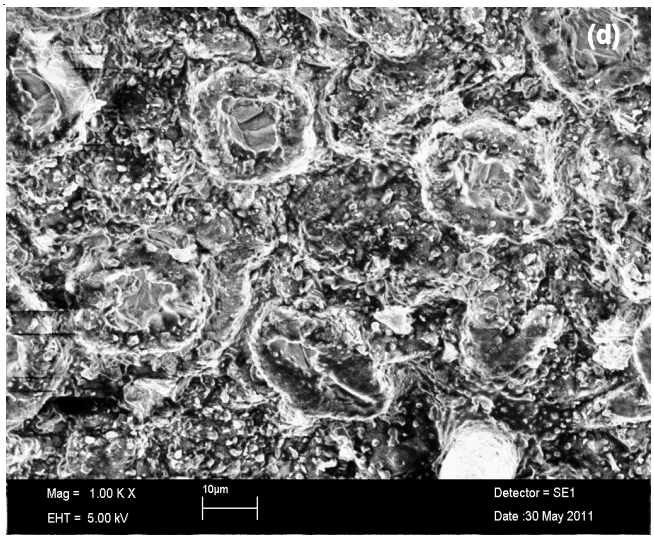


Fig. 1(d). SEM Micrograph of Banyan tree leaves after adsorption of methyl orange

Freundlich isotherm: The Freundlich isotherm is a result of the assumption that the adsorption occurs on a heterogeneous surface and non-uniform distribution of the heat of adsorption takes place over the adsorbent surface[14,15].

The linear transformation of Freundlich isotherm[10] is given as (eqn. 2):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

where, q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium dye concentration in solution (mg/L) and K_f and n are Freundlich constants.

The plot of ln C_e *versus* ln q_e for malachite green is shown in Fig. 2 and the values of the parameters (n and K_f) calculated from slope and the intercept of these plots are listed in Table-1.

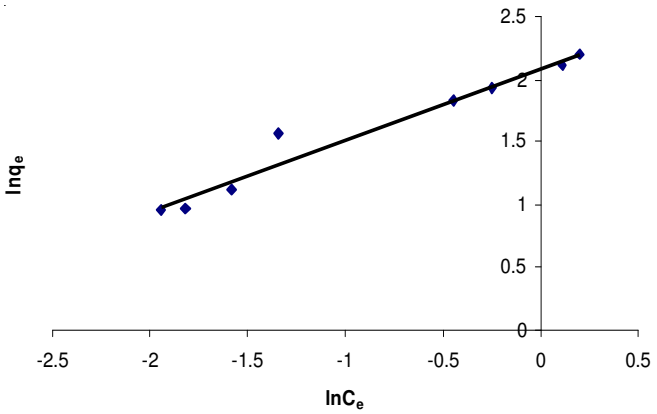


Fig. 2. Freundlich isotherm for the adsorption of malachite green on Banyan leaves

TABLE-1
FREUNDLICH PARAMETERS FOR THE ADSORPTION OF MG, MB AND MO DYES ON BANYAN LEAVES

T (K)	Dyes	n	K_f (mg/g)	R^2
298	Malachite green (MG)	1.786	8.059	0.969
	Methylene blue (MB)	1.796	6.020	0.966
	Methyl orange (MO)	1.968	0.296	0.921
308	Malachite green (MG)	1.408	8.044	0.988
	Methylene blue (MB)	1.970	5.558	0.933
	Methyl orange (MO)	2.159	0.283	0.973

The values of K_f (Table-1) decrease with increase in temperature, which reflects exothermic[5] nature of the adsorption process for all the dyes. It is also clear from the table that values of 'n' for all the dyes are greater than unity. These higher values of 'n' are indicative of the fact that adsorption of these dyes on Banyan leaves is favourable.

Langmuir isotherm: The Langmuir[16] isotherm proposes that the coverage of adsorbate molecules on a solid surface occurs in a monolayer. It is assumed that once the adsorbent site is covered with the dye molecules, no further adsorption can take place at that site. It also suggests that all the adsorption sites are of equivalent energy.

The linear form of Langmuir isotherm[17] is expressed as (eqn. 3):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + a_L \frac{C_e}{K_L} \quad (3)$$

where, K_L and a_L are Langmuir constants. Langmuir plot at 298 K for malachite green is shown in Fig. 3.

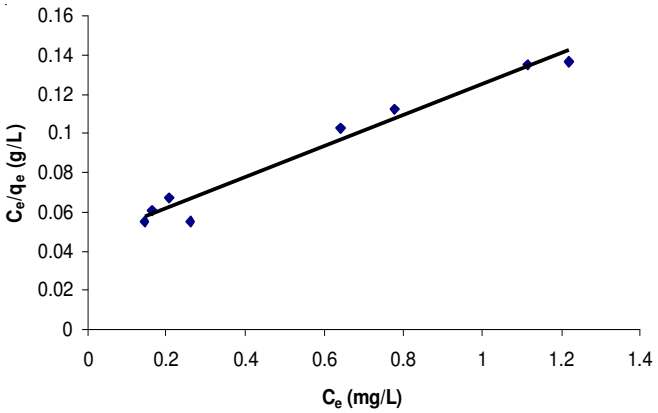


Fig. 3. Langmuir isotherm for the adsorption of malachite green on Banyan leaves

The adsorption capacity qm can be calculated as the inverse of the slope (eqn. 4) of this plot.

$$q_m = \frac{K_L}{a_L} \quad (4)$$

The important characteristic of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L, which is defined as eqn. 5:

$$R_L = \frac{1}{1 + K_L C_e} \quad (5)$$

The value of R_L obtained in the present studies (Table-2) is $0 < R_L < 1$ showing the adsorption process to be favourable[17]. The values of a_L and K_L decrease with temperature for all the dyes. On comparing the regression coefficients obtained for Freundlich and Langmuir models it can be very well predicted that the Freundlich isotherm is more favoured for the adsorption of all the dyes on Banyan leaves.

TABLE-2
LANGMUIR PARAMETERS FOR THE ADSORPTION OF MG, MB AND MO DYES ON BANYAN LEAVES

T (K)	Dyes	q_m (mg/g)	K_L (L/mg)	a_L (L/mg)	R_L (g/L)	R^2
298	Malachite green	12.674	21.834	1.722	0.246	0.962
	Methylene blue	13.514	11.357	0.839	0.153	0.940
	Methyl orange	2.863	0.1217	0.042	0.351	0.892
308	Malachite green	17.760	14.598	0.821	0.261	0.948
	Methylene blue	12.579	10.416	0.828	0.165	0.889
	Methyl orange	2.564	0.1076	0.041	0.369	0.971

Dubinin Rudushkevish isotherm: The adsorption data was also applied to the linear form of Dubinin Rudushkevish (DR) model[18] (eqn. 6).

$$\ln q_e = \ln X_m - K_{DR} \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

where, ε, X_m is monolayer capacity[19] of adsorbent and K_{DR} is constant related to adsorption potential.

The graph plotted between ln q_e *versus* ε^2 for malachite green is shown in Fig. 4 and the values of K_{DR} and X_m are obtained from the slope and intercept, respectively.

TABLE-4
KINETIC PARAMETERS FOR THE ADSORPTION OF MG, MB AND MO ON BANYAN LEAVES AT 298 K

Dye	q_e (exp) mg g^{-1}		q_e (cal) mg g^{-1}		k × 10^{-3}		R^2	
	1st	2nd	1st	2nd	1st (min^{-1})	2nd (dm^3/mg/min)	1st	2nd
Malachite green	2.432	2.432	0.528	2.52	0.105	0.363	0.967	0.998
Methylene blue	4.775	4.775	1.694	4.81	0.355	0.467	0.983	0.999
Methyl orange	1.870	1.870	1.293	2.27	0.139	0.095	0.963	0.995

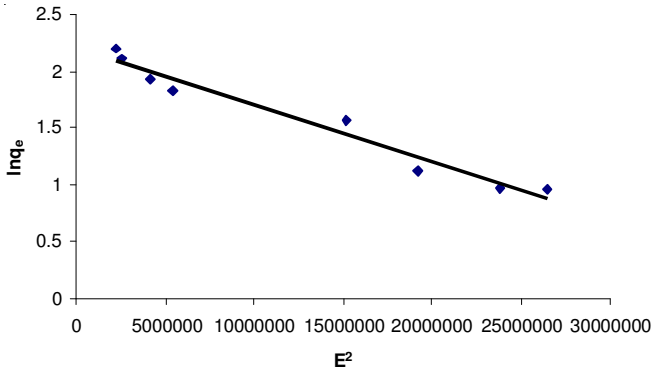


Fig. 4. Dubinin Rudushkevish isotherm for the adsorption malachite green on Banyan leaves

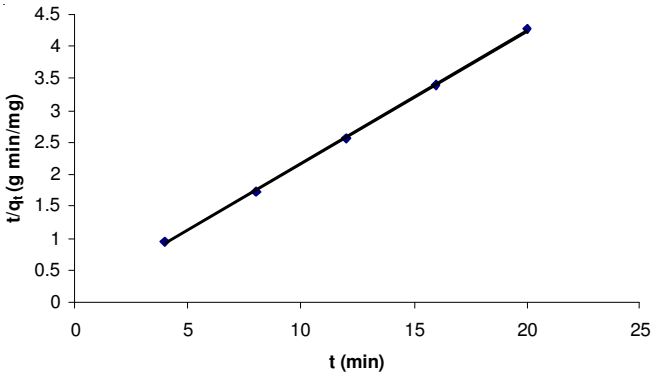


Fig. 5. Plot for pseudo second order kinetic model for the adsorption of malachite green on Banyan leaves

The mean sorption energy is calculated by the following equation (eqn. 8).

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (8)$$

The values of X_m, K_{DR} and E are given in the Table-3. The adsorption process accompanied with the energy (E) < 8 kJ/mol have been ascribed to be of physical nature[20]. The value of heat of adsorption ≤ 3.2 kJ/mol obtained in the present investigations, thus indicate physical nature of the adsorption process for all the three dyes.

TABLE-3
D-R PARAMETERS FOR THE ADSORPTION OF MG, MB AND MO DYES ON BANYAN LEAVES

T (K)	Dyes	X_m (mg/g)	K_{DR}	E (kJ/mol)	R^2
298	Malachite green (MG)	9.075	-5E-08	3.162	0.967
	Methylene blue (MB)	8.859	-1E-07	2.236	0.950
	Methyl orange (MO)	1.708	-2E-05	0.158	0.821
308	Malachite green (MG)	9.659	7E-08	2.672	0.978
	Methylene blue (MB)	8.092	-9E-08	2.357	0.820
	Methyl orange (MO)	0.479	-2E-05	0.158	0.977

Kinetics and mechanism: To investigate kinetic order and mechanism of the adsorption process pseudo first order (eqn. 9), pseudo second order (eqn.10) and intraparticle diffusion model (eqn.11) were employed.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \quad (10)$$

$$q_t = k_{id}\sqrt{t} + I \quad (11)$$

The results of adsorption (Table-4) show that the pseudo second order model (Fig. 5) provides a better fit for all the dyes as compared to that given by pseudo first order kinetic model.

Furthermore, the experimental value of adsorption capacity q_e compares well with that of calculated from pseudo second order kinetic model. This evidence also supports that the adsorption of all the three dyes on Banyan leaves follow pseudo second order kinetics indicating the occurrence of both the external as well as internal mass transfer during the adsorption process[21].

In order to investigate the number of steps involved in the adsorption process, the experimental data was subjected to regression (piecewise) analysis. The resultant four linear segments (Fig. 6) indicate that adsorption of these dyes on Banyan tree leaves is taking place in four steps which are as follows: (i) Transfer of solute from the bulk of the solution to the boundary layer (bulk diffusion); (ii) Transport of solute from the boundary layer to the surface of the material (film diffusion); (iii) Transfer of solute from the adsorbent surface to active intraparticle sites (intraparticle diffusion); (iv) Interaction between solute molecules and the available adsorption sites on the internal surface of the adsorbent.

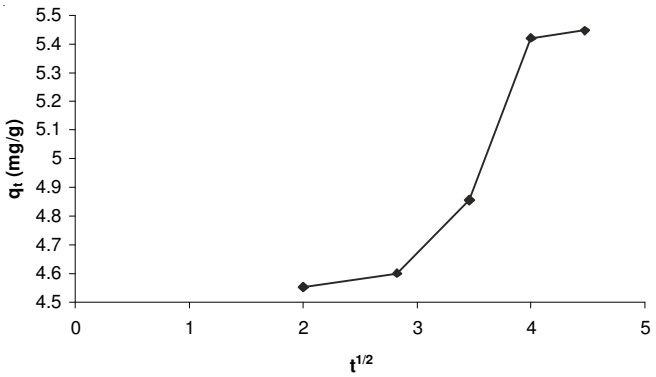


Fig. 6. Plot of piece wise regression analysis for the adsorption of malachite green on Banyan leaves

The rate of adsorption process is controlled by one or more of these steps. The first and last steps are usually considered

to be rapid[22] and film diffusion, pore diffusion or a combination of both may be the rate controlling steps. In order to decide, which one is the rate limiting step, intraparticle diffusion model was applied to the experimental data.

Yuh[23] suggested that it is crucial for q_t *versus* $t^{1/2}$ plot to go through the origin (*i.e.* I = 0.00) if the intraparticle diffusion is the only rate limiting step. Any value of I greater than zero can be attributed to difference in rate of mass transfer during initial and final stages. The values of intercepts (I) obtained for malachite green, methylene blue and methyl orange are 3.583, 4.197 and 0.484 mg/g, respectively (Fig. 7). This suggests that film diffusion and pore diffusion are concurrently responsible for controlling rate of the adsorption process[24].

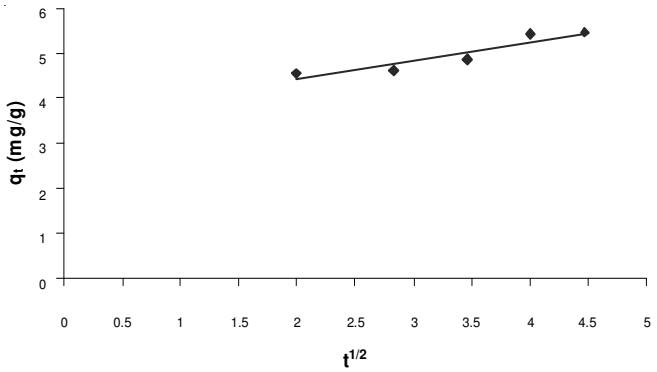


Fig. 7. Plot of intraparticle diffusion model for the adsorption of malachite green on Banyan leaves

Thermodynamic studies: Thermodynamic parameters ΔG, ΔH and ΔS were calculated by the following equations (eqs.12, 13 and 14).

$$\Delta G = RT \ln K_L \quad (12)$$

where, K_L is Langmuir constant.

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad (13)$$

where, K_2 and K_1 are Langmuir constants at 308 K and 298 K, respectively.

$$\Delta G = \Delta H - T\Delta S \quad (14)$$

The values of ΔG, ΔH and ΔS obtained from the adsorption data of all these dyes are given in Table-5. The negative values of ΔG and ΔH for the adsorption of malachite green and methylene blue show that the adsorption process of these two dyes is spontaneous and exothermic. The negative value of ΔS can be attributed to the loss of translational degrees of freedom of the adsorbate molecules after adsorption.

TABLE-5
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF VARIOUS DYES ON BANYAN LEAVES

T (K)	Dyes	ΔG (Kj/mol)	ΔH (Kj/mol)	ΔS (Kj/mol K)
298	Malachite green	-7.638	-30.722	-0.077
	Methylene blue	-6.019	-6.595	-1.932
	Methyl orange	5.216	-9.440	-0.049
308	Malachite green	-6.865	-30.722	-0.077
	Methylene blue	-6.001	-6.595	-1.932
	Methyl orange	5.708	-9.440	-0.049

Removal efficiency of the adsorbent: Removal efficiency of the adsorbent was calculated in terms of % removal (eqn.15) of the dyes from aqueous solutions under the given experimental conditions.

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (15)$$

where, C_i and C_e have the same meanings as mentioned in the above text.

The percentage removal of malachite green, methylene blue and methyl orange obtained in the present studies are 98.00, 96.00 and 23.80 %, respectively.

Conclusion

The sky-scraping percentage removal of malachite green and methylene blue in just 20 min suggests that Banyan tree leaves can effectively be used for removal of these dyes from aqueous solution. Adsorption data is well described by Freundlich model indicating heterogenous surface of the adsorbent. Mean sorption energy (≤ 3.2 kJ/mol) calculated from Dubinin Rudushkevish model indicates physical nature of the adsorption process. Adsorption of all the three dyes on Banyan tree leaves follows pseudo second order kinetics indicating that external and internal mass transfer are taking place simultaneously. Intraparticle diffusion model with non zero intercept indicates film diffusion and pore diffusion to be the rate controlling steps.

REFERENCES

1. S. Chakrabarti and B.K. Dutta, *J. Colloid. Interf. Sci*., **286**, 807 (2005).
2. I.D. Mall, V.C. Srivastava, N.K. Agarwal and I.M. Mishra, *Colloid. Surf. A: Physicochem. Engg. Aspects*, **264**, 17 (2005).
3. S. Srivastava, R. Sinha and D. Roy, *Aquat. Toxicol.*, **66**, 319 (2004).
4. J. Zhao, X. Wang, L. Zhang, X. Hou, Y. Li and C. Tang, *J. Hazard. Mater.*, **188**, 231 (2011).
5. J. Zhang, Y. Li, C. Zhang and Y. Jing, *J. Hazard. Mater.*, **150**, 774 (2008).
6. L.S. Oliveira, A.S. Franca, T.M. Alves and S.D.F. Rocha, *J. Hazard. Mater.*, **155**, 507 (2008).
7. N. Daneshvar, M. Ayazloo, A.R. Khataee and M. Pourhassan, *Bioresour. Technol.*, **98**, 1176 (2007).
8. O. Tunay, *Water Sci. Technol.*, **34**, 9 (1996).
9. K. Wu, Y. Xie, J. Zhao and H. Hidaka, *J. Mol. Cat. A: Chem.*, **144**, 77 (1999).
10. R. Ahmad, *J. Hazard. Mater.*, **171**, 767 (2009).
11. M. Balsamo, F.D. Natale, A. Erto, A. Lancia, F. Montagnaro and L. Santoro, *J. Hazard. Mater.*, **187**, 371 (2011).
12. W. Zou, K. Li, H.X. Bai, H. Shi and R. Han, *J. Chem. Eng.*, **56**, 1882 (2011).
13. W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun and M.F. Hsieh, *Chemosphere*, **45**, 51 (2001).
14. H.M.F. Freundlich, *Physikalische Chemie*, **57**, 385 (1906).
15. A. Mittal, J. Mittal, A. Malviya, D. Kaur and V.K. Gupta, *J. Colloid. Interf. Sci.*, **343**, 463 (2010).
16. I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).
17. F. Renault, N. Morin-Crini, F. Gimbert, P.M. Badot and G. Crini, *Bioresou. Technol.*, **99**, 7573 (2008).
18. T. Sismanoglu, *Colloid. Surf. A*, **297**, 38 (2007).
19. H. Tahir, *Afr. J. Biotechnol.*, **9**, 8206 (2010).
20. M.E. Argun, S. Dursun, C. Ozdemir and M. Karatas, *J. Hazard. Mater.*, **141**, 77 (2007).
21. A.K. Jain, V.K. Gupta, A. Bhatnagar and Suhas, *J. Hazard. Mater.*, **101**, 31 (2003).
22. B.H. Hameed and M.I. Al-Khaiary, *J. Hazard. Mater.*, **153**, 701 (2008).
23. S.H. Yuh, *Water Resour.*, **37**, 2323 (2003).
24. Z. Bekci, C. Ozveri, Y. Seki and K. Yurdakoc, *J. Hazard. Mater.*, **154**, 254 (2008).