African Journal of Biotechnology Vol. 7 (21), pp. 3906-3911, 5 November, 2008
Available online at http://www.academicjournals.org/AJB
ISSN 1684–5315 © 2008 Academic Journals

Full Length Research Paper

Removal of fast green dye (C.I. 42053) from an aqueous solution using *Azadirachta indica* leaf powder as a low-cost adsorbent

Hajira Tahir*, Uzma Hammed, Qazi Jahanzeb and Muhammad Sultan

Department of Chemistry, University of Karachi, Pakistan.

Accepted 19 September, 2008

***Azadirachta indica* (neem) leaf powder was used as an adsorbent for the removal of textile dye from aqueous solution. The adsorption of dye on *A. indica* was found to be dependent on contact time, dye concentration and amount of adsorbent. Spectrophotometric technique was used for the measurement of concentration of dye before and after adsorption. The removal data were fitted on Langmuir and Freundlich adsorption isotherm equations. The values of their corresponding constants were determined from the slope and intercepts of their respective plots. The adsorption isotherm data will employ to calculate the thermodynamic parameters like (ΔG) Gibb's free energy, (ΔH) change in enthalpy and (ΔS) entropy. The values of percent removal and K_D for Fast green dye on neem leaf powder was also calculated at temperatures ranging from 303-318 K.**

Key words: Adsorption, dye, *Azadirachta indica,* adsorption isotherms, thermodynamics of adsorption.

INTRODUCTION

Many industries like plastics, paper, textile and cosmetics use dyes to color their products. These dyes are common water pollutants and they may be frequently found in trace quantities in industrial wastewater. Their presence in water, even at very low concentrations, is highly visible and undesirable. In addition, many dyes are difficult to degrade due to their complex aromatic structure and they tend to persist in the environment and creating serious water quality and public health problems. Therefore, it would be advantageous to develop technologies to eliminate them. A number of conventional biological treatment processes are not very effective for treating a dye wastewater owing to low biodegradability of dyes. They are usually treated by physical or chemical processes. There are various methods for dye removals which include coagulation and chemical oxidation, membrane separation process, electrochemical, reverse osmosis and aerobic and anaerobic microbial degradation but all of these methods suffer from one or other limitations, and none of them were successful for completely removing the color from wastewater. Dyes can be effectively removed by adsorption process in which dissolved dye compounds were attached to the surface of adsorbents. Researchers have exploited many low cost and biodegradable effective adsorbents. They were obtained from natural resources for the removal of different dyes from aqueous solutions at different operating conditions. Some of the adsorbent materials that have been used with varying success include rice husk (Malik, 2003; Mahejabeen and Hajira, 2007), cornelian cherry, apricot stone, almond shell (Demirbas et al., 2004; Demirbas et al., 2002), cotton stalks (Attia et al., 2004), coir pith (Namasivayam and Kadirvelu, 1994), wood (Poots et al., 1978), sunflower stalks (Sun and Xu, 1997), and orange peel (Arami et al., 2005) were successfully employed for the removal of dyes from aqueous solutions. In the present investigation, *Azadirachta indica* (neem) leaf powder was used as an adsorbent for the removal of textile dye from aqueous solution.

MATERIALS AND METHODS

Preparation of the adsorbent

The neem belongs to the meliaceae family and is native to Indian sub-continent. Its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household

*Corresponding author. E-mail: hajirat@uok.edu.pk. Tel: 092-333-3621470. Fax: 092- 21-6832216.

Table 1. Optimization for the amount of adsorbent (*Azadirachta indica* leaf powder) in the adsorption of fast green.

Amount of neem leaf powder (g)	Ce (mol/L)	Adsorption (%)	K_D (mol/g)
0.1	3.50×10^{-4}	70.00	21.00
0.2	4.13×10^{-4}	82.60	24.72
0.3	4.23×10^{-4}	84.60	25.38
0.5	4.30×10^{-4}	86.00	25.87
0.8	4.52×10^{-4}	90.40	27.12
1.0	4.63×10^{-4}	92.60	27.78
1.5	4.34×10^{-4}	86.70	26.04

Table 2. Optimization of the concentration of dye in the adsorption of fast green from aqueous solution using *Azadirachta indica* leaf powder as adsorbent.

Concentration of dyes (x 10^{-4} mol/L)	Ce (mol/L)	Adsorption (%)	K_D (mol/g)
1.7	1.5×10^{-4}	87.6	26.3
1.8	1.7×10^{-4}	92.7	27.8
4.2	3.1×10^{-4}	73.4	22.0
6.0	5.3×10^{-4}	88.3	26.5
8.6	7.3×10^{-4}	84.7	25.4

pesticide. The trees are also known as an air purifier. The medicinal and germicidal properties of the neem tree have been put to use in a variety of applications. The mature neem leaves used in the present investigation were collected from the trees in University of Karachi area. They are washed thrice with water to remove dust and water soluble impurities and are dried until the leaves become crisp. The dried leaves were powdered and further washed with distilled water till the washings are free of color and turbidity. Then the neem leaf powder was dried in an oven at 60℃ ± 2℃ and then placed in desiccator for the adsorption studies.

Adsorbate

Fast green dye (C.I 42053) was used as an adsorbate. Stock solution of Fast green dye (mol.wt: 808.86 g) having strength $1x10^{-2}$ was prepared in double distilled water. For the determination of λ_{max} of dye, the solution of strength of $1x10^{-5}$ mol/dm^3 concentrations were prepared. Experimental solutions of desired concentration were prepared by successive dilutions. The absorbance of solutions was measured on spectrophotometer at wave length 622 nm.

Determination of optimum amount of adsorbent

In order to find out the optimum amount of adsorbent at which maximum adsorption takes place, 30 ml of $5x10^{-4}$ mol/dm^3 fast green dye solution was taken in a series of flasks with different quantity of adsorbent; 0.1, 0.2, 0.3, 0.5, 0.8, 1.0 and 1.5 g of neem leaf powder. The solution of dye was kept on a shaking incubator for 30 min at 120 rpm for shaking.

Determination of optimum concentration of adsorbate

For the determination of optimum concentration of dyes, solutions of different concentrations of dye were prepared. 30 ml of dye solution was placed in respective flasks with optimum amount of neem leaf powder for 30 min.

Determination of optimum shaking time

For the determination of effect of time for the adsorption of fast green dye on neem leaf powder, the optimum amount of adsorbent (1.0 g) was added in respective flasks with 30 ml of optimum concentration of dye solution (1.8 mol/dm^3) for different intervals of time.

Adsorption at different temperature

30 ml of dye solution having different concentrations were place in flasks. Optimum amount of neem leaf powder was added in each shaking flask containing different concentration of dye solutions. These flasks were placed in the thermostatic water bath at desired temperature under the optimized conditions. After the specific shaking time period, the solutions were filtered using Whatman no. 42 filter paper and analyzed by using UV-visible spectrophotometer for the determination of concentration of dye remaining in solution. These experiments were repeated at various temperatures in the range of 30 to 45°C at the step of 5°C. The dye concentration retained in the adsorbent phase was calculated using equation 1.

$$Q_e = (C_0 - C_e) V/W \quad (1)$$

Where C_o and C_e are the initial and equilibrium concentrations (M), respectively, of dye in solution, while V is the volume (ml), and W is the weight (g) of the adsorbent.

RESULTS AND DISCUSSION

Adsorption of Fast Green dye which is acidic in nature was studied on neem leaf powder under the optimize conditions of amount of adsorbent, adsorbate, shaking time and temperatures. The results are shown in Tables 1, 2 and 3. The results were indicated that maximum adsorption that took place is about 92.6% using 1.0 g of

Table 3. Optimization for the shaking time in the adsorption of fast green from aqueous solution using *Azadirachta indica* leaf powder as adsorbent.

Time (min)	Ce (mol/L)	Adsorption (%)	K_D (mol/g)
5.0	4.3×10^{-4}	86.20	25.86
10	4.5×10^{-4}	90.00	27.00
15	4.5×10^{-4}	91.00	27.30
20	4.6×10^{-4}	92.36	27.70
30	4.8×10^{-4}	97.00	29.10
40	4.7×10^{-4}	94.00	28.20
50	4.6×10^{-4}	93.60	28.08
60	4.5×10^{-4}	91.50	27.45

Table 4. Langmuir parameters of adsorption of fast green using *Azadirachta indica* leaf powder as adsorbent.

Temperature	Intercept C = 1/K.Vm	Slope m = 1/Vm	K = 1/C.Vm	Vm = 1/m
303 K	0.264	-43.48	-164.38	-0.023
308 K	0.277	-68.19	-247.53	-0.014
313 K	0.227	-39.47	-173.58	-0.025
318 K	0.196	12.38	--63.29	-0.081

adsorbent. The distribution constant (K_D) value at this amount is 27.78 (mol/g). The adsorption that occurred with 0.1 g is 70.0%. The difference in % adsorption of this dye on the surface of neem leaf powder and bentonite may be due to the presence of more or less irregular and defective edges. These edges play significant role on the adsorption phenomenon. These edges strike the unsaturated part of the dye and accelerate the removal of dye molecules (Khan et al., 2002; Tahir and Uddin, 2003). These types of observations were also observed for the adsorption of organic acids on the surface of finely divided charcoal (Khan et al., 1991, 1994).

The effect of dye concentration on adsorption was carried out under the optimized conditions of amount of adsorbent (1.0 g), volume of adsorbate (30 ml) and shaking time (30 min) and the results are summarized in Table 2. For neem leaf powder as adsorbate, the adsorption increased with increase in concentration of dye, then it drops and again increases. The maximum and minimum adsorption values were obtained at concentrations of 1.8×10^{-4} mol.dm^{-3} and 4.2×10^{-4} mol.dm^{-3}, respectively. Table 3 illustrates the adsorption of dye at different time duration. The Maximum and minimum values of adsorption of dye from aqueous solution on neem leave powder (adsorbent) were obtained at 30 min (Ce 4.85 X 10^{-4} mol/L, % adsorption 97.0%) and 5.0 min (Ce 4.3 X10^{-4} mol/L, % adsorption 86.2), respectively. The values of K_D increased with increase in time. When a pure liquid is in contact with solid, the state of affairs at the interface between solid and the liquid will be different from that in the interior part of the liquid. The number of molecule, which will be adsorbed at the surface of solid or liquid from solutions, will be directly proportional to the concentration. During the period of adsorption after a shorter or longer duration, equilibrium will be established between molecules in the bulk place and adsorbed phase.

Many theories of adsorption were put forward to explain the phenomena of adsorption. Langmuir, Freundlich and and Dubinin-Radushkevich (D-R) adsorption isotherms are some of them. The Langmuir adsorption isotherm is the best known model and most frequently utilized to determine the adsorption parameters. The well known langmuir equation is (Langmuir, 1918) given below:

$$C_s/X_m = 1/KV_m + C_s/V_m \qquad (2)$$

Where, K is the adsorption coefficient or Langmuir constant, V_m is the monolayer capacity, X_m is the amount of dye required to form the monolayer over the surface of adsorbent and C_S is the equilibrium concentration.

A straight line was obtained by plotting C_S/X/m versus C_S. The slopes and intercept of these plots are represented as $1/V_m$ and $1/K.V_m$. Experiments were accomplished at different temperatures ranging from 303 to 318 K. The Plots are shown in Figure 1 and the results are summarized in Table 4. The increase in the K values with the rise in temperature for fast green-neem leaf powder system predicts strong interaction between adsorbent and adsorbate. It reveals that the adsorption affinity of fast green dye at neem leaf powder increased with the rise in temperature, so adsorption is highly favorable at high temperatures. All the adsorption system obey Langmuir adsorption isotherm except at 303 K for fast green-neem leaf powder system. The monolayer

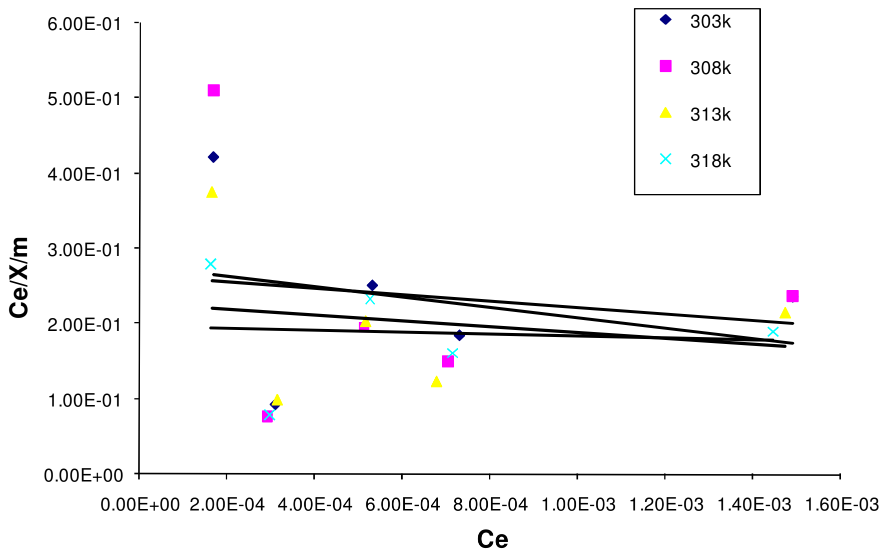

Figure 1. Langmuir adsorption isotherm for fast green using *Azadirachta indica* leaf powder as adsorbent.

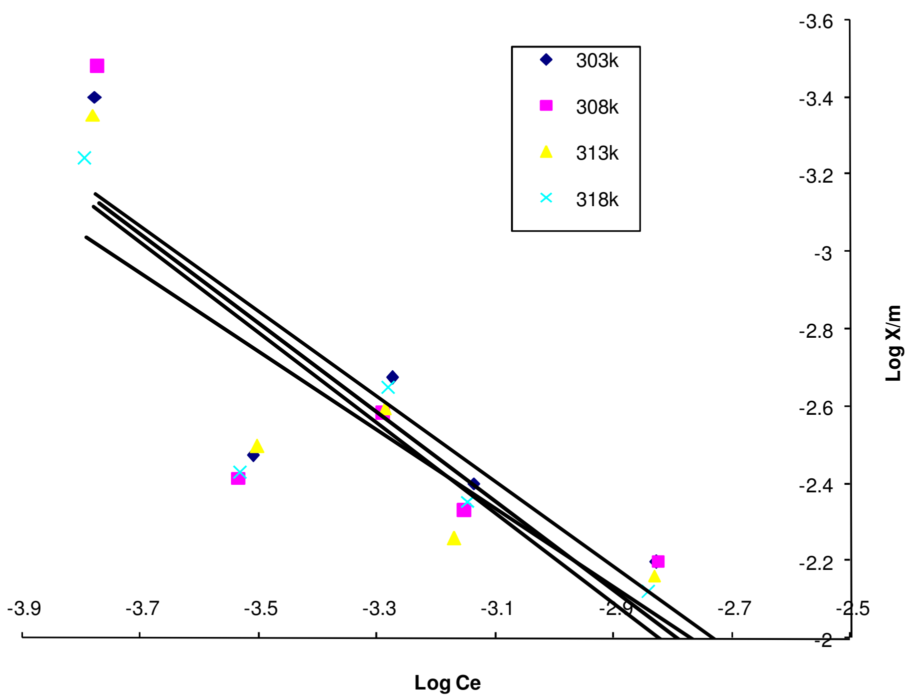

Figure 2. Freundlich adsorption isotherm for fast green using *Azadirachta indica* leaf powder as adsorbent.

capacity (V_m), for fast green-neem leaf powder system decreased with the increase in temperature, indicating high affinity of dye at low temperatures.

The Freundlich isotherm is expressed in the form of Eq. (3):

$$\text{Log}X/m = \log K + 1/n \log Cs \quad (3)$$

Where, X/m is the amount adsorbed per unit mass of the adsorbate, C_s the equilibrium concentration, and $1/n$ and K are constants.

Figure 2 depicts the Freundlich plots obtained at various temperatures studied for the present system. Values of K and n were computed from the respective slopes and intercepts of their plots and are listed in Table

Table 5. Freundlich parameters of adsorption of fast green using *Azadirachta indica* leaf powder as adsorbent.

Temperature	Intercept (log K)	K	Slope m = 1/n	n
303 K	0.814	6.510	1.016	0.984
308 K	1.298	19.86	1.168	0.856
313 K	1.218	16.54	1.152	0.868
318 K	1.010	10.24	1.101	0.908

Table 6. Thermodynamic parameters of adsorption of fast green using *Azadirachta indica* leaf powder as adsorbent.

Concentration (mol/L)	ΔH^o	ΔS^o	ΔG^o			
			303 K	308 K	313 K	318 K
1.8×10^{-4}	0.2543	0.1950	-2575.69	-2654.78	-2632.47	-2606.35
4.2×10^{-4}	0.1059	0.4284	-1986.23	-1887.66	-2098.67	-1974.13
6.0×10^{-4}	0.0371	0.8371	-2455.05	-2407.80	-2466.41	-2556.56
8.6×10^{-4}	0.1959	0.2684	-2348.25	-2294.62	-2234.47	-2411.94
1.7×10^{-3}	0.2020	0.3056	-2435.96	-2476.16	-2486.51	-2474.89

Table 7. Removal (%) of fast green dye at different temperatures using *Azadirachta indica* leaf powder as adsorbent.

Concentration (mol/L)	Removal (%)			
	303 K	308 K	313 K	318 K
1.8×10^{-4}	92.7	93.9	91.8	89.4
4.2×10^{-4}	73.4	69.5	74.8	70.2
6.0×10^{-4}	88.3	85.4	85.9	87.5
8.6×10^{-4}	84.7	81.8	78.7	82.9
1.7×10^{-3}	87.6	87.6	86.5	85.0

5. The constant *K* is related to the degree of adsorption, while *n* provides the rough estimation of the intensity of the adsorption. The decrease in the values of K with the rise in temperature reveals that adsorption affinity for fast green on neem leaf powder system decreased with rise in temperature, showing the less adsorption tendency at higher temperatures.

Thermodynamic parameters

In order to fully understand the nature of adsorption, the thermodynamic studies play an important role. This paper also presents the thermodynamics parameters related to the adsorption of dye such as free energy change (ΔG), enthalpy change (ΔH) and entropy changes (ΔS), which are tabulated in Table 6 by using the following eauations:

$$\Delta G = -RT\ln K_D \quad (7)$$

$$\ln k = \Delta S/R - \Delta H/RT \quad (8)$$

$$\Delta G = \Delta H - T\,\Delta S \quad (9)$$

The values of ΔH and ΔS were calculated from the slope and intercept of the linear variation of ln K_D with reciprocal of temperature (1/T). The values of ΔG for fast green- neem leaf powder system are negative at different temperatures. The negative value of ΔG shows the spontaneous behavior of adsorption process. While the values of ΔH, positive for fast green-neem leaf powder system, show the endothermic nature of adsorption process. The values of ΔS were also positive for fast green-neem leaf powder system.

Conclusion

From the present studies we can conclude that *A. indica* (Neem) leaves can be used as a low-cost, natural adsorbent compared to commercial adsorbent for the removal (Table 7) of fast green dye.

REFERENCES

Arami M, Limaee NY, Mahmoodi NM, Tabrizi NS (2005). Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. J. Colloid Interface Sci. 288: 371-376.

Attia AA, El-Hendawy AA, Khedr SA, El-Nabarawy TH (2004). Textural properties and adsorption of dyes onto carbons derived from cotton stalks. Adv. Sci. Technol. 22: 411-426.

Demirbas E, Kobya M, Oncel S, Sencan S (2002). Removal of Ni (II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Bioresour. Technol. 84: 291-293.

Demirbas E, Kobya M, Senturk E, Ozkan T (2004). Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water SA 30: 53-539.

Khan AR, Uddin F, Ahmed Z (2002). Adsorption behavior of citric acid from aqueous solution on activated charcoal. Pak. J. Sci. Ind. Res. 45: 82-85.

Khan AR, Uddin F, Ali S (1994). Adsorption studies of tartaric acid from aqueous solution on charcoal. Pak. J. Sci. Ind. Res. 37: 40-42.

Khan AR, Uddin F, Khan GU (1991). Adsorption of glycolic and lactic acids from aqueous solutions on charcoal, Pak. J. Sci. Ind. Res. 34: 163-166.

Langmuir I (1918). The adsorption of gases on plane surfaces of glass mina and platinum. J. Am. Chem. Soc. 40: 1361-1365.

Mahejabeen M, Hajira T (2007). Determination of levels of fluoride and trace metal ions in drinking waters and remedial measures to purify water. Afr. J. Biotechnol. 6: 2541-2549.

Malik PK (2003). Use of activated carbons prepared from sawdust and rice husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes Pigments 56: 239-249.

Namasivayam C, Kadirvelu K (1994). Coir pith, an agricultural waste by-product, for the treatment of dyeing wastewater. Bioresour. Technol. 48: 79-81.

Poots VJP, McKay G, Healy JJ (1978). Removal of basic dye from effluent using wood as an adsorbent. J. Water Pollut. Contr. Fed. 50: 926-939.

Sun G, Xu X (1997). Sunflower stalks as adsorbents for color removal from textile wastewater. Indian Eng. Chem. Res. 36: 808-812.

Tahir H, Uddin F (2003). Comparative statistical approach for the assessment of pollution of heavy metals in rawal lake water and main streams entering raw lake. Saudi J. Chem. Soc. 7: 167-174.