Asian Journal of Chemistry; Vol. 24, No. 5 (2012), 2187-2190

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Adsorption Studies of Acid Blue-92 from Aqueous Solution by Activated Carbon Obtained from Agricultural Industrial Waste-Cocoa (*Theobroma cacao*) Shell

C. THEIVARASU* and S. MYLSAMY

Department of Chemistry, PSG College of Technology, Coimbatore-641 004, India

*Corresponding author: Fax: +91 422 2573833; Tel: +91 422 2572177, E-mail: theivarasu@yahoo.co.in

(*Received*: 19 May 2011; *Accepted*: 19 December 2011) AJC-10857

The present study investigates the ability of cocoa (*Theobroma cacao*) shell activated carbon for the removal of acid blue-92 dye from waste water. Batch studies were performed to evaluate the influence of various experimental parameters like initial pH, contact time, initial concentration and adsorbent dose. Equilibrium isotherms were analyzed by Langmuir and Freundlich isotherm models. The adsorption data are best described by Langmuir isotherm model followed by Freundlich model. The pseudo-first order and pseudo-second order were used to describe the kinetic data. The experimental data fitted well to the pseudo-second order kinetic model. Results implied that cocoa shell activated carbon may be suitable as an adsorbent for the removal of acid blue-92 from aqueous solutions.

Key Words: Adsorption, Acid blue-92, Cocoa shell, Kinetics, Isotherm.

INTRODUCTION

Industries such as paper, textile, plastic, rubber, cosmetics, pharmaceuticals and food use synthetic dyes to colour their products[1]. More than 0.7 million tons of dyes are consumed per year in the industries worldwide[2]. A considerable percentage of these dyes go into the effluent during the dyeing process and affects the photosynthetic activity and may cause toxic to certain forms of aquatic life[3]. Various treatment processes such as ozonation[4], coagulation/flocculation[5], ultrafiltration[6], oxidation[7] and adsorption[8] have been widely investigated to remove dyes from waste waters. Among these methods adsorption using activated carbon was found most efficient method for the removal of synthetic dyes from aqueous effluents[9]. Due to the higher cost and regeneration problems of activated carbon, researchers are showing interests in using low cost adsorbents from agricultural wastes for dye removal[10].

In this paper it was proposed to use cocoa shell, an agricultural waste as a precursor for the preparation of activated carbon material. Cocoa shell activated carbon (CSAC) adsorbent was successfully used to remove acid blue-92 (AB-92) dye from aqueous solution. Equilibrium and kinetic data for the adsorption process of the acid blue-92 dye onto this adsorbate was investigated.

EXPERIMENTAL

Preparation of adsorbent: Dried cocoa shell collected from local agricultural field was carbonized with concentrated sulphuric acid in the weight ratio of 1:1 (w/v). The activation was performed by heating the sample for 7 h in a muffle furnace at 550 ºC. After carbonization and activation, the carbon obtained was washed with distilled water until a constant pH was reached. Then the sample was dried at 110 ºC for overnight in a hot air oven. The carbonized material was taken out, grounded and sieved to 150 μm size and stored in a vacuum dessicator.

Preparation of dye solution: Stock solution of acid blue-92 was prepared by dissolving 1 g of dye in 1 L of distilled water to give concentration of 1000 mg/L. The serial dilutions say 10, 20, 30, 40 mgL^{-1} were made by diluting the dye stock solution in accurate proportions. The pH of dye solutions were adjusted with 0.1 M NaOH or 0.1 M HCl using a pH meter.

Batch adsorption experiments: Adsorption experiments were carried out in temperature controlled orbital shaker at a constant speed of 125 rpm at 35 ºC using 250 mL conical flasks containing 100 mg of cocoa shell activated carbon with 50 mL of dye solutions. All the experiments (except the study of pH effect) were carried out at pH of 3. After agitating the flasks for predetermined time intervals samples were withdrawn from the flasks. The adsorbents were separated from the solution by centrifugation (REMI make) at 2000 rpm for 5 min. The absorbance of the supernatant solution was estimated to determine the residual dye concentration[11], measured at λ_{max} = 567 nm spectrophotometrically using Elico make UV-Visible spectrophotometer.

The adsorption isotherms were specified at pH 3 for adsorption of acid blue-92 onto cocoa shell activated carbon at 35 ºC. Adsorption data obtained from the effect of initial concentration and contact time were employed in testing the applicability of isotherm and kinetic equations, respectively.

RESULTS AND DISCUSSION

Effect of agitation time and initial concentration: The effect of agitation time and dye concentration on removal of acid blue-92 by cocoa shell activated carbon at 35 ºC was presented in Fig. 1. The equilibrium time for acid blue-92 was found to 60, 90, 120 and 150 min for 10, 20, 30 and 40 mgL^{-1} respectively. The uptake of dye after equilibrium (q_e) was 8.89, 14.48, 20.71 and 26.40 mgg^{-1} for 10, 20, 30 and 40 mgL^{-1} respectively. The results showed that adsorption capacity was found to increase with increasing contact time and attained maximum value at 4 h for higher concentration of adsorbate. There was no significant change in equilibrium concentration after 4 h and therefore, for further studies, the time for attaining equilibrium was set as 4 h.

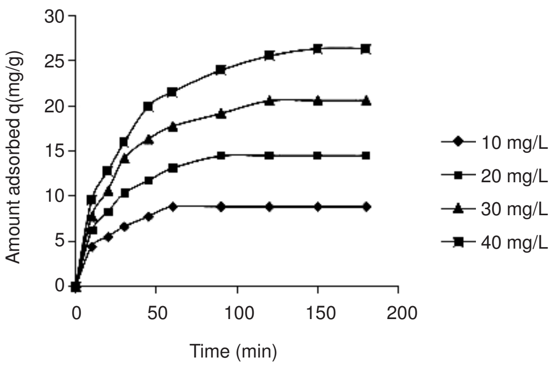

Fig. 1. Effect of agitation time on adsorption-initial concentration variation (Temp.: 308 K; Initial pH = 3; Adsorbent dosage: 100 g/50 mL)

Effect of adsorbent dosage: The effect of various amounts of cocoa shell activated carbon was studied by varying the weight of carbon from 100 mg to 1000 mg without changing the volume of acid blue-92 dye solution (50 mL) with constant speed of 125 rpm for 4 h (Fig. 2). Similarly the pH (3) and temperature (35 ºC) was kept constant. The percentage adsorption increases with increase of adsorbent dosage. It is evident that by increasing the adsorbent dosage, the number of valuable adsorption sites and surface area increases[12]. Thus, adsorption increases with increase of adsorbent dosage.

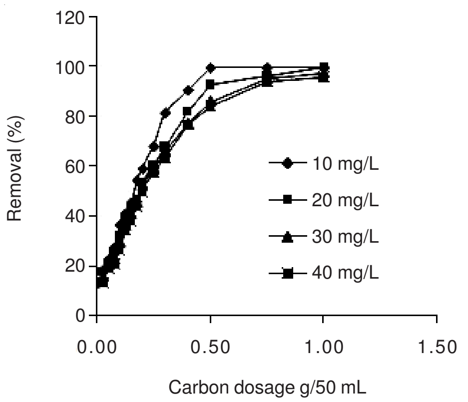

Fig. 2. Effect of adsorbent dose on the removal of acid blue-92 onto cocoa shell activated carbon (Temp: 308 K; Initial pH = 3; Agitation time: 4 h)

Effect of pH: The pH is one of the most important factor for controlling the adsorption of dye on to the adsorbent. The pH of the system exerts influence on the adsorptive uptake of adsorbate molecules. The effect of solution pH was studied between 2 to 10, initial pH controlled by the addition of 0.1 M HCl or 0.1 M NaOH and agitated with 100 mg of adsorbent for 4 h at 35 ºC. The effect of initial pH of dye solution on the adsorption of acid blue-92 for initial dye concentration of 30 mg/L was illustrated in Fig. 3. The interaction between the sorbate and sorbent is affected by pKa of dye. When the solution pH value is above the pKa of dye (pKa for acid blue-92 is 3.2), the adsorption decreases due to the electrostatic repulsion between dissociated adsorbate and adsorbent surface[13]. The maximum uptake of acid blue-92 by cocoa shell activated carbon was obtained at pH 3. So, pH 3 was chosen for the study on adsorption isotherm.

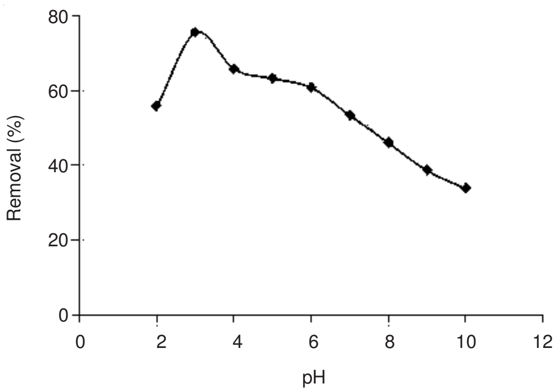

Fig. 3. Effect of pH on the removal of acid blue-92 onto cocoa shell activated carbon (Temp: 308 K; Initial pH = 3; Agitation time: 4 h; Concentration: 30 mg/L)

Adsorption isotherm

Langmuir isotherm: Langmuir theory is based on the assumption that it predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent[14].

Linear form of Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{b}Q_0 + \frac{C_e}{Q_o} \quad (1)$$

where, C_e is equilibrium constant of dye (mg/L), q_e is amount of dye adsorbed at equilibrium (mg/g), Q_0 is Langmuir constant related to adsorption capacity (mg/g) and b is Langmuir constant related to energy of adsorption capacity (L/mg). The linear plot of C_e/q_e *versus* C_e is shown in Fig. 4. The constants Q_0 and b can be calculated from slope and intercept of the plot and the values are tabulated in Table-1. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (R_L) to determine high affinity adsorption. R_L is calculated as follows:

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

where, C_o is the initial dye concentration (mg/L). R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) (or) unfavourable ($R_L > 1$)[15]. In the present investigation, the R_L values were less than one which shows the adsorption process was favourable.

TABLE-1
RESULTS OF ISOTHERM PLOTS FOR THE ADSORPTION OF ACID BLUE-92 ON COCOA SHELL ACTIVATED CARBON

Temperature (K)	Langmuir isotherm				Freundlich isotherm		
	Q_m (mg/g)	b × 10^{-3} (L/mg)	R^2	R_L	K_f (mg/g)	l/n	R^2
308	28.57	20.5	0.996	0.1944-0.3915	4.27	0.338	0.954

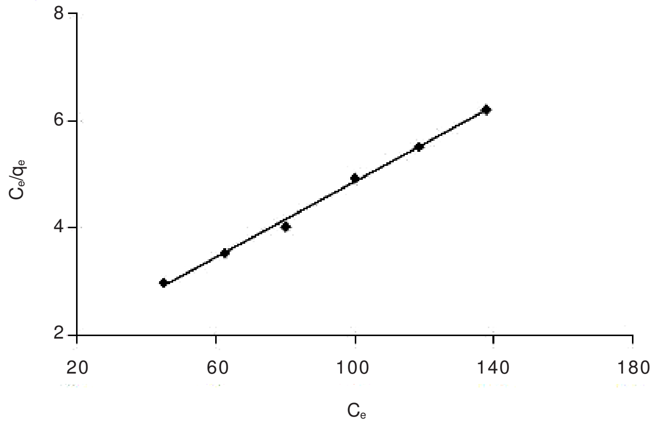

Fig. 4. Langmuir plot for the removal of acid blue-92 onto cocoa shell activated carbon (Temp: 308 K; Initial pH = 3; Agitation time: 4 h; Adsorbent dosage: 100 mg/50 mL)

Freundlich isotherm: The Freundlich isotherm based on multilayer adsorption on heterogeneous surface[16]. Linear form of Freundlich model is:

$$\log C_e = \log k_f + \frac{1}{n}\log C_e \quad (3)$$

where, q_e is dye concentration in solid at equilibrium (mg/g), C_e is dye concentration in solution at equilibrium (mg/L), k_f (L/mg) and 1/n are adsorption capacity at unit concentration and adsorption intensity, respectively. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favourable (0 < 1/n < 1), unfavourable (1/n > 1). The linear plot of log q_e *versus* log C_e was shown in Fig. 5. The values of 1/n and k_f can be calculated from the slope and intercept respectively and the results are given in Table-1. The value of 1/n was less than one indicating the favourable adsorption[17]. Langmuir adsorption is more appropriate to explain the nature of adsorption with correlation coefficient of 0.996 rather Freundlich model shows poor fit (R^2 = 0.954).

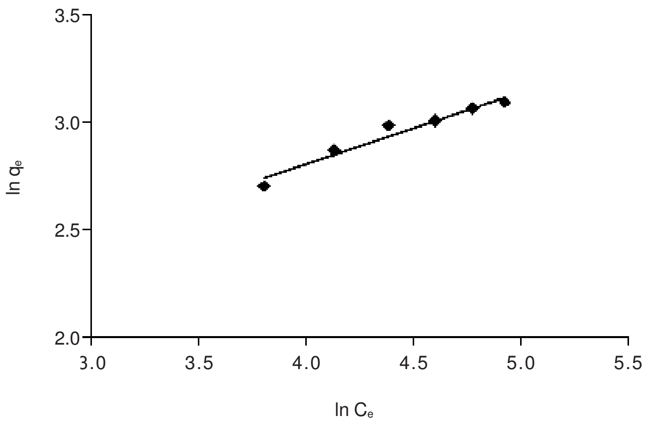

Fig. 5. Freundlich plot for the removal of acid blue-92 onto cocoa shell activated carbon (Temp: 308 K; Initial pH = 3; Agitation time : 4 h; Adsorbent dosage : 100 mg/50 mL)

Adsorption kinetics: Kinetic studies are necessary to optimize different operation condition for the sorption of dyes. The kinetics of acid blue-92 onto cocoa shell activated carbon was analyzed using pseudo-first order and pseudo-second order kinetic models.

Pseudo-first order kinetic model: It is based on the fact that the change in dye concentration with respect to time is proportional to the power one[18]. The differential equation is described as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

where, q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t, respectively and k_1 is the rate constant (min^{-1}) of pseudo-first order kinetic model.

The integrated linear form of the model is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (5)$$

A plot of log (q_e-q_t) *versus* t gives a linear line (Fig. 6) from which the values of k_1 and q_e can be determined from the slope and intercept respectively (Table-2). This value showed that the q_e calculated was not equal to q_e experimental, although the values of R^2 are satisfactory. This shows that the kinetics for the entire process did not follow the pseudo-first order model.

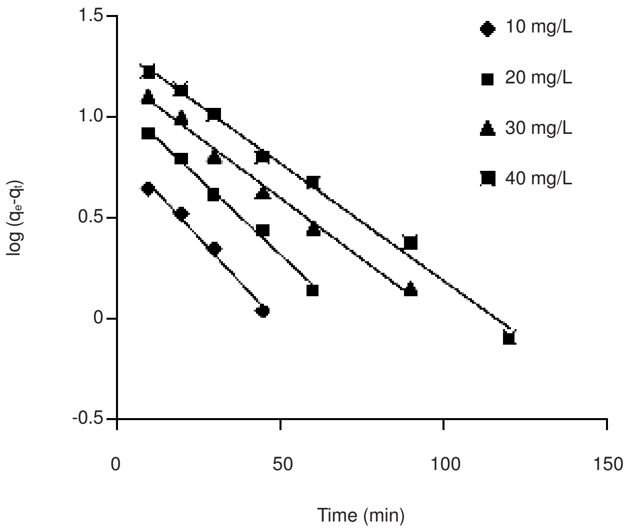

Fig. 6. Pseudo-first order plot-Initial acid blue-92 concentration variation (Temp: 308 K; Initial pH = 3; Adsorbent dosage: 100 mg/50 mL)

Pseudo-second order kinetic model: The adsorption mechanism over a complete range of the contact time is explained by the pseudo-second order kinetic model[19]. The differential equation is described as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

TABLE-2
RESULTS OF KINETIC PLOTS FOR THE ADSORPTION OF ACID BLUE-92 ON COCOA SHELL ACTIVATED CARBON AT 308 K

Concentration (mg/L)	Pseudo-first order				Pseudo-second order			
	$K_1 \times 10^{-2}$ (min^{-1})	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	R^2	$K_2 \times 10^{-3}$ (g/mg min)	$q_{e(cal)}$ (mg/g)	h	R^2
10	3.91	8.89	7.03	0.999	9.8	9.6	0.9	0.997
20	3.45	14.48	12.22	0.989	4.0	16.1	1.04	0.997
30	2.76	20.71	16.07	0.989	2.1	23.8	1.19	0.998
40	2.53	26.4	23.01	0.989	1.3	31.2	1.20	0.998

where, q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t, respectively and k_2 is the rate constant of pseudo-second order adsorption (g/mg min).

The linearized form of the above model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

The initial adsorption rate, h (mg/g min), as $t \rightarrow 0$ can be defined as:

$$h = k_2 q_e^2 \qquad (8)$$

A plot of t/q_t *versus* t gives a linear relationship (Fig. 7), from which q_e and k_2 can be determined from the slope and intercept of the plot respectively (Table-2). The calculated values of q_e show good agreement with experimental data. The correlation coefficient R^2 was close to unity. Thus the sorption of acid blue-92 by cocoa shell activated carbon could be approximated more appropriately by the pseudo-second order model, supporting the assumption of chemisorptions as the rate-limiting mechanism through sharing or exchange of electrons between sorbent and sorbate[20].

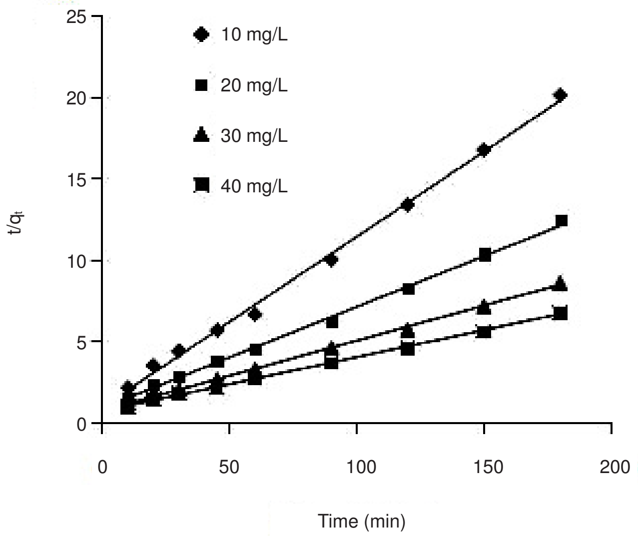

Fig. 7. Pseudo-second order plot-initial acid blue-92 concentration variation (Temp: 308 K; Initial pH = 3; Adsorbent dosage: 100 mg/ 50 mL)

Conclusion

It is reasonable to conclude that the present investigation focuses on the adsorption of acid blue-92 from aqueous solution using cocoa shell activated carbon as low-cost adsorbent. The adsorption characteristics have been examined by initial pH, contact time, initial concentration and adsorbent dose. The experimental data were evaluated by the Langmuir and Freundlich isotherms. Equilibrium data were well fitted to Langmuir model followed by Freundlich isotherm model. Kinetic studies showed that the adsorption process followed the pseudo-second order model. Based on the data of present study, it could be employed that cocoa shell activated carbon is an effective adsorbent for the removal of acid blue-92 from aqueous solution.

REFERENCES

1. Z. Zhang, R.E. Levin, J.L. Pinkham and K. Shetty, *Proc. Biochem.*, **34**, 31 (1999).
2. R. Ahamad and R. Kumar, *Appl. Surf. Sci.*, **257**, 1628 (2010).
3. A. Mittal, J. Mittal, A. Malviya and V.K. Gupta, *J. Coll. Interf. Sci.*, **340**, 16 (2009).
4. M. Muthukumar and N. Selvakumar, *Dyes Pigments*, **62**, 221 (2004).
5. S. Papic, N. Koprivanac, A.L. Bozic and A. Metes, *Dyes Pigments*, **62**, 291 (2004).
6. S. Chakraborty, S. De, J.K. Basu and S. Dasgupta, *Desalination*, **174**, 73 (2005).
7. V.L. Grimaa and M.C. Guiterrez, *Chemosphere*, **62**, 106 (2006).
8. D. Suns, X. Zhang, Y. Wu and X. Liu, *J. Hazard. Mater.*, **181**, 335 (2010).
9. N. Kannan and M.M. Sundaram, *Dyes Pigments*, **51**, 25 (2001).
10. M. Namasivayam, R. Radhika and S. Suba, *Waste Manag.*, **21**, 381 (2001).
11. A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, ELBS, London, edn. 3 (1969).
12. A.H. Mahri, A. Makki and A. Eslami, *Am. J. Appl. Sci.*, **1**, 321 (2004).
13. P.N. Palanisamy and P. Sivakumar, *Desalination*, **249**, 388 (2009).
14. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
15. S. Manocha, V.B. Chauhan and L.M. Manocha, *Carbon Sci.*, **3**, 133 (2002).
16. H.M.F. Freundlich, *Z. Phys. Chem.*, **57**, 385 (1906).
17. R.K. Trey Bell, Mass Transfer Operations, McGraw Hill, New York, edn. 10 (1998).
18. S. Lagergren, *Kung Sven. Veten. Hand.*, **24**, 1 (1898).
19. Y.S. Ho and G. McKay, *Proc. Biochem.*, **34**, 450 (1999).
20. Z. Belala, M. Jeguirim, M. Belhachemi, F. Addoun and G. Trouve, *Desalination*, **271**, 80 (2011).