

Removal of Disperse Dyes from Aqueous Solution Using Sawdust and BDTDA-Sawdust

P. B. Rai, S. S. Banerjee, and R. V. Jayaram

Department of Chemistry, Institute of Chemical Technology, University of Mumbai, Mumbai, India

The adsorption of two disperse dyes, disperse blue 56 and disperse red from aqueous solution onto sawdust (SD) and benzyldimethyltetradecyl ammonium (BDTDA) treated sawdust has been studied. The effect of initial concentration of dyes, pH, and contact time has been studied. The pH had a considerable influence on adsorption and optimum pH for adsorption of disperse dyes is found to be in the range of 2–3. The experimental data were analyzed using Langmuir and Freundlich adsorption isotherm equations. The experimental data were fitted well to pseudo first order kinetic model with $R^2 > 0.99$. The results indicate that sawdust modified with surfactant can be employed as a low cost alternative to commercial activated carbon for the removal of disperse dyes.

Keywords Adsorption, sawdust, BDTDA treated sawdust, disperse dyes, Langmuir equation, Freundlich equation

1 INTRODUCTION

India is one of the largest producers and end user of dyes and pigments and caters to the need of various industrial segments, viz. textiles, tannery, paper, paints and plastics, etc. The effluent discharges from industries have color and are reported to have low BOD and high COD. Untreated color can cause hazards to the environment due to the presence of large number of contaminants. Some of dyes are carcinogenic and mutagenic because they were formerly made of hazardous chemical such as benzidine, metals, etc.^[1] The discharge of colored wastes into receiving water bodies not only affect their aesthetic nature but also interferes with transmission of sunlight there by reducing photo synthetic activity.^[2] This disturbs the natural equilibrium by affecting aquatic life and food chain.

Due to chemical stability of dye components, conventional wastewater treatment technologies are often ineffective for handling wastewater containing synthetic dyes.^[3] Adsorption on activated carbon has been proven to be effective process for dye removal it is an expensive adsorbent. Consequently, numerous low cost alternatives to activated carbon have been proposed including peanut hulls,^[4] waste coir pith,^[5] and barley husk,^[6] sawdust.^[7,8]

Since the disperse dyes are low soluble in water and does not have significant charge on them which makes it difficult to remove from wastewater. Sawdust is inherently hydrophilic, thus, the surface of sawdust has to be modified to improve the efficacy for adsorption of disperse dyes. The treatment of surface of sawdust with cationic surfactant makes it organophilic thereby increasing the affinity for disperse dyes.

The objective of the present work is to evaluate the effectiveness of the BDTDA treated sawdust in removal of disperse dyes from aqueous solution. The effect of initial concentration, pH and time on the adsorption of dyes by sawdust and BDTDASD were investigated. The Langmuir and Freundlich isotherm equations were used to fit the equilibrium data.

2 MATERIALS AND METHODS

2.1 Materials

Sawdust was procured from the local timber saw mill, Thane, India. It was washed several times with distilled water to remove water-soluble impurities. It was then dried at 80°C for 24 hours. After drying, it was sieved using ASTM standard sieves 100 mesh to obtain particle size of ≥ 150 micron and stored in airtight container for further use.

The disperse dyes used in the adsorption studies were disperse red (C.I. No. 11079), disperse blue 56 (C.I. No. 63285) were provided by Clariant chemicals, India. These dyes were commercial grade and used as an adsorbate without further purification. Cationic surfactant samples were purchased from Aldrich Chemical Co. All other reagents used were analytical grade purchased from Merck, India.

Received 20 July 2006; Accepted 13 September 2006.

Address correspondence to R. V. Jayaram, Department of Chemistry, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400019, India. E-mail: rai_uict@yahoo.co.in or rvjayaram@udct.org

2.2 Modification of Sawdust with Cationic Surfactant

30 g of sawdust was treated with 1000 ml of benzyl dimethyltetradecyl ammonium bromide (BDTDAB) solution in 2 l flask at concentration of 0.01 M in an amount slightly excess than cation exchange capacity (CEC) of sawdust (170 mM/Kg). The mixture was agitated with mechanical stirrer at 250 rpm for 24 hours. After agitation, it was then washed with distilled water repeatedly until free of halide ions as indicated by precipitation test with AgNO_3 . The sample was dried in oven at 80°C for 24 hours. It was then sieved using ASTM standard sieves 100 mesh to obtain particle size of ≥ 150 micron stored in air tight container.

2.3 Adsorption Studies

Batch experiments were carried out by agitating 100 mg of adsorbent with 100 ml of solution containing desired concentration of dye placed in series of Erlenmeyer flask of 250 ml capacity. The effect of pH was studied by adjusting the pH of solution with 0.1 N HCl and 0.1 N NaOH. After shaking for 3 hours in an orbital shaker (200 rpm) the solutions were centrifuged and the final pH of solutions was measured. The solutions were centrifuged and the supernatant liquid was analyzed by absorbance measurements at the respective λ_{max} using UV-Visible Jasco spectrophotometer V-530, Japan with 1 cm quartz cell for the quantitative estimation of the dye.

To study the effect of contact time and temperature, experiments were carried out by treating 1 g of SD and BDTDASD with 1000 ml of dye solution containing 150 mg of disperse red and 150 mg of disperse blue-56 at pH 7 in fully baffled reactor fitted with overhead stirrer (200 rpm) and temperature controller ($\pm 2^\circ\text{C}$). After definite time interval the samples were withdrawn and centrifuged at 8,000 rpm for 10 minutes and concentration of dyes were determined in supernatant. The amount of dye adsorbed q (mg/g), was calculated by following mass balanced relationship,

$$q = (C_o - C_e) v/m,$$

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

2.4 Characterization Methods

The cation exchange capacity of sawdust was determined with methylene blue method.^[9] The Brunauer- Emmet-Teller (BET) surface area (m^2/g) was obtained by nitrogen adsorption-desorption isotherm at -196°C in ASAP 2010 Apparatus Micromeritics Co., USA. Surface texture study of sawdust was done with scanning electron microscopy (SEM) using Philips XL-30 instrument (the Netherlands). Infrared spectra were recorded on FT-IR spectrometer Jasco FT-IR 420 (Japan). The spectra were recorded at a resolution of 4 cm^{-1} per second.

3 RESULT AND DISCUSSION

3.1 Characterization of the Adsorbents

The SD was characterized by standard techniques^[10] and the characteristics of SD are given in Table 1. The SEM photomicrograph of untreated and BDTDA treated SD are shown in Figures 1 and 2. Figure 1 clearly reveals the porous nature of SD, Figure 2 shows the change in texture of SD on treatment due to the presence of BDTDA on the surface.

The FT-IR spectra were recorded in the region $400-4000 \text{ cm}^{-1}$. FTIR spectra of sawdust and surfactant treated sawdust were shown in Figures 3 and 4. The strong band at 3460 cm^{-1} is due to -OH stretching. The band at 1634 cm^{-1} is attributed H-O-H bending. The band at 2356 cm^{-1} is attributed to -OH stretching. The bands at 2928 cm^{-1} corresponds to symmetric and asymmetric stretching vibration of - CH_2 group. It can be seen that FT-IR of BDTDA-SD that the intensity of band at 3460 in SD due to -OH stretching has decreased considerably after surfactant treatment. This confirms the ion exchange mechanism of -OH with cationic surfactant. Also the band 1458 cm^{-1} correspond to - CH_2 bending adjacent to $> \text{N}^+ <$ BDTDASD.^[11]

3.2 Effect of Initial Adsorbate Concentration

Adsorption of disperse dyes viz. disperse red, disperse blue-56 on sawdust and surfactant treated sawdust were studied and the effect of initial dye concentration on adsorption are shown in Figure 5 and 6. It can be seen that adsorption of disperse dye increases with increase in initial dye concentration. This indicates that initial concentration of dye plays an important role in adsorption. As other variables such as adsorbent dosage,

TABLE 1
Physical characteristics of sawdust

Element	% Composition	% Volatile matter	pH _{pzc}	Particle size (micron)	BET surface area (m^2/g)
C	50				
N	1.2	7.5	5.5	≥ 150	12.50
O	6.2				

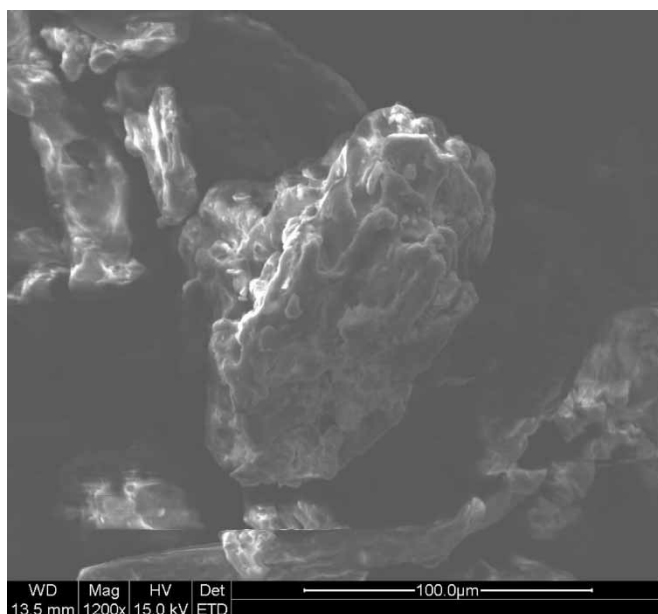


FIG. 1. SEM photomicrograph of untreated SD.

pH, agitation speed, kept constant, the dye concentration affect diffusion of dye molecule through the solution to surface of adsorbent. Higher concentration resulted in higher driving force of concentration gradient. This driving force accelerated the diffusion of dye from solution to the adsorbent.^[8] However, after particular concentration saturation takes place, this may be due to monolayer formation on active sites of the adsorbent surface.

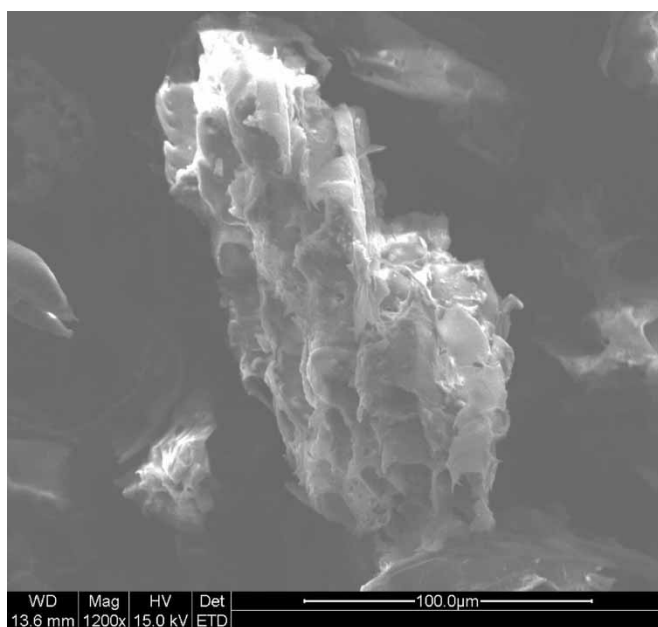


FIG. 2. SEM photomicrograph of BDTDASD.

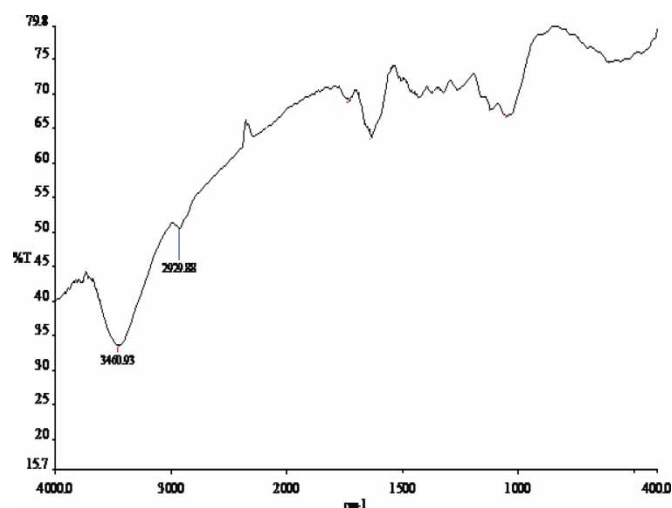


FIG. 3. FTIR spectra of untreated SD.

3.3 Effect of pH

The effect of pH on the adsorption of disperse dyes (disperse red, disperse blue-56) onto sawdust and BDTDA treated sawdust from aqueous solution is shown in Figures 7 and 8. It was observed that maximum adsorption of both the dyes was achieved at pH 2. As the pH increases from 2 to 5 adsorption of disperse dye on SD and BDTDASD decreases considerably. Thereafter from pH 5–10, the adsorption of disperse dye remains almost constant for BDTDASD and continues to decrease for SD.

At lower pH positive charge dominates the surface of adsorbent, thereby increasing the electrostatic attraction between negatively charge dye species and positively charged adsorption sites and causing an increase in adsorption.^[12] The high adsorption of BDTDASD is due to high affinity of $-N^+(R)_3$ of surfactant modified sawdust for the dye anions. When pH of the solution increases the positive charge on solution

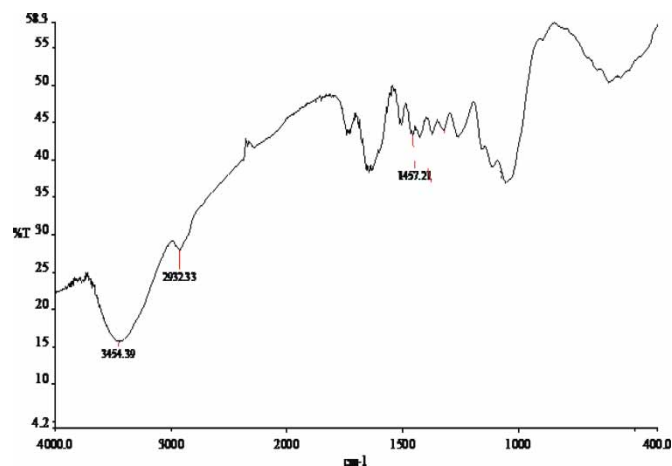


FIG. 4. FTIR spectra of BDTDASD.

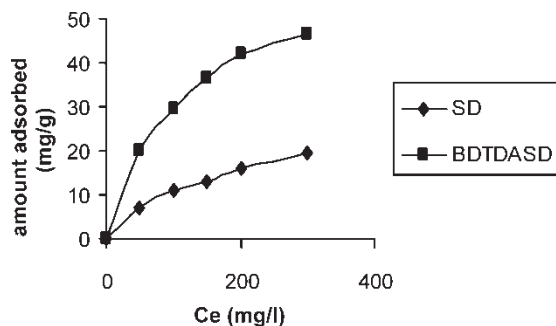


FIG. 5. Effect of initial concentration of disperse blue-56 on SD and BDTDA SD.

interface decreases and adsorbent surface appears negatively charged. This does not favor adsorption due to electrostatic repulsion. At the same time, presence of excess OH⁻ ion in alkaline medium will compete with dye anion for the adsorption site.^[13] But still adsorption takes place at high pH this can be due to hydrophobic interaction between dyes and hydrophobic sites on adsorbent.

3.4 Adsorption Isotherms

The analysis of equilibrium data for the adsorption of disperse dyes onto surfactant modified SD has been done using the linear forms of Langmuir and Freundlich isotherm equation.^[14,15]

The linear form Langmuir isotherm equation can be represented as

$$C_e/q_e = 1/Q_0b + C_e/Q_0, \quad [1]$$

where,

q_e = equilibrium concentration of adsorbate in solid phase (mg/g),

C_e = equilibrium concentration of adsorbate in liquid phase (mg/L),

Q_0, b = Langmuir constant.

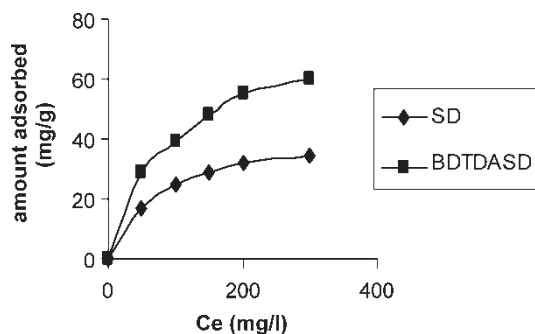


FIG. 6. Effect of initial concentration of disperse red on SD and BDTDA SD.

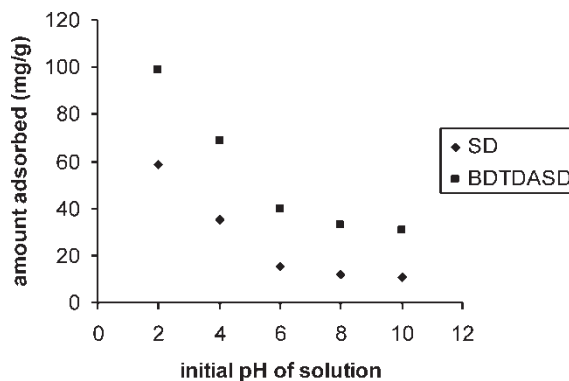


FIG. 7. Effect of initial pH of disperse blue-56 on SD and BDTDASD.

Freundlich isotherm equation is another most widely used experimental equation in adsorption measurements and is given by

$$\log q_e = \log K_f + 1/n \log C_e, \quad [2]$$

where,

C_e = equilibrium concentration of the solute in solution (mg/L),

q_e = amount adsorbed at equilibrium and

K_f = constants for given adsorbate/adsorbent.

Linear plots of $\log q_e$ against $\log C_e$ and C_e/q_e against C_e (plots not shown) for two disperse dyes yielded the constant of Freundlich and Langmuir co efficient as shown in Table 2. Both Langmuir and Freundlich isotherm were found to be fit well to the experimental data with former being slightly better as indicated by R^2 values.

3.5 Adsorption Kinetics

Kinetic models were examined to investigate the mechanism and the potential rate controlling process such as mass transfer and chemical reaction. The pseudo first order and pseudo second order kinetics kinetic model were used to analyze the adsorption kinetic for disperse dyes. The two kinetic models and their linear form are as follows:

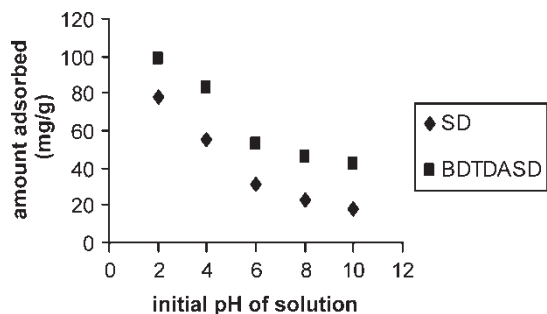


FIG. 8. Effect of initial pH of disperse red on SD and BDTDASD.

TABLE 2
Adsorption isotherm constants for adsorption of disperse dyes onto SD and BDTDASD

Freundlich constant					Langmuir constant				
Adsorbate	Adsorbent	K_f	n	R^2	Adsorbate	Adsorbent	Q_0	b	R^2
Disp blue	SD	1.016	1.87	.972	Disp blue	SD	28.8	0.171	.996
	BDTDASD	5.273	2.48	.981	Disp blue	BDTDASD	57.1	0.018	.992
Disp red	SD	5.39	2.93	.957	Disp red	SD	39.3	0.026	.998
	BDTDASD	13.3	3.25	.985	Disp red	BDTDASD	68.4	0.014	.995

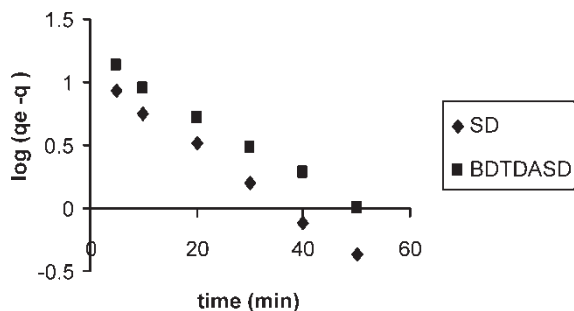


FIG. 9. Pseudo first order plot for disperse blue-56 on SD and BDTDASD.

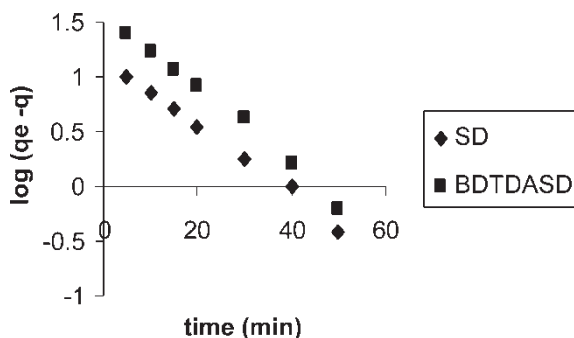


FIG. 10. Pseudo first order plot for disperse red on SD and BDTDASD.

3.5.1 Pseudo First Order Kinetic Model

The adsorption of disperse dyes onto SD and BDTDASD may involve chemical adsorption, the sorption kinetics may be described by pseudo first order equilibrium^[16]

$$dq/dt = k_1(q_e - q), \tag{3}$$

where k_1 is the rate constant, integrating Equation (3) for the boundary condition $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ and rearranging yields the linear time dependent function,

$$\log(q_e - q) = \log q_e - k_1/2.303t. \tag{4}$$

3.5.2 Pseudo Second Order Kinetic Model

A pseudo second order kinetic model may also be described the kinetic of adsorption. According to Hamadi et al.^[17] the differential equation for this reaction is,

$$dq/dt = k_2(q_e - q)^2. \tag{5}$$

Integrating Equation (5) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ and rearranging in the linear form,

$$t/q = 1/k_2 q_e^2 + t/q_e, \tag{6}$$

where q_e and q are the amount adsorbed at equilibrium and time t , respectively. Figures 9 and 10 shows linear plots of pseudo first order model for disperse blue and disperse red. The values of k_1 , k_2 , and R^2 are given in Table 3. The result shows good agreement of experimental data with pseudo first order model. As can be seen from Table 3 the correlation co

TABLE 3
Kinetic parameter for the adsorption of disperse dyes onto SD and BDATA SD

Pseudo first order kinetic constant				Pseudo first order kinetic constant			
Adsorbate	Adsorbent	K_1 (min^{-1})	R^2	Adsorbate	Adsorbent	K_2 ($\text{mg}^{-1} \text{min}^{-1}$)	R^2
Disp blue	SD	0.0474	0.992	Disp blue	SD	0.0029	0.953
	BDTDASD	0.0518	0.995	Disp blue	BDTDASD	0.000142	0.923
Disp red	SD	0.0502	0.997	Disp red	SD	0.000235	0.964
	BDTDASD	0.0656	0.995	Disp red	BDTDASD	0.000041	0.923

efficient for pseudo first order kinetic model were greater than 0.99 for all cases and calculated values of q_e were good agreement the experimental data. It can be therefore inferred that both the dye adsorption system followed pseudo first order kinetic model.

CONCLUSION

The present study shows that surfactant treated sawdust can be used as adsorbent for the removal of disperse dyes from aqueous solution.

The surface charge on adsorbent and solution pH plays significant role in influencing the capacity of adsorbent towards dye ions. Decreases in the pH of solution leads to significant increase in adsorption capacities of disperse dyes on SD and BDTDASD.

The adsorbed amount of dyes increased with increase in contact time and reached equilibrium after 60 minutes. The equilibrium time is independent of initial dye concentration.

The equilibrium data have been analyzed using both Freundlich and Langmuir equations. The Langmuir isotherm showed best fit for adsorption of disperse dyes on SD and BDTDASD to equilibrium data over entire concentration range studied.

The adsorption of disperse dyes is found to be following pseudo first order kinetic model.

REFERENCE

- [1] Ozacar, M. and Sengil, A.I. (2003) Adsorption of reactive dyes on calcined alunite solution. *J. Hazard. Mat.*, 98: 211–224.
- [2] Namasivayam, C., Radhika, R., and Suba, S. (2001) Uptake of dyes by promising locally available agricultural solid waste: Coir pith. *Waste Management*, 21: 381–387.
- [3] Forgacs, E., Cserhati, T., and Oros, G. (2004) Removal of synthetic dyes from wastewater: a review. *Environmental International*, 30: 953–971.
- [4] Ernst, W.R. (1979) Adsorption of textile dyes from aqueous solution by activated carbon from peanut hulls; Georgia Institute of Technology, Atlanta.
- [5] Namasivayam, C., Kumar, M.D., Selvi, K., Begun, R.A., Vanathi, T., and Yamuna, R.T. (2001) Waste coir pith—A potential biomass for the treatment of dyeing wastewater. *Biomass and Bioenergy*, 21: 477–483.
- [6] Robinson, T., Chandran, B., and Nigam, P. (2002) Removal of dyes from an artificial textile dye effluent by two agricultural waste residue, corncob and barley husk. *Environmental International*, 28: 29–33.
- [7] Garg, V.K., Amita, M., Kumar, R., and Gupta, R. (2004) Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rosewood sawdust: a timber industry waste. *Dyes Pigments*, 63: 243–250.
- [8] Ozacar, M. and Sengil, A.I. (2005) Adsorption of metal complex dyes from aqueous solution by pine sawdust. *Bioresource Technol.*, 96: 791–795.
- [9] Taylor, R.K. (1985) Cation exchange in clays and mud rocks by methylene blue. *J. Chemical Technol. Biotechnol.*, 35: 195.
- [10] Vogel, A.I. (1989) *Text Book of Qualitative Chemical Analysis*, 5th edn; ELBS Publication: London.
- [11] Nakanishi, K. and Solomon, P. (1977) *Infrared Absorption Spectroscopy*; Holden-Day, Inc.: San Francisco.
- [12] Ozcan, A.S. and Ozcan, A. (2004) Adsorption of acid dyes from aqueous solution onto acid activated bentonite. *J. Colloid Interface Sci.*, 276 (1): 39–46.
- [13] Wu, Z., Ahn, I.S., Lee, C.H., Kim, J.H., Shul, Y.G., and Lee, K. (2004) Enhancing the organic dye adsorption on porous xerogels. *Colloid Surface A*, 240 (1–3): 157–164.
- [14] Langmuir, I. (1916) The constitution and fundamental properties of solid and liquid. *J. Am. Chem. Soc.*, 38 (11): 2221–2295.
- [15] Freundlich, H.M.F. (1906) Uber die adsorption losungen zetschrift fur physikalische chemie. *J. Phys. Chem.*, 57: 385–470.
- [16] Lagergren, S. (1898) About the theory of so called adsorption of soluble substances. *Ksver Vetwrskapsakad Hand I*, 898 (24): 1–6.
- [17] Ho, Y.S. and McKay, G. (1999) Pseudo second order kinetic model for sorption processes. *Process Biochem.*, 34: 451–465.

Copyright of Journal of Dispersion Science & Technology is the property of Taylor & Francis Ltd and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.