Adsorptive removal of phthalate ester (Di-ethyl phthalate) from aqueous phase by activated carbon: A kinetic study

S. Venkata Mohan, S. Shailaja, M. Rama Krishna, P.N. Sarma *

Biochemical and Environmental Engineering Center, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Abstract

Adsorptive studies were carried out on Di-ethyl phthalate (DEP) removal from aqueous phase onto activated carbon. Batch sorption studies were performed and the results revealed that activated carbon demonstrated ability to adsorb DEP. Influence of varying experimental conditions such as DEP concentration, pH of aqueous solution, and dosage of adsorbent were investigated on the adsorption process. Sorption interaction of DEP onto activated carbon obeyed the pseudo second order rate equation. Experimental data showed good fit with both the Langmuir and Freundlich adsorption isotherm models. DEP sorption was found to be dependent on the aqueous phase pH and the uptake was observed to be greater at acidic pH.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Phthalate; Di-ethyl phthalate; Adsorption; Activated carbon; HPLC; Kinetic models; Isothermal models

1. Introduction

Phthalates are mainly used as plasticizers for cellulosic and some vinyl ester resins. Other uses of phthalates are in ceramic, paper, cosmetic, ink, and paint industries. These industries discharge phthalates in their wastewaters. Phthalates are known to be chemicals, which are hazardous to human health and fertility as they can be readily adsorbed through the skin. They have been linked to birth defects, organ damage, infertility, and cancer. They are also known to be among the endocrine-disrupting compounds [1,2]. Di-ethyl phthalate (DEP) is one of the important molecules in the family of phthalate esters, which has wide industrial applications. USEPA [3] estimated that 300 metric tonnes of DEP would be released annually to surface water as a result of manufacturing, use, or disposal, based on 1977 production data. DEP is used to manufacture industrial products as solvent [4]. DEP is designated as a toxic pollutant under the Clean Water Act and is also regulated under the Emergency Planning and Community Right-to-Know Act, Comprehensive Environmental Response, Compensation and Liability Act, and the Resource Conservation and Recovery Act

[5]. The destruction of phthalates may be achieved by biological treatments [6,7] or photocatalytic techniques [8]. However, the main drawbacks of these biological processes are that the complete degradation/removal is seldom achieved [9]. Therefore, nondestructive techniques seem to be attractive [10–13]. Among the various treatments, adsorption process has an edge over the other methods due to its sludge-free, clean operation and complete removal from the dilute solutions [14]. Adsorption onto the activated carbon is proved to be one of the effective and reliable physicochemical nondestructive treatment methodology [15]. Relatively few studies are reported with reference to adsorption process for phthalate removal from aqueous phase [16–19].

This study focuses on the adsorption of DEP onto the activated carbon from aqueous phase. The effect of various parameters such as contact time, initial concentration, carbon dosage, and operation pH has been investigated. The kinetic data on sorption studies are processed to understand the sorption mechanism of DEP onto the activated carbon.

2. Materials and methods

2.1. Chemicals

Activated charcoal of geometric mean (Gm) size 70 μ (surface area, 500 m²/g; Methyle Blue adsorption, 180 mg/g; loss

* Corresponding author. Tel.: +91 40 271 931 59.
E-mail addresses: kousik@iictnet.org, sarma1950@yahoo.com (P.N. Sarma), vmohan_s@yahoo.com (S. Venkata Mohan).
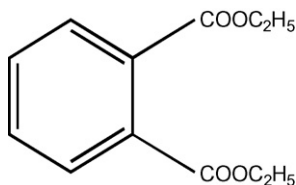
Fig. 1. Structure of Di-ethyl phthalate (DEP).

on drying, 10% (120 °C); residue on ignition, 5% (600 °C)) (E-Merck) was used as an adsorbent in this study. Analytical grade DEP (purity >99%, E-Merck) was used in all the experiments. Its molecular weight is 222.24 has a boiling point of 298–299 °C and aqueous solubility of 1.1 g/l. The structure of DEP is shown in Fig. 1. Stock solution of DEP was prepared by dissolving 50 mg in 1000 ml of double glass distilled water. The stock solution was then appropriately diluted to get the test solution of desired DEP concentration.

2.2. Batch sorption experiments

Batch sorption experiments were performed adopting bottle point method as described by Venkata Mohan et al. [20,21]. In this method, each independent bottle represented one point on the graph containing the adsorbent and DEP mixture in order to get accurate results. A series of 250 ml stopper glass bottles with 0.1 g of activated carbon are taken and 100 ml of solution containing DEP concentration of 0.5, 1.0, 2.0, and 3.0 mg/l. DEP is added in separate bottles and the adsorption mixture was agitated for a pre-determined time period (200 min) using horizontal shaker (temperature, 30 °C; agitation, 100 rpm; activated carbon, 0.1 g; contact time (till equilibrium), 120 min; pH 7.0). Sorption kinetics were determined by analyzing uptake of the DEP from aqueous solution at different time intervals of 30, 60, 90, 120, 150, 180, and 200 min. Isothermal studies were conducted to determine the sorption capacity and intensity by adding various doses of sorbent (0.2–1.0 g) and agitated the reaction mixture for the equilibrium time (temperature, 30 °C; agitation, 100 rpm; DEP, 1.0 mg; adsorption (contact) time, 120 min; pH 7.0). Influence of the aqueous phase pH on DEP sorption was studied by adjusting the reaction mixture to different initial pH values from 2 to 10.5 (concentration, 10 mg DEP; activated carbon, 0.1 g/l; temperature, 30 °C; agitation, 100 rpm; contact time, 120 min). Aqueous phase pH was maintained using 0.1 M HCl and 0.1 M NaOH solutions.

2.3. Analysis

The residual DEP concentration in the aqueous phase was analyzed by high-performance liquid chromatography (HPLC) with acetonitrile and water as eluents (9:1) using reverse phase C18 column (250 mm × 4.6 mm, 5 μ particle size) and UV–vis detector at 225 nm (flow rate of 0.5 ml/min; 20 μl sample). The pH was maintained using a pH meter (Denver, model 20, USA).
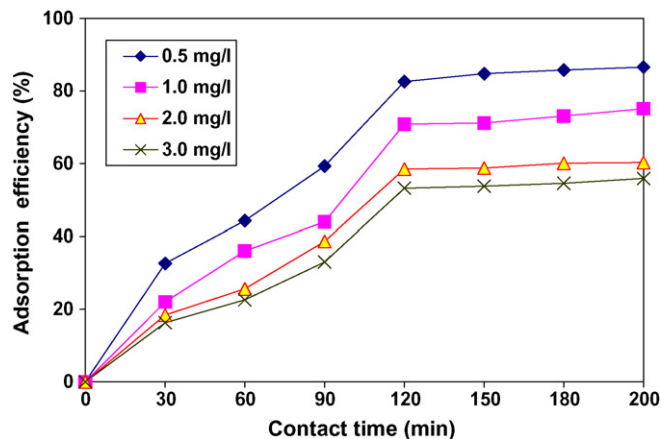

Fig. 2. Variation of DEP sorption onto *activated carbon* (a) Influence of contact time on the sorption capacity [temperature, 30 °C; agitation, 100 rpm; activated carbon, 0.1 g/l; pH 7.0].

3. Results and discussion

3.1. Sorption kinetics

The effect of contact time on the adsorptive removal of DEP was depicted in Fig. 2. The rate of DEP removal was rapid initially and slowed down gradually after it attained equilibrium. After 120 min there is almost no adsorption, that is rate of adsorption is almost zero. The initial rapid sorption was perhaps due to participation of specific functional groups and active surface sites [14,21] in the adsorptive removal of the DEP. A large fraction of the DEP was removed within 120 min of the contact time in all the experiments studied. The DEP removal efficiency (120 min) showed a decreasing trend gradually from 82.6 to 53.2% with increase in the aqueous phase DEP concentration from 0.5 to 3.0 mg/l. The effect of the dosage of activated carbon on the sorption removal of DEP was studied at 10 mg/l of DEP concentration (Fig. 3). DEP sorption increased with the
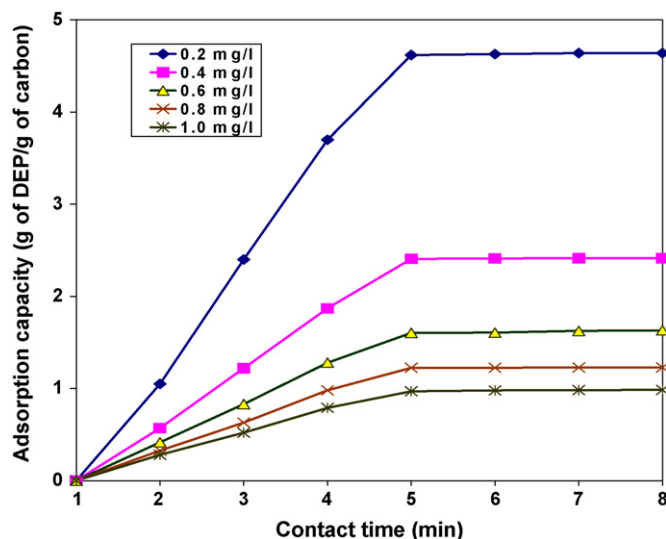

Fig. 3. Influence of activated carbon dose on the sorption capacity [temperature, 30 °C; agitation, 100 rpm; concentration, 1.0 mg/l DEP; pH 7.0; contact time, 120 min].
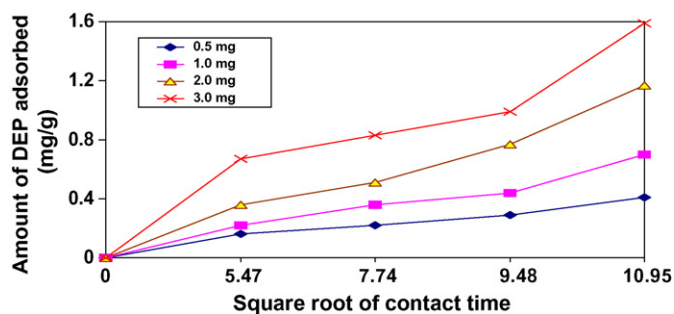
Fig. 4. Intraparticle diffusion model of activated carbon–DEP sorption system [temperature, 30 °C; agitation, 100 rpm; activated carbon, 0.1 g; pH 7.0].

Table 1
Summary of sorption data evaluated by different kinetic models

Kinetic model	Initial DEP concentration (mg/l)	Rate constant	R^2
Pseudo second order kinetic models	0.5	5.74 g/mg min	0.9747
	1.0	4.03 g/mg min	0.9486
	2.0	2.55 g/mg min	0.9554
	3.0	1.48 g/mg min	0.9311
Intraparticle diffusion model	0.5	0.06 mg/g min$^{0.5}$	0.9664
	1.0	1.08 mg/g min$^{0.5}$	0.9980
	2.0	1.78 mg/g min$^{0.5}$	0.9832
	3.0	2.31 mg/g min$^{0.5}$	0.9705

increase of the dosage of adsorbent. The highest unit adsorption capacity was observed at 1.0 mg/l of activated carbon. The sorption kinetic data obtained from DEP-activated carbon system was studied with different kinetic models [22,23] namely the intraparticle diffusion model [14,22,24] and the pseudo kinetic models [23].

3.1.1. Intraparticle diffusion model

The basic assumption with intraparticle diffusion model is that the film diffusion was negligible and intraparticle diffusion was the only rate-controlling step [14,20,23]. The mathematical expression for the intraparticle diffusion model [24] might be represented as

$$q_t \approx k_p t^{0.5} \tag{1}$$

where q_t represents the fraction of DEP removed (mg/g), k_p represents intraparticle diffusion rate constant (mg/g min$^{0.5}$) and $t^{0.5}$ denotes square root of contact time (min). According to Eq. (1) the plot of fraction of DEP removal (q_t) versus the square root of contact time ($t^{0.5}$) would yield a straight line passing through the origin if the adsorption process obeyed the intraparticle diffusion model. Sorption kinetic data was processed to determine whether intraparticle diffusion was rate limiting (Fig. 4). The plots obtained were of general type, that is, initial curved portion with a final linear portion. The initial curved portions might be attributed to the boundary layer diffusion effect [25], while the final linear portions might be due to intraparticle diffusion effects [25,26]. The sorption data indicated that the sorption removal of the DEP from aqueous phase on to activated carbon was rather a complex process, involving both boundary layer diffusion and intraparticle diffusion. The slope of the linear portion was defined as a rate parameter (k_p) and characteristic of the rate of adsorption in this region where intraparticle diffusion was rate limiting is depicted in Table 1.

3.1.2. Pseudo kinetic models

The pseudo first and second order kinetic models assume that sorption is a chemical reaction and the sorption rate could be determined, respectively, by the pseudo first order and second order reaction rate equations [14].

$$dq_t/dt = k_1(q_e - q_t)^2 \tag{2}$$

$$dq_t/dt = k_2(q_e - q_t)^2 \tag{3}$$

where q_e (mg/g) is the solid phase concentration of the DEP at equilibrium, q_t (mg/g) the average solid phase concentration of DEP at contact time t (min) and k_1 (min^{-1}) and k_2 (g/mg min) are the pseudo first order and pseudo second order rate constants, respectively. If the sorption followed the pseudo first order rate equation, a plot of $\ln(q_e - q_t)$ against contact time 't' should be a straight line. Similarly, t/q_t should change linearly with time 't' if the sorption process obeyed the pseudo second order rate equation. The derived rate constants for both intraparticle diffusion and pseudo second order models with the correlation coefficient R^2 are depicted in Table 1. The intraparticle diffusion model generated the best fit with the sorption kinetic data for the investigated DEP-activated carbon adsorption systems, among the three kinetic models evaluated. The correlation coefficients obtained for intraparticle diffusion model and pseudo second order model were larger than 0.9. The modified pseudo second order equation showed next good fit with the sorption data (>0.9). In the case of pseudo first order rate model, all the correlation coefficients obtained were above 0.63 and less than 0.83 indicating the limited applicability of this model for the investigated activated carbon adsorption system. The DEP-activated carbon system was confining to the intraparticle diffusion model along with modified pseudo second order equation. Reported studies showed that the pseudo second order rate equation was a reasonably good fit of the data over the entire fractional approach to equilibrium and therefore was employed extensively in the study of adsorption kinetics [22,23,26–29]. The applicability of intraparticle diffusion model suggested that adsorptive process of DEP onto the activated carbon is rather a complex process involving both boundary layer and intraparticle diffusion [23,24]. It could be also presumed from the discussion that the modified pseudo second order equation was potentially a generalized kinetic model for the adsorption system under study. The rate constants k_2 [pseudo second order rate constant, g/(mg min)] decreased with increase in the initial concentration of the DEP in the adsorption systems.

3.2. Adsorption equilibrium

Both Langmuir and Freundlich adsorption isotherm models were used for the analysis of the DEP-activated carbon adsorption system. The rearranged Langmuir adsorption isotherm
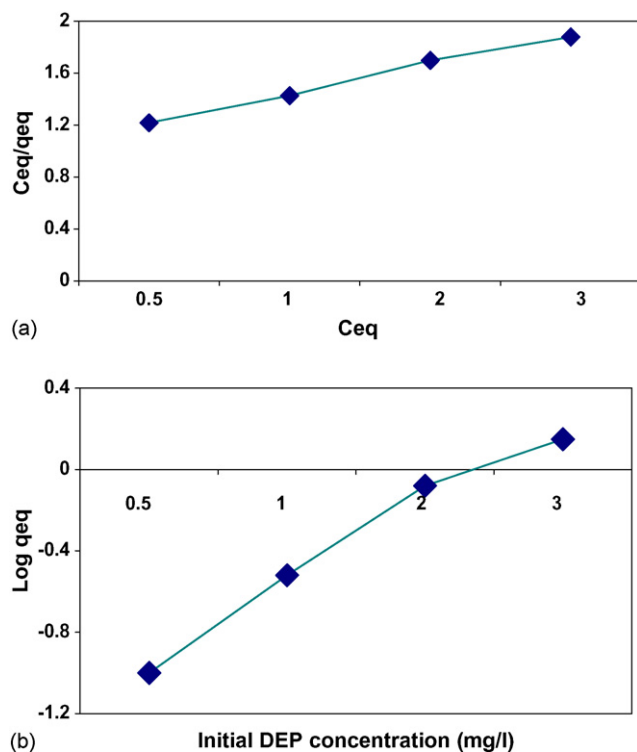
Fig. 5. (a) Langmuir adsorption isotherm plot for activated carbon–DEP sorption system. [Temperature, 30 °C; agitation, 100 rpm; activated carbon, 0.1 g; pH 7.0]. (b) Freundlich adsorption isotherm plot for activated carbon–DEP sorption system [temperature, 30 °C; agitation, 100 rpm; activated carbon, 0.1 g; pH 7.0].

model for evaluating the monolayer adsorption phenomena as depicted in Eq. (4) was used to calculate the maximum adsorption capacity of the adsorbent Q_m (mg/g) and a constant (k_a) related to the affinity of the binding sites (l/mg).

$$C_{eq}/q_{eq} = [1/k_a Q_m] + [C_{eq}/Q_m] \tag{4}$$

The fit of experimental data to linear form of Langmuir adsorption isotherm model shown in Fig. 5(a) with R^2 of 0.9947 indicated the validity of the model for the present system. Hall et al. [30] and Venkata Mohan [31] showed that essential characteristics of a Langmuir adsorption isotherm equation could be expressed in terms of a dimensionless constant called as separation factor or equilibrium factor or equilibrium parameter, 'R_s' which is defined by the following equation,

$$R_s = 1/(1 + K_a C_0) \tag{5}$$

where R_s is the dimensionless constant separation factor; 'a' the Langmuir constant as defined earlier (1/mg); and C_0 is the initial solute concentration (mg/l). The separation factor was calculated using the Langmuir isotherm model constants [24,29,30]. By the value of separation factor the nature of the isotherm could be assessed by the following classification [32]:

$R_s > 1$: unfavorable isotherm;
$R_s = 0$: linear isotherm;
$0 < R_s < 1$: favorable isotherm;
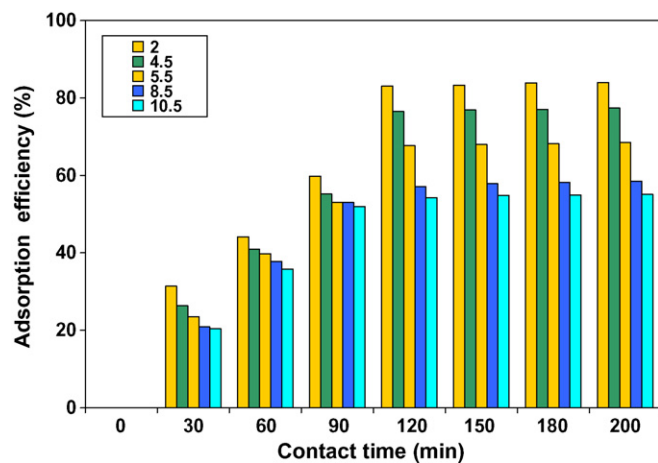$R_s < 0$: irreversible isotherm.

Fig. 6. Influence of aqueous phase pH on sportive removal of DEP [temperature, 30 °C; agitation, 100 rpm; activated carbon, 0.1 g; concentration, 1.0 mg/l DEP].

'R_s' was calculated for the linearized Langmuir adsorption isotherm and found to be 0.77, which can be considered to be a favorable condition.

Freundlich adsorption isotherm model used to study the non-ideal adsorption involving heterogeneous adsorption phenomena was evaluated by the linearized Eq. (6) form

$$Log(q_{eq}) = [1/n \log C_{eq}] + [\log k_f] \tag{6}$$

where k_f and $1/n$ are empirical constants. The fit of experimental data to linear form of Freundlich model is seen in Fig. 5(b) with R^2 of 0.977. On the basis of R^2 values Langmuir model seems to fit better than Freundlich model to DEP-activated carbon adsorption system.

3.3. Influence of pH

Batch sorption experiments were carried out at variable pH values in the range of 2–10.5 to assess the adsorption capacity of DEP (DEP concentration, 1.0 mg/l; activated carbon, 100 mg/l; contact time, 120 min). The removal efficiency was measured after equilibrium contact time (120 min) and the data is depicted in Fig. 6. It is evident from the experimental data that the process of DEP adsorptive is highly dependent on the pH. The extent of adsorption decreased markedly as the pH of the test solution is increased from 2.0 to 10.5. The highest adsorption values were observed at acidic pH 2.0. According to Ayranci and Bayram [17], adsorption phenomena of phthalates can be explained on the basis of hydrophobic and dispersion effects. The hydrophobicity of groups attached to phthalic acid for the formation of esters increases in the order dimethyl phthalate < diethyl phthalate < diallyl phthalate. The sorption phenomena of DEP sorption at neutral pH can be attributed to the hydrophobic interactions which are characterized as unusually strong attraction by Moreno-Castilla [33], between hydrophobic sites of carbon surface and apolar alkyl or allyl groups of phthalates determine the observed order of rate and extent of adsorption [17]. At acidic pH the protonated effect of surface functional groups such as amino, carboxyl, thiol etc., imparted positive charge on the surface [34]. The sorption inhibition observed at basic pH range might be

attributed to the increase of hydroxyl ion leading to formation of aqua-complexes thereby retarding the sorption [20].

4. Conclusions

Batch sorption studies were performed on the removal of DEP from aqueous phase using activated carbon as adsorbent. Adsorption studies showed varied sorption capacity of DEP. Effect of pH and the dosage of activated carbon were studied. DEP-activated carbon interaction showed good fit with pseudo second order rate equation. Isothermal data fitted well with both Langmuir and Freundlich isotherm models.

References

[1] D.B. Peakall, Phthalate esters: occurrence and biological effects, Residue Rev. 54 (1975) 1–41.

[2] J. Ejlerstsson, B. Svensson, A review of the possible degradation of polyvinyl chloride (PVC) plastics and its components phthalic acid esters and vinyl chloride under anaerobic conditions prevailing in landfills, Department of Water and Environmental Studies, Linkoping University, Sweden, 1995, p. 20.

[3] US EPA, Exposure and risk assessment for phthalate esters: Di(2-ethylhexyl) phthalate, di-*n*-butyl phthalate, dimethyl phthalate, diethyl phthalate, di-*n*-octyl phthalate, butyl benzyl phthalate, Final report, Washington, DC, US Environmental Protection Agency (EPA-440/4-81-020), 1981b.

[4] Environmental Protection Agency, National Oceanic and Atmospheric Administration, www.epa.gov/ceppo.

[5] Department of Labor, Occupational Health and Safety Administration, Washington, DC, www.osha.gov.

[6] B.V. Chang, C.S. Liao, S.Y. Yuan, Anaerobic degradation of diethyl phthalate, di-n-butyl phthalate and di-(2-ethyl hexyl) phthalate from river sediment in Taiwan, Chemosphere 55 (4) (2004) 533–538.

[7] S. Venkata Mohan, S. Shailaja, M. Ramakrishna, K.B. Reddy, P.N. Sarma, Bioslurry phase degradation of DEP contaminated soil in periodic discontinuous mode operation: influence of augmentation and substrate partition, Process Biochem. 41 (3) (2006) 644–652.

[8] C.A. Staples, T.F. Parkerton, D.R. Peterson, A risk assessment of selected phthalate esters in North American and Western European surface waters, Chemosphere 40 (2000) 885–891.

[9] D.K. Singh, K. Rastogi, Adsorptive removal of basic dyes from aqueous phase onto activated carbon of used tea leaves: a kinetic and thermodynamic study, J. Environ. Sci. Eng. 46 (2004) 293–302.

[10] R.J. Stephenson, J.B. Sheldon, Coagulation and precipitation of a mechanical pulping effluent, Water Res. 30 (1996) 781–792.

[11] J.A. Laszlo, Removing acid dyes from textile wastewater using biomass for decolourization, Am. Dyest. Rep. 83 (1994) 17–21.

[12] J.H. Churchley, Removing of dye wastewater colour from sewage effluent. The use of full scale ozone plant water, Sci. Tech. 30 (1994) 275–284.

[13] Y. Fu, T. Viraraghavan, Removal of cango red from an aqueous solution by fungus *Aspergillus niger*, Environ. Res. 7 (2002) 239–247.

[14] S. Venkata Mohan, J. Karthikeyan, Removal of lignin and tannin aqueous solution by adsorption onto activated charcoal, Environ. Pollut. 1–2 (1997) 183–197.

[15] M. Sankar, G. Sekaran, S. Sadulla, T. Ramasami, Removal of diazo and triphenylmethane dyes from aqueous solutions through an adsorption process, J. Chem. Technol. Biotechnol. 74 (1999) 337–344.

[16] H.P. Herbert, F.H. Zeng, Adsorption of phthalates by activated sludge and its biopolymers, Environ. Technol. 25 (7) (2004) 757–761.

[17] E. Ayranci, E. Bayram, Adsorption of phthalic acid and its esters onto high-area activated carbon-cloth studied by in situ UV-Spectroscopy, J. Hazard. Mater. (2000) 147–153.

[18] N. Adhoum, L. Monser, Removal of phthalates on modified activated carbon, Sep. Purif. Technol. 38 (2004) 233–239.

[19] M. Bodzek, M. Dudziak, K. Luks-Betlej, Application membrane techniques to water purification. Removal of phthalates, Desalination 162 (2004) 121–128.

[20] S. Venkata Mohan, N. Chandrasekhar Rao, K. Krishna Prasad, J. Karthikeyan, Treatment of simulated reactive yellow 22 (azo) dye effluents using *Spirogyra* species, Waste Manage. 22 (2002) 575–582.

[21] S. Venkata Mohan, S.V. Ramanaiah, B. Rajkumar, P.N. Sarma, Biosorption of fluoride from aqueous phase onto algal *Spirogyra* IO1 and evaluation of adsorption kinetics, Bioresour. Technol. 98 (2007) 1006–1011.

[22] X. Yang, B. Al-Duri, Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon, J. Colloid Interface Sci. 287 (2005) 25–34.

[23] M. Yalcin, A. Gurses, C. Dogar, M. Sozbilir, The adsorption kinetics of cethyl tri methyl ammonium bromide (CTAB) onto powdered active carbon, Adsorption 10 (2004) 339–348.

[24] S. Venkata Mohan, N. Chandrasekhar Rao, J. Karthikeyan, Adsorption removal of direct azo dye aqueous phase onto coal based sorbents—a kinetic and mechanistic study, J. Hazard. Mater. 90 (2) (2002) 189–204.

[25] C.Y. Chang, W.T.T. Sai, C.H. Ing, C.H. Chang, Adsorption of polyethylene glycol (PEG) from aqueous solution onto hydrophobic zeolite, J. Colloid Interface Sci. 260 (2003) 273–279.

[26] C.L. Brierley, H.L. InEhrlich, C.L. Brierly (Eds.), Microbial Mineral Recovery, McGraw-Hill, New York, 1990, pp. 303–324.

[27] L.E. Malaskie, A.C.R. Dean, in: B. Molesky (Ed.), Metals-Sequestering Biochemicals, Biosorption of Heavy Metals, CRC press, Boca Raton, FL, 1990, pp. 199–248.

[28] S. Hunt, B.In. Eeeles, S. Hunt (Eds.), Diversity of Biopolymers Structure and Its Potential for Ion-bonding Applications, Immobilization of Ions by Biosorption, Ellies Horword, Chichester, 1996, pp. 15–45.

[29] S. Venkata Mohan, S.V. Ramanaiah, B. Rajkumar, P.N. Sarma, Removal of fluoride from aqueous by biosorption onto algal biosorbent *Spirogyra sp*-IO1: Sorption mechanism elucidation, J. Hazard. Mater. 141 (2007) 465–474.

[30] K.R. Hall, L.C. Eagleton, A. Acriros, T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.

[31] S. Venkata Mohan, Removal of textile dye colour from aqueous solution by adsorption onto coal/coal based sorbents, Ph.D. Thesis, Sri Venkateswara University, Tirupati, India, 1997.

[32] T.W. Weber, P.K. Chakravorti, Pore and solid diffusion models for fixed adsorbers, J. Am. Inst. Chem. Eng. 20 (1974) 226–237.

[33] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon 42 (2004) 83–94.

[34] T. Ilhami, B. Gulay, Y. Emine, B. Gokben, Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto micro algae *Chlamydomonas reinhardtii*, J. Environ. Manage. 77 (2005) 85–92.