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Modeling the mechanism, equilibrium and kinetics for the adsorption of Acid Orange 8 onto surfactant-modified clinoptilolite: The application of nonlinear regression analysis

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Abstract

Adsorption of Acid Orange 8 onto surfactant-modified clinoptilolite was studied conducting batch experiment system. Effect of pH, dye concentration and contact time on the adsorption was evaluated. Equilibrium adsorption data were analyzed by Langmuir, Freundlich, Redlich–Peterson and Koble–Corrigan isotherm equations using nonlinear regression analysis. The adsorption was analyzed using pseudo-first-order and pseudo-second-order kinetic models and pseudo-second-order model provided the best correlation of the experimental data. Adsorption process was found to be controlled by both surface and particle diffusions.

Keywords: Dye removal; Nonlinear regression; Chi-square test; Adsorption; Isotherm; Kinetics

1. Introduction

Dyestuff is used widely in textile industry in order to color the products. Water contamination resulted from dyeing and finishing in textile industry is a major concern since it can cause serious environmental problems due to its high color content. The dyes used in the textile industries include several structural varieties such as acidic, reactive, basic, disperse, azo, diazo, anthraquinone-based and metal complex dyes [1]. Among these, azo dyes are characterized by the presence of the N=N linkage [2] and they are constituting about 20–40% of the total dyes used for coloring [3].

Conventional chemical [4–6] and biological [7–9] treatments have been applied for the removal of dyes from textile wastewater, but these processes are insufficient in removing dye contaminants since dyes are stable to light, heat and oxidizing agents [10]. One of the powerful treatment processes for the removal of dyes from water with a low cost is adsorption [11]. Activated carbon is used mostly for adsorption process but it is very expensive and there is a growing search activity for cheap and efficient alternate natural materials including bentonite and zeolite. Armagan et al. [12,13] showed that surface modification with quaternary amine improves the dye removal efficiency of zeolite, and modified zeolites are comparable to activated carbon.

In this study, surface of clinoptilolite, a natural zeolite mineral, was modified using HTAB chemical and adsorption of Acid Orange 8 onto surfactant-modified clinoptilolite was investigated in a batch system. Equilibrium and kinetic parameters of experimental data were calculated using nonlinear regression with the help of Data Fit (Version 8) software program. Chi-square test was used to evaluate the models which have best fit with experimental data.

2. Materials and methods

The clinoptilolite sample used as an adsorbent in this study was obtained from Esen Foreign Trade Company of Turkey.

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Table 1
Chemical analysis of clinoptilolite

Constituent	Weight (%)
SiO_2	74.4
Al_2O_3	11.5
Fe_2O_3	1.1
K_2O	5.0
MgO	0.5
Na_2O	0.6
CaO	2.0
TiO_2	0.1
MnO_2	<0.001
P_2O_5	0.02
Loss of ignition	5.85

Cation exchange capacity of clinoptilolite is 0.95–1.4 meq/g and its bulk density is 900–1100 kg/m^3. Chemical composition of the clinoptilolite sample is shown in Table 1. A quaternary amine hexadecyltrimethylammonium bromide (HTAB, $C_{19}H_{42}BrN$) was used for modifying the surface of clinoptilolite. HTAB was purchased from Sigma (USA), and specified to be of 99% purity with a molecular weight of 346.46 g. Clinoptilolite crushed and classified to the diameter of 0.6–1.0 mm was conditioned with 2×10^{-2} M HTAB solution for 2 h at room temperature, washed with pure water and dried at 100 °C for 2 h. Acid Orange 8 (AO8) was supplied from Sigma–Aldrich (Germany). The chemical structure and properties of AO8 are given in Fig. 1 and Table 2, respectively.

The adsorption experiments of AO8 on modified clinoptilolite were performed using a batch method. Adsorption experiments were conducted in 50 ml glass vials with 2% solid concentration for the modified clinoptilolite. Adsorption experiments were carried out with Gallenkamp orbital shaker at 200 rpm for the temperatures 30, 40 and 50 °C. The solution pH was adjusted with NaOH or HCl solutions using Jenway pH meter. The equilibrium concentrations of dye were determined using Jenway spectrophotometer and adsorbed amount of dye was calculated by the difference between the initial and remaining concentrations at equilibrium.

3. Results

3.1. Optimum adsorption conditions

Adsorption equilibrium is governed by several operational factors such as the nature of solute and adsorbent as well as the pH and temperature of the medium. Optimization of such operational parameters is the first step toward the understanding of the process [14].

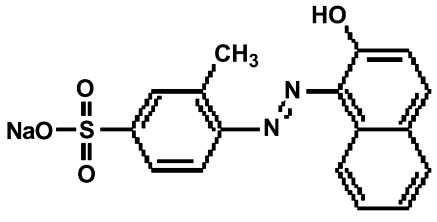

Fig. 1. Structure of Acid Orange 8.

Table 2
Properties of Acid Orange 8

Property	
Chemical formula	$C_{17}H_{13}N_2NaO_4S$
Molecular weight	364.35 g
Structure	Azo
CAS number	5850-86-2
Color index number	15575
Dye content	65%
λ_{max} (nm)	490

In order to determine optimum adsorption conditions, the effect of pH, initial dye concentration and contact time was investigated. Initial pH value of solution is one of the most important factors influencing the dye adsorption. Fig. 2 shows the effect of pH on adsorption capacity of AO8 on modified clinoptilolite at different initial solution pHs for the dye concentration of 25 mg/l and at 30 °C. As seen in Fig. 2, maximum color removal was observed at pH 3. Above pH 3 adsorption capacity is decreasing, since electrostatic attraction decreases between the positively charged clinoptilolite surface and anionic dye molecule at higher pH values [15].

The effect of initial dye concentration on the AO8 adsorption by modified clinoptilolite was investigated in the range of 25–200 mg/l of initial dye concentrations. As shown in Fig. 3, with increasing initial dye concentration from 25 mg/l to 200 mg/l, the amount of dye adsorbed gets increased from 3.11 to 18.98 mg/g for the contact time of 20 min. The effect of contact time on adsorption process was investigated at various initial dye concentrations at 30 °C. It can be seen from Fig. 3 that the adsorption of AO8 occurred very quickly within the first 5 min and this may be indicative of chemical adsorption [16]. After 5 min a gradual increase occurred with increasing contact time up to 20 min after which a maximum value of adsorption capacity was attained.

3.2. Equilibrium isotherms

In the present study the Langmiur, Freundlich, Reclich–Peterson and Koble–Corrigan isotherm models were used to

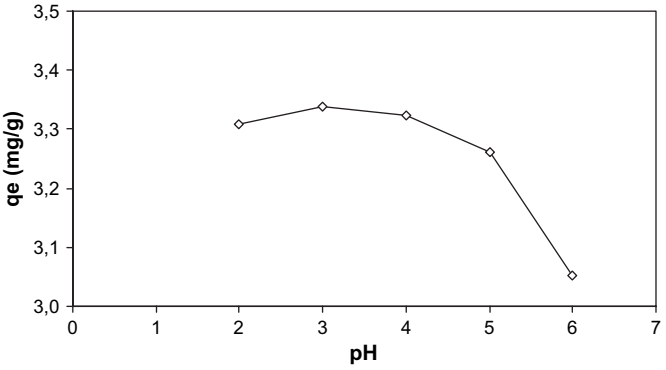

Fig. 2. The effect of pH on the adsorption of Acid Orange 8 (solid ratio: 2%, temperature: 30 °C, agitation rate: 200 rpm, and C_0: 25 mg/l).

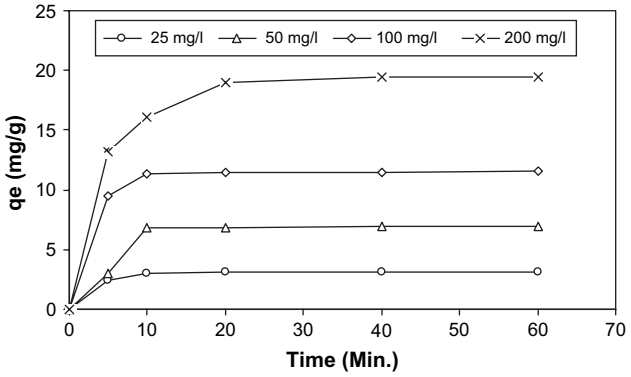

Fig. 3. Effect of initial dye concentration and contact time (solid ratio: 2%, temperature: 30 °C, and agitation rate: 200 rpm).

describe the adsorption equilibrium. Isotherm studies were conducted at an equilibrium time of 20 min and temperature of 30 °C.

Nonlinear least square optimization technique was applied and isotherm parameters were determined with the help of Data Fit software program. The Chi-square test was used as a criterion for the quality of fitting. In this test, squared difference between the experimental data and calculated data is divided by the calculated data obtained from the model. The Chi-square test can be represented by

$$\chi^2 = \sum \frac{(q_{e_{\text{exp.}}} - q_{e_{\text{mod.}}})^2}{q_{e_{\text{mod.}}}} \tag{1}$$

where $q_{e_{\text{exp.}}}$ and $q_{e_{\text{mod.}}}$ (mg/g) are the experimental value and model calculation of adsorption capacity, respectively. The value of χ^2 is used to evaluate the fit of the isotherm to experimental data, where smaller the χ^2, better is the fit.

According to Langmuir isotherm model adsorption takes place at specific homogeneous sites within the adsorbent and once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir equation can be written in the following form:

$$q_e = \frac{QK_{\text{L}}C_{\text{e}}}{1 + K_{\text{L}}C_{\text{e}}} \tag{2}$$

where q_e (mg/g) and C_{e} (mg/l) are the amounts of adsorbed dye per unit weight of clinoptilolite and equilibrium dye concentration in solution. Q (mg/g) is the maximum amount of adsorbed dye per unit weight of clinoptilolite and K_{L} (l/mg) is the adsorption equilibrium constant. Q represents a practical limiting adsorption capacity when the surface of clinoptilolite is fully covered with dye molecules.

The empirical Freundlich model based on adsorption on a heterogeneous surface is given below by Eq. (3).

$$q_e = K_{\text{F}}C_{\text{e}}^{1/n} \tag{3}$$

Here K_{F} and n are the Freundlich constants. K_{F} and n are indicators of adsorption capacity and adsorption intensity, respectively.

The three parameter Koble–Corrigan (K–C) model is the combination of Langmuir and Freundlich models and is given by Eq. (4). This model is valid when $m > 1$ [17].

$$q_e = \frac{AC_{\text{e}}^m}{1 + BC_{\text{e}}^m} \tag{4}$$

Similarly, Redlich–Peterson (R–P) model has three constants and it has been proposed to improve the fit by Langmuir and Freunlich models. Eq. (5) reduces to a linear isotherm at low surface coverage, to the Freundlich isotherm at high adsorbate concentration and to the Langmuir isotherm when $\beta = 1$ [18].

$$q_e = \frac{K_{\text{RP}}C_{\text{e}}}{1 + a_{\text{RP}}C_{\text{e}}^{\beta}} \tag{5}$$

where K_{RP}, a_{RP} and β are the R–P parameters. Value of β is between 0 and 1.

The isotherm constants, their correlation coefficients and value of Chi-square test are listed in Table 3. Value of n constant of Freundlich isotherm ($n = 1.37$) model suggests that AO8 is favorably adsorbed by modified clinoptilolite [19]. By comparing the results presented in Table 3, it is shown that the Langmuir, R–P and K–C isotherms have higher correlation coefficient ($R^2 = 0.9970$) than Freundlich model ($R^2 = 0.9924$). It can be seen that the K–C model yields a better fit than the R–P and Langmuir models, as reflected by a χ^2 value of 0.0866, 0.0952 and 0.0970, respectively.

3.3. Kinetic studies

In order to analyze the adsorption kinetics for the adsorption of AO8, the pseudo-first- and second-order kinetic models

Table 3
Comparison of equilibrium isotherm models

Isotherm	Values
Langmuir	
Q	44.05
K_{L}	0.0047
R^2	0.9967
χ^2	0.0970
Freundlich	
K_{F}	0.46
N	1.37
R^2	0.9924
χ^2	0.2259
R–P	
K_{RP}	0.2061
a_{RP}	0.0049
β	0.99
R^2	0.9967
χ^2	0.0952
K–C	
A	0.18
B	0.0045
m	1.03
R^2	0.9967
χ^2	0.0866

were applied for the temperatures of 30, 40 and 50 °C. The pseudo-first-order kinetic equation based on adsorption equilibrium capacity is expressed in the following form [20].

$$q_t = q_1\left(1 - e^{-k_1 t}\right) \quad (6)$$

Here q_1 and k_1 are constants of pseudo-first-order kinetic model. q_1 and k_1 were determined by nonlinear regression and are given in Table 4.

The pseudo-second-order kinetic model can be written in the following form [20].

$$q_t = \frac{t}{(1/k_2 q_2^2) + (t/q_2)} \quad (7)$$

Values of constants q_2 and k_2 were determined by using Data Fit 8 software and are given in Table 5.

The correlation coefficients (R^2) of the pseudo-first-order model are lower than that of the pseudo-second-order model. The R^2 values for pseudo-second-order model are very close to 1, thus suggesting that the kinetics of Acid Orange 8 adsorption can be described by the pseudo-second-order model. Therefore, the Acid Orange 8 adsorption by clinoptilolite is most likely to be controlled by chemisorption process [21,22].

The rate constant k_2 for pseudo-second-order model decreases with increasing initial dye concentration, which is consistent with the study of Ho and Chiang [23]. q_2 values in Table 5 shows that the equilibrium sorption capacity of Acid Orange 8 increases with increasing temperature which indicates that a higher temperature favors AO8 adsorption onto the clinoptilolite.

3.4. Adsorption mechanism

Determination of adsorption mechanism is required for design purposes and the intraparticle model is commonly used for identifying the adsorption mechanism. Intraparticle equation is written as

$$q_t = k_d t^{1/2} + C \quad (8)$$

The intraparticle diffusion plot for AO8 adsorption is given in Fig. 4. From the figure it can be observed that there are two linear portions. These two linear portions in the intraparticle model suggest that the adsorption process consists of both surface adsorption and intraparticle diffusion. While the initial linear portion of the plot is the indicator of boundary layer effect, the second linear portion is due to intraparticle diffusion [24]. The intraparticle diffusion parameter (k_d) was calculated from the slope of the second linear portion and is given in Table 6. k_d value of Acid Orange 8 adsorption was increased with increasing temperature. The value of C (Table 6) gives an idea about the thickness of the boundary layer, the larger the intercept the greater is the boundary layer effect [25]. Increasing of temperature leads to the increase in boundary layer effect for the adsorption of AO8.

External mass transfer is characterized by the initial solute uptake, and initial sorption rate (K_s) can be calculated from the slope of plot of C/C_0 versus time [26]. The adsorption capacity of AO8 onto clinoptilolite versus contact time is illustrated in Fig. 5. Adsorption of AO8 onto clinoptilolite occurred rapidly within first 10 min of contact time and equilibrium is achieved at 20 min (Fig. 3). In this work, it is assumed that external mass transfer occurs in the first 10 min, and K_s values were calculated as $(C_{10}/C_0)/10$ and are given in Table 6.

Boyd model was used to determine the actual rate-controlling step for the adsorption of AO8. The Boyd kinetic model is written as

Table 4
Pseudo-first-order kinetic constants for AO8 adsorption onto clinoptilolite

Temperature (°C)	C_0 (mg/l)	q_1 (mg/g)	k_1 (l/min)	R^2	χ^2
30	25	3.30	1.5311	0.8388	0.023
	50	10.07	7.8981	0.8911	0.451
	100	11.95	1.0894	0.8435	0.045
	200	20.80	2.7675	0.9754	0.040
40	25	3.31	1.3878	0.8237	0.062
	50	7.58	0.8224	0.9654	0.023
	100	13.88	2.0142	0.9564	0.401
	200	28.85	0.9831	0.9099	1.249
50	25	2.85	0.6983	0.9541	0.004
	50	7.62	1.0213	0.7592	0.278
	100	17.21	3.3342	0.9437	1.382
	200	32.90	0.7675	0.8650	1.695

Table 5
Pseudo-second-order kinetic constants for AO8 adsorption onto clinoptilolite

Temperature (°C)	C_0 (mg/l)	q_2 (mg/g)	k_2 (g/mg min)	R^2	χ^2
30	25	3.20	0.3322	0.9996	0.039
	50	7.41	0.0402	0.9884	0.112
	100	11.68	0.1309	0.9998	0.082
	200	20.32	0.0220	0.993	0.088
40	25	3.22	0.3593	0.9996	0.044
	50	7.60	0.1520	0.9999	0.003
	100	13.51	0.0517	0.9995	0.087
	200	28.87	0.0339	0.9996	0.048
50	25	2.82	0.6438	0.9999	0.002
	50	7.87	0.0743	0.9989	0.089
	100	16.59	0.024	0.9987	0.192
	200	32.47	0.059	0.9999	0.0916

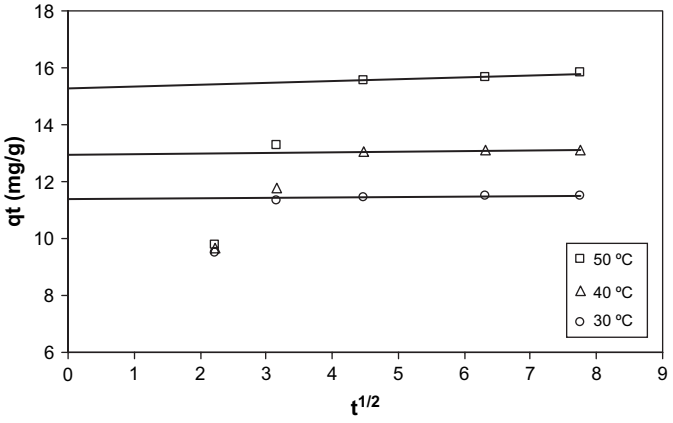

Fig. 4. Plots of intraparticle diffusion model.

Table 6
Intraparticle diffusion model parameters

Temperature (°C)	C (mg/g)	k_d (mg/g min$^{0.5}$)	K_s (min^{-1})
30	11.38	0.018	0.0774
40	12.96	0.022	0.0765
50	15.26	0.070	0.0735

$$F = 1 - \frac{6}{\pi^2} \exp(-\mathrm{Bt}) \tag{9}$$

$$F = -\frac{q_t}{q_e} \tag{10}$$

where F is the fraction of solute adsorbed at any time t and Bt is mathematical function of F. q_t and q_e are amounts of AO8 adsorbed at any time t and infinite time, respectively. In this study, q_2 values of pseudo-second-order model were used as q_e to calculate F values. After substituting Eq. (10) in Eq. (9), Boyd model can be written as below.

$$\mathrm{Bt} = -0.4977 - \ln(1 - F) \tag{11}$$

The Bt values were calculated from Eq. (11) and plotted against time as shown in Fig. 5. It can be seen from Fig. 5, linear plots which do not pass through the origin indicate that film diffusion governs the rate limiting process [27].

4. Conclusions

The amount of dye adsorbed onto surfactant-modified clinoptilolite was found to vary with pH, initial concentration and contact time. Equilibrium was achieved in about 20 min and maximum adsorption capacity was observed at pH 8. Error analysis showed that the Koble–Corrigan model best fits the equilibrium adsorption data. The adsorption kinetics followed the pseudo-second-order model at all time intervals. Adsorption process was found to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages.

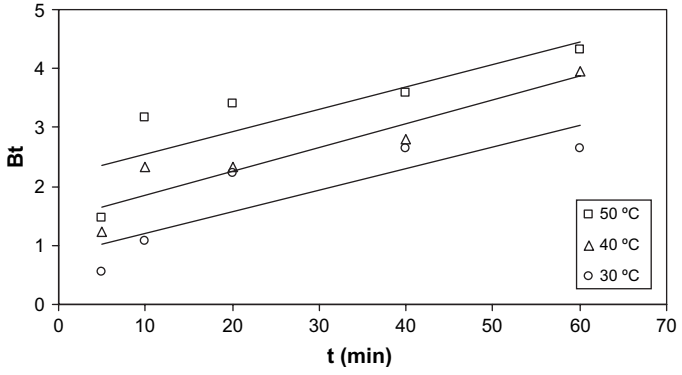

Fig. 5. Plots of Boyd model.

References

[1] Banat IM, Nigam P, Singh D, Marchant R. Microbial decolorization of textile-dye-containing effluents: a review. Bioresource Technology 1996;58:217–27.
[2] Saquib M, Muneer M. Titanium dioxide mediated photocatalyzed degradation of a textile dye derivative, Acid Orange 8, in aqueous suspensions. Desalination 2003;155:255–63.
[3] Wu J, Eitman MA, Law SE. Evaluation of membrane filtration and ozonation processes for treatment of reactive dye wastewater. Journal of Environment Engineering 1998;12(3):272–7.
[4] Hyun TK, Chulhwan P, Eung BS, Sangyong K. Decolorization of disperse and reactive dye solutions using ferric chloride. Desalination 2004;161:49–58.
[5] Daneshvar N, Aleboyeh A, Khataee AR. The evaluation of electrical energy per order for photooxidative decolorization of four textile dye solutions by the kinetic model. Chemosphere 2005;59:761–7.
[6] Hyun TK, Chulhwan P, Jeongmok Y, Sangyong K. Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. Journal of Hazardous Materials 2004;B112:95–103.
[7] Bell J, Buckley CA. Treatment of textile dye in the anaerobic baffled reactor. Water SA 2003;29(2):129–34.
[8] Kapdan IK, Ozturk R. Effect of operating parameters on color and COD removal performance of SBR. Sludge age and initial dyestuff concentration. Journal of Hazardous Materials 2005;B123:217–22.
[9] Renmin G, Yi D, Mei L, Chao Y, Huijun L, Yingzhi S. Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. Dyes and Pigments 2005;64:187–92.
[10] Ozcan A, Ozcan AS. Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite. Journal of Hazardous Materials 2005;B125:252–9.
[11] Shawabkeha AR, Tutunjib MF. Experimental study and modeling of basic dye sorption by diatomaceous clay. Applied Clay Science 2003;24:111–20.
[12] Armagan B, Ozdemir O, Turan M, Celik MS. The removal of reactive azo dyes by natural and modified zeolites. Journal of Chemical Technology and Biotechnology 2003;78:725–32.
[13] Ozdemir O, Armagan B, Turan M, Celik MS. Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals. Dyes and Pigments 2004;62:49–60.
[14] Mitali S, Pradip KA, Bhaskar B. Modelling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters. Journal of Colloid and Interface Science 2003;266:28–32.
[15] Malik PK. Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. Journal of Hazardous Materials 2004;B113:81–8.
[16] Özcan AS, Erdem B, Özcan A. Adsorption of Acid Blue 193 from aqueous solutions onto Na–bentonite and DTMA–bentonite. Journal of Colloid and Interface Science 2004;280:44–54.
[17] Aksu Z, Isoglu IA. Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. Process Biochemistry 2005;40:3031–44.
[18] Stephen JA, Quan G, Ronan M, Pauline AJ. Comparison of optimised isotherm models for basic dye adsorption by kudzu. Bioresource Technology 2003;88:143–52.
[19] Malik PK. Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes and Pigments 2003;56:239–49.
[20] Ho YS. Effect of pH on lead removal from water using tree fern as the sorbent. Bioresource Technology 2005;96:1292–6.
[21] Banat F, Sameer AA, Leema AM. Utilization of raw and activated date pits for the removal of phenol from aqueous solution. Chemical Engineering and Technology 2004;27(1):80–6.
[22] Chairata M, Saowanee R, Bremnerb JB, Rattanaphani V. An adsorption and kinetic study of lac dyeing on silk. Dyes and Pigments 2005;64:231–41.
[23] Ho YS, Chiang CC. Sorption studies of Acid Dye by mixed sorbents. Adsorption 2001;7:139–47.

[24] Sarkar M, Acharya PK, Bhaskar B. Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters. Journal of Colloid and Interface Science 2003;266:28–32.
[25] Kannan K, Sundaram MM. Kinetics and mechanism of removal of Methylene Blue by adsorption on various carbons—a comparative study. Dyes and Pigments 2001;51:25–40.
[26] Vadivelan V, Vasanth KK. Equilibrium, kinetics, mechanism, and process design for the sorption of Methylene Blue onto rice husk. Journal of Colloid and Interface Science 2005;286:90–100.
[27] Gupta VK, Ali I. Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste. Water Research 2001;35(1): 33–40.