JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Equilibrium, Kinetics, and Thermodynamics of Dye Removal Using Alginate in Binary Systems

Niyaz Mohammad Mahmoodi*

Department of Environmental Research, Institute for Color Science and Technology, Tehran, Iran

ABSTRACT: In this paper, dye adsorption properties of alginate in binary systems were investigated. Physical characteristics of alginate were studied using Fourier transform infrared and scanning electron microscopy. Three textile dyes, Basic Violet 16 (BV16), Basic Red 18 (BR18), and Basic Blue 41 (BB41) were used as model compounds in single and binary systems. The effects of alginate dosage, initial dye concentration, and pH on dye removal were elucidated at 25 °C. The dye adsorption isotherm, kinetics, and thermodynamics were studied. The presence of functional groups such as hydroxyl and carboxyl groups was detected. It was found that BV16, BR18, and BB41 followed the Langmuir and extended Langmuir isotherms in single and binary systems, respectively. The adsorption kinetics of dyes was found to conform to pseudosecond order kinetics in both single and binary systems. The thermodynamic data showed that dye adsorption onto alginate was spontaneous, endothermic, and a physisorption reaction. On the basis of the data of the present investigation, one could conclude that the alginate being a biocompatible, eco-friendly, and low-cost adsorbent might be a suitable alternative to remove dyes from colored aqueous solutions.

INTRODUCTION

The presence of numerous dyes with various chemical properties in surface and underground waterways has been of concern for the public and governments all around the world. The discharge of dye-bearing wastewater into natural waterways causes damage to the aesthetic nature of the environment.[1−3] In addition, dyes may drastically affect the photosynthetic phenomenon for aquatic life due to reduced light penetration.[4,5] As a result, the removal of dyes from waste effluents has become environmentally important.[6,7] Several methods such as adsorption, photocatalysis, electrochemical, etc. have been used to remove dyes from the aqueous phase.[1−7]

The adsorption process is considered to be superior to other techniques because of low cost, simplicity of design, availability, and ability to treat dyes. Alginate is a natural carbohydrate polymer and has the capacity to remove toxic pollutants. Biopolymers are known to have an affinity for metal ions and the use of alginate as an adsorbent for the recovery of valuable metal ions as well as removal of toxic metal ions has been studied.[8,9] Alginate has carboxyl groups capable of forming complexes with metal ions. Alginate is derived from several genera of brown algae. One of the important properties of alginate is the ability to form hydrogels.[11,12] An aqueous solution of alginate is readily transformed into a hydrogel on addition of metallic divalent cations. Alginate is often used for immobilization of biological entities.[13,14] Calcium alginate immobilized microbial cultures have been used to remove dyes.[15,16] The important contribution of alginate to certain biological entities such as algae has been reported for the uptake of heavy metal ions.[17,18] Activated carbons immobilized in calcium alginate beads are used for dye removal.[15]

A literature review showed that alginate has not been used to remove dyes from binary systems. This paper deals with the characterization and dye adsorption properties of alginate in single and binary systems. Three textile dyes were used as model compounds. The effects of operational parameters such as alginate dosage, initial dye concentration, and pH on dye removal in single and binary systems were studied. In addition, isotherms, kinetics, and thermodynamics of dye adsorption were investigated.

MATERIALS AND METHODS

Alginate was obtained from the Kitotak Co. Cationic dyes, Basic Violet 16 (BV16), Basic Red 18 (BR18), and Basic Blue 41 (BB41), were achieved from Ciba and ICI Ltd. and used without further purification (Figure 1). All other chemicals were of analar grade and purchased from Merck (Germany).

The functional group of the alginate was studied using Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer Spectrophotometer Spectrum One) in the range (450 to 4000) cm^{-1}. The morphological structure of the alginate was examined by scanning electron microscopy (SEM) using a LEO 1455VP scanning microscope.

The dye adsorption measurements were conducted by mixing the adsorbent in jars containing 200 mL of a dye solution (50 $mg\ L^{-1}$), pH 8, agitation speed of 200 rpm, and 25 °C for 20 min. The change on the absorbance of all solution samples was monitored and determined at certain time intervals during the adsorption process. At the end of the adsorption experiments, the solution samples were centrifuged and the dye concentration was determined. The maximum wavelength (λ_{max}) used for determination of the residual concentration of BV16, BR18, and BB41 in the supernatant solution using UV−vis spectrophotometry (CECIL 2021) were (545, 488, and 605) nm, respectively.

The effect of alginate dosage on dye removal in single and binary systems was investigated by contacting 200 mL of dye solution (50 $mg\ L^{-1}$) at room temperature (25 °C) and pH 8 for

Received: November 29, 2010
Accepted: April 20, 2011
Published: May 03, 2011

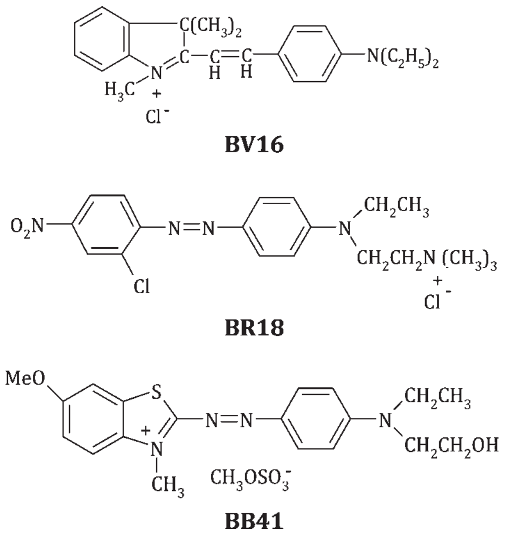


Figure 1. Chemical structure of cationic dyes.

20 min. Different amounts of alginate [(2 to 8) g L^{-1}] were applied. The samples were centrifuged, and the concentration in the supernatant dye solution was analyzed.

The effect of initial dye concentration on dye removal in single and binary systems was studied. Experiments were conducted at different dye concentrations [(25, 50, 75, and 100) mg L^{-1}], 6 g L^{-1} of alginate, pH 8, and 200 mL of dye solution. The samples were centrifuged, and the concentration in the supernatant dye solution was analyzed.

The effect of pH on dye removal in single and binary systems was studied. The solution pH was adjusted by adding a small amount of H_2SO_4 or NaOH. Experiments were conducted at different pH values (2−8), 6 g L^{-1} of alginate, and 200 mL of dye solution (50 mg L^{-1}). The samples were centrifuged, and the concentration in the supernatant dye solution was analyzed.

Dye concentrations were calculated as follows. For a binary system, components A and B were measured at λ_1 and λ_2, respectively, to give optical densities of d_1 and d_2[19]

$$C_A = (k_{B2}d_1 - k_{B1}d_2)/(k_{A1}k_{B2} - k_{A2}k_{B2}) \qquad (1)$$

$$C_B = (k_{A1}d_2 - k_{A2}d_1)/(k_{A1}k_{B2} - k_{A2}k_{B2}) \qquad (2)$$

where k_{A1}, k_{B1}, k_{A2}, and k_{B2} are the calibration constants for components A and B at the two wavelengths λ_1 and λ_2, respectively.

■ RESULTS AND DISCUSSION

Physicochemical Characterization. The Fourier transform infrared (FTIR) spectrum of alginate (Figure 2) shows that the peak positions are at (3422, 2916, 2151, 1625, 1418, and 1296) cm^{-1}. The band at 3422 cm^{-1} is due to OH stretching, whereas the bands at (1625 and 1418) cm^{-1} reflect the carbonyl group stretching and C═C stretching. The band at 1296 cm^{-1} corresponds to C−O stretching.[20,21]

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of adsorbent surfaces. It is useful for determining the particle shape, porosity, and appropriate size distribution of the adsorbent. Scanning electron micrographs of alginate are shown in Figure 3. From Figure 3, it is clear that alginate has a considerable number of pores where there is a good possibility for dyes to be trapped and adsorbed.

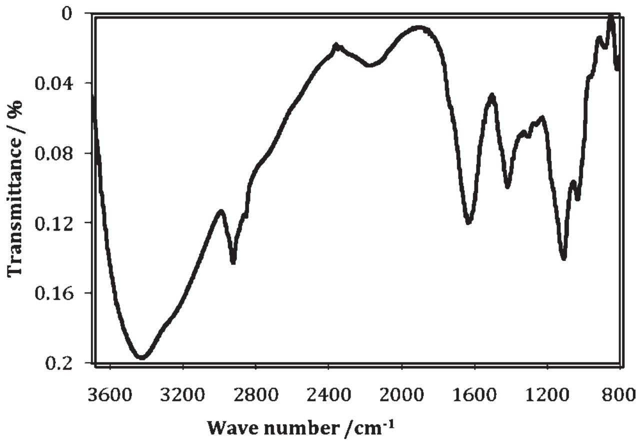


Figure 2. FT-IR spectrum of alginate.

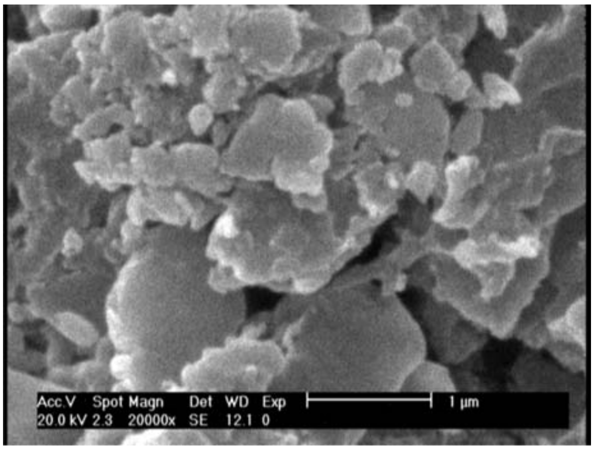


Figure 3. SEM image of alginate.

Effect of Operational Parameters on Dye Removal. *Effect of Adsorbent Dosage.* A plot of dye removal (%) versus adsorbent dosage (g L^{-1}) is shown in Figure 4. The increase in adsorption with adsorbent dosage can be attributed to an increased adsorbent surface and the availability of more adsorption sites. However, if the adsorption capacity is expressed in milligrams adsorbed per gram of material, the capacity decreases with the increasing amount of adsorbent. This may be attributed to overlapping or aggregation of adsorption sites, resulting in a decrease in total adsorbent surface area available to the dye and an increase in diffusion path length.[22]

Dye Concentration Effect. The effect of dye concentration on dye removal using alginate is shown in Figure 5. The equilibrium capacity decreases with an increase in the initial dye concentration. This can be attributed to active sites on the adsorbent for dye removal decreasing when the dye concentration increases. The amount of the dye adsorbed onto alginate increases with an increase in the initial dye concentration at a constant amount of adsorbent. This is due to the increase in the driving force of the concentration gradient with the higher initial dye concentrations. At low initial dye concentrations, the adsorption of dyes by

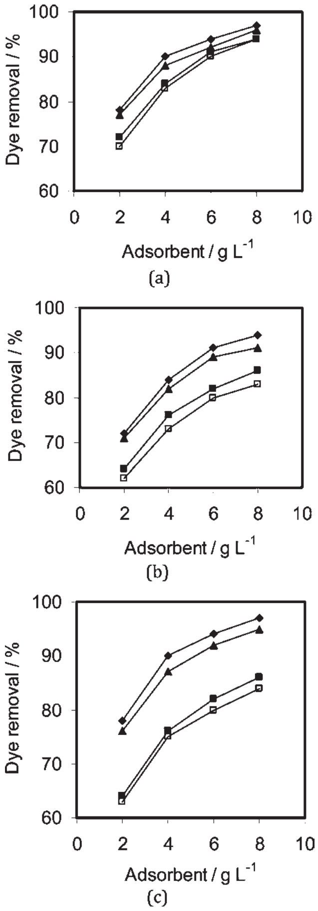


Figure 4. Effect of adsorbent dosage on dye removal by alginate (a) BV16 + BR18 [♦: BV16(sin), ■: BR18(sin), ▲: BV16(bin), □: BR18(bin)], (b) BV16 + BB41 [♦: BV16(sin), ■: BB41(sin), ▲: BV16(bin), □: BB41(bin)], (c) BR18 + BB41 [♦: BR18(sin), ■: BB41(sin), ▲: BR18(bin), □: BB41(bin)].

alginate is very intense and reaches equilibrium very quickly. This indicates the possibility of the formation of monolayer coverage of the molecules at the outer interface of the alginate. At a fixed alginate dosage, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower dye concentrations, the ratio of the initial number of dye moles to the available adsorption sites is low. At higher concentrations, the number of available adsorption sites becomes lower, and subsequently the removal of dyes depends on the initial concentration. At high concentrations, it is not likely that dyes are only adsorbed in a monolayer at the outer interface of the adsorbent.[23−26]

Effect of pH. The effect of the initial pH on the dye removal in single and binary systems is shown in Figure 6. The adsorption capacity increases when the pH increases. The maximum adsorption of basic dyes occurs at pH 8. Alginate is comprised of various functional groups such as hydroxyl and carboxyl groups which are affected by the pH of solutions. Therefore, at various pH values, electrostatic attraction as well as the ionic properties and structure of dye molecules and alginate could play very important roles in the dye adsorption on alginate. At pH 8, a considerably high electrostatic attraction exists between the negatively charged surface of the adsorbent, due to the ionization of functional groups of the adsorbent and positively charged cationic dye molecules. As the pH of the system decreases, the number of positively charged sites increases. A positively charged site on the adsorbent does not favor the adsorption of cationic dyes due to electrostatic repulsion.[27] Thus, the effective pH for adsorption of cationic dyes (BV16, BR18, and BB41) onto alginate was 8, and it was used in further studies.

Adsorption Isotherm. *Single Systems.* Adsorption isotherms investigate the relation between the mass of dye adsorbed at constant temperature per unit mass of adsorbent and liquid phase dye concentration at equilibrium. It presents how a dye can be distributed between the liquid and solid phases at various equilibrium concentrations. Different factors such as the number of compounds in the solution, their relative adsorbabilities, initial concentration of adsorbate in the solution, and the degree of competition among solutes for adsorption sites determine the shape of the isotherm. Adsorption isotherms provide information on how an adsorption system proceeds and indicate how efficiently a given adsorbent interacts with adsorbate.[28]

Several models such as those of Langmuir, Freundlich, and Tempkin have been used in the literature to describe experimental data in order to optimize the design of an adsorption system to remove dyes from solutions.

The Langmuir equation often describes monolayer adsorption. This model assumes a uniform energy of adsorption and a single layer of adsorbed solute at a constant temperature. The Langmuir model is the most frequently employed model and is given by[29]

$$q_e = Q_0 K_L C_e / (1 + K_L C_e) \tag{3}$$

where q_e, C_e, Q_0, and K_L are the amount of solute adsorbed at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), the concentration of adsorbate at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), maximum adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), and Langmuir constant ($\text{L}\cdot\text{mg}^{-1}$), respectively.

Equation 3 can be rearranged to a linear form

$$C_e/q_e = 1/K_L Q_0 + C_e/Q_0 \tag{4}$$

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter, R_L, which is defined by the following equation:[30]

$$R_L = 1/(1 + K_L C_0) \tag{5}$$

where C_0 is the initial dye concentration. The nature of the adsorption process can be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

To study the applicability of the Langmuir isotherm for dye adsorption onto alginate, a linear plot of C_e/q_e against C_e was plotted. The values of Q_0, K_L, and R^2 (coefficient of determination) are shown in Table 1.

The Freundlich equation is one of the well-known models applicable for a single solute system. It is an empirical equation used to describe the distribution of solute between solid and aqueous phases at a point of saturation. The basic assumption of this model is that there is an exponential variation in site energies of the adsorbent and also surface adsorption is not the rate limiting step. The strength of the linear relationship can be expressed by the correlation coefficient. Its value is used to evaluate how the Freundlich model represents the experimental data.[31]

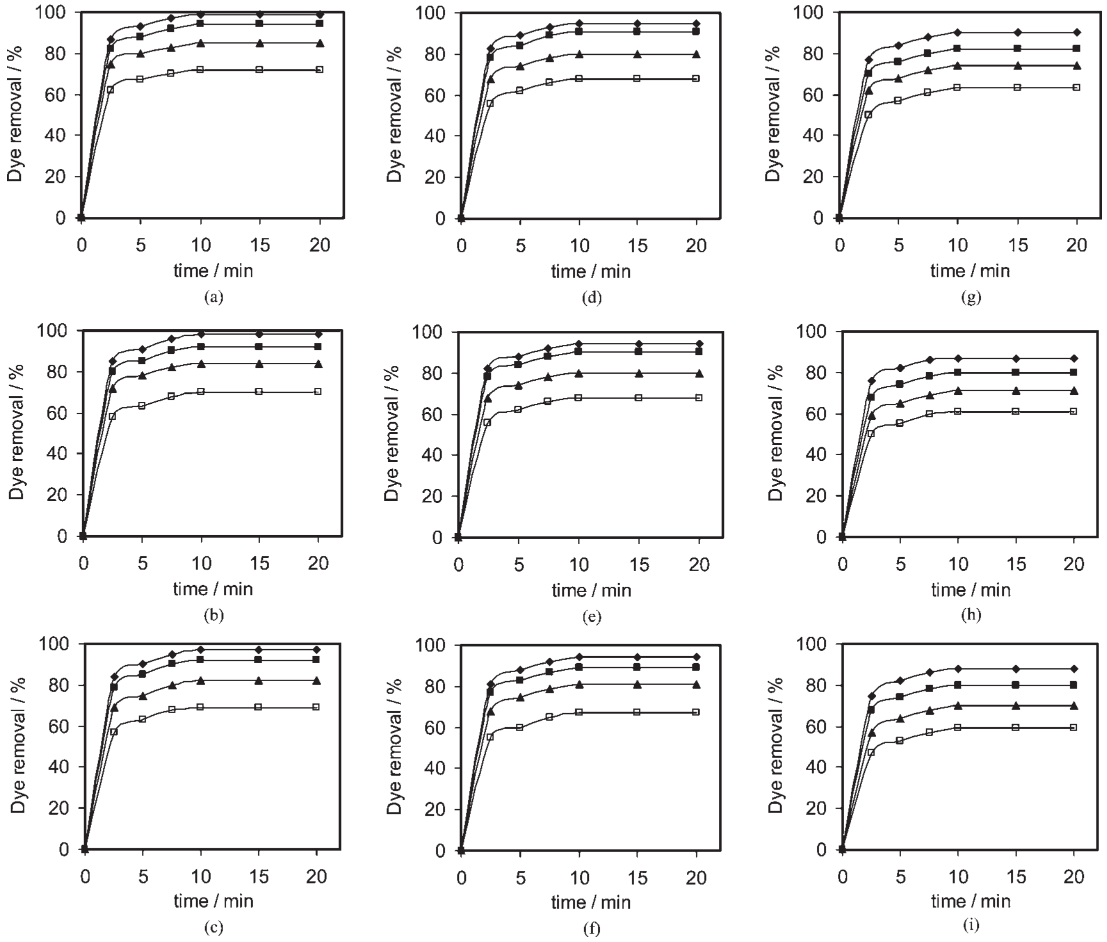


Figure 5. Effect of dye concentration on dye removal by alginate (a) BV16 (sin), (b) BV16 (BV16 + BR18), (c) BV16 (BV16 + BB41), (d) BR18 (sin), (e) BR18 (BV16 + BR18), (f) BR18 (BR18 + BB41), (g) BB41 (sin), (h) BB41 (BV16 + BB41), and (i) BB41 (BR18 + BB41) (♦: 25 mg L^{-1}, ■: 50 mg L^{-1}, ▲: 75 mg L^{-1}, □: 100 mg L^{-1}).

The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. The Freundlich isotherm can be expressed by[32−35]

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F is the adsorption capacity at unit concentration (L·g^{-1}) and $1/n$ is adsorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), and unfavorable ($1/n > 1$). Equation 6 can be rearranged to a linear form

$$\log q_e = \log K_F + (1/n)\log C_e \tag{7}$$

To study the applicability of the Freundlich for dye adsorption onto alginate, linear plot of log q_e versus log C_e was plotted. The values of K_F, n, and R^2 are shown in Table 1.

The Tempkin isotherm is given as

$$q_e = RT/b \ln(K_T C_e) \tag{8}$$

which can be linearized as

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{9}$$

where

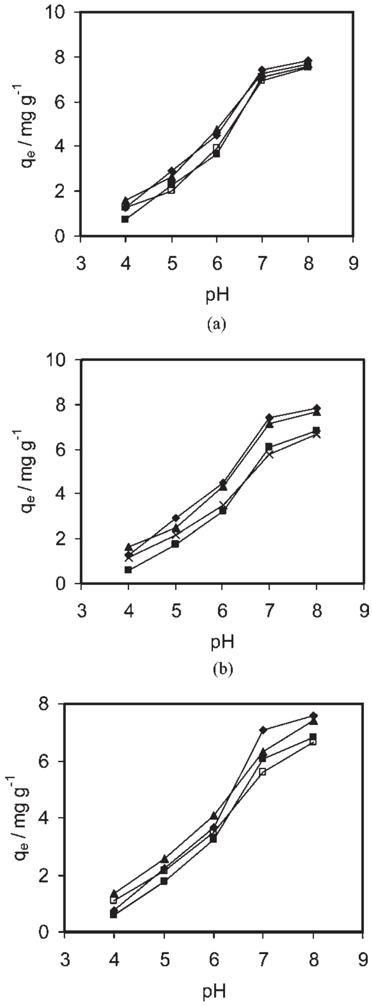
$$B_1 = RT/b \tag{10}$$

The Tempkin isotherm contains a factor that explicitly takes into account adsorbing species−adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all molecules in the layer decreases linearly with coverage due to adsorbent−adsorbate interactions and (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.[36,37] K_T is the equilibrium binding constant (L·mg^{-1}) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption. The R and T are the gas constant (8.314 J·mol^{-1}·K^{-1}) and the absolute temperature (K), respectively.

To study the applicability of the Tempkin isotherm for dye adsorption onto alginate, a linear plot q_e versus ln C_e are plotted. The values of K_T, B_1, and R^2 are shown in Table 1.

The R^2 values showed that the dye removal isotherm using alginate in single system did not follow the Freundlich and Tempkin isotherms (Table 1). The linear fit between C_e/q_e versus C_e for the Langmuir isotherm model in single systems showed that the dye removal isotherm could be approximated with the Langmuir model (Table 1). This means that the adsorption of cationic dyes takes place at specific homogeneous sites and a one layer adsorption onto the alginate surface in the single systems.

Binary Systems. In this work, an extended Langmuir model (eq 11), Freundlich and Tempkin isotherm (single system equation) models were employed to fit the experimental data.[38]



(a)

(b)

(c)

Figure 6. Effect of pH on dye removal by alginate (a) BV16 + BR18 [♦: BV16(sin), ■: BR18(sin), ▲: BV16(bin), □: BR18(bin)], (b) BV16 + BB41 [♦: BV16(sin), ■: BB41(sin), ▲: BV16(bin), □: BB41(bin)], (c) BR18 + BB41 [♦: BR18(sin), ■: BB41(sin), ▲: BR18(bin), □: BB41(bin)].

The extended Langmuir isotherm is given as

$$q_{e,i} = (K_{L,i}Q_{0,i}C_{e,i})/(1 + \sum K_{L,i}C_{e,i}) \tag{11}$$

where $K_{L,i}$ is the adsorption equilibrium constant of dye i in the mixed dye system.

In adsorption from binary dye solutions, the amounts of dye adsorbed can be expressed as

$$q_{e,1} = (K_{L,1}Q_{0,1}C_{e,1})/(1 + K_{L,1}C_{e,1} + K_{L,2}C_{e,2}) \tag{12-1}$$

$$q_{e,2} = (K_{L,2}Q_{0,2}C_{e,2})/(1 + K_{L,1}C_{e,1} + K_{L,2}C_{e,2}) \tag{12-2}$$

According to eqs 12-1 and 12-2, we have

$$(K_{L,2}C_{e,2})/(K_{L,1}Q_{0,1}) = (q_{e,2}C_{e,2})/(q_{e,1}Q_{0,2}) \tag{13}$$

After rearrangement, a linear form of the extended Langmuir model in binary dye systems was obtained.

$$(C_{e,1}/q_{e,1}) = (1/K_{L,1}Q_{0,1}) + (C_{e,1}/Q_{0,1}) + (q_{e,2}C_{e,1}/q_{e,1}Q_{0,2}) \tag{14-1}$$

$$(C_{e,2}/q_{e,2}) = (1/K_{L,2}Q_{0,2}) + (C_{e,2}/Q_{0,2}) + (q_{e,1}C_{e,2}/q_{e,2}Q_{0,1}) \tag{14-2}$$

According to eq 14 the values of $C_{e,1}/q_{e,1}$ has a linear correlation with $C_{e,1}$ and $C_{e,1}q_{e,2}/q_{e,1}Q_{0,2}$ if the adsorption obeys the extended Langmuir model. By using eq 14 as the fitting model, the isotherm parameters of an individual dye in the binary dye solutions were estimated and are listed in Table 2. It can be seen that the isotherms of an individual dye in the binary dye systems followed the extended Langmuir model. Figure 7 shows the adsorption isotherms of dyes.

The R^2 values showed that the dye removal isotherm using alginate in binary systems followed the extended Langmuir model (Table 1). This means that the adsorption of cationic dyes takes place at specific homogeneous sites and a one layer adsorption onto the alginate surface in the binary systems.

Adsorption Kinetics. Adsorption kinetics provides information regarding the mechanism of adsorption that is important for the efficiency of the process. It is important to know the rate of adsorption during removing pollutants from wastewater to

Table 1. Isotherm Constants for Dye Adsorption on Alginate at Different Dye Concentrations from Single and Ternary Systems (Q_0/mg.g^{-1}; K_L/L·mg^{-1}; K_F/L·g^{-1}; K_T/L·mg^{-1}; and B_1/mg·g^{-1})

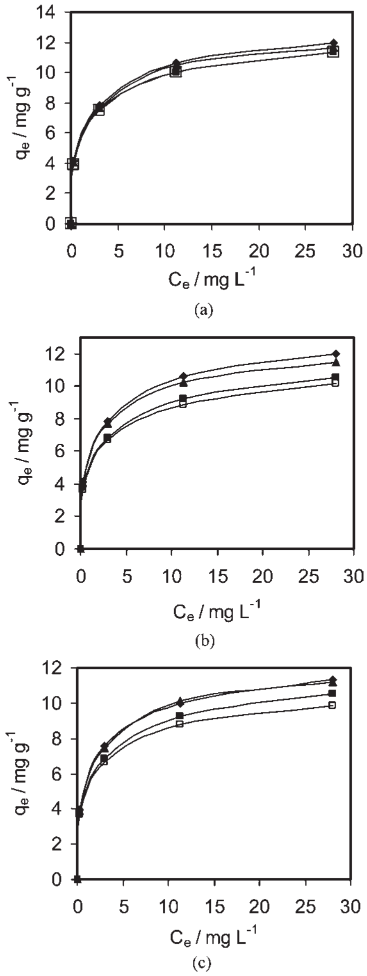
			isotherms								
system	dye		Q_0	K_L	R^2	K_F	n	R^2	K_T	B_1	R^2
				Langmuir			Freundlich			Tempkin	
single	BV16		12.438	0.772	0.997	5.837	4.316	0.991	42.441	1.690	0.995
	BR18		12.255	0.351	0.999	4.053	3.117	0.942	5.214	2.266	0.989
	BB41		12.254	0.158	0.998	2.732	2.552	0.980	1.713	2.560	0.996
				extended Langmuir			Freundlich			Tempkin	
binary	BV16+BR18	BV16	12.270	0.572	0.998	5.086	3.768	0.981	16.455	1.907	0.991
		BR18	12.484	0.294	0.999	3.750	2.896	0.943	3.745	2.431	0.989
	BV16+BB41	BV16	12.180	0.487	0.999	4.678	3.512	0.967	10.268	2.034	0.996
		BB41	121.225	0.124	0.999	2.332	2.377	0.974	1.218	2.664	0.998
	BR18+BB41	BR18	12.315	0.300	0.999	3.702	2.888	0.945	3.694	2.418	0.982
		BB41	11.415	0.149	0.999	2.539	2.607	0.972	1.585	2.396	0.997

Table 2. Kinetic Constants for Dye Adsorption on Alginate at Different Dye Concentrations from Single and Binary Systems (Dye/mg·L^{-1}; $(q_e)_{Exp}$/mg·g^{-1}; $(q_e)_{Cal}$/mg·g^{-1}; k_1/min^{-1}; k_2/g·mg^{-1}·min^{-1}; and K_p/mg·g^{-1}·min$^{-1/2}$)

			pseudofirst order			pseudosecond order			intraparticle diffusion		
system	dye	$(q_e)_{Exp}$	$(q_e)_{Cal.}$	k_1	R^2	$(q_e)_{Cal.}$	k_2	R^2	k_P	I	R^2
single						BV16					
	25	4.125	2.924	0.496	0.948	4.172	1.101	0.999	0.839	1.253	0.680
	50	7.833	5.640	0.490	0.951	7.930	0.546	0.999	1.597	2.356	0.685
	75	10.625	7.198	0.478	0.933	10.741	0.431	0.999	2.157	3.239	0.678
	100	12	8.545	0.458	0.943	12.165	0.316	0.999	2.457	3.541	0.695
						BR18					
	25	3.958	2.841	0.491	0.950	4.001	1.093	0.999	0.807	1.193	0.684
	50	7.583	5.781	0.483	0.959	7.692	0.485	0.999	1.557	2.220	0.699
	75	10	7.558	0.470	0.960	10.152	0.355	0.999	2.058	2.905	0.703
	100	11.333	8.993	0.451	0.969	11.534	0.259	0.999	2.358	3.154	0.723
						BB41					
	25	3.750	2.824	0.488	0.963	3.801	1.033	0.999	0.769	1.104	0.696
	50	6.833	5.126	0.473	0.958	6.930	0.535	0.999	1.404	1.996	0.700
	75	9.250	7.156	0.461	0.964	9.398	0.352	0.999	1.913	2.635	0.712
	100	10.500	8.802	0.445	0.981	10.718	0.242	0.999	2.210	2.799	0.741
BV16 + BR18						BV16					
	25	4.000	3.044	0.492	0.955	4.137	0.982	0.999	0.835	1.215	0.691
	50	7.500	5.642	0.481	0.948	7.770	0.510	0.999	1.567	2.278	0.691
	75	10.250	7.820	0.476	0.957	10.650	0.358	0.999	2.154	3.084	0.697
	100	11.667	9.320	0.448	0.961	11.876	0.244	0.999	2.426	3.239	0.724
						BR18					
	25	3.917	2.820	0.490	0.951	3.965	1.093	0.999	0.798	1.178	0.685
	50	7.500	5.471	0.484	0.953	7.599	0.543	0.999	1.533	2.236	0.690
	75	10.000	7.558	0.470	0.960	10.152	0.355	0.999	2.058	2.905	0.703
	100	11.333	8.993	0.451	0.969	11.534	0.259	0.999	2.358	3.154	0.723
BV16 + BB41						BV16					
	25	4.042	3.023	0.490	0.956	4.095	0.981	0.999	0.527	1.200	0.692
	50	7.667	5.826	0.484	0.958	7.776	0.486	0.999	1.573	2.250	0.698
	75	10.250	8.063	0.470	0.964	10.417	0.319	0.999	2.119	2.927	0.711
	100	11.500	10.435	0.536	0.975	11.696	0.277	0.999	2.392	3.233	0.718
						BB41					
	25	3.625	2.910	0.567	0.974	3.667	1.316	0.999	0.739	1.100	0.681
	50	6.667	5.038	0.470	0.960	6.766	0.534	0.999	1.372	1.936	0.703
	75	8.875	6.965	0.456	0.966	9.025	0.349	0.999	1.841	2.501	0.717
	100	10.167	9.247	0.518	0.969	10.352	0.287	0.999	2.122	2.810	0.726
BR18 + BB41						BR18					
	25	3.917	2.912	0.493	0.961	3.968	1.303	0.999	0.802	1.164	0.692
	50	7.417	5.429	0.483	0.954	7.513	0.542	0.999	1.517	2.206	0.691
	75	10.125	7.870	0.475	0.969	10.277	0.339	0.999	2.091	2.908	0.708
	100	11.167	9.039	0.443	0.963	11.377	0.242	0.999	2.330	2.060	0.730
						BB41					
	25	3.667	2.780	0.485	0.964	3.717	1.029	0.999	0.753	1.074	0.699
	50	6.667	5.038	0.470	0.960	6.766	0.534	0.999	1.372	1.936	0.703
	75	8.750	7.107	0.458	0.976	8.913	0.329	0.999	1.826	2.414	0.727
	100	9.833	8.141	0.434	0.976	10.040	0.252	0.999	2.068	2.616	0.743

optimize the design parameters because the kinetics of the system controls the adsorbate residence time and reactor dimensions. As a result, predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design.[39]

In order to design a fast and effective model, investigation was made on the adsorption rate. Several kinetics models (pseudofirst order, pseudosecond order, and intraparticle diffusion) are used to test the experimental data such as the examination of the controlling mechanism of the adsorption process.[40,41]



(a)

(b)

(c)

Figure 7. Adsorption isotherms for dyes on alginate (a) BV16 + BR18 [♦: BV16(sin), ■: BR18(sin), ▲: BV16(bin), □: BR18(bin)], (b) BV16 + BB41 [♦: BV16(sin), ■: BB41(sin), ▲: BV16(bin), □: BB41(bin)], (c) BR18 + BB41 [♦: BR18(sin), ■: BB41(sin), ▲: BR18(bin), □: BB41(bin)].

The pseudofirst order equation is generally represented as follows:[42,43]

$$\mathrm{d}q_t/\mathrm{d}t = k_1(q_e - q_t) \tag{15}$$

where q_t and k_1 are the amount of dye adsorbed at time t ($mg\,g^{-1}$) and the rate constant of pseudofirst-order kinetics (min^{-1}), respectively. After integration by applying conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, then eq 15 becomes

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t \tag{16}$$

Straight-line plots of $\log(q_e - q_t)$ versus t for the adsorption of BV16, BR18, and BB41 in single and binary systems onto alginate at different dye concentrations have been tested to obtain the rate parameters. The calculated q_e ($(q_e)_{Cal}$), k_1, and R^2 at different dye concentrations values were calculated and are given in Table 2.

Data were applied to the Ho and MacKay's pseudosecond order kinetic rate equation which is expressed as[42,44]

$$\mathrm{d}q_t/\mathrm{d}t = k_2(q_e - q_t) \tag{17}$$

where k_2 is the rate constant of pseudosecond order ($\mathrm{g \cdot mg^{-1} \cdot min^{-1}}$). On integrating eq 17

$$t/q_t = 1/k_2{q_e}^2 + (1/q_e)t \tag{18}$$

To understand the applicability of the pseudosecond order model, linear plots of t/q_t versus t under dye concentrations for the adsorption of dyes in single and binary systems onto alginate are shown in Figure 8. The calculated q_e ($(q_e)_{Cal}$), k_2, and R^2 were calculated and are given in Table 2.

The possibility of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion model as

$$q_t = k_p t^{1/2} + I \tag{19}$$

where k_p and I are the intraparticle diffusion rate constant ($\mathrm{mg \cdot g^{-1} \cdot min^{-1/2}}$) and intercept ($\mathrm{mg \cdot g^{-1}}$), respectively.

Values of I (Table 2) give an idea about the thickness of the boundary layer; that is, the larger the intercept, the greater is the boundary layer effect. According to this model, a plot of uptake should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step.[45,46] When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and shows that intraparticle diffusion is not the only rate limiting step, but also other kinetic processes may control the rate of adsorption, all of which may be operating simultaneously.

The R^2 values demonstrate that the pseudofirst order and intraparticle diffusion kinetic models do not play a significant role in the uptake of the dye by alginate (Table 2). The linear fit between the t/q_t versus contact time (t) and the calculated coefficient of determination for the pseudosecond order kinetic model show that the cationic dye removal kinetics can be approximated as pseudosecond order kinetics (Table 2). In addition, the experimental q_e ($(q_e)_{Exp}$) values agree with the calculated ones ($(q_e)_{Cal}$), obtained from the linear plots of the pseudosecond order model (Table 2).

Adsorption Thermodynamics. Thermodynamic parameters including change in the Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are the actual indicators for practical application of an adsorption process. According to the values of these parameters, what process will occur spontaneously can be determined.

The thermodynamic parameters were determined using the following equations:[47]

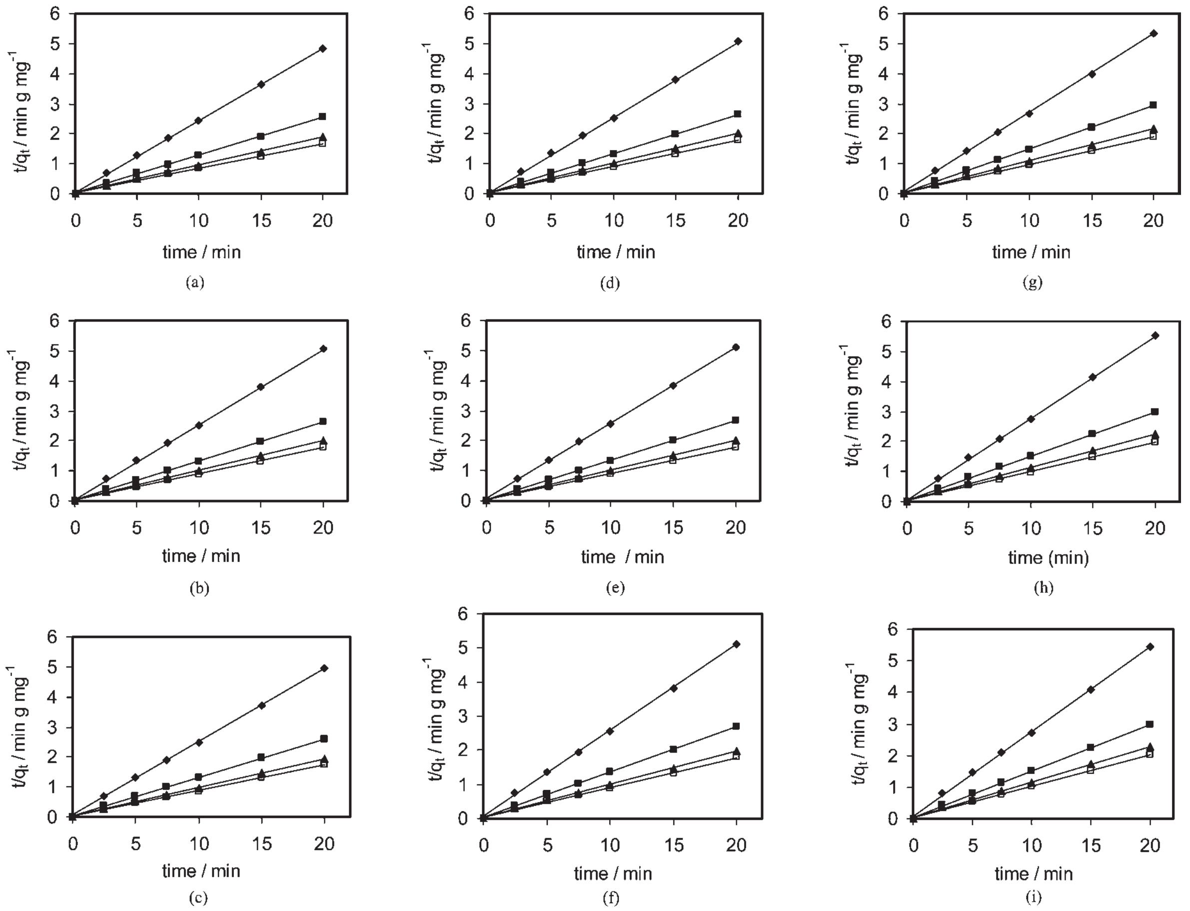
$$\Delta G = \Delta H - T\Delta S \tag{20}$$

$$K_c = C_A/C_S \tag{21}$$

$$\ln K_c = (\Delta S/R) - (\Delta H/RT) \tag{22}$$

where K_c, C_A, and C_S are the equilibrium constant, the amount of dye adsorbed on the adsorbent of the solution at equilibrium ($\mathrm{mol \cdot L^{-1}}$), and the equilibrium concentration of dye in the solution ($\mathrm{mol \cdot L^{-1}}$), respectively.

The obtained thermodynamic parameters are given in Table 3. The positive value of ΔH suggests an endothermic reaction. The positive value of ΔS suggests the increased randomness at the solid/solution interface during the adsorption of dyes onto alginate. The negative values of ΔG imply the spontaneous nature of the adsorption process. Further, the decrease in the values of ΔG with increasing temperature indicates the adsorption is more spontaneous at higher temperatures.



(a) (d) (g) (b) (e) (h) (c) (f) (i)

Figure 8. Pseudosecond order adsorption kinetics of dye removal by alginate (a) BV16 (sin), (b) BV16 (BV16 + BR18), (c) BV16 (BV16 + BB41), (d) BR18 (sin), (e) BR18 (BV16 + BR18), (f) BR18 (BR18 + BB41), (g) BB41 (sin), (h) BB41 (BV16 + BB41), (i) BB41 (BR18 + BB41) (◆: 25 mg·L^{-1}, ■: 50 mg·L^{-1}, ▲: 75 mg·L^{-1}, □: 100 mg·L^{-1}).

Table 3. Thermodynamic Parameters of Dye Adsorption on Alginate from Single and Binary Systems

system	dye	ΔH/kJ·mol^{-1}	ΔS/J·mol^{-1}·K^{-1}	ΔG/kJ·mol^{-1} 298 K	308 K	318 K	328 K
single	BV16	11.136	−45.083	−2.299	−2.750	−3.200	−3.651
	BR18	11.822	43.905	−1.261	−1.700	−2.139	−2.578
	BB41	5.903	17.488	0.692	0.517	0.342	0.168
BV16+BR18	BV16	13.547	50.731	−1.571	−2.078	−2.586	−3.093
	BR18	10.520	38.585	−0.979	−1.364	−1.750	−2.136
BV16+BB41	BV16	12.944	48.967	−1.648	−2.138	−2.627	−3.117
	BB41	5.392	14.697	1.013	0.866	0.719	0.572
BR18+BB41	BR18	9.500	34.293	−0.719	−1.062	−1.405	−1.748
	BB41	4.512	11.670	1.034	0.917	0.801	0.684

Generally, the change in free energy for physisorption is between (−20 to 0) kJ·mol^{-1}, but chemisorption is in the range of (−80 to −400) kJ·mol^{-1}.[48] The values of ΔG obtained in this study are within the ranges of a physisorption reaction.

■ CONCLUSION

Equilibrium, kinetic, and thermodynamic studies were conducted for the adsorption of BV16, BR18, and BB41 from aqueous solutions onto alginate in single and binary systems. The results of adsorption showed that alginate can be effectively used as a biosorbent for the removal of cationic dyes. The alginate biosorbent exhibited high sorption capacities toward BV16, BR18, and BB41. The equilibrium data showed that the experimental data were correlated reasonably well by the Langmuir and the extended Langmuir isotherm models in single and binary systems, respectively. The kinetic studies were performed based on pseudofirst order, pseudosecond order, and intraparticle diffusion models. The data indicated that the adsorption kinetics of dyes on alginate followed the pseudosecond order model at different dye concentrations. Thermodynamic studies indicated the presence of an energy barrier in the adsorption process and an endothermic process. On the basis of the data of the present study, one could conclude that the alginate is an eco-friendly adsorbent for dye removal from colored textile wastewater.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +98 021 22969771. Fax: +98 021 22947537. E-mail: nm_mahmoodi@aut.ac.ir; nm_mahmoodi@yahoo.com.

REFERENCES

(1) Bulut, Y.; Aydin, H. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination* **2006**, *194*, 259–267.

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

(3) Mahmoodi, N. M.; Arami, M.; Zhang, J. Preparation and photocatalytic activity of immobilized composite photocatalyst (titania nanoparticle/activated carbon). *J. Alloy. Compd.* **2011**, *509*, 4754–4764.

(4) Mahmoodi, N. M.; Arami, M.; Bahrami, H.; Khorramfar, S. The effect of pH on the removal of anionic dyes from colored textile wastewater using a biosorbent. *J. Appl. Polym. Sci.* **2011**, *120*, 2996–3006.

(5) Maljaei, A.; Arami, M.; Mahmoodi, N. M. Decolorization and aromatic ring degradation of colored textile wastewater using indirect electrochemical oxidation method. *Desalination* **2009**, *249*, 1074–1078.

(6) Sanghi, R.; Bhattacharya, B. Review on decolorisation of aqueous dye solutions by low cost adsorbents. *Color Technol.* **2002**, *118*, 256–269.

(7) Malik, P. K. Use of activated carbons prepared from sawdust and rice—husk for adsorption of acid dyes: a case study of Acid Yellow 36. *Dyes Pigments* **2003**, *56*, 239–249.

(8) Deans, J. R.; Dixon, B. G. Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers. *Water Res.* **1992**, *26*, 469–472.

(9) Davis, T. A.; Volesky, B.; Mucci, A. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* **2003**, *37*, 4311–4330.

(10) Atkins, E. D. T. *Polyscaccharides: Topics in Structure and Morphology*; VCH Verlag:Weinheim, Germany, 1985.

(11) Mihailovic, D; Saponjic, Z.; Radoic, M.; Radetic, T.; Jovancic, P.; Nedeljkovic, J.; Radetic, M. Functionalization of polyester fabrics with alginates and TiO_2 nanoparticles. *Carbohydr. Polym.* **2010**, *79*, 526–532.

(12) Gilson, C. D.; Thomas, A. J. Encapsulation of lactic acid bacteria with alginate/starch capsules. *Biotechnology* **1997**, *62*, 227–232.

(13) Martinse, A.; Skijak-Braek, A.; Smidsrod, O. Alginate as immobilization material: I. Correlation between chemical and physical properties of alginate gel beads. *Biotechnol. Bioeng.* **1989**, *33*, 79–89.

(14) Shin, E. W.; Rowell, R. M. Cadmium ion sorption onto lignocellulosic biosorbent modified by sulfonation: the origin of sorption capacity improvement. *Chemosphere* **2005**, *60*, 1054–1061.

(15) Aravindhan, T.; Fathima, N. N.; Rao, J. R.; Nair, B. U. Equilibrium and thermodynamic studies on the removal of basic black dye using calcium alginate beads. *Colloids Surf.* **2007**, *299*, 232–238.

(16) Ramsay, J. A.; Mok, W. H. W.; Luu, Y. S.; Savage, M. Decoloration of textile dyes by alginate-immobilized *Trametes versicolor*. *Chemosphere.* **2005**, *61*, 956–964.

(17) Schiewer, S.; Fourest, E.; Chong, K. H.; Volesky, B.; Jerez, C. A.; Vargas, T.; Toledo, H.; Wiertz, J. V. *Biohydrometallurgical Processing*; University of Chile: Chile, 1995.

(18) Yamuna, R. T.; Namasivayam, C. Dye removal from wastewater by adsorption on 'waste' Fe(III)/Cr(III) hydroxide. *Waste Management* **1994**, *14*, 643–648.

(19) Choy, K. K. H.; Porter, J. F.; McKay, G. Langmuir Isotherm Models Applied to the Multicomponent Sorption of Acid Dyes from Effluent onto Activated Carbon. *J. Chem. Eng. Data* **2000**, *45*, 575–584.

(20) He, J.; Ma, W.; He, J.; Zhao, J.; Yu, J. C. Photooxidation of azo dye in aqueous dispersions of H_2O_2/FeOOH. *Appl. Catal. B Environ.* **2002**, *39*, 211–220.

(21) Pavia, D. L.; Lampman, G. M.; Kaiz, G. S. *Introduction to Spectroscopy: A Guide for Students of Organic Chemistry*; W.B. Saunders Company: New York, 1987.

(22) Alley, E. R. *Water Quality Control Handbook*; McGraw-Hill Education: London, 2000; pp 125−141.

(23) Crini, G.; Badot, P. M. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Prog. Polym. Sci.* **2008**, *33*, 399–447.

(24) Dutta, P. K.; Bhavani, K. D.; Sharma, N. Adsorption for dyehouse effluent by low cost adsorbent (chitosan). *Asian Textile J.* **2001**, *10*, 57–63.

(25) Chiou, M. S.; Li, H. Y. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere* **2003**, *50*, 1095–1105.

(26) Chatterjee, S.; Chatterjee, S.; Chatterjee, B. P.; Das, A. R.; Guha, A. K. Adsorption of a model anionic dye, eosin Y, from aqueous solution by chitosan hydrobeads. *J. Colloid Interface Sci.* **2005**, *288*, 30–35.

(27) Low, K. S.; Lee, C. K. Quaternized rice husk as sorbent for reactive dyes. *Bioresour. Technol.* **1997**, *12*, 121–125.

(28) Ng, C.; Losso, J. N.; Marshall, W. E.; Rao, R. M. Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water system. *Bioresorce. Technol.* **2002**, *85*, 131–133.

(29) Langmuir, I. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* **1916**, *38*, 2221–2295.

(30) Das, S. K.; Bhowal, J.; Das, A. R.; Guha, A. K. Adsorption behavior of Rhodamine B onrhizopus oryzae biomass. *Langmuir* **2006**, *22*, 7265–7272.

(31) Choy, K. K. H.; Porter, J. F.; McKay, G. Intraparticle diffusion in single and multicomponent acid dye adsorption from wastewater onto carbon. *Chem. Eng. J.* **2004**, *103*, 133–145.

(32) Wu, C. H. Adsorption of reactive dyes onto carbon nanotubes: Equilibrium, kinetics and thermodynamics. *J. Hazard. Mater.* **2007**, *144*, 96–98.

(33) Kunwar, P. S.; Dinesh, M.; Sarita, Sinha.; Tondon, G. S.; Gosh, D. Color Removal from Wastewater Using Low-Cost Activated Carbon Derived from Agricultural Waste Material. *Ind. Eng. Chem. Res.* **2003**, *42*, 1965–1976.

(34) Woodard, F. *Industrial Waste Treatment Handbook*; Butterworth-Heinemann: Boston, 2001; pp 376−451.

(35) Freundlich, H. M. F. Uber die adsorption in lasugen. *Phys. Chem.* **1906**, *57*, 385–470.

(36) Tempkin, M. J.; Pyzhev, V. Recent modification to Langmiur isotherms. *Acta Physiochim. USSR* **1940**, *12*, 217–222.

(37) Kim, Y. C.; Kim, I.; Choi Rengraj, S.; Yi, J. Arsenic removal using mesoporous alumina prepared via a templating method. *Environ. Sci. Technol.* **2004**, *38*, 924–31.

(38) Asku, Z.; Tezar, S. Biosorption of reactive dyes on the green alga *Chlorella vulgaris*. *Process Biochem.* **2005**, *40*, 1347–1361.

(39) Ho, Y. S. Adsorption of heavy metals from waste streams by peat. Ph.D. Thesis; The University of Birmingham: Birmingham, U.K., 1995.

(40) Lagergren, S. Zur theorie der sogenannten adsorption geloster stoffe. K. Sven. *Vetenskapsakad. Handl.* **1898**, *24*, 1–39.

(41) Ho, Y. S. Sorption studies of acid dye by mixed sorbents. *Adsorption* **2001**, *7*, 139–147.

(42) Ho, Y. S. Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* **2004**, *59*, 171–177.

(43) Ho, Y. S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465.

(44) Ozcan, A.; Ozcan, A. S. Adsorption of Acid Red 57 from aqueous solutions onto surfactant-modified sepiolite. *J. Hazard. Mater.* **2005**, *125*, 252–259.

(45) Senthilkumaar, S.; Kalaamani, P.; Porkodi, K.; Varadarajan, P. R.; Subburaam, C. V. Adsorption of dissolved reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste. *Bioresour. Technol.* **2006**, *97* (14), 1618–1625.

(46) Weber, W. J.; Morris, J. C. Kinetics of adsorption on carbon from solution. *J. Sanitary Eng. Div. Am. Soc. Civ. Eng.* **1963**, *89* (SA2), 31–60.

(47) Ozcan, A.; Oncu, E. M.; Ozcan, A. S. Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite. *Colloid Surf. A: Physicochem. Eng. Aspects* **2006**, *277*, 90–97.

(48) Jaycock, M. J.; Parfitt, G. D. *Chemistry of Interfaces*; Ellis Horwood Ltd.: Chichester, U.K., 1981.