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Removal of anionic dyes from aqueous solution by modified alginate

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ABSTRACT

In this study, alginate as a low-cost and eco-friendly adsorbent was modified to remove dyes from wastewater. Modification of alginate was done using ethylenediamine. Fourier transform infrared was used to study the characteristic of alginate and modified alginate. The presence of functional groups such as hydroxyl, carboxylate, and amine groups was detected. Modified alginate was used to remove Direct Red 23 (DR 23), Direct Red 31 (DR 31), and Direct Red 80 (DR 80) from aqueous solution. The effect of three parameters such as adsorbent dosage, pH, and inorganic salts on dye removal was investigated at room temperature (26°C). During the dye removal study, the dye adsorption isotherm and kinetic were studied. It was found that DR 23 and DR 80 followed with Tempkin isotherm and DR 31 followed with Langmuir isotherm. In addition, the adsorption kinetic of dyes was found to fit into pseudo-second-order kinetics. Based on the obtained data from the current investigation, it could be concluded that the modified alginate as a biocompatible green material and low-cost adsorbent might be an appropriate alternative to remove anionic dyes from colored wastewater.

Keywords: Alginate; Modification; Biopolymer; Wastewater

1. Introduction

Control of water pollution has been one of the most important challenging subjects in research area currently [1]. Dyes are one of the important classes of pollutants which could discharge from textile, leather, food processing, dyeing, cosmetics, paper, etc. [2,3]. Not only any amount of dye in wastewater is noticeable but also it can be toxic. So it is very important topic from environmental view to remove dye from wastewater before reuse it again [4]. A number of methods such as chemical coagulation, chemical oxidation, photochemical degradation, membrane filtration, etc. have been used to remove dyes from the aqueous phase. The chemical coagulation process effectively decolorizes insoluble dyes, but it is not suitable for soluble dyes. Chemical oxidation is an operative process but expensive. Photochemical degradation in aqueous solution is probable to growth slowly. Biological treatment is mostly unsuccessful in removing color from wastewater since most dyes are toxic to the organisms used in such processes. On the other hand, each of the mentioned methods has its limitations and none of them has been effective in entirely removing the

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color from wastewater. Because the above technologies did not show effective success, the low-cost treatment methods have been studied for a long time [5].

The adsorption process is considered as the most important one because of low cost, ease of design, accessibility, and ability to treat dyes [6,7]. During different investigations, the greatest used adsorbents are clay minerals, activated carbon, and polymers [8]. Alginate is a biopolymer that is considered be biocompatible, nontoxic, biodegradable and low-cost. It can be characterized as an anionic copolymer comprised of mannuronic acid (M block) and guluronic acid (G block) units arranged in an irregular block-wise pattern of varying proportions of GG, MG, and MM blocks [9]. Many studies confirmed that alginate is an effective adsorbent for cationic dyes from wastewaters [6,8,10,11].

A literature review showed that alginate has not been used for removal of anionic dyes. In this paper, chemical modification of alginate by ethylenediamine as a means to discuss the ability to remove anionic dyes was studied. Direct Red 23 (DR 23), Direct Red 31 (DR 31), and Direct Red 80 (DR 80) were used as model compounds. The effect of working parameters such as modified alginate amount, pH, and presence of salts on dye removal was studied. In addition, isotherm and kinetic of dye adsorption were investigated.

2. Experimental

2.1. Materials

Ethylenediamine was supplied by Merck from Germany. Adjusting of pH was carried out using H_2SO_4 and NaOH, which were obtained from Merck (Germany). Anionic dyes including DR 23, DR 31, and DR 80 were supplied by Ciba. The chemical structure and characteristic of dyes are shown in Fig. 1 and Table 1, respectively.

Table 1
The chemical characteristic of dyes

Generic name	Abbreviation	$\lambda_{\max}$ (nm)
Direct Red 23	DR 23	502
Direct Red 31	DR 31	513
Direct Red 80	DR 80	542

2.2. Preparation of modified alginate

Modification of alginate was carried out as follows: 30 mL of water and 1 mL of ethylenediamine were added to 2 g of alginate powder. The above mixture was stirred by stirrer at room temperature for 2 min. Then the mixture was irradiated using microwave for 10 min. Finally, the product of reaction was dried at 40℃ for 48 h in oven [12]. Fig. 2 shows the schematic formation of reaction.

2.3. Characterization of alginate and modified alginate

The Fourier transform infrared (FTIR) was applied in order to characterize alginate and the modified alginate. FTIR spectrum (Perkin-Elmer Spectrophotometer Spectrum One) in the range 4,000–450 cm^{-1} was studied. FTIR spectra for raw alginate and modified one are shown in Fig. 3. The peak appearing at 3,442 cm^{-1} corresponds to the stretching vibration of hydroxyl groups. The presence of peaks at 820 and 890 cm^{-1}

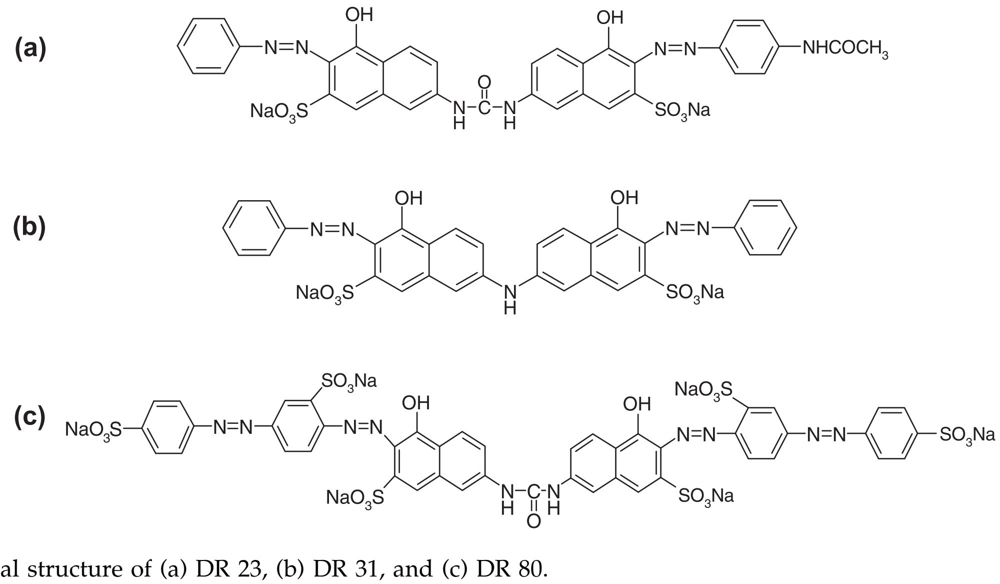

Fig. 1. Chemical structure of (a) DR 23, (b) DR 31, and (c) DR 80.

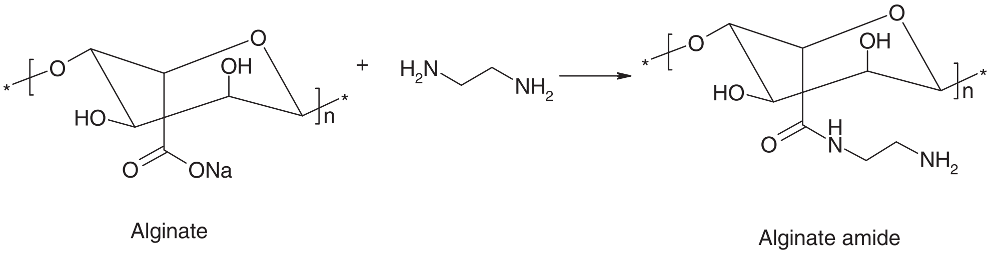

Fig. 2. The schematic reaction for modification of alginate using ethylenediamine.

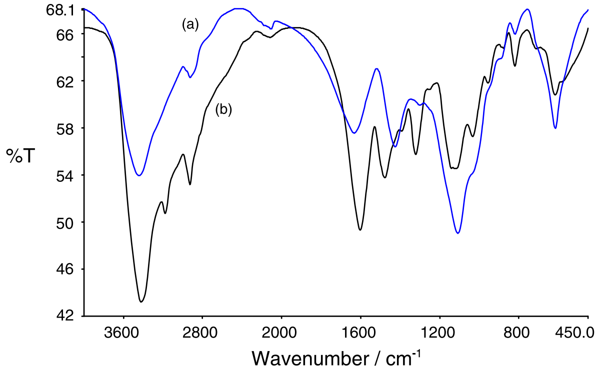

Fig. 3. FTIR spectra (a) alginate and (b) modified alginate.

indicates the existence of guluronic and mannuronic acid, respectively [13]. The band at 2,927 cm^{-1} is belonging to C–H stretching [14]. The peaks which appear at 1,633 and 1,426 cm^{-1} are correlated to asymmetric and symmetric stretching vibration of carboxylate [15,16]. The existence of peak at 3,180 cm^{-1} in FTIR spectrum of modified alginate can be related to secondary amide. Also, the band that is detected at 713 cm^{-1} is related to out-of-plane bending of N–H. The peak that appears at 1,034 cm^{-1} is attributed to the stretching of C–N in amine [17].

2.4. Analytical methods

The dye removal efficiency (R) of the dye was calculated as follows

$$R = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

where C_0 and C_t are the initial concentration and concentrations of the dye at time t (mg/L), respectively.

The mass of dye adsorbed per unit mass of the adsorbents (q) at any time ($C = C_t$) and at equilibrium ($C = C_e$) was calculated from the Eq. (2).

$$q = \frac{(C_0 - C)V}{m} \tag{2}$$

q (mg/g) is the adsorbed amount of acid dyes in the solid phase at equilibrium ($q = q_e$) and time t (min) ($q = q_t$), respectively. V indicates the volume of dye solution (L) and m is the weight of the adsorbent (g).

3. Results and discussion

3.1. The influence of adsorbent amount

In order to study the effect of adsorbent amount on removal of dye, different quantities of alginate and modified alginate (0.1–0.4 g) were added to 250 mL of each dye solution, while the primary dye concentration was 50 mg/L and pH was equal to 2. Then each solution was stirred by jar test at room temperature for 60 min at a stirring speed of 200 rpm.

After equilibrium, the solution samples were centrifuged and the concentration in the supernatant dye solution was measured using spectrophotometer. The percentage of dye removal vs. time for different adsorbent amounts is shown in Fig. 4. It is clearly found that alginate has not adsorbed any anionic dyes, while the modified alginate removed a large percentage of dyes in each dye sample solution. Based on Fig. 4, it is clear that the effect of adsorbent dosage plays an important role in adsorption process for anionic dye removal.

3.2. The influence of pH

One of the most important parameters in dye removal from the wastewaters is the pH of the solution. The pH of the solution effects on surface charge of adsorbent followed by the degree of ionization of dye in solution [18]. To study the effect of pH, different pH values (2, 5, 8, and 10) were used. Effect of initial pH on the dye removal is shown in Fig. 5. As shown in Fig. 5, the adsorption capacity increases when pH decreases. The maximum adsorption of DR 23, DR 31, and DR 80 occur at pH 2. It could be concluded that at lower pH more protons will be available to protonate amino groups of the modified alginate to form groups NH_3^+, thus increasing

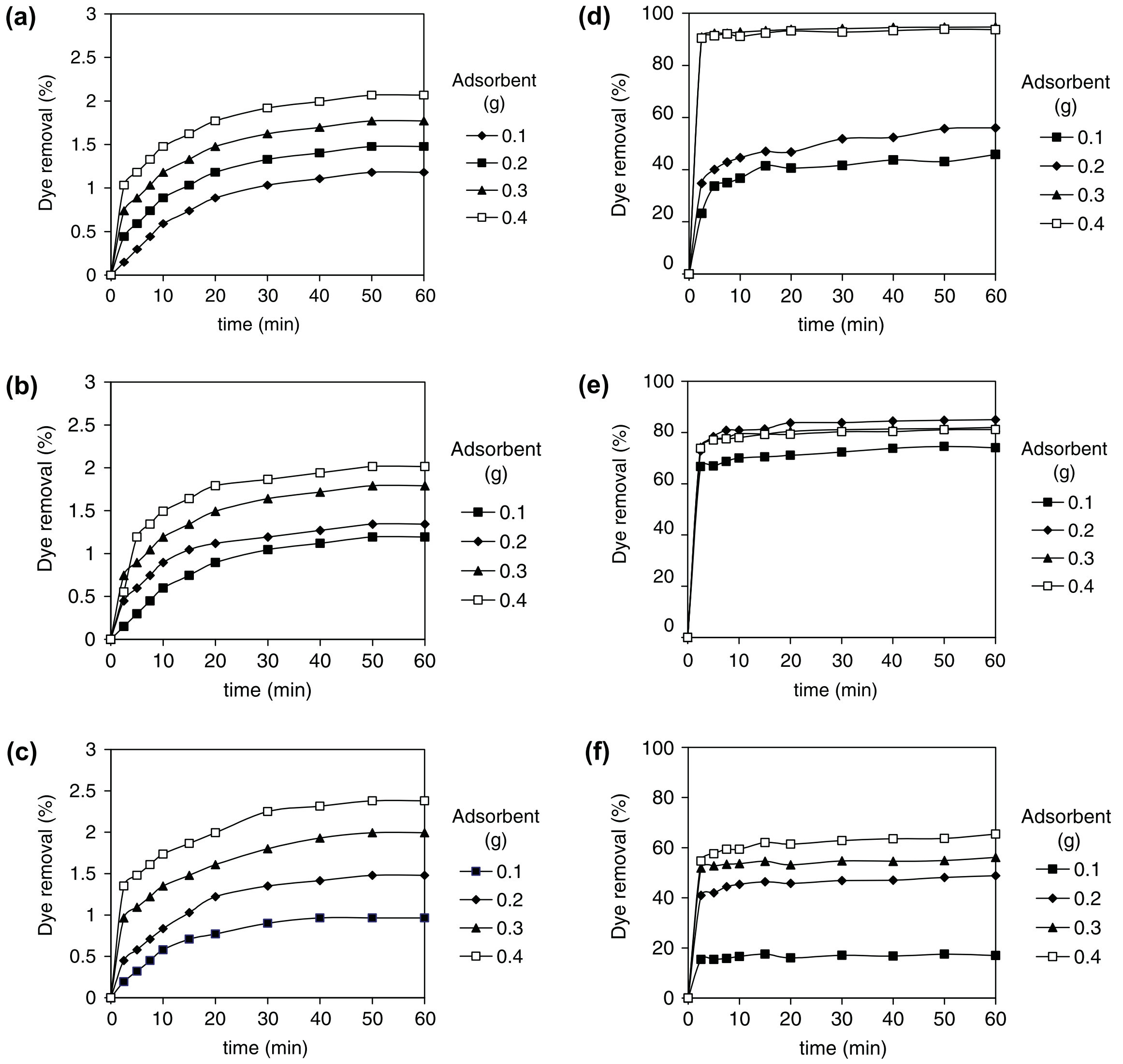

Fig. 4. Effect of adsorbent dosage on dye removal by alginate ((a) DR 23, (b) DR 31, and (c) DR 80) and modified alginate ((d) DR 23, (e) DR 31, and (f) DR 80).

electrostatic attractions between negatively charged dye anions and positively charged adsorption sites, and causing an increase in dye adsorption [19].

3.3. The effect of salts

The presence of salts as inorganic ions is very common in dye-containing industrial wastewater. These ions could compete for the active sites on the adsorbent surface or neutralize the adsorbent and, consequently, decrease the dye adsorption efficiency [20]. To study the effect of the presence of dissolved inorganic anions on adsorption of dyes, the effect of NaCl, $NaHCO_3$, Na_2CO_3, and Na_3PO_4 as the most important salts was investigated.

Fig. 6 shows that the dye removal capacity of dyes by modified alginate is decreased in the presence of salts, because these salts have small molecules and compete with dyes in adsorption onto modified alginate.

3.4. Adsorption kinetics

Adsorption which is a physiochemical process involves mass transfer of a solute from liquid phase to the adsorbent surface. Kinetic study provides important information about the mechanism of dye adsorption onto modified alginate [21]. In order to study the mechanism of sorption, characteristic constants of sorption were determined using pseudo-first-order of

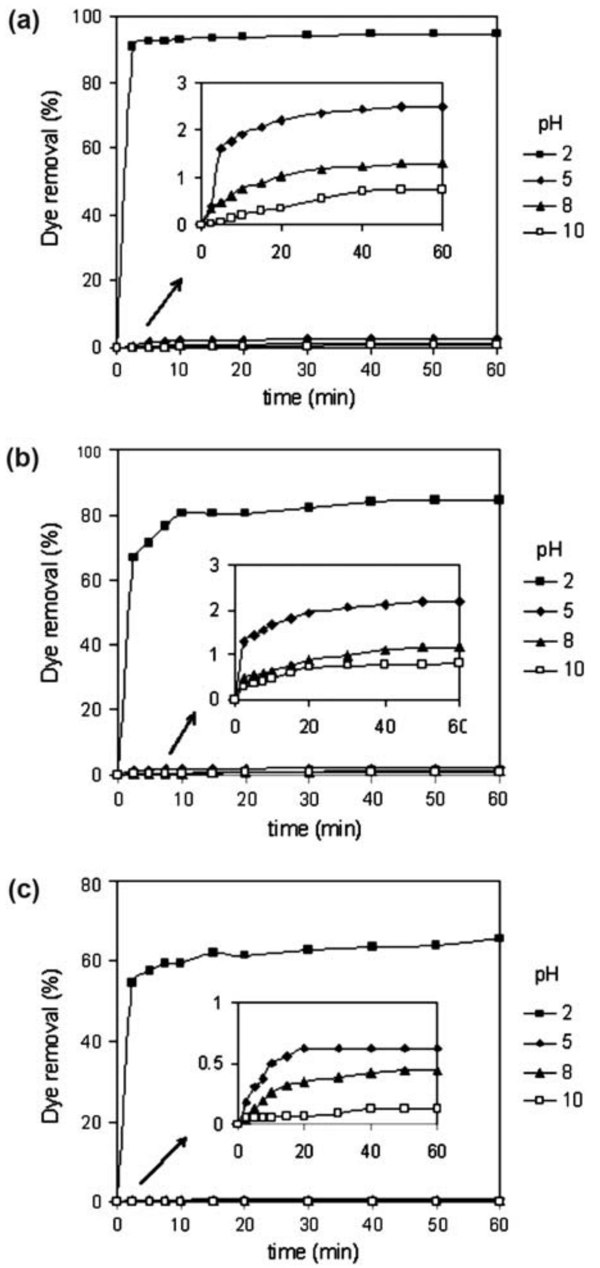

Fig. 5. Effect of pH on dye removal by the modified alginate (a) DR 23, (b) DR 31, and (c) DR 80.

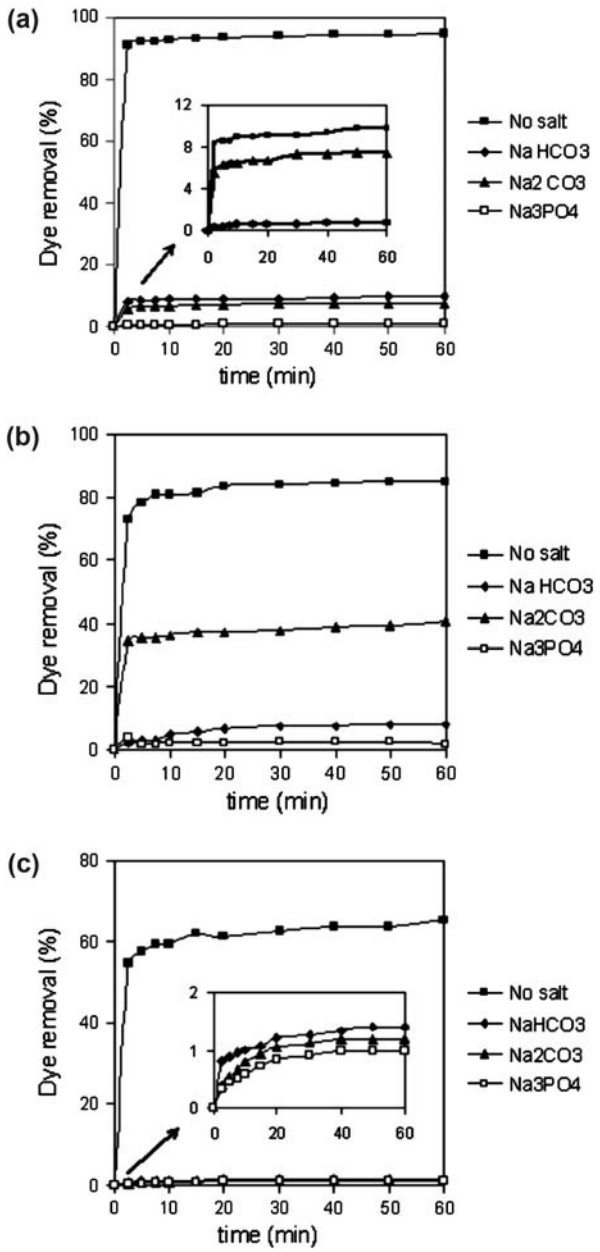

Fig. 6. Effect of salts on dye removal by the modified alginate (a) DR 23, (b) DR 31, and (c) DR 80.

Lagergren, pseudo-second-order equation, and intraparticle model.

The first-order rate equation of Lagergren [22] is as below:

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

where k_1 is the constant rate of first-order adsorption (min^{-1}). Eq. (2) shows the integrating of Eq. (3) for the boundary conditions $t = 0$ to $t = t$:

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

The second-order kinetic model is expressed as [23]:

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

which k_2 is the equilibrium constant rate of pseudo-second-order adsorption (g/mg min). The linearized integrated form of (5) is given as:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \qquad (6)$$

The probability of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle model as below:

$$q_t = k_p t^{1/2} + c \qquad (7)$$

where k_p is the intraparticle diffusion constant rate and c is the intercept.

To understand the applicability of pseudo-first-order, pseudo-second–order, and intraparticle diffusion models, linear plots of $\log(q_e - q_t)$ vs. contact time (t), t/q_t vs. contact time (t) (Fig. 7), and q_t against $t^{1/2}$ with different amount of adsorbent are plotted and the values of k_1, k_2, k_p, c, and r^2 (correlation coefficient values of all kinetics models) and the calculated q_e ($(q_e)_{cal}$) are shown in Table 2. All the experimental data showed better agreement with pseudo-second-order kinetic model in terms of higher correlation coefficient values ($r^2 > 0.9974$) and closer values between $q_{e,\ cal}$ and $q_{e,\ exp}$.

3.5. Adsorption isotherm

Adsorption isotherm models were commonly employed to show the relationship between the equilibrium solute concentration in bulk solution and its amount adsorbed per unit of adsorbent at constant temperature [24].

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

The Langmuir equation treats the interaction between the adsorbent and the adsorbate as a linear, reversible, and monolayer chemical reaction. This equation is a relatively straightforward model that assumes that the adsorbent surface is completely homogeneous, that each adsorbent site can bind a maximum of one adsorbate molecule, and that there are no interactions between molecules of the adsorbate. The Langmuir adsorption model can be expressed in the following form [25]:

$$q_e = Q_0 K_L C_e / (1 + K_L C_e) \qquad (8)$$

where Q_0 is the maximum adsorption capacity (mg/g) and K_L is Langmuir constant (L/mg).

The linear form of Langmuir equation is:

$$C_e/q_e = 1/K_L Q_0 + C_e/Q_0 \qquad (9)$$

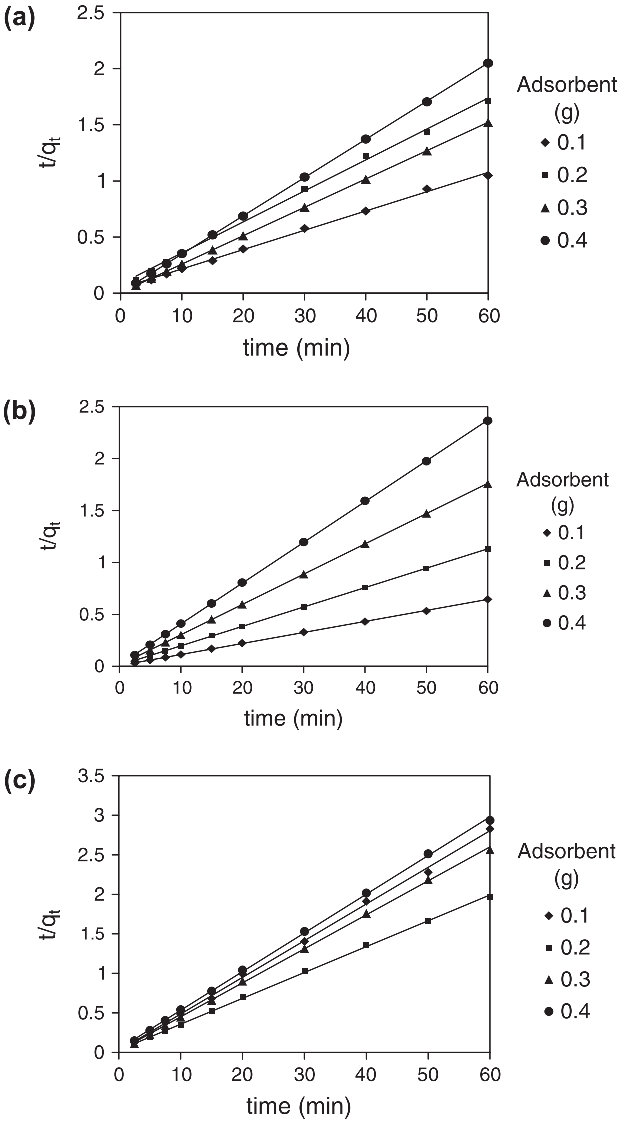

Fig. 7. Pseudo-second-order dye adsorption kinetics onto alginate amide (a) DR 23, (b) DR 31, and (c) DR 80.

The Freundlich isotherm model suggests a monolayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. This equation is helpful in quickly providing some general information about the affinity of a compound to be adsorbed. The Freundlich model is given by [25,26]:

$$q_e = K_F C_e^{1/n} \qquad (10)$$

Eq. (10) can be rearranged to a linear form:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (11)$$

Table 2
Kinetics constants for pseudo-first-order, pseudo-second-order, and intraparticle diffusion models

Adsorbent (g)	$(q_e)_{exp}$	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
		$(q_e)_{cal}$	k_1	${r_1}^2$	$(q_e)_{cal}$	k_2	${r_2}^2$	K_p	c	${r_3}^2$
DR 23										
0.10	57.27	29.27	0.05	0.76	58.10	0.01	0.99	5.69	20.62	0.70
0.20	35.02	19.86	0.08	0.87	36.21	0.01	0.99	3.42	12.93	0.71
0.30	39.44	3.68	0.10	0.78	39.55	0.13	1.00	2.86	23.72	0.35
0.40	29.27	2.24	0.09	0.51	29.36	0.17	1.00	2.11	17.66	0.34
DR 31										
0.10	93.16	22.54	0.10	0.81	94.34	0.01	0.99	7.33	51.32	0.43
0.20	53.11	9.77	0.09	0.83	53.53	0.04	1.00	4.20	29.3	0.43
0.30	34.17	4.44	0.07	0.71	34.29	0.07	1.00	2.59	19.57	0.39
0.40	25.36	1.42	0.02	0.22	25.48	0.10	1.00	1.92	14.58	0.38
DR 80										
0.10	1.20	4.17	0.09	0.54	21.58	0.09	0.99	1.67	11.96	0.41
0.20	30.50	6.53	0.06	0.67	30.69	0.04	0.99	2.50	15.92	0.47
0.30	23.39	2.69	0.04	0.40	23.25	0.09	0.99	1.71	13.49	0.37
0.40	20.44	4.25	0.05	0.65	20.44	0.05	0.99	1.63	10.67	0.46

where K_F is the adsorption volume at unit concentration and $1/n$ is adsorption intensity. K_F and $1/n$ are to be estimated from the intercept and slope of the Freundlich isotherm, respectively.

The Tempkin isotherm model suggests an equal distribution of binding energies over the number exchanging sites on the surface. The distribution of these energies depends on the number of functional groups on the dye molecule and the adsorbent surface. There is equal distribution of maximum binding energy during the adsorption process. The decline in the heat of adsorption is linear but not logarithmic in nature.

The Tempkin isotherm is given as:

$$q_e = RT/b\ln(AC_e) \tag{12}$$

The linear form of Tempkin isotherm can be written as:

$$q_e = B_1 \ln A + B_1 \ln C_e \tag{13}$$

where $B = RT/b$, T is the absolute temperature (K) and R is the universal gas constant (8.314 J/mol K). A is the equilibrium binding constant and B is corresponding to the heat of sorption [27].

The Q_0, K_L, K_F, n, A, B_1, and r^2 (correlation coefficient) are given in Table 3. The Tempkin isotherm is found to fit quite well with the experimental data for both DR 23 and DR 80 in accordance with the linear correlation coefficient (r^2). But the r^2 values for DR 31 indicate that the Langmuir isotherm is most appropriate for adsorption of this dye on alginate amide.

4. Conclusion

The adsorption of DR 23, DR 31, and DR 80 was studied onto alginate and modified alginate. The results of adsorption showed that alginate cannot be

Table 3
Isotherm constants for dye adsorption on alginate amide

	Langmuir isotherm			Freundlich isotherm			Tempkin isotherm		
	Q_0	K_L	r^2	K_F	n	r^2	A	B_1	r^2
DR 23									
	17.48	−0.27	0.98	79.98	−0.42	0.96	0.01	−11.52	0.98
DR 31									
	39.23	−0.49	0.99	88.71	−0.25	0.99	0.002	−12.53	0.99
DR 80									
	5.12	−0.06	0.87	1,651.9	−1.41	0.92	0.02	−22.42	0.99

used as an adsorbent for the removal of anionic dyes, but modified alginate effectively adsorbed anionic dyes from aqueous solution. The adsorption kinetics studies of dyes on alginate amide were achieved based on pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The data specified that the adsorption kinetics of dyes on alginate amide followed the pseudo-second-order model. The equilibrium data showed that the experimental data were correlated reasonably well by Tempkin isotherm model for DR 23 and DR 80, and Langmuir isotherm model for DR 31. The results showed that the alginate amide as the modified alginate being a biocompatible, eco-friendly, and low-cost adsorbent might be a suitable material for elimination of anionic dyes from colored aqueous solutions.

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