Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.905978

54 (2015) 2765–2776
May

Taylor & Francis
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Removal of methylene blue dye using biodegradable hydrogel and reusing in a secondary adsorption process

Ghada A. Mahmoud[a,*], Sahera F. Mohamed[b], Hala M. Hassan[c]

[a]*National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt, Tel. +20 1065495895; email: ghadancrrt@yahoo.com*
[b]*Microbial Biotechnology Department, National Research Center, Dokki, Cairo, Egypt*
[c]*Textile Technology Department, Industrial Education College, Beni-Suef City, Egypt*

Received 24 November 2013; Accepted 27 February 2014

ABSTRACT

Sodium alginate poly itaconic acid (NaAlg/IA) hydrogel was prepared by free radical polymerization using gamma radiation. Characterization of the hydrogel was done by thermogravimetric and Infrared analysis. The hydrogel was used for removal of methylene blue dye (MB) about 85% of dye was removed. The experimental data have been modeled by Langmuir, Freundlich, and Temkin, the adsorption data were well described by the Freundlich model. The adsorption kinetic was studied and the pseudo-second-order reaction was better than pseudo-first-order reaction for low concentrations of MB and vice versa. The calculated dimensionless separation factor R_L was 0.1 indicates favorable adsorption process. Thermodynamic parameters suggest that the adsorption is physical process ($\Delta H^\circ = -17.87\,\text{kJ/mol}$), spontaneous, and exothermic in nature. After adsorption, the NaAlg/IA hydrogel-loaded MB was applied to secondary adsorption of acid fast red dye (AFR) at suitable conditions. Successful results were obtained about 74% of AFR was removed due to the altered surface structures of the used adsorbents.

Keyword: Alginate; Itaconic acid; Hydrogel; Secondary adsorption; Waste dyes

1. Introduction

In recent years, pollution from dye wastewater has become a serious environmental problem due to the variety uses of dyes [1]. Colored organic effluent is produced in the textile, paper, plastic, leather, food, and mineral processing industries [2]. The effluents of the manufacturing and textile industries are discarded into rivers and lakes, changing their biological life [3,4]. Disposal of these effluents into water can be toxic to aquatic life [5].

Adsorption technology is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent [6–9]. But recycling of the used adsorbents is a problem, where, large amount of solvent is used to wash and recover adsorbents. So, a novel way has been investigated to use of used adsorbents [10]. Since, the surface structures of adsorbents have been changed after adsorption of some contaminant, the used adsorbents can be applied to adsorb other pollutants in suitable conditions [11].

Different methods using low-cost adsorbents for dye removal have been developed successfully

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*Corresponding author.

[12–20]. In recent years, particular interest has been devoted to hydrogels exhibiting phase transitions in response to changes in external conditions such as pH, ionic strength, temperature, and electric currents, known as the intelligent hydrogels. These hydrogels are suitable for dyes removal due to their hydrophilic nature and three-dimensional polymeric network which can imbibe large amounts of water [21].

Alginate is a high molecular weight polysaccharide extracted from various species of brown algae. It is a linear, anionic block copolymer heteropolysaccharide consisting of 1,4 linked β-D-mannuronic acid (M) and α-L-guluronic acid (G), The primary structure of alginate depending on the producing species, and for marine sources, on seasonal and geographical variations. Alginate salts are important hydrocolloids that are capable of both thickening and gelling water [22]. However, they are prone to enzymatic degradation and suffer from limitations in fabrication, which limits its application in some fields. Grafting is a well-established and powerful method for the development of natural–synthetic polymer hybrid materials.

Itaconic acid (IA) is one of the monomers, which is readily available at low cost. It is obtained from renewable resources by fermentation with *Aspergillus terrus* using carbohydrate materials as molasses and hydrolyzed starch [23,24]. Poly IA is interesting as a polyelectrolyte having two ionizable groups (–COOH–), with different pKa values, which can form H-bonds. These groups bring additional capability of chelate formation under certain cases.

It was reported for first time [25] the optimum condition for graft copolymerization of IA onto sodium alginate (NaAlg) by using benzoyl peroxide. The same hydrogel NaAlg/IA was synthesized by gamma radiation, as a pH-sensitive hydrogel and used as a sorbent for removal of Pb^{2+} ions from aqueous solution [26]. In this study, the same NaAlg/IA hydrogel was used for dyes removal and to identify various important parameters on the removal of methylene blue (MB) from its aqueous solution. The cationic dyes loaded hydrogels were used to removal of acid fast red dye (AFR). Kinetic and isotherm models were used for the quantitative description and prediction of the dyes uptake behavior of this hydrogel.

2. Materials and methods

2.1. Materials

Marine brown seaweed *Turbinaria decurrens*, collected in summer season, from jizan coast-KSA, was used for extraction of alginate. Dried seaweed crushed and silted (10–20 mesh). Reagent grade IA purity 99% (Merck, Germany) was used as received. The other chemicals such as dyes were reagent grade and used without further purification, the structures of dyes were shown in Fig. 1. For pH adjustment throughout the experiment, hydrochloric acid and/or sodium hydroxide solutions were used as necessary.

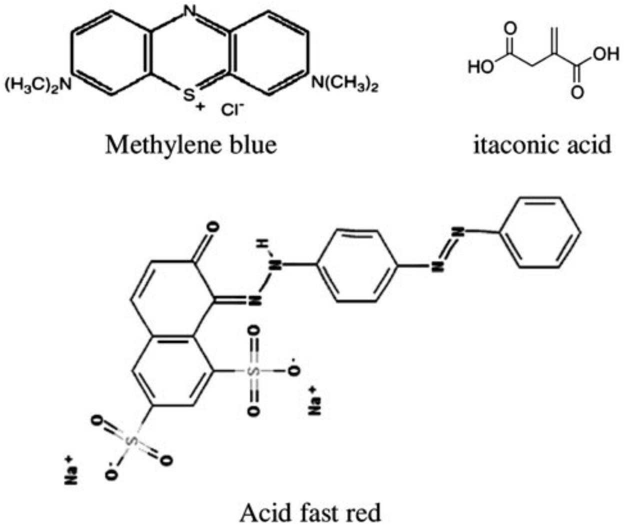

Fig. 1. Molecular structures of dyes.

2.2. Extraction of NaAlg from marine brown seaweed

NaAlg was extracted from *T. decurrens*, as shown in Fig. 2 and purified as described before [26]. The precipitate, NaAlg, collected and dried to constant weight. A sample of NaAlg was hydrolyzed by using formic acid in a sealed tube in a boiling water bath for 12 h. The hydrolase was analyzed by using HPLC.

2.3. Preparation of hydrogel

The NaAlg/IA hydrogels were synthesized by the free radical polymerization. An aqueous solution of 20% IA was mixed with 10% NaAlg. Then they were irradiated at different radiation doses 5, 10, and 20 kGy, at room temperature, with a ^{60}Co source at a dose rate of 3.065 kGy/h at the National Center for Radiation Research and Technology, Cairo, Egypt. The hydrogel was purified by washing in excess water so that unreacted chemicals were leached out then air dried at room temperature.

2.4. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analysis was performed on both free and dye-loaded

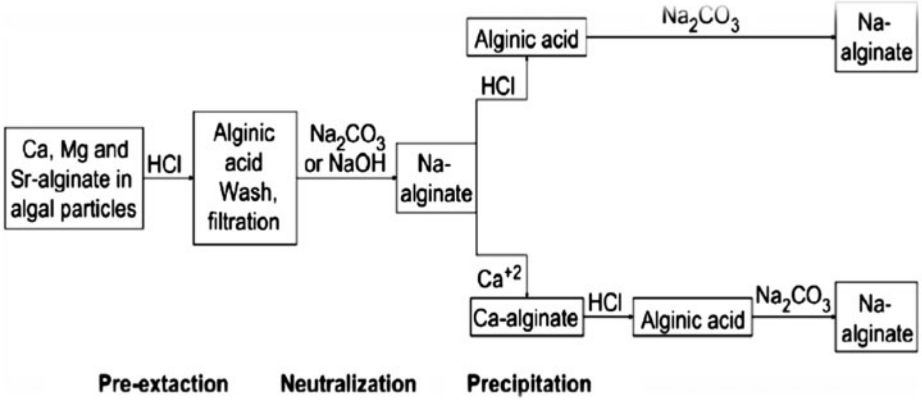

Fig. 2. Schematic showing alginate extraction procedure from algae.

hydrogel. FTIR analysis was performed on KBr discs with 2% finely ground sample analyzed on an FT/IR300e (Jasco) spectrophotometer within the range 400–4,000 cm^{-1} using a KBr window.

2.5. The swelling measurements

The clean, dried, and weighed hydrogel was soaked in bidistilled water at room temperature for different intervals time durations. The sample was removed and the excess water on the surface was removed by blotting quickly with filter paper and reweighed. The swelling ratio was calculated as follows:

$$\text{Swelling}\,(\text{mg/g}) = \frac{M_s - M_d}{M_d} \tag{1}$$

where M_d and M_s are the masses of dry and swelled hydrogel, respectively.

To investigate swelling behavior at various pH, the samples were swollen in several buffer solutions at room temperature in the same way as mentioned above.

2.6. Thermogravimetric analysis

Shimadzu thermogravimetric analysis (TGA) system of type TGA-50 was used for measurement of TGA. The nitrogen gas flow at constant rate was about 50 ml/min to prevent thermal oxidation processes of polymer samples. The heating rate was 10°C/min from ambient up to 600°C.

2.7. Adsorption studies

Batch adsorption experiments were carried out at different temperatures changed between 30 and 60°C. Exactly 100 ml of MB solution of known initial concentration (20–100 mg/dm^3) and pH 9 was shaken at the certain agitation speed (250 rpm) with 1gm dose of the dried hydrogel for 1,440 min. The percentage removal of the dye was calculated using the following relationship:

$$\text{Removal}\,(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

where C_o and C_t (both in mg/dm^3) are the initial dye concentration and the dye concentration at any time, respectively.

The adsorption capacity q_t (mg/g) at any time was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{3}$$

where V is the volume of the solution (dm^3), W is the mass of the dry hydrogel used (g).

The concentration of MB dye was determined by using Perkin–Elmer 601 single beam UV–Vis spectrophotometer at λ max of 665 nm with a quartz cell of 1.0 cm optical length.

The effects of various medium pH (2.0–12.0) on desorption of MB-loaded (NaAlg/IA) hydrogel were studied at ambient temperature. The final desorbed MB concentrations in solution were analyzed using the same method as mentioned above.

The adsorption capacities of (NaAlg/IA) hydrogel-loaded MB dye and free-loaded NaAlg/IA hydrogel for removal of AFR were investigated at various medium pH ranged from 2.0 to 10.0 at ambient temperature. The initial concentration of AFR was

100 mg/dm^3 and final AFR concentrations were calculated at a wavelength of 555 nm.

3. Results and discussion

3.1. Swelling measurements

3.1.1. Measuring of the maximum swelling time

In order to test the suitability of the hydrogel, the swelling behavior has been studied as a function of time and is shown in Fig. 3. It is concluded that the hydrogel swelling in water increases with time till it reached equilibrium swelling value after 5 h. The swelling increases as the content of SA also increases due to the introduction of more hydrophilic groups. So, the produced hydrogel of 3% SA content is suitable to be used for the adsorption process of MB in immersion time 5 h.

3.1.2. Effect of initial solution pH

The different compositions of the prepared hydrogel were tested for swelling behavior as a function of pH at different irradiation doses and are shown in Fig. 4. It was found that the swelling ratio increases with increasing the pH of medium in all compositions. At lower pH values (below the pKa of carboxylic groups, approximate 4.6), the carboxylic groups are protonated to –COOH groups, and the hydrogen bonds between –COOH and –OH groups are formed, which result in a decrease of swelling ratios.

When pH value is increased over 4.6, the carboxylic groups become ionized and the electrostatic repulsion between the molecular chains is predominated which leads to the network more expanding. It was also observed from Fig. 4 that as when the irradiation dose of the prepared hydrogel increases from 5 to 10 kGy, little increase in the swelling ratio was observed. But the hydrogel prepared by irradiation dose 15 kGy showed the lowest swelling affinity. The number of cross-linking in the hydrogel increases by radiation which reduces the free volumes between the macromolecular chains, meanwhile, the diffusion of water into the matrix becomes difficult [27]. It can be concluded that a high amount of absorbed dose decreases the number–average molar mass between cross-links, while a low amount of absorbed dose increase the number–average molar mass between cross-links.

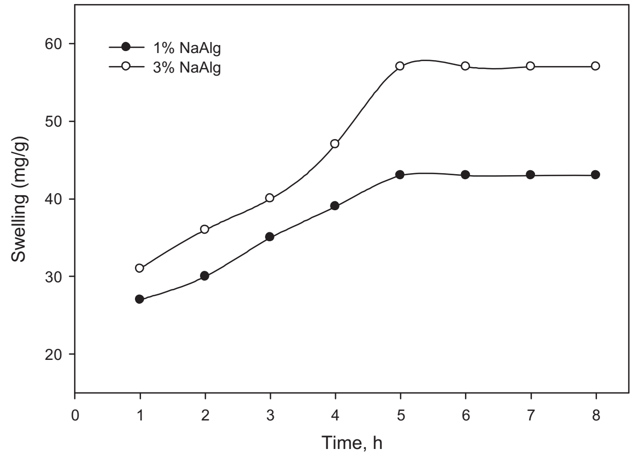

Fig. 3. Effect of time on the swelling of NaAlg/IA hydrogel.

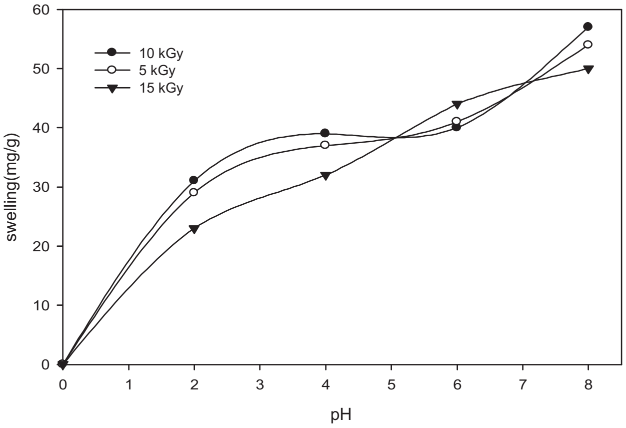

Fig. 4. Effect of pH on the swelling of NaAlg/IA hydrogel at different irradiation doses.

3.1.3. TGA

To investigate the thermal properties of free and dye-loaded NaAlg/IA hydrogel, their thermograms were recorded, and they are given in Fig. 5. The figure shows the same decomposition behavior for free- and loaded-MB hydrogel. For free-loaded NaAlg/IA hydrogel (Fig. 5(a)) a characteristic three-step thermogram was observed at 32–120, 228, and 393 °C. The first step of weight loss (7%) is attributed to moisture loss. The major weight loss (59%) occurs in the second step which may be attributed to degradation of intermolecular side chain. The third step of the weight loss attributed to decomposition of the backbone polymer. For MB-loaded NaAlg/IA hydrogel (Fig. 5(b)) the characteristic three-step thermogram was observed at 128, 237, and 400 °C. It can be concluded that, A little increase of thermal resistance was

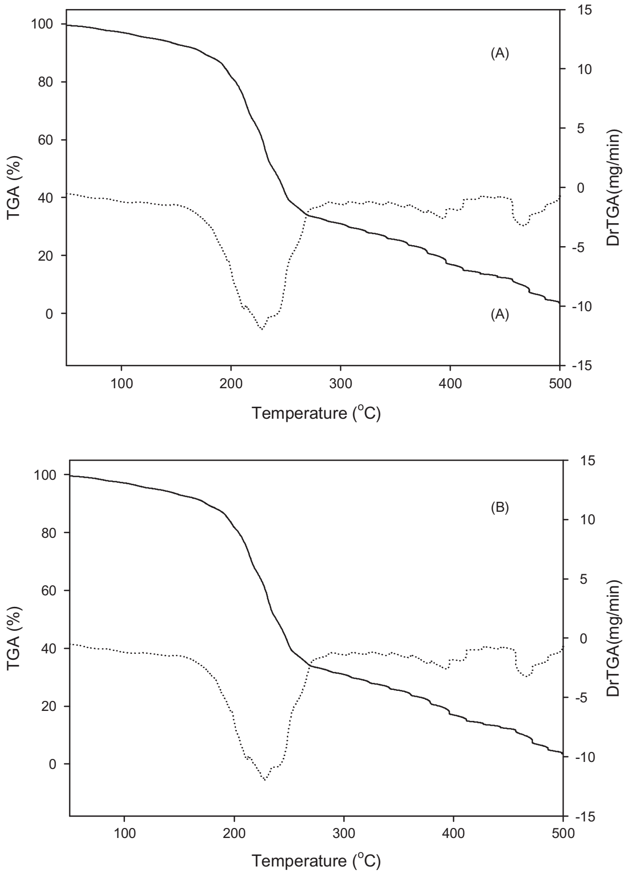

Fig. 5. TGA of free (a) and dye-loaded (b) NaAlg/IA hydrogel.

observed for dye-loaded NaAlg/IA hydrogel than the free one.

3.1.4. Spectroscopic analysis studies

FTIR analysis was performed on both free- and dye-loaded NaAlg/IA hydrogel and is shown in Fig. 6. In the free hydrogel (Fig. 6(a)) the band at 1,712 cm^{-1} is corresponding to C=O group of carboxylic acid group and a broad band at 3,373 cm^{-1} was due to the O–H group. IR spectrum of the dye-loaded hydrogel (Fig. 6(b)) consisted of four regions; the broad –OH stretching band shifted to 3,337 cm^{-1} indicated the intramolecular hydrogen bonding between NaAlg/IA hydrogel chains and the dye molecules, –CH stretching region at 2,800–3,000 cm^{-1}, carbonyl group stretching region at 1,713 cm^{-1}, and fingerprint bands below 1,550 cm^{-1}. The region between 1,500 and 1,800 cm^{-1} is a special range to evaluate the degree of saponification of the gel after binding with dye. A new band at 1,599 cm^{-1} due to the carboxylate ion groups which confirm the binding of the hydrogel with the dye.

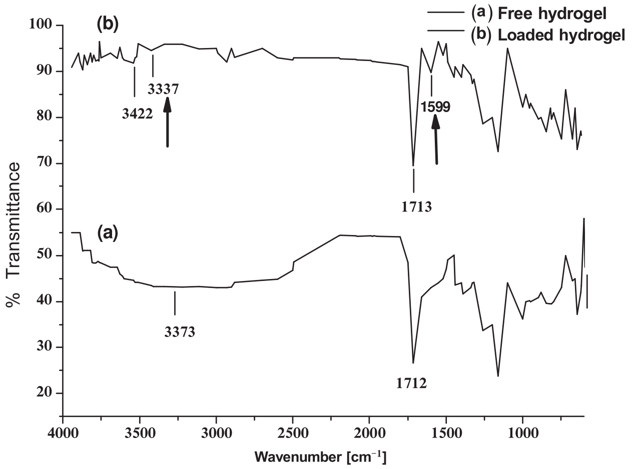

Fig. 6. FTIR Spectra of dye-loaded (a) and free (b) NaAlg/IA hydrogel.

3.2. Investigation of adsorption parameters

The adsorption process of MB on NaAlg/IA hydrogel characterization have been discussed considering the effect of different factors.

3.2.1. Initial dye concentration and contact time

The effect of contact time on the adsorption of MB dye onto NaAlg/IA hydrogel was investigated at different initial dye concentration (40–100 $\mathrm{mg/dm}^3$) and is shown in Fig. 7. It can be noticed that the removal of dye by adsorption on NaAlg/IA hydrogel was found to be rapid at the initial period of contact time and then to slowdown with time until it reaches equilibrium. The initial high rate of adsorption may be due to the attractive forces between the dye molecule such as Vander Waals forces and electrostatic attractions; fast diffusion onto the external surface was followed by fast pore diffusion into the intraparticle matrix to attain equilibrium at 80 min [28]. Also it can be seen from Fig. 7 that the percentage of dye adsorbed increases with the increase in the initial dye concentration, but the time required to reach equilibrium is independent of the initial MB concentration. The concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases [29,30].

3.2.2. Adsorption kinetics

Adsorption kinetics is an important characteristic for evaluating the efficiency of adsorption. The dynamics of sorption describes the rate of MB uptake

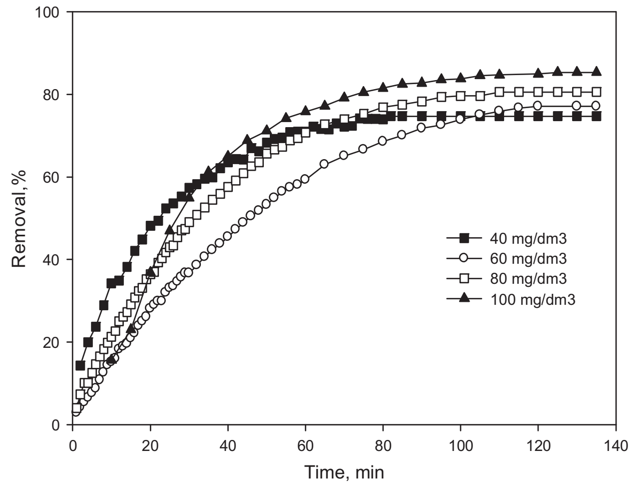

Fig. 7. Effect of contact time on the removal percent of MB by NaAlg/IA hydrogel at different initial dye concentrations and pH 9.

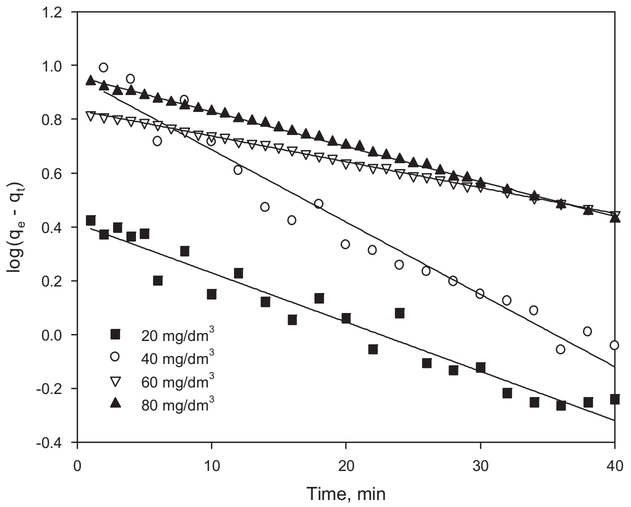

Fig. 8. Pseudo-first-order plot for the removal of MB by NaAlg/IA hydrogel at different initial MB concentrations.

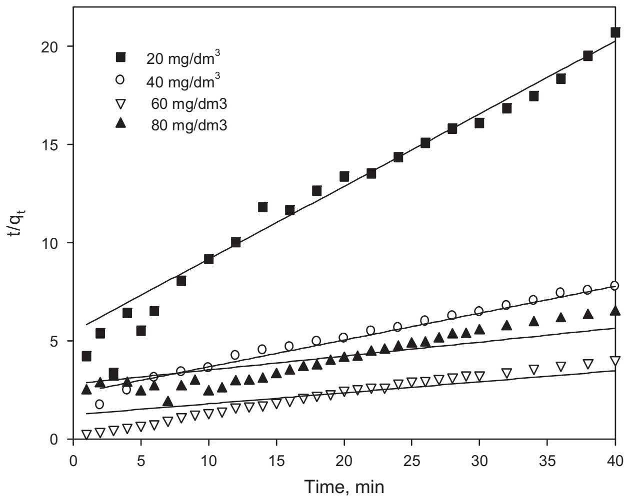

Fig. 9. Pseudo-second-order plot for the removal of MB by NaAlg/IA hydrogel at different initial MB concentrations.

on NaAlg/IA hydrogel and this rate controls the equilibrium time. In order to study the controlling mechanisms of the adsorption process, different kinetic models have been used to test the experimental kinetic data. The sorption dynamics of the adsorption by NaAlg/IA hydrogel was tested with the Lagergren pseudo-first-order [31], the chemisorptions pseudo-second-order [32], and the intraparticle diffusion mode [33].

The linearized form of the pseudo-first-order equation of Lagergren is generally expressed as follows:

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

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g). k_1 is the rate constant of pseudo-first-order adsorption. The plot of log ($q_e - q_t$) vs. t should give a linear relationship and is shown in Fig. 8; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

The pseudo-second-order kinetic model is represented by the following linear equation:

$$\frac{t}{q_t} = \frac{1}{k_2\,q_e^2} + \frac{1}{q_e}t \tag{5}$$

$$h = k_2 q_e^2 \tag{6}$$

where q_e, q_t, and t have the same meaning as explained above. k_2 is the overall rate constant of pseudo-second-order sorption (g/mg/min) and h represents the initial adsorption rate (mg/g min). If pseudo-second-order kinetics is applicable, the plot of t/q_t against t of Eq. (6) should give a linear relationship and is shown in (Fig. 9); q_e and k_2 can be determined from the slope and intercept of the plot. Several steps are involved in the sorption of sorbate by a sorbent. The mechanism of adsorption of a sorbate on a sorbent follows a series of steps. As it is known, adsorption proceeds in several steps involving transport of the solute from solution to the surface of the solid particles and diffusion of the solute into the interior of the pores which is usually a slow process [34].

Table 1 presents results obtained for the pseudo-first-order and pseudo-second-order model. Upon correlation of the kinetic data with the above two rate models, all of the kinetic data of low concentrations (20 and 40 mg/dm^3) are used for modeling with pseudo-second-order rate model but for modeling with pseudo-first-order rate model, higher initial concentrations (60 and 80 mg/dm^3) have been used and the same behavior was found for the calculated values of q_e(cal) (mg/g) for all four initial concentrations of MB. Thus the pseudo-second-order reaction is better than pseudo-first-order reaction for low concentrations of MB and vice versa.

Weber and Morri's intraparticle diffusion model, which is the most widely applied for sorption, has been studied. Based on this, it can be determined whether intraparticle diffusion is rate limiting for the sorption process or not.

The intraparticle diffusion rate constant k_{id} (mg g^{-1} min$^{-1/2}$) is given by the following equation:

$$q_t = k_{id} t^{0.5} \quad (7)$$

According to Weber and Morris [33], when intraparticle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of q_t vs. $t^{0.5}$ yield straight lines passing through the origin and the slope gives the rate constant k_{id}. According to the presented results (Fig. 10), the linear plots of q_t vs. $t^{0.5}$ did not pass through the origin; the intraparticle diffusion plot showed multi-linearity and is related by three straight lines. The deviation of the straight lines from the origin may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption [35]. The first stage, could be attributed to the diffusion of MB through the solution to the external surface of NaAlg/IA hydrogels and through the boundary layer to the surface of hydrogels. The second described diffusion of the solute into the interior of the pores. The third described the final equilibrium for which the intraparticle diffusion started to slow down due to the low concentration decreased by increasing the contact time owing to the smaller pores. Further, it showed that the intraparticle diffusion was not the rate-limiting step.

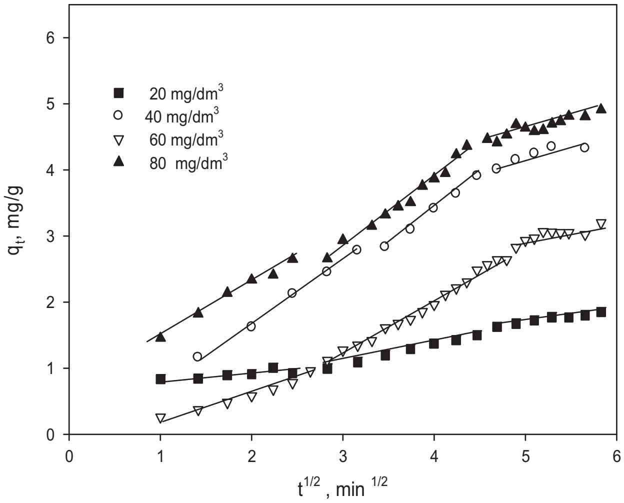

Fig. 10. Intraparticle diffusion plot for the removal of MB by NaAlg/IA hydrogel at different initial MB concentrations.

3.2.3. Effect of NaAlg concentration

The effect of hydrogel composition on the dye removal has been studied as show in Fig. 11. The alginate concentration in the hydrogel played an observable role in the adsorption efficiency. As increasing the NaAlg percentage in the hydrogel the adsorption process also increased. That is could be referred to increasing the functional groups responsible for interaction with cationic groups on the dye as the mechanism discussed above.

Table 1
Pseudo-first-order and pseudo-second-order kinetic parameters for the removal of MB by NaAlg/IA hydrogel at different initial MB concentrations (mg/dm^3)

		Pseudo-first-order model			Pseudo-second-order model			
Initial conc. (mg/dm^3)	$q_{e,exp}$ (mg g^{-1})	$k_1 \times 10^{-2}$ (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	$k_2 \times 10^{-3}$ (min^{-1})	$q_{e,cal}$ (mg g^{-1})	h (mg/g min)	R^2
20	2.50	4.21	2.85	0.9484	3.32	2.59	22.27	0.9829
40	6.05	6.19	9.03	0.9534	8.14	7.31	434.97	0.9965
60	6.81	2.49	7.16	0.9986	2.57	17.82	816.11	0.9123
80	9.16	3.26	9.47	0.9978	2.19	12.77	357.13	0.8924

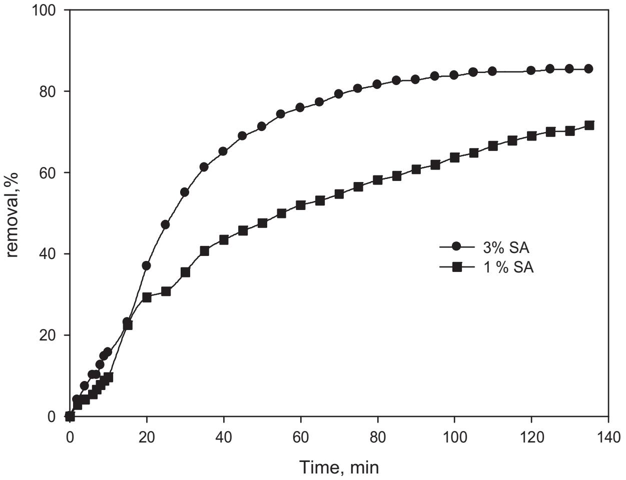

Fig. 11. The effect of NaAlg content on the removal of MB dye onto NaAlg/IA hydrogel at pH 9 and initial dye concentration = 80 mg/dm^3.

3.2.4. Isotherm analysis

The equilibrium isotherm was fundamental in describing the interactive behavior between the solutes and adsorbent. In this work, the equilibrium data for MB on NaAlg/IA hydrogel was modeled with the Langmuir (Eq. (8)), the linear form of the Freundlich (Eq. (9)), and Temkin (Eq. (10)) isotherm models.

$$\frac{C_e}{q_e} = \frac{a_L}{K_L} C_e + \frac{1}{K_L} \tag{8}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}$$

$$q_e = B \ln A + B \ln C_e \tag{10}$$

where C_e (mg/dm^3) is the equilibrium MB concentration in solution, q_e (mg/g) is the MB concentration in the adsorbent, a_L (dm^3/mg) and K_L (dm^3/g) are the Langmuir constants, and a_L is related to the adsorption energy. K_F (dm^3/g) is the Freundlich constant, and $1/n$ is the heterogeneity factor. B is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), $B = RT/b$, R the gas constant (8.314 J/mol K), b is Temkin isotherm constant, and T the absolute temperature (K).

The Langmuir model (Eq. (8)) represents a monolayer sorption process onto a homogenous surface, whereas the Freundlich model (Eq. (9)) assumes that the sorbent surface is heterogeneous in nature with an exponential distribution of active sites when an unlimited number of sorption sites are available. The Temkin isotherm equation (Eq. (10)) assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy [36].

The three isotherm model parameters were evaluated, the values of the correlation coefficient (R^2) were 0.98, 0.99, and 0.79 for Langmuir, Freundlich, and Temkin isotherm models, respectively, which indicate the Freundlich expression, provided a better linearity than the other isotherm models. This means the sorption of MB on NaAlg/IA hydrogel is heterogeneous energy distribution. The result also shows that the value of n is greater than unity ($n = 1.43$) indicating that the dye is favorably adsorbed on NaAlg/IA hydrogel.

The effect of isotherm shape can also be used to predict whether an adsorption system is "favorable" or "unfavorable." The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L which is defined by the following relationship [37]:

$$R_L = \frac{1}{1 + a_L C_0} \tag{11}$$

where R_L is a dimensionless separation factor, C_o the initial MB concentration (mg/dm^3), and a_L is the Langmuir constant (dm^3/mg). The value of R_L indicates the shape of the isotherm which is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L value for the adsorption of MB onto NaAlg/IA hydrogel is 0.10, indicating that the adsorption was a favorable process. This is in great agreement with the findings regarding to n value.

On the other hand, the correlation coefficient of Temkin model was ($R^2 = 0.79$) showing the poorest fit to the experimental adsorption equilibrium data. This means the adsorption of MB on the NaAlg/IA hydrogel is complex process, probably forming multi layers and even closing some of the pores. So, it can be conclude that the Freundlich isotherm model was more suitable for the experimental data than other isotherms.

3.2.5. Thermal effect

The dependence of the adsorption capacity of MB on the temperature has been investigated at 30, 40, 50, and 60°C and is shown in Fig. 12. It shows that with the increase in temperature from 30 to 40°C the

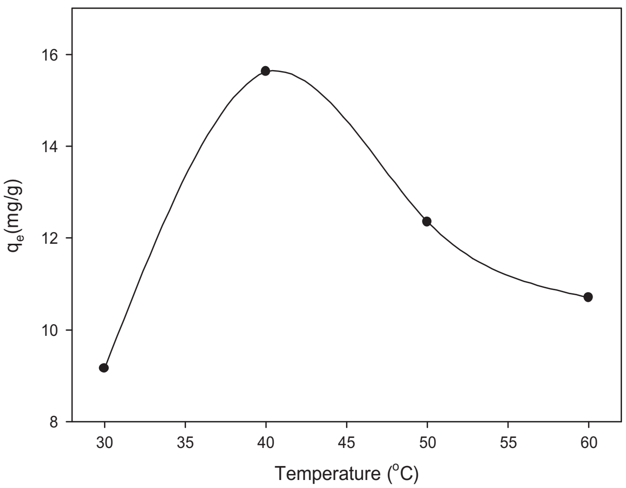

Fig. 12. Effect of solution temperature on the adsorption of MB dye onto NaAlg/IA hydrogel (initial dye concentration = 80 mg/dm^3, contact time = 80 min, and pH 9).

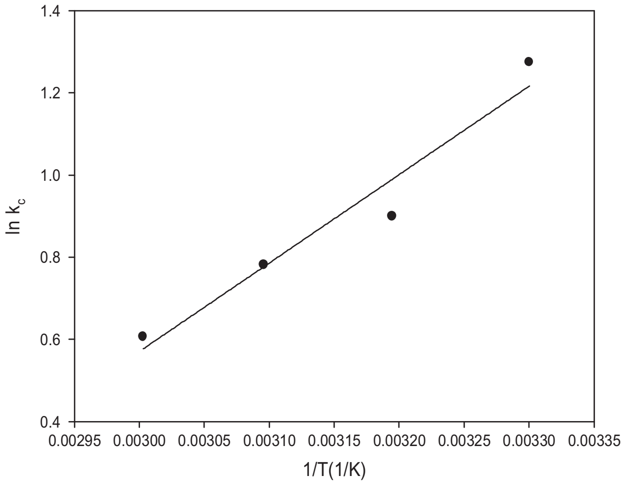

Fig. 13. Effect of solution temperature on the adsorption kinetic of MB dye onto NaAlg/IA hydrogel (initial dye concentration = 80 mg/dm^3, contact time = 80 min, and pH 9).

adsorption was increased, where above 40℃ a decreasing was occurred. The adsorption capacity increases with the increase in temperature from 30 to 40℃ due to two factors; firstly increasing the diffusion rate of the adsorbate molecules across the external boundary layer and the internal pores of the adsorbent particle, secondly, the decreases in case viscosity of the solution for highly concentrated suspensions. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [38]. A possible mechanism of the interaction is the reaction between the chromophore groups such as alcoholic, carboxylic of the NaAlg/IA hydrogel, and the cationic group in the dye molecule; such a reaction could be favored at moderate temperatures. A hydrogen bond can occur between OH groups of NaAlg/IA hydrogel and nitrogen atom of dye; electrostatic attractive forces between cationic dye ions and the surface of NaAlg/IA hydrogel. A decreasing in adsorption was occurred by increasing in temperature above 40℃, due to volume collapse upon warming. It has been shown that a number of hydrogels demonstrate nearly continuous volume transition from low temperature, highly swollen gel network to be collapsed at high temperature. This behavior indicates that this sorption process is exothermic process. Similar results were observed before with other sorbents [39].

3.2.6. Thermodynamic study

The thermodynamic parameters; Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°); for the sorption of MB onto NaAlg/IA hydrogel at various temperatures were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. The change in enthalpy (ΔH°) and entropy (ΔS°) are calculated using the van't Hoff [40]:

$$ln\, k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

where $k_c = F_e/(1 - F_e)$, and $F_e = (C_o - C_e)/C_o$, T is the temperature in degree K, and R is the gas constant [8.314 J/mol K]. The values of ΔH° and ΔS° have been computed from the slope and the intercept of the plot of $\ln k_c$ vs. $1/T$ (Fig. 13) which gives a straight line with acceptable coefficient of determination ($R^2 = 0.95$). The value of ΔH° is −17.87 kJ/mol suggests that the reaction is exothermic and its value was lower than 40 kJ/mol indicating physically controlled process. Generally, the enthalpy change due to chemisorption takes value between 40 and 120 kJ/mol [41]. Thus, the value of heat of adsorption ΔH° obtained in this study indicates that adsorption is due to physisorption and the interaction between NaAlg/IA hydrogel and MB is mainly electrostatic interaction. The values of ΔS° at 30, 40, 50, and 60℃ were −48.39, −49.62, −48.83, and −48.63, respectively, the negative value of ΔS° shows that decreasing randomness at the solid/liquid interface during the adsorption of MB on NaAlg/IA hydrogel, indicated the adsorption was not favorable at higher temperatures.

The values of the standard Gibbs free energy change were estimated using the following equation.

$$\Delta G^\circ = -RT \ln k_c \tag{13}$$

The values of ΔG° at 30, 40, 50, and 60°C were −48.39, −49.62, −48.83, and −48.63, respectively; indicate that this adsorption process is spontaneous in nature whereby no energy input from outside of the system is required [42]. The decrease in the values of ΔG° with an increase in temperature indicates that the adsorption process of MB on NaAlg/IA hydrogel becomes more favorable at low temperatures.

3.2.7. Secondary adsorption of AFR onto NaAlg/IA hydrogel-loaded MB

The surface structures and charge of NaAlg/IA hydrogel have been changed after covered by a layer of MB, however, NaAlg/IA hydrogel-loaded MB dye NaAlg/IA-MB can be applied to adsorb other type of dyes at suitable conditions. MB is cationic dye so, the MB-loaded hydrogels were tried to remove AFR as a model of anionic dyes.

The most important factor that affects either desorption of MB dyes or adsorption of AFR is pH of medium. So, effects of medium pH on desorption of NaAlg/IA-MB and adsorption AFR onto NaAlg/IA hydrogel was investigated and shown in Fig. 14. It was found that, at pH 6, a little desorption of MB dyes from NaAlg/IA hydrogel and applicable adsorption of AFR onto NaAlg/IA hydrogel. However, pH 6 was used in the second adsorption processes.

The secondary adsorptions of AFR onto NaAlg/IA-MB were performed at various initial concentrations of MB-loaded NaAlg/IA hydrogel and shown in Fig. 15. It can be observed that, as the contact time increased the removal percent also increased until reached the equilibrium after 180 min. AFR removal percent was between 62 and 74% depends on the loaded amount of MB which are applicable results. After adsorption of MB on the surfaces of NaAlg/IA hydrogel were covered with a layer of canionic dyes, which could adsorb anionic AFR through electrostatic interaction. It can be concluded that the removal percent of AFR by NaAlg/IA-MB was in connection with the amount of MB dyes loaded on NaAlg/IA hydrogel.

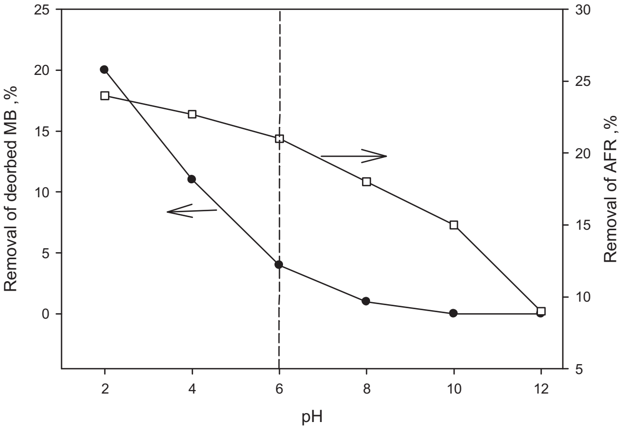

Fig. 14. Effect of pH on desorption of MB dye from NaAlg/IA hydrogel and adsorption of AFR onto NaAlg/IA hydrogel at ambient temperature.

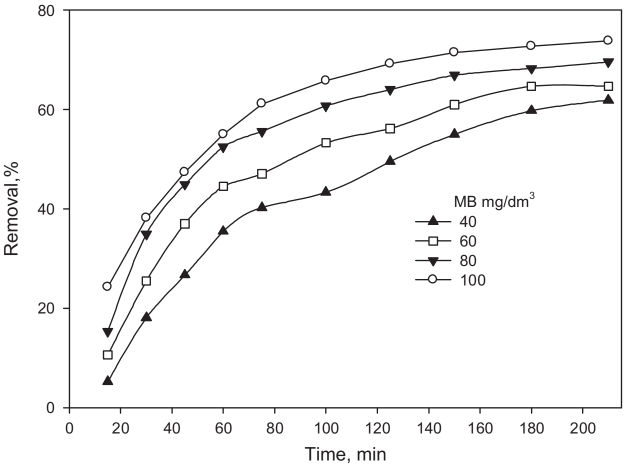

Fig. 15. Effect of contact time on the removal percent of AFR by (NaAlg/IA)-MB hydrogel at pH 6.

4. Conclusions

NaAlg and IA hydrogel was prepared by free radical polymerization using gamma radiation. The prepared hydrogels NaAlg/IA were confirmed using FTIR and TGA. The swelling equilibrium was occurred after 5 h at pH 8. The NaAlg/IA hydrogel was successfully evaluated for adsorption of MB dye, it was found that the concentration of adsorbed dye increased with the increase in the initial dye concentration and alginate content in the hydrogel. The equilibrium data are well fitted by Freundlich isotherm model with favorable dimensionless separation factor. The sorption of MB onto NaAlg/IA hydrogel follows pseudo-second-order kinetic model. Thermodynamic studies have shown the spontaneous and exothermic nature of NaAlg/IA hydrogel for the removal of MB. The NaAlg/IA hydrogel-loaded MB was employed to remove AFR as a second adsorption from aqueous solutions and showed high removal percent at suitable conditions. This means the second adsorption was an efficient and economical way for reuse of the NaAlg/IA hydrogel.

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