Preparation and Characterization of Polyalginate–Glutaraldehyde Membranes—Swelling Analysis by Microcalorimetry and Adsorption Kinetics of Cationic Dye

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ABSTRACT: Thin crosslinked polyalginate–glutaraldehyde membranes were prepared and characterized by Fourier-transformed infrared spectroscopy, thermal analysis (TG/DTG), and X-ray diffractometry. Microcalorimetric analyses have pointed out that water swellings of the membranes are slightly exothermic, and the swelling energies decrease with increasing temperature. The membranes were tested for the adsorption of methylene blue (MB) dye from aqueous solutions. The adsorption capacity of the membranes increased with increasing initial MB concentration and decreased with increasing temperature. It was observed that the MB adsorption kinetic data were best fitted by the Avrami model. Intraparticle diffusion of MB into the interior of the membranes was detected after 60 min of contact time. The MB adsorption on the membranes was also evaluated by three new 2^2 full factorial designs (36 experiments). It was found that binary interactions between initial dye concentration and temperature are statistically important for MB adsorption on the membranes. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 857–865, 2010

Key words: polyalginate membranes; microcalorimetry; dyes; multivariate modeling

INTRODUCTION

The textile industries release more than 0.2 million of tons of salts in the environment every year.[1] Unless properly treated, the dyes present in wastewaters can affect photosynthetic activity because of reduced light penetration and may also be toxic to certain forms of aquatic life.[2,3] Therefore, they must be removed before discharge. The accumulation and concentration of pollutants from aqueous solutions by the use of materials is termed sorption.[4,5] Biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons and can reduce dye concentration to ppb levels.[5] In this instance, polysaccharides have proven to be effective sorbents for use in industrial applications.[6]

Alginic acid is a copolymer of 1,4-linked β-D-mannuronic and α-L-guluronic acid residues, each containing one carboxylate group per monomeric unit (Fig. 1). Different species of alginates contain different percentages of mannuronic acid (M) and guluronic acid (G), with an average M : G ratio of 1 : 5.[6] The hydroxyl groups have been found to play an important role not only to cation exchange capacity but also to the affinity of the material toward different ions in solution.[6,7]

In general, the microstructures of the powders and beads polysaccharides are probably not porous enough and the surface areas are usually small. Particular advantages of the membranes are relating to their good tensile strengths (up to 1.0 MPa) and convenience to handling in experimental procedures. In addition, their large contact areas, short diffusion paths, low pressure drops, and very short residence times for adsorption are also potential advantages over powder-like biosorbents.[7]

All polymers contain a small amount of water, which is absorbed during synthesis, processing, or storage. Various natural and synthetic polymers, which have hydrophilic groups such as hydroxyl, carboxyl, and carbonyl, have strong or weak interaction with water. The nature of water in hydrophilic membranes is of the most importance in understanding their dynamic and equilibrium swelling behavior as well as in analyzing solute transport and other diffusive properties of such systems. Bound water in the water-insoluble hydrophilic polymers, such as alginates, breaks hydrogen bondings between the hydroxyl groups of the polymers. Water can "plasticize" the polymer matrix or form stable bridges through hydrogen bonding, resulting in an antiplasticizing effect. Important kinetic and energetic aspects of water interaction with polymers can be

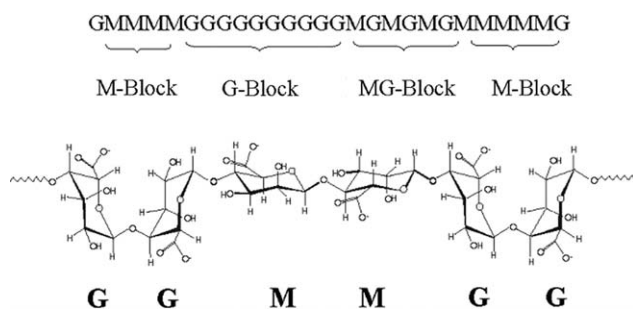*Correspondence to:* A. R. Cestari (cestari@ufs.br).

Figure 1 Polymeric structure of alginate having M-, G- and MG blocks.

observed calorimetrically.[8] In spite of extensive researches on swelling of polymers, information concerning energetic aspects at water/polymer interfaces is difficult to find in polymer literature.

On the other hand, the extent of dye adsorption depends on many factors, such as the nature of the adsorbent, the kind of the adsorbate molecules, and solution conditions, such as the initial concentration of the solute, temperature, and the adsorption pH value. Therefore, experimental procedures are the only manner to evaluate the interactions of membrane–adsorbate in solution.[1–5]

Statistical methods of experimental design and system optimization such as factorial design and response surface analysis have been applied to different adsorption systems because of their capacities to extract relevant information from systems while requiring a minimum number of experiments.[9–11] Multivariate methods are capable of measuring interaction at the solid/solution interface as well as the individual effect of each experimental factor on response properties of interest in the most precise way possible. However, as far as we know, despite the large number of adsorption works using polymeric membranes, the roles of changes of important experimental parameters, such as the solute concentration in solution and temperature, as well as their binary interactions on dyes adsorptions are few and scattered.

In this work, thin crosslinked polyalginate membranes were prepared and characterized. Microcalorimetry was used to study quantitative and energetic aspects of the water swelling of the membranes. The role of the adsorption kinetic parameters was evaluated using new multivariate factorial designs.

EXPERIMENTAL

Materials

All chemicals were all of analytical grade and used without further purification. Sodium alginate (Viscosity average of about 100 kDa) and the methylene

blue dye (hereafter described as MB for simplicity) were provided by Sigma. Glutaraldehyde (GA; 50 wt % content in water), hydrochloric acid (35.5 wt % content), and acetone were purchased from Synth (Brazil).

Preparation of thin alginate membranes

About 5 g of sodium alginate was dissolved in 100 mL of water at 50°C under overnight stirring. The gel was homogenized mechanically and was cast on polyethylene plates forming a thin layer. A homemade spacer was used to prepare membranes with similar thicknesses (about 14 μm). The membranes were washed with methanol and water several times until constant values for water conductivity. The dry films formed were peeled off the polyethylene plates and immersed into an acetone solution containing 5.0 wt % GA and 1.0 wt % HCl for the crosslinking of the films for 24 h. The crosslinked films were then taken out of the solution and washed with 0.1 mol L^{-1} NaOH aqueous solution to remove HCl from solution and several times with an excess amount of deionized water at 50°C for 24 h and then dried under vacuum for 24 h. The films prepared were used as membranes.

Characterization of the membranes

Fourier transformed infrared spectroscopy (FTIR) spectra of the membranes were taken on an Spectrum BX FTIR spectrophotometer (Perkin Elmer), using the diffuse reflectance method. X-ray diffractograms (DRX) analyses were performed in a Rigaku diffractometer, in the 2Θ range from 5° to 80° (accumulation rate of 0.02 min^{-1}), using Cu Kα radiation. Thermal analysis (TG/DTG) was determined with a SDT 2960 thermobalance (TA Instruments); each membrane sample was run at a scanning rate of 10°C min^{-1} under a nitrogen atmosphere from room temperature to 800°C or until constant mass loss detection. DSC
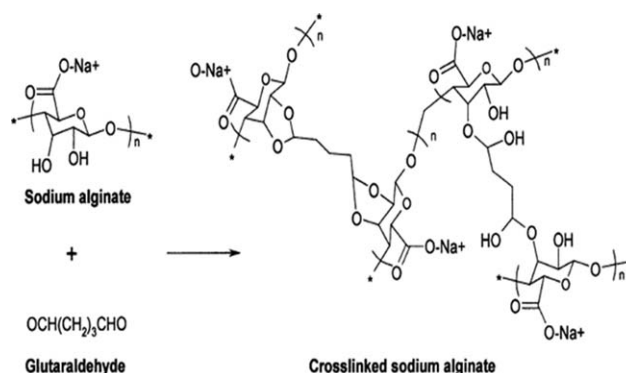

Figure 2 Cross-linking reaction of alginate using glutaraldehyde.

analyses were performed in sealed Al pans, in a calorimeter from TA Instruments, from room temperature to 400°C in a nitrogen atmosphere.

Microcalorimetric measurements

Microcalorimetric determinations were performed in a C80 microcalorimeter (SETARAM), which is capable of maintaining a baseline of ± 0.12 µW with a temperature stability of $\pm 10^{-4}$°C. Experimental determinations were performed using the membrane (thin Teflon®) as described elsewhere.[11] Briefly, a polyalginate–glutaraldehyde membrane was cut into 1.00×1.00 cm^2 sections, and 3.0 mL of deionized water was put into the lower and the upper part of the calorimetric vessel, respectively. Calorimetric output is of thermal power (dq/dt; mW) as a function of time (t; s), and consequently, the integral of this data to time t is equal to the interaction energy (J). The thermal effect of thin Teflon® membrane breaking for the empty cell was found to be negligible. The calorimetric experiments were carried out at 25 (two repetitions), 35 (two repetitions), 45 (three repetitions), and 55°C (three repetitions). The adsorbed water amounts (WAs) were determined according to the following formula: WA (%) = [(wet membrane mass − dried membrane mass) × 100]/(dried membrane mass).

Adsorption experiments

The kinetic adsorption experiments were performed by isothermal batch procedures, from 25 to 55°C, using pH 8.0 MB 1.00×10^{-3} mol L^{-1} borate/HCl buffered solutions from 2.50×10^{-5} to 1.60×10^{-3} mol L^{-1}. In each experiment, 50 mL of dye solution was added in a dark glass flask containing a selected crosslinked membrane, which was previously cut into square pieces of 6.25 cm^2. The flask was shaken continuously on a selected temperature using a termostatized bath (precision of ± 0.1°C) from Micronal (Brazil). At a predetermined time, a sample of solution was taken, and the MB concentrations were determined spectrophotometrically at $\lambda_{max} = 663$ nm. All determinations were carried out in triplicate runs.

The adsorbed MB quantities were calculated using the expression:[12]

$$q_t = \frac{(C_i - C_t)V}{m},$$ (1)

where q_t is the fixed quantity of MB dye per gram of membrane at a given time t in mol g^{-1}, C_i is the initial concentration of dye in mol L^{-1}, C_t is the concentration of dye at a given time t in mol L^{-1}, V is the volume of the solution in L, and m is the mass of the membrane in g.

Factorial designs calculations

Full 2^2 factorial designs were performed to evaluate the importance of the initial MB concentration and adsorption temperature on the adsorptions of MB on crosslinked membranes. The responses evaluated were the maximum adsorption amount (q_t^{max}).

Principal and interaction effect values are easily calculated from factorial design results. Both types of effects are calculated using the eq. (2).[13]

$$\text{Effect} = \bar{R}_{+,i} - \bar{R}_{-,i},$$ (2)

where $\bar{R}_{+,i}$ and $\bar{R}_{-,i}$ are average values of N_f for the high (+) and low (−) levels of each factor, respectively. For principal or main effects, the above averages simply refer to the results at the high (+) and low (−) levels of the factor whose effect is being calculated independent of the levels of the other factors. For binary interactions, $\bar{R}_+$ is the average of results for both factors at their high and low levels, whereas $\bar{R}_-$ is the average of the results for which one of the factors involved is at the high level and the other is at the low level. In general, high-order interactions are calculated using the above equation by applying signs obtained by multiplying those for the factors involved, (+) for high and (−) for low levels. If duplicate runs are performed for each individual measurement, as done in this work, standard errors (E) in the effect values can be calculated by:[13]

$$E = \{\Sigma(d_i)^2/8N\}^{1/2},$$ (3)

where d_i is the difference between each duplicate value and N is the number of distinct experiments performed.

The statistical calculations (t-tests, F-tests, analysis of variance, and multiple regressions) were performed using the software packages ORIGIN® and the Statistica®, both release 7.0.

RESULTS AND DISCUSSION

Characterization of the membranes

The membranes were transparent before and after the crosslinking reaction. The crosslinking reaction is related to the competition between the swelling reaction by the water absorbed into the hydrophilic membranes and reaction between the —OH and O=CH— groups of both the membranes and GA, due to the swelling of the membrane, accompanying the increase in the intermolecular distance, make the membrane unfavorable for tight crosslinking (Figure 2).[14] In general, alcohols as weak nucleophiles have limited reactivity toward an aldehyde under neutral conditions. However, under acidic conditions, the carbonyl
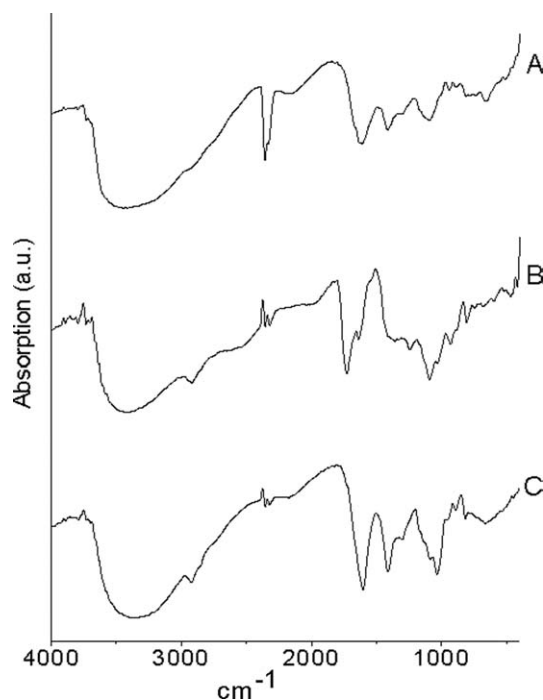
Figure 3 FTIR spectra of the alginate membranes before (A), and after (B) the cross-linking reaction, and after interaction with the methylene blue dye (C).

oxygen is protonated, strongly polarizing the carbonyl group. The oxygen lone-pair electrons from alcohol can readily attack the activated carbonyl group, resulting in rapid addition of an alcohol to the aldehyde. There are two hydroxyls in each of the uronic acid residues. In the presence of HCl, the nucleophilic addition of hydroxyls from polyhexuronic acid to aldehyde initially yields an oxonium ion. Deprotonation of the alcoholic oxonium produces a neutral hemiacetal tetrahedral intermediate. Further protonation of the hemiacetal hydroxyl by hydrochloric acid converts it into a good leaving group. The loss of water from the hemiacetal results in an intermediate carbocation. The second equivalent alcohol undergoes nucleophilic addition to the polarized carbonyl group of the carbocation, generating protonated acetal. Loss of a proton yields neutral acetal product. Because the second hydroxyl group is in close proximity and due to the excluded volume effect of macromolecules in dilute solution, it is more thermodynamically favorable to add the hydroxyl from the same hexuronic acid monomer to the carbocation than any other hydroxyls from the nearby polymer chain. To generate predominantly intermolecular crosslinking, the chemical crosslinker should be tetrafunctional, as is the case with 1,5-pentanedial, which is capable of reacting with four hydroxyl groups, forming two acetal linkages between two hexuronic acid monomers from adjacent polymer chains.[15]

The FTIR spectra are shown in Figure 3. Sodium alginate showed two strong absorption bands at 1630

and 1420 cm^{-1} due to carboxyl anions (asymmetric and symmetric stretching vibrations, respectively).[15] A "shoulder band" of C—H stretching at 2910 cm^{-1} is observed as well.[16] The peak observed at 3420 cm^{-1} corresponds to O—H stretching vibrations of Na-Alginate. For the crosslinked membranes, the sharp peak at 1100 cm^{-1} represents the C—O—C stretching vibration due to crosslinking of Na-Alginate membrane; with increasing reaction time more —OH groups transformed into —C—O—C— groups (acetal linkage). Also, the peak at 2910 cm^{-1} (C—H stretching) became stronger confirming the crosslinking reaction by GA. In the spectrum (C), after adsorption of MB, new peaks at 1610 and 1413 cm^{-1} were observed due to the symmetric and asymmetric stretching formed by the reaction of —COOH groups with sodium ions used in the buffered solutions.[12]

The TG/DTG curves are presented in Figure 4. The thermal processes are related to dehydration (25–100°C), decomposition (170–350°C), and carbonaceous residue burn (350–800°C) residue.[17,18] The curves of the noncrosslinked membranes and the
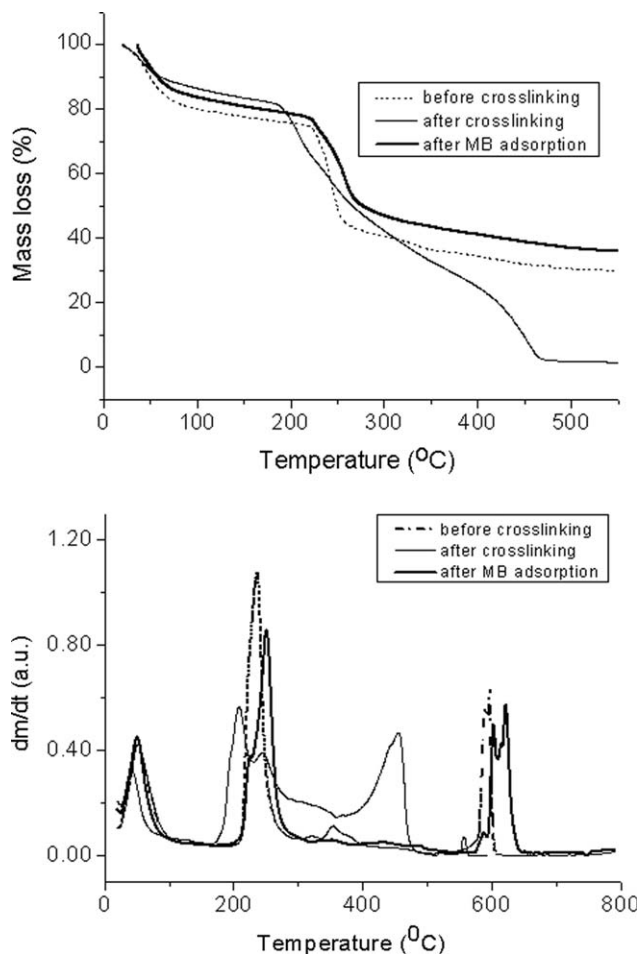

Figure 4 TG (upper part) and DTG (lower part) curves of the alginate membranes before, and after the cross-linking reaction, and after interaction with the methylene blue dye.
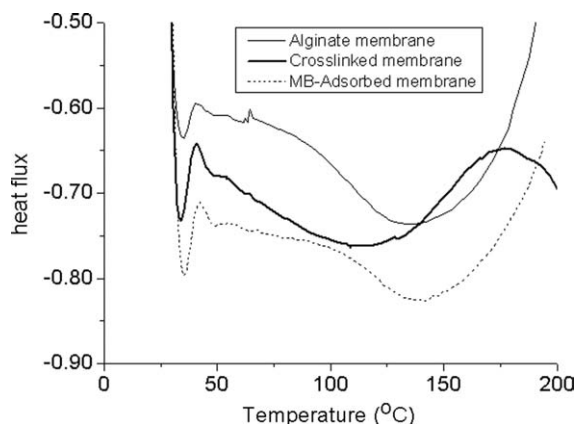
Figure 5 DSC curves of the alginate membranes before, and after the cross-linking reaction, and after interaction with the methylene blue dye.

MB-adsorbed membranes are relatively similar to each other. The TG curve for the crosslinked membranes presents a lower residue than the other membranes used in this work.

In Figure 5 we can see the DSC thermograms of the alginate membranes. It is observed initial endothermic peaks at about 40°C, because of dehydration of membranes. The glass transition temperature (T_g) for all membranes was about 50°C. Additional broad endothermic peaks from 100 to 200°C were also observed, because of partial decomposition reactions of the polymeric chains of the membranes.[17]

The DRX of original, crosslinked and MB-adsorbed alginate membranes are shown in Figure 6. The diffractograms suggest amorphous nature of the membranes, with broad peaks at about $2\Theta = 12°$. The reduction of this peak for both the crosslinked and
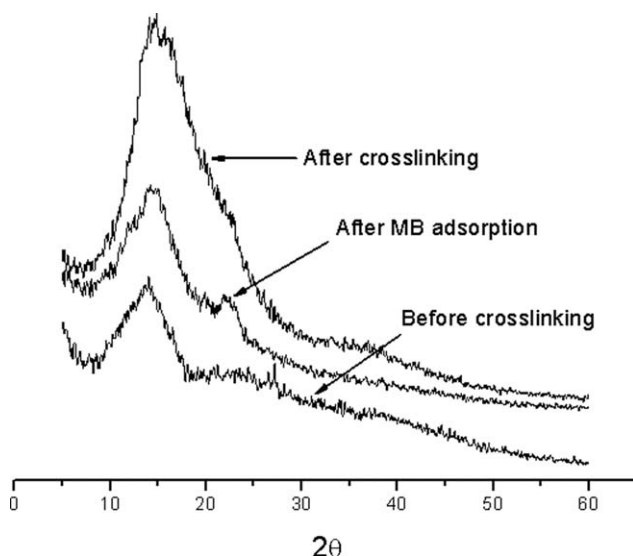

Figure 6 DRX diffractograms of the alginate membranes before, and after the cross-linking reaction, and after interaction with the methylene blue dye.
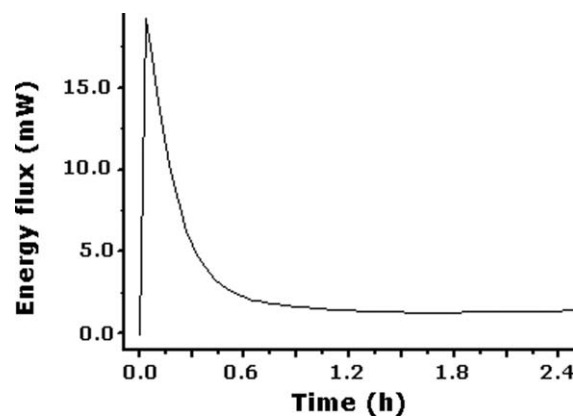

Figure 7 Typical water swelling profile of the polyalginate-glutaraldehyde membranes by means of isothermal heat-conduction microcalorimetry.

the MB-adsorbed membrane suggests the occurrence of the crosslinking reaction. It is a well-known fact that the polymer chains are in close compaction with one another and thus a reduction in the cluster space may be encountered.[19] This suggests shrinkage in cell sizes or intersegmental spacing and the presence of relatively large free volumes in the crosslinked membranes structures. On the other hand, an additional peak at $2\Theta = 22°$ appeared in the MB-adsorbed membrane diffractogram suggests partial reorganization of the structure of the crosslinked membranes after the MB dye interaction.[19]

Microcalorimetric results

The typical profile of the microcalorimetric interaction processes is illustrated in Figure 7. The base line used for the integrations was selected as linear from first to last point, joining the two extreme points selected on the curves. The interaction energy values and the reaction time required to yield are presented in Table I. The water swelling reactions are slightly exothermic, and interaction energies decrease as temperature increases. The WA amounts of adsorbed water increased as temperature increases. The

TABLE I
Swelling Parameters of 1.00 cm² Polyalginate–Glutaraldehyde Membrane in Relation to Temperature

Temperature (°C)	Average interaction time (min)[a]	Average WA (%)[b]	Average interaction energy (J cm⁻²)[c]
25	150	70	0.400
35	147	94	0.250
45	145	137	0.090
55	145	150	0.010

[a] Average standard deviation (%) = 3.5.
[b] Average standard deviation (%) = 4.8.
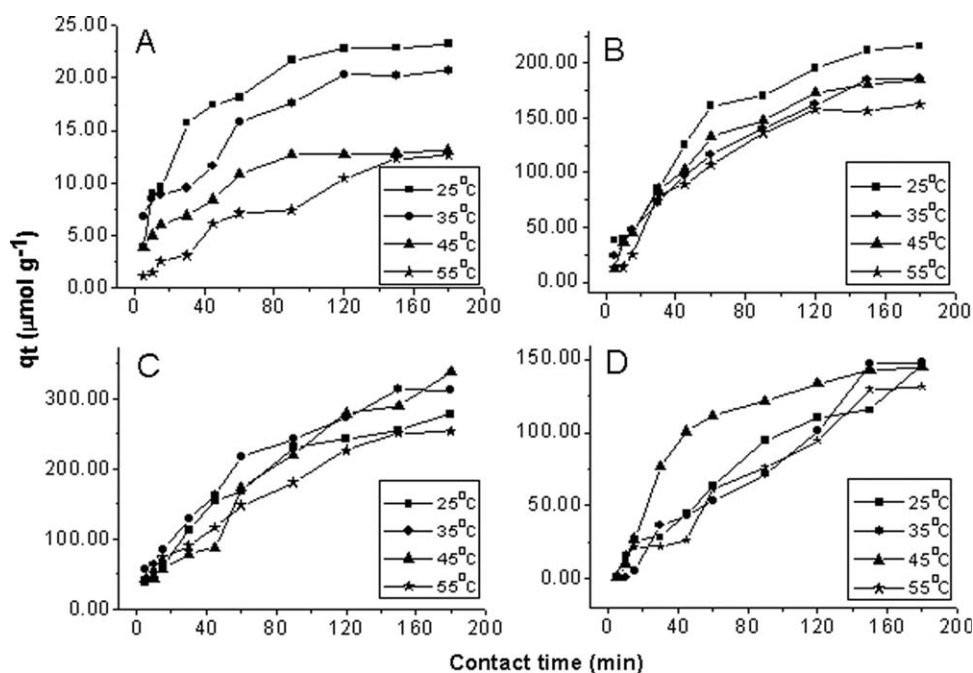[c] Average standard deviation (%) = 5.1.

Figure 8 Adsorption profiles of methylene blue on the cross-linked membranes in relation to the contact time, at different temperatures. Initial dye concentration: (A) $= 2.50 \times 10^{-5}$, (B) $= 5.30 \times 10^{-5}$, (C) $= 2.50 \times 10^{-4}$ and (D) $= 1.00 \times 10^{-3}$ mol L^{-1}.

reaction time did not present variations in relation to temperature. These microcalorimetric results are in agreement with diffusion of fluidic phase (water) into the membranes. The solvent transport through polymer membranes is generally described following an adsorption–diffusion mechanism, where molecules first diffuse from the bulk phase to the membrane surface. Next, they adsorb to the sites on the membrane surface and in the membrane pores. The adsorbed molecules diffuse through the membrane, driven by the chemical potential gradient within the pores.[20]

The MB dye interaction on the crosslinked alginate membranes

The adsorption processes typically take place taking into account two main aspects. First, the adsorbate is transferred from the solution to the adsorbent surface. The last stage is related to the diffusion of the dye-adsorbed molecules within the pores of material, binding the pores and capillary spaces.[21,22]

The effect of the initial concentration of MB on adsorption is shown in Figure 8. The amount of adsorbed dye increases with time, and it remains constant after an equilibrium contact time of about 200 min. Raising the initial MB concentration in solution from 2.50×10^{-5} to 2.50×10^{-3} mol L^{-1} allows the crosslinked membranes to reach their maximum adsorption capacities. It is observed that the MB adsorption increased from 25 to 45°C and decreased from 45 to 55°C. These results seem to indicate that the MB adsorption process is an endothermic process

from 25 to 45°C and exothermic from 45 to 55°C. Similar trends in adsorption of MB adsorption using biosorbents were also observed earlier.[23–25]

Kinetic modeling of MB adsorption on the crosslinked membranes

To find appropriate sorption treatments, several models can be used to express the mechanism of solute sorption onto an adsorbent. However, determination of the adsorption rates as a function of the contact time and temperature represents a challenge in the kinetic adsorption modelings. To try overcoming the limitations cited above, a three-parameter kinetic equation was used in this work.

The adsorption is visualized using the Avrami exponential function shown in eq. (4),[26]

$$q_t = q_t^{\max}(1 - \exp^{-[k_{Av}t]^n}), \qquad (4)$$

where $q_t^{\max}$ is the maximum adsorption capacity for a given adsorption system, k_{Av} is the Avrami kinetic constant, and n is another constant, which is related to the kinetic order. The linearized form of this equation is presented in eq. (5):

$$\ln\left(\ln\left(\frac{q_t^{\max}}{q_t^{\max} - q_t}\right)\right) = n\ln k_{Av} + n\ln t. \qquad (5)$$

The slopes and intersections values of the $\ln(\ln(q_e^{\max}/q_e^{\max} - q_t))$ versus $\ln t$ plots (data not shown) provide the n and $\ln k_{Av}$ values, respectively.

TABLE II
Kinetic Parameters of the Avrami Kinetic Model for Adsorption of the Methylene Dye on 1.00 cm^2 Polyalginate–Glutaraldehyde Membrane

T (°C)	$C_i/10^{-4}$ (mol L^{-1})	$k_{\text{Av},1}/10^{-2}$ (min^{-1})	n_1	$k_{\text{Av},2}/10^{-2}$ (min^{-1})	n_2	$k_{\text{Av},3}/10^{-2}$ (min^{-1})	n_3	$k_{\text{Av},4}/10^{-2}$ (min^{-1})	n_4	Δq_t (%)
25	0.25	6.06	1.44	3.23	0.69	2.29	1.25	11.82	0.46	8.3
35		1.98	0.40	0.07	0.13	2.98	1.01			1.3
45		1.54	0.45	2.07	1.25	1.67	0.51	0.66	5.19	2.4
55		0.45	0.65	1.43	1.54	0.20	0.15	0.99	1.76	7.2
25	0.53	2.36	1.56	1.92	1.11					2.9
35		0.73	0.26	1.67	0.80	1.14	2.34			3.2
45		5.53	0.93	9.35	0.35	3.24	0.85			7.0
55		0.06	0.32	1.36	0.91	1.98	3.91	4.57	0.61	4.7
25	2.50	41.0	0.50	1.63	0.99					1.0
35		0.20	0.17	1.82	0.88	1.36	1.81			4.1
45		0.02	0.05	0.22	0.51	1.21	1.78	1.21	1.23	6.6
55		1.54	0.24	1.22	0.72	1.19	1.92			5.5
25	10.0	5.18	0.34	4.61	0.69	1.14	1.52	1.20	2.38	8.3
35		2.34	4.40	0.61	0.78	0.96	2.99			8.4
45		3.89	2.90	2.55	1.61	2.38	0.94			11.2
55		5.65	3.44	0.07	0.26	11.1	2.02			8.6

Average standard deviation of the results (%) = 5.4.

From inspection of the linearized curves, the presence of three or four segments, in relation to the contact time, is strongly suggested. Therefore, three or four independent values of n_i ($i = 1$–4) and $k_{\text{Av}(i)}$ ($i = 1$–4) should also be considered. The Avrami kinetic parameters are shown in Table I. The calculated n_i and $k_{\text{Av}(i)}$ Avrami constants are different from 25 to 55°C. Therefore, the MB adsorption parameters seem to present both temperature and contact time.

The applicability of the Avrami kinetic model was evaluated using normalized standard deviations (Δq_t), in relation to the experimental and calculated values of q_t ($q_{t,\text{exp}}$ and $q_{t,\text{calc}}$), according to eq. (6).[27]

$$\Delta q_t(\%) = 100x\sqrt{\frac{\sum[(q_{t,\text{exp}} - q_{t,\text{calc}})/q_{t,\text{exp}}]^2}{(a - 1)}}, \quad (6)$$

where a is the number of experimental points in each experimental curve. In general, good agreements of the experimental and calculated data were found (Δq_t less than 10%).

A particle diffusion model, described by eq. (5), was also used here to evaluate the presence of pore diffusion of MB onto the alginate membranes:[28,29]

TABLE III
Intraparticle Model Parameters for Adsorption of the Methylene Dye on 1.00 cm^2 Polyalginate–glutaraldehyde Membrane

T (°C)	$C_i/10^{-4}$ (mol L^{-1})	$k_{\text{dif},1}/10^{-6}$ (mol g^{-1} min^{-1})	$k_{\text{dif},2}/10^{-7}$ (mol g^{-1} min^{-1})	$k_{\text{dif},3}/10^{-6}$ (mol g^{-1} min^{-1})	$k_{\text{dif},4}/10^{-6}$ (mol g^{-1} min^{-1})	$I/10^{-5}$ (mol g^{-1})
25	0.25	4.05	13.92			5.10
35		1.05	9.59			3.52
45		1.48	0.92	1.19		1.91
55		1.79	1.73	1.79	6.66	−0.29
25	0.53	4.22				3.94
35		1.77	34.81	1.93		0.18
45		9.96	2.49			−3.01
55		3.08	11.69			−1.93
25	2.50	2.92	1.20			4.74
35		2.74				4.22
45		8.33	2.84			1.45
55		1.46	2.32			1.09
25	10.0	0.84	1.42			−3.34
35		19.67	1.16	1.95		−0.49
45		26.20	7.45			−3.52
55		1.70	0.16			−2.47

Average standard deviation of the results (%) = 5.7.

TABLE IV
Factors and Levels Used in the Continuous Factorial Design Study

Factors	Levels					
	(−)	(+)	(−)	(+)	(−)	(+)
C—Dye conc./10^{-3} (mol L^{-1})	$C_1 = 0.01$	$C_2 = 0.05$	$C_2 = 0.05$	$C_3 = 0.50$	$C_3 = 0.50$	$C_4 = 1.00$
T—Temperature (°C)	$T_1 = 25$	$T_2 = 35$	$T_2 = 35$	$T_3 = 45$	$T_3 = 45$	$T_4 = 55$

$$q_t = k_{dif}t^{1/2} + I, \qquad (7)$$

where k_{dif} is the pore diffusion rate constant and I is the intercept.

If the intraparticle diffusion is involved in the adsorption process, then a plot of $t^{1/2}$ versus q_t (details not shown) would result in linearized segments. The particle diffusion would be the controlling step if this line passed through the origin.[24] When the plots do not pass through the origin, this is indicative of some degree of boundary layer control. Therefore, the intraparticle diffusion is not the only rate-controlling step but also other processes (typically physical and/or chemical interactions) take place simultaneously. The values of the intercepts (I) give an idea about the boundary layer thickness: the larger the intercept, the greater is the boundary layer effect. The boundary layer resistance is affected by the rate of adsorption and increase in contact time, which reduces the resistance and increases the mobility of dye during adsorption. However, some negative values of the intercepts shown in Table II at 55°C suggest that the dyes adsorption boundary layer effect closes to minimum values at higher adsorption temperatures.

Evaluation of dyes adsorption kinetics by multivariate analysis

The variables and levels used in factorial design study are shown in Table III. The results of the factorial design analysis are shown in Table IV, and the principal and interaction effects are presented in Table V. The effects errors have presented values less than $q_t^{max} = 1.00 \times 10^{-5}$ mol g^{-1}. However, if the interaction terms are left out of the effect

TABLE VI
Values of the Effects and the Polynomial Modeling for the Continuous Factorial Design Study

	Effect, q^{max}/ 10^{-4} (mol g^{-1})	Polynomial modeling, q^{max}/ 10^{-4} (mol g^{-1})
C_1	0.47	$0.46 + 0.24C$
T_1	−0.01	
$C_1 - T_1$	0.01	
Average	0.46	
C_1	0.43	$0.39 + 0.21C - 0.063T - 0.03C.T$
T_2	−0.13	
$C_1 - T_2$	−0.07	
Average	0.39	
C_1	0.26	$0.27 + 0.13C - 0.05T$
T_3	−0.11	
$C_1 - T_3$	−0.09	
Average	0.27	
C_2	5.72	$3.56 + 2.86C + 0.31T - 0.30C.T$
T_1	0.62	
$C_2 - T_1$	0.61	
Average	3.56	
C_2	6.87	$4.04 + 3.44C + 0.17T + 0.27C.T$
T_2	0.35	
$C_2 - T_2$	0.55	
Average	4.04	
C_2	−17.2	$16.9 + 0.86C - 12.4T - 12.8C.T$
T_3	2.55	
$C_2 - T_3$	0.01	
Average	16.9	
C_3	−4.95	$3.94 - 2.48C + 0.31T - 0.30C.T$
T_1	0.62	
$C_3 - T_1$	−0.61	
Average	3.94	
C_3	−6.01	$4.47 - 3.01C + 0.22T - 0.23C.T$
T_2	0.44	
$C_3 - T_2$	0.45	
Average	4.47	
C_3	0.44	$4.84 + 0.22C - 0.15T - 3.45C.T$
T_3	−0.29	
$C_3 - T_3$	6.90	
Average	4.84	

TABLE V
Values of q^{max} (mol g^{-1}) for the Continuous Factorial Design Study

C_1	T_1	$q^{max}/10^{-4}$	C_2	T_1	$q^{max}/10^{-4}$	C_3	T_1	$q^{max}/10^{-4}$
−	−	0.24	−	−	0.70	−	−	5.81
+	−	0.70	+	−	5.80	+	−	1.47
−	+	0.21	−	+	0.70	−	+	7.06
+	+	0.70	+	+	7.06	+	+	1.49
C_1	T_2		C_2	T_2		C_3	T_2	
−	−	0.21	−	−	7.04	−	−	7.06
+	−	0.70	+	−	7.06	+	−	1.49
−	+	0.15	−	+	0.51	−	+	7.95
+	+	0.51	+	+	7.95	+	+	1.47
C_1	T_3		C_2	T_3		C_3	T_3	
−	−	0.15	−	−	50.8	−	−	7.95
+	−	0.51	+	−	7.95	+	−	1.47
−	+	0.14	−	+	0.31	−	+	1.33
+	+	0.31	+	+	8.80	+	+	8.80

calculations (data not shown), all effect errors increase significantly.

The experimental factors of multivariate MB adsorption have shown different behaviors in relation to the levels of the factors "concentration" and "temperature." In general, the principal effect of "concentration factor" increases the q_t^{max} responses for lower temperatures (25 and 35°C). However, the opposite effect was verified mainly for adsorption experiments performed up to 35°C. This is an indication that the dye adsorption on the membranes was favored at lower temperatures.

The effects the "concentration" and "temperature" effects present a complex behavior. This found seems to be related to different aspects of the quantitative adsorption of MB on the membranes, such as surface adsorption, as well as pore and/or intraparticle diffusion.[2] The high adsorption capacities at low temperatures have been attributed to the exothermic nature of the adsorption processes from aqueous solutions.[5] The "temperature effect" presents only a marginal importance in relation to the effect errors.

Interactive effects ($C_i - T_i$, in Table VI) are also present statistically importance in the multivariate results. The interaction of the dye adsorption is also determined by interactive effects and not by the principal "concentration" and "temperature" effects alone.

The quantitative polynomial models for q_t^{max} are shown in Table IV. They were written in terms of the statistically significant effects in Table III.[13] The predicted versus observed graphical correlations (data not shown) have shown good correlations for the observed and predicted values of q_t^{max} of the dye adsorption.

CONCLUSIONS

In this study, thin polymeric alginate membranes were synthesized and crosslinked with glutaraldehyde in acidic medium. Changes of some membranes characteristics, before both the crosslinking reaction and adsorption of MB, were evidenced. The calorimetric results have pointed out that water swelling reactions are slightly exothermic, and interaction energies decreased with increasing temperature.

Adsorptions of the MB dye on the membranes increase with the increasing of initial dye concentration and decrease with the increasing of temperature. The intraparticle diffusion model has suggested several diffusion steps in relation to the contact time and temperature.

The continuous multivariate analysis was used to evaluate quantitative principal and interactive roles of temperature and the initial MB concentration on the maximum MB adsorption. The principal roles of the "concentration" and "temperature" effects seem to be related to different aspects of the methylene dye on the membranes, such as surface adsorption, as well as pore and/or intraparticle diffusion. The new continuous multivariate analysis has suggested that the MB adsorption is influenced by statistically important interactions of the variables "concentration" and "temperature" and not by their principal effects alone.

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