

Removal of Paraquat Pesticide from Aqueous Solutions Using a Novel Adsorbent Material Based on Polyacrylamide and Methylcellulose Hydrogels

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Received 16 July 2008; accepted 4 February 2009

DOI 10.1002/app.30339

Published online 2 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This research studied the characteristics of poly(acrylamide) and methylcellulose (PAAm-MC) hydrogels as a novel adsorbent material for removal of pesticide paraquat, from aqueous solution, with potential applications in curbing environmental risk from such herbicides. PAAm-MC hydrogels with different acrylamide (AAM) and MC concentrations were prepared by a free-radical polymerization method. The capability of the hydrogels in removing paraquat dichloride from aqueous solution was determined using UV-Vis analysis. The scanning electron microscopy method was used to study the morphological properties of the hydrogels, and swelling degree (Q) of the hydrogels was also measured. The entrapped MC in PAAm chains provoked significant changes in morphological, hydrophilic, and adsorption properties of the PAAm-MC hydrogels. The adsorption capacity of hydrogels was

strongly influenced by AAM, MC, and paraquat concentrations with the highest adsorption capacity ($q_{\text{eq}} = 14.3 \text{ mg g}^{-1}$) was observed for hydrogels synthesized with 6.0% AAM with 0.75% MC swollen in 45.7 mg L^{-1} of paraquat solution. Freundlich model performed better than Langmuir model in describing the adsorption isotherm of PAAm-MC/paraquat system, implying a heterogeneous surface. These results suggest that PAAm-MC hydrogels are potentially viable adsorbents for removal of paraquat pesticide from aqueous solution and cleaning water contaminated with dyes, heavy metals, and others pesticides. © 2009 Wiley Periodicals, Inc. *Journal of Appl Polym Sci* 114: 2139–2148, 2009

Key words: hydrogels; poly(acrylamide); biodegradable; paraquat pesticide; adsorption

INTRODUCTION

Polymeric gels are physically or chemically cross-linked networks of polymer chains, within which low molecular weight liquid is immobilized, thus the amount of solvent present within the network is much higher than the amount of polymer constituting the network.¹ Specifically, xerogels that swell in aqueous medium are known as “hydrogels.”^{2–4} Intelligent or smart hydrogels have been developed as stimuli-responsive materials, which can undergo vol-

ume changes in response to changes in temperature, pH, and ionic strength.^{5–7}

Methylcellulose (MC) comprises a family of cellulose ethers in which methyl substitution occurs with or without additional functional substitutions. Additionally, MC is a carbohydrate polymer that is biodegradable and soluble in water.⁸ It can form aqueous solution and, more importantly, has demonstrated a unique ability to form reversible physical gels when heated above a particular temperature due to hydrophobic interactions.^{9,10} Environmental pollutants in water caused by waste products from industries increased the need of novel polymeric materials with the purpose of removing and separating toxic heavy metal ions through complexation and ion exchange mechanisms.¹¹

Hydrogels containing amide, amine, carboxylic acid, and ammonium groups can bind metal ions and be good polychelators for water purification applications.¹² Additionally, researchers have exploited many biodegradable and effective adsorbents obtained from natural resources for the removal of contaminants (dyes, heavy metals, and pesticides)

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Contract grant sponsor: National Council for Scientific and Technological Development (CNPq-Brazil); contract grant numbers: 141695/2006-5, 202430/2006-5.

Contract grant sponsors: National Nanotechnology Laboratory for Agriculture (LNNA) - Embrapa Agricultural Instrumentation, Embrapa-Brazil (Labex Program and MP1 Project), FINEP/LNAA and CAPES-Brazil.

Journal of Applied Polymer Science, Vol. 114, 2139–2148 (2009)
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from aqueous solutions at different operating conditions.¹³ Akkaya and Ulusoy¹⁴ investigated the dependency on ion concentration and temperature for the removal of Pb^{2+} , UO_2^{2+} , and Th^{4+} from hydrogels based on chitosan entrapped in poly(acrylamide) (PAAm) chains. Li and Bai¹⁵ for instance, studied the application of chitosan–cellulose hydrogel beads as adsorbent materials for Cu adsorption from aqueous solutions.

Pesticides and herbicides present a wide array of substances, some of which pose significant potential risk to human health.¹⁶ Indiscriminate use of herbicides and pesticides, especially “over-application,” contaminates surface water. Studies have shown that conventional drinking water treatments are not effective in removing pesticides like metolachlor and terbutylazine.¹⁷ Adsorption is a common technique used to remove a wide variety of organic pollutants including pesticides.¹⁸

The herbicide, paraquat (1,1-dimethyl-4,4-dipyridinium dichloride), also known as methyl viologen, is an especially onerous herbicide if it accumulates in the environment. It has been applied widely despite the fact that it is one of the most toxic substances used in agriculture.¹⁹ As a result, there have been many authenticated cases of residual paraquat detection in water sources.²⁰ Its residues are considered as a potent health risk, because it is a highly persistent molecule.^{21,22}

The aim of this study was to develop a fast, simple, and reproductive preparation procedure for hydrogels based on PAAm and MC using only one-step synthesis and biodegradable, nontoxic, and low-cost materials. Moreover, most of the articles related with polysaccharide hydrogels used for scavengers process are synthesized based on two or more steps,^{23,24} being necessary the modification of the polysaccharide with some vinyl methacrylate reagent, which increases the cost, toxicity, and time of preparation. Additionally, in this specific case, the double bonds from vinylic compost are attached to the polysaccharide structure (specifically hydroxyl groups), which certainly will decrease the number of free hydroxyl groups and the mobility of the polysaccharide macromolecules. As a consequence, the hydrophilic, adsorption, and biodegradability properties can be affected. Another important advantage of the use of PAAm-MC hydrogels as compared with other hydrogels is that the acrylamide (AAM)-based materials are already being used in agriculture as carriers of agrochemicals and soil conditioners.^{25–27}

The objective of this study was to analyze the capability of biodegradable hydrogels constituted by PAAm and MC for removing paraquat dichloride from aqueous solution. The kinetics of paraquat sorption was determined using UV–Vis measurements. In addition, morphological and hydrophilic

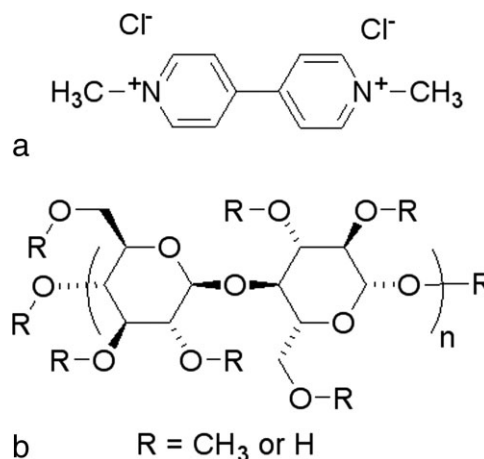


Figure 1 Structures of (a) paraquat dichloride and (b) MC.

properties of PAAm-MC hydrogels were also characterized.

EXPERIMENTAL

Materials

AAM (99%) was obtained from Fluka; *N,N'*-methylene-bis-acrylamide (MBAAM, 99%) used as a cross-linking agent was acquired from Aldrich; and *N,N,N',N'*-tetramethylethylene-diamine (99%) used as a catalyst; and sodium persulfate (SP, $\geq 98\%$) used as an initiator were purchased from Sigma. Biodegradable MC (number-average molecular weight $40,000 \text{ g mol}^{-1}$, viscosity 400 cP, 27.5–31.5% in methoxy groups and 68.5–72.5% in hydroxyl groups, data from supplier's specifications) was obtained from Aldrich. Structures of paraquat dichloride (PESTANAL[®], analytical standard, Riedel-de Haën) and MC are shown in Figure 1. Paraquat dichloride has a UV–Vis maximum absorbance at wavelength 258 nm. The chemical formula and molecular weight of paraquat dichloride are $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{N}_2$ and 257.2 g mol^{-1} , respectively. All reagents were used as received.

Preparation of PAAm–MC hydrogels

The PAAm–MC hydrogels were prepared by a free-radical polymerization method.^{28–30} Briefly, AAM [3.6, 6.0, or 9.0 (in wt %), MBAAM ($8.55 \mu\text{mol mL}^{-1}$), *N,N,N',N'*-tetramethylethylene-diamine ($3.21 \mu\text{mol mL}^{-1}$)], MC (0, 0.25, 0.5, 0.75, or 1.0 wt %) were placed in a bottle and homogenized by mixing. After preparation of mixture, it was deoxygenated by N_2 bubbling for 25 min. Then, aqueous SP (final concentration of $3.38 \mu\text{mol mL}^{-1}$), also deoxygenated, was added to initiate the polymerization reaction.

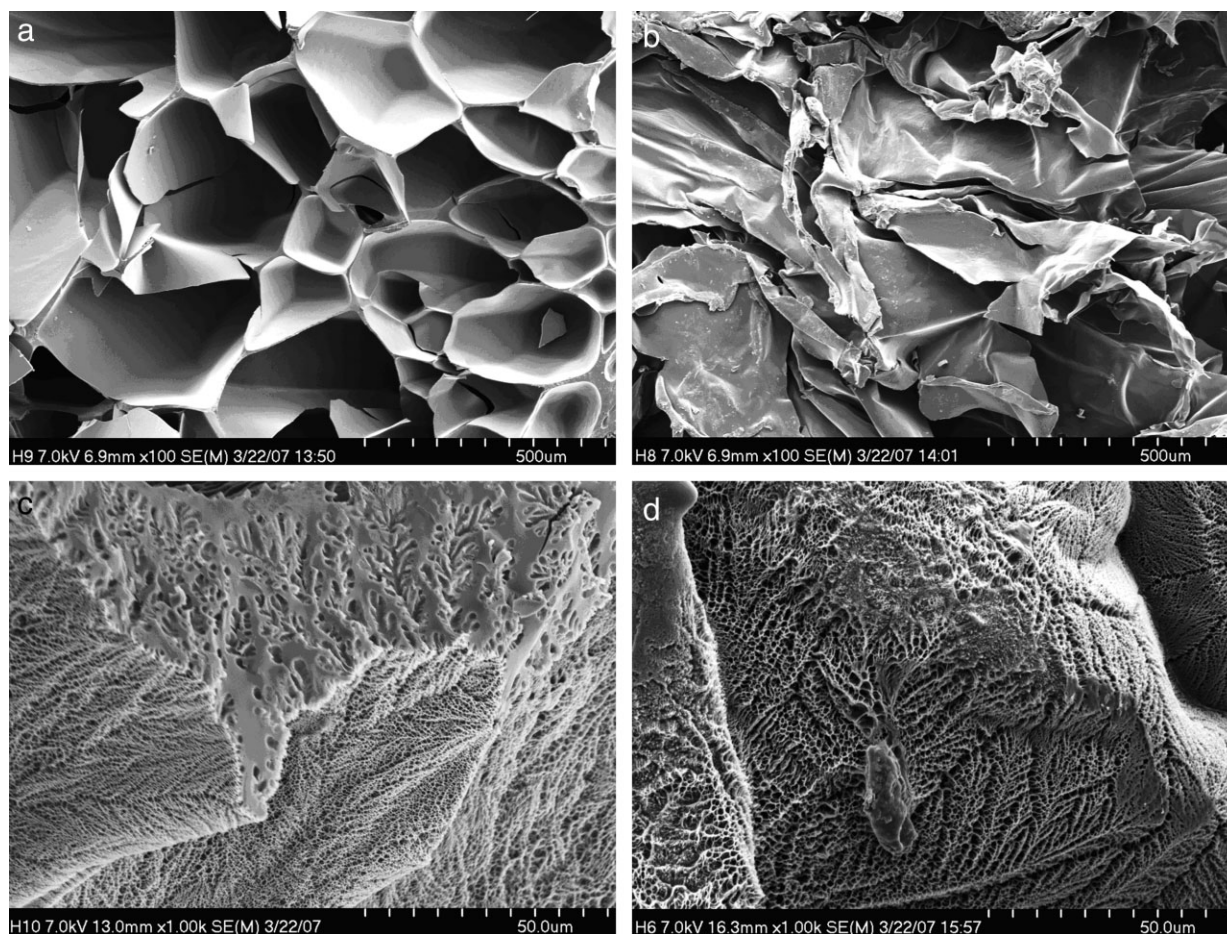


Figure 2 SEM micrographs of PAAm hydrogels with (a) 6.0% AAm and (b) 6.0% AAm with 1.0% MC swollen in water. (c, d) SEM micrographs of hydrogels prepared with 6.0% AAm with 1.0% MC, swollen in paraquat concentrations of 10.1 and 37.5 mg L⁻¹, respectively. All hydrogels were lyophilized after the swelling process.

spectra applying a typical standardization curve ($R^2 = 0.9991$). Such analytical curves were used to determine the concentration of paraquat after interaction with different PAAm–MC hydrogels.

Effects of the initial concentration of paraquat, MC, and the effect of PAAm content in hydrogel were studied. Paraquat aqueous solutions were prepared in the concentration range of 4.6–45.7 ppm (mg L⁻¹). The amount of adsorbed paraquat per gram of the hydrogels was determined by using the following equation:

$$q_t = \frac{[(C_0 - C_t)] \times V}{W} \quad (1)$$

where q_t is the amount of paraquat adsorbed onto PAAm or PAAm–MC hydrogels (mg g⁻¹) based on dry gel weight, C_0 and C_t are the concentrations of the paraquat in the initial solution and the aqueous phase after adsorption process for a certain period of time t , respectively (mg L⁻¹). V is the volume of the aqueous phase (L), and W is the amount of dry PAAm–MC hydrogels used (g).

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species between liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage, and the possibility of interaction between the adsorbate species.³²

Results obtained from the adsorption isotherm were evaluated by means of the Langmuir and Freundlich adsorption models. The Langmuir equation is applicable to homogeneous sorption where the sorption of each sorbate molecule on to the surface has equal sorption activation energy and it is represented by eqs. (2) and (3):

$$q_{eq} = \frac{K_L C_{eq}}{1 + \alpha_L C_{eq}} \quad (2)$$

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_L} + \frac{\alpha_L}{K_L} C_{eq} \quad (3)$$

where C_{eq} is the solution paraquat concentration at equilibrium (mg g⁻¹), q_{eq} is the maximum paraquat

adsorption on hydrogel (mg g^{-1}), K_L (L g^{-1}), and α_L (L mg^{-1}) are the Langmuir isotherm constants.

The sorption data were analyzed according to the linear form of eq. (3) in which constants were evaluated from the slope α_L/K_L and intercept $1/K_L$ of the linear plot of $C_{\text{eq}}/q_{\text{eq}}$ versus C_{eq} .

The Freundlich adsorption model, which assumes that the adsorption occurs on heterogeneous surfaces, can be expressed using eq. (4):

$$\ln q_{\text{eq}} = \ln K_F + \frac{1}{n} \ln C_{\text{eq}} \quad (4)$$

where K_F (L g^{-1}) and n (mg L^{-1}) are constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity of adsorption). Values of K_F and n were calculated from the intercept and slope of the plot of $\ln q_{\text{eq}}$ versus $\ln C_{\text{eq}}$.

RESULTS AND DISCUSSION

Surface morphology observation by SEM

SEM micrographs of PAAm hydrogels with 6.0% AAm and 6.0% AAm plus 1.0% MC swollen in water are shown in Figure 2(a,b). The hydrogels shown in Figure 2(a) had high porous structure with well-defined shapes exhibiting some spread in pore size. Jin et al.³³ obtained SEM images with similar surface morphology, but larger three-dimensional pores when they used synthetic poly(*N*-vinylpyrrolidone) hydrogels. The structure was also similar to that of synthetic poly(*N*-isopropylacrylamide) (PNI-PAAm) hydrogels synthesized with different *N*-isopropylacrylamide monomer and MBAAM cross-linker agent.³⁴

The SEM image of PAAm–MC hydrogel [Fig. 2(b)] presents a clear difference in morphology compared with PAAm hydrogel shown in Figure 2(a). It is very likely attributable to the presence of the second polymer (polysaccharide MC) entrapped in the PAAm network; the leaf-like structure seen in SEM images is characteristic of polysaccharides.^{35,36} The presence of paraquat inside PAAm–MC hydrogels was characterized by SEM and is shown in Figure 2(c,d) where the pesticide adsorption capacity of hydrogels was clearly demonstrated. It can be observed that the paraquat adsorption provokes significant changes in size and morphologies of the porous. The analysis reveals a decrease in porous size in relation to the PAAm–MC matrix. What it is probably occurring is that the paraquat molecules are distributed around or inside the membrane porous, contributing for matrix compaction. Such variation may imply changes in hydrophilic properties (water absorption) and consequently in the physical–chemical properties of the hydrogels. The influence of par-

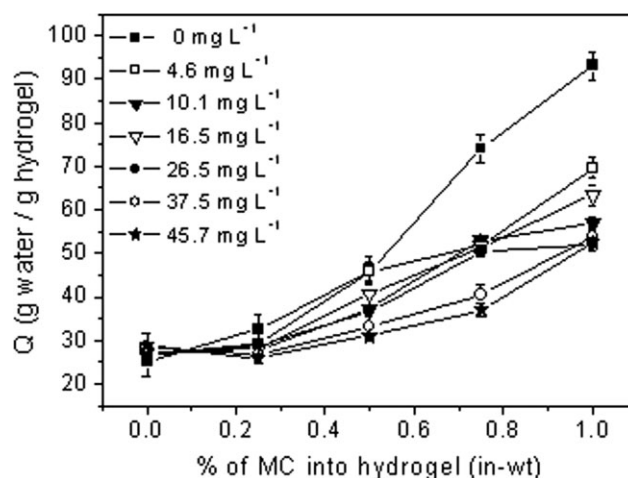


Figure 3 Dependence of swelling degree (Q) as a function of concentration of MC in PAAm hydrogel prepared with 6.0% AAm in distilled water and paraquat aqueous solution at concentrations noted.

aquat on hydrophilic properties of PAAm–MC hydrogels will be discussed in the next section.

Swelling degree (Q) of hydrogels

The dependence of swelling degree (Q) as a function of concentration of MC in PAAm hydrogel prepared with 6.0% AAm is shown in Figure 3. It can be observed that Q values abruptly increase when concentration of MC in feed solution increases. The Q values ($C_0 = 0 \text{ mg L}^{-1}$, i.e., water) increases from 25.0 ± 1.8 to $93.1 \pm 3.1 \text{ g/g}$ when the concentration of MC was increased from 0 to 1.0%. This trend is attributed to the increase in the hydrogel hydrophilicity (and thus the increase in water absorption capacity) due to incorporation of hydroxyl groups from MC segments. This trend in hydrophilicity due to incorporation of hydrophilic groups was also observed in other works.^{37,38}

The effects of varying initial paraquat concentration on swelling degree (Q) properties for hydrogels prepared with 6.0% AAm with and without MC were investigated and shown in Figure 4, whereby a decrease in the Q values was observed when the initial paraquat concentration was increased. When the PAAm–MC hydrogels are in constant contact with solutions containing paraquat, molecular interactions between cationic groups (from the paraquat) and anionic groups (via the MC) may occur. Thus, the relative number of hydroxyl groups in the free MC (without interaction with paraquat) decreased and consequently the water absorption capacity also decreased. Thus, the largest decrease in Q was observed in hydrogels with hydrogels prepared with 1.0% MC. In addition, a slight increase in Q values was observed for hydrogels prepared with PAAm

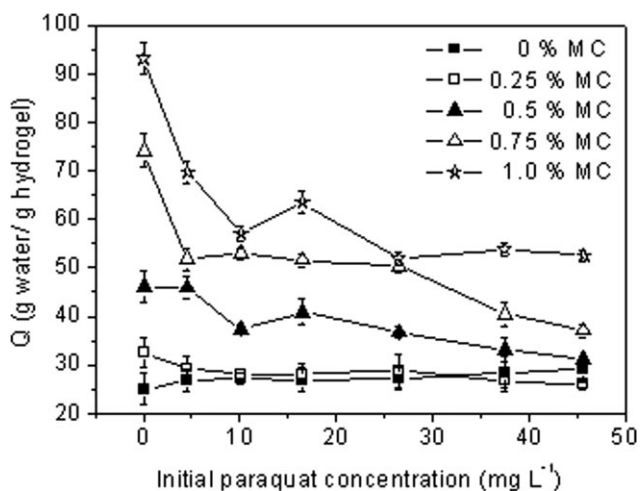


Figure 4 Effects of varying initial paraquat concentration on swelling degree (Q) properties for hydrogels prepared with 6.0% AAm with and without MC, at $25.0 \pm 0.1^\circ\text{C}$.

chains only, which was in favor of water absorption by the presence of ionic groups from the paraquat.

Adsorption of paraquat

Adsorption of the paraquat pesticide from water solution was investigated in different concentrations of paraquat, AAm, and MC. The initial concentration of the paraquat varied between 4.6 and 45.7 mg L^{-1} ($1 \text{ mg L}^{-1} = 1 \text{ ppm}$), whereas the AAm and MC concentrations varied between 3.6 and 9.0% and 0 and 1.0% , respectively. To ensure equilibrium, adsorption tests were carried out for 96 h at $25.0 \pm 0.1^\circ\text{C}$.

In a batch adsorption system, total paraquat concentration (C_T , mg L^{-1}) is:

$$C_T = C_H + C_S \quad (5)$$

where C_H (mg L^{-1}) is the paraquat concentration absorbed by hydrogel and C_S (mg L^{-1}) is the paraquat concentration in the solution. Thus, the concentration of adsorption paraquat by hydrogel was calculated using eq. (6) and the individual values were then derived using the standard curve previously obtained ($R^2 = 0.9991$).

Figure 5(a, b) shows the adsorption behavior of paraquat as a function of time for different hydrogels, with two different initial concentrations of paraquat: 10.1 and 37.5 mg L^{-1} . The decrease in paraquat concentration with time was observed for both conditions, as expected. Of significance, the adsorption of paraquat in hydrogels without MC was low compared with hydrogels containing MC. The PAAm hydrogel showed a decrease in paraquat concentration of 22.5% from 10.1 to 7.8 mg L^{-1} at lower initial concentration [Fig. 5(a)] and a 5.6% decrease from 37.5 to 35.4 mg L^{-1} at higher initial

concentration [Fig. 5(b)]. For hydrogels synthesized with MC, the paraquat adsorption capacity of the hydrogels increased abruptly. For example, paraquat concentrations decreased significantly, by $65 - 77\%$, for all concentrations of MC studied. In addition, the highest adsorption capacity was observed for hydrogel with 0.5% MC ($C_0 = 10.1 \text{ mg L}^{-1}$) and 0.75% MC ($C_0 = 37.5 \text{ mg L}^{-1}$).

Adsorption capacity of an adsorbent material depended on the concentration of the adsorbed molecule, together with other process parameters.³⁹ The dependence of amount of paraquat adsorbed (q_t) as a function of time for hydrogels with different amount of MC is shown in Figure 6(a). The general trend confirms that an increase in q_t resulted from increased MC concentration. This can be explained by the greater number of hydroxyl groups inherent in the MC. As previously mentioned, the adsorption was likely due to paraquat–MC interactions. The maximum adsorption capacity was highest for

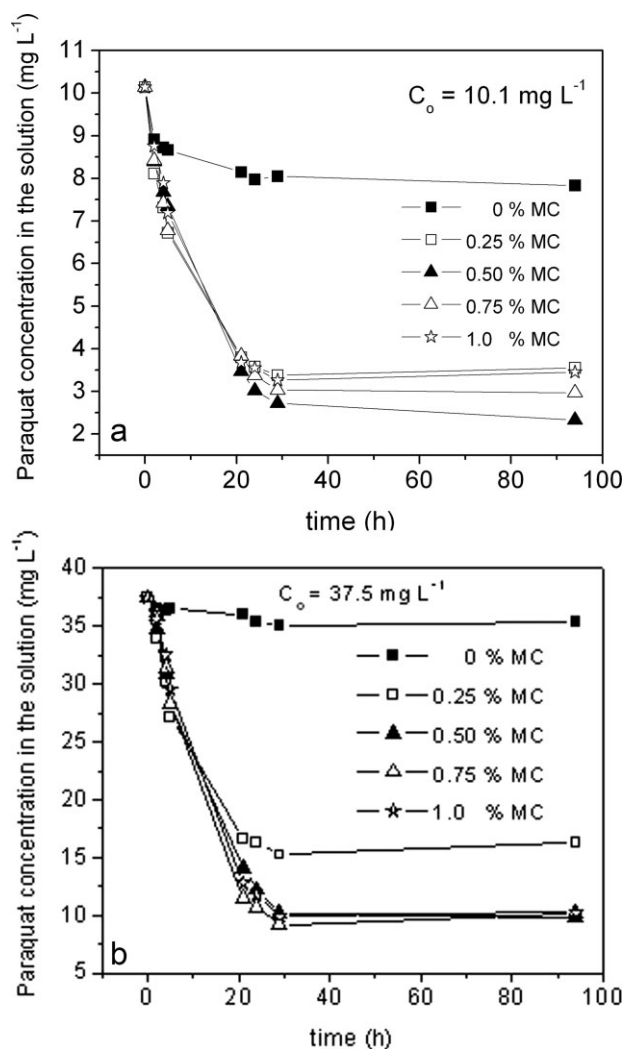


Figure 5 Adsorption behavior of paraquat as a function of time for different hydrogels, with two different initial concentrations of paraquat: (a) 10.1 and (b) 37.5 mg L^{-1} .

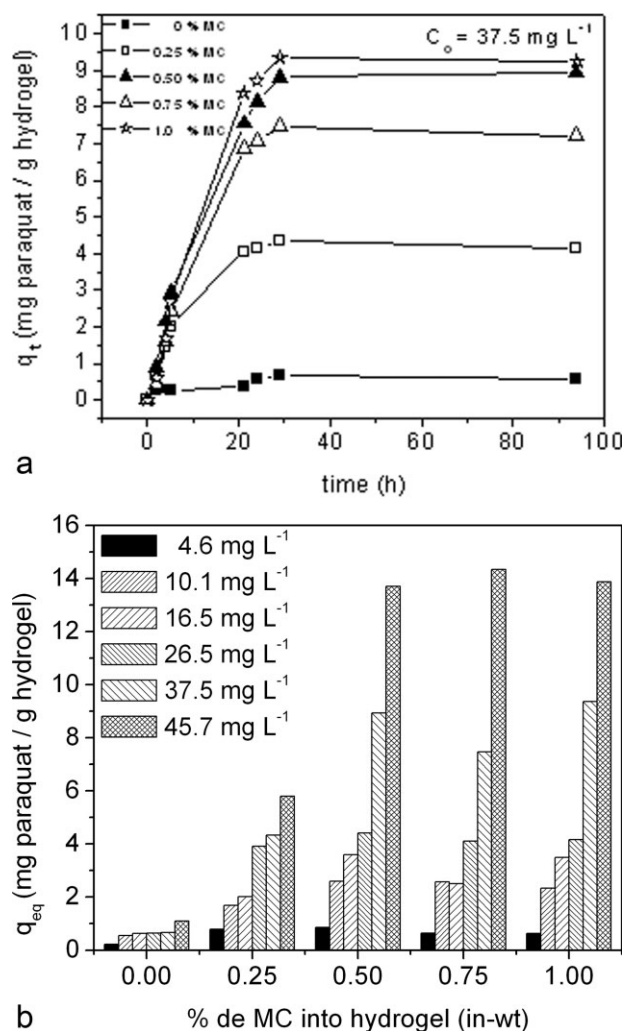


Figure 6 (a) Dependence of amount of paraquat adsorbed (q_t) as a function of time for hydrogels with different amount of MC at $25.0 \pm 0.1^\circ\text{C}$, AAm = 6.0 %, $C_0 = 37.5 \text{ mg L}^{-1}$. (b) Dependence of maximum paraquat adsorption (q_{eq}) as a function the amount of MC in the PAAm hydrogel for different C_0 concentrations.

hydrogels with 6.0% AAm with 1.0% MC, around 9.5 mg/g^{-1} for $C_0 = 37.5 \text{ mg L}^{-1}$.

The dependence of maximum paraquat adsorption (q_{eq}) as a function of the amount of MC in the PAAm hydrogel for different C_0 concentrations is shown in Figure 6(b). The maximum paraquat adsorption for PAAm hydrogel (0% MC) was 1.0 mg g^{-1} . The low adsorption could be attributed to the absence of hydroxyl groups entrapped in PAAm chains. The paraquat molecules were absorbed into hydrogels by interaction with amide groups proceeding PAAm chains. The maximum paraquat adsorptions for PAAm–MC hydrogels were 5.8, 13.7, 14.3, and 13.9 mg g^{-1} for MC concentrations of 0.25, 0.5, 0.75, and 1.0%, respectively. The q_{eq} values were practically constant for MC concentrations equal or

greater than 0.5%. Perhaps because of overabundance of hydroxyl groups relative to paraquat molecules.

Figure 7 shows the influence of AAm content on paraquat adsorption (q_t) of the hydrogels synthesized with constant MC concentration (0.5 %). The AAm concentration range was set at 3.6, 6.0, and 9.0%. It is clear that the amount of AAm was an important factor that affected paraquat adsorption. The q_{eq} values decreased when the AAm concentration increased from 3.6 to 9.0% in the feed solutions; specifically for hydrogels with 3.6, 6.0, and 9.0% AAm, q_{eq} was 13.1 , 8.9 , and 6.7 mg g^{-1} , respectively. Corresponding to this, these same hydrogels showed a decrease in swelling, Q , with increasing AAm concentration likely due to more rigidity in the PAAm chains and, consequently, to the lower water adsorption capability. Q values were 64.7 ± 2.3 , 46.1 ± 3.7 , and $29.7 \pm 1.8 \text{ g/g}$ for 3.6, 6.0, and 9.0% AAm, respectively. The adsorption trend in these PAAm–MC hydrogels is that greater compaction decreases the paraquat adsorption capacity.

The fitted lines of the data modeled using the Freundlich and Langmuir isotherms for the adsorption of paraquat from aqueous solution are shown in Figures 8 and 9. Fitted adsorption parameters of Freundlich isotherm model and their corresponding R^2 are listed in Table I. Based on R^2 values, the Freundlich model fits the paraquat adsorption data better than the Langmuir model.

The parameter K_F is a constant for the system and is related to the bonding energy; generally defined as an adsorption or distribution coefficient, it represents the quantity of paraquat adsorbed on the hydrogel. The parameter $1/n$ is also a measure of the adsorption intensity or surface heterogeneity.^{40,41}

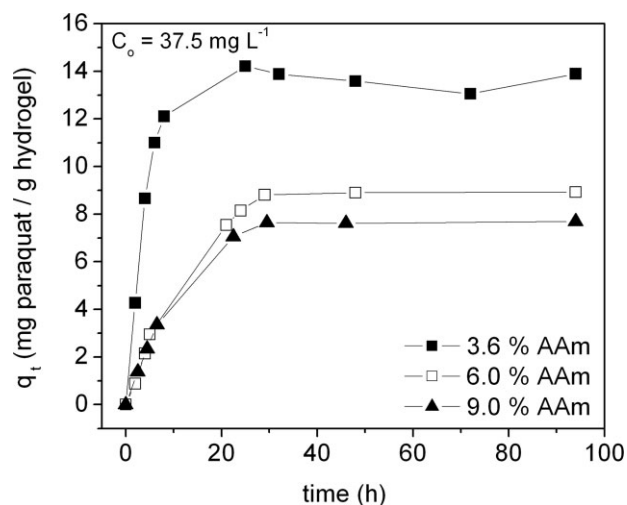


Figure 7 Influence of AAm content on paraquat adsorption (q_t) of the hydrogels synthesized with constant MC concentration, $25.0 \pm 0.1^\circ\text{C}$, MC = 0.5%. $C_0 = 37.5 \text{ mg L}^{-1}$.

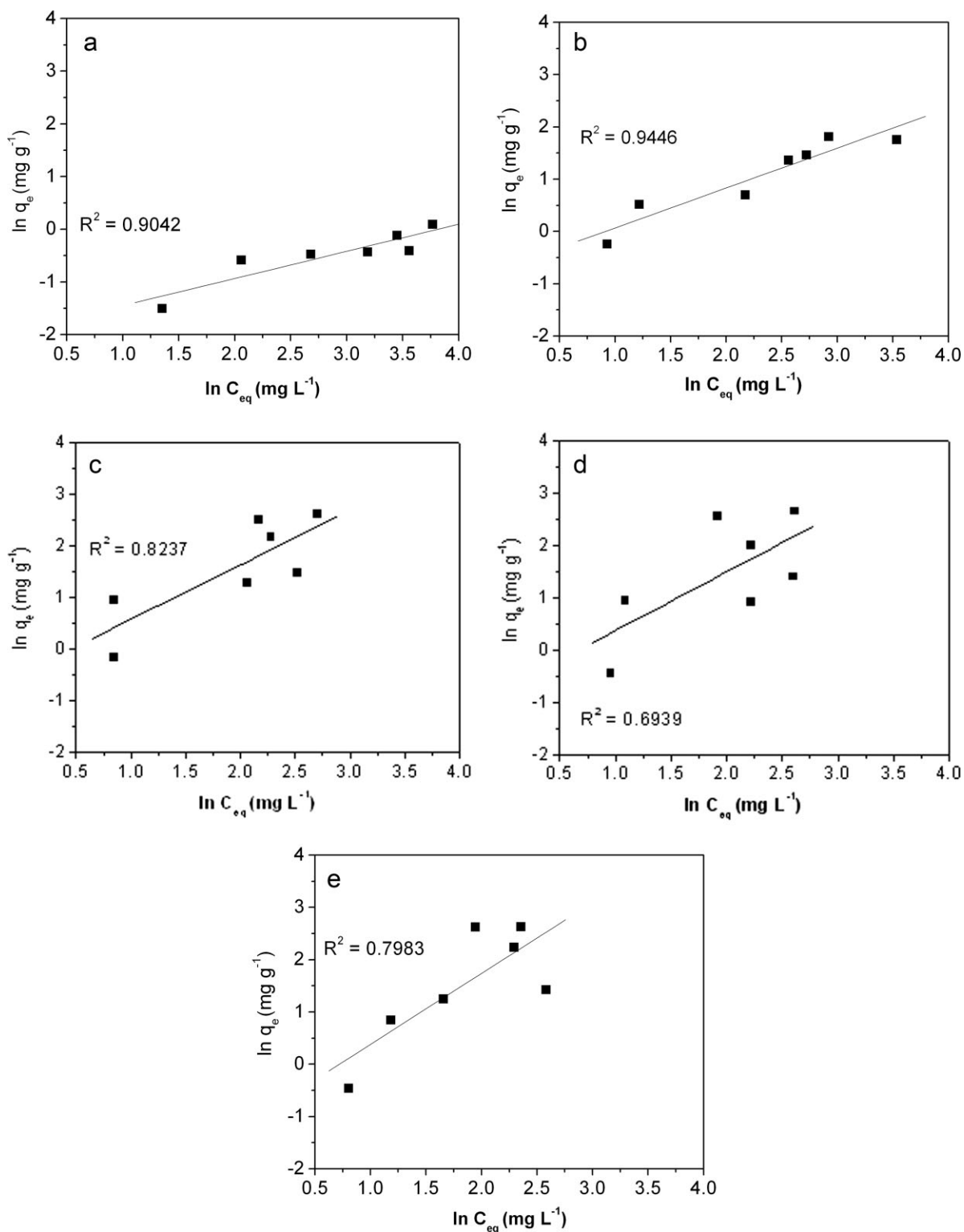


Figure 8 Fitted lines of the data modeled using the Freundlich isotherms for the adsorption of paraquat from aqueous solution: (a) 6.0% AAm; (b) 6.0% AAm with 0.25% MC; (c) 6.0% AAm with 0.5% MC; (d) 6.0% AAm with 0.75% MC; and (e) 6.0% AAm with 1.0% MC.

Figure 10 shows the dependence of K_F and $1/n$ parameter for PAAm hydrogels synthesized with different MC content. As observed, K_F increased with increasing MC concentration in the feed solution

until reaching a maximum value ($K_F = 0.619 \text{ L g}^{-1}$) for hydrogel (with MC = 0.5 %). Above this MC concentration K_F decreases. This fact is related to saturation of hydroxyl groups due to interaction with

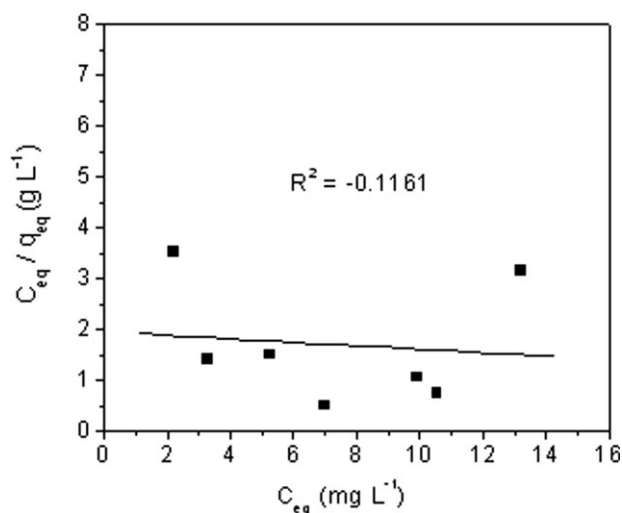


Figure 9 Fitted lines of the data modeled using the Langmuir isotherm for the adsorption of paraquat from aqueous solution for 6.0% AAm with 1.0% MC hydrogel.

paraquat molecules. Additionally, $1/n$ values showed that paraquat adsorption is more favorable ($1/n < 1$) for hydrogels with MC concentration below 0.5%. The maximum paraquat adsorption was obtained when $1/n \approx 1$; therefore, hydrogel constituted by 6.0% AAm and 0.5% MC.

CONCLUSIONS

SEM micrographs of PAAm hydrogels showed that their surfaces were porous because of well-defined shapes of varying pore sizes. The presence of MC changes hydrogel morphology, especially pore structure, giving a leaf-like appearance to the surface. Indications of paraquat adsorption on PAAm–MC hydrogels were observed by significant modifications in morphology.

Swelling degree (Q) trends had abrupt increases as a function of increases in MC within the feed solution. Q values decreased when the initial paraquat

TABLE I
Parameters of the Freundlich Model for the Adsorption of Paraquat From Aqueous Solution for Hydrogels With 6.0% AAm and Different MC Concentrations

	Freundlich constants			R^2
	K_F ($L g^{-1}$)	n ($mg L^{-1}$)	$1/n$ ($L mg^{-1}$)	
6.0% AAm	0.140	1.939	0.516	0.9042
6.0% AAm with 0.25% MC	0.498	1.309	0.764	0.9446
6.0% AAm with 0.5% MC	0.619	0.943	1.060	0.8231
6.0% AAm with 0.75% MC	0.475	0.889	1.125	0.6939
6.0% AAm with 1.0% MC	0.377	0.737	1.357	0.7983

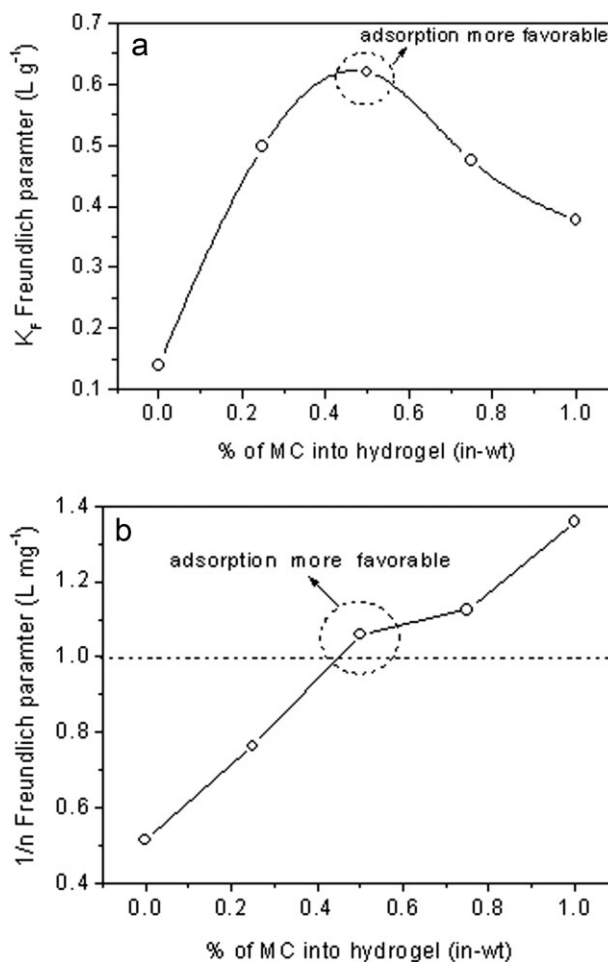


Figure 10 Dependence of (a) K_F and (b) $1/n$ parameter for PAAm hydrogels synthesized with different MC content.

concentration was increased. The adsorption capacity of hydrogels changed significantly as a result of their AAm, MC, and paraquat concentrations. The highest adsorption capacity ($q_{eq} = 14.3 mg g^{-1}$) was observed for hydrogels synthesized with 6.0% AAm and 0.75% MC, swollen in $45.7 mg L^{-1}$ of paraquat. The paraquat adsorption capacity of polymers was increased by decreasing the AAm concentration, increasing the MC concentration (until saturation of hydroxyl groups), and increasing paraquat concentrations. In modeling analysis, the Freundlich isotherm model performed the best fitting for this PAAm–MC/paraquat system.

These results suggest that PAAm–MC hydrogels are promising materials that can be applied as absorbents for the removal of contaminants (dyes, heavy metals) from aqueous solution, which is very important for environmental protection strategies. More specifically, this study has clearly shown that PAAm–MC hydrogels can be used in the removal of pesticides from aqueous solutions.

References

1. Srivastava, A.; Jain, E.; Kumar, A. *Mater Sci Eng A* 2007, 464, 93.
2. Ylmaz, Z.; Kavakli Akkaş, P.; Şen, M.; Güven, O. *J Appl Polym Sci* 2006, 102, 6023.
3. Wu, Q.; Tian, P. *J Appl Polym Sci* 2008, 109, 3470.
4. Xu, K.; Wang, J.; Chen, Q.; Yue, Y.; Zhang, W.; Wang, P. *J Colloid Interface Sci* 2008, 321, 272.
5. Bagheri Marandi, G.; Esfandiari, K.; Biranvand, F.; Babapour, M.; Sadeh, S.; Mahdavinia, G. R. *J Appl Polym Sci* 2008, 109, 1083.
6. Sahoo, S. K.; De, T. K.; Ghosh, P. K.; Maitra, A. *J Colloid Interface Sci* 1998, 206, 361.
7. Moradi, O.; Modarress, H.; Noroozi, M. *J Colloid Interface Sci* 2004, 271, 16.
8. Stephen, A. M.; Philips, G. O.; Williams, P. A. *Food Polysaccharides and Their Applications*, Marcel Dekker: New York, 1995.
9. Haque, A.; Morris, E. R. *Carbohydr Polym* 1993, 22, 161.
10. Ramesh Babu, V.; Sairam, M.; Hosamani, K. M.; Aminabhavi, T. M. *Carbohydr Polym* 2007, 69, 241.
11. Kok Yetimoglu, E.; Kahraman, M. V.; Ercan, O.; Akdemir, Z. S.; Kayaman Apohan, N. *React Funct Polym* 2007, 67, 451.
12. Lee, W. F.; Yuan, W. Y. *J Appl Polym Sci* 2000, 77, 1760.
13. Yi, J.-Z.; Zhang, L.-M. *Bioresour Technol* 2008, 99, 2182.
14. Akkaya, R.; Ulusoy, U. *J Hazard Mater* 2008, 151, 380.
15. Li, N.; Bai, R. *Sep Purif Technol* 2005, 42, 237.
16. Ayranci, E.; Hoda, N. *Chemosphere* 2005, 60, 1600.
17. Griffini, O.; Bao, M. L.; Burrini, D.; Santianni, D.; Barbieri, C.; Pantani, F. *Aqua* 1999, 48, 177.
18. Sarkar, B.; Venkateswralu, N.; Nageswara Rao, R.; Bhattacharjee, C.; Kale, V. *Pest Manage Sci* 2007, 60, 340.
19. Bromilow, R. H. *Pest Manage Sci* 2004, 60, 340.
20. Ritter, L.; Solomon, K.; Sibley, P.; Hall, K.; Keen, P.; Mattu, G.; Linton, B. *J Toxicol Environ Health* 2002, 65, 1.
21. Hamadi, N. K.; Swaminathan, S.; Chen, X. D. *J Hazard Mater* 2004, 112, 133.
22. Souza, D.; Machado, S. A. S.; Pires, R. C. *Talanta* 2006, 69, 1200.
23. Ferreira, L.; Vidal, M. M.; Geraldies, C. F. G. C.; Gil, M. H. *Carbohydr Polym* 2000, 41, 15.
24. Reis, A. V.; Guilherme, M. R.; Cavalcanti, O. A.; Rubira, A. F.; Muniz, E. C. *Polymer* 2006, 47, 2023.
25. Abraham, J.; Pillai, V. N. R. *J Appl Polym Sci* 1996, 60, 2347.
26. Orts, W. J.; Sojka, R. E.; Glenn, G. M. *Ind Crop Prod* 2000, 11, 19.
27. Sojka, R. E.; Bjorneberg, D. L.; Entry, J. A.; Lentz, R. D.; Orts, W. J. *Adv Agron* 2007, 92, 75.
28. Wang, B.; Xu, X.-D.; Wang, Z.-C.; Cheng, S.-X.; Zhang, X.-Z.; Zhuo, R.-X. *Colloids Surf B* 2008, 64, 34.
29. Kundakci, S.; Üzümlü, O. B.; Karadağ, E. *React Funct Polym* 2008, 68, 458.
30. Aouada, F. A.; de Moura, M. R.; Rubira, A. F.; Muniz, E. C.; Fernandes, P. R. G.; Mukai, H.; da Silveira, A. C. F.; Itri, R. *Eur Polym J* 2006, 42, 2781.
31. Singh, B.; Chauhan, N. *Food Hydrocolloid* 2003, 23, 928.
32. Chen, C.; Li, X.; Zha, D.; Tan, X.; Wang, X. *Colloid Surf A* 2007, 302, 449.
33. Jin, S.; Liu, M.; Zhang, F.; Chen, S.; Niu, A. *Polymer* 2006, 47, 1526.
34. Zhang, X.-Z.; Wu, D.-Q.; Chu, C.-C. *Biomaterials* 2004, 25, 3793.
35. Cunha, P. L. R.; Castro, R. R.; Rocha, F. A. C.; Paula, R. C. M.; Feitosa, J. P. A. *Int J Biol Macromol* 2005, 37, 99.
36. de Moura, M. R.; Guilherme, M. R.; Campese, G. M.; Radovanovic, E.; Rubira, A. F.; Muniz, E. C. *Eur Polym J* 2005, 41, 2845.
37. Çaykara, T.; Akçakaya, I. *Eur Polym J* 2006, 42, 1437.
38. Şen, M.; Kantoğlu, O.; Güven, O. *Polymer* 1999, 40, 913.
39. Kaşgöz, H. *Colloid Surf A* 2005, 266, 44.
40. Coles, C. A.; Yong, R. N. *Eng Geol* 2006, 85, 19.
41. Tsai, W. T.; Lai, C. W.; Hsien, K. J. *Chemosphere* 2004, 55, 829.