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Polyacrylamide and methylcellulose hydrogel as delivery vehicle for the controlled release of paraquat pesticide

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Abstract PAAm–MC hydrogels as a potential delivery vehicle for the controlled release of paraquat pesticide was investigated, as they play an essential role to use hydrogels in controlled release technology. The release kinetics of paraquat was determined using UV–Vis measurements. The release mechanism of paraquat from PAAm–MC hydrogels was investigated through a semi-empirical model proposed by Ritger and Peppas. In general, the initial rate of paraquat release was fast, decreasing after several days, hence indicating that paraquat on the surface (or close to) of hydrogels diffused rapidly after the initial swelling of the gel. Later, the cumulative release occurred in a very controlled and sustained manner, with the paraquat concentration maintaining constant from 15 to 46 days. The paraquat release capacity was dependent on the swelling of the matrix and the density of the network chains. The curves obtained from Peppas's model presented good linearity ($R^2 \geq 0.999$), indicating that such model can be applicable to analyze the systems. The n values for the pesticide release from hydrogels indicate that paraquat release has Fickian and non-Fickian diffusion, depending of hydrogel formulation. The values of k showed that the release of paraquat becomes slower when the MC and AAm concentration increases. Finally, to the best of our knowledge, we report a hydrogel-based vehicle (first carrier) that is able to prolong the sustained release of paraquat pesticide up to 45 days, which is essential for its application in controlled release systems.

Abbreviations

π	Osmotic pressure defined by Donnan equilibrium theory
μ	Chemical potential
AAm	Acrylamide
Abs	Absorbance
C	Mobile ion concentration
C_R	Cumulative release
G	Gibb's free energy
k	Constant incorporating structural and geometric characteristics of the macromolecular polymeric system and the pesticide
M_∞	Amount of paraquat loaded onto the hydrogel
MBAAm	*N*,*N*′-methylene-bis-acrylamide
MC	Methylcellulose
M_t	Cumulative amount of paraquat released at time "t"
n	Release exponent representing the release mechanism
P	Pressure
PAAm	Polyacrylamide
q_{eq}	Maximum paraquat adsorption
R	Universal gas constant

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R^2	Linear regression coefficient
SD	Standard deviation
SEM	Scanning electron microscopy
T	Absolute temperature
TEMED	*N*,*N*,*N*′,*N*′-tetramethylethylene-diamine
UV–Vis	Ultraviolet–visible
V	Volume
wt%	Weight percent or mass percent

Introduction

Over the past decades, hydrogel polymers have attracted a great deal of attention as potential delivery vehicles for the controlled release applications [1–3]. Hydrogels are three-dimensional hydrophilic macromolecular networks, which can absorb water many times their dry mass and significantly expand in their volume [4]. The ability of hydrogels to undergo substantial swelling and collapsing in response to the presence and absence of water [5] allows for their potential application in different fields [6–8]. Special applications are in biomedical application [9] and in pharmaceutical controlled release technology [10–12]. However, there are few publications on their application in the agricultural field [13]. In arid areas, the use of hydrogels in sandy soils (macroporous medium) may increase the water-holding capacity, thus improving the quality of plants. Hydrogels in soil applications facilitate an increased water sorption, minimizing the irrigation frequency and water loss due to evaporation. Additionally, in agricultural areas, it is advantageous to have a hydrogel that can encapsulate a toxic pesticide or micronutrient so as to regulate its safe release to the environment [14].

The main problem with conventional agrochemical applications is using greater amounts of agrochemicals over a long period than what is actually needed, possibly leading to crop damage and environmental contamination [15]. Controlled release polymer matrix systems offer a number of potential advantages, not only to avoid treating excess amounts of active substances, but also to offer the most suitable technical solution in special fields of application [13].

The purpose of controlled release systems is to protect the supply of the agent to allow the automatic release of the agent to the target at a controlled rate and to maintain its concentration in the system within the optimum limits over a specified period of time, thereby providing great specificity and persistence without diminishing efficiency. Controlled release of agrochemicals (pesticides, herbicides, nutrients) is used to maintain the local concentration of active ingredients in the soil and to reduce runoff [15].

In a previous study [16], we analyzed the physicochemical properties of the network based on cross-linked polyacrylamide (PAAm) and polysaccharide methylcellulose (MC), and their capacity to remove pesticide from an aqueous solution through the kinetics of paraquat sorption using UV–Vis spectrophotometric technique. Continuing from that work, we now report on the PAAm–MC hydrogels as potential delivery vehicles for the controlled release of paraquat pesticide, as they play an essential role to use hydrogels in controlled release technology. The release kinetics of paraquat was also determined using UV–Vis measurements. The morphological characterization was evaluated by scanning electron microscopy (SEM). In addition, the release mechanism of paraquat from PAAm–MC hydrogels was investigated through a semi-empirical model proposed by Ritger and Peppas.

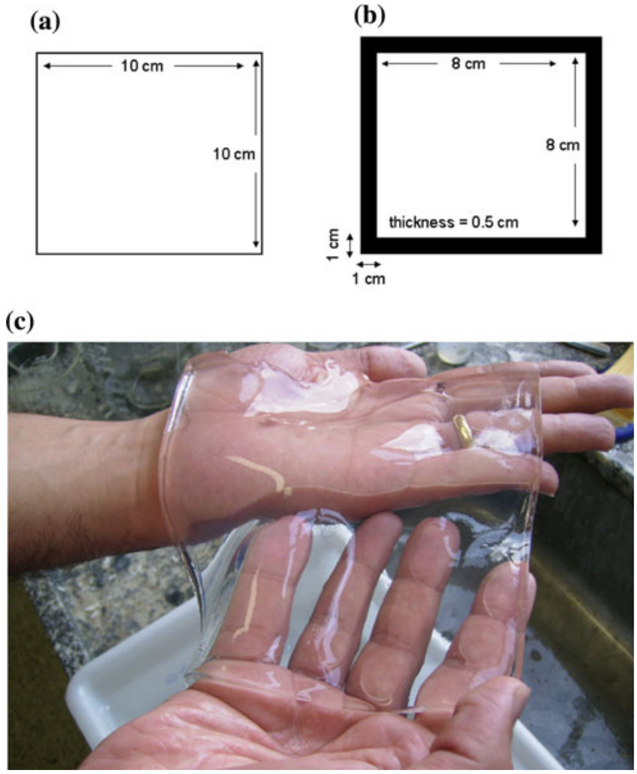
Experimental

Materials

Acrylamide (AAm, 99%) was obtained from Fluka; *N*,*N*′-methylene-bis-acrylamide (MBAAm, 99%) used as cross-linker was acquired from Aldrich; and *N*,*N*,*N*′,*N*′-tetramethylethylene-diamine (TEMED, 99%) used as catalyst agent, and sodium persulfate (SP, ≥98%), used as initiator, were purchased from Sigma. Biodegradable methylcellulose (MC, number-average molecular weight 40,000 g mol^{-1}, viscosity 400 cP, 27.5–31.5% in methoxy groups; 68.5–72.5% in hydroxyl groups, data from the supplier's specifications) was obtained from Aldrich. Paraquat dichloride (PESTANAL®, analytical standard) was purchased from Riedel-de Haën. Paraquat dichloride has a UV–Vis maximum absorbance at 258 nm wavelength. The chemical formula and molecular weight of Paraquat dichloride are $C_{12}H_{14}Cl_2N_2$ and 257.2 g mol^{-1}, respectively. All reagents were used as received.

Preparation of PAAm–MC hydrogels

The synthesis of PAAm–MC hydrogels was published elsewhere [16]. AAm (6.0; 9.0 or 12.0 in-wt%), MC (0; 0.25; 0.5; 0.75 and 1.0 in-wt%), MBAAm, and TEMED were placed in a bottle and homogenized by stirred mixing. The MBAAm and TEMED concentrations were fixed at 1.0 mol% relative to the AAm amount and 3.21 μmol mL^{-1}, respectively. After the mixture was prepared, it was deoxygenated by N_2 bubbling for 25 min. Then, aqueous sodium persulfate (final concentration of 3.38 μmol mL^{-1}), also deoxygenated, was added to initiate the polymerization reaction.



Scheme 1 Experimental apparatus for the hydrogels syntheses: **a** glass plates; **b** rubber gasket; and **c** photo of hydrogel composed of PAAm and MC in membrane form after dialysis process: [AAm] = 6.0 in-wt%; [MC] = 1.0 in-wt%

The resulting solution was quickly placed between two glass plates (Scheme 1a) separated by a rubber gasket (Scheme 1b) and kept at room temperature. The system was kept closed by means of metallic straps for 24 h at ambient temperature (ca. 25 °C). At this stage, the complete polymerization/cross-linking of AAm occurred. After 24 h, the hydrogels, in a membrane form (Scheme 1c), were removed from the plates. Then, these membranes (final thickness $\approx$ 9 to 10 mm) were freed from the unreacted chemicals by dialysis with distilled/deionized water for 10 days. The polymeric network PAAm–MC was used to study the controlled release of paraquat pesticide at different AAm and MC compositions.

Morphological characterization by SEM

Scanning electron microscopy was performed on the PAAm–MC sample to obtain information on the hydrogels pore structure. The swollen hydrogel was removed from water, freezing it quickly in liquid nitrogen, followed by lyophilization [17] at −55 °C for 24 h. After the lyophilization process, the dried sample was deposited onto an aluminum stub and sputter-coated with gold for 60 s to enhance conductivity. The morphology was investigated using a Hitachi (model S 4700) Scanning Electron Microscope with an accelerating voltage of 7.0 kV. The hydrogel was scanned at a magnification of 500×.

Loading of paraquat pesticide onto hydrogels

For the paraquat loading, each hydrogel was dried and soaked in the paraquat aqueous solution at 37.48 ppm (mg L^{-1}) and maintained at controlled temperature (25.0 ± 0.1 °C) for 30 h. Next, the swollen paraquat-loaded hydrogel was removed and the amount of paraquat that remained in the solution was determined by the UV measurements at $\lambda = 258$ nm based on previously built analytical curve (linear regression coefficient, $R^2 = 0.9991$). The regression equation was Abs 258 nm = −0.06134 + 0.06377 [paraquat]. The analytical curve had a linearity range between 0 and 44 ppm.

The amount of paraquat loaded onto each hydrogel was determined using Eq. 1:

$$[\text{Paraquat}]_{\text{loaded}} = [\text{Paraquat}]_{\text{before loading}} - [\text{Paraquat}]_{\text{after loading}}$$
$$[\text{Paraquat}]_{\text{loaded}} = 37.48 - [(\text{Abs}_{258\,\text{nm}} + 0.06134)/0.06377] \tag{1}$$

where $[\text{Paraquat}]_{\text{before loading}}$ and $[\text{Paraquat}]_{\text{after loading}}$ are the paraquat concentrations in the solution before and after the gel-loading process.

Controlled release of paraquat pesticide at different conditions

The experiments for releasing the paraquat from the hydrogel were performed at 25.0 °C, using distilled and deionized water as release medium under static conditions. Aliquots were removed and placed in the quartz cell to measure the UV intensity absorbances. Then, the aliquot was put back into the sample solution. Measurements were performed in triplicate and the error bars indicated the standard deviation ($n = 3$). At the end of each experiment sequence for the one specific hydrogel ($n = 1$), the medium was removed and then replaced. For the second sequence ($n = 2$), another previously loaded hydrogel was inserted into this fresh medium [18].

The cumulative release of paraquat pesticide at different time intervals (C_R) was obtained from the following equation:

$$C_R = \frac{M_t}{M_\infty} \times 100 \tag{2}$$

where M_t is the cumulative amount of paraquat released at time “t” and M_∞ is the amount of paraquat loaded onto the hydrogel.

To analyze the release mechanism, a semi-empirical equation presented by Ritger and Peppas [19, 20] was used:

$$\frac{M_t}{M_\infty} = kt^n \tag{3}$$

where the M_t/M_∞ is the fractional release, k is a constant incorporating structural and geometric characteristics of the macromolecular polymeric system and the pesticide, and n is designated as the release exponent representing the release mechanism.

Equation 3 expounds the data analysis of Fickian or non-Fickian diffusional release from polymeric delivery systems [21]. For $n = 0.45$–0.5, for hydrogels with slab geometry, the solute release is diffusion controlled and follows a Fickian mechanism. For $0.5 < n < 1$, a non-Fickian diffusion or anomalous diffusion behavior is considered. When the $n = 1$, the transport is driven exclusively by chain relaxation.

Results and discussion

Release of paraquat pesticide from PAAm–MC hydrogels

The release of chemicals entrapped in a hydrogel occurs only after water penetrates the network to swell the polymer and dissolve the chemicals, followed by diffusion along the aqueous pathways to the surface of the device. The release of chemicals is closely related to the swelling characteristics of the hydrogels, which in turn is a key function for the chemical architecture of the hydrogels [22]. Scheme 2 shows the schematic representations of loading and the paraquat release process, which are directly correlated with the swelling capability of hydrogels. For instance, in the loading process, there is water and paraquat sorption. For the release case, the water sorption contributes to the pesticide desorption due to two main factors: (1) difference in chemical potential [23] (Eq. 4), and (2) osmotic pressure defined by Donnan equilibrium theory [24] (Eq. 5).

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \tag{4}$$

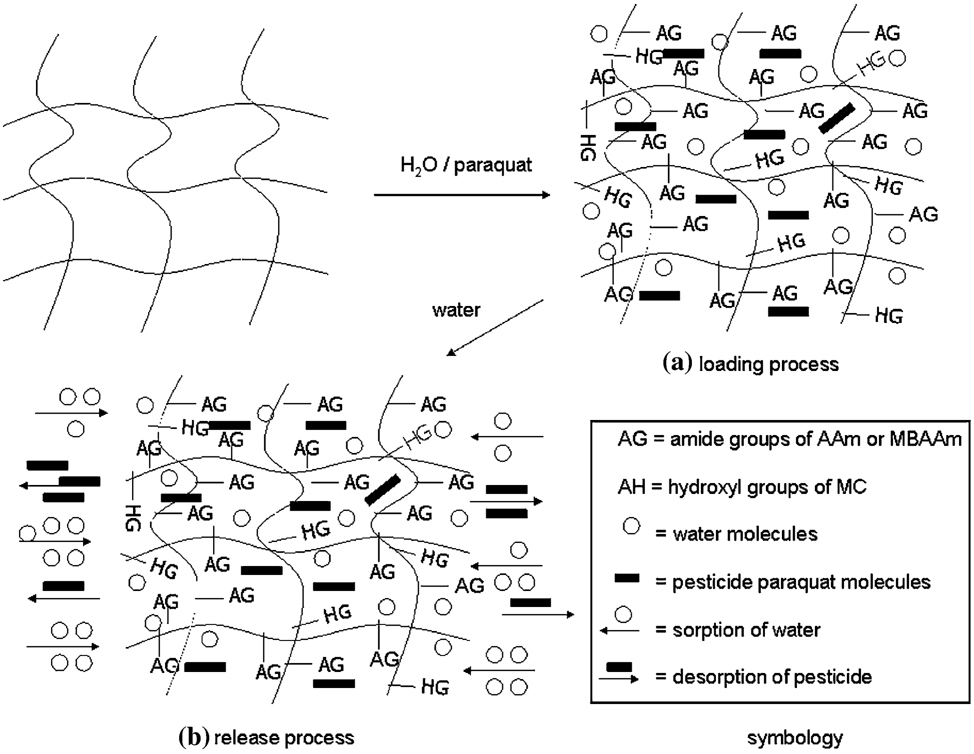
where G is the Gibb's free energy, n_i is the amount of component i, V is the volume, and P is the pressure. The subscripts indicate that temperature, pressure, and the amount of all other components are maintained constant.

$$\pi_{\text{ion}} = RT\sum_i \left(C_i^{\text{g}} - C_i^{\text{s}}\right) \tag{5}$$

where C_i is the mobile ion concentration of species i, and superscripts "g" and "s" represent the gel and solution phase, respectively. R is the universal gas constant and T is the absolute temperature.

Controlling pests often require periodic pesticide applications to the crop using conventional formulations, e.g., powders, granules, or concentrated emulsions. These

Scheme 2 Schematic representations of **a** loading process showing the sorption of water and paraquat; and **b** release process showing the sorption of water and desorption of paraquat



lead to significant levels of environmental pollution due to the extensive quantities of pesticide applied, required for prolonged effectiveness [25]. According to the literature [26], controlled release systems for pesticides involve advanced pesticide delivery technologies, highlighting new means for reducing toxicity, increasing efficacy, lessening the environmental impact from pesticides and pesticide applications, reducing potential transportation hazards, and facilitating new product development.

In this study, the hydrogels presented high loading capability of paraquat pesticide (Table 1). The pesticide was not chemically attached to the polymeric chain and the only likely interactions were ionic attractions. The hydrogels loaded up to 82% of paraquat, in relation to the amount of paraquat available in the loading solution. The maximum paraquat adsorption (q_{eq}) in hydrogels without MC was low, when compared with hydrogels containing MC, of around 0.7 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 the hydrogels by interaction with amide groups proceeding from PAAm chains. The general trend indicated that an increase in q_{eq} resulted from an increased MC concentration due to the greater number of hydroxyl groups inherent in the MC. In these conditions, the adsorption was likely due to paraquat–MC interactions. It was also observed that an increased AAm concentration provoked a decrease in the q_{eq} values [16].

Table 1 Parameters obtained from kinetics of paraquat sorption using UV–Vis spectrophotometric technique for hydrogel with various AAm and MC concentrations at 25.0 °C

Hydrogel	[Paraq]^{BF}	[Paraq]^{AL}	APL (ppm)	PPL (%)	q_{eq} (mg/g)
(6.0–0)[a]	37.48	35.04	2.44	6.49	0.7
(6.0–0.25)	37.48	15.22	22.26	59.39	4.3
(6.0–0.5)	37.48	9.77	27.71	73.91	8.9
(6.0–0.75)	37.48	9.16	28.32	75.54	7.5
(6.0–1.0)	37.48	9.90	27.58	73.58	9.4
(9.0–0.5)	37.48	8.06	29.42	78.42	6.7
(12.0–0.75)	37.48	6.70	30.78	82.07	7.2

[a] [AAm] = 6.0 in-wt% and [MC] = 0 in-wt%

[Paraquat]^{BF} = paraquat concentration in the solution before the gel-loading process

[Paraquat]^{AF} = paraquat concentration in the solution after the gel-loading process

APL (ppm) = amount of paraquat loaded onto each hydrogel

PPL (%) = percentage of paraquat loaded onto each hydrogel in relation to the amount of paraquat available in the loading solution

q_{eq} (mg/g) = maximum paraquat adsorption on hydrogel

Analytical curve: Abs 258 nm = −0.06134 + 0.06377 [paraquat], $R^2 = 0.9991$

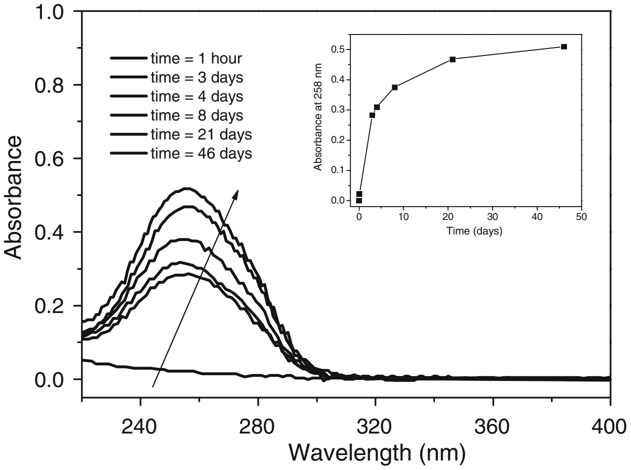


Fig. 1 UV–Vis absorption spectra recorded during the release of pesticide from a specific hydrogel: [AAm] = 6.0 in-wt%; [MC] = 1.0 in-wt%. Spectra were recorded at different times: 0.0417 (1 h); 3; 4; 8; 21; 46 days. Inset: *Graph* of absorbance at $\lambda = 258$ nm versus time showing their kinetic behavior of paraquat release

Figure 1 presents the UV–Vis absorption spectra recorded during the release of paraquat pesticide from the hydrogel composed of 6.0% AAm and 1.0% MC. Figure 1 (Inset) shows the absorbance increase at 258 nm (maximum absorption) as a function of time of the same hydrogel, indicating that its release was controlled over time (up to 45 days). As a consequence, PAAm–MC hydrogel can be considered as a potential delivery vehicle for controlled release application of agrochemicals, especially in the case of paraquat pesticide.

The solute diffusion out of a porous hydrogel matrix is dependent on the pore sizes within the matrix of the gel [27], which, in turn, is affected by several parameters, including, mainly, the degree of cross-linking, chemical structure of the composing monomers, monomer concentration and hydrophilicity, and, when applicable, the type as well as intensity of the external stimuli [28]. The porosity of PAAm and MC hydrogels was observed in Fig. 2, where a porous honeycomb-like structure with many well-defined shapes exhibiting a homogeneous pore size distribution can be seen.

The varying effects of PAAm and MC contents on releasing paraquat from PAAm–MC hydrogels were investigated in details and their results will be now discussed. Figure 3 shows the amount of paraquat released as a function of time for PAAm–MC hydrogels prepared with 6.0% AAm using different MC contents. In general, the initial rate of paraquat release was fast, and after several days it decreased. This fact indicates that paraquat on the hydrogels surface (or close to) diffused rapidly from the initial swelling of the gel [18, 29]. Later, paraquat was released slowly from the hydrogels, up to 45 days. The

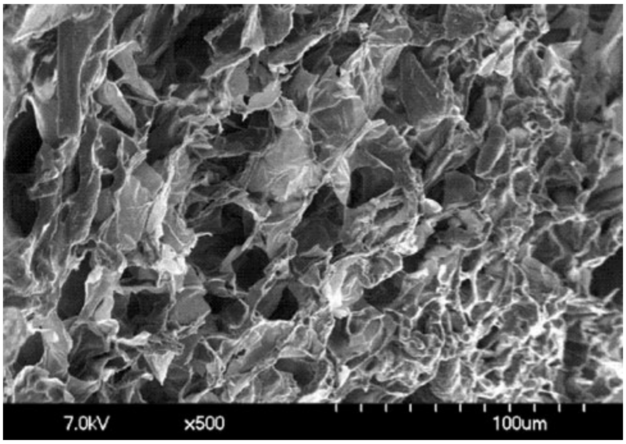


Fig. 2 Scanning electron microscopy image showing the honeycomb-like porous structure of the PAAm–MC hydrogel. The gel was lyophilized after swelling in distilled water at 25.0 °C. The micrograph was obtained at ×500 magnification applying an accelerating voltage of 7.0 keV. The size of the bar is 100 μm: [AAm] = 6.0 in-wt%; [MC] = 1.0 in-wt%

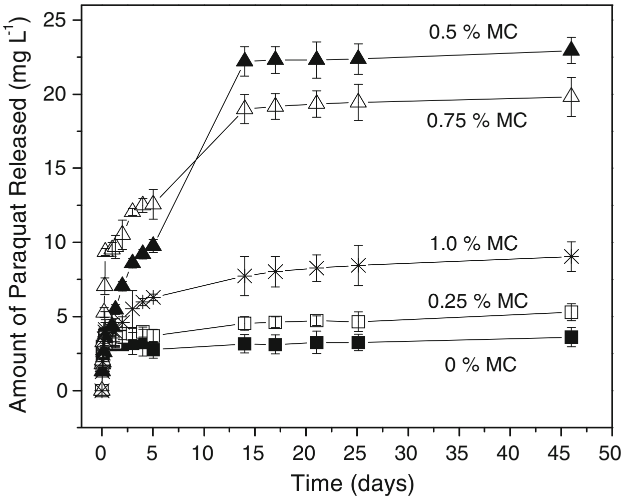


Fig. 3 Profiles of amount of paraquat released as a function of time for PAAm–MC hydrogels with different MC concentrations: [MC] = 0; 0.25; 0.5; 0.75; and 1.0 in-wt%, [AAm] = 6.0 in-wt%, and $C_0 = 37.48$ mg L^{-1}. Error bars represent standard deviations for the three measurements (mean ± SD, $n = 3$)

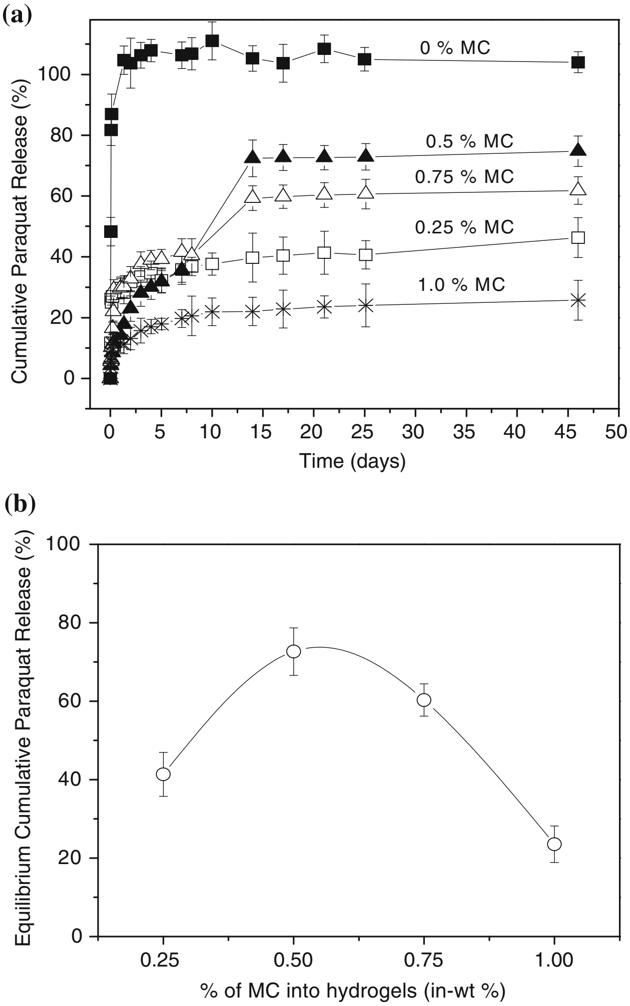


Fig. 4 **a** Profiles of paraquat release as a function of time, and **b** dependence of equilibrium cumulative paraquat release as a function of MC concentration for PAAm and MC hydrogels: $C_0 = 37.48$ mg L^{-1}, and [AAm] = 6.0 in-wt%. Error bars represent standard deviations for the three measurements (mean ± SD, $n = 3$)

content of MC significantly affects the amount of paraquat released, where the maximum release, close to 23 mg L^{-1}, was observed when an intermediate content of MC (0.5%) was used.

Figure 4 shows the effect of MC percentage on the kinetic behavior of cumulative paraquat release. It is possible to see in Fig. 4a that the paraquat release from the hydrogel constituted of 6.0% AAm is 100% after 1 day. This fast release is attributed to the hydrophobic weak interactions between cationic groups (from the paraquat) and amide groups from the PAAm chains. The figure also reveals that the cumulative release occurred in a very controlled and sustained manner, where the concentration of paraquat after 15 days was maintained constant up to 46 days. It was also observed that the quantity of paraquat release increases from 41.3 ± 5.6 to 72.6 ± 6.1% when the amount of MC in the gel-forming solution increases in the range of 0.25–0.5 (in-wt%), Fig. 4b. By increasing MC content of the matrix, swelling of the matrix also increased due to the more hydrophilic nature of MC, conducing to the percentage increase of the released paraquat. Similar observations have been noticed by Rokhade et al. [30].

The release profiles indicate that the amounts of paraquat released decreased in the hydrogel prepared with MC concentration above 0.5%. At higher concentrations of MC (beyond 0.5 g) the density of network chains increases so much that both the diffusion of solvent molecules and relaxation of macromolecular chains are reduced. Similar behaviors have been observed in other studies on the characterizations of hydrogel hydrophilicity [15, 31]. This explains the hydrogels drop in the release capability. Moreover, one of the primary factors in the application of hydrogels as a delivery vehicle for the controlled release of pesticide is the loading percentage effect on the solute release rate because a larger hydrogel loading can facilitate the relaxation of macromolecular chains [15]. In addition, the results of paraquat removal from aqueous solutions using PAAm and MC hydrogels, recently published by our group [16], indicated that paraquat adsorption is more favorable in hydrogels prepared with an MC concentration of around 0.5%.

In general, the hydrogels did not release the total loaded paraquat because of the strong interaction of the paraquat–hydrogel matrix, specifically between the hydroxyl and amide groups (from MC and PAAm, respectively) with cationic regions from the paraquat. Controlled release systems studied by Sing et al. [22] and Alemzadeh and Vossoughi [32] presented similar behavior.

Figure 5 shows the effects of acrylamide concentration on the cumulative paraquat release from PAAm–MC hydrogels prepared with different AAm and MC combinations. The releasing kinetic and the released quantity can be controlled until 40–45 days and up to 75% by adjusting the PAAm and MC contents in the gel-forming solution. In both cases, it was observed that as the polymeric matrix becomes rigid due to the increase in the concentration of acrylamide in the hydrogels, from 6.0 to 9.0% (Fig. 5a) and from 6.0 to 12.0% (Fig. 5b), the cumulative paraquat release decreased. This tendency was also reported by Işiklan [1], where the author explained that the decreases in the cumulative release are due to the increasing of the monomer concentration, which gives rise to a compact network of the polymer; hence the free volume reduces, and the penetration of water molecules and diffusion of pesticide molecules become difficult.

In accordance to Singh et al. [33], the primary requisites for using agrochemicals to control the environment and health hazards are by means of the controlled release and sustained manner. Also, PAAm-type hydrogels must act as carriers for herbicidal agents and hydrogels, such as in water preservation systems (soil conditioning), hence inducing aggregation, diminishing water evaporation, and promoting plant growth [34]. Moreover, acrylamide was selected due to its industrial importance and its better known properties [35]. Consequently, the hydrogels studied in this work have enormous potential to be applied in agriculture fields.

Additionally, to our knowledge, we report in this study a hydrogel-based vehicle (first carrier) that is able to prolong the sustained release of paraquat pesticide up to 45 days.

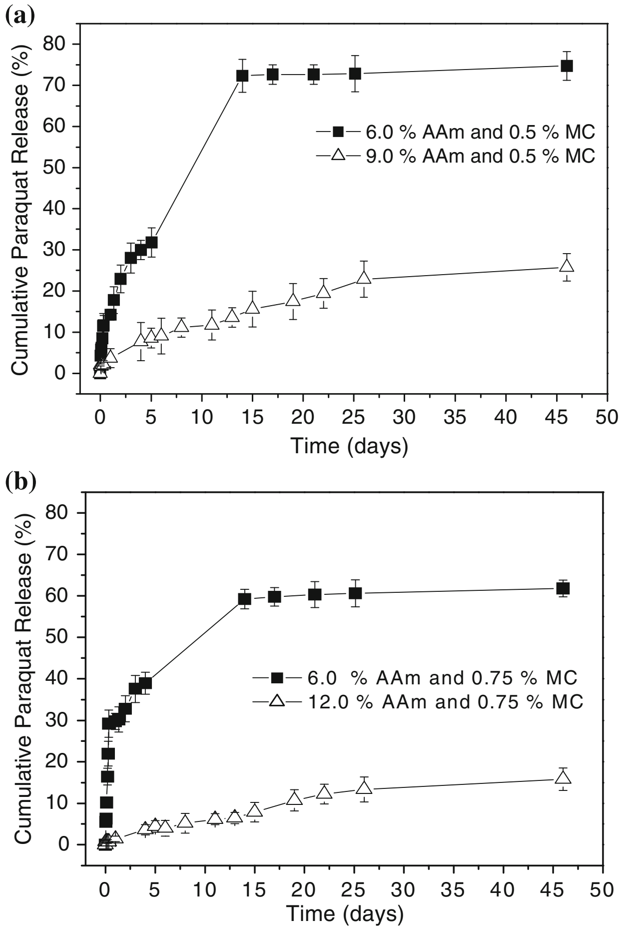


Fig. 5 Profiles of paraquat release from hydrogels constituted by PAAm and MC as a function of time in different conditions: **a** 6.0% AAm and 0.5% MC, 9.0% AAm and 0.5% MC; **b** 6.0% AAm and 0.75% MC, 12.0% AAm and 0.75% MC. $C_0 = 37.48$ mg L^{-1}. Error bars represent standard deviations for the three measurements (mean ± SD, $n = 3$)

Mathematical modeling of paraquat release

Hydrogels have a unique combination of characteristics that make them useful in controlled delivery applications. Due to their hydrophilicity, hydrogels can imbibe large amounts of water (>90 in-wt%). Therefore, the molecule's release mechanisms from hydrogels are very different from hydrophobic polymers. Both simple and sophisticated models have been previously developed to predict the release of an active agent from a hydrogel device as a function of time. The most widely applicable mechanism for describing solute release from hydrogels is diffusion-controlled release [36]. Fick's law of diffusion with either constant or variable diffusion coefficients is commonly used in modeling diffusion-controlled release [21, 22, 37]. Although there are a number of reports dealing with the mathematical modeling of controlled release from swellable

Table 2 Parameters k and n obtained for paraquat pesticide release from hydrogels synthesized with various AAm and MC concentrations at 25.0 °C: $C_0 = 37.48$ mg L^{-1}

Hydrogel	k (h^{-1})	n	Mechanism
(6.0–0)[a]	0.529 ± 0.0308	0.44 ± 0.02	Fickian
(6.0–0.25)	0.0678 ± 0.0008	0.44 ± 0.03	Fickian
(6.0–0.5)	0.0404 ± 0.0010	0.50 ± 0.02	Fickian
(6.0–0.75)	0.0541 ± 0.0021	0.63 ± 0.01	Anomalous
(6.0–1.0)	0.0375 ± 0.0010	0.58 ± 0.04	Anomalous
(9.0–0.5)	0.0147 ± 0.0302	0.34 ± 0.08	More-Fickian
(12.0–0.75)	0.00533 ± 0.00010	0.38 ± 0.09	More-Fickian

[a] [AAm] = 6.0 in-wt% and [MC] = 0 in-wt%

polymeric systems, no single model successfully predicts all the experimental observations [33].

The values of release exponent "n" and gel characteristic constant "k" calculated using Eq. 3 for the release dynamics of pesticide from the PAAm–MC hydrogels are in Table 2. The curves obtained from Eq. 3 presented good linearity (regression coefficient, $R^2 \geq 0.999$), indicating that Peppas's model can be applicable to analyze the systems. The values of n remained in a range corresponding to Fickian diffusion ($n = 0.45$–0.5) until MC = 0.5% for AAm concentration equal to 6.0% (in-wt). After this concentration, the paraquat release occurred through the non-Fickian diffusion. Non-Fickian or anomalous diffusion occurs when the diffusion and relaxation rates are comparable. Thus, the paraquat release depends on two simultaneous rate processes, water migration into the beads and diffusion through continuously swelling hydrogels [20]. The values of k showed that the release of paraquat becomes slower when the MC and AAm concentration increases.

Conclusion

In order to investigate the hydrogels controlled release capacity, it was loaded with paraquat and the release kinetics was studied by UV–Vis spectroscopy as a function of the chemical composition of the hydrogel, i.e., acrylamide and MC content. SEM micrograph of PAAm and MC hydrogel presented a porous honeycomb-like structure with many well-defined shapes exhibiting a homogeneous pore size distribution. The results showed that the pesticide paraquat was successfully loaded and released from different hydrogels. Hydrogels presented high loading capability of paraquat pesticide, up to 82% of paraquat in relation to the amount of paraquat available in the loading solution.

In general, the initial paraquat release rate was fast, and after several days it decreased, indicating that paraquat on the hydrogels surface (or close to) diffused rapidly after the initial swelling of the gel. Later, the cumulative release occurred in very controlled and sustained manner, when the paraquat concentration after 15–25 days maintained constant up to 46 days. The paraquat release capacity was increased from 41.3 ± 5.6 to 72.6 ± 6.1% by increasing the MC concentration in the range of 0.25–0.5 (in-wt%), the swelling of the matrix also increased due to a more hydrophilic nature of MC. However, a decrease was observed in the release rate of the hydrogel prepared from the gel-forming solution with MC concentration above 0.5%, because the density of the network chains increases so much that both the diffusion of solvent molecules and relaxation of macromolecular chains are reduced. Thus, as the polymeric matrix becomes rigid due to the concentration increase of acrylamide in the hydrogels, the cumulative paraquat release decreased.

The curves obtained from Peppas' model presented good linearity ($R^2 \geq 0.999$), indicating that such model is applicable to analyze the systems. The n values for the release of pesticide from hydrogels indicate that paraquat release has Fickian and non-Fickian diffusion, depending on the MC content. The values of k showed that the release of paraquat becomes slower when the MC and AAm concentrations increase.

Finally, to our knowledge, we report a first carrier on hydrogel-based vehicle that is able to prolong the sustained release of paraquat pesticide up to 45 days, essential for its application in controlled release systems.

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