

Application of Polysaccharide Hydrogels in Adsorption and Controlled-Extended Release of Fertilizers Processes

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ABSTRACT: This article studied the applicability of poly(acrylamide) and methylcellulose (PAAm-MC) hydrogels as potential delivery vehicle for the controlled-extended release of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ and potassium phosphate (KH_2PO_4) fertilizers. PAAm-MC hydrogels with different acrylamide (AAM) and MC concentrations were prepared by a free radical polymerization method. The adsorption and desorption kinetics of fertilizers were determined using conductivity measurements based on previously built analytical curve. The addition of MC in the PAAm chains increased the quantities of $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 loaded and extended the time and quantities of fertilizers released. Coherently, both loading and releasing processes were strongly influ-

enced by hydrophilic properties of hydrogels (AAM/MC mass proportion). The best sorption (124.0 mg $\text{KH}_2\text{PO}_4/\text{g}$ hydrogel and 58.0 mg $(\text{NH}_4)_2\text{SO}_4/\text{g}$ hydrogel) and desorption (54.9 mg $\text{KH}_2\text{PO}_4/\text{g}$ hydrogel and 49.5 mg $(\text{NH}_4)_2\text{SO}_4/\text{g}$ hydrogel) properties were observed for 6.0% AAM–1.0% MC hydrogels (AAM/MC mass proportion equal 6), indicating that these hydrogels are potentially viable to be used in controlled-extended release of fertilizers systems. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2291–2298, 2012

Key words: adsorption; conductimetric measurements; controlled-extended release of fertilizers; polysaccharide hydrogels; swelling degree

INTRODUCTION

Controlled/extended desorption systems (also known as controlled release systems) were first studied and applied to evaluate the controlled release of drugs. The main objective of these systems is to always keep an optimal dosage in the body, reducing costs, dosage frequency, toxic effects, thus increasing the efficiency of the drug.¹ This concept can also be extended to agriculture such as in the controlled-extended desorption of fertilizer through low-cost biodegradable carrier vehicles, produced from simple and reproductive synthesis.

The most commonly used biodegradable carrier vehicles are hydrogels which are capable of storing

large amounts of fertilizer, gradually releasing it into the soil, retaining the fertilizers concentration longer and in optimal conditions. This avoids unnecessary expenses and minimizes the environmental impacts² caused by overuse of fertilizers in the plantations. Therefore, biodegradable hydrogels have received much attention from the agricultural sector in recent years, such as: controlled-extended release of agricultural inputs,^{3–6} soil conditioners,^{7,8} and erosion control.⁹ The use of conditioners has contributed to increase the water retention capacity in the soil, reducing the irrigation frequency, minimizing costs, and helping to improve the yield in cultures.⁷ Hydrogels are three-dimensional hydrophilic macromolecular networks, which can absorb water many times their dry mass and significantly expand in their volume.^{10–12} For these and other applications, there is substantial interest in obtaining hydrogels from renewable and biodegradable sources.

In this regard, several studies published in the literature were conducted to obtain hydrogels from polysaccharide materials.^{13–16} Due to its high number of hydroxyl and carboxylic groups, polysaccharides can improve the hydrophilic properties of the hydrogels, in addition to increasing biodegradability or making the hydrogels biodegradable.¹⁷

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This article studied the applicability of poly(acrylamide) and methylcellulose (PAAm-MC) hydrogels as potential delivery vehicle for the controlled-extended release of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and potassium phosphate (KH_2PO_4) fertilizers. Adsorption and release processes were investigated by conductimetric method.

EXPERIMENTAL

Synthesis of hydrogels

Acrylamide (AAM, 99%) was obtained from Fluka (St. Louis, MO). Biodegradable methylcellulose (MC, number-average molecular weight $40,000 \text{ g mol}^{-1}$, viscosity 400 cP, 27.5–31.5% in methoxy groups; 68.5–72.4% in hydroxyl groups, data from supplier's specifications) was obtained from Aldrich (St. Louis, MO). The polyacrylamide (PAAm) and methylcellulose (MC) semi-interpenetrating networks or semi-IPN hydrogels were obtained according to the procedure described by Aouada et al.^{17,18} Five hydrogels were synthesized with different compositions of AAM and MC: [AAM] = 6.0; 9.0; and 12.0 in wt % and [MC] = 0.5 and 1.0 in wt % describes the composition of the feed reaction mixture, i.e., the concentration of the monomer AAM and MC in the reaction mixture, Table I. After the synthesis, the hydrogels were then purified by dialysis using distilled water for 10 days. In this process, the species that did not undergo polymerization or did not participate in the reaction were eliminated from the hydrogel.^{17,19,20}

Acrylamide is carcinogenic to experimental mice and rats, causing tumors at multiple organ sites in both species when given in drinking water or by other means.²¹ In addition, except for the differences related to the metabolism of acrylamide and its metabolites, few qualitative differences are expected between humans and rats with respect to absorption, distribution, and excretion, in part because acrylamide is highly water soluble.²² Despite the monomer acrylamide presented some toxicity, in the synthesis of hydrogels, the monomers acrylamide are polymerized to the polyacrylamide polymer. In the literature, the polyacrylamide hydrogels or composites containing polyacrylamide are being proposed for use as biomaterials.^{23–25}

Detection of fertilizers by conductimetric measurements

In the conductivity measurement of an ionic solution, the physical property, determined in practice, is the resistance. In summary, electrolyte ionic conductivity is a measure of the current that it can conduct, and the current is the transfer rate of an electric charge. Since the electrical charge is conducted

TABLE I
AAM and MC Concentrations in Feed Solutions Used in (AAM-MC)^a Hydrogel Synthesis: $V_{\text{Final}} = 0.03 \text{ L}$

Hydrogels	Acrylamide (AAM) (g)	Methylcellulose (MC) (g)	AAM/MC mass proportion
(6.0–1.0)	1.80	0.30	6
(9.0–0)	2.70	0	–
(9.0–0.5)	2.70	0.15	18
(9.0–1.0)	2.70	0.30	9
(12.0–1.0)	3.60	0.30	12

^a Corresponds to AAM and MC concentrations, both in wt %.

through the electrolyte by the ions, then the conductance of an electrolyte depends on the amount or proportion of charge that the ions can conduct.²⁶ For the measurements performed to approach the maximum of the real conditions, the apparatus was calibrated before any experimental measurement. The solution of potassium chloride (KCl) at 0.01 mol L^{-1} (conductivity = 1.409 mS cm^{-1} at 25.0°C) was used as standard for the equipment calibration. The cell constant (K) experimentally determined was around 1.014. Conductimetric properties were investigated using a conductivity meter Horiba, model ES-12.

Adsorption of fertilizers onto PAAm-MC hydrogels

The study of adsorption of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and potassium phosphate KH_2PO_4 fertilizers was performed by inserting a previously dried hydrogel in a given solution of $(\text{NH}_4)_2\text{SO}_4$ at 1867 mg L^{-1} or KH_2PO_4 at 1970 mg L^{-1} . The decrease of fertilizer concentration in medium was investigated as a function of time. After a certain period of time, the hydrogels were removed from solution, and the loaded amount of each fertilizer was obtained by the difference between the initial concentration of the solution (before insertion of the hydrogel) and the concentration in the solution after a time “ t ” of immersion of the gel, eq. (1)^{27,28}:

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

where q_t is the amount of fertilizer 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 fertilizer 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).

After each measurement, the hydrogels were replaced in the fertilizer solution. The concentrations of the fertilizer in the solutions were determined by

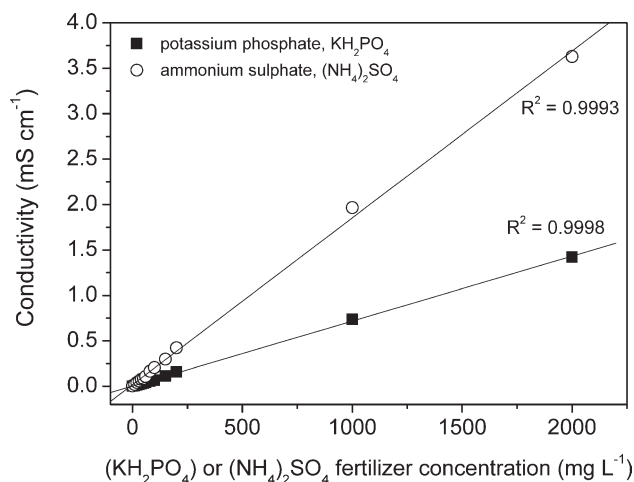


Figure 1 Analytical calibration curves for potassium phosphate (KH_2PO_4) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) fertilizers with good correlation coefficient of 0.9998 and 0.9993, respectively. The regression equations were conductivity = $1.54 \times 10^{-6} + 7.15 \times 10^{-7} [(\text{NH}_4)_2\text{SO}_4]$ and conductivity = $1.61 \times 10^{-5} + 1.84 \times 10^{-6} [\text{KH}_2\text{PO}_4]$. Both analytical curves had linearity ranges between 0 and 2000 mg L^{-1} .

conductimetric measurements based on previously built analytical curve.² The linear regression coefficients for fertilizers $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 were 0.9993 and 0.9998, respectively.

Swelling degree

PAAm-MC hydrogels with different AAm and/or MC formulations were allowed to swell in fertilizer aqueous solution with different concentrations. The swelling degree (at equilibrium conditions) was calculated by the ratio between weights of the swollen and dried hydrogel. Measurements were performed in triplicate at $25.0 \pm 0.1^\circ\text{C}$ and the error bars indicate the standard deviation ($n = 3$).

Controlled-extended release of $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 fertilizers in water

After quantifying the sorption of the fertilizers, their release in deionized water was studied. The hydrogel was then removed from the fertilizer solution after sorption equilibrium, and added to a container containing a known volume of deionized water ($V = 0.03 \text{ L}$). At specific “ t ” times, the hydrogels were removed from solution and the conductivity of the solution was measured, which was converted in terms of concentration through the analytical calibration curve. After each measurement, the hydrogels were replaced in the solution.

The desorption results were quantified as a function of time in terms of cumulative desorption (CD) using eq. (2)^{29,30}:

$$CD(\%) = \frac{AR_t}{AL_\infty} \times 100 \quad (2)$$

where AR_t is the amount of fertilizer released by the hydrogel at time t and AL_∞ is the total amount of fertilizer loaded by the hydrogel.

RESULTS AND DISCUSSION

Study of the fertilizers adsorption process

The concentrations of the fertilizers in the solutions were determined using a conductimetric technique,² based on previously constructed calibration curves, shown in Figure 1. The sorption kinetics was monitored until the equilibrium state, and after this state, there is no incorporation of the fertilizer by the gel. The hydrogels remained immersed for 48 h in solutions of potassium phosphate KH_2PO_4 or ammonium sulfate solution $(\text{NH}_4)_2\text{SO}_4$ with concentrations of 1970–1867 mg L^{-1} , respectively.

In this study, the concentration effects of AAm and MC in the sorption capacity of equilibrium hydrogels were investigated and their results are shown in Table II. For fertilizer KH_2PO_4 , the highest rate of sorption was found for 6.0% AAm and 1.0% MC hydrogel ($124.0 \pm 15.9 \text{ mg KH}_2\text{PO}_4/\text{g hydrogel}$). This specific hydrogel has the lowest AAm/MC mass proportion, AAm/MC = 6. On the other hand, the lesser was found for 12.0% AAm and 1.0% MC hydrogel ($26.2 \pm 1.3 \text{ mg KH}_2\text{PO}_4/\text{g hydrogel}$). This hydrogel has AAm/MC mass proportion equal to 12. When comparing the fertilizer sorption capability of the hydrogel by two fertilizers, it is observed that the sorption of KH_2PO_4 is greater than $(\text{NH}_4)_2\text{SO}_4$ fertilizer, indicating that its interaction with the polymer matrix is more effective. The fertilizer was not chemically attached to the polymeric chain and the only likely interactions were ionic attractions. The overall behavior showed an increase in the rates of the loaded fertilizer with the increased concentration of MC due to the increased number of hydroxyl groups from the MC chains. However, the fertilizer sorption capability decreased when concentration of AAm in feed solution increased. This fact is related

TABLE II
Values of Maximum Load of $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 Fertilizer for Different Hydrogels After 48 h of Immersion Time

(AAm-MC) hydrogel	mg $(\text{NH}_4)_2\text{SO}_4/\text{g hydrogel}$	mg $\text{KH}_2\text{PO}_4/\text{g hydrogel}$
(6.0–1.0)	58.0 ± 6.7	124.0 ± 15.9
(9.0–0)	13.2 ± 1.1	31.6 ± 0.8
(9.0–0.5)	20.2 ± 2.2	43.9 ± 4.2
(9.0–1.0)	36.7 ± 6.0	76.4 ± 7.7
(12.0–1.0)	15.4 ± 2.0	26.2 ± 1.3

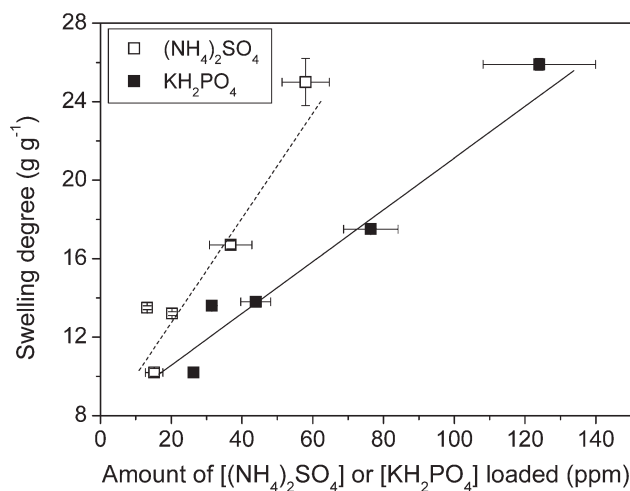


Figure 2 Relationship between swelling degree and amount of fertilizers loaded onto hydrogels prepared with different AAm and MC concentration. Error bars represent standard deviations for the three measurements (mean \pm SD, $n = 3$).

to the decrease in water absorption caused by increase of network rigidity. Thus, the increase in AAm/MC mass proportion causes a decrease in fertilizer sorption. This is good indicative that the fertilizer sorption is also strongly influenced by hydrophilicity of the hydrogels as well as synthesis conditions, i.e., the AAm/MC mass proportion, Figure 2.

Controlled-extended release of fertilizers

When the hydrogel loaded with agrochemical species (herbicides, fungicides, fertilizers, etc.) is placed in contact with water, by chemical potential differences (chemical spontaneity), the water molecules tend to diffuse into the polymer matrix through the interaction mainly with hydroxyl groups, resulting in a chemical competition between agrochemicals/water with the matrix. As a result, the agrochemical molecules are diffused from the matrix (aqueous media), achieving the controlled-extended desorption. In this way, 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.

Figure 3(a,b) shows the dependencies of the release quantities and the cumulative release of the KH_2PO_4 fertilizer as a function of concentration of methylcellulose ($[\text{AAm}] = 9.0$ in wt % and as a function of concentration of acrylamide ($[\text{MC}] = 1.0$ in wt %), respectively. Figure 4(a,b) shows the same kinetic studies performed for $(\text{NH}_4)_2\text{SO}_4$ fertilizer for the same hydrogels indicated in Figure 3. In general, the initial fertilizer release rate was fast, and it decreased after about 5–6 h, indicating that fertilizer

on the hydrogels surface (or close to) diffused rapidly from the initial swelling of the gel. Later, the cumulative release occurred in very controlled and sustained manner, in which the concentration of fertilizer after 24 h was maintained constant up to 78 h. It was also observed that an increased AAm concentration provoked a decrease in the quantities of $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 released. This tendency was previously reported,^{20,31} which the authors attributed to the increase in network compaction; hence the free volume reduces, and the penetration of water molecules and diffusion of fertilizer molecules become difficult. In this sense, the increase of MC content increased the release capability due to the increase in hydrophilicity of the matrix. For instance, the released amounts of the fertilizer KH_2PO_4 were 30.8 ± 1.0 ; 35.4 ± 2.5 ; 41.0 ± 1.0 mg/g for the concentrations of MC equal to 0; 0.5; and 1.0 in wt %, respectively. These results showed that a decrease in AAm/MC mass proportion provokes a pronounced increase in the released amounts of the fertilizer.

The hydrogels presented desorption kinetics very distinct from each other, what reflects in a significant variation in the total amount of fertilizer desorbed. Thus, by controlling the synthesis conditions of the hydrogel, it is possible to control the release process of the fertilizer, releasing it more or less depending on the interests of those applying it. This makes the PAAm-MC hydrogel extremely interesting as a carrier vehicle for controlled-extended desorption systems.

When analyzing the Tables II to IV, it is observed that the sorption and desorption results (both in %) are antagonistic. This occurs because the cumulative rate of desorption is related to the ratio of the amount of desorbed fertilizer by the hydrogel and the total amount of fertilizer sorbed by the hydrogel, eq. (2). Therefore, increasing the concentration of MC increases the sorption capacity due to strong interactions of the OH^- groups from the MC with the NH_4^+ cations proceeding of $(\text{NH}_4)_2\text{SO}_4$, contributing to increase of the desorption time (sustained to up to 78 h). The same gains in the desorption kinetics were observed for fertilizer KH_2PO_4 . These results showed that PAAm-MC hydrogels are potentially viable to be used in systems of release and extended desorption of fertilizers. In addition, in accordance to literature, the primary requisites for using agrochemicals to control the environment and health hazards are by means of the controlled release and sustained manner.³²

Both KH_2PO_4 and $(\text{NH}_4)_2\text{SO}_4$ released from the hydrogel constituted of 9.0% AAm is almost 100%. This trend was attributed to the hydrophobic weak interactions between K^+ and NH_4^+ and amide groups from the PAAm chains.²⁰ In the case of KH_2PO_4 one, around 98% of the fertilizer that was

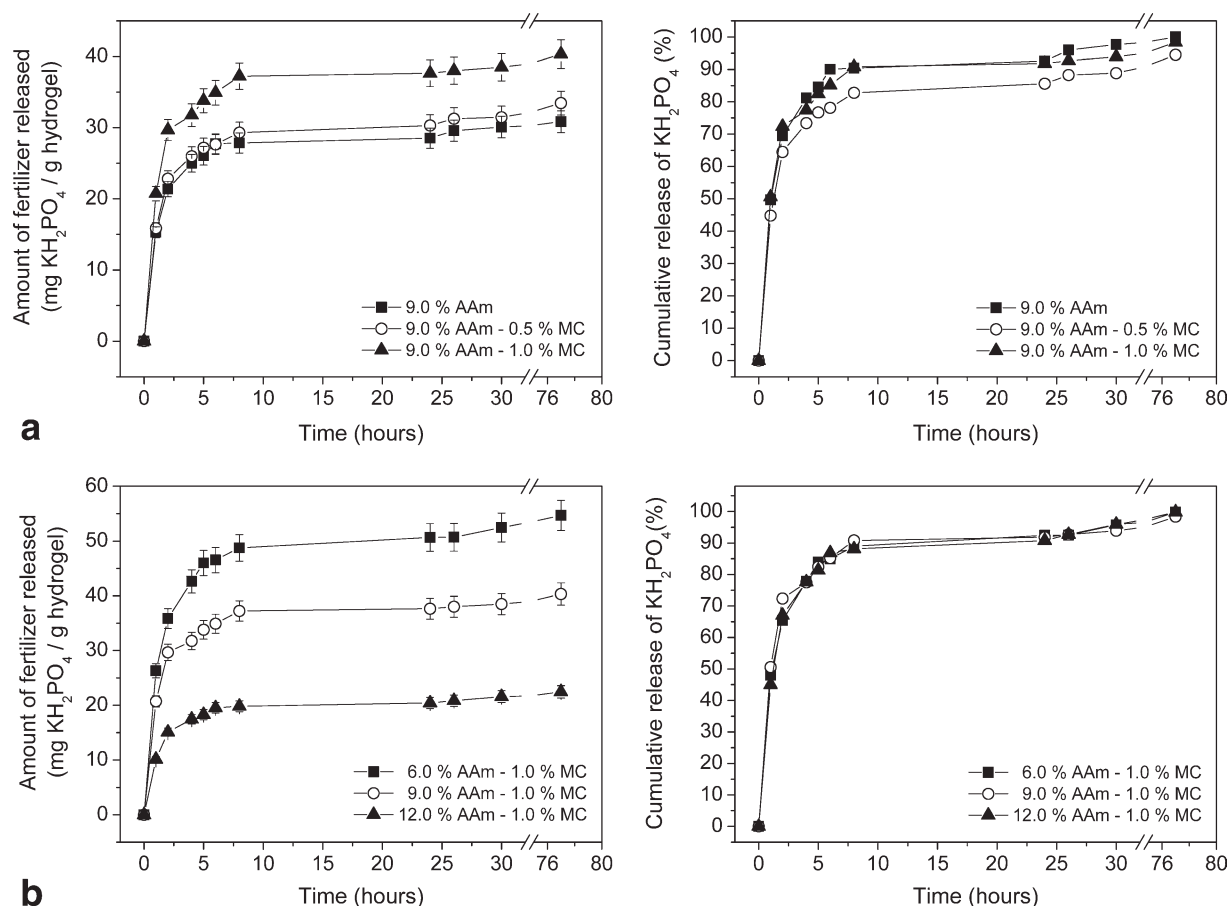


Figure 3 Profiles of potassium phosphate (KH_2PO_4) release from hydrogels constituted by PAAm and MC as a function of time in different conditions: (a) [AAm] = 9.0 in wt % with 0; 0.5; and 1.0 MC in wt %, and (b) [MC] = 1.0 in wt % with 6.0; 9.0; and 12.0 AAm in wt %. Error bars represent standard deviations for the three measurements (mean \pm SD, $n = 3$).

sorbed is desorbed to the aqueous phase and around 2% of fertilizer was retained in the hydrogel.

Increasing the concentration of AAm, and consequently AAm/MC mass proportion, negatively affects the sorption and also significantly reduces the amount of fertilizers released due to the little interaction between its amide groups ($-\text{CONH}_2$) with the cations of the fertilizer. Accordingly, 6.0% AAm and 1.0% MC hydrogel had a lowest cumulative release ($44.3 \pm 1.2\%$ for KH_2PO_4 and $85.5 \pm 2.7\%$ for $(\text{NH}_4)_2\text{SO}_4$). As discussed earlier, this behavior is related to the lowest AAm/MC mass proportion.

Comparatively, it is observed that release of $(\text{NH}_4)_2\text{SO}_4$ occurred more effectively than KH_2PO_4 , which indicates a low fertilizer/hydrogel interaction (Tables III and IV). The cumulative release results that exceed the value of 100% may be related to some impurities in the medium, whether it is a result of the purification process of the gel or during the measurements performed, since conductivity is a technique that measures the mobility of ions in solution, not of a specific species.²⁶

Isotherms of adsorption

The Langmuir isotherm 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 the eq. (3):

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

where C_{eq} is the solution fertilizer concentration at equilibrium (mg L^{-1}), q_{eq} is the maximum fertilizer adsorption on hydrogel (mg g^{-1}), K_L (L g^{-1}) and α_L (L mg^{-1}) are the Langmuir isotherm constants.

The Freundlich adsorption model, which assumes that the adsorption occurs on heterogeneous surfaces, and can be expressed using the 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).

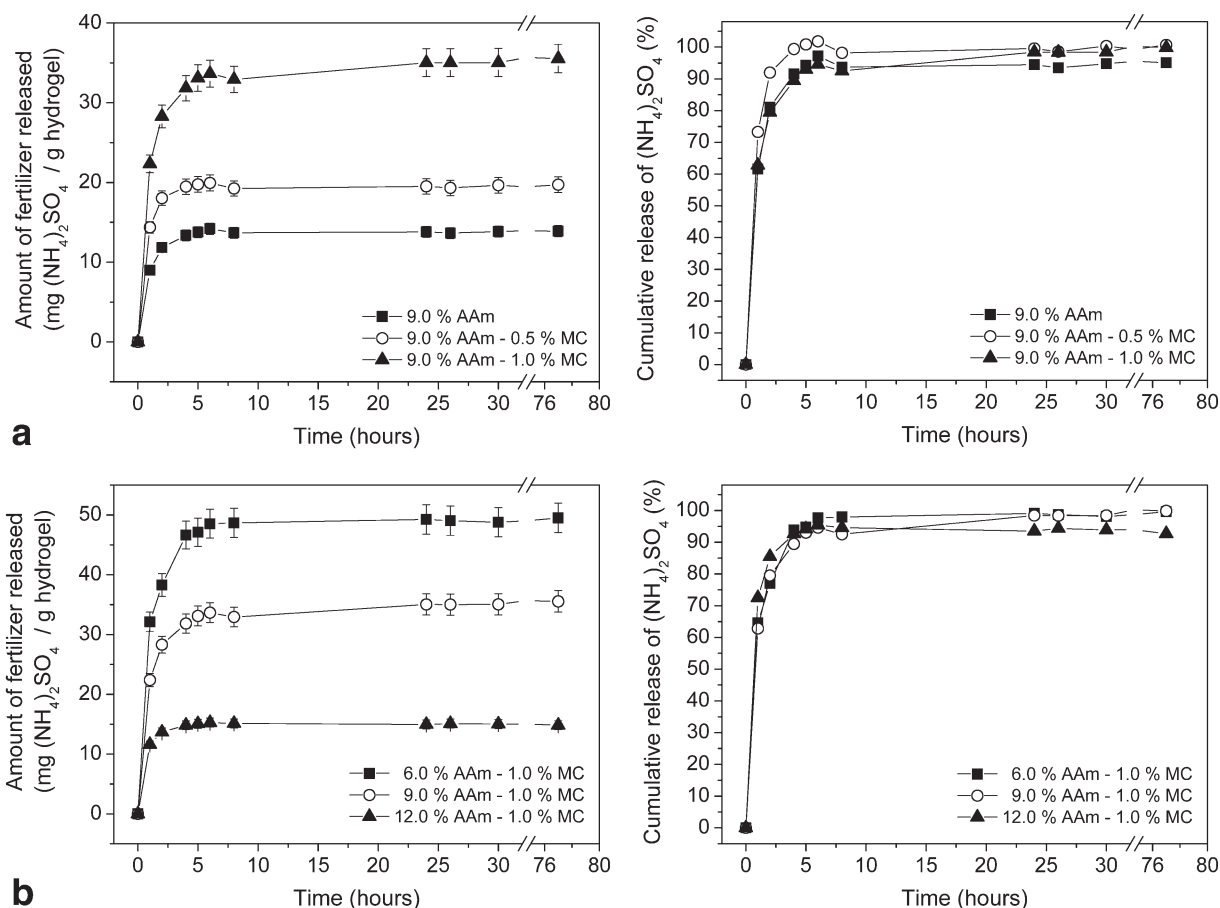


Figure 4 Profiles of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ release from hydrogels constituted by PAAm and MC as a function of time in different conditions: (a) $[\text{AAM}] = 9.0$ in wt % with 0; 0.5; and 1.0 MC in wt %, and (b) $[\text{MC}] = 1.0$ in wt % with 6.0; 9.0; and 12.0 AAm in wt %. Error bars represent standard deviations for the three measurements (mean \pm SD, $n = 3$).

Values of K_F and n were calculated from the intercept and slope of the plot of $\ln q_{\text{eq}}$ versus $\ln C_{\text{eq}}$.

The fitted lines of the data modeled using the Freundlich and Langmuir isotherms for the adsorption of fertilizers from hydrogels composed by 6.0% AAm and 1.0% MC are shown in Figure 5. The initial concentration of the fertilizers varied between 50 and 2000 mg L⁻¹. Based on R^2 values, the Freundlich model fits the both fertilizers better than the Langmuir model. It was possible to determine the K_F and n Freundlich parameters. The K_F parameters calcu-

lated were 1.271 and 1.176 L g⁻¹ for $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 fertilizers, respectively. In addition, the values of n parameter for $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 fertilizers were 1.727 and 1.641.

CONCLUSIONS

Because it is a simple technique, highly reproducible, low cost, and allows a direct detection without previous treatment of the analyte, the conductivity technique was extremely efficient in this study. It

TABLE III
Cumulative Release and Amount of KH_2PO_4 Fertilizer Released for Different Hydrogels

(AAM-MC) hydrogel	Cumulative release (%)	Amount of fertilizer released (mg KH_2PO_4)/g hydrogel
(6.0-1.0)	44.3 \pm 1.2	54.9 \pm 7.9
(9.0-0)	97.5 \pm 1.4	30.8 \pm 1.0
(9.0-0.5)	80.6 \pm 4.1	35.4 \pm 2.5
(9.0-1.0)	50.4 \pm 0.8	41.0 \pm 1.0
(12.0-1.0)	85.5 \pm 2.7	22.4 \pm 0.7

TABLE IV
Cumulative Release and Amount of $(\text{NH}_4)_2\text{SO}_4$ Fertilizer Released for Different Hydrogels

(AAM-MC) hydrogel	Cumulative release (%)	Amount of fertilizer released (mg $(\text{NH}_4)_2\text{SO}_4$)/ g hydrogel
(6.0-1.0)	85.3 \pm 2.2	49.5 \pm 4.8
(9.0-0)	106.8 \pm 2.7	14.1 \pm 0.2
(9.0-0.5)	97.0 \pm 3.4	19.6 \pm 1.5
(9.0-1.0)	96.7 \pm 2.9	35.5 \pm 6.3
(12.0-1.0)	99.4 \pm 0.8	15.3 \pm 0.8

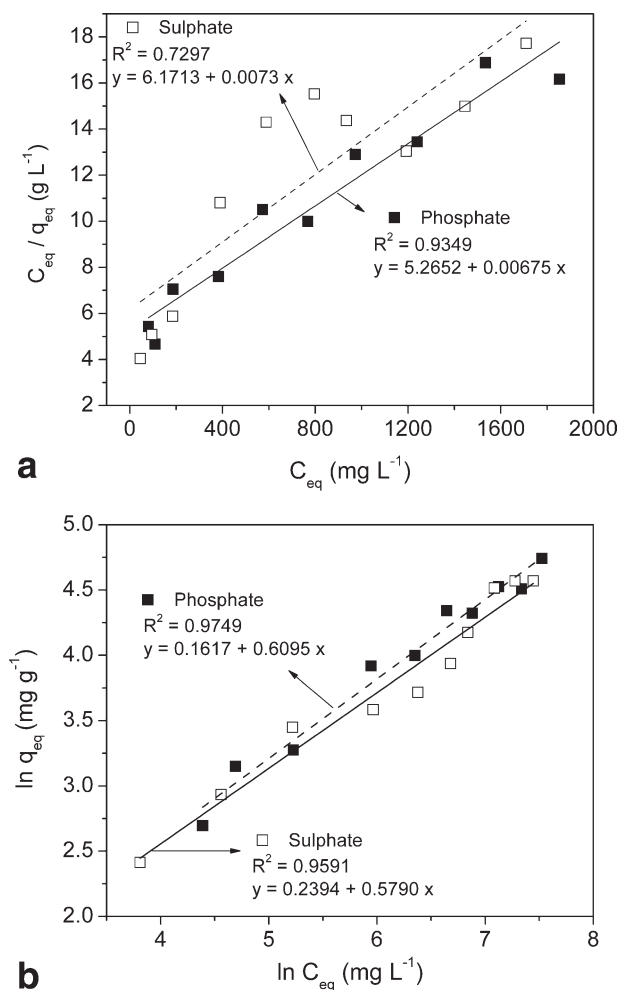


Figure 5 Fitted lines of the data modeled using the (a) Langmuir and (b) Freundlich isotherms for the adsorption of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ and potassium phosphate KH_2PO_4 for hydrogel containing 6.0% AAm and 1.0% MC.

was possible to quantify the sorption and desorption of the $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 from the hydrogels in aqueous solution by conductimetric measurements, even in small amounts (at mg L^{-1} level).

Sorption and desorption controlled-extended studies indicated that such processes are strongly dependent on the concentration of AAm and MC. There was an important gain on the amounts of sorbed and desorbed fertilizers by the increasing in MC conc. and/or decreasing in AAm conc., indicating that the fertilizers sorption and desorption mechanism can be controlled by controlling the hydrophilicity of the hydrogels.

Based on the results presented (increasing quantities of $(\text{NH}_4)_2\text{SO}_4$ and KH_2PO_4 loaded and extended the time and quantities of fertilizers released), the addition of MC in the PAAm chains makes the PAAm-MC hydrogels potentially viable to be used in systems of release and extended desorption of fertilizers.

NOMENCLATURE

AAm	acrylamide (wt %)
PAAm or poly(AAm)	poly(acrylamide) (wt %)
MC	methylcellulose (wt %)
$(\text{NH}_4)_2\text{SO}_4$	ammonium sulfate (mg L^{-1})
(KH_2PO_4)	potassium phosphate (mg L^{-1})
KCl	potassium chloride (mol L^{-1})
K	cell constant
q_t	amount of fertilizer adsorbed onto PAAm or PAAm-MC hydrogels based on dry gel weight (mg g^{-1})
C_0	concentration of the fertilizer in the initial solution (mg L^{-1})
C_t	concentration of the fertilizer in the aqueous phase after adsorption process for a certain period of time t (mg L^{-1})
V	volume of the aqueous phase (L)
w	amount of dry PAAm-MC hydrogels (g)
CD	cumulative desorption (%)
AR_t	amount of fertilizer released by the hydrogel at time t (mg g^{-1})
AL_∞	amount of fertilizer loaded by the hydrogel (mg g^{-1})

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