

Pectin-Based Polymer Hydrogel as a Carrier for Release of Agricultural Nutrients and Removal of Heavy Metals from Wastewater

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ABSTRACT: A pectin-based hydrogel was used as a remover of Cu^{2+} and Pb^{2+} ions from water and wastewater and in the release of phosphate, potassium, and urea. The swelling studies in either aqueous or saline solutions were analyzed at different pressures, and the prediction of profile of water and solute transports was further analyzed on basis of transport process by diffusion in swellable polymer networks. The hydrogel composed of 0.10 g mL^{-1} final polymer concentration showed an excellent absorption capacity for removal of Cu^{2+} and Pb^{2+} from the solution: 120 mg Cu^{2+} and 130 mg Pb^{2+} per g hydrogel, both at pH 5.5. The hydrogel help to con-

serve water in a pressure range in which a variety of horticultural plants can absorb it. The release process of urea, phosphate, and potassium from the hydrogels is controlled by non-Fickian mechanism with a tendency to macromolecular relaxation. This type of hydrogel is an interesting system for applications in which the efficient use of water is required and release of fertilizers for agriculture. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3146–3154, 2010

Key words: diffusion; drug delivery systems; hydrogel; kinetic (polym.); polysaccharides

INTRODUCTION

Pectin (Pec) is a natural chemical compound with heterogeneous structure which is basically formed by smooth and hairy regions having various unit of polymers such as the poly(1→4) α -D-galacturonic acid.^{1,2} Pec has been generally found in citric fruits, principally in the lemon. Therein, such polysaccharide has been commonly used in feed compositions³ and pharmaceutical industry.^{4–7} Its structure has high amounts of ionic groups, assigning as an excellent polymer matrix for superabsorbent hydrogel

synthesis. Superabsorbent hydrogels are chemically or physically crosslinked polymer network having excellent absorption properties in various aqueous solutes. The efficiency of the swelling rate of hydrogels depends on thermodynamic factors which can be influenced by the specific characteristics of both, hydrogels and solutes.^{8,9} Classes of hydrogels known as superabsorbent materials have been widely used on wastewater and water treatment^{10,11} and soil conditioning¹² due to their excellent water uptake and, consequently, diffusion of different solutes into the polymer matrix. Other characteristics of superabsorbent hydrogels are attributed to high amounts of ionic groups, network flexibility, and porous structure.¹³ By this logic, such materials have been widely applied as towel paper, surgical materials, bandage, membranes, and so forth.¹⁴ The diffusion of aqueous solutes toward the inside of the hydrogel structures is directly related to swelling rate. The flow of fluids inwards and outwards hydrogels allows their use as either absorbent or releasers of inorganic and organic solutes.¹⁵ In recent years, the polysaccharide-based superabsorbent hydrogels appear as a viable

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ecologically economically alternative, aiming at either soil conditioning or water and wastewater treatment. The main characteristics which have been assigned for the use of polysaccharide-based superabsorbent hydrogels are their non-toxicity, biodegradability, availability, and efficiency of application.¹⁶ In this work, the swelling rate of the Pec-based superabsorbent hydrogel at different conditions of pH, temperature, and compositions was studied. Furthermore, the removal of Cu²⁺ and Pb²⁺ from water and the release of phosphate, potassium, and urea were carried out.

EXPERIMENTAL

Materials

Pectin (Spectrum-PE100, $M_W \cong 202,000 \text{ g mol}^{-1}$), glycidyl methacrylate 97% (GMA, Aldrich, $M_W = 142.15 \text{ g mol}^{-1}$), chloridric acid (HCl, Synth), sodium persulfate 99% (SP, Vetec), ethanol 99.5% (Nuclear), acrylamide 99% (AAm, Aldrich), and sodium acrylate (NaAAc, Aldrich) were used. The buffer solutions were previously prepared with deionized water. Other reagents were all of analytical grade and were used without previous purification.

Synthesis of hydrogels

Twelve grams of Pec were dissolved in 480 mL distilled-deionized water. The pH of the solution was adjusted to 3.5 with the addition of concentrated HCl. Next, 1.29 mL GMA was added to the solution under constant and vigorous stirring, keeping the temperature at 60°C for 12 h. Then, the 10 mL final mixture was precipitated in 100 mL ethanol and separated by centrifugation. The precipitate was cooled with liquid nitrogen at -180°C and lyophilized (Martin Christ, Freeze Dryer, Alpha 1-2/LD) at -60°C for 12 h. On the other hand, the modified pectin (M-Pec) hydrogel was synthesized by the following procedure: known amount of M-Pec were dissolved in 500 mL water. Soon after, a solution with known amounts of AAm, AAc, and 10 mmol L⁻¹ SP was added. Then, the mixture was introduced into a cylindrical glass tube and heated at 75°C for 30 min. After that, the cylindrical hydrogels were taken out from the tubes and immersed in distilled-deionized water for 24 h and then washed. After, the M-Pec hydrogels were dried out at room temperature until reaching constant weight. The labels (15-50-35)-0.10 and (15-50-35)-0.05 were used to describe the hydrogel formulation. The values inserted in parenthesis correspond to the mass percentages of M-Pec (15%), AAm (50%), and NaAAc (35%). The values 0.10 and 0.05 (both given

in g mL⁻¹) correspond to final polymer concentrations used in the hydrogel-forming solutions.

Swelling kinetics in aqueous and saline solutions

Swelling kinetics was carried out in buffer solutions of pH 2, 4, 6, 8, and 10. The ionic strength for each solution was adjusted by using a 0.125 mol L⁻¹ NaCl solution. The hydrogels were swollen to equilibrium and measured on an analytical grade balance. The values for the swelling index (I) were obtained from the following relation:^{12,17}

$$I = \frac{m_t - m_d}{m_d} = \frac{m_{\text{H}_2\text{O}}}{m_d} \quad (1)$$

where m_t is the weight of the hydrogel swollen at a specific time, and m_d is the weight of the dried M-Pec-co-AAm-co-AAc hydrogel. Each measurement was carried out by replicates. The swelling kinetic behavior of the M-Pec-co-AAm-co-AAc hydrogel was studied in saline solutions of NaCl, CaCl₂, and KCl with concentrations ranging from 0.03 to 0.06 mol L⁻¹ at 25°C. By assuming that the Cl⁻ ions were common for all the salts used, the main effects observed in the swelling index can be analyzed by the presence of Na⁺, Ca²⁺, and K⁺ ions. The quantitative values for the swelling index were determined by using eq. (1).

Water uptake mechanisms

The diffusional coefficient (n) is a parameter which describes the water diffusion mechanism into hydrogels.¹⁸ The plot of the diffused water rate into the M-Pec-co-AAm-co-AAc hydrogel (M_t/M_∞) versus time (t) gives the n values. The values of n were determined by using eq. (2).¹⁹⁻²¹

$$\frac{M_t}{M_\infty} = kt^n \quad (2)$$

where M_t is the mass of the water absorbed by the hydrogel at a specific time, M_{eq} is the mass of the water absorbed by the hydrogel at a infinity time, and k is a proportionality constant derived from the hydrogel network.

Water uptake at different pressures

The measurements of water uptake at different pressures can help to predict the capacity of the hydrogels to conserve water when they are exposed in an environment in which the gel-to-plant water transport is given by difference in pressure between the soil and the root of the vegetal. To this end, the hydrogel samples were introduced into a vessel with

Richard membrane-covered walls. Water was taken out from hydrogel by increasing the pressure and subsequently removed from the vessel by diffusion through the membrane. The pressure Ψ ranged from 0 to 4000 hPa. The water uptake was analyzed from dependence of the water retention θ (kg water per kg hydrogel) on the pressure Ψ . Quantitative results were estimated by means of van Genuchten's model,²² represented by

$$\theta = f(\psi) = \theta_r + (\theta_s - \theta_r) \times [1 + (\alpha \times \psi)^n]^{-m} \quad (3)$$

where θ (kg kg⁻¹) represents the water retention curve defining the water content as a function of the pressure Ψ (hPa), θ_s and θ_r are residual and saturated water contents, m is a numerically fitted parameter, and α and n are curve shape parameters.

Release of phosphate, potassium, and urea from Hydrogel

Phosphate, potassium, and urea were embedded into the polymer matrix during the synthesis of the M-Pec-co-AAm-co-AAc hydrogel according to amounts shown in Table I. Each dried polymer matrix, loaded with urea, potassium, or phosphate, was immersed into a 100-mL glass cell with 60 mL water. The cell was connected to a conductivity electrode. The water ionic conductivities after releasing the nutrients, at different swelling time of the hydrogel, were measured by a digital conductivity meter (Cornindigital 311 conductivity) at 25°C under a magnetic stirring of 30 rpm.

Removal of Pb²⁺ and Cu²⁺ ions from aqueous medium

The absorption studies of Pb²⁺ and Cu²⁺ from aqueous environments by M-Pec-co-AAm-co-AAc hydrogel were carried out according to the following procedure: the store solutions of either 100 mg L⁻¹ Pb(NO₃)₂ or 100 mg L⁻¹ Cu(NO₃)₂ were previously prepared. Fifty milligrams dried hydrogel with particle sizes ranging from 300 to 425 μ m were introduced into 50 mL of a either Pb²⁺ or Cu²⁺ store solution. The percentages of metallic ions diffused into the hydrogel at specified time were determined from eq. (4):

$$A(\%) = \frac{(C_0 - C_{eq})}{C_{eq}} \times 100 \quad (4)$$

where $A(\%)$ is the percentage of metal absorbed by the hydrogel, C_0 and C_{eq} are the initial and equilibrium concentrations for each residual metal in solution, respectively. $A(\%)$ was determined by the difference between the initial and the final concentrations of metal solutions.

TABLE I
Feed Compositions of Urea, Potassium and Phosphate onto the Hydrogels

Hydrogel formulation (g mL ⁻¹)	Urea (g mL ⁻¹)	Potassium (g mL ⁻¹)	Phosphate (g mL ⁻¹)
(10-40-50)-0.10	0.01	0.01	0.01
(15-50-35)-0.10	0.01	0.01	0.01
(20-40-40)-0.10	0.01	0.01	0.01
(15-50-35)-0.05	0.005	0.05	0.05
(20-40-40)-0.05	0.005	0.05	0.05

The absorption capacity of the hydrogel was determined through eq. (5):

$$q_{eq} = \frac{C_0 - C_{eq}}{m} V \quad (5)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations for each metal in solution, respectively; m is the mass of the dried hydrogel and V is the volume of the metal ions-containing solutions.

RESULTS AND DISCUSSIONS

Swelling index for the M-Pec-co-AAm-co-AAc hydrogel in distilled water

Hydrogels formed only of Pec and NaAAc were not appropriate for swelling studies because they were highly brittle over the experiments. The lower mechanical properties of such hydrogels can be improved with the addition of AAm. Figure 1(a) shows the swelling curves for the M-Pec-co-AAm-co-AAc superabsorbent hydrogel on different compositions of Pec, AAm, and NaAAc. For this hydrogel formulation, the final polymer concentration was 0.10 g mL⁻¹. The swelling index values were 52.21 for (10-40-50)-0.10 hydrogel, 71.08 for (20-40-40)-0.10 hydrogel, and 90.21 for (15-50-35)-0.10 hydrogel. The higher swelling index value was assigned to the (15-50-35)-0.10 hydrogel followed by the hydrogels (20-40-40)-0.10 and (10-40-50)-0.10, respectively. Although (10-40-50)-0.10 hydrogel possessed higher amount of NaAAc, the lower Pec content contributed to decrease the swelling index. Anion-anion electrostatic repulsion forces generated on the ionized groups at both the Pec network and the acrylate (AAc) groups expands the formed hydrogel network, thus allowing the diffusion of either inorganic or organic solutes toward the inside hydrogel.²³ The (20-40-40)-0.10 hydrogel absorbed water efficiently up to 200 min after immersion in distilled water. On the other hand, the (15-50-35)-0.10 hydrogel reached the best swelling performance after 480 min of immersion.

Figure 1(b) shows the swelling indices for the (15-50-35) and (20-40-40) M-Pec-co-AAm-

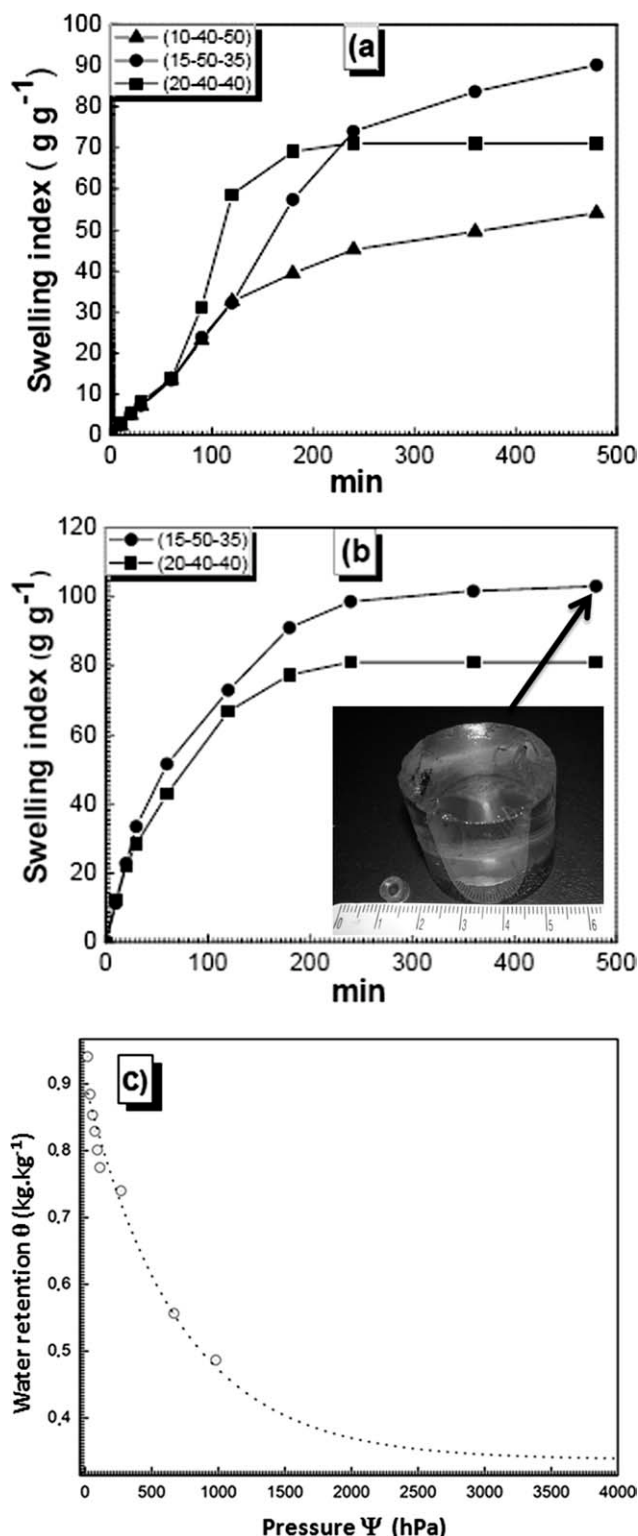


Figure 1 Swelling index curves *versus* time for the M-Pec-co-AAm-co-AAc hydrogels. 0.10 (a) and 0.05 g mL⁻¹(b) final polymer concentration, and (c) curve of water retention θ defining the water content as a function of the pressure Ψ (hPa, hectoPascals).

co-AAc hydrogel with 0.05 g mL⁻¹ final polymer concentration. The swelling indices for the (15-50-35)-0.05 and (20-40-40)-0.05 hydrogel were

103.06 and 81.08, respectively, after it being immersed in water for 480 min. A picture of (15-50-35)-0.05 hydrogel in dried state and swollen for 480 min is shown in inset. Comparing with the results shown in Figure 1(a), the swelling index increased by decreasing the final polymer concentration. The decrease in the final polymer concentration from 0.10 to 0.05 mg L⁻¹ decreases the density of the polymer network and improves the electrostatic effects. In this logic, the stronger electrostatic repulsion between Pec and AAc, the easier the diffusion of water and solutes into the hydrogel network due to formation of a porous structure. Table II shows the maximum swelling index to the M-Pec-co-AAm-co-AAc hydrogel swollen to equilibrium at 25°C. As it can be seen, the maximum swelling index were higher for the (15-50-35)-0.05 g mL⁻¹ hydrogel, confirming that the polymer network density has influenced significantly the swelling rate during the hydrogel expansion. Finally, all the hydrogels studied were considered as superabsorbent material which may be efficiently used as either soil conditioning or remover of heavy metals.

Horticultural plants can absorb water from soils due to a difference in pressure between the soil and the root that can occur in a range of 0 to 4000 hPa (not applicable to all plant species) in which there is no excessive use of energy.

Figure 1(c) shows a curve of water retention θ (kg kg⁻¹) defining the water content (kg water per kg hydrogel) as a function of the pressure Ψ (hPa) for the (15-50-35)-0.05 g mL⁻¹ hydrogel. The saturated moisture (θ_s) and residual moisture (θ_r) at 4000 hPa were 0.567 and 0.333 kg kg⁻¹, respectively. The ability of hydrogel help to conserve water residues in a pressure range in which a variety of horticultural plants can absorb water makes it an attractive for soil conditioning.

Water diffusion mechanism into M-Pec-co-AAm-co-AAc hydrogels

The swelling profile for the M-Pec-co-AAm-co-AAc hydrogel was studied by plotting the water rate curves into hydrogel (M_t/M_∞) versus

TABLE II
Maximum Swelling Index for the M-Pec-co-AAm-co-AAc Hydrogel Swollen to Equilibrium in Distilled Water for 24 h at 25°C

Hydrogel formulation (g mL ⁻¹)	Maximum swelling index
(10-40-50)-0.10	115.87 ± 5.67
(15-50-35)-0.10	130.11 ± 8.67
(20-40-40)-0.10	91.58 ± 3.67
(15-50-35)-0.05	643.67 ± 20.67
(20-40-40)-0.05	416.93 ± 15.67

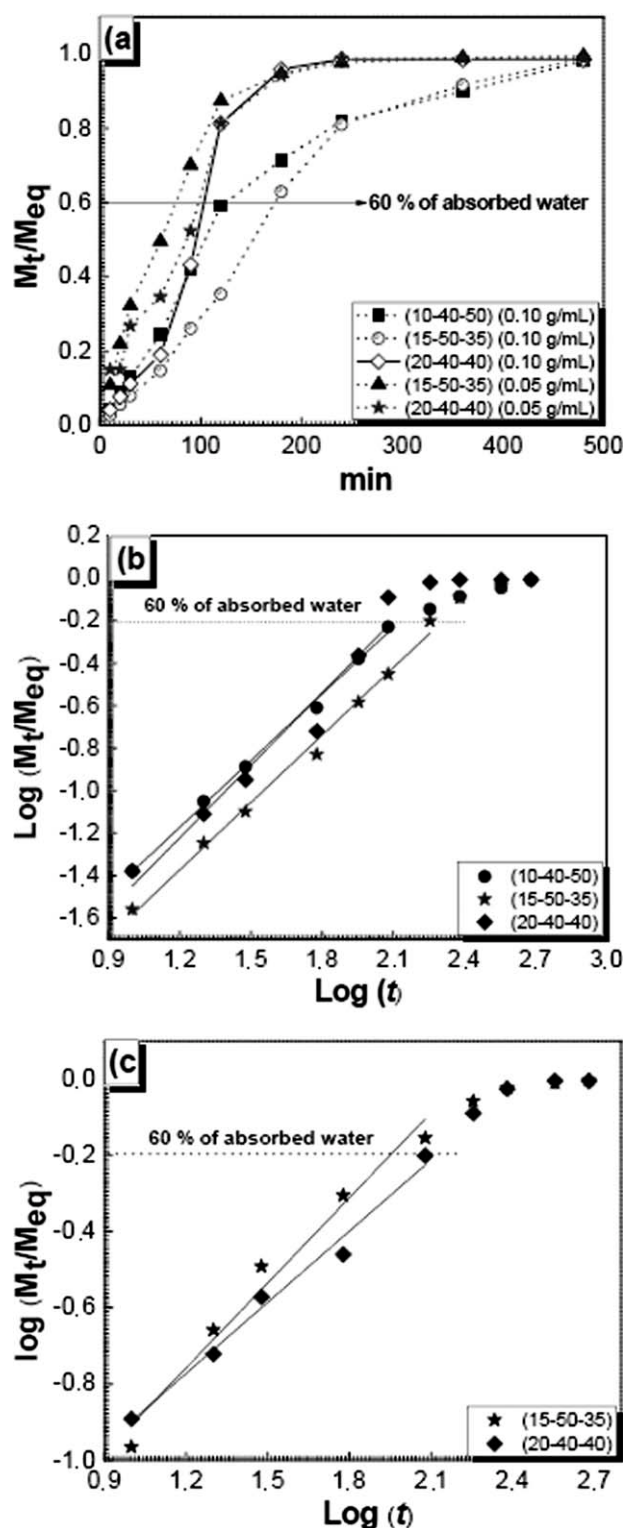


Figure 2 Diffused water rate into the M-Pec-co-AAm-co-AAc hydrogels at different formulations (a). Logarithm curves for the (10-40-50), (15-50-35) and (20-40-40) hydrogels with 0.1 g mL^{-1} final polymer concentration (b) and for the (15-50-35) and (20-40-40) hydrogels with 0.05 g mL^{-1} final polymer concentration (c).

time (t) as shown in Figure 2(a). The n values were obtained from the linear regression curves shown in Figure 2(b,c). The n values are dependents on the hydrogel geometric form that affects the water diffusion mechanism into hydrogel. In this work, the M-Pec-co-AAm-co-AAc hydrogels were synthesized in cylindrical forms. The n values for each released solute were characterized on basis of transport process by diffusion in swellable polymer networks. It is important to report that the n is a parameter depending on the geometrical shape of the hydrogel matrix, because of the progression in the swollen-dry boundary throughout the swelling process. In this contribution, cylinder-shaped hydrogels were used to study water transport mechanism. This implies that the values of the n parameter have the following conceptual meanings: (i) $n = 0.45$ for Fickian diffusion (Case I), (ii) $0.45 < n < 0.89$ for anomalous transport, contribution of Fickian diffusion and controlled relaxation, (iii) $n = 0.89$ for zero order (Case II), contribution of controlled relaxation of the polymer chains, and (iv) $n > 0.89$ for super Case II, contribution of the macromolecular relaxation of the polymer chains. Here, the water diffusion mechanism is specifically conducted by macromolecular relaxing. The n values described in Table III indicate the water absorption profile with variation of the polymer compositions in the hydrogel. The values of n ranged from 0.6 to 1.0 when the hydrogel possesses a 0.1 g mL^{-1} final polymer concentration, indicative of non-Fickian diffusion with a tendency to macromolecular relaxation. This result was attributed to the increase of the ionized groups (COO^-) of either Pec structure or acrylic acid. As described earlier, the electrostatic repulsion among the polymer segments induces the expansion of the three-dimensional hydrogel network. The values of n for the (15-50-35)-0.05 and (20-40-40)-0.05 M-Pec-co-AAm-co-AAc hydrogels were higher than 1, suggesting that the water absorption profile was exclusively driven by macromolecular relaxation mechanism.

TABLE III
Difusional Exponent (n) for the M-Pec-co-AAm-co-AAc Hydrogels with Different Amounts of M-Pec, AAm, and AAc at 25°C

Hydrogel formulation (g mL^{-1})	Difusional exponent (n)	Kinetic Adjust (R^2)
(10-40-50)-0.10	1.0106	0.9975
(15-50-35)-0.10	0.8161	0.9973
(20-40-40)-0.10	0.6800	0.9849
(15-50-35)-0.05	1.0692	0.9960
(20-40-40)-0.05	1.1382	0.9576

TABLE IV
Difusional Exponent (n) for the M-Pec-co-AAm-co-AAc Hydrogels Swollen to Equilibrium in 0.01, 0.03, and 0.06 mol L⁻¹ Saline Solutions at 25°C

Hydrogel Formulation (g mL ⁻¹)	Expoente difusional (n)								
	KCl (mol L ⁻¹)			CaCl (mol L ⁻¹)			NaCl (mol L ⁻¹)		
	0.01	0.03	0.06	0.01	0.03	0.06	0.01	0.03	0.06
(10-40-50)-0.10	0.915	0.766	0.786	0.584	0.521	0.408	0.621	0.661	0.651
(15-50-35)-0.10	0.842	0.833	0.692	0.620	0.676	0.581	1.018	0.898	0.842
(20-40-40)-0.10	0.760	0.764	0.665	0.658	0.496	0.452	0.944	0.867	0.787
(15-50-35)-0.05	0.762	0.677	0.631	0.596	0.550	0.438	0.452	0.843	0.676
(20-40-40)-0.05	0.866	0.822	0.775	0.721	0.594	0.426	0.823	0.724	0.663

Swelling kinetics for M-Pec-co-AAm-co-AAc hydrogels in saline solutions

The values of n for the hydrogels swollen in 0.01, 0.03, or 0.06 mol L⁻¹ saline solutions are described in Table IV. The values of n obtained after immersion of the hydrogel in both NaCl and KCl saline solutions were close to 1. This result indicates that the water diffusion into the hydrogel structure was driven by non-Fickian transport with a tendency to macromolecular relaxation mechanism. Additionally, the values of n in both NaCl and KCl saline solutions were equivalent to those in distilled water, thus suggesting that there was no water loss by the M-Pec-co-AAm-co-AAc superabsorbent hydrogel in the presence of the salts. A small water loss was only observed by using the calcium chloride salt (CaCl₂). In this case, the Ca²⁺ divalent ions may form complex with the carboxylate groups of the hydrogel by way of intermolecular ionic bonds that result in an increase in the crosslinking rate, and consequently, a decrease in the water uptake.

pH effects on the absorption studies of Pb²⁺ and Cu²⁺

To perform absorption tests of solutes by hydrogels, it is necessary to consider the properties of the hydrogel such as water uptake capacity, chemical structure, reagent concentrations, and crosslinking rate. In addition, the properties of solutes such as pH, initial concentration, temperature, and ionic strength, should be analyzed. After immersion of a hydrogel in aqueous solution, the water molecules diffuse firstly inwards the hydrogel due to hydrophilicity of the polymer chain. It follows that the COOH groups dissociate to form COO⁻ and expand the polymer networks. Afterwards, it generates a concentration gradient on the hydrogel-water interface which promotes the diffusion of metal ions into the hydrogel polymer network.¹⁹ By this sense, the metal ions can be removed from aqueous solutions by variation of the either chemical structure nature of the hydrogel or ionic size of the metallic ions.¹⁰

Figure 3 shows the absorption capacity of Pb²⁺ (a) and Cu²⁺ (b) from aqueous solutions (in mg metal per g hydrogel) versus pH by Ma-Pec-co-AAm-co-AAc hydrogel with formulations of (10-40-50), (15-50-35) and (20-40-40). The ionic characteristic of the hydrogel was strongly affected by variation of the pH and ionic strength. There was a significant increase of the absorption capacity of Pb²⁺ and Cu²⁺

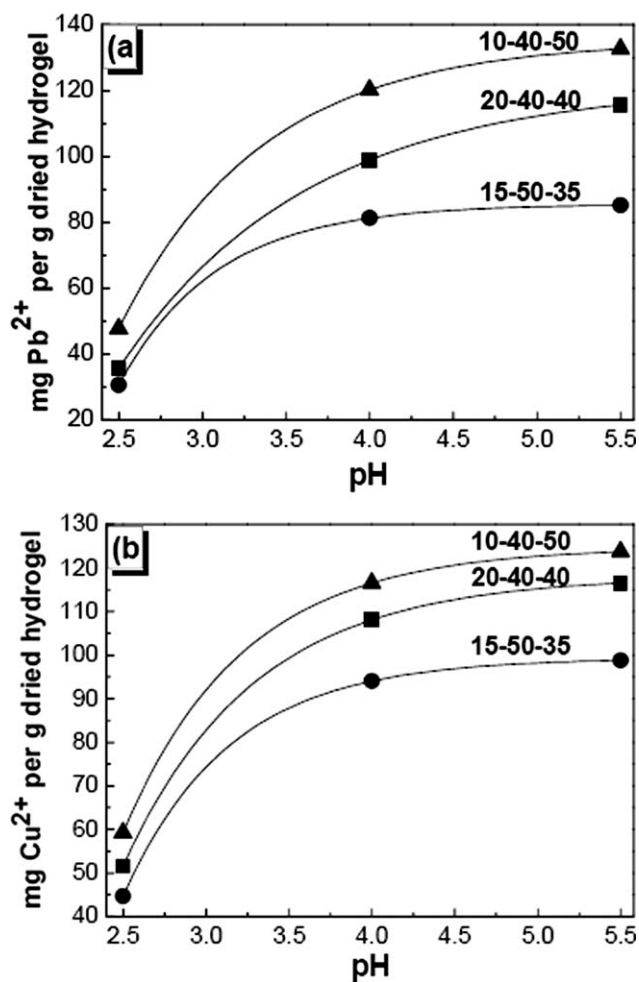


Figure 3 Absorption capacity of Pb²⁺(a) and Cu²⁺ (b) versus pH into the (10-40-50), (15-50-35) and (20-40-40) M-Pec-co-AAm-co-AAc hydrogels. The final polymer concentration was 0.10 g mL⁻¹.

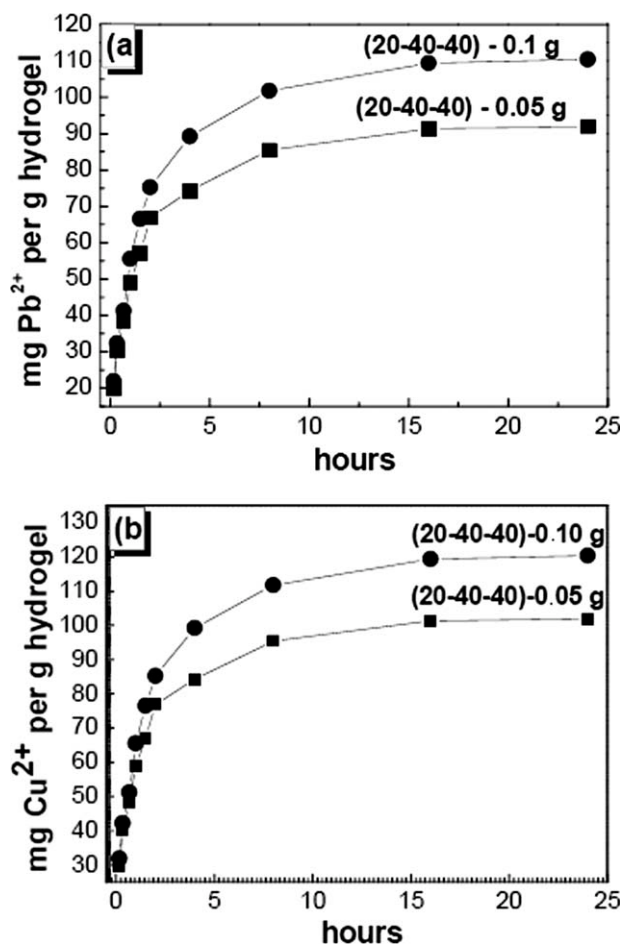


Figure 4 Absorption capacity of Pb^{2+} (a) and Cu^{2+} (b) versus the contact time into the $(20-40-40)-0.10 \text{ g mL}^{-1}$ and $(20-40-40)-0.05 \text{ g mL}^{-1}$ M-Pec-co-AAm-co-AAc hydrogels.

in the $(10-40-50)$ hydrogel with pH increasing from 2.5 to 5.5, attributed to occurrence of electrostatic interactions between the hydrogel groups and the metal ions.

Absorption kinetics of Pb^{2+} and Cu^{2+}

The absorption capacity curves for Pb^{2+} and Cu^{2+} in $(20-40-40)-0.10 \text{ g mL}^{-1}$ hydrogel (a) and $(20-40-40)-0.05 \text{ g mL}^{-1}$ hydrogel (b) are shown in Figure 4. The higher the polymer density of the hydrogel, $[(20-40-40)-0.10 \text{ g mL}^{-1}$ hydrogel], the rather higher were the absorption capacities for the Pb^{2+} and Cu^{2+} ions. It was attributed to the increase of the amount of ionized groups issued from the AAc structure at the hydrogel polymer network. Therein, the absorption capacities for the $(10-40-50)-0.10 \text{ g mL}^{-1}$ M-Pec-co-AAm-co-AAc hydrogel were 120 mg Cu^{2+} and 130 mg Pb^{2+} per g hydrogel, both at pH 5.5. In conclusion, the higher the amount of AAc groups at the hydrogel network, the higher was their swelling capacity. As a result, the absorption capacity efficiencies for the

Pb^{2+} and Cu^{2+} ions were greater in AAc-richer hydrogels. The M-Pec-co-AAm-co-AAc hydrogels could be applied on wastewater and water treatment aiming at the removal of heavy metals.

Release of phosphate, potassium, and urea

Release systems by hydrogels as a polymer matrix have been widely applied on soil conditioning. The three-dimensional hydrophilic structure of these materials allows solutes diffusion through their swollen polymer network, enabling them to be an effective system to carry agricultural nutrients throughout environmental systems. The agricultural nutrients have been very important for the enrichment of either deserted or poorly nutritious soils. The release profiles of agricultural nutrients from hydrogels are generally well described by several mathematical models. Such systems are dependent on parameters such as the polymer compositions, crosslinking, and swelling degree of the hydrogels used as polymer matrix. Also, the diffusional properties of the solutes employed should be considered.¹⁹ As previously described, the release of agricultural nutrients occurs mainly by diffusional process. However, the chemical-physical interactions between the hydrogels and solutes can affect the final results. By assuming that the release results are influenced by partition effects, the mathematical models are view as semi-empiric models which follow a release kinetic for the first 60% of the released solute.²³ By this logic, the profiles of release for the agricultural nutrients from the M-Pec-co-AAm-co-AAc hydrogels can be efficiently determined only by the first 60% of the released solute, by applying eq. (2). The quantitative values of the concentration of phosphate, potassium and urea were determined by employing analytical curves.

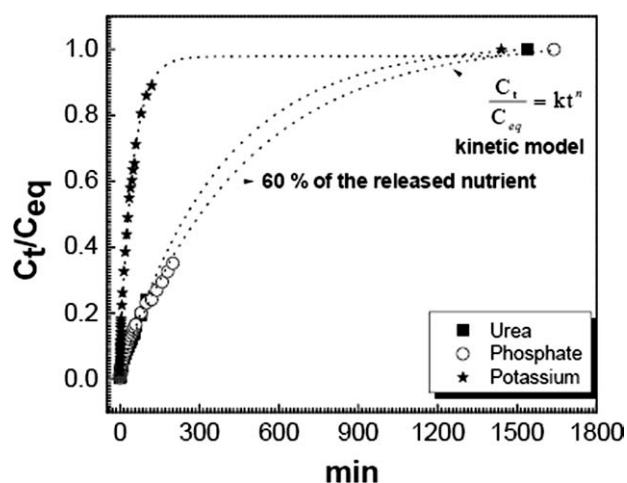


Figure 5 Fractional release curves of urea, phosphate and potassium from the $(15-50-35)$ hydrogel at 25°C .

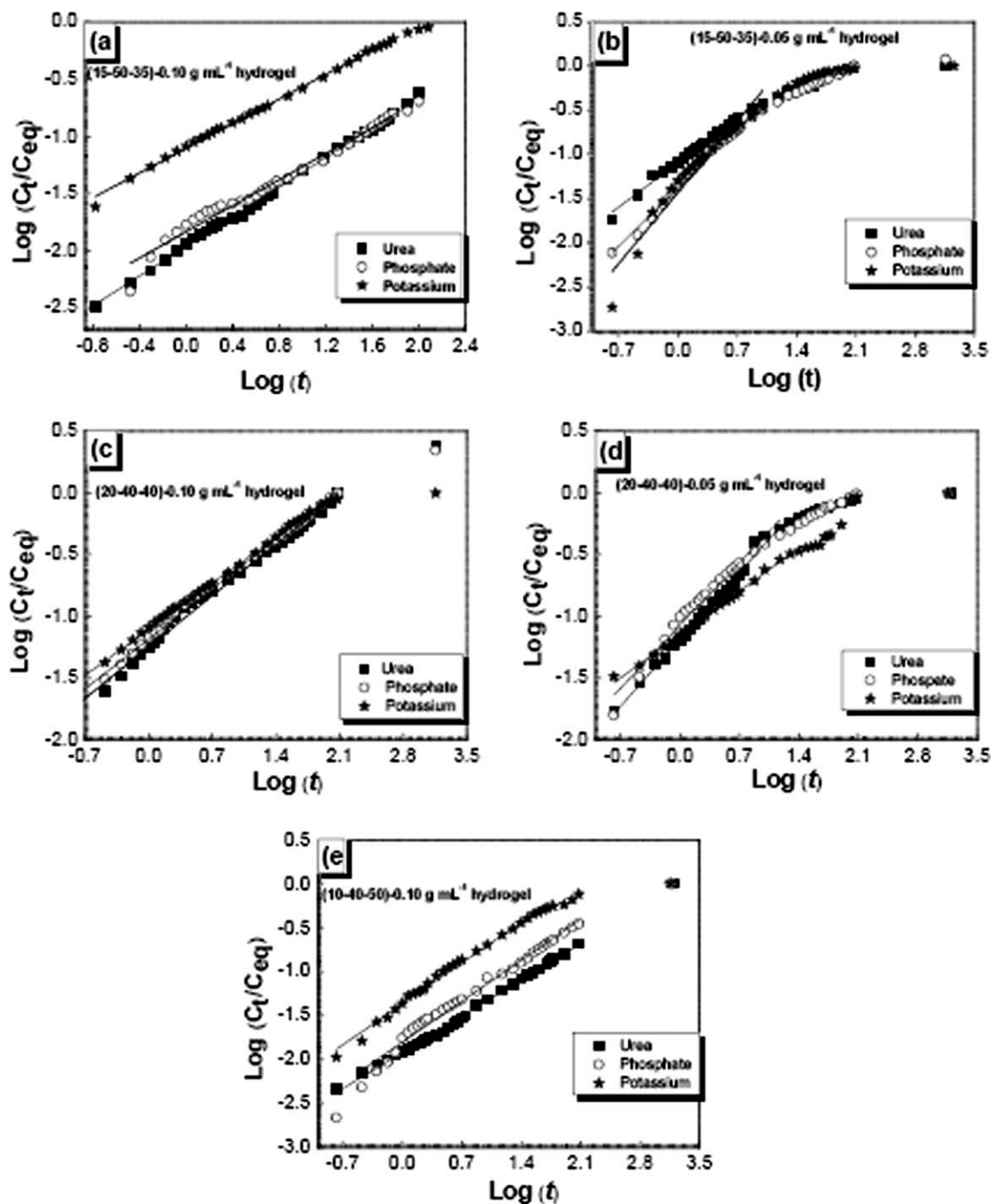


Figure 6 Logarithm curves for the fractional release of urea, phosphate and potassium from the (15–50–35)–0.10 g mL⁻¹ (a), (15–50–35)–0.05 g mL⁻¹ (b), (20–40–40)–0.1 g mL⁻¹ (c), (20–40–40)–0.05 g mL⁻¹ (d), and (10–40–50)–0.1 g mL⁻¹ (e) hydrogels.

Figure 5 shows the fractional release curves for the phosphate, potassium, and urea from the (10–40–50)–0.10 g mL⁻¹ Ma–Pec–co–AAm–co–AAc hydrogel at 25°C. The spotted lines describe the kinetic model plotted according to eq. (2) and the circle points describe the experimental release data. The n values were obtained from the logarithm curves shown in Figures 6(a–e). The values of n

ranged from 0.5 to 0.6 for all the solutes studied, as shown in Table V. The release of phosphate, potassium and urea from the hydrogels was driven by anomalous transport with a tendency to macromolecular relaxation mechanism. This result is in accordance to the kinetic results for the water diffusion. Moreover, the release of phosphate and potassium was slightly improved by increasing the

TABLE V
Diffusional Exponent (n) for Release of Urea, Phosphate, and Potassium from M-Pec-co-AAm-co-AAc Hydrogels at Temperature 25°C

Hydrogel formulation (g mL ⁻¹)	Urea		Potassium		Phosphate	
	n	R^2	n	R^2	n	R^2
(10-40-50)-0.10	0.585	0.997	0.663	0.992	0.664	0.983
(15-50-35)-0.10	0.647	0.998	0.539	0.996	0.571	0.975
(20-40-40)-0.10	0.593	0.984	0.552	0.996	0.577	0.992
(15-50-35)-0.05	0.717	0.990	1.150	0.949	0.951	0.990
(20-40-40)-0.05	0.773	0.991	0.565	0.993	0.723	0.968

AAc groups at the hydrogel, for example, the (10-40-50)-0.10 g mL⁻¹ hydrogel. On the other hand, by decreasing the amount of AAc at the hydrogel, a light increase in the release of urea was observed. The M-Pec-co-AAm-co-AAc hydrogels can be applied on either removal of heavy metals from water and wastewater or soil conditioning, particularly for the release of agricultural nutrients and water. They also present the opportunity to be simultaneously employed as remover of toxic materials and in release of agricultural nutrients and water.

CONCLUSIONS

The hydrogel help to conserve water in a pressure range in which a variety of horticultural plants can absorb it. In metal removing by hydrogel, it was found that the M-Pec-co-AAm-co-AAc hydrogels had an excellent performance for removal of Cu²⁺ and Pb²⁺ from the solution. Such attribute makes these hydrogels suitable for uses in treatments of either industrial wastewater or contaminated rivers. The release of urea, phosphate, and potassium from the hydrogels was controlled by anomalous mechanism with a tendency to macromolecular relaxation mechanism, thus corroborating the data of water penetration kinetic. There was a discrete increase of the release of phosphate and potassium from AAc-loader hydrogel. On the other hand, there was an increase of the release of urea from hydrogel with lower AAc content. M-Pec-co-AAm-co-AAc hydrogels are said to be a versatile system for applications in which the efficient use of water is required and release of fertilizers for agriculture.

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