

Biodegradable Hydrogel as Delivery Vehicle for the Controlled Release of Pesticide

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1. Introduction

1.1 Agrochemical controlled release goals

Controlled release is a chemical activation method, which is provided to specific plant species at preset rates and times. Different polymers are largely used to control the delivery rates, mobilities, and the chemicals period of effectiveness. The main benefit of the controlled release method is that if fewer chemicals are used for the protected plants over the predetermined period, then there is a lesser effect on the other plant species, while reducing leaching, volatilization, and degradation. The macromolecular nature of polymers is the key to chemical loss reduction throughout the production. Controlled release polymer systems can be divided into two categories. In the first, the active agent is dissolved, dispersed, or encapsulated within the polymeric matrix or coating. Its release takes place through diffusion or after biological or chemical breakdown of the polymer. In the second category, the active agent either constitutes a part of the macromolecular backbone or is attached to it. Here its release is the result of biological or chemical cleavage of the bond between the polymer and the bioactive agent [Mitrus et al., 2009].

The main problem with conventional agrochemical applications is using greater amounts of agrochemicals, over a long period of time, than what is actually needed, possibly leading to crop damage and environmental contamination [Bajpai & Giri, 2003]. Controlled release polymer matrix systems offer numerous 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 [Wang et al., 2007]. The objective 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 losses due to run off.

Controlled release systems for pesticides involve advanced pesticide delivery technologies, highlighting new means to reduce toxicity, increase efficacy, lessen the environmental

impact from pesticides and pesticide applications, reduce potential transportation hazards, as well as facilitating new product development [Abd El-Rehim et al., 2005].

1.2 Use of hydrogels in controlled release

Over the past decades, hydrogel polymers have attracted a great deal of attention as potential delivery vehicles for controlled release applications. For instance, Kenawy, 1998 obtained a series of polyacrylamide gel derivatives by transamidation of crosslinked polyacrylamide polymer with various diamine of different structures such as ethylenediamine, hydrazine hydrate, etc. The amount of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide released from acrylamide formulations was monitored by UV-spectrophotometric analyses at 25 °C in water solution buffered at pH 4, 7 and 9. Results showed that the release rate of 2,4-D is dependent of pH of the medium: it was slower in acidic medium than in neutral or alkaline medium. The best release rate was found for crosslinked polyacrylamide hydrogels amidated with bis-(3-aminopropyl) poly (tetrahydrofuran) 1100 (BAPPTHF-1100), close to 600 mg.

Kulkarny et al., 2000 investigated the encapsulation and release of a natural liquid pesticide 'neem (*Azadirachta Indica A. Juss.*) seed oil' designated as NSO, using sodium alginate (Na-Alg) as a vehicle carrier after crosslinking with glutaraldehyde (GA). The higher NSO release rates were observed for higher NSO loading. An increase in the degree of crosslinking of the precipitated Na-Alg polymer resulted in a significant decrease of NSO release from the beads. The empirical parameter n values calculated for the release of NSO from the beads were between 0.70 to 0.94, indicating that the diffusion deviates slightly from Fickian transport and the kinetic constant k values are considerably small, indicating the absence of any interactions between the polymer and the active ingredient. The k values further show a decrease with the increase in crosslinking and also an increase with the increase in NSO loading.

Işıklan, 2004 investigated the effects of the bead preparation conditions, such as percent of carboxymethylcellulose (NaCMC), insecticide carbaryl:NaCMC ratio, crosslinker concentration and kaolin clay addition as filler on carbaryl release. The copper-carboxymethylcellulose (CuCMC) beads were prepared by the ionotropic crosslinking of NaCMC with copper ions. The beads were characterized by carbaryl encapsulation efficiency, bead diameter, scanning electron microscopy, equilibrium swelling degree and carbaryl release kinetics. The beads diameter decreased from 2.08 to 1.74 mm when car:NaCMC ratio was increased from 1:1 to 1:8. The authors attributed this effect to the hydrodynamic viscosity concept, i.e. as the car:NaCMC ratio increases the carbaryl content in the bead decreases and the interfacial viscosity of the polymer droplet in the crosslinker solution also decreases. The higher carbaryl release rates were observed for lower car:NaCMC ratio, higher NaCMC percent and higher kaolin addition. Also, the increase in CuCl₂ concentration resulted in a significant decrease of carbaryl release from the beads.

Singh et al., 2009 studied the release of thiram, a dithiocarbamate fungicide, from starch-alginate-clays beads with different compositions by varying the amount of kaolin and bentonite clays. The beads with diameters between 1.07 and 1.34 mm had a high loading capacity of thiram fungicide, up to 97.49 ± 1.27 %. The maximum release of thiram was of about 10 mg after 300 h. The decrease to 6.9 mg and 6.3 mg, in the presence of kaolin and bentonite due to differences, is the ability of montmorillonite (the clay mineral in bentonites) for intercalation, whereas kaolin does not intercalate thiram. Moreover, the presence of kaolin and bentonite in starch-alginate bead formulation retarded the release of the

fungicide thiram; with the release slower for bentonite-based formulations than for formulations containing kaolin.

Roy et al., 2009 prepared biopolymer microspheres of sodium alginate and starch using CaCl_2 as a crosslinker, which are promising to function as carriers for the controlled release of the pesticide chlorpyrifos. The microspheres show greater swelling with increasing wt% of alginate and decreasing wt% of starch, hence exhibiting an optimum water uptake at a definite composition of beads (57.3 wt% alginate and 42.7 wt% starch). The biopolymeric beads show that their swelling ratio significantly decreases with increasing crosslinking. The polymer beads show great potential for the release of chlorpyrifos, while the fractional release increases with increasing wt% of alginate and decreases with increasing content of starch. However, an optimum fractional release for a bead composition is obtained with more alginate and less starch. The cumulative release occurred in a controlled and sustained manner up to 14 days.

1.3 Hydrogels properties

Hydrogels are three-dimensional hydrophilic macromolecular networks that can absorb water many times their dry mass and significantly expand in their volume [Aouada et al., 2006; Moura et al., 2006; Aouada et al., 2009a]. The ability of hydrogels to undergo substantial swelling and collapsing in response to the presence and absence of water allows for their potential application in different areas, including the biomedical [Jayakumar et al., 2010; Melchels et al., 2010], cosmetic [Angus et al., 2006; Lee et al., 2009] and agrochemical fields [Pourjavadi et al., 2009]. The structural integrity of hydrogels depends on crosslinks established between the polymer chains through covalent bonds, hydrogen bonding, van der Waals interactions, or physical entanglements [Park et al., 1993]. The stability of the gel structure is due to a delicate balance between the hydrogen bonds and the degree of shrinking, with the swelling highly dependent on factors such as temperature, pH, pressure and electric fields.

Hydrogels are formed by physical or chemical crosslinks of homopolymers or copolymers, which are appropriately used to give the three-dimensional structures their specific mechanical and chemical characteristics. Hydrogels can be classified into different groups based on their [Deligkaris et al., 2010]:

- physical structure: amorphous, semi crystalline, hydrogen bonded or supramolecular;
- electric charge: ionic (charged) or neutral;
- crosslink: physically or chemically crosslinked;
- responses to external effects: stimulus-sensitive and -insensitive ones;
- origin: synthetic and natural.

2. Characterization of hydrogels

To characterize the hydrogels, the most common techniques used are water uptake [Lohakan et al., 2010; Wang et al., 2010]; mechanical properties [Baker et al., 2010; Jiang et al., 2010; Xu et al., 2010]; scanning electron microscopy (SEM) [Moura et al., 2009; Ferrer et al., 2010; Gao et al., 2010; Li et al., 2010; Zhao et al., 2010]; Fourier transform infrared (FTIR) spectroscopy [Kim et al., 2010; Wang & Wang, 2010]; nuclear magnetic resonance (NMR) [Yin et al., 2010]; differential scanning calorimetry (DSC) [Castelli et al., 2008; Rao et al., 2010]; thermogravimetric analysis (TGA) [Rodkate et al., 2010]; structural properties [Panic et al., 2010] through average molar mass between crosslinks (M_c), crosslink density (q), and

number of elastically effective chains, completely included in a perfect network, per unit volume (V_e); and controlled release of drugs [Koutroumanis et al., 2010; Liu & Lin, 2010; Sajeesh et al., 2010; Tanigo et al., 2010]; and agrochemicals [Saraydin et al., 2000; Bajpai & Giri, 2003; Bajpai et al., 2006; Wang et al., 2007; Pourjavadi et al., 2009].

3. Preparation of hydrogels and their application in pesticide controlled release

Our research group has recently focused on the preparation and characterization of polyacrylamide (PAAm) and methylcellulose (MC) biodegradable hydrogels, as potential delivery vehicles for the controlled release of paraquat pesticide, since they play an essential role in the use of hydrogels in controlled release technology.

3.1 Mechanism to form and prepare the PAAm and MC hydrogels

In a simplified preparation process of acrylamide hydrogel by the free radical copolymerization of acrylamide (AAm) and a divinyl crosslinker, e.g. N,N'-methylene-bis-acrylamide (MBAAm), linear polymers are first formed in the solution during the fast propagation step, and later crosslinked with other molecules through their pendent double bonds and additional monomer units [Stepto, 1998]. According to Karadag et al., 2005 the polymerization of vinyl monomers, such as AAm and MBAAm in the presence of ammonium persulfate and N,N,N',N'- tetramethylethylene-diamine (TEMED), is first initiated by the reaction between ammonium persulfate and TEMED, in which the TEMED molecule is left with an unpaired valance electron. The activated TEMED molecule can combine with an AAm and/or crosslinker molecule, in which the unpaired electron is transferred to the monomeric units so that they then become reactive. Thus, another monomer or co-monomer can be attached and activated in the same way. The poly(AAm) or other copolymer hydrogel can continue growing indefinitely, with the active centre continually shifted to the free end of the chain.

The synthesis of PAAm-MC hydrogels was reported in the literature [Aouada et al., 2009a; Aouada et al., 2010]. AAm (3.6 - 21.7 in w:v%), MC (0 - 1.0 in w:v%), MBAAm, and TEMED were placed in a bottle and homogenized by stirred mixing. TEMED concentration was fixed at $3.21 \mu\text{mol mL}^{-1}$. After the mixture was prepared, it was deoxygenated by N_2 bubbling for 25 min. Then, aqueous sodium persulfate (final conc. of $3.38 \mu\text{mol mL}^{-1}$), also deoxygenated, was added to initiate the polymerization reaction. The resulting solution was quickly placed between two glass plates separated by a rubber gasket 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 1), were removed from the plates. These membranes (final thickness $\approx 9 - 10 \text{ mm}$) were then freed from the unreacted chemicals by dialysis with distilled/deionized water for 10 days. The polymeric network PAAm-MC was used to study the hydrophilic properties of the hydrogels and pesticide paraquat sorption from the aqueous solution. Polymeric networks were made by chemically induced polymerization through free radical mechanism, in which SP radical species generates the reactive sites on the MC, AAm and MBAAm. Due to the polyfunctionality of the crosslinker MBAAm, it has four reactive sites which can be linked to the radical on the methylcellulose and to the poly(acrylamide). Scheme 2 presents the formation of crosslinked network structures based on poly(acrylamide) and methylcellulose.

3.2 Some physical-chemistry properties of PAAm-MC hydrogels

3.2.1 Hydrophilic properties

The hydrophilic properties of PAAm-MC hydrogels were investigated by measuring their water uptake (WU). For the water uptake studies, the swollen hydrogels in membrane form were cut into cylindrical shapes of 13 mm and the average of dry hydrogels used was of approximately 150 mg. WU values were obtained by the mass ratio of the swollen hydrogel to dried hydrogel. Measurements were performed in replicate at 25.0 °C to check reproducibility and the error bars indicate the standard deviation ($n = 3$).

Figure 1 shows the dependences of WU as a function of the immersion time of the hydrogels swelled in distilled water.

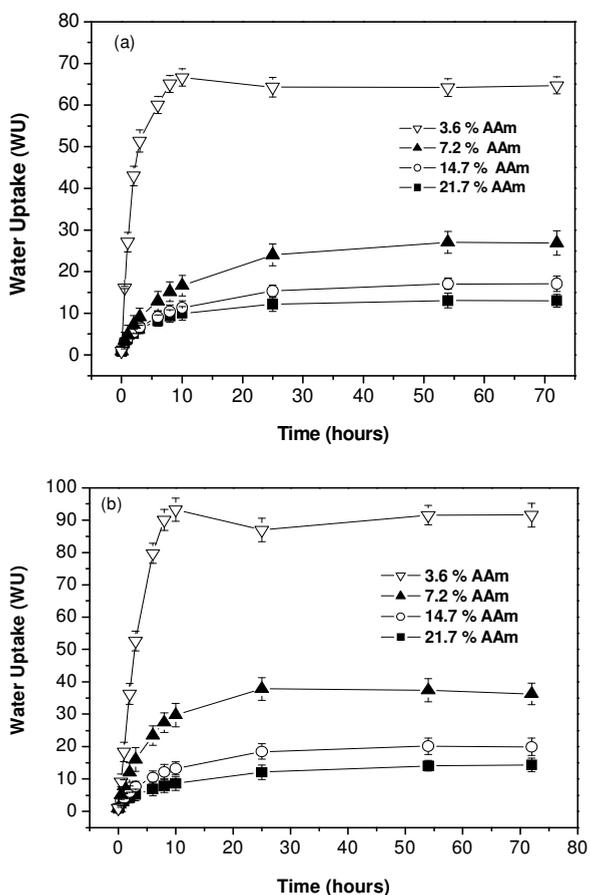


Fig. 1. Dependence of water uptake as a function of time for: (a) PAAm-MC0.5 and (b) PAAm-MC1.0, in distilled water (pH = 6.7), at 25.0 °C. Different concentrations of AAm were tested as indicated. Error bars represent standard deviations for the three experiments.

Changes on equilibrium in WU values as a function of the AAm concentration in the feed solution are shown in Figure 2. It can be pointed out that the value of WU decreases

abruptly when the concentration of AAm in the gel-forming solution increases. This reduction is related to the increase of network rigidity, where the flexibility of a hydrogel network is directly related with the amount of total water absorbed by the hydrogel [Aouada et al., 2006]. The highest WU value obtained for 3.6 % AAm and 1.0 % MC, was of around 90 g/g. Also, the WU values abruptly increased when the concentration of MC in feed solution was increased. This trend is attributed to the increase in the hydrogel hydrophilicity (thus the increase in water absorption capacity) due to the incorporation of hydroxyl groups from MC segments. This tendency was also observed in the PAAm/poly(γ -glutamic acid) hydrogels studied by Rodríguez et al., 2006.

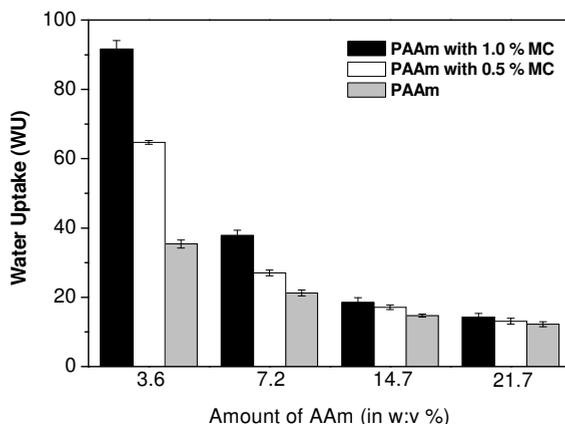


Fig. 2. Dependence of equilibrium water uptake as a function of acrylamide for PAAm, PAAm-MC0.5 and PAAmMC1.0 hydrogels, in distilled water (pH = 6.7), at 25.0 °C. Error bars represent standard deviations for the three experiments.

3.2.2 Mechanical properties

Uniaxial compression measurements were performed on equilibrium swollen hydrogels after their preparation. Compression tests were performed using a universal testing machine (Instron, Model 5500R, Canton, MA). Hydrogel compression was measured using a 1.27 cm diameter cylindrical probe. The probe was attached to the upper jaw of the Instron machine. The crosshead speed was of 12.0 mm min⁻¹ with a 100 N load.

The measurements were conducted up to 30% compression of hydrogel. In this case, the maximum load (σ_{\max}) of hydrogels was recorded. The modulus of elasticity (E) was calculated by Eq. (1), where F is the force and A is the cross-sectional area of the strained specimen. The relative strain (λ) was calculated from Eq. (2), where ΔL is the change in thickness of the compressed hydrogel and L_0 is the initial thickness. Six tests were run for each gel.

$$\sigma = \frac{F}{A} = E(\lambda - \lambda^{-2}) \quad (1)$$

$$\lambda = \frac{\Delta L}{L_0} \quad (2)$$

The effective (or apparent) cross-linking density, ν_e , was obtained from the slope of linear dependence of σ versus $(\lambda - \lambda^{-2})$, Eq. (3), where R is the universal gas constant, T is the temperature in absolute scale, $\phi_{g,0}$ and ϕ_g are the polymer volume fractions of the hydrogel in the relaxed state and in the swollen state, respectively.

$$\sigma = RT \left(\frac{\phi_{g,0}}{\phi_g} \right)^{2/3} \phi_g \nu_e (\lambda - \lambda^{-2}) \quad (3)$$

The length of the effective chains between crosslinking points (N) is related to the effective cross-linking density ν_e by Eq. (4):

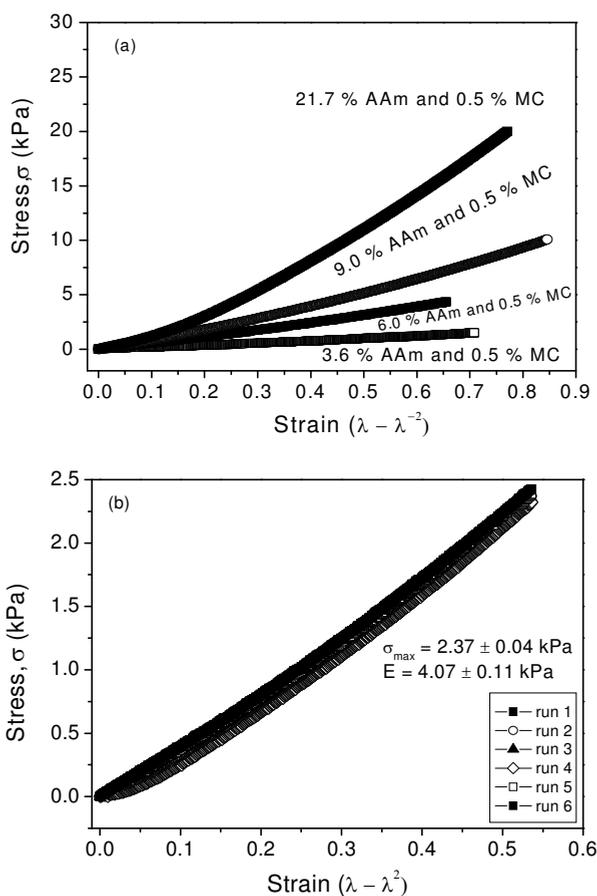


Fig. 3. Measured force and stress as a function of Strain $(\lambda - \lambda^{-2})$ at 25 °C for hydrogels synthesized with (a) $[MC] = 0.5$ in w:v%, $[MBAAM] = 8.6 \mu\text{mol mL}^{-1}$ and different AAm concentrations; (b) $[AAm] = 6.0$ in w:v%, $[MBAAM] = 10.0 \mu\text{mol mL}^{-1}$, $[MC] = 0.75$ in w:v% [Aouada et al., 2009b].

$$N = (\nu_e V_l)^{-1} \quad (4)$$

where V_l is the molar volume of the segment, which is taken as the molar volume of water ($18 \text{ cm}^3 \text{ mol}^{-1}$).

To evaluate the mechanical properties of the PAAm and PAAm-MC hydrogel, the maximum load (σ_{\max}) and modulus of elasticity (E) of the hydrogels were measured. Representative stress-strain curves for the hydrogels tested with uniaxial compression are shown in Fig. 3, where the linearity between force and strain can be observed. The reproducibility of the stress-strain experiments is shown in Fig. 3b.

The linear correlation indicates that elastic deformation occurred, i.e. the strain is recoverable after removing the applied stress. In the most elementary form, recoverable strain means that if the hydrogel is under an applied load, the polymer chains are rearranged to accommodate the deformation. At the same time, retractive elastic force develops in the polymer networks because of their tendency to return to their original formation [Buchholz & Graham, 1997].

The dependence of maximum load as a function of acrylamide concentration for hydrogels with different methylcellulose concentrations is shown in Fig. 4.

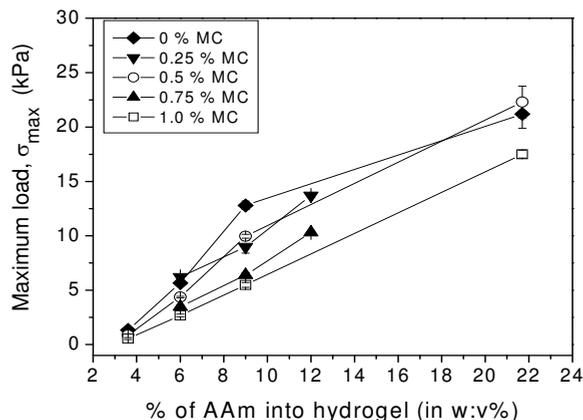


Fig. 4. Measured force and stress as a function of Strain ($\lambda - \lambda^{-2}$) at 25°C for hydrogels synthesized with (a) $[\text{MC}] = 0.5$ in w:v%, $[\text{MBAAm}] = 8.6 \mu\text{mol mL}^{-1}$ and different AAm concentrations; (b) $[\text{AAm}] = 6.0$ in w:v%, $[\text{MBAAm}] = 10.0 \mu\text{mol mL}^{-1}$, $[\text{MC}] = 0.75$ in w:v% [Aouada et al., 2009b].

The increase in mechanical property values was observed when the amount of acrylamide in the feed solution was increased. These results corroborate with the swelling degree results (see Table 1), where increasing AAm concentration and consequently, the rigidity of the networks, results in decreasing water-uptake. Maximum load and modulus of elasticity properties decrease with increasing MC concentration. The maximum load of the (3.6-8.6-MC) hydrogels, where MC is the methylcellulose concentration, were 1.35 ± 0.14 , 0.89 ± 0.05 and 0.55 ± 0.09 kPa for $M = 0, 0.5$ and 1.0 (in w:v%), respectively. For the same hydrogel, the modulus of elasticity values were 1.85 ± 0.08 , 1.43 ± 0.06 and 1.06 ± 0.15 kPa. Such a decrease is attributed to the increase of network hydrophilicity from an increase of hydroxyl groups entrapped in the PAAm network. Additionally, when the MC concentration was increased from 0 to 1.0 (in

w:v%), the decrease in the mechanical property values was more pronounced in hydrogels with low AAm concentration, demonstrating that the water-uptake (from interactions with hydrophilic groups present in MC chains) depends on PAAm flexibility.

Hydrogels*	SD (g/g)	σ_{\max} (kPa)	E (kPa)	ν_e ** (10^{-4} mol cm $^{-3}$)	N **
(3.6-8.6-0)	35.4 ± 4.3	1.35 ± 0.14	1.85 ± 0.08	4.13	134.46
(3.6-8.6-0.5)	64.0 ± 2.3	0.89 ± 0.05	1.43 ± 0.06	3.89	142.79
(3.6-8.6-1.0)	92.0 ± 3.1	0.55 ± 0.09	1.06 ± 0.15	3.25	170.68
(6.0-8.6-0)	25.7 ± 0.7	5.65 ± 0.16	5.44 ± 0.19	10.92	50.88
(6.0-8.6-0.25)	30.3 ± 1.9	6.23 ± 0.11	6.12 ± 0.22	12.98	42.81
(6.0-8.6-0.5)	42.0 ± 3.7	4.37 ± 0.08	5.82 ± 0.04	13.76	40.37
(6.0-8.6-0.75)	85.0 ± 2.7	3.74 ± 0.13	4.79 ± 0.11	14.33	38.78
(6.0-8.6-1.0)	98.1 ± 2.4	2.68 ± 0.12	3.61 ± 0.14	11.33	49.06
(6.0-4.3-0.75)	211.2 ± 10.2	0.79 ± 0.03	1.48 ± 0.03	6.00	92.67
(6.0-6.4-0.75)	109.9 ± 4.5	1.45 ± 0.05	2.54 ± 0.05	8.28	67.13
(6.0-10.0-0.75)	104.1 ± 8.6	2.37 ± 0.04	4.07 ± 0.11	13.02	42.66
(6.0-12.8-0.75)	105.4 ± 6.8	2.70 ± 0.09	3.64 ± 0.12	11.70	47.50
(6.0-17.1-0.75)	98.1 ± 6.2	2.98 ± 0.09	3.85 ± 0.19	12.08	46.00
(9.0-8.6-0)	18.8 ± 0.5	12.8 ± 0.39	13.48 ± 0.32	24.38	22.79
(9.0-8.6-0.25)	26.9 ± 0.5	8.99 ± 0.59	11.24 ± 0.52	22.91	24.25
(9.0-8.6-0.5)	29.7 ± 1.8	9.96 ± 0.18	10.16 ± 0.38	21.40	25.96
(9.0-8.6-0.75)	49.5 ± 4.5	6.39 ± 0.22	7.89 ± 0.33	19.71	28.19
(9.0-8.6-1.0)	57.8 ± 2.4	5.49 ± 0.22	7.43 ± 0.32	19.54	28.43
(12.0-8.6-0.25)	21.0 ± 0.5	13.71 ± 0.17	16.15 ± 0.20	30.31	18.33
(12.0-8.6-0.75)	33.7 ± 0.9	10.32 ± 0.07	14.02 ± 0.16	30.80	18.03
(21.7-8.6-0)	12.2 ± 0.2	21.25 ± 1.32	27.50 ± 1.11	43.06	12.90
(21.7-8.6-0.5)	13.0 ± 0.1	22.34 ± 1.46	24.60 ± 1.00	39.35	14.12
(21.7-8.6-1.0)	14.0 ± 0.2	17.50 ± 0.36	20.53 ± 1.05	36.26	15.32

* the notation (AAm-MBAAm-MC) will be used to characterize the composition of hydrogels.

** calculated based on the SD and E average values.

Table 1. AAm, MBAAm, and MC concentrations in feed solutions used in hydrogel synthesis and numerical values of mechanical properties [Aouada et al., 2009b].

The properties σ_{\max} and E can be correlated to the effective crosslinking density (ν_e) and length of the effective chains between crosslinking points (N), for which it was observed in Table 1 that ν_e values increases and N decreases when the σ_{\max} and E increase. The highest ν_e values were found for hydrogels synthesized with (21.7-8.6-MC). Consistently, these hydrogels presented lower N values, whereas higher AAm and MBAAm contents decreased the mobility of polymer chains within the gel, and thereby a higher loading was required for

compressing the hydrogel. Two different behaviours were observed in the variation of modulus of elasticity as a function on MBAAm crosslinker concentration. Firstly, modulus of elasticity increased with increasing crosslinker density from 4.3 to 8.6 $\mu\text{mol mL}^{-1}$. When the crosslinker density is increased, the water-absorption capacity of the hydrogels decreases significantly. Secondly, at MBAAm concentrations higher than 8.6 $\mu\text{mol mL}^{-1}$, a decrease in modulus of elasticity was observed. In this condition, additional polymeric chains, essentially constituted of MBAAm crosslinking, can be formed and entrapped in the hydrogel network. Due to high hydrophilicity, MBAAm chains have lower mechanical properties when compared with PAAm and PAAm-MC.

3.2.3 Morphological properties

Morphological properties of equilibrium swollen PAAm-MC hydrogels were investigated using a Hitachi scanning electron microscope (model S 4700) with 200 X magnification and an accelerating voltage of 15 keV. The samples were removed from the water and quickly frozen by immersion in liquid nitrogen. The hydrogels were freeze-dried at 80 °C to maintain their porous structure without any collapse. After 48 h lyophilization, the dried sample was deposited onto an aluminium stub and sputter-coated with gold for 60 s to enhance conductivity.

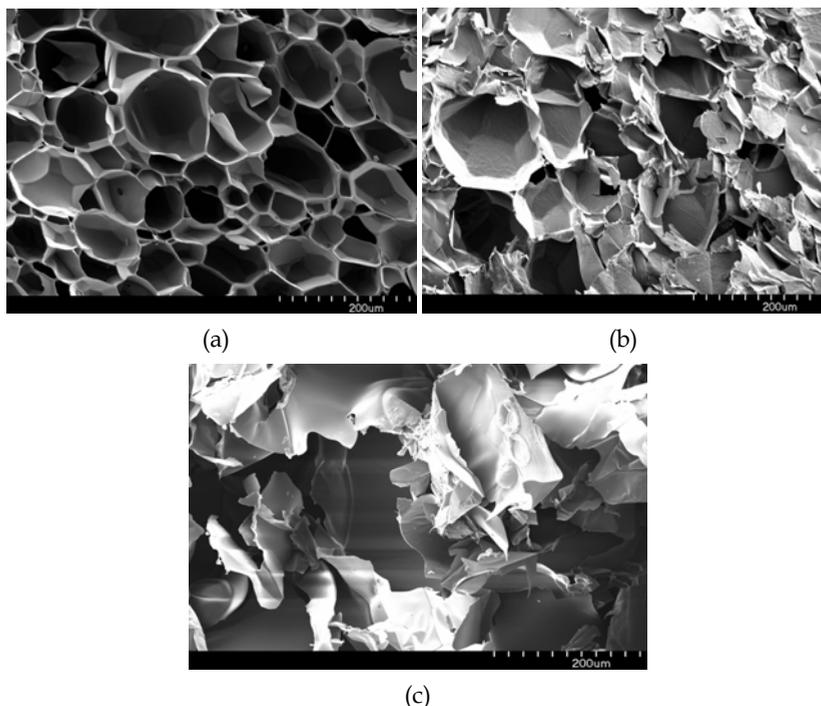


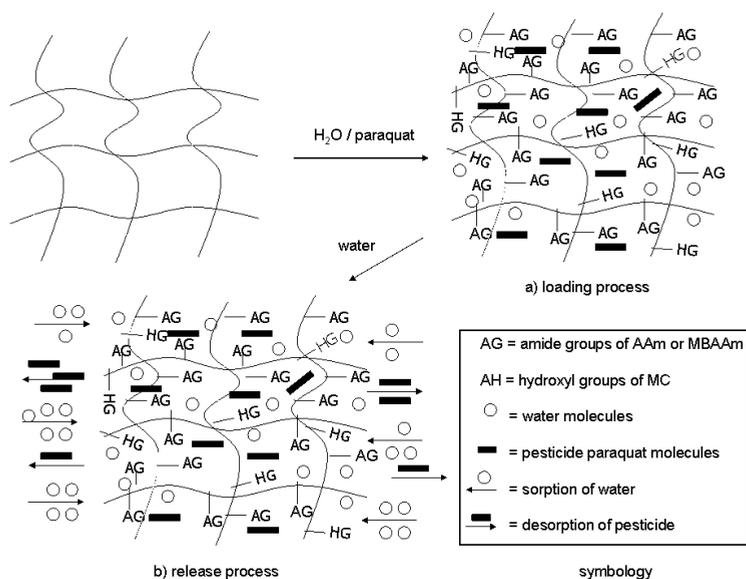
Fig. 5. SEM micrographs for semi-IPN hydrogels: (a) PAAm3.6-MC0.0; (b) PAAm3.6-MC0.5 and (c) PAAm3.6-MC1.0. The gels were lyophilized after swelling in distilled water at 25.0 °C. All micrographs were taken at 200 X magnification.

Scanning electron microscopy technique was used to analyze the morphology of PAAm and PAAm-MC hydrogels. Average pore size values were estimated by considering at least 20 individual pore size values [Tang et al., 2007]. The SEM image of PAAm3.6 MC0.0 (3.6 % AAm and 0 % MC), shown in Fig. 5a, indicates the formation of homogeneous and highly porous material with a mean pore size of $90 (\pm 20) \mu\text{m}$. The addition of MC into the solution-forming hydrogel caused morphological changes, mainly in the size and shape of the pores. From the SEM micrographs shown in Fig. 5b and 5c, it was possible to see that hydrogel pores are more foliaceous, larger, and highly heterogeneous than those shown in Fig. 5a. Due to the pore formation with high heterogeneity, it is not possible to accurately estimate the pore size of these hydrogels.

3.3 Pesticide controlled release from PAAm-MC hydrogels

3.3.1 Controlled release principles

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 [Singh et al., 2008]. Scheme 3 shows the schematic representations of loading and the paraquat release process, which are directly correlated with the swelling capacity of the 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 [Shang et al., 2008] (Eq. 5), and (2) osmotic pressure defined by the Donnan equilibrium theory [Liang et al., 2009] (Eq. 6).



Scheme 3. Schematic representations of (a) the loading process showing the sorption of water and paraquat; and (b) the release process showing the sorption of water and desorption of paraquat.

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (5)$$

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

$$\pi_{ion} = RT \sum_i (C_i^g - C_i^s) \quad (6)$$

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.

3.3.2 Effects of AAm and MC concentration on paraquat pesticide release

Hydrogels presented high loading capacity for paraquat pesticide. The pesticide was not chemically attached to the polymeric chain and the only likely interactions were ionic attractions. The hydrogels were 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, which was 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 an 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 probably due to paraquat-MC interactions. It was also observed that an increased AAm concentration provoked a decrease in the q_{eq} values [Aouada et al., 2009a]. The varying effects of AAm and MC contents on releasing paraquat from PAAm-MC hydrogels were investigated in details and their results will be now discussed. Fig. 6 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. Later, paraquat was released slowly from the hydrogels, up to 45 days. The content of methylcellulose significantly affects the amount of paraquat released, where the maximum release, close to 23 mgL⁻¹, was observed when an intermediate content of MC (0.5 %) was used.

Fig. 7 shows the effect of methylcellulose percentage on the kinetic behaviour of cumulative paraquat release. It is possible to see in Fig. 7a 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 the 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, in which 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 w:v%), Fig. 7b. By increasing the

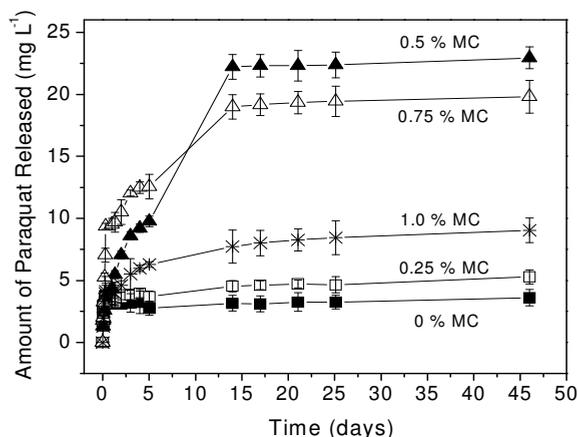
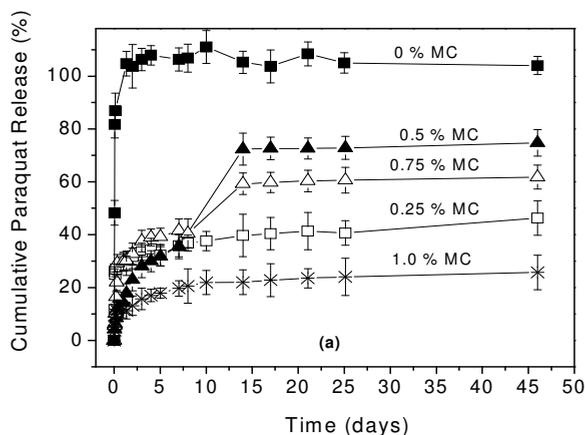


Fig. 6. Profiles of the amount of paraquat released as a function of time for PAAm-MC hydrogels with different MC concentrations: [MC] = 0; 0.25; 0.5; 0.75 and 1.0 in w:v%, [AAm] = 6.0 in w:v%, and $C_0 = 37.48 \text{ mg L}^{-1}$. Error bars represent standard deviations for the three measurements (mean \pm S.D., $n = 3$) [Aouada et al., 2010].

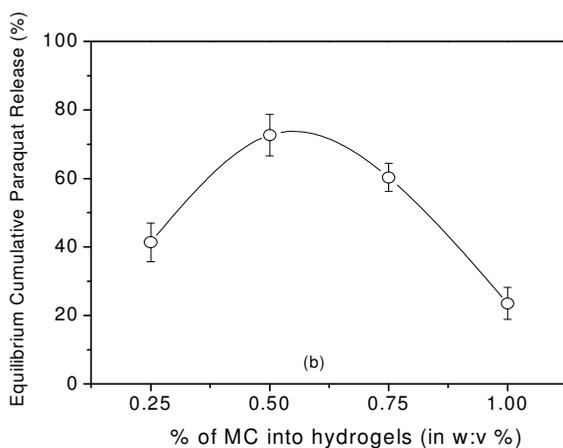
MC content of the matrix, the swelling of the matrix also increased due to the more hydrophilic nature of MC, leading to the percentage increase of the released paraquat. Similar observations have been noticed by Rokhade et al., 2007. The release profiles indicate that the amounts of paraquat released 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 behaviours have been observed in other studies on the characterizations of hydrogel hydrophilicity [Graiver et al., 1995; Bajpai & Giri, 2003]. This explains the drop in the hydrogels release capacity. 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. In addition, the results of paraquat removal from aqueous solutions using PAAm and MC hydrogels, recently published by our group [Aouada et al., 2009a], indicated that paraquat adsorption is more favourable 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 Alemzadeh & Vossoughi, 2002 and Sing et al., 2008 presented similar behaviours.

Fig. 8 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 up to 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. 8a) and from 6.0 to 12.0 % (Fig. 8b), the



(a)



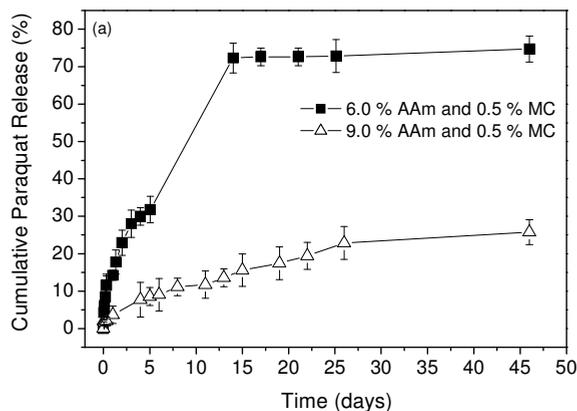
(b)

Fig. 7. (a) profiles of paraquat release as a function of time, and (b) dependence of equilibrium cumulative paraquat release as a function of methylcellulose concentration for PAAm and MC hydrogels: $C_0 = 37.48 \text{ mg L}^{-1}$, and $[\text{AAm}] = 6.0$ in w:v%. Error bars represent standard deviations for the three measurements (mean \pm S.D., $n = 3$) [Aouada et al., 2010].

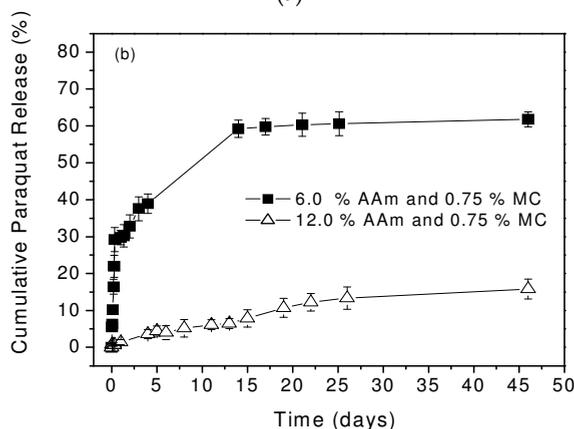
cumulative paraquat release decreased. This tendency was also reported by Işıkkan, 2007, where the author explained that the decreases in the cumulative release are due to the increasing of the monomer concentration, which gives rise to a compact network of the polymer, hence the free volume reduces and the penetration of water molecules and diffusion of pesticide molecules become difficult.

In accordance with Singh et al., 2009, the primary requisites for using agrochemicals to control the environment and health hazards are by means of 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 [Siyam, 1994]. Moreover, acrylamide was selected due to its industrial importance and its better known properties [Kenawy, 1998]. Consequently, the hydrogels studied in this work have enormous potential to be applied in agriculture fields.



(a)



(b)

Fig. 8. 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. $C_0 = 37.48 \text{ mg L}^{-1}$. Error bars represent standard deviations for the three measurements (mean \pm S.D., $n = 3$) [Aouada et al., 2010].

3.3.3 Mathematical modeling of paraquat release from PAAm and MC hydrogels

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 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 the diffusion-controlled release [Lin & Metters, 2006]. Fick's law of diffusion with either constant or variable diffusion coefficients is commonly used in modeling diffusion-controlled release [Andreopoulos & Tarantili, 2001]. Although there are a number of reports dealing with the mathematical modeling through swelling controlled release polymeric systems, no single model successfully predicts all the experimental observations [Singh et al., 2009].

The values of release exponent " n " and gel characteristic constant " k " calculated using Eq. 7 for the release dynamics of pesticide from the PAAm-MC hydrogels are in Table 2.

$$\frac{M_t}{M_\infty} = k t^n \quad (7)$$

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.

The curves obtained from Eq. 3 presented good linearity (regression coefficient, $R^2 \geq 0.999$), indicating that the Peppas 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 w:v%). 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 [Ritger & Peppas, 1987]. The values of k showed that the release of paraquat becomes slower when the MC and AAm concentration increases.

Hydrogel	k (h ⁻¹)	n	Mechanism
(6.0-0)*	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

* [AAm] = 6.0 in w:v% and [MC] = 0 in w:v%.

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. [Aouada et al., 2010].

4. Final remarks

Controlled release polymer matrix systems offer numerous 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. The objective 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.

The book chapter reported the use of biodegradable hydrogels as a potential delivery vehicle for the controlled release of pesticide. PAAm-MC hydrogels presented high loading capacity of paraquat pesticide, up to 82 % of paraquat, in relation to the amount of paraquat available in the loading solution. The release mechanism of paraquat from hydrogels was investigated through a semi-empirical model proposed by Ritger and Peppas. The release of pesticides entrapped in a hydrogel occurs only after water penetrates the network to swell the polymer and dissolve the pesticides, 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. Pesticide diffusion capacity out of hydrogel was dependent on the swelling of the matrix and the density of the network chains, i.e. MC/AAm ratio and pore sizes. The values of k showed that the release of paraquat becomes slower when the MC and AAm concentration increases.

Further work is in progress with fertilizers (NPK-type) and other pesticides using PAAm-MC and novel hydrogels as matrix, aiming to understand the controlled release process. In this sense, works are also underway to investigate the kinetic behaviour (release mechanism, cumulative release, etc...) of paraquat release from PAAm and MC in soil in a greenhouse to confirm the applicability of these hydrogels as delivery vehicles for the controlled release of agrochemicals.

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MCT/FINEP, FAPESP, CNPq, Capes, Embrapa.

6. References

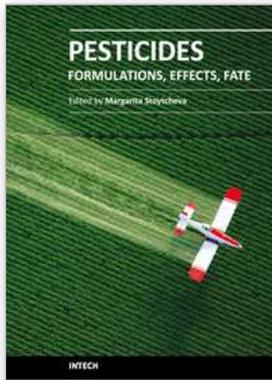
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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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