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Original Research

PAA-Based Hybrid Organic-Inorganic Fertilizers with Controlled Release

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Abstract

Poly(acrylic acid) (PAA)-based controlled release fertilizers with ammonium nitrate or carbamide were prepared using microwave irradiation. The obtained hydrogels were characterized by swelling behavior and ammonium ion release. It has been found that at higher amounts of crosslinker (N,N`-methylenebisacrylamide), the hydrogel network chains became less flexible. It causes a decrease in the swelling ratio of the hydrogel. The swelling of hydrogels containing ammonium nitrate decreased with increased concentrations of ammonium nitrate. The reason is the presence of ionic groups during agrochemicals' release in water. These ions prevent water molecules from diffusion into the hydrogels, thus decreasing the swelling capacity of the hydrogels. The release rate is the highest during the first 24 hours, then reaches a plateau.

Keywords: slow-release fertilizers, hydrogels, PAA, swelling behavior

Introduction

The use of controlled-release fertilizers causes an increase in their efficiency, reduces soil toxicity, minimizes the potential negative effects associated with overdosage and reduces the frequency of the application [1-5]. Controlled-release fertilizers have been known for several years. It has been estimated that the percentage of the fertilizer dose recovered by plants when applied in conventional forms may amount to only 30 to 50% [1]. The control of fertilizer release keeps the fertilizer concentration at effective levels in the soil solution and releases the fertilizer when the plant most needs it. As a result of this control we observed maximal utilization of the fertilizer from plant systems, a remarkable decrease with respect to fertilizer application rate, the least possible losses of the fertilizer through volatilization or leaching, prevention of seeding damage and full protection of the ecosystem in the case of biodegradable carriers [2, 3].

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In our studies, a new type of controlled release fertilizer that enables control over both release rate and release pattern was developed. A dry mixture of soluble fertilizer is contained in the polymeric matrix. Two main processes govern the release of nutrients from the hydrogels matrix: water penetrates through the pores into the dry mixture, forming a distinct and sharp wetting front. The process starts with a 'burst' of water into the matrix; fertilizers leave the matrix through pores either by diffusion alone or by diffusive and convective flows [6-9].

In this paper, nitrogen-containing fertilizers were entrapped in a hydrogel structure prepared from acrylic acid and cross-linked by N,N'-methyleno-bisacryloamide.

Experimental Procedures

Materials

Acrylic acid (AA), ammonium nitrate (AN), carbamide (CA), N,N`-methylenebisacrylamide (NMBA), ammonium persulphate (APS), sodium hydroxide, hydrochloric acid,

Table 1. Description of PAA/fertilizer hydrogels.

Sample No.	Initiator concentration [wt. %]	Crosslinker concentration [wt. %]	Carbamide concentration [wt. %]					Ammonium nitrate concentration [wt. %]				
			a	b	c	d	e	f	g	h	i	j
1	0.2	0.1	-	-	30	-	-	-	-	30	-	-
2	0.2	0.2	-	-	30	-	-	-	-	30	-	-
3	0.2	0.3	10	20	30	40	50	10	20	30	40	50
4	0.2	0.4	-	-	30	-	-	-	-	30	-	-
5	0.2	0.5	-	-	30	-	-	-	-	30	-	-
6	0.2	0.6	-	-	30	-	-	-	-	30	-	-

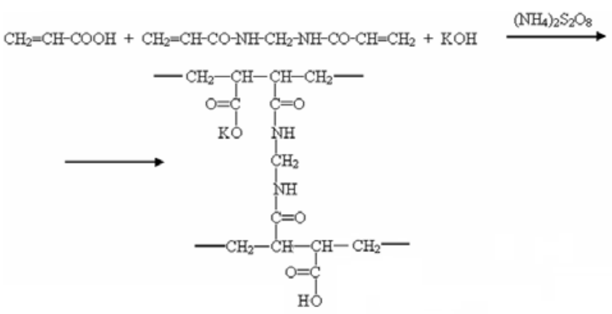
sodium chloride and calcium chloride (analytical grade) were used without further purification. In swelling measurements 0.9 wt. % NaCl and 0.9 wt.% $MgCl_2$ solutions were used.

Preparation

The synthesis of poly(acrylic acid) (PAA) hydrogel (Figs. 1a and 1b) was performed as follows: an appropriate amount of monomer acrylic acid (AA) was added to the solution containing KOH. The degree of AA neutralization is ca. 70%. The mixture of PAA and KOH was cooled slowly until the temperature dropped to 30ºC, then an agrochemical, initiator ammonium persulfate (APS) and crosslinker N,N'-methyleno-bisacryloamide (NMBA) were added. After polymerization dry hydrogel samples were disintegrated into fraction 0.5-2.0 mm.

A description of samples used in this work is given in Table 1.

a



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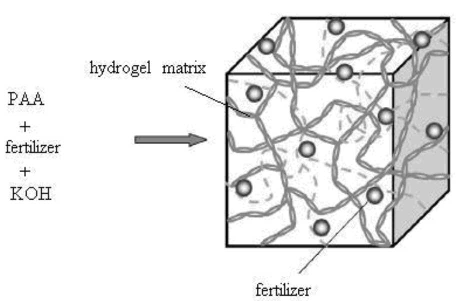

Fig. 1. a. Synthesis of PAA hydrogel. b. Synthesis of PAA/fertilizer hydrogels.

Swelling Measurement

A 1.0 g polymer sample was dispersed in 500 ml distilled water (or salt solution) for swelling equilibrium. After 1 h, the swollen sample was filtered. The water in the bag surface was removed and weighed. The swelling ratio (Q, g/g) was calculated as follows:

$$Q = \frac{w - w_0}{w}$$

...where w was polymer weight after swelling, and w_0 was polymer weight before swelling [4, 5].

Agrochemical Release

Fertilizer release was measured by immersing the membranes in distilled water at 25°C. The amount of desorbed agrochemicals vs. time was determined by photometry at 260 nm and compared with the standard curve.

Results and Discussion

Effect of Crosslinker

The swelling behavior of the absorbent polymer depends on the composition of the polymer and the characteristic of the external solution. Crosslinker concentration is an important swelling control factor. To investigate the effect of the crosslinker on the swelling characteristics of the gel, the concentration of NMBA in the feed mixture was varied in the range 0.5-3.0 [wt. %] (Fig. 2). At higher amounts of NMBA the hydrogel network chains became less flexible. It causes a decrease in the swelling ratio of the hydrogel [4, 5, 9].

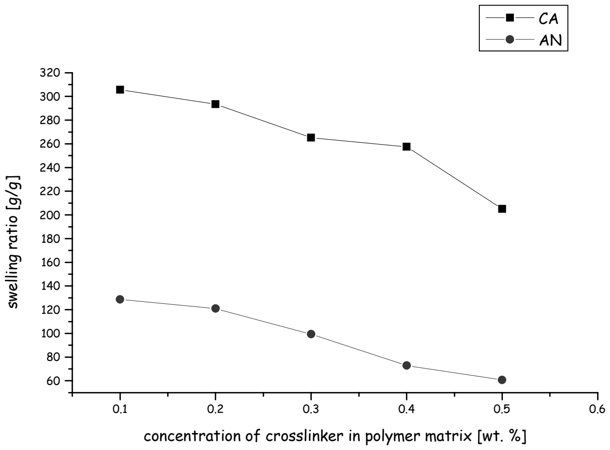

Fig. 2. The dependence of swelling ratio upon the concentration of crosslinker in dried hydrogels (samples CA: 1c-6c and AN: 1h-6h).

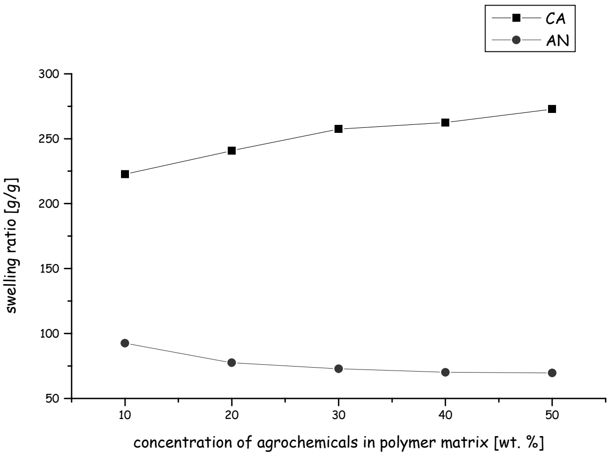

Fig. 3. The dependence of swelling ratio upon the concentration of fertilizers in dried hydrogels (samples CA: 3a-3e and AN: 3f-3j).

Effect of the Concentration of Fertilizers in Polymer Matrix

The equilibrium swelling behaviour of the concentration of agrochemicals in hydrogels was studied as a function of fertilizer concentration on the polymeric matrix (Fig. 3). The swelling rate of hydrogels with carbamide is higher than the swelling rate of hydrogels containing ammonium nitrate. The swelling studies indicated that the swelling degree of hydrogels in water increased with an increased concentration of carbamide (hydrogels with carbamide are highly porous). Moreover, their pore numbers were highly dependent on carbamide concentration in hydrogels. During drying, part of carbamide decomposes and operates as a blowing agent in the polymer matrix. The pore morphology of hydrogels can be related to their water uptake capacity. As large hydrogel pores lead to a larger contact of the networkwalls with water molecules, then the larger average pore size of hydrogels implies higher water uptake [10-13]. The change of neutralization degree of AA resulting from the addition of basic urea may also play a role. The swelling of hydrogels containing ammonium nitrate deceased with increased concentration of AN. The reason for this effect is the presence of ionic groups during agrochemical's release in water. These ions prevent water molecules from diffusing into the hydrogels, thus decreasing the swelling capacity of the hydrogels [11, 13-15].

Effects of Various Salt Solutions

The presence of ions in the swelling medium has a profound effect on the swelling behaviour of the hydrogel. In this work the salts added - NaCl and $MgCl_2$ - were found to exert a 'salting out' effect. The addition of each of the salts at increasing concentrations also resulted in decreasing the swelling ratio [4, 15, 16]. The effects of salt concentrations are illustrated in Figs. 4 and 5. Bivalence ion salts have a stronger 'salting out' effect on the hydrogel swelling ratio than monovalent ion salts. Bivalent ions caused additional

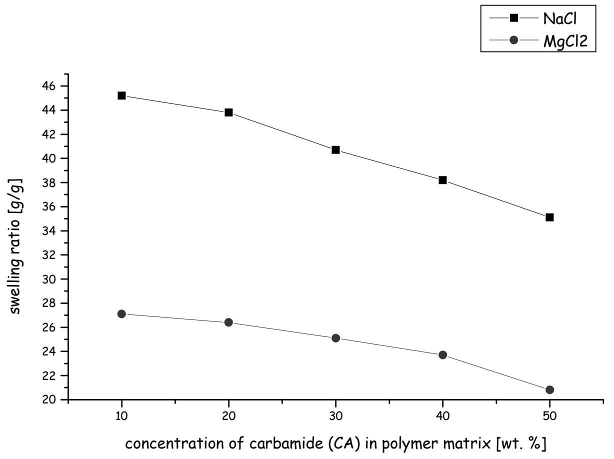

Fig. 4. The dependence of swelling ratio upon the concentration of carbamide in dried hydrogels (samples 3a-3e).

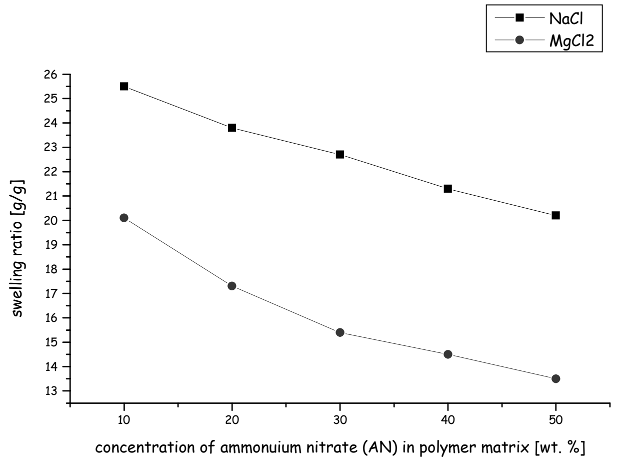

Fig. 5. The dependence of swelling ratio upon the concentration of ammonium nitrate in dried hydrogels (samples 3f-3j).

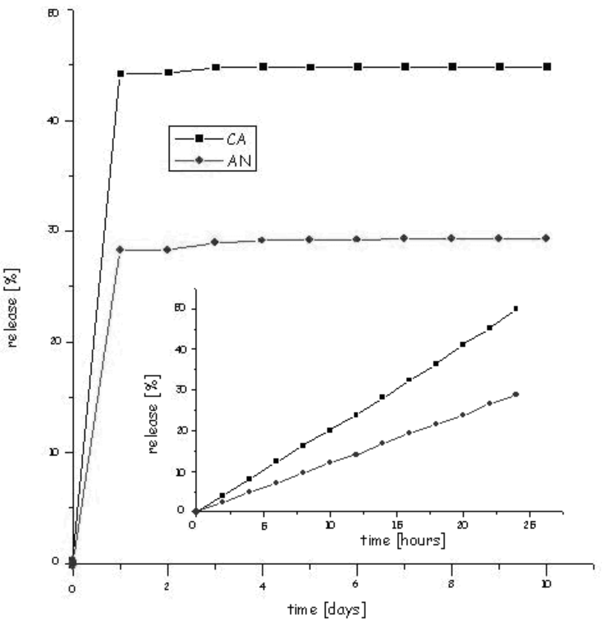

Fig. 6. The dependence of ammonium ions release ratio upon the time (samples 3c, 3h).

crosslinking of the polymer matrix and decreased the swelling ratio. Increasing ionic concentration reduces the mobile ion concentration difference between the polymer gel and external medium (osmotic swelling pressure) which, in turn, reduces gel volume, i.e. the gel shrinks [17-19].

Release Study

The release of compounds from hydrogels involves several processes: penetration of release medium into the polymeric network, dissolution of the dispersed fertilizers and release of the compounds from the hydrogel under swelling conditions. Hydrogels under consideration act in an aqueous environment as membranes – they release active substances until a concentration's equilibrium between the matrix inner space and water solution is reached. The release of agrochemicals from hydrogel is closely related to its water sorption [4, 21-24]. The highly swelled hydrogel should release a greater amount of solute trapped within the gel. The release profiles of agrochemicals are shown in Fig. 6. As would be expected for a water-soluble fertilizer, release of ammonium nitrate reached maximum the first day. Similar to ammonium nitrate, carbamide had high initial nitrogen release from polymer matrix - not surprising as urea is a water-soluble product. After the first day the release rate slowed because of the ionic concentration increases in swelling medium, which reduces the release rate.

Conclusions

Hydrogels made of acrylic acid and cross-linked by N,N'-methyleno-bisacryloamide were prepared and applied as matrices for CA and AN fertilizers. It was observed that water absorption capacity is a function of the cross-linking degree of the system. Based on the results obtained, one can conclude that the swelling behaviour of the absorbent polymer depends on the composition of the polymer and the characteristics of the external solution. At higher amounts of NMBA the hydrogel network chains became less flexible. It causes a decrease in the swelling ratio of the hydrogel. The swelling rate of hydrogels with carbamide is higher than the swelling rate of hydrogels containing ammonium nitrate. The swelling studies indicated that the swelling degree of hydrogels in water were increased with an increased concentration of carbamide (hydrogels with carbamide are highly porous). Moreover, their pore numbers were highly dependent on the concentration of carbamide in hydrogels. Further studies are underway to explain the structure/release profile effects in detail [25].

Acknowledgements

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