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In the present work slow-release phosphorus fertilizers were prepared by formation of crosslinked acrylic acid networks, modified by poly(ethylene glycol). The effect of polymerization conditions on swelling capacity was investigated. The results showed that the swelling capacity was affected by concentration of the fertilizer and amount of poly(ethylene glycol). Morphological analysis (SEM) shows the large surface of the hydrogels matrix. Besides, relationship between the release profiles and swelling capacity was observed. The influence of PEG macrochains in the polymer networks on fertilizer ions migration from hydrogel matrix to water has been discussed.

Keywords Hydrogels; poly(acrylic acid); slow-release fertilizers; swelling capacity

Introduction

Superabsorbents are crosslinked hydrophilic polymers that can efficiently absorb and retain aqueous fluids up to thousands of times their own weight, and the water is hardly bound [1]. One of the possible applications of superabsorbent polymers is associated with the controlled release fertilizers. They are able to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant [4,5]. The optimized combination of superabsorbents and slow-release fertilizers may improve nutrition of plants, and mitigate at the same time the environmental impact from water-soluble fertilizers, reduce evaporation losses, and lower frequency of irrigation [6–9]. Besides, superabsorbent polymers can be used for the restoration of degraded lands. They increase the plant available water in the soil which enables the plants to survive longer under water stress. Superabsorbents amendment to soils reduces the evapotranspiration rate of the plants and induce a significantly higher growth rate in plants [2,3]. In polymeric slow release systems two main processes

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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 the pores either by diffusion alone or by diffusive and convective flows [10–13].

In this paper, KH_2PO_4 – containing fertilizers were entrapped into a hydrogel structure prepared from acrylic acid, cross-linked by N,N′-methyleno-bisacryloamide, and modified by poly(ethylene glycol).

Experimental Details

Materials

Monopotassium phosphate (KH_2PO_4), Acrylic acid (AA), N,N′-methylenebisacrylamide (NMBA), ammonium persulphate (APS), and KOH were obtained from POCh Gliwice, Poland. Poly(ethylene glycol) (PEG) was acquierd from Sigma Aldrich. All the chemicals were of analytical grade and used without further purification.

Hydrogel Preparation

The synthesis of PAA hydrogel was performed as follows: an appropriate amount of monomer acrylic acid was added to the solution containing KOH. The mixture was APS and crosslinker NMBA, as well as PEG and phosphorus fertilizers were added. The synthesis of hydrogel in aqueous was carried out under microwave irradiation at 600 W for 5 minutes.

Synthesis route of PAA/PEG hydrogels with KH_2PO_4 were is schematically illustrated in Figure 1.

Description of samples used in this work is given in Table 1.

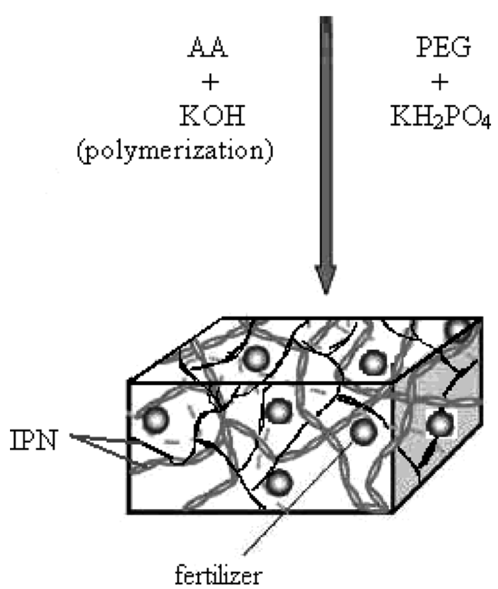


Figure 1. Synthesis of PAA/PEG hydrogels with fertilizer.

Table 1. Description of PAA/fertilizer hydrogels

Sample no.	PEG concentration [wt.%]	KH2PO4 concentration [wt.%]					
		a	b	c	d	e	f
1	0	0	10	20	30	40	50
2	5	0	10	20	30	40	50
3	10	0	10	20	30	40	50
4	15	0	10	20	30	40	50

Swelling Measurements

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

$$Q = \frac{w - w_0}{w_0} \tag{1}$$

where w was the weight of polymer after swelling, and w_0 was the weight of polymer before swelling [14–16].

Morphological Analysis

Structure of silver-coated hydrogels was examined using a scanning electron microscope Hitachi S-4700.

Agrochemical's Release

Fertilizers release was measured by immersing the membranes in distilled water at 25°C. The amount of desorbed agrochemicals vs. time was determined by photometric method at 260 nm.

Results and Discussion

Effect of the Concentration of PEG in Polymer Matrix

The effect of PEG content on water absorption was shown in Figure 2.

It can be seen that water absorption generally decreased as PEG content increased.

This effect can be explained by decreasing the available free volumes within the hydrogel by PEG macrochains. The second reason for reduced swelling capacity may be that PEG terminal –OH groups react with strongly hydrophilic –COOH groups of PAA, but there was no ester absorption bond at the FTIR spectra [19–26].

Finally, interpenetrating PAA/PEG network serves as a physical barrier (Fig. 3) for mass transfer, and reduces the rate of water diffusion into the core and the nutrient diffusion outside the core, thus provided the slow release fertilizers with a good controlled-release property [17,18].

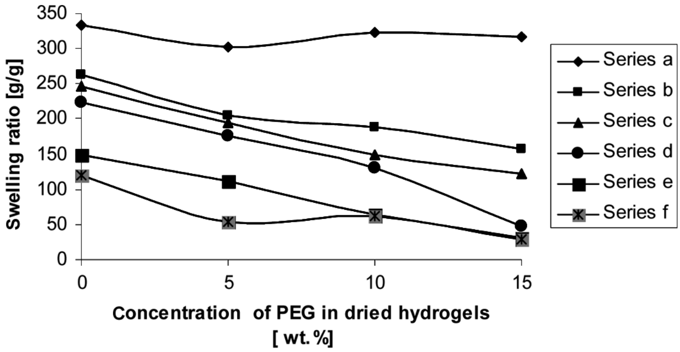


Figure 2. The dependence of swelling ratio upon the concentration of PEG in dried hydrogels.

Effect of the Concentration of KH_2PO_4 in Polymer Matrix

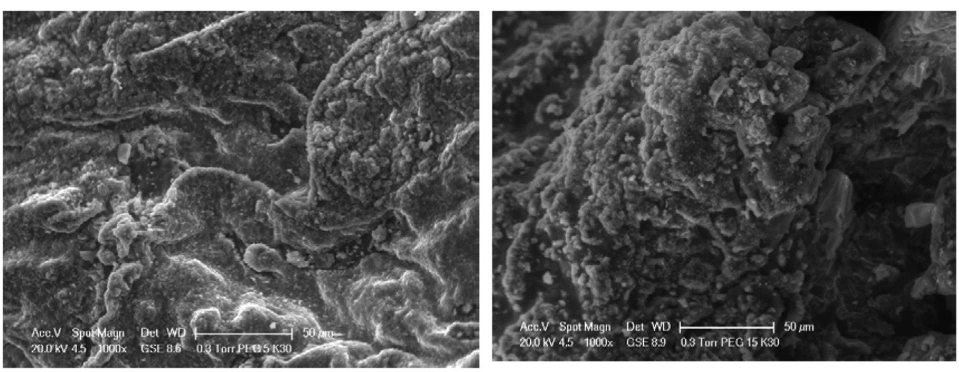
The presence of ions in the swelling medium has a profound effect on the swelling behaviour of the hydrogel. In this work the fertilizer added was found to exert a 'salting out' effect. The addition of the agrochemical at increasing concentration also resulted in a decrease of the swelling ratio [15,18,27]. The effect of fertilizer concentration is illustrated in Figure 4.

Swelling ratio decreases with an increase of concentration of KH_2PO_4 because ionic groups prevent water molecules from diffusion into the hydrogels, thus, the swelling capacity of the hydrogels decreases [18,32,33].

Besides, an increase of the ionic concentration reduces the mobile ion concentration difference between the polymer gel and external medium (osmotic swelling pressure) which, in turn, reduces the gel volume, i.e., the gel shrinks [28–31].

Release Study

The superabsorbent polymers could absorb a lot of water and translate into hydrogel, and then the agrochemicals dissolved in the water could be absorbed into



(a) (b)

Figure 3. SEM microphotographs of dried hydrogel: (a) hydrogel contain 5 wt.% PEG and 30 wt.% KH_2PO_4 (b) hydrogel contain 15 wt.% PEG and 30 wt.% KH_2PO_4.

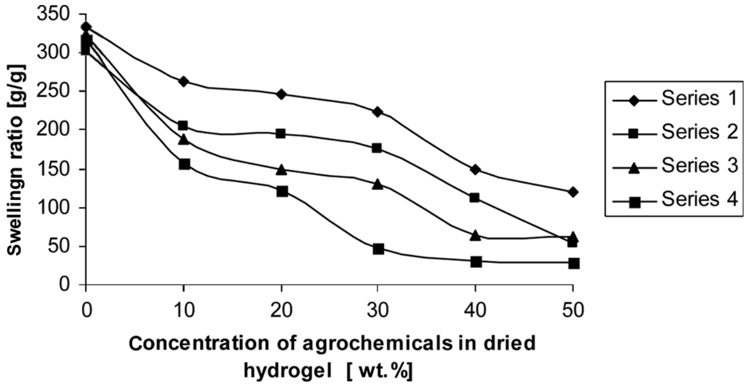


Figure 4. The dependence of swelling ratio upon the concentration of fertilizers in dried hydrogels.

it or adsorbed on its surface. The absorbed phosphorus fertilizers could be slowly released out or desorbed with the exchange of free water between the hydrogel and the solution, therefore, a slow release property is achieved [6,27,34–36].

P_2O_5 release behavior from the PAA/PEG hydrogel is shown in Figure 5.

Whereby more than 56% of phosphorus was released within 24 hours from PAA hydrogel, the phosphorus release rate from the PAA/PEG matrix was lower. PEG macrochains in the polymer network hinderd fertilizer ions migration from hydrogel matrix to water – an increased concentration of PEG in superabsorbent caused reduction of available free volumes within the hydrogel.

After the first day the release rate slowed down because of the ionic concentration increases in swelling medium which, in turn, reduces the release rate. Importantly, the time of phosphorus release was within the recommended in agriculture

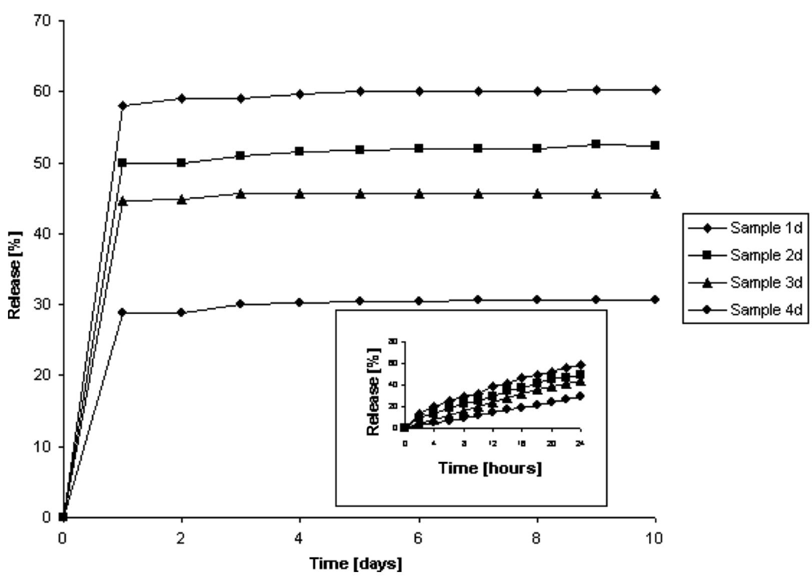


Figure 5. The dependence of P_2O_5 release ratio upon the time.

procedures, although the tests were made in water. It can be assumed that the time of phosphorus release in soil will be much longer [6,27] – such studies are in progress.

Conclusion

A new type of slow release KH_2PO_4 – containing fertilizer was synthesized by aqueous solution polymerization of AA using NMBA as a crosslinker, sodium persulfate as an initiator and PEG as a modifier. It can be seen that more than 56% of phosphorus was released within 24 hours from PAA hydrogel, the phosphorus release rate from the PAA/PEG matrix was lower. PEG macrochains in the polymer network hinderd fertilizer ions migration from hydrogel matrix to water – an increased concentration of PEG in superabsorbent caused reduction of available free volumes within the hydrogel.

The results of the present work indicate that PAA-based hydrogels display excellent water-retention capabilities, which make them suitable candidates for agriculture applications.

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