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Composite Materials for Controlled Release of Mineral Nutrients and Humic Substances for Agricultural Application

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Controlled release fertilizers based on superabsorbents containing lignohumate and conventional mineral fertilizer (NPK) were prepared. Their water absorption was supported by the presence of lignohumate (LH) and suppressed by the presence of NPK. The release of mineral nutrients was prolonged up to four weeks in the case of increased content of NPK. The addition of LH had negligible influence on the release of P and N. The release of LH was partially suppressed by the higher content of NPK. The release of nutrients from all used samples was connected with the strong increase of conductivity and weak increase of pH values. The application of superabsorbents supported growth of corn. The length of roots was probably more influenced by better water management, while the growth of above-ground plant was more affected by release of nutrients.

Keywords: Lignohumate; Fertilizer; Superabsorbent; Swelling; Release

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1 INTRODUCTION

Humic substances are the principal components of organic soil matter. They affect biological uptake and bioaccumulation of toxic chemicals in plants as well as the pollution of underground water supplies. They influence soil fertility and stabilize soil aggregates. Due to their colloidal and poly-functional character, these substances play important roles in the mobility and bioavailability of nutrients and contaminants in the environment (Bryan *et al.* 2007; Frimmel *et al.* 2002; Lee and Sung 2014; Tan 2014). Humic substances play irreplaceable role from agronomical point of view. Most agricultural soils have gradually lost much of this capacity as the use of heavy machinery and synthetic fertilizers have replaced careful soil utilization and natural fertilization (Novotny *et al.* 1999; Shepherd *et al.* 2001; Lal 2004; Sedlacek and Klucakova 2009; Klucakova 2014), therefore, it must now be supported artificially. This is the main reason why they are used as additives in fertilizing products (Garcia *et al.* 1994; Piccolo and Mbaghwu 1997; Albiach *et al.* 2001; Madejon *et al.* 2001; Shepherd *et al.* 2001). Although their water soluble complexes with toxic metals can be absorbed by plants more easily which has inhibiting effect on their growth (Pacheco and

Havel 2001; Chu *et al.* 2008; Klucakova and Pekar 2003; Klucakova and Novackova 2014; Klucakova and Veznikova 2016), humic substances have a beneficial effect on soil quality and plant growth (Zhang *et al.* 2005; Bharadwaj *et al.* 2007; Liu *et al.* 2007; Bai *et al.* 2010; Klucakova 2010; Enev *et al.* 2014). However, humic substances are suitable for agricultural application only if care is taken to ensure limited dosing. This means that humic substances should have a certain concentration which should not be exceeded. This can be accomplished by using fertilizer systems that are capable of providing controlled release of nutrients (Du *et al.* 2006; Mo *et al.* 2006; Bai *et al.* 2010; Klucakova 2010; Davidson and Gu 2012).

Superabsorbent polymers have the unique ability to absorb and retain relatively large amounts of water or water solutions in their structure (Raju and Raju 2001; Raju *et al.* 2002; Li *et al.* 2004; Dadhaniya *et al.* 2006; Nnadi and Brave, 2011). Therefore, they are able to regulate soil moisture. Swelling behavior of superabsorbents studied in this work is described in detail in Supplementary 1.

Humic substances as a source of organic carbon for composite fertilizer have been studied by several authors (Li *et al.* 2005; Zhang *et al.* 2005, 2006; Mo *et al.* 2006; Liu *et al.* 2007; Chu *et al.* 2008; Gao *et al.* 2013). Zhang *et al.* (2005, 2006) used sodium humate in combination with poly(acrylic acid-co-acrylamide) and later in combination with attapulgite. They investigated the release of humate into distilled water and reported that a material containing humate caused sturdier roots and stems. Gao *et al.* (2013) synthetized and characterized controllable agricultural superbasorbent based on poly(acrylic acid-co-acrylamide) and sodium humate. Li *et al.* (2005) and Mo *et al.* (2006) incorporated sodium humate into poly(acrylic acid) as a kind of functional filler and studied its influence on water absorption. Chu *et al.* (2008) dealt with the influence of potassium humate on the swelling properties of a poly(acrylic acid-co-acrylamide)/ potassium humate superabsorbent. Liu *et al.* (2007) combined poly(acrylic acid) with chitosan and sodium humate. A review of Mikula *et al.* 2020) presents current achievements in the field of fertilizers with controlled release of microelements, which, apart from the main fertilizer components, are also very significant for proper plant growth.

In the light of the above-mentioned works and their results, our study investigates the development of multifunctional superabsorbent composite materials containing commercial NPK fertilizer as a source of mineral constituents and lignohumate as organic functional materials in combination with poly(acrylic acid-co-acrylamide) as polymer providing high water retention. In comparison with composite materials combining humic substance with mineral fertilizers (Erro *et al.* 2007) and fertilizers coated by polymers (Davidson and Gu 2012), our systems should combine advantages of controlled release of nutrients (organic and mineral) with the ability of swell (water conservation).

The aim of this work was to investigate the release of active substances in the prepared superabsorbents in order to optimize their composition for further pot experiments. Superabsorbent materials enriched by mineral fertilizer and lignohumate are investigated. The novelty of our work lay in the combination of mineral and organic fertilizer and the connection with high ability to absorb water. This work is a complex study covering all aspects of this type of composite materials: swelling and water absorption, release of mineral and organic fertilizers, repeated leaching (washing) of nutrients and application of prepared composite materials in pot experiments.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Chemicals

Eight different samples of superabsorbent polymers were synthesized through the rapid solution polymerization of partially neutralized acrylic acid (AA; Sigma Aldrich, St. Louis, MO, USA) under normal atmospheric conditions. Potassium peroxydisulfate (KPS; Sigma Aldrich, St. Louis, MO, USA) was used as an initiator and *N,N*-methylenebisacrylamide (MBA, Sigma Aldrich, St. Louis, MO, USA) as a crosslinking agent. Powders of potassium lignohumate (LH; Amagro s. r. o., Prague, Czech Republic) and NPK 20-8-8 (NPK, Lovochemie a.s., Lovosice, Czech Republic).

2.1.2 Preparation of superabsorbents

Weight quantity of AA (57 g) was dissolved in distilled water (100 cm^3). AA solution (25 cm^3) was neutralized by 10 cm^3 of 8.5M potassium hydroxide solution (KOH, Penta). Powders of LH and NPK were dispersed in this mixture and crosslinked by MBA (0.016 g). Then the initiator KPS was added (0.5 g). The mixture was continuously heated and stirred until reaching of cca 85 °C then highly viscous mixture was removed from the beaker and replaced to an oven for 24 hours which was settled up on 80 °C. Dried product was crushed by hammer into small pieces (Mo *et al.* 2006). The compositions of prepared samples are described in detail in Tables 1 and 2.

2.2 Methods

2.2.1 Releasing experiments

Samples in form of xerogel were mixed with distilled water in the ratio 50 mg : 100 cm^3. Releasing of active substances was monitored in time by means of several methods. The time development of pH and conductivity was measured using a S47 SevenMulti pH and conductivity meter (Mettler Toledo, Greifensee, Switzerland). The amounts of released K and P was determined by means of ICP-OES (an Ultima 2 ICP-OES spectrometer, Horiba, ThermoFisher Scientific, Waltham, MA, USA). Concentrations of anions (NO_3^- and PO_4^{3-}) were monitored using (a 850 Professional IC Anion-MCS ion chromatography system, Metrohm AG, Herisau, Switzerland).

The release of LH was measured by means of an U-3900H UV/Vis spectrometer (Hitachi, Tokyo, Japan). In order to determine the amounts of N, P and K in LH and NPK, their solutions in distilled water (1 g/dm^3) were analyzed by means of ICP-OES (Horiba Ultima 2, Thermo Fisher Scientific, Waltham, MA USA) and ion chromatography (see above).

2.2.2 Leaching experiments

This experiment was done in order to determine the release of nutrients in repeated leaching of superbsorbents. Samples in form of xerogel were mixed with distilled water in the ratio 400 mg : 100 cm^3. After one hour, the leachate was decanted and replaced by 100 cm^3 of fresh distilled water. Whole process was repeated fifteen times. Obtained leachates were analyzed by the same way as in the case of releasing experiments.

2.2.3 Pot experiments

The model soil was prepared by mixing of peat (200 g), kaolin (120 g), silica sand (1660 g) and $CaCO_3$ (20 g). Corn seeds were extracted in 0.05M NaClO (5 min) in order to remove pickling agent and washed by distilled water. After 24 hours, the seeds were placed separately into curled up paper towels and covered by distilled water (5 days at 28 ± 2 °C). The germinated seeds were placed into the 250 g of model soil mixed with 1 g of xerogel and 40 cm^3 of water (3 seeds into 1 pot). The pots were placed in the growing box at 26 ± 2 °C with periodical watering. Shoot and root were separated and individually measured.

All experiments were triplicated and average values are presented in this study.

3 RESULTS AND DISCUSSION

3.1 Releasing experiments

Active components were released from hydrogels progressively (Figure 1). In beginning, the release was partially influenced by the swelling of hydrogel. The cumulative amount of the nutrient increased in time up to the achievement of stable concentration in the leachate. The content of potassium in samples was a combination of potassium coming from NPK and LH, added in samples as active components, and KOH and KPS used in the preparation of hydrogels. While the amounts of potassium coming from KOH and KPS were the same for all samples, they differed in the contents of NPK and LH. Sample A contained lower amount of NPK and no LH. The release of K from this sample corresponded with its content in the hydrogel. The majority of potassium was released in one week and the following release rate was very low. The increased content of NPK in hydrogels B and D thus resulted in the increased cumulative release of potassium. In this case, the addition of LH had negligible influence (samples B and D). In contrast, the addition of LH supported the release of K from sample C. The release of K from samples B, C, D and H was retarded after two or three weeks (Figure 1a). The release of P (Figure 1b) and NO_3^- (Figure 1c) was strongly dependent on the contents of NPK. In the case of increased content of NPK (samples B and D) the release was prolonged up to four weeks. The addition of LH had negligible influence on the release of P and $NO_3^-$from samples B and D. In contrast, The release of P from sample C was prolonged in the comparison with the sample A containing the same initial amount of NPK. The release of LH (which was primarily added in hydrogels as a source of organic carbon) was partially suppressed by the higher content of NPK (sample D). In this case, the release was stopped after three days, while it continued for more than two months in samples C and H (Figure 2). The release of nutrients from all used samples was connected with a strong increase of conductivity and weak increase in pH values.

Erro *et al.* (2007) developed a fertilizer based on humic substances and NPK (without polymers). Their results showed that nutrients were released into water in about 30 minutes (K and N) or two hours (P), while the release of ammonia ions was slower with a maximum achieved in several days. The amount of nitrogen released was enhanced by the addition of straw. Du et al. (2006) studied the release of K, N, and P from polymer coated fertilizers which could be released up to two months in the dependence on the temperature and thickness of surface polymer layer. Nutrients release was the fastest into water, than into water saturated sand. Similarly, Davidson and GU (2012) studied the release of nutrients from fertilizers coated e.g.by polyactic acids and wax. The release of urea was stopped in 20 days in both cases. Zhan *et al.* (2004) investigated the release of phosphate from superabsorbent polymer based on PVA, H_3PO_4 and Na_2CO_3 provided. The proportion of released phosphate increased during first day up to 26.5 %. No release was detected during second day. After that the release increased from 26,5 to 47 % during third day of experiment. On the 28th day, the total proportion of released phosphate was 79 %. The authors concluded that the results were due to the enrichment of the surface layer and the slow diffusion of phosphate encapsulated inside the material. In contrast, the release of sodium humate from superabsorbents based on AA, acrylamide and attapulgite was stopped after several days in dependence on the content of humate (Zhang *et al.* 2005). However, the use of acrylamide is problematic because of its toxicity (Matoso *et al.* 2019; Spencer *et al.* 2018; Spencer and Schaumburk 1974a, 1974b). We performed some experiments with superabsorbents containing acrylamide but the results did not show any improvement in their properties in comparison with samples used in this work.

3.2 Leaching experiments

The gradual leaching of active components from hydrogels can be characterized by measurement of conductivity. Obtained results are shown in Figure 3. In our study, the development of amounts of individual ions in leachates corresponded with conductivity values which did not change after seven washing cycles. An exception was the leaching of LH which can be extracted for ten washing cycles. This means that if the hydrogel is applied in soil with very good supply of water the active components can be repeatedly washed out from the surroundings of plant roots. The leaching of nutrients from fertilizer prepared and studied by Erro *et al.* (2007) was in most cases faster. The release of phosphate was completed after three cycles and that of potassium after for cycles. In contrast, no nitrogen was leached after seven cycles.

3.3 Pot experiments

The influence of superabsorbent application on corn growth is shown in Figure 4. A possitive effect on corn height was observed for all prepared samples. As can be seen in Figure 4, the growth of shoots was much slower in soil without superabsorbent and no changes in plant height were observed after two weeks. In contrast, higher content of NPK in superabsorbent enriched by LH had the most positive effect on corn growth. It was confirmed that the presence of LH in superabsorbent supported corn growth but it was lower in comparison with the application of superabsorbents containing NPK. This effect was partly the result of better water management and partly the result of the slow supply of nutrients from NPK and LH. The improvement of plant growth as a result of the more effective utilization of water was confirmed also by Raju and Raju (2001), Abedi-Koupai and Asadkazemi (2006), and Dorraji *et al.* (2010) who applied superabsorbents without addition of nutrients. The application of fertilizer without superabsorbent polymer supported the growth of wheat (Erro *et al.* 2007), but the growth was small than that induced by composite materials in our study. Chatzistathisa *et al.* (2020) compared effects between manure application and a controlled-release fertilizer on the growth and nutrient uptake of *Olea europaea* L. They concluded that the total plant biomass and total per plant macronutrient were significantly higher in the case of controlled-release fertilizer due to higher biomass production. Zhao *et al.* (2019) demonstrated that the combination of fertilizers with superabsorbens improved soil fertility, increased soil nutrient supply capacity, and yield of tomatoes. Four different types of controlled-release fertilizers were used in container-grown ornamental plants (Japanese spirea) and abrovitae by Grable *et al.* (2017). The most positive effect on the growth was observed for the prototype blends with experimental polymer coatings. They produced a deeper green foliage and higher shoot dry weight in comparison with others. Similarly, Girardi *et al.* (2005) observed positive effect of slow-release fertilizers on growth of containerized citrus nursery trees and Silva et al. (2017) concluded that associating organo-mineral fertilization with the organo-mineral fertilizer slow release of nutrients can ensure greater yield of lavender essential oil and had a noticeable impact on its chemical composition.

Our results showed that higher contents of NPK in superabsorbent without LH (sample B) had slightly inhibiting effect. This could be the result of a greater release of nutrients which cannot be effectively utilized in the first days of growth. A similar effect was observed by Nnadi and Brave (2011) who used polymers based on carboxymethyl cellulose sodium salt and several commercial starch powders. Higher amounts of this polymer in soil resulted in lower plant height as well as smaller plant weight.

In contrast, the combination of LH and higher amount of NPK had a synergic effect on corn growth. Material containing only LH (sample H) affected corn growth positively in comparison with plant grown withaut application of superabsorbent but its effect was weaker.

Figge *et al.* (1995) used expanded clay and porous ceramics (as materials to enhance water management) in combination with manure, KH_2PO_4, and KCl (as nutrients) in order to improve plant growth in minespoils. They observed that germination and growth of plants were improved if the materials were applied on the surface but no benefit was observed in the case of mixing.

The influence of our composite materials on root growth was different. The best results were obtained with sample A containing only a small content of NPK without LH. It seems that water management is more important for root growth than the addition of nutrients. The addition of LH had negative effect in the case of low NPK content. Root growth was slightly improved if a higher content of NPK was combined with the addition of LH. In contrast, the results with sample H which contained LH without NPK were the best (with the exception of those with sample A). The negative effect of humic substances on the growth of plants and roots was described by Rastghalam *et al.* (2011). The effect was more important in the case of plant growth (in comparison with roots). In contrast, Zhang *et al.* (2005) observed that the roots and stems of grass were sturdier if superabsorbent containing sodium humate was applied in soil (compared with grass grown without such application). This discrepancy can be explained by the existence of an optimal level of humic addition. If the addition of humic substances increases above, a certain threshold, negative effects on nutrient uptake and plant growth can be observed (Pannucio *et al.* 2001).

4 CONCLUSIONS

In this work, several different superabsorbents containing lignohumate and conventional mineral fertilizer (NPK) were prepared. Their swelling behaviour, release of nutrients, periodic washing out and the influence on the growth of corn were studied. It was found that the swelling was relatively fast and it was completed in 24 h. While the addition of NPK surpressed the water absorption, the sweling was supported by the presence of LH. Simultaneously, the swelling influenced the release of nutrients from superabsorbents during the first day. The release of mineral nutrients corresponded with their contents in different samples. The higher content of NPK resulted in the prolongation of the release of nutrients. The addition of LH had negligible influence on the release of P and N. In contrast, the amount of released K incresed due to the potassium content in added LH. On the other hand, the release of LH was partially suppressed by the higher content of NPK. In leaching experiments, realised be repeated washing out of active substances from hydrogels, the mineral nutrients were washed out after seven cyles and LH after ten cycles. In general, the application of superabsorbents supported growth of corn. Better water management and a slow supplying by nutrients had possitive effect on the height of plants. The length of roots is probably influenced more by better water management. The combination of superabsorbent polymers with NPK and LH in suitable amounts can improve soil properties, water management, nutrient uptake and growth of plants. Such materials can be utilized mainly in problematic areas with dry soils and low levels of organic matter and nutrient elements.

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Table 1. Composition of superabsorbent hydrogels – starting materials

Sample	A	B	C	D	H
AA (g)	14.25	14.25	14.25	14.25	14.25
MBA (g)	0.016	0.016	0.016	0.016	0.016
KPS (g)	0.5	0.5	0.5	0.5	0.5
KOH (g)	4.75	4.75	4.75	4.75	4.75
NPK (g)	0.6602	6.602	0.6602	6.602	0
LH (g)	0	0	1	1	1
H_2O (g)	35	35	35	35	35

Table 2. Composition of superabsorbent xerogels – active components

Sample	**A**	**B**	**C**	**D**	**H**
K (% wt.)	17.34	14.91	17.57	15.17	17.92
N (% wt.)	0.67	5.07	0.82	5.02	0.20
P (% wt.)	0.11	0.88	0.11	0.85	0.00
LH (% wt.)	0.00	0.00	4.72	3.69	4.87

FFIGURE CAPTIONS

Fig. 1. The release of K (left) and P (right) from studied materials in the dependence on time

Fig. 2. The release of LH from studied materials in the dependence on time

Fig. 3. The conductivity of aqueous leachates for samples A and C in the dependence on washing cycle

Fig. 4. The time development of the height of corn (left) and the final lengths of roots for the used superabsorbents (right). The blank experiment is without application of superabsorbent

Supplementary 1. Swelling experiments

Supplementary 2. Pictures of xerogels and swollen hydrogels

Supplementary 3. The time development of plant growth

Supplementary 4. The time development of root growth

Composite Materials for Controlled Release of Mineral Nutrients and Humic Substances for Agricultural Application

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Controlled release fertilizers based on superabsorbents containing lignohumate and conventional mineral fertilizer (NPK) were prepared. Their water absorption was supported by the presence of lignohumate (LH) and suppressed by the presence of NPK. The release of mineral nutrients was prolonged up to four weeks in the case of increased content of NPK. The addition of LH had negligible influence on the release of P and N. The release of LH was partially suppressed by the higher content of NPK. The release of nutrients from all used samples was connected with the strong increase of conductivity and weak increase of pH values. The application of superabsorbents supported growth of corn. The length of roots was probably more influenced by better water management, while the growth of above-ground plant was more affected by release of nutrients.

Keywords: Lignohumate; Fertilizer; Superabsorbent; Swelling; Release

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1 INTRODUCTION

Humic substances are the principal components of organic soil matter. They affect biological uptake and bioaccumulation of toxic chemicals in plants as well as the pollution of underground water supplies. They influence soil fertility and stabilize soil aggregates. Due to their colloidal and poly-functional character, these substances play important roles in the mobility and bioavailability of nutrients and contaminants in the environment (Bryan *et al.* 2007; Frimmel *et al.* 2002; Lee and Sung 2014; Tan 2014). Humic substances play irreplaceable role from agronomical point of view. Most agricultural soils have gradually lost much of this capacity as the use of heavy machinery and synthetic fertilizers have replaced careful soil utilization and natural fertilization (Novotny *et al.* 1999; Shepherd *et al.* 2001; Lal 2004; Sedlacek and Klucakova 2009; Klucakova 2014), therefore, it must now be supported artificially. This is the main reason why they are used as additives in fertilizing products (Garcia *et al.* 1994; Piccolo and Mbaghwu 1997; Albiach *et al.* 2001; Madejon *et al.* 2001; Shepherd *et al.* 2001). Although their water soluble complexes with toxic metals can be absorbed by plants more easily which has inhibiting effect on their growth (Pacheco and

Havel 2001; Chu *et al.* 2008; Klucakova and Pekar 2003; Klucakova and Novackova 2014; Klucakova and Veznikova 2016), humic substances have a beneficial effect on soil quality and plant growth (Zhang *et al.* 2005; Bharadwaj *et al.* 2007; Liu *et al.* 2007; Bai *et al.* 2010; Klucakova 2010; Enev *et al.* 2014). However, humic substances are suitable for agricultural application only if care is taken to ensure limited dosing. This means that humic substances should have a certain concentration which should not be exceeded. This can be accomplished by using fertilizer systems that are capable of providing controlled release of nutrients (Du *et al.* 2006; Mo *et al.* 2006; Bai *et al.* 2010; Klucakova 2010; Davidson and Gu 2012).

Superabsorbent polymers have the unique ability to absorb and retain relatively large amounts of water or water solutions in their structure (Raju and Raju 2001; Raju *et al.* 2002; Li *et al.* 2004; Dadhaniya *et al.* 2006; Nnadi and Brave, 2011). Therefore, they are able to regulate soil moisture. Swelling behavior of superabsorbents studied in this work is described in detail in Supplementary 1.

Humic substances as a source of organic carbon for composite fertilizer have been studied by several authors (Li *et al.* 2005; Zhang *et al.* 2005, 2006; Mo *et al.* 2006; Liu *et al.* 2007; Chu *et al.* 2008; Gao *et al.* 2013). Zhang *et al.* (2005, 2006) used sodium humate in combination with poly(acrylic acid-co-acrylamide) and later in combination with attapulgite. They investigated the release of humate into distilled water and reported that a material containing humate caused sturdier roots and stems. Gao *et al.* (2013) synthetized and characterized controllable agricultural superbasorbent based on poly(acrylic acid-co-acrylamide) and sodium humate. Li *et al.* (2005) and Mo *et al.* (2006) incorporated sodium humate into poly(acrylic acid) as a kind of functional filler and studied its influence on water absorption. Chu *et al.* (2008) dealt with the influence of potassium humate on the swelling properties of a poly(acrylic acid-co-acrylamide)/ potassium humate superabsorbent. Liu *et al.* (2007) combined poly(acrylic acid) with chitosan and sodium humate. A review of Mikula *et al.* 2020) presents current achievements in the field of fertilizers with controlled release of microelements, which, apart from the main fertilizer components, are also very significant for proper plant growth.

In the light of the above-mentioned works and their results, our study investigates the development of multifunctional superabsorbent composite materials containing commercial NPK fertilizer as a source of mineral constituents and lignohumate as organic functional materials in combination with poly(acrylic acid-co-acrylamide) as polymer providing high water retention. In comparison with composite materials combining humic substance with mineral fertilizers (Erro *et al.* 2007) and fertilizers coated by polymers (Davidson and Gu 2012), our systems should combine advantages of controlled release of nutrients (organic and mineral) with the ability of swell (water conservation).

The aim of this work was to investigate the release of active substances in the prepared superabsorbents in order to optimize their composition for further pot experiments. Superabsorbent materials enriched by mineral fertilizer and lignohumate are investigated. The novelty of our work lay in the combination of mineral and organic fertilizer and the connection with high ability to absorb water. This work is a complex study covering all aspects of this type of composite materials: swelling and water absorption, release of mineral and organic fertilizers, repeated leaching (washing) of nutrients and application of prepared composite materials in pot experiments.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Chemicals

Eight different samples of superabsorbent polymers were synthesized through the rapid solution polymerization of partially neutralized acrylic acid (AA; Sigma Aldrich, St. Louis, MO, USA) under normal atmospheric conditions. Potassium peroxydisulfate (KPS; Sigma Aldrich, St. Louis, MO, USA) was used as an initiator and *N,N*-methylenebisacrylamide (MBA, Sigma Aldrich, St. Louis, MO, USA) as a crosslinking agent. Powders of potassium lignohumate (LH; Amagro s. r. o., Prague, Czech Republic) and NPK 20-8-8 (NPK, Lovochemie a.s., Lovosice, Czech Republic).

2.1.2 Preparation of superabsorbents

Weight quantity of AA (57 g) was dissolved in distilled water (100 cm^3). AA solution (25 cm^3) was neutralized by 10 cm^3 of 8.5M potassium hydroxide solution (KOH, Penta). Powders of LH and NPK were dispersed in this mixture and crosslinked by MBA (0.016 g). Then the initiator KPS was added (0.5 g). The mixture was continuously heated and stirred until reaching of cca 85 °C then highly viscous mixture was removed from the beaker and replaced to an oven for 24 hours which was settled up on 80 °C. Dried product was crushed by hammer into small pieces (Mo *et al.* 2006). The compositions of prepared samples are described in detail in Tables 1 and 2.

2.2 Methods

2.2.1 Releasing experiments

Samples in form of xerogel were mixed with distilled water in the ratio 50 mg : 100 cm^3. Releasing of active substances was monitored in time by means of several methods. The time development of pH and conductivity was measured using a S47 SevenMulti pH and conductivity meter (Mettler Toledo, Greifensee, Switzerland). The amounts of released K and P was determined by means of ICP-OES (an Ultima 2 ICP-OES spectrometer, Horiba, ThermoFisher Scientific, Waltham, MA, USA). Concentrations of anions (NO_3^- and PO_4^{3-}) were monitored using (a 850 Professional IC Anion-MCS ion chromatography system, Metrohm AG, Herisau, Switzerland).

The release of LH was measured by means of an U-3900H UV/Vis spectrometer (Hitachi, Tokyo, Japan). In order to determine the amounts of N, P and K in LH and NPK, their solutions in distilled water (1 g/dm^3) were analyzed by means of ICP-OES (Horiba Ultima 2, Thermo Fisher Scientific, Waltham, MA USA) and ion chromatography (see above).

2.2.2 Leaching experiments

This experiment was done in order to determine the release of nutrients in repeated leaching of superbsorbents. Samples in form of xerogel were mixed with distilled water in the ratio 400 mg : 100 cm^3. After one hour, the leachate was decanted and replaced by 100 cm^3 of fresh distilled water. Whole process was repeated fifteen times. Obtained leachates were analyzed by the same way as in the case of releasing experiments.

2.2.3 Pot experiments

The model soil was prepared by mixing of peat (200 g), kaolin (120 g), silica sand (1660 g) and $CaCO_3$ (20 g). Corn seeds were extracted in 0.05M NaClO (5 min) in order to remove pickling agent and washed by distilled water. After 24 hours, the seeds were placed separately into curled up paper towels and covered by distilled water (5 days at 28 ± 2 °C). The germinated seeds were placed into the 250 g of model soil mixed with 1 g of xerogel and 40 cm^3 of water (3 seeds into 1 pot). The pots were placed in the growing box at 26 ± 2 °C with periodical watering. Shoot and root were separated and individually measured.

All experiments were triplicated and average values are presented in this study.

3 RESULTS AND DISCUSSION

3.1 Releasing experiments

Active components were released from hydrogels progressively (Figure 1). In beginning, the release was partially influenced by the swelling of hydrogel. The cumulative amount of the nutrient increased in time up to the achievement of stable concentration in the leachate. The content of potassium in samples was a combination of potassium coming from NPK and LH, added in samples as active components, and KOH and KPS used in the preparation of hydrogels. While the amounts of potassium coming from KOH and KPS were the same for all samples, they differed in the contents of NPK and LH. Sample A contained lower amount of NPK and no LH. The release of K from this sample corresponded with its content in the hydrogel. The majority of potassium was released in one week and the following release rate was very low. The increased content of NPK in hydrogels B and D thus resulted in the increased cumulative release of potassium. In this case, the addition of LH had negligible influence (samples B and D). In contrast, the addition of LH supported the release of K from sample C. The release of K from samples B, C, D and H was retarded after two or three weeks (Figure 1a). The release of P (Figure 1b) and NO_3^- (Figure 1c) was strongly dependent on the contents of NPK. In the case of increased content of NPK (samples B and D) the release was prolonged up to four weeks. The addition of LH had negligible influence on the release of P and $NO_3^-$from samples B and D. In contrast, The release of P from sample C was prolonged in the comparison with the sample A containing the same initial amount of NPK. The release of LH (which was primarily added in hydrogels as a source of organic carbon) was partially suppressed by the higher content of NPK (sample D). In this case, the release was stopped after three days, while it continued for more than two months in samples C and H (Figure 2). The release of nutrients from all used samples was connected with a strong increase of conductivity and weak increase in pH values.

Erro *et al.* (2007) developed a fertilizer based on humic substances and NPK (without polymers). Their results showed that nutrients were released into water in about 30 minutes (K and N) or two hours (P), while the release of ammonia ions was slower with a maximum achieved in several days. The amount of nitrogen released was enhanced by the addition of straw. Du et al. (2006) studied the release of K, N, and P from polymer coated fertilizers which could be released up to two months in the dependence on the temperature and thickness of surface polymer layer. Nutrients release was the fastest into water, than into water saturated sand. Similarly, Davidson and GU (2012) studied the release of nutrients from fertilizers coated e.g.by polyactic acids and wax. The release of urea was stopped in 20 days in both cases. Zhan *et al.* (2004) investigated the release of phosphate from superabsorbent polymer based on PVA, H_3PO_4 and Na_2CO_3 provided. The proportion of released phosphate increased during first day up to 26.5 %. No release was detected during second day. After that the release increased from 26,5 to 47 % during third day of experiment. On the 28th day, the total proportion of released phosphate was 79 %. The authors concluded that the results were due to the enrichment of the surface layer and the slow diffusion of phosphate encapsulated inside the material. In contrast, the release of sodium humate from superabsorbents based on AA, acrylamide and attapulgite was stopped after several days in dependence on the content of humate (Zhang *et al.* 2005). However, the use of acrylamide is problematic because of its toxicity (Matoso *et al.* 2019; Spencer *et al.* 2018; Spencer and Schaumburk 1974a, 1974b). We performed some experiments with superabsorbents containing acrylamide but the results did not show any improvement in their properties in comparison with samples used in this work.

3.2 Leaching experiments

The gradual leaching of active components from hydrogels can be characterized by measurement of conductivity. Obtained results are shown in Figure 3. In our study, the development of amounts of individual ions in leachates corresponded with conductivity values which did not change after seven washing cycles. An exception was the leaching of LH which can be extracted for ten washing cycles. This means that if the hydrogel is applied in soil with very good supply of water the active components can be repeatedly washed out from the surroundings of plant roots. The leaching of nutrients from fertilizer prepared and studied by Erro *et al.* (2007) was in most cases faster. The release of phosphate was completed after three cycles and that of potassium after for cycles. In contrast, no nitrogen was leached after seven cycles.

3.3 Pot experiments

The influence of superabsorbent application on corn growth is shown in Figure 4. A possitive effect on corn height was observed for all prepared samples. As can be seen in Figure 4, the growth of shoots was much slower in soil without superabsorbent and no changes in plant height were observed after two weeks. In contrast, higher content of NPK in superabsorbent enriched by LH had the most positive effect on corn growth. It was confirmed that the presence of LH in superabsorbent supported corn growth but it was lower in comparison with the application of superabsorbents containing NPK. This effect was partly the result of better water management and partly the result of the slow supply of nutrients from NPK and LH. The improvement of plant growth as a result of the more effective utilization of water was confirmed also by Raju and Raju (2001), Abedi-Koupai and Asadkazemi (2006), and Dorraji *et al.* (2010) who applied superabsorbents without addition of nutrients. The application of fertilizer without superabsorbent polymer supported the growth of wheat (Erro *et al.* 2007), but the growth was small than that induced by composite materials in our study. Chatzistathisa *et al.* (2020) compared effects between manure application and a controlled-release fertilizer on the growth and nutrient uptake of *Olea europaea* L. They concluded that the total plant biomass and total per plant macronutrient were significantly higher in the case of controlled-release fertilizer due to higher biomass production. Zhao *et al.* (2019) demonstrated that the combination of fertilizers with superabsorbens improved soil fertility, increased soil nutrient supply capacity, and yield of tomatoes. Four different types of controlled-release fertilizers were used in container-grown ornamental plants (Japanese spirea) and abrovitae by Grable *et al.* (2017). The most positive effect on the growth was observed for the prototype blends with experimental polymer coatings. They produced a deeper green foliage and higher shoot dry weight in comparison with others. Similarly, Girardi *et al.* (2005) observed positive effect of slow-release fertilizers on growth of containerized citrus nursery trees and Silva et al. (2017) concluded that associating organo-mineral fertilization with the organo-mineral fertilizer slow release of nutrients can ensure greater yield of lavender essential oil and had a noticeable impact on its chemical composition.

Our results showed that higher contents of NPK in superabsorbent without LH (sample B) had slightly inhibiting effect. This could be the result of a greater release of nutrients which cannot be effectively utilized in the first days of growth. A similar effect was observed by Nnadi and Brave (2011) who used polymers based on carboxymethyl cellulose sodium salt and several commercial starch powders. Higher amounts of this polymer in soil resulted in lower plant height as well as smaller plant weight.

In contrast, the combination of LH and higher amount of NPK had a synergic effect on corn growth. Material containing only LH (sample H) affected corn growth positively in comparison with plant grown withaut application of superabsorbent but its effect was weaker.

Figge *et al.* (1995) used expanded clay and porous ceramics (as materials to enhance water management) in combination with manure, KH_2PO_4, and KCl (as nutrients) in order to improve plant growth in minespoils. They observed that germination and growth of plants were improved if the materials were applied on the surface but no benefit was observed in the case of mixing.

The influence of our composite materials on root growth was different. The best results were obtained with sample A containing only a small content of NPK without LH. It seems that water management is more important for root growth than the addition of nutrients. The addition of LH had negative effect in the case of low NPK content. Root growth was slightly improved if a higher content of NPK was combined with the addition of LH. In contrast, the results with sample H which contained LH without NPK were the best (with the exception of those with sample A). The negative effect of humic substances on the growth of plants and roots was described by Rastghalam *et al.* (2011). The effect was more important in the case of plant growth (in comparison with roots). In contrast, Zhang *et al.* (2005) observed that the roots and stems of grass were sturdier if superabsorbent containing sodium humate was applied in soil (compared with grass grown without such application). This discrepancy can be explained by the existence of an optimal level of humic addition. If the addition of humic substances increases above, a certain threshold, negative effects on nutrient uptake and plant growth can be observed (Pannucio *et al.* 2001).

4 CONCLUSIONS

In this work, several different superabsorbents containing lignohumate and conventional mineral fertilizer (NPK) were prepared. Their swelling behaviour, release of nutrients, periodic washing out and the influence on the growth of corn were studied. It was found that the swelling was relatively fast and it was completed in 24 h. While the addition of NPK surpressed the water absorption, the sweling was supported by the presence of LH. Simultaneously, the swelling influenced the release of nutrients from superabsorbents during the first day. The release of mineral nutrients corresponded with their contents in different samples. The higher content of NPK resulted in the prolongation of the release of nutrients. The addition of LH had negligible influence on the release of P and N. In contrast, the amount of released K incresed due to the potassium content in added LH. On the other hand, the release of LH was partially suppressed by the higher content of NPK. In leaching experiments, realised be repeated washing out of active substances from hydrogels, the mineral nutrients were washed out after seven cyles and LH after ten cycles. In general, the application of superabsorbents supported growth of corn. Better water management and a slow supplying by nutrients had possitive effect on the height of plants. The length of roots is probably influenced more by better water management. The combination of superabsorbent polymers with NPK and LH in suitable amounts can improve soil properties, water management, nutrient uptake and growth of plants. Such materials can be utilized mainly in problematic areas with dry soils and low levels of organic matter and nutrient elements.

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Table 1. Composition of superabsorbent hydrogels – starting materials

Sample	A	B	C	D	H
AA (g)	14.25	14.25	14.25	14.25	14.25
MBA (g)	0.016	0.016	0.016	0.016	0.016
KPS (g)	0.5	0.5	0.5	0.5	0.5
KOH (g)	4.75	4.75	4.75	4.75	4.75
NPK (g)	0.6602	6.602	0.6602	6.602	0
LH (g)	0	0	1	1	1
H_2O (g)	35	35	35	35	35

Table 2. Composition of superabsorbent xerogels – active components

Sample	A	B	C	D	H
K (% wt.)	17.34	14.91	17.57	15.17	17.92
N (% wt.)	0.67	5.07	0.82	5.02	0.20
P (% wt.)	0.11	0.88	0.11	0.85	0.00
LH (% wt.)	0.00	0.00	4.72	3.69	4.87

FFIGURE CAPTIONS

Fig. 1. The release of K (left) and P (right) from studied materials in the dependence on time

Fig. 2. The release of LH from studied materials in the dependence on time

Fig. 3. The conductivity of aqueous leachates for samples A and C in the dependence on washing cycle

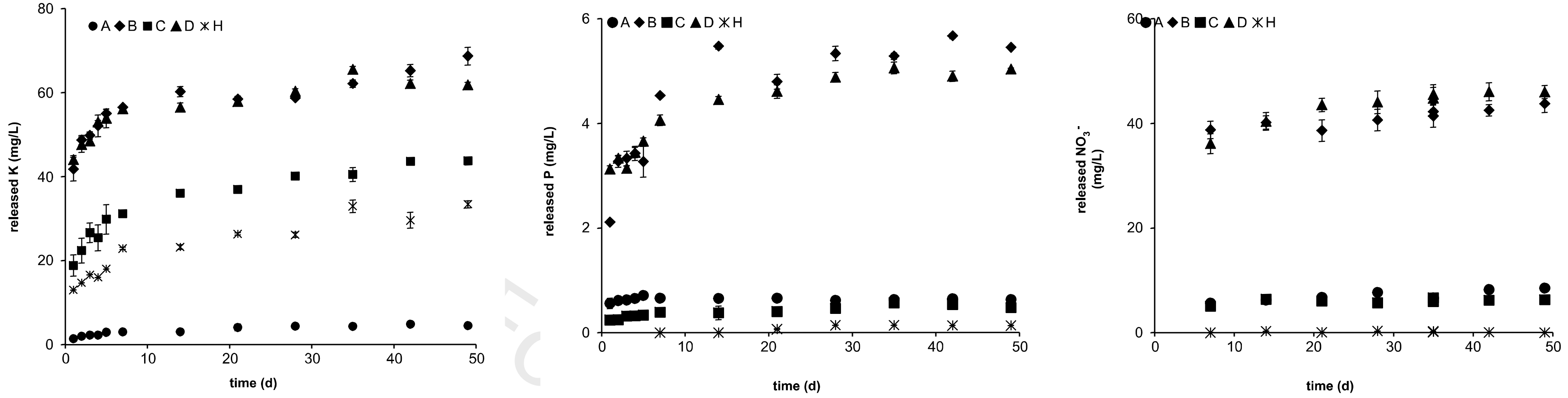
Fig. 4. The time development of the height of corn (left) and the final lengths of roots for the used superabsorbents (right). The blank experiment is without application of superabsorbent

Supplementary 1. Swelling experiments

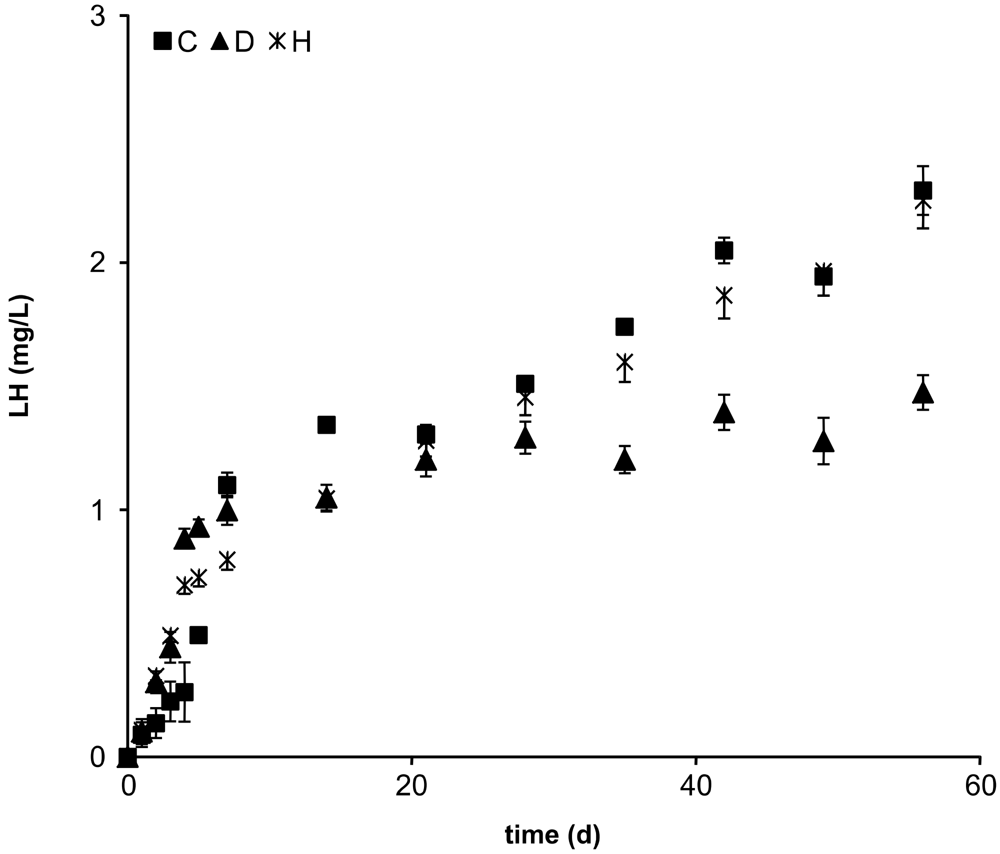
Supplementary 2. Pictures of xerogels and swollen hydrogels

Supplementary 3. The time development of plant growth

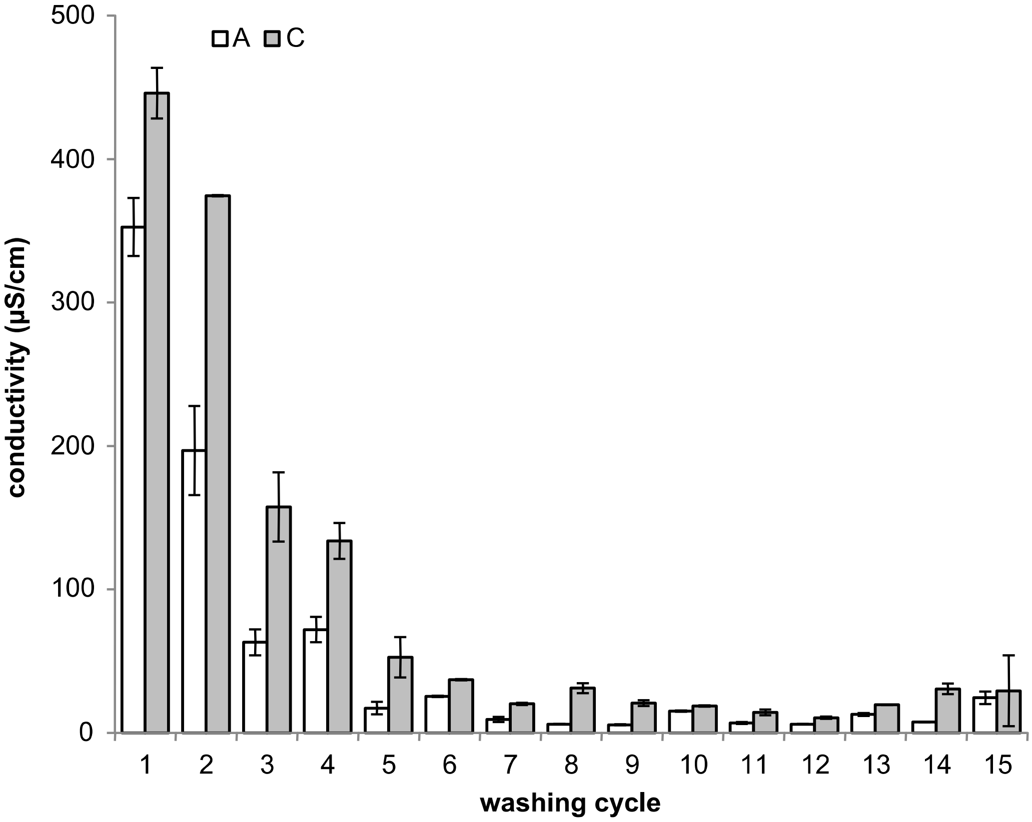
Supplementary 4. The time development of root growth

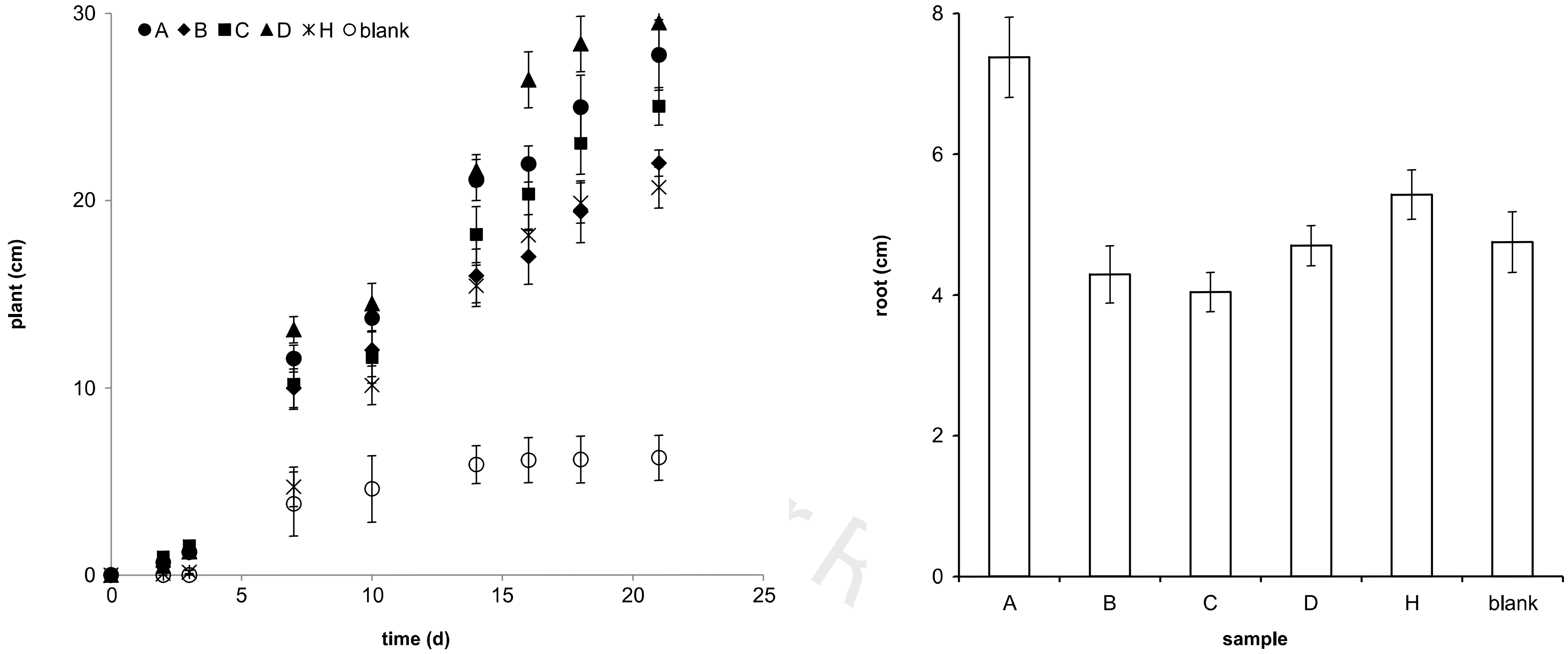


released K (mg/L)
time (d)
A B C D H
released P (mg/L)
time (d)
A B C D H
released NO_3^- (mg/L)
time (d)
A B C D H



■C ▲D ⁎H
LH (mg/L)
time (d)
0
1
2
3
0
20
40
60


A
C
conductivity (µS/cm)
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
washing cycle



A B C D H blank
plant (cm)
time (d)
root (cm)
sample
A
B
C
D
H
blank

Supplementary 1. *Swelling experiments*

Samples in form of xerogel were mixed with distilled water in the ratio 50 mg : 100 cm^3. The swelling degree was determined on the basis of weight increase after 24 hours.

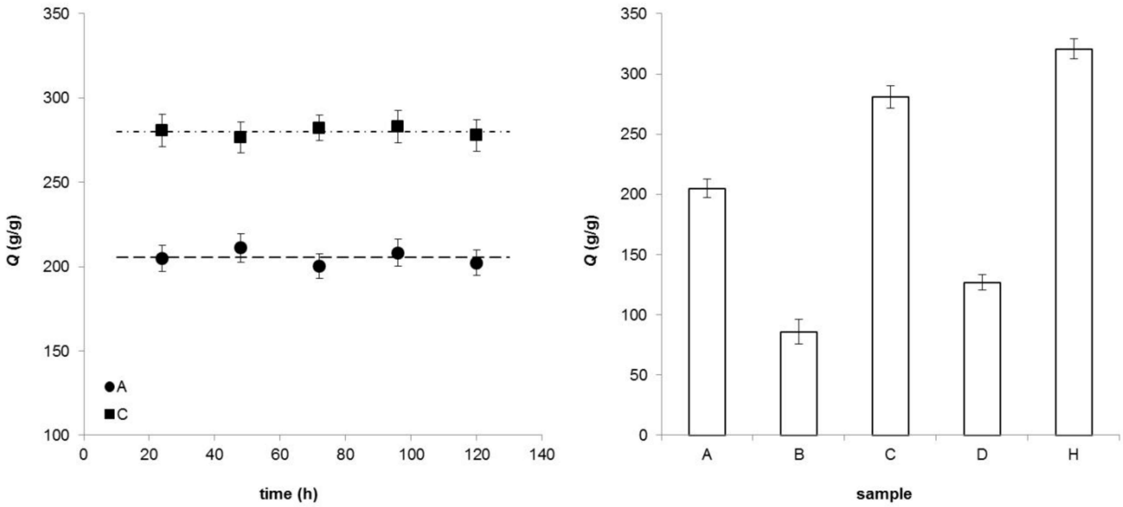
The weight increase caused by the absorption of water was expressed as the so-called swelling degree Q. It was calculated as the amount of absorbed water (expressed as the difference between the weight of hydrogel $m_{hydrogel}$ and the weight of xerogel $m_{xerogel}$) normalized on the weight of xerogel (Wu *et al.* 2000; Raju *et al.* 2002; Li *et al.* 2004a, 2004b, 2005; Chu *et al*., 2008; Dadhaniya *et al.* 2006; Marandi *et al.* 2006; Mo *et al.* 2006; Zhang *et al.* 2006a, 2006b, 2007; Liu *et al.* 2007; Gao *et al.* 2013):

$$Q = \frac{m_{\text{hydrogel}} - m_{\text{xerogel}}}{m_{\text{xerogel}}}.$$

The swelling degrees obtained for prepared samples are showed in Figure 1. We can see that swelling was completed in one day therefore the values obtained after 24 h were considered as the swelling characteristics of the samples. This relatively fast equilibration agrees with the findings of other authors (Wu *et al.* 2000; Raju *et al.* 2002; Dadhaniya *et al.* 2006). Dadhanyia *et al.* (2006) observed maximum swelling degree after 20 h. Some superabsorbent polymers prepared by Raju *et al.* (2002) achieved the maximum swelling degrees instantly, others in 45 minutes. Similarly, equilibrium was observed after 30-60 minutes for starch-*graft*-polyacryl-amide/kaolinite composites (Wu *et al.* 2000). Some authors reported that the time taken for equilibrium swelling increased with the increase in particle size (Raju *et al.* 2002; Marandi *et al.* 2006). The results presented in this work are average values for polydisperse systems.

The swelling of all prepared samples was relatively pronounced. The lowest values were obtained for samples containing higher amounts of NPK which caused the depression of swelling. In contrast, the addition of LH supported the absorption of water which resulted in the greatest degree of swelling in sample H (without NPK) and an increase in swelling degree for samples containing combination of NPK and LH (C and D) in comparison with samples enriched by NPK alone LH (A and B). The positive effect of humic substances on swelling was observed in recent works (Li *et al.* 2005; Chu *et al.* 2008; Gao *et al.* 2013). Superabsorbents containing potassium or sodium humate (Li *et al.* 2005; Liu *et al.* 2007; Gao *et al.* 2013) evinced both a higher swelling rate and a greater amount of absorbed water.

However, some authors noted that the efficiency of humic addition to enhance swelling reached a maximum value that the addition of higher amounts of humic substances had no additional influence on swelling (Gao *et al.* 2013) or, conversely, began to have a negative influence (Li *et al.* 2005; Mo *et al.* 2006; Liu *et al.* 2007; Chu *et al.* 2008). A recommended allowance of humic substances differed between 3 and 30 % wt. Mo *et al.* (2006) showed that with the addition of superabsorbent (1% wt.) water retention in soil increased 31 times, and 40 times with the addition of superabsorbent enriched with sodium humate. The increase in moisture in soil enriched by superabsorbent polymers was observed in recent work (Bai *et al.* 2010). Our content of LH was in the lower limit. The increase in ionic strength usually suppressed the ability of hydrogel to absorb water and their degrees of swelling decreased in the presence of salts (Liu *et al.* 2007; Chu *et al.* 2008).



The time development of the swelling degree *Q* for samples A and C (left) and the values of *Q* after 24 h for all studied samples (right)

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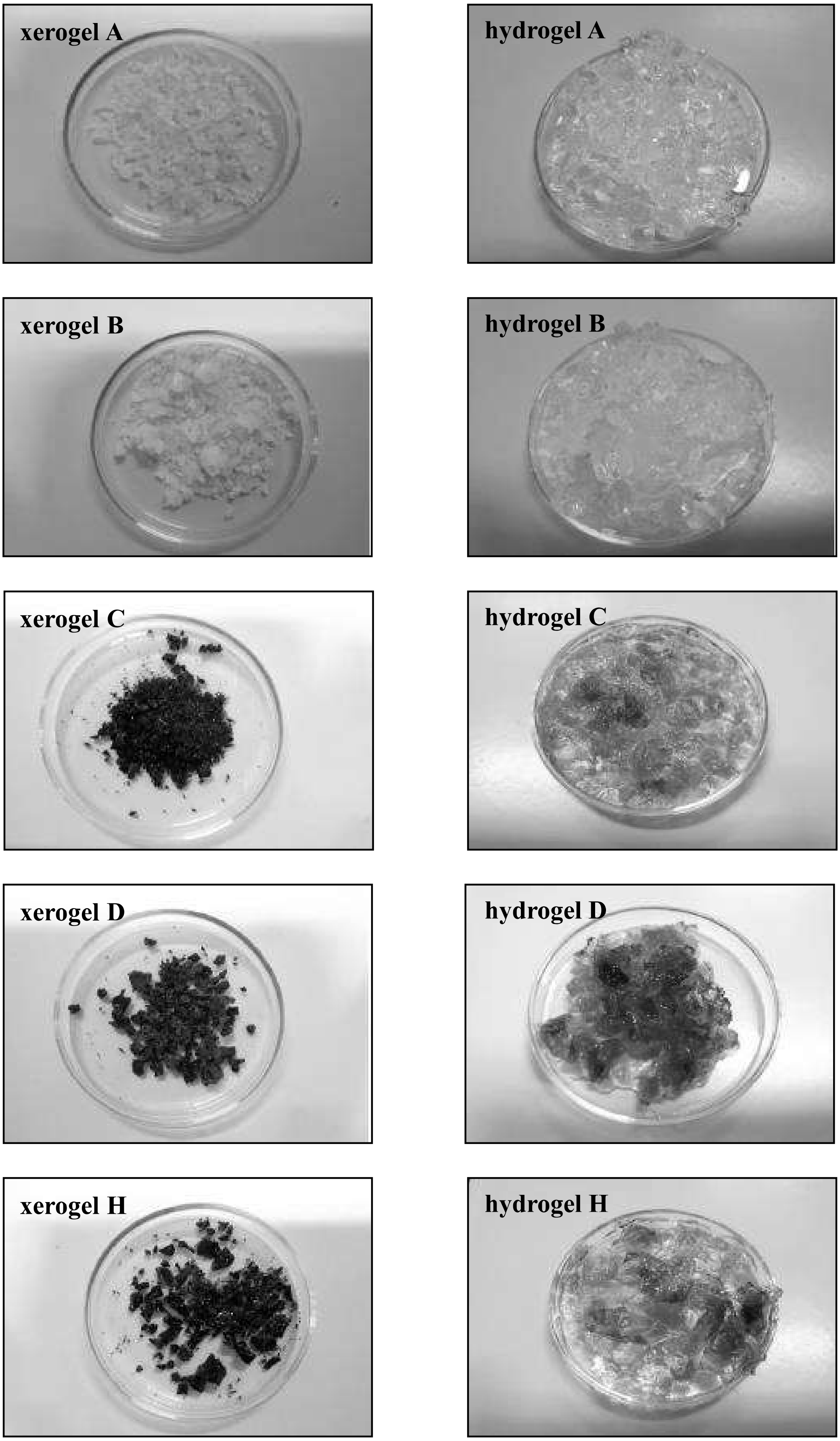
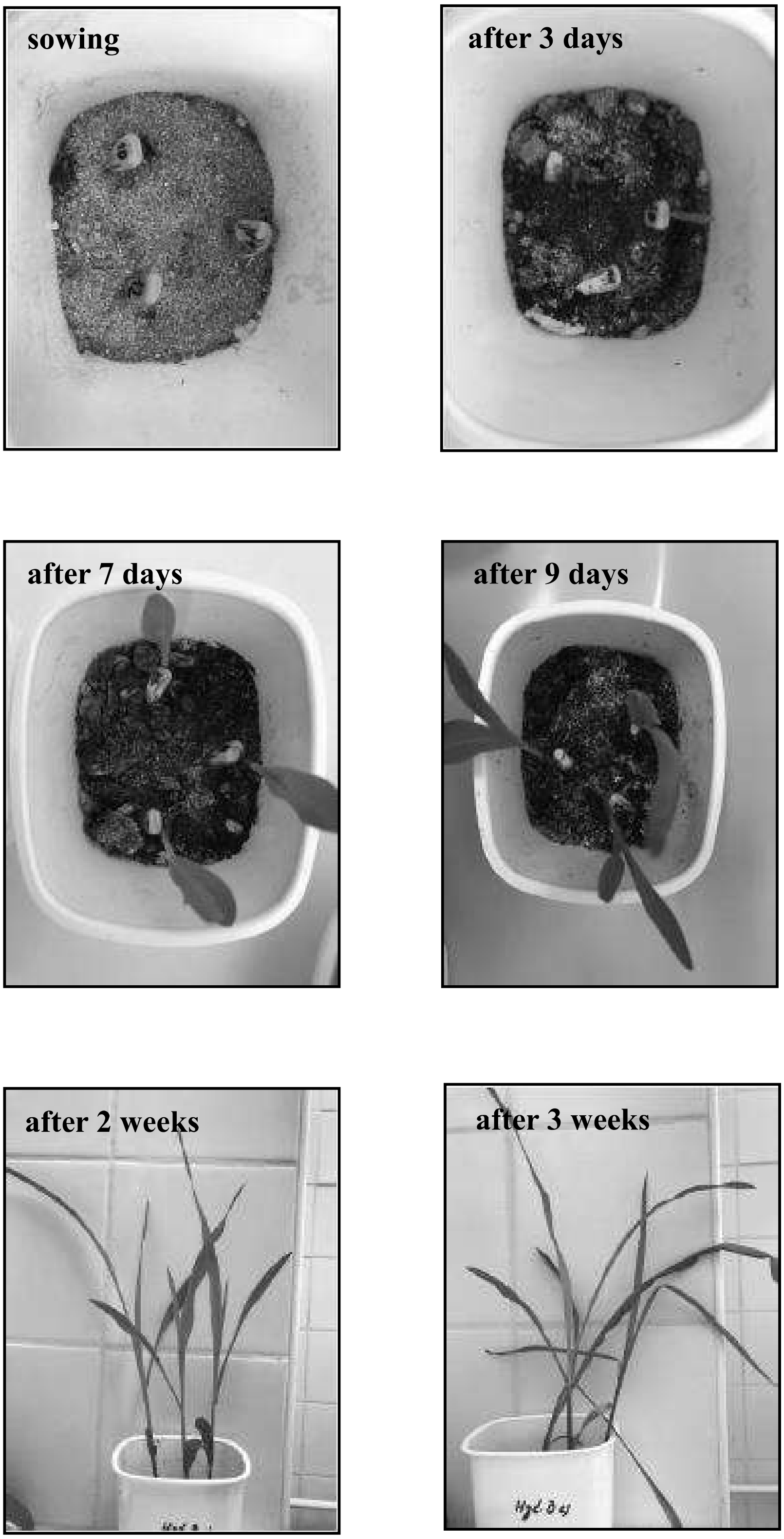


Supplementary 2. *Dry xerogels (left) and swollen hydrogels (right)*

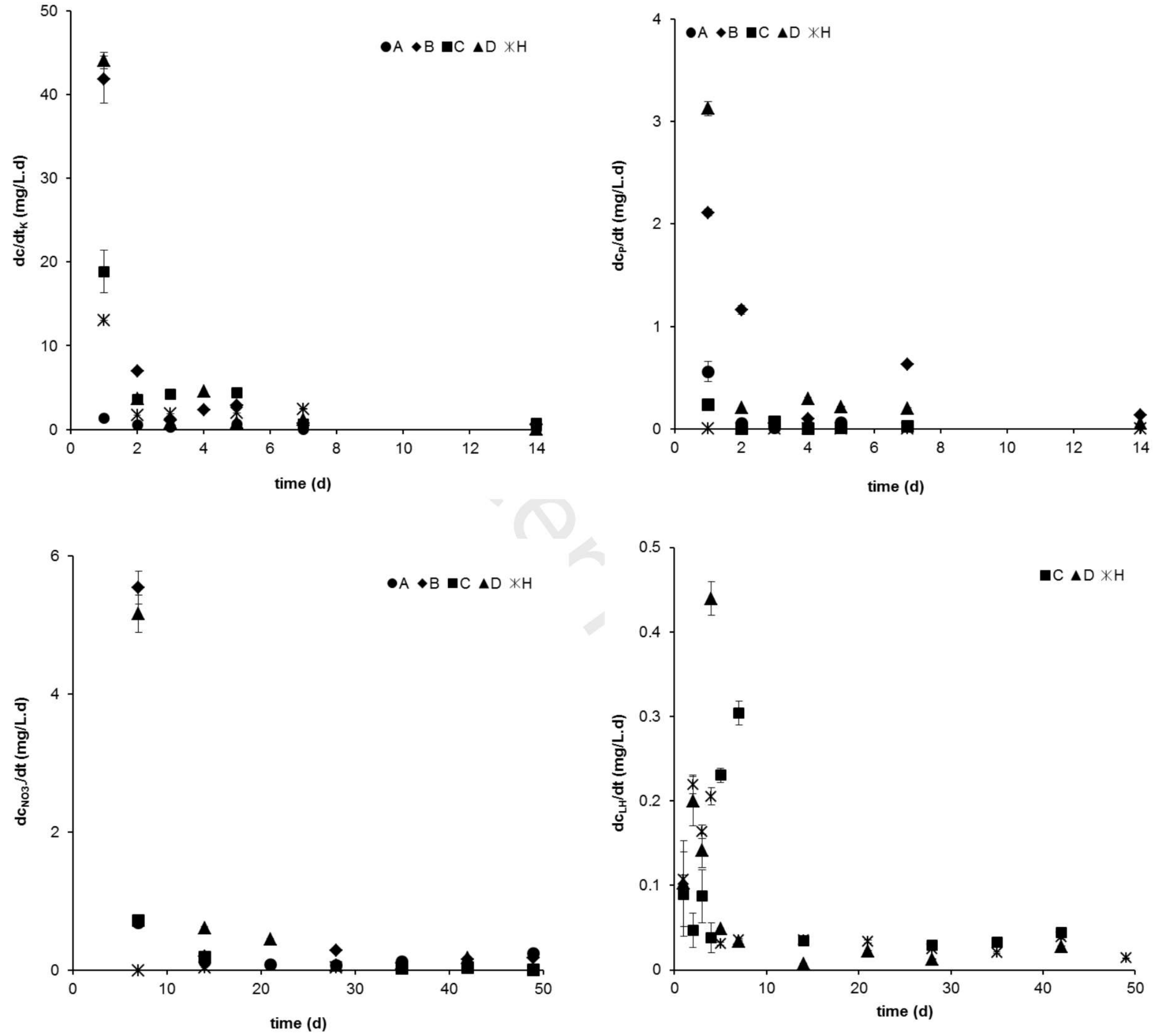
Supplementary 4. *The time development of root growth*



Supplementary 3. *The time development of plant growth*

Supplementary 5. *Release rate*

The rates of release were calculated as the change of the concentration in the leachate in given time. As can be seen, the highest rates were observed in the initial phase of experiment and gradually decreased. The main decrease was recorded in first two weeks.



The time development of the release rates dc/dt for K, P, NO_3^- and LH.