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Biodegradable Superabsorbent Hydrogel IncreasesWater Retention Properties of Growing Media and Plant Growth

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Abstract

Superabsorbent hydrogels are a particular class of gels, obtained by chemical stabilization of hydrophilic polymers in a tridimensional network. Hydrogels have been widely proposed over the last 40 years for agricultural use with the aim to ameliorate water availability for plants, by increasing water holding properties of growing media (soils or soilless substrates). Most of the traditional hydrogels on the market are acrylate-based products, thus not biodegradable. Due to the increasing attention for environmental protection issues, biodegradable hydrogels arise lively interest for potential commercial application in agriculture. In this study, we evaluated a novel class of cellulose-based superabsorbent hydrogels, totally biodegradable and biocompatible, for agricultural use. The objectives of the tests carried out were: 1) to verify the ability of the hydrogel to modify the water retention properties of the growing media (soils and soilless substrates); 2) to study the effects on the growth of plants grown on media amended with the hydrogel. Water retention curve of a sandy soil amended with 0, 0.5, 1.0 and 2.0% (w/w) of hydrogel was determined using a Richard's pressure plate apparatus. The hydrogel modified the soil water retention properties. The soil moisture at field capacity increased with the highest hydrogel percentage up to 400% compared to the not amended soil, and at wilting point (-15 bar) was similar to that at field capacity of the not amended soil. When added to perlite, a low water holding capacity soilless substrate, 1 or 2% (w/w) of hydrogel increased the container capacity of 28 and 48%, respectively, with no decrease of air capacity. Tests revealed absence of phytotoxicity of the hydrogel, and cultivation trials on cucumber (on soil) and sweet basil (in soilless conditions) showed a general overall enhancement of plant growth and quality when hydrogel was added to growing media. The tested hydrogel showed to be suitable for potential use in agriculture. Its employment should be further evaluated under a cost-effective perspective.

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Keywords: agriculture; soil moisture release curve; perlite; sweet basil; cucumber.

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1. Introduction

Synthetic hydrophilic polymers (hydrogels) are a particular class of gels, obtained by chemical stabilization of hydrophilic polymers in a tridimensional network. Hydrogels are characterized by the ability to absorb and retain quantities of liquids (swelling) much greater, in terms of weight, than the initial weight of the material (Horie et al., 2004).Hydrogels have been widely proposed for horticultural purposes over the last 40 years with the basic idea to use the swelling and water release properties to ameliorate water availability for plants. Several possible agricultural applications of hydrogels have been defined (Zohuriaan-Mehr and Kabiri, 2008). Hydrogels have been successfully used as soil improvers to increase the water-holding capacity and/or nutrient retention of sandy soils, with a possible reduction of irrigation frequency, compaction tendency and water run-off (Abd El-Rehim et al., 2004). Hydrogels found applications as slow release fertilizers (Teodorescu et al., 2009), although addition of fertilizers salts generally implies a reduced hydration of polyacryamide gels and affects physical properties of gel-amended media (Bowman et al., 1990). Hydrogel-based pesticide release devices have also become very popular, and a number of patents based on this particular agricultural applications of hydrogels have been developed (Rudzinski et al., 2002).

Most of the traditional hydrogels on the market are acrylate-based products, thus not biodegradable and regarded as potential pollutants for the soil. Due to the increasing attention for environmental protection issues, biodegradable hydrogels arise lively interest for potential commercial application in agriculture (Cannazza et al., 2014).

In the present study, we evaluated a novel class of cellulose-based superabsorbent hydrogels, totally biodegradable and biocompatible (Demitri et al., 2008), for agricultural use. The objectives of the tests carried out were: 1) to verify the ability of the hydrogel to modify the water retention properties of the growing media (soils or soilless substrates); 2) to study the effects on the growth of two vegetable crops - cucumber (on soil) and sweet basil - grown on media amended with the hydrogel.

2. Material and Methods

The biodegradable superabsorbent cellulose-based hydrogel used in this study was obtained in the framework of ColGel Project (contract grant number L297/9400, Italian Ministry of University and Research). Briefly, two cellulose derivatives, sodium carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC), were used for superabsorbent hydrogel preparation; citric acid (CA), a cross-linking agent able to overcome toxicity and costs associated with other cross-linking reagents, was selected in a heat activated reaction. Details of the chemical aspects of this novel hydrogel are reported by Demitri et al. (2008).

2.1. Test 1: Effects of hydrogel on the moisture release curve of a sandy soil

The purpose of this test was to evaluate the effect of the hydrogel amendment on the moisture release curve of a sandy texture soil. A typical sandy soil(91.5% sand, 4.2% silt and 4.3% clay) from an agricultural area of the Apulia region (Zapponeta– FG, south-eastern coast of Italy), characterized by intense vegetable production industry, was used. Moisture release curves of soil amended with increasing percentages of the polymer (0, used as untreated control, 0.5, 1 and 2% w:w) were determined using a Richard's pressure plate apparatus. Five soil water potential values (-0.1, -0.33, -1.0, -5.0 and - 15.0 bar, corresponding to pF 2.0, 2.5, 3.0, 3.7 and 4.2, the latter representing the conventional "wilting point") were tested and the soil moisture at the different potential values was measured gravimetrically according to the following equation:

$$GWC\ (\%) = ((W_w - W_d)/W_d)*100 \qquad (1)$$

GWC = gravimetric water content on a dry weight basis;
W_w= wet weight of the soil sample at a specific water potential value;
W_d = dry weight (105 °C) of the soil sample.

Measurements at each water potential valuefor each of the soil and hydrogel combinations were replicated on threee samples for a total of 60 samples analyzed.

2.2. Test 2: Effects of hydrogel on hydrological and physical properties of perlite

The objective of this test was to determine the effects of the hydrogel on some of the most important hydrological and physical properties of perlite, under an agronomic point of view. This material, characterized by high porosity and relatively low water holding capacity, was selected as one of the most used component for soilless growing media preparation. A rapid method for determining physical properties of undisturbed substrate (Bragg and Chambers, 1988) was used in the test. Pots (1300 mL volume, V_1) were filled with perlite (Agrilit 3, Perlite Italiana), perlite + 1% and perlite + 2% of hydrogel (percentages of hydrogel are expressed on a weight basis, considering the moisture of the substrate, approximately 0.5%, as it was on the bag at the moment of the use). Three pots (three replications) per each of the perlite and hydrogel combinations were used. Briefly, the pots filled with the substrates were accommodated in a tank and subsequently submerged to the soil line with water. Pots were left submerged for 24 h, then subjected to three cycles of submersion (30 min) and run-off (60 min). After the last cycle of submersion, holes in the bottom of the submerged pots were plugged before their removal from the tank. The weight of the saturated substrate (W_w) was determined The holes were unplugged and the drainage water was measured (V_2). After this, pots were placed in an oven at 105 °C until reaching a constant weight, and the dry weight of the substrate (W_d) was determined. Bulk density (BD), water container capacity (WCC), air filled porosity (AFP) and total porosity (TP) were determined, according to the following equations:

$$BD\ (g{\cdot}cm^3) = W_d / V_1 \quad (2)$$
$$WCC\ (\%\ volume) = ((W_w - W_d) / V_1) * 100 \quad (3)$$
$$AFP\ (\%\ volume) = (V_2 / V_1) * 100 \quad (4)$$
$$TP\ (\%\ volume) = AFP + WCC \quad (5)$$

Data were subjected to one-way analysis of variance (ANOVA) using the general linear model procedure for a completely randomized design (SAS Institute, Cary, NC); means were separated by LSD test with $P \leq 0.05$ considered to be statistically significant.

2.3. Test 3: Effects of hydrogel on plant growth

A phytotoxicity test and two cultivation trials were carried out to evaluate the absence of phytotoxicity of the hydrogel and the effects of growing medium (soil or soilless substrate) amended with hydrogel on growth and physiological traits of plants.

Phytotoxicity test

The phytotoxicity test was performed according to Zucconi et al. (1985). Seeds of radish (*Raphanus sativus* L. var. *radicula* Pers.), cucumber (*Cucumis sativus* L.), alyssum (*Alyssum* spp.) and Centaurea (*Centaurea* spp.), were placed in Petri dishes (15 seeds per dish). Dishes were filled with 10 mL of distilled water (control) or with hydrogel (previously reduced in powder) saturated with water. Dishes were placed in a growth chamber (Conviron PGW 36) at 25 °C for 72 h in dark conditions. Six replications (dishes) were adopted per each treatment of a single species. The germination index (G_{index})was determined according with the following equation:

$$G_{index} = ((G / G_o) * (L / L_o)) * 100 \quad (6)$$

G and L = number of germinated seeds and root length in presence of hydrogel, respectively;
G_0 and L_0 = number of germinated seeds and root length in the control conditions, respectively.

Cultivation trials

Both the cucumber and basil cultivation trials were carried out in a greenhouse at the experimental farm “La Noria” (Mola di Bari) of the Institute of Sciences of Food Productions - National Research Council (CNR – ISPA).

Cucumber trial. Plastic pots (9 L volume) were filled with a sandy soil amended with 2 $g \cdot L^{-1}$ of hydrogel or not. Pots were placed on trough benches raised from the ground. Fertigation was provided with a drip-irrigation system and automated with a timer. The irrigation schedule was adjusted in order to bring back the substrates at the maximum water holding capacity at each irrigation (this event made known by the appearance of drainage from the pots). Cucumber (cv. Marketer, Vilmorin) seedlings were transplanted at the 3rd true leaf stage, and grown according to the local practice for this crop. The experiment provided four treatments: NO-HYDROGEL (not amended soil); HYDROGEL (soil amended with hydrogel); NO-HYDROGEL-STRESS and HYDROGEL-STRESS (plants of both treatments were subjected to suspension of irrigation for 24 h at 34 days after transplant (DAT) and then used for measurements, with the specific objective to assess the effects of hydrogel on plants subjected to controlled water stress). A completely randomized block design was adopted, with three replications per treatment and each replication including five plants. On 35 DAT, plant height, total fresh biomass and leaf area were measured. The plant water status was assessed by measuring leaf dry matter percentage, water potential (using a Sholander pressure chamber), osmotic potential (using a Micro-osmometer, Automatic 13/13 DR – AUTOCAL, Roebling, Germany) and turgor potential (calculated as water potential – osmotic potential) on plants of treatments subjected to controlled water stress.

Data were subjected to one-way analysis of variance (ANOVA) using the general linear model procedure (SAS Institute, Cary, NC); means were separated by LSD test with $P \leq 0.05$ considered to be statistically significant.

Basil trial. Plastic pots (0.35 L volume) were filled with perlite (Agrilit3, Perlite Italiana), perlite + 3% hydrogel or perlite + 6% hydrogel (percentages of hydrogel are expressed on a weight basis, considering the moisture of the substrate as it was on the bag at the moment of the use, approximately 0.5%). Seeds (six per pot) of basil ('Grand Vert', Vilmorin) were sown and pots were placed on ebb-and-flow benches in greenhouse. Pots were manually overhead irrigated with water until the emission of the first true leaf, and subsequently subirrigated (ebb and flow technique) with a complete nutrient solution (NS). Irrigation schedule provided from three to nine fertigations per day, according to the growth stage of the crop. At each subirrigation event, substrates were allowed to absorb the NS for 15 minutes, then the NS left in the bench was collected and used for subsequent irrigations. Growth analysis to determine the total fresh weight of plants were performed at 46 and 63 days after sowing (DAS), the last representing the end of the crop cycle (commercial stage of plants). A complete randomized experimental design was adopted, with seven replicates per treatment and each replication including seven pots (subsamples).

Data were subjected to one-way analysis of variance (ANOVA) using the general linear model procedure (SAS Institute, Cary, NC); means were separated by LSD test with $P \leq 0.05$ considered to be statistically significant.

3. Results and discussion

3.1. Effects of hydrogel on moisture release curve of a sandy soil

The presence of the polymer in the sandy soil dramatically altered the soil water holding capacity (Fig. 1). At a suction pressure of pF 2.0 (-0.1 bar), hydrogel at the lowest dose nearly doubled the moisture content of the not amended soil, while at the highest hydrogel dose the water content exceeded 50%, which is even higher than a clay soil with a good structure characterized by considerable water retention capacity. In previous studies, the addition of traditional hydrophilic polymer to sandy soil changed the water holding capacity to be comparable to silty clay or loam soils (Johnson, 1984; Hutterman et al., 1999).

At soil field capacity (pF 2.5; -0.33 bar), the moisture percentage increased by 60% compared to the control with 0.5% hydrogel, was tripled by the 1% hydrogel and more than quadrupled with the highest dose of hydrogel (Fig. 1).

At a suction pressure of pF 3.0 (-1.0 bar), the water content of the soil amended with the polymer was always higher than the not amended control (increments of 25, 80 and 267%, respectively, with 0.5, 1 and 2% of hydrogel).

Finally, by applying a pressure of -15 bar (pF 4.2), no significant differences were observed between the control and the soil amended with the lowest hydrogel doses (0.5 and 1%), while with the highest dose of hydrogel (2%) the soil water content was 10.1%, similar to the moisture of the not amended soil at field capacity.

Therefore, the results show a good response of the medium supplemented with the polymer in terms of higher soil water content, especially at the higher potential values.Shahid et al. (2012) found that the water retention of a sandy loam soil was increased up to approximately 60 to 100% at field capacity with the application of 0.1 to 0.4 % (w:w) of a poly-acrylamide-based superabsorbent hydrogel, with the water retention increase depending on the quantity of the hydrogel. Similar results were demonstrated on a sandy soil amended with hydrogel, although a reduction of the hydrogel effect with increasing the soil salinity was outlined, confirming a common problem of hydrogels (Dorraji et al., 2010). Beside the positive effects that the increased water holding capacity of sandy soils could have on plant water availability, addition of hydrophilic polymer to poor water retention soils is a possible procedure that could prevent water loss in sandy soils due to drainage, with significant impact on the reduction of potential sources of groundwater pollution due to percolation phenomena of fertilizer solutions in areas of intense agricultural activity.

3.2. Effects of hydrogel on hydrological and physical properties of perlite

The results showed a clear influence of the hydrogel in increasing the container capacity (the maximum amount of water present in the substrate after saturation and at the end of the dripping), with a WCC increase of 27.9% and 47.7% compared to the not amended perlite, respectively, with 1 and 2% of the hydrogel, while no differences were observed among treatments with regard to AFP, BD and TP (Table 1).

The increase of the water retention capacity of the substrate under examination was achieved without compromising the high air capacity, which represents a distinctive feature of some granular substrates such as perlite. However, the water holding capacity of perlite is considered excessively low if compared with an ideal substrate (De Boodt and Verdonk, 1972; Abad et al., 2001), making necessary for most applications using this material in mix with components with higher water retention (i.e. peat). Effects of a novel biopolymer used for the amendment of a soilless substrate indicated a significant improvement of the water availability of soilless growing media (Singh et al., 2011). Although the obtained results are encouraging with regard to the possibility to ameliorate the water retention properties of porous soilless substrates, it should be taken into account that growing plants in soilless conditions implies the use of fertilizers solutions with the related increase of the overall salt level in the substrate. As reported by Cannazza et al. (2014), in a study focused on the same class of hydrogel used in the present research, the hydrogel swelling is reduced with increasing electrical conductivity; therefore,we can expect a reduced ability to improve the water retention capacity of the substrates in actual cultivation conditions, especially when the substrate electrical conductivity tends to increase with the progress of the crop cycle.

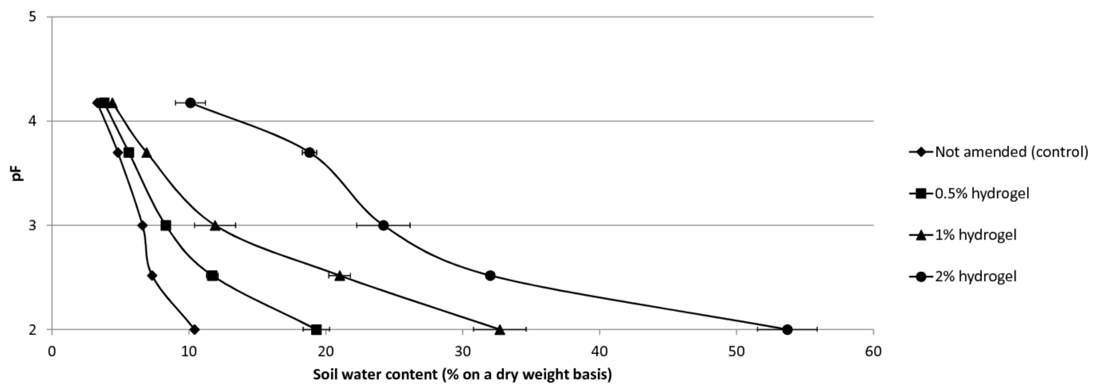

Fig. 1. Water retention curve of a sandy soil not amended or amended with 0.5, 1.0 and 2.0% (w:w) of a biodegradable hydrogel. Lateral bars represent ± standard error (n=3).

Table 1. Water container capacity (WCC), air filled porosity (AFP), total porosity (TP) and bulk density of perlite not amended or amended with 1 or 2% of hydrogel.

Substrate	WCC (% volume)	AFP (% volume)	TP (% volume)	BD (g/cm^3)
Perlite	28.3 c	44.2	72.6	0.141
Perlite + 1% hydrogel	36.2 b	38.9	75.1	0.136
Perlite + 2% hydrogel	41.8 a	37.5	79.3	0.134
Significance[1]	***	ns	ns	ns

[1]Mean values within columns followed by the same letters were not significantly different at 5% level according to LSD test (P= 0.05); ns, not significant; ***, significant at 0.1% level, respectively.

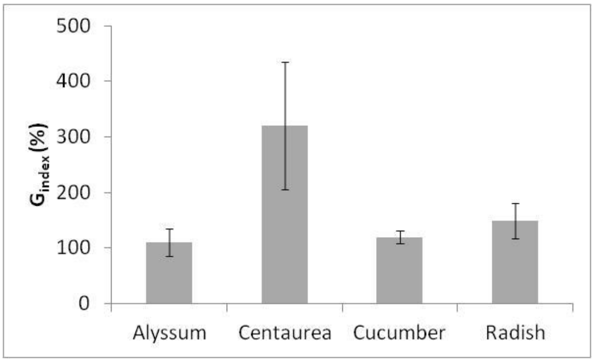

Fig. 2: Germination index (G_{index}) of four species germinated in presence of a biodegradable hydrogel. Vertical bars represent ± standard error. (n=6).

3.3. Effects of hydrogel on plant growth

Neither the seeds of vegetable or ornamental species showed any symptom of phytotoxicity in presence of the hydrogel. On average, the G_{index} was in fact well above 60% for all the four species tested (Fig. 2), this being the limit to consider not phytotoxic the superabsorbent polymer tested (Zucconi et al., 1985).The Centaurea showed a G_{index} very high since the root development and the average number of seeds germinated in the presence of hydrogel were significantly higher than the control.

Obviously, the absence of phytotoxicity represents the first requirement when approaching to the use of an innovative material as growing media component. Under this point of view, we can consider the use of this innovative hydrogel absolutely safe for plants.

Results from the cucumber cultivation trial showed an overall enhanced growth of plants subjected to hydrogel treatment at the moment of the analysis (Table 2).With the hydrogel, the plants had higher height (180 vs 158 cm), total fresh biomass (1753 vs 913 g), leaf, stems and fruit fresh biomass (468 vs 285 g, 427 vs 264 and 858 vs 364, respectively), and leaf area (14275 vs 8770 cm^2) (Table 2).

The plants grown in the presence of hydrogel and subjected to a controlled water stress (suspension of irrigation for 24 h) showed a greater hydration of the leaf tissue, as shown by the lower dry matter percentage of the leaves (18.5 vs 16.5%, respectively, in absence and presence of the hydrogel) (Fig. 3A). This result was confirmed by the higher leaf water potential value (-10.3 vs -8.7 bar) and turgor potential (2.3 vs 3.7 bar) in HYDROGEL treatment (Fig. 3B and 3C). No differences were observed in leaf osmotic potential. The presence of hydrogel provided, even in the absence of irrigation, a certain water availability for the plants, which resulted in turn in greater leaf turgidity.

The results confirm the positive effects of hydrogels often reported on the plant growth promotion and the reduction of the detrimental effects of water stress (Akhter et al., 2004; Shahid et al., 2012). However, in the period following the moment of the analysis, the differences in the water content of the substrates gradually reduced (data not shown), indicating the possible changes in the swelling capacity of the hydrogel. This behavior has been observed in other previous studies and is probably associated with the frequent dehydration and hydration cycles, typical of irrigation management of vegetable crops, and the increase in the substrate salinity due to the contribution of fertilizer salts (Frantz et al., 2005). It remains important, however, the promoting growth and limiting water stress effects observed during the first stage of the crop cycle, with significant repercussions on the potential earliness of the production.

Table 2. Growth parameters of cucumber plants grown on sandy soil not amended or amended with hydrogel at 35 day after transplant (2 g·L^{-1} of soil).

Treatment	Plant height (cm)	Total fresh biomass (g/plant)	Leaf fresh biomass (g/plant)	Stem fresh weight (g/plant)	Fruit fresh weight (g/plant)	Leaf area (cm^2/plant)
NO HYDROGEL	158	913	285	264	364	8770
HYDROGEL	180	1753	468	427	858	14275
Significance[1]	***	***	***	***	***	***

[1]*** significant at 0.1%. level

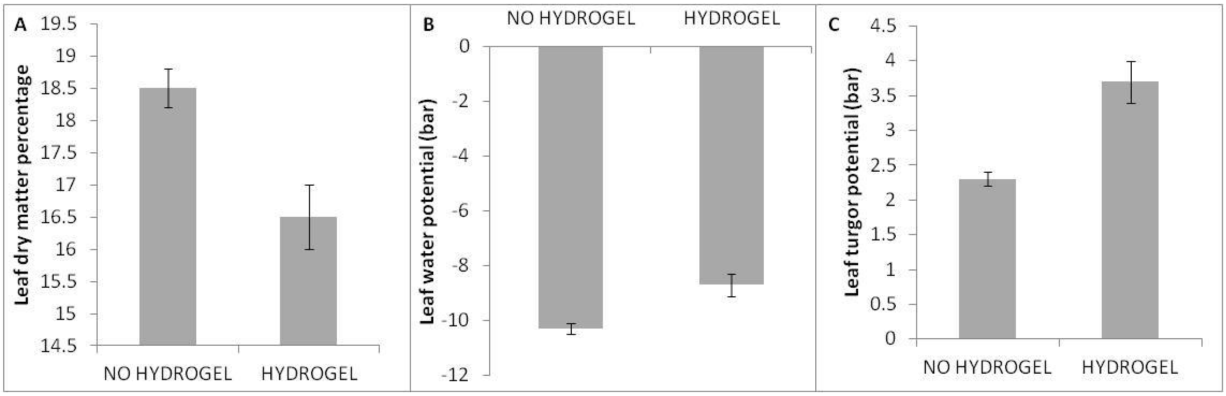

Fig.3. Effects of hydrogel on leaf dry matter percentage (A), leaf water potential (B) and leaf turgor potential (C) of cucumber plants subjected to 24 h of suspension of irrigation. Vertical bars represent ± standard error (n=3).

The sweet basil plants grown on perlite amended with hydrogel showed an enhanced growth in terms of fresh biomass at 46 DAS (Table 3). However, the effect of the hydrogel tended to drastically decrease in the final part of the basil growing cycle, thus no significant differences were observed at 63 DAS. The progressive loss of effectiveness ofhydrogels used for containerized plant production in soilless conditions has been well documented. Theoretical analysis of the potential benefits from hydrogels confirmed the potential benefit early in bedding plant containerized production (less frequent irrigations and more rapid plant production) with little to no benefit later in production and in post-production (Frantz et al., 2005).

Table 3. Fresh weight of sweet basil plants grown on perlite not amended or amended with hydrogel (3 and 6%, w:w) at 46 and 63 days after sowing (DAS).

Hydrogel in the perlite (%)	Fresh weight 46 DAS (mg/plant)	Fresh weight 63 DAS (g/plant)
0	750 b	11.44
3	1170 a	12.64
6	1330 a	13.04
Significance[1]	***	ns

[1]Mean values within columns followed by the same letters were not significantly different at 5% level according to LSD test (P= 0.05); ns, not significant; ***, significant at 0.1% level, respectively..

4. Conclusions

The innovative hydrogel tested in this study showed the positive properties generally documented for others traditional hydrogels, with the advantage of its biodegradable nature. We documented beneficial effects on water retention properties of a sandy soil and perlite (soilless substrate), both recognized as poor water retention substrates, and on plant growth. Soilless cultivation conditions could lead to a progressive loss of effectiveness of the hydrogel, due to theperiodic dehydration and hydration cycles and the high fertilization rate. The tested hydrogel showed to be suitable for potential use in agriculture, with potential benefit in particular for short growing cycle crops. Its employment should be further evaluated under a cost-effective perspective.

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