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# Eco-friendly whey/polysaccharide-based hydrogel with poly(lactic acid) for improvement of agricultural soil quality and plant growth

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## ABSTRACT

A set of renewable and biodegradable hydrogels based on acid whey and cellulose derivatives blended with poly (lactic acid) (PLA) were designed as eco-friendly biopolymeric material for sustainable agricultural applications. The physico-chemical properties of the hydrogel were evaluated using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and rheological measurements. The effect of the whey/poly-saccharide/PLA hydrogel on soil quality improvement (water retention study, biodegradability, loading capacity and release of the fertilizers) and the growth pattern of *Raphanus sativus* and *Phaseolus vulgaris* has been also studied. The addition of PLA has been found to improve mechanical properties of the hydrogel. The introduction of 20% wt PLA extended decomposition time of hydrogels by 25% which makes the material more stable in the environment and maintaining the soil humidity for longer. The increasing the amount of PLA led to a rise in hydrogel viscosity brought about better entrapment efficiency of the fertilizers (86-92% for  $\text{KNO}_3$  and 87-96% for urea, resp.) compared to control (82% for  $\text{KNO}_3$  and 85% for urea, resp.). The novel hydrogels with swelling ratio of up to 500% showed potential as a sustainable water reservoir for plants improving water retention capacity of the soil by 30%.

**Keywords:** Acid whey, water retention, hydrogel, sustainability, poly(lactic acid)

## 1. Introduction

Hydrogel materials are set to gain in importance over time as soil conditioners for the agricultural sector, especially in locations where water is in limited supply [1]. Apart from providing plants with essential moisture, another benefit of the hydrogel is its ability to controlled release of nutrients or agrochemicals to maximize soil usage and increase the crop yields [2]. However, the majority of commercial hydrogels currently in use agriculturally are primarily based on polyacrylamide and acrylate derivatives, which stem from the production of petroleum and prove difficult to degrade in soil [3]. These factors clearly raise issues relating to environmental sustainability. In their search to find safer alternatives, many researchers have investigated biopolymers as a potential replacement for synthetic materials in efforts to produce biodegradable and environmentally friendly hydrogels [4-6]. Bio-based hydrogel can be obtained from a large number of biopolymers of food origin (proteins, polysaccharides) [4,7] or renewable bioresources [8] (e.g., industrial by-products or derivatives from agricultural crops) like cellulose, hemicellulose, lignin [5,9,10], cassava starch or natural rubbers [11]. Hydrogels derived from natural sources offer distinctive benefits over synthetic form, such as safety, low cost, sustainability and environmentally friendly properties [5].

In this study, the novel material for hydrogel production is acid whey, a by-product of the dairy industry arising from the manufacture of cream cheese and Greek yogurt. While sweet whey has commercial uses in products such as nutritional supplements, a major proportion of acid whey from dairy industry is discarded as effluent, constituting a form of pollution [12]. In this context, acid whey has been used as a base material of the hydrogel to find its effective use and address the associated pollution, whereas contemporary hydrogel production utilizes water instead. Acid whey also has the potential to act as a nutritive agent for boosting the growth, yield and quality of crops, a consequence of the high content of organic compounds present, thereby enhancing the quality of the soil and promoting beneficial microorganisms in it [13]. Another benefit of acid whey is to correct the pH of alkaline soils through its inherent acidic pH (4.0-5.1) [14].

The cellulose derivatives - carboxymethyl cellulose sodium salt (CMCNa) and hydroxyethyl cellulose (HEC) represent biopolymeric materials of the hydrogel with excellent absorption properties, that are obtained by the etherification of cellulose, the most abundant, naturally occurring carbohydrate and the main constituent of plants and natural fibres [15]. Cellulose stands out for its biodegradability, nontoxicity, sustainability and very good swelling properties, making it an ideal material for a hydrogel intended for agricultural use [9]. Nevertheless, the cellulose-based hydrogels usually show poor mechanical properties and considerable biodegradability in a soil environment [16]. The high content of whey in the hydrogel also makes it very susceptible to microbial attack, potentially accelerating the rate of degradation [17]. Therefore, the low-molecular-weight poly(lactic acid) (PLA) was selected as a more stable biopolymeric material with the aim of heightening the stability of the whey-CMCNa/HEC hydrogel and maintaining humidity in the soil for a long period. PLA is a well-known biodegradable aliphatic polyester derived from 100% renewable resources, thus it constitutes a sustainable material for producing environmentally-friendly hydrogels. PLA has already been widely deployed in biopolymer hydrogels produced for the pharmaceutical and foodstuff sectors [18,19]. There is a general lack of data in the literature, though, on PLA use in biopolymer-based hydrogels for agricultural applications.

The primary aim of this study is to discern how the biodegradability and swelling properties of the novel hydrogel are affected by the presence of PLA, as well as the effect exerted by whey-based hydrogel on soil quality improvement and plant growth.

## **2. Material and methods**

### *2.1. Materials*

Acid whey was sourced from the production of cream cheese. Car-boxymethyl cellulose sodium salt (CMCNa), viscosity 1500-3000 cP, 1% (25 °C), and 2-hydroxyethyl cellulose (HEC), viscosity 1500-2500 cP, 2% (25 °C) (Sigma-Aldrich, Italy) were applied as precursors for hydrogel synthesis. Citric acid in anhydrous form (CA, Sigma-Aldrich, Italy) was employed as a natural and non-toxic cross-linker [20]. Low-molecular-weight PLA (Mw 7700 g/mol, PDI = 1.64) was synthesized from lactic acid (L(+)-LA 80% pure (LA), Lach-Ner, Czech Republic) by a polycondensation reaction described below. Acetone p.a. (Lach-Ner, Czech Republic) was used as a solvent of synthesized PLA. Urea (Lach-Ner, Czech Republic) and potassium nitrate (KNO<sub>3</sub>, Sigma-Aldrich, Italy) were used for preparation of the solutions for gauging the loading capacity and release of fertilizers.

## 2.2. PLA synthesis

The low-molecular-weight PLA was synthesized from LA in accordance with procedure described in the literature [21,22]. The amount of 400 mL of LA was dosed into a three-necked round-bottom flask equipped with a Teflon stirrer and placed in an oil bath and heated at 160 °C for 3 h to remove water; for this purpose, a magnetic stirrer (Phoenix RSM-02 HP) with heating was connected to a laboratory apparatus for distillation under reduced pressure (20 kPa). The reaction vessel was disconnected from the vacuum pump and 0.5% wt of the catalyst Tin(II) 2-ethylhexanoate (related to the initial mass of the reactants) was added into it dropwise under continuous stirring at 300 rpm. The flask was then reconnected to the vacuum source at 100 Pa, and the reaction continued for 48 h at 160 °C. The resulting product was cooled to room temperature and dissolved in 200 mL acetone. The polymer solution was consequently precipitated in a mixture of chilled methanol/distilled water at the ratio of 1:1 (v/v) and filtrated by centrifugation at 13000 rpm. This process of dissolution and precipitation was repeated twice more. The final product was washed with distilled water and dried at 45 °C for 48 h. The synthesized PLA was characterized by GPC analysis (PL-GCP 220 chromatographic system, Agilent).

## 2.3. Preparation of hydrogel samples

Whey/polysaccharide based hydrogel samples were prepared by esterification-crosslinking mechanism with citric acid according to procedure described in the previous work [17] with slight modification. The schematic diagram of hydrogel preparation and its application is presented in Fig. 1. A mixture of the CMCNa and HEC, at a ratio of 3:1 in weight and total polymer concentration of 3% wt, was dissolved in the liquid acid whey under continuous stirring (RW 20 digital, IKA, 500 rpm) at laboratory conditions (22-24 °C) until a highly viscous solution had been obtained. After that, 15% wt of the crosslinker CA and relevant amount of PLA in paste form (5, 10, 15 and 20% wt) in relation to the amount of the cellulose derivatives, was then doped into the gel and stirred on a high-performance dispersing mixer (T 25 digital, IKA, Ultra-Turrax). The obtained whey-CMC/HEC/PLA gel was dried at 60 °C for 24 h and stored at 4 °C. Designation and composition of hydrogel samples used in this study are shown in Table S1 (Supplementary material).

## 2.4. Hydrogel characterization

### 2.4.1. Morphology

The surface and inner texture of the hydrogel samples were investigated by scanning electron microscopy (SEM). Dried hydrogels were sputter-coated with gold using Sputter coater Quorum Q300TT in a vacuum of  $3 \times 10^{-1}$  atm of argon gas and analysed on a Nova NanoSEM 450 unit set to an operating voltage of 10 kV.

### 2.4.2. Porosity measurement

The solvent replacement method was adopted to measure porosity as described in other works [23,24]. Dried hydrogel samples ( $M_d$ ) were immersed in a pycnometer full of absolute ethanol ( $M_1$ ) for 24 h and weighed after any excess ethanol on the surface had been blotted off ( $M_2$ ). Porosity ( $P$ ) was calculated from Eq. (1) below:

$$P(\%) = \frac{M2 - Md}{\rho V} \times 100 \quad (1)$$

where  $V$  is the volume of the hydrogel and  $\rho$  is the density of the absolute ethanol. Volume was calculated according to Eq. (2):

$$V = \frac{M1 - M2 + Md}{\rho} \quad (2)$$

#### 2.4.3. Gel fraction

Dried samples ( $w_0$ ) were immersed in deionized water at the ratio of 1000:1 for 48 h; the water was periodically changed to remove the sol fraction. The samples were dried to constant weight ( $w_1$ ) at 60 °C and the gel fraction ( $GF$ ) subsequently calculated in accordance with Eq. (3) [25]:

$$GF(\%) = \frac{w_1}{w_0} \times 100 \quad (3)$$

#### 2.4.4. Rheology

Rheological measurements of swollen hydrogel particles (150-200  $\mu\text{m}$  in diameter) were performed using a rotational rheometer (Physica MCR 502, Anton Paar GmbH, Austria) set up with parallel-plate geometry (PP 20/MRD/TI/S,  $d = 20$  mm), at 25 °C. The viscoelastic properties of the samples were studied by carrying out frequency-sweep and strain-sweep oscillation tests. The latter were conducted at  $\omega = 1.0$  rad/s at the strain amplitude of 0.01%, whereas the frequency sweep tests were performed across the frequency range of 0.1-40 Hz at the same strain setting.

#### 2.4.5. Structural properties

The chemical structure of the novel hydrogel was investigated by using Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy.

The infrared spectra of the whey-CMCNa/HEC/ PLA-based hydrogel were recorded using Thermo NICOLET 6700 spectrophotometer via the ATR technique, equipped with a diamond crystal, which was set to the resolution of 2  $\text{cm}^{-1}$  and range of absorbance of 400-4000  $\text{cm}^{-1}$  at room temperature [26].

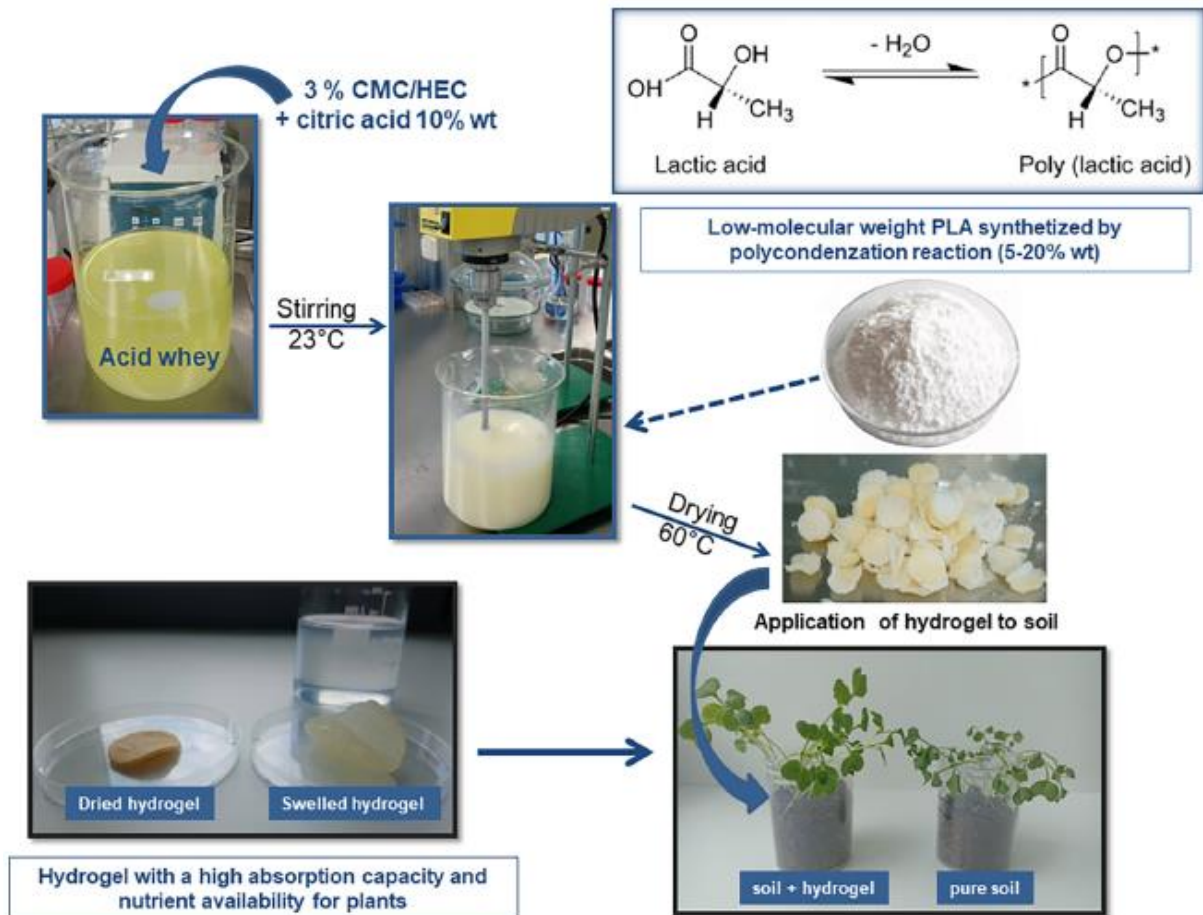


Fig. 1. Schematic illustration of the whey-CMCNa/HEC/PLA-based hydrogel preparation and its application.

#### 2.4.6. Swelling properties

The maximum capacity of the hydrogel for water absorption in distilled water and soil extract (pH ~5.8, EC < 30  $\mu\text{S}\cdot\text{cm}^{-1}$ ) was determined according to published research [5]. Preparing the soil extract involved adding 20 g of soil into 1000 mL of deionized water, and the resultant suspensions were shaken in a reciprocal shaker for 24 h. Afterwards the suspension was poured into a centrifuge tube and centrifuged at 1400g for 10 min. The liquid obtained was utilized in the experiment.

Swelling capacity (SC) was determined by weighing the samples prior to and following immersion in the distilled water/soil extract for 24 h by the following Eq. (4):

$$\text{SC (\%)} = \left( \frac{M_s - M_d}{M_d} \right) \times 100 \quad (4)$$

where  $M_s$  and  $M_d$  are the masses of the swollen and dried samples (g), respectively.

The efficacy of the prepared hydrogel to retain water in soil was assessed by analysis of the water evaporation ratio (WER) [27]. Commercial garden soil containing 30% clay, 40% silt and 30% sand was dried at 45 °C until it had reached constant weight. Subsequently, 1 g of the dried hydrogel (2 mm in diameter) was thoroughly mixed with 50 g of the dried soil and transferred into a plastic pot. Pure soil was used as the control. Each pot was weighed, then 50 mL of distilled water added and the weight recorded again. The samples were stored at room temperature and their weight measured every 3 days until no detectable weight loss was observed. Values for WER were derived from Eq. (5):

$$\text{WER (\%)} = \left( \frac{M_i - M_t}{M_s} \right) \times 100 \quad (5)$$

where  $M_i$  is the weight of the sample after adding the water,  $M_t$  refers to the weight of the sample after the specified time intervals, and  $M_s$  is a weight of the soil used. Repeating the above experiment for SC and WER facilitated investigation of the reusability of the hydrogels in soil.

#### 2.4.7. Loading capacity of a fertilizer and the entrapment efficiency of the hydrogel

In this work, the impact of the content of PLA on the loading capacity (LC) of the given fertilizer, potassium nitrate ( $\text{KNO}_3$ ) and urea was evaluated according to the procedure as described in the literature [28]. In brief, the dried hydrogels were soaked in 250 mL of aqueous 0.1 M solution supplemented with the fertilizer for 24 h to discern maximum absorption over time. The amount of the fertilizer loaded (LC) was obtained by this Eq. (6):

$$\text{LC (\%)} = \left( \frac{M_n - M_0}{M_0} \right) \times 100 \quad (6)$$

where  $M_n$  is the weight (in milligrams) of the previously dried hydrogel after being soaked for time  $n$  in the solution, while  $M_0$  is the initial weight of the dried hydrogel.

Entrapment efficiency (EE) was estimated to be the difference between the initial quantity of the loaded solution and the free/unen-trapped quantity of the fertilizer in the solution, with respect to the total quantity incorporated in the hydrogel [29]. *EE* was calculated as follows:

$$\text{EE (\%)} = \frac{(W_d - W_i)}{W_0} \times 100 \quad (7)$$

where  $W_d$  is the mass of the fertilizer-loaded dried hydrogel,  $W_i$  is the initial weight of the dried hydrogel, and  $W_0$  refers the amount of  $\text{KNO}_3$ / urea incorporated.

#### 2.4.8. Release of the fertilizer from the hydrogel

The release of  $\text{KNO}_3$  and urea from the hydrogel samples was tested in soil extract. The process commenced with recording the weight of the dried hydrogel supplemented with the fertilizer, and then placing the material in 250 mL of the soil extract. At scheduled time intervals, the amount of  $\text{KNO}_3$  released was determined by variation of the conductivity of the release media, and the consequent values informed a calibration plot. The amount of urea released was quantified by treating 3 mL of the release media with 4-dimethylamino benzaldehyde (40 mmol/L) and measuring absorbance spectroscopically at 245 nm on a UV spectrophotometer (Cary 300 UV/Vis Agilent, UK). Values for the  $\text{KNO}_3$  and urea released were calculated according to Eqs. (8) and (9), respectively [4,30].

$$\text{KNO}_3 \text{ release (\%)} = \frac{W_f - W_r}{W_r} \times 100 \quad (8)$$

where  $W_f$  is the mass of a  $\text{KNO}_3$ -loaded hydrogel sample and  $W_r$  is the weight of  $\text{KNO}_3$ .

$$\text{Urea release (\%)} = \frac{\lambda_{\infty} - \lambda_t}{\lambda_{\infty}} \times 100 \quad (9)$$

where  $\lambda_{\infty}$  and  $\lambda_t$  represent the absorbance of urea released at equilibrium at certain times ( $t$ ), respectively; the release studies were performed in triplicate.

#### 2.4.9. Biodegradation

The dried samples were accurately weighed (to the nearest 0.001 g) and buried at a 5 cm depth from the surface in a pot containing commercial soil. The samples were kept at room temperature for 30 days. Tap water was added regularly during the experiment to counteract drying of soil through evaporation. The weight of each sample was taken at 5-day intervals, followed by cleaning with water and drying at 45 °C for 24 h. The difference in weight loss of the samples indicated the extent of degradation. The degree of degradation (D) was calculated by Eq. (10) given below:

$$D (\%) = \left( \frac{W_i - W_f}{W_i} \right) \times 100 \quad (10)$$

where,  $W_i$  is the initial weight of the sample prior to degradation and  $W_f$  refers to its weight after specific time intervals of biodegradation.

The release of CO<sub>2</sub> during the biodegradation process in soil was monitored using gas chromatography (GC) (Agilent 7890) according to a procedure described in the previous work [17]. From the CO<sub>2</sub> concentration discerned, the percentage of mineralization ( $M$ ) was calculated with respect to the carbon content of the initial samples in accordance with Eq. (11):

$$M (\%) = \frac{m_{gc}}{m_s w_c} \quad (11)$$

where  $m_{gc}$  (mg) is the mass of carbon evolved as CO<sub>2</sub> determined by GC analysis,  $m_s$  (mg) is the weight of the sample and  $w_c$  is the percentage ( $w/w$ ) of carbon in the material investigated using total organic carbon analyser (TOC-L, Shimadzu).

#### 2.4.10. Effect of hydrogel application on plant growth

Experiments were conducted to verify the influence of the hydrogel on the vitality of plants and its capacity for conserving water in soil. The hydrogel HPLA10 (approx. 2 mm in diameter) was mixed at the extent of 0.5, 1.5 and 3.0% in 100 g of dried soil. Soil absent of the hydrogel served as a control. The soil mixture was placed in containers and 10 seeds of *Raphanus sativus* var. *sativus* and 7 seeds (per pot) of *Phaseolus vulgaris* were sown in each soil sample. The experiment was performed in triplicate for each plant and soil mixture. The pots were continuously irrigated with tap water for the first two weeks and exposed to laboratory conditions at 25 °C. After this period, no more water was added, and the vitality and survival rate of the plants under drought conditions were observed. The experiment ceased when all the plants under test had completely wilted.

The effect of different amounts of PLA on plant growth was performed by the same procedure, with 1.5% w/w of hydrogel samples containing PLA at 5, 10 and 20%. The rate of germination and the heights of growing plants (from the level of the soil to the top of the highest leaf) were recorded from



the commencement of germination at certain time intervals and over the course of the ensuing 25 days.

#### 2.4.11. Effect of biodegraded products on soil quality

The impact exerted by biodegraded components of the hydrogel on soil quality was studied by carrying out soil analysis before the hydrogel underwent biodegradation and afterwards. Macro analysis of the soil was performed in terms of its pH, total carbon and nitrogen content on a carbon and nitrogen (TC/TN) analyser (TOC-L, Shimadzu).

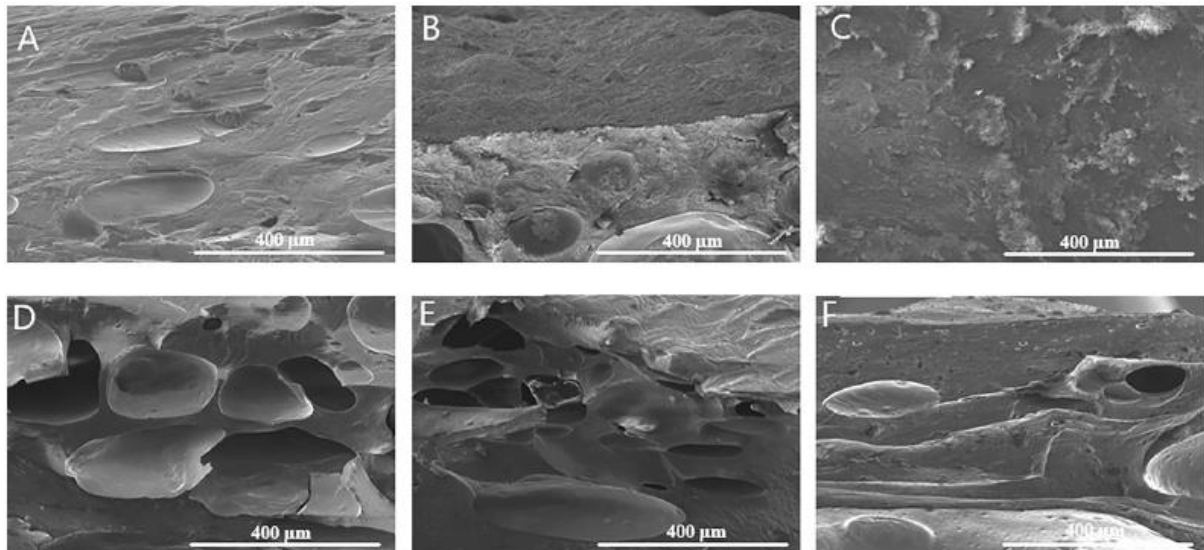
### **3. Results and discussion**

#### *3.1. Morphology, mechanical and structural properties*

The SEM images in **Fig. 2** depict how the presence of PLA affected the morphology of the hydrogel. The hydrogel HPLA0 (**Fig. 2A**) and HPLA20 (**Fig. 2C**) differed in the appearance of their surfaces, as the former possessed a smooth, wave-like structure with shallow pores of 100-200  $\mu\text{m}$ , while the hydrogel with PLA was characterized by a rough surface with small protrusions, caused by the PLA incorporated in the hydrogel matrix. Variation was also discernible in their cross sections (**Fig. 2D-F**). The structure of HPLA0 was porous and sponge-like, with pores of 100-400  $\mu\text{m}$  in size. These pores are favourable for absorbing and retaining water molecules that diffused into the network of the hydrogel, leading to a higher swelling ratio and effective retention of water in the soil environment [31]. Addition of synthesized PLA reduced this porosity, as is evident in **Fig. 2D-F**, where the pores shrank and disappeared, and the internal structure became more compact apparently due to the higher viscosity of the samples containing PLA and the greater cross-link density between CMCNa/HEC, CA and PLA.

The porosity of the hydrogel directly affected its durability, swelling properties, loading capacity and release of the fertilizer [30]. The results in **Table 1** show that porosity decreased in parallel with rise in the concentration of PLA due to the higher density of cross-links in the polymeric structure. Such diminished porosity restricted release of the fertilizer, and consequently heightening control in release kinetics. The gel fraction is defined as the percentage of dry polymer remaining in the hydrogel after swelling [25]. As detailed in **Table 1**, the GF values for the hydrogels varied according to the content of PLA. The greater the amount of PLA present, the higher the value for GF, resulting in reduced swelling and a more rigid polymer network.

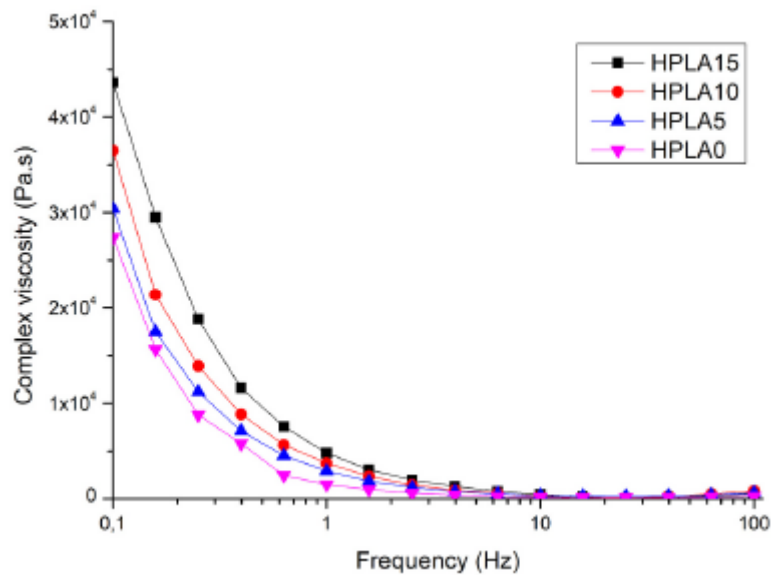
The viscosity of the material helps to define the ability of the hydrogel to resist deformation in response to stress [32]. The rheological data in **Fig. 3** reveal that viscosity decreased in line with increase in frequency, and the hydrogel tended to retain elasticity at lower frequencies of load. The least viscosity was observed for hydrogel HPLA0, since the lesser formation of cross-link points meant the cross-link density of the hydrogel was decreased, weakening its mechanical properties. The presence of water molecules inside the hydrogel structure altered the rheological properties of the hydrogels, making the hydrogel softer under mechanical stress and vice versa. The hydrogel samples with PLA proved to be resistant to ambient stress after swelling due to a higher degree of crosslinking, which make the hydrogel structure more stable in the swollen state.



**Fig. 2.** SEM analysis of the surfaces (A, B, C) and inner structures (D, E, F) of the hydrogels. A and D refer to hydrogel absent of PLA, B and E are the hydrogel HPLA10, and C and F pertain to the hydrogel HPLA20.

**Table 1** Porosity and gel fraction of the hydrogel formulations; the data refer to mean values  $\pm$  SD ( $n = 3$ ).

Sample	HPLA 0	HPLA 5	HPLA 10	HPLA 15	HPLA 20
Porosity (%)	56.5 $\pm$ 2.8	52.3 $\pm$ 2.1	45.3 $\pm$ 1.4	35.5 $\pm$ 1.2	31.2 $\pm$ 2.1
Gel fraction (%)	67.7 $\pm$ 1.5	72.5 $\pm$ 1.7	78.3 $\pm$ 2.1	80.5 $\pm$ 1.6	84.2 $\pm$ 1.5



**Fig. 3.** Dependency of complex viscosity on frequency after 24 h of swelling for the whey/polysaccharide-based hydrogel samples with different concentrations of PLA.

The chemical structure of the whey/polysaccharide/PLA based hydrogels were studied using FTIR spectroscopy as shown in **Fig. 4a**. The reference material (the hydrogel without PLA) shows a broad

peak at 3000-3700  $\text{cm}^{-1}$ , attributed to the stretching vibration of —OH ascribed to the COOH groups of CA and cellulose derivatives CMCNa and HEC [33]. The band at 3347  $\text{cm}^{-1}$  gives information concerning the intermolecular hydrogen bonds in the cellulose structure. The absorption band at 2934  $\text{cm}^{-1}$  is a characteristic of a cross-linked hydrogel and pertains to C—H stretching vibration of the —CH<sub>2</sub> and —CH<sub>3</sub> groups [17]. The peak at 1757  $\text{cm}^{-1}$  is attributed to the stretching of hydrogen-bonded C—O and the one at 1632  $\text{cm}^{-1}$  denotes carbonyl band of free carboxylic acid groups and the carbonyl band of ester formed during cross-linking [34]. The sharp peak at 1538  $\text{cm}^{-1}$  is attributed to the presence of free —COOH groups, while 1420  $\text{cm}^{-1}$  pertains to the stretching vibration of COO and is an indication of the carboxyl groups of CMCNa [33,35]. The peak at 1264  $\text{cm}^{-1}$  denotes the stretching vibration of a C—C bond formed during reaction between CA and cellulose derivatives [17]. The characteristic peak at 1072  $\text{cm}^{-1}$  is typical for the absorption bands of CMCNa, related to the C—O stretching vibration of the alcoholic group [33]. The substitution of cellulose derivatives as well as their crosslinking being seen as an ether C—O—C stretching vibration from ~910  $\text{cm}^{-1}$  (for unsubstituted cellulose) to ~887  $\text{cm}^{-1}$  for cross-linked CMCNa/HEC samples [33]. The presence of the synthesized low-molecular-weight PLA in the hydrogel was confirmed with typical spectra of PLA, which were in agreement with the results reported elsewhere [22]. The peak located at 2994 and 2944  $\text{cm}^{-1}$  represent asymmetric and symmetric —CH— stretching. The absorbance band at 1757  $\text{cm}^{-1}$  is attributed to the C—O stretching vibration. The peak at 1264  $\text{cm}^{-1}$  was assigned to the C—O stretching of the ester groups and carboxylic acid's oligomers. The region between 1300 and 1050  $\text{cm}^{-1}$  showed four intensive absorption peaks indicating C-O-C stretching. The peaks located at 869 and 755  $\text{cm}^{-1}$  corresponded to —C—C— stretching.

### 3.2. Swelling capacity

The ability of hydrogels to absorb water is a crucial property for agricultural purposes. The amount of water that can be retained in the hydrogel matrix directly correlates with the concentration of hydrophilic groups [20] and cross-link density [36,37]. Figs. 5 and 6 show a decrease in the kinetics of swelling which occurred alongside increase in the concentration of PLA in the hydrogel structure (SR 505 > 480 > 475 > 444%, respectively). HPLA20 showed the least extent of equilibrium swelling, in turn giving rise to a more rigid structure. It is evident that PLA slowed the movement of water within the hydrogel matrix, at the expense of improving the stability of the hydrogel in the soil environment. Hydrogel HPLA0, in contrast, was more hydrophilic and its porous morphology enhanced the diffusion of water into its network. The hydrogel reached the SR of up to 505%, which indicates its potential as a soil conditioner.

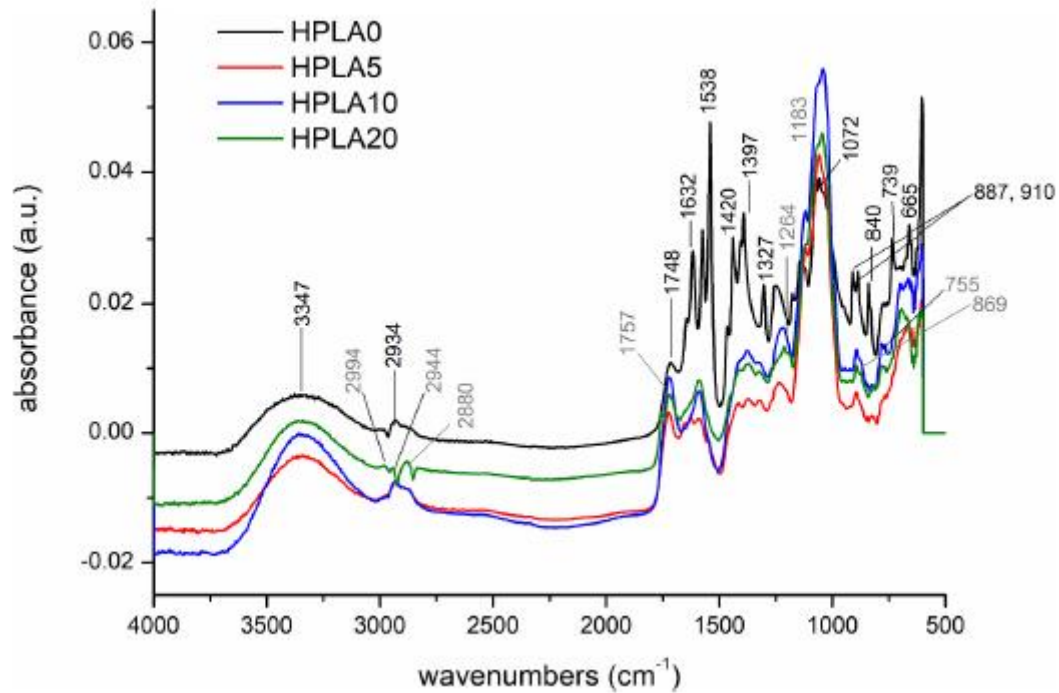


Fig. 4. FTIR spectra of whey-CMC/HEC-based hydrogel and hydrogel with different concentrations of PLA (HPLA0-HPLA20).

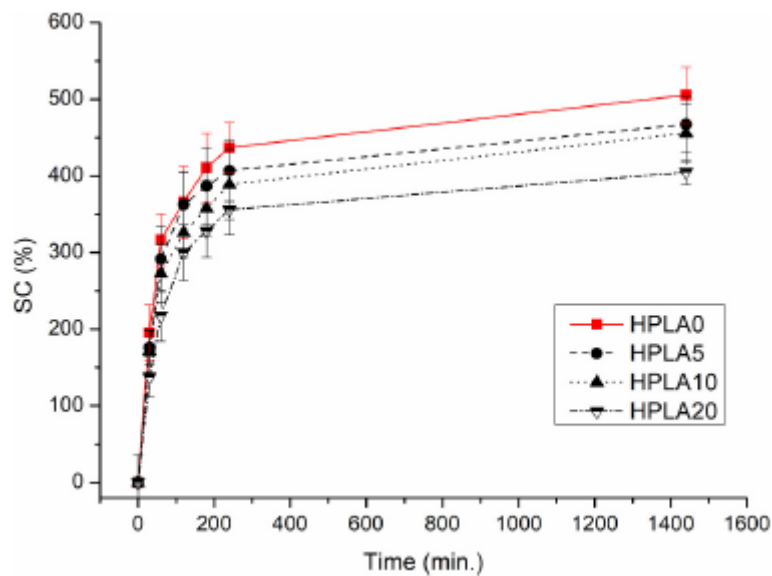


Fig. 5. Swelling kinetics of the hydrogel samples in distilled water at room temperature; the data refer to mean values  $\pm$  SD ( $n = 3$ ).

Similar findings for swelling behaviour were observed in the soil extract (Fig. 6), although the SC values for both of these samples were slightly reduced, since CMCNa as an ionic polyelectrolyte had the potential for sensitivity to the concentration of ions in the soil extract. This behaviour was a consequence of an imbalance in charge between the inner and outer environments of the hydrogel, known as the Gibbs-Donnan effect [38]. The increasing the ionic strength of the external solution (soil extract) decreases the difference between the concentration of ion species in the hydrogel and in the external solution, and thus, the water uptake decreases [39]. Therefore, it should be noted that the

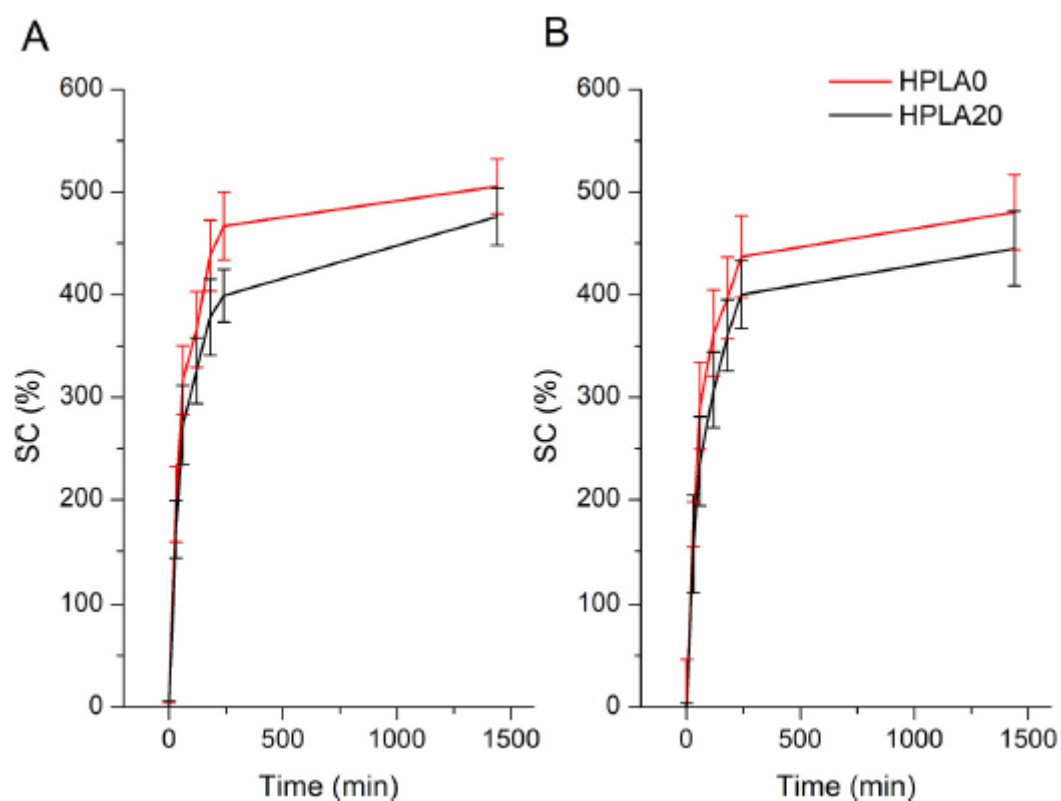
swelling behaviour of the hydrogel could be altered to suit the external stimuli (changes in temperature, pH or ionic strength) of the absorption media in the surrounding environment [40,41].

### 3.3. Water retention study in soil

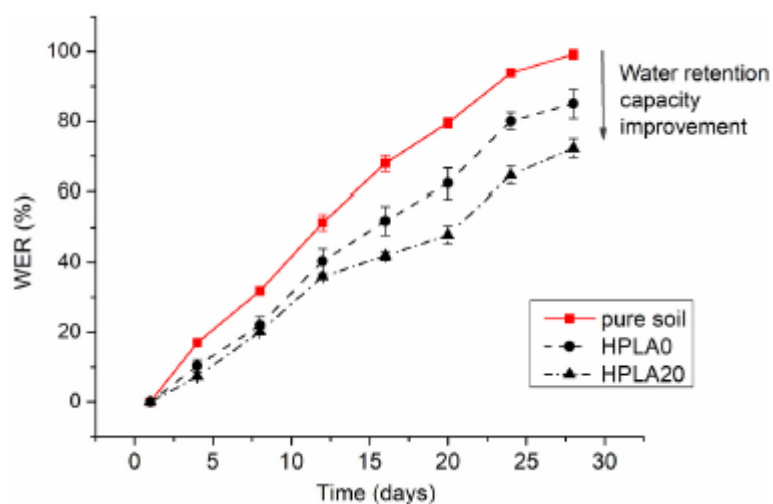
Water retention in soil constitutes an important property with positive effects on improving soil quality, increasing the survival rate of seedlings and promoting the growth of plants [1]. The trends in **Fig. 7** show water evaporation ratio (WER) from the soil over the course of 30 days. Water evaporation is a direct loss into the atmosphere in the form of water vapour as mediated by ambient conditions such as humidity, air temperature and the water retention capacity of the soil [27]. The data reveal that the application of the hydrogel to the soil increased the quantity of water retained by all of the formulations for a sustained period. The soil amended with hydrogel HPLA20 demonstrated better retention ability (almost 30% higher) compared to pure soil (almost 100% water loss through evaporation after 30 days than soil with the hydrogel HPLA0 (85%) and HPLA20 (72%), respectively). The variances in the trends potentially arose through the presence of the carboxylic groups and PLA of the crosslinked materials of different structures in the soil, which heightened water retention as a consequence of increase in half-bound and bound water in the polymer structure [37]. However, it is worth noting that each hydrogel particle was surrounded by earth particles under the limited pressure of the soil environment, which may have influenced the water-holding capacity of the samples [42].

### 3.4. Loading capacity of the hydrogel and fertilizer release

The fertilizer application such as nitrogen (*N*) and potassium nitrate ( $\text{KNO}_3$ ) is an essential part of agriculture to optimise production. *N* and  $\text{KNO}_3$  improve the quality of the harvest, support the formation of protein and resistance to disease, and increase water-use efficiency [31,43]. Additionally,  $\text{KNO}_3$  aids the absorption of critical nutrients such as calcium, magnesium and phosphorus, while also combatting salinity [44]. However, about 40-70% of such nutrients degrade in the environment when applied directly, resulting in large economic losses [43,44]. The effect of hydrogel application and its chemical structure on the loading capacity and entrapment efficiency of the fertilizer is presented in **Table 2**. All the formulations demonstrated that the presence of the low-molecular-weight PLA led to a rise in viscosity and formation of hydrogel matrix with small, mesh-like pores, which limited loading of  $\text{KNO}_3$ /urea solution. The hydrogel samples HPLA5-HPLA20 had proportionately less loading capacity showing general trend of loading  $60 > 55.4 > 55.3 > 51\%$  for urea loaded-hydrogel and  $76 > 75 > 71 > 69\%$  for  $\text{KNO}_3$  loaded-hydrogel respectively. The decrease in LC of the hydrogel could also be affected by the amount of CMCNa/HEC in the hydrogel which exhibited the potential for high sensitivity to the concentration of ions in water. At high ionic strength, the presence of such ions increases the osmotic pressure of the hydrogel, causing water to desorb from the hydrogel [12]. It is noteworthy, therefore, that the swelling behaviour of the hydrogel could be altered based on the concentration of the fertilizer solution. Nevertheless, the presence of the PLA in hydrogel matrix enhanced its crosslinking structure resulting in greater EE of the loaded hydrogel. As the data in **Table 3** show, with PLA concentration at higher levels, more of the fertilizer would be available for encapsulation and the better the entrapment efficiency. Sample HPLA20 exhibited a higher EE after loading with  $\text{KNO}_3$  (92%) and urea (96%) respectively, compared to control (HPLA0) with EE 86% for urea loaded and 85% for  $\text{KNO}_3$ -loaded hydrogel.



**Fig. 6.** Swelling capacity of the hydrogel samples without PLA (HPLA0) and with PLA (HPLA20) in distilled water (A) and the soil extract (B); the data refer to mean values  $\pm$  SD ( $n = 3$ ).



**Fig. 7.** Water evaporation ratio (%) in pure soil and soil containing the hydrogel formulations HPLA0 and HPLA20; the data refer to mean values  $\pm$  SD ( $n = 3$ ).

**Table 2** Loading capacity and entrapment efficiency of KNO<sub>3</sub> and urea in the whey-CMC/HEC/PLA hydrogel formulations; data refer to mean values ( $n = 3$ ) with a SD up to 10%.

	Fertilizer	HPLA0	HPLA5	HPLA10	HPLA15	HPLA20
Loading capacity (%)	KNO <sub>3</sub>	76.2	75.1	74.3	71.1	69.3
	Urea	66.1	60.3	55.4	55.3	51.3
Entrapment efficiency (%)	KNO <sub>3</sub>	82.4	86.1	88.5	90.5	92.4
	Urea	85.8	87.3	90.3	95.3	96.0

The graphs illustrated in **Fig. 8** give information about the ability of the loaded hydrogels to absorb and maintain the water inside their structures. As shown in **Fig. 8A-C**, the presence of loaded  $\text{KNO}_3$  and urea in the hydrogel matrix limited the hydrogel water uptake ability, especially with increasing PLA concentration. Moreover, there was a significant reduction in swelling behaviour when urea was loaded to the hydrogel. The largest weight ratio between swollen and dried state of the hydrogel was observed in hydrogel HPLA0 (17.9), HPLA0/ $\text{KNO}_3$  (11.9) and HPLA0/urea (7.35), respectively. This reduction in SC is probably a result of decreasing of  $\text{KNO}_3$  and urea diffusion rate inside the hydrogel matrix [45]. Such differences in the swelling ability can be also ascribed to variation in the chemical structures of the fertilizer, including distinct interactions with the 3D polymer network of the hydrogel. Increase in the concentration of PLA brought about reduction in the release of urea, most likely triggered by interactions between the urea and PLA, alongside variation in media displacement within the hydrogel structure.

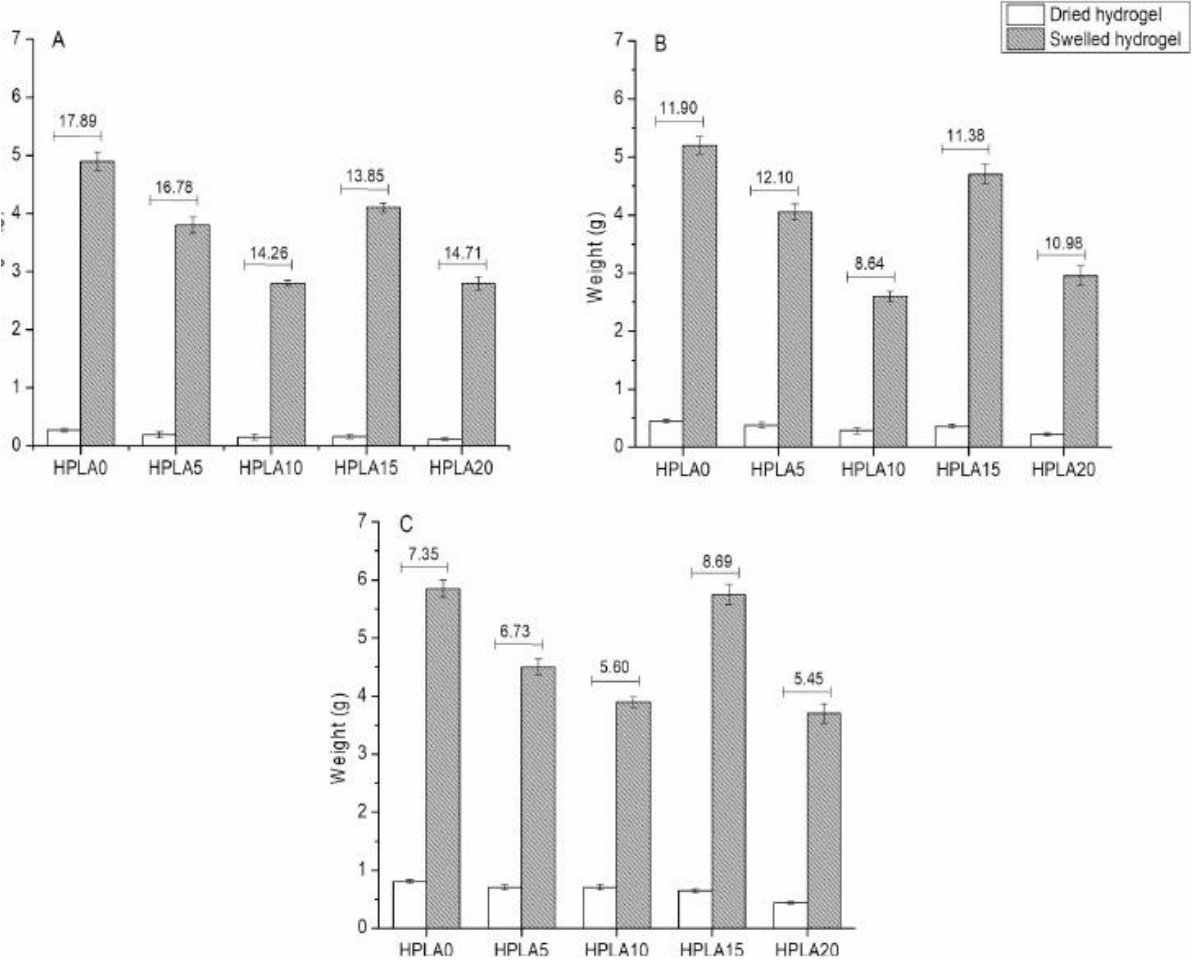
**Table 3** Effect of hydrogel application in soil (1, 2 and 5% w/w HPLA10) on the heights of growing plants (cm). Control represents soil without hydrogel.

Height of plants (cm)						
	<i>Raphanus sativus</i> var. <i>Sativus</i> (n = 12)			<i>Phaseolus vulgaris</i> (n = 7)		
	Day 5	Day 10	Day 25	Day 5	Day 10	Day 25
Control	2.1 ± 0.5	6.5 ± 0.8	9.3 ± 1.2	2.0 ± 2.0	13.0 ± 1.0	22.1 ± 1.7
1%	5.0 ± 0.3	8.3 ± 0.9	9.7 ± 1.8	5.6 ± 0.3	16.1 ± 2.3	24.2 ± 1.1
2%	4.7 ± 1.0	8.3 ± 1.2	9.9 ± 1.3	2.4 ± 0.8	16.8 ± 1.8	24.0 ± 2.0
5%	4.1 ± 0.5	7.8 ± 0.7	9.4 ± 1.5	2.2 ± 0.9	17.0 ± 1.3	24.5 ± 1.9

The ionic strength could also have an effect on the reduction SC through the presence of the polyelectrolyte CMCNa in the polymer network, bringing about a Gibbs-Donnan effect between the hydrogel and the surrounding solution [10]. Furthermore, a decreasing trend in reduction of water uptake was observed for  $\text{KNO}_3$ /urea loaded hydrogel formulation with PLA. The hydrophobic nature of PLA was likely to reduce the amount of water displaced within the polysaccharide chains. However, no a direct correlation has been found between the amount of PLA and the reduction in water as even the control shows a reduction after loading with the fertilizers as well.

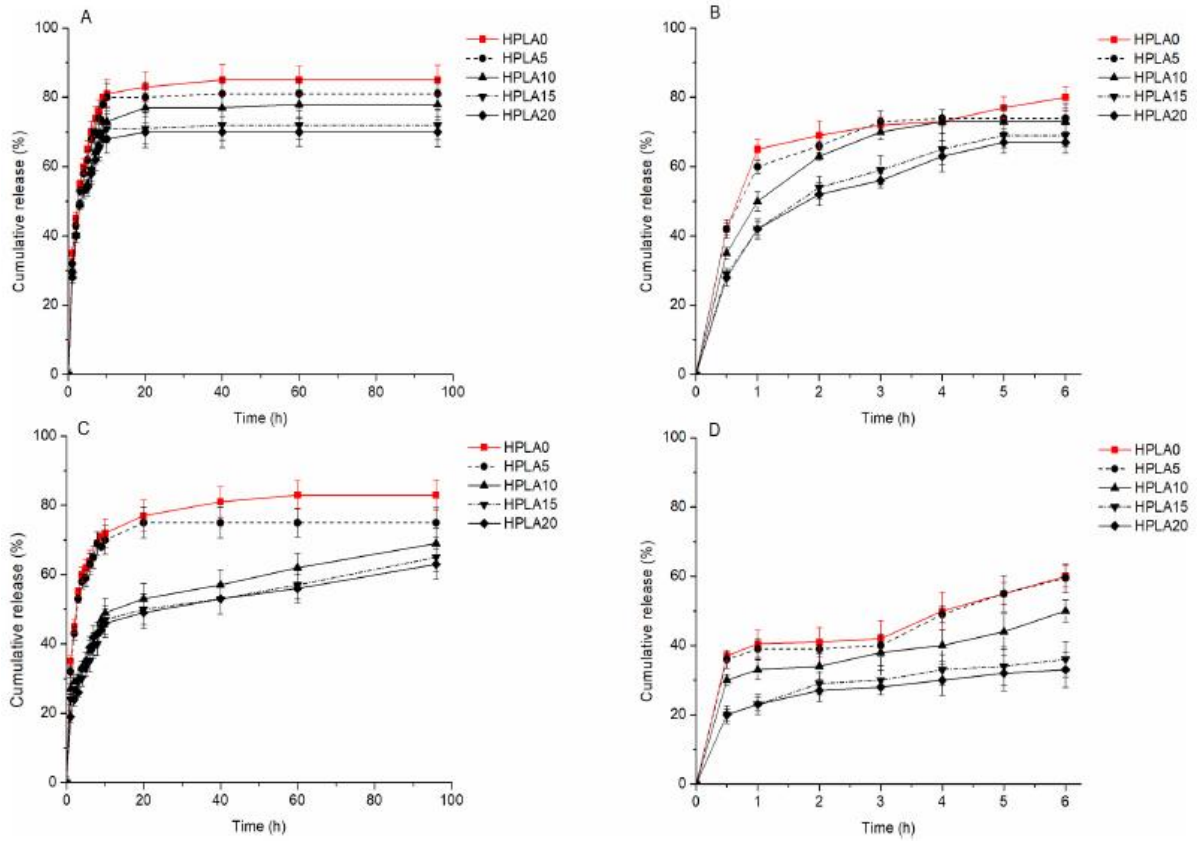
The plots in **Fig. 9** show the cumulative release rate of the  $\text{KNO}_3$ /urea fertilizer from the hydrogel during the first days after application to the soil. When the fertilizer-loaded whey-CMC/HEC/PLA hydrogel is allowed to contact with release medium, the water penetrates the surface of hydrogel releasing the  $\text{KNO}_3$  and urea [45]. The trends in **Fig. 10A** show an intensive initial burst in which up to 50% of the loaded  $\text{KNO}_3$  was released, followed by a slow phase which culminated in up to 85% of the initial amount being released within 96 h. This initial rapid release was probably a result of higher pore size of a swelled hydrogel caused by the electrostatic repulsive effect between the carboxylated groups of CMCNa and HEC and molecules of the fertilizer were released easily from the hydrogel matrix. This obviously resulted in rapid diffusion of the entrapped  $\text{KNO}_3$  from the hydrogel to the exterior release medium, in accordance with Fickian or non-Fickian diffusion [46]. The release of the fertilizer from the hydrogel is also closely related to hydrophilic behaviour of CMCNa/HEC, since the polymer network could absorb a large amount of water, leading to widespread relaxation of the network chains and the subsequent heightened release of  $\text{KNO}_3$ . The presence of PLA and crosslink density of the hydrogel is

intimately related to the degree of swelling and consequently, the release behaviour of the hydrogel [46]. The crystalline nature of the PLA and the hydrogen bonds, that form during crosslinking, had the positive effect of limiting the initial burst, which in turn affected the media uptake and kinetics.

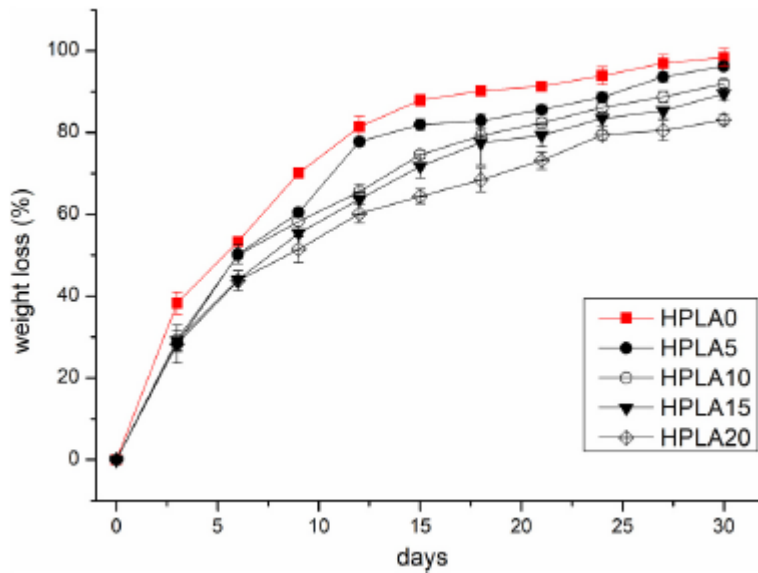


**Fig. 8.** Impact of PLA and fertilizer content on swelling behaviour expressed in weight (g); A) hydrogels without fertilizer, B) hydrogels with KNO<sub>3</sub>, C) hydrogels with urea; the values reported indicate the weight ratio between the states of swelled and dried; data refer to mean values ± SD (*n* = 3).





**Fig. 9.** Release trends of the fertilizers from the hydrogel to soil A) cumulative release of  $\text{KNO}_3$  during 96 h, B) release of  $\text{KNO}_3$  during the first 6 h, C) cumulative release of urea during 96 h, D) release of urea during the first 6 h; data refer to mean values  $\pm$  SD ( $n = 3$ ).



**Fig. 10.** Biodegradation of the hydrogel samples in garden soil using soil burial method; the data refer to mean values  $\pm$  SD ( $n = 3$ ).

At 96 h, about 67% cumulative release was attained for KNO<sub>3</sub>-loaded hydrogel HPLA20 (**Fig. 9A, B**). The similar trends were observed for urea-loaded hydrogels with PLA (**Fig. 9C, D**). However, the release behaviour of the urea from the hydrogel was significantly slower (about 33% of cumulative release (CR) was observed for urea-loaded HPLA20 after 96 h compared to control (CR=60%)). It can also be attributed to variation in the chemical structures of the fertilizers leading to distinct interactions with the 3D polymer network of the hydrogel. In addition, the release rate of fertilizers was significantly affected by the difference in PLA concentration. The increasing concentration of PLA brought about reduction in the release of fertilizer most likely triggered by interactions between the KNO<sub>3</sub>/urea and CMC/HEC/PLA, alongside variation in media displacement within the crosslinked hydrogel structure.

### *3.5. Biodegradability*

#### *3.5.1. Evaluation of biodegradability by soil burial test*

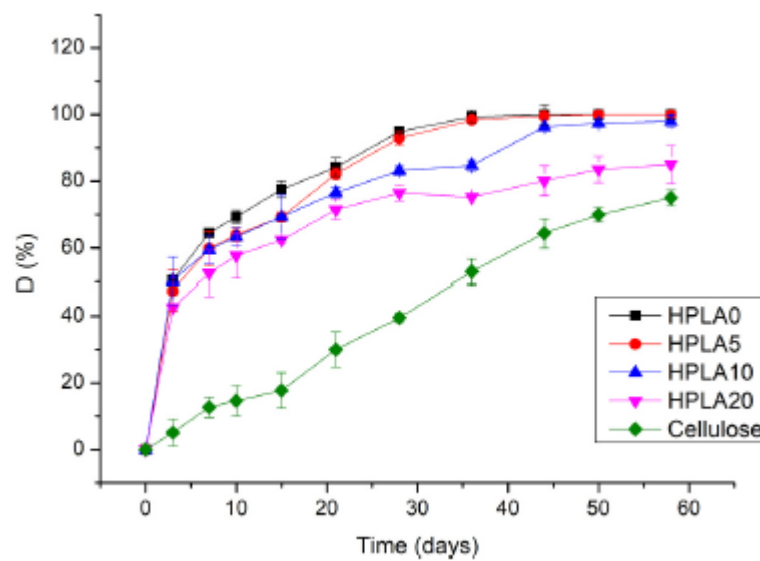
Biodegradation of the hydrogel material in a soil environment is a desirable property to ensure its safe use in agricultural applications. As the biopolymer hydrogel based on acid whey and polysaccharides constitutes ideal source of nutrients for soil microorganisms, the rate of degradation can be accelerated. Plots in **Fig. 10** detail the effect of PLA addition on the weight loss of hydrogels during 30 days in soil using the soil burial test. The control sample (HPLA0) was found to degrade from 98% in soil within 30 days. The addition of low-molecular-weight PLA at 5, 10, 15 and 20% wt enhanced the stability of the hydrogel in the given environment for an extended period; nevertheless, the all the formulations still exhibited very good biodegradability (83-96% upon 30 days of study). It should be taken into account, though, that the degradation of PLA could be influenced by various factors like size and geometry of the sample, degree of crystallinity, molecular weight or environmental conditions such as temperature, pH and microbial activity [47,48]. Based on the results is evident, that hydrogels based on acid whey are applicable in agriculture or horticulture as a valuable source of nutrients in the initial phase of plant cultivation.

#### *3.5.2. Evaluation of biodegradation by GC*

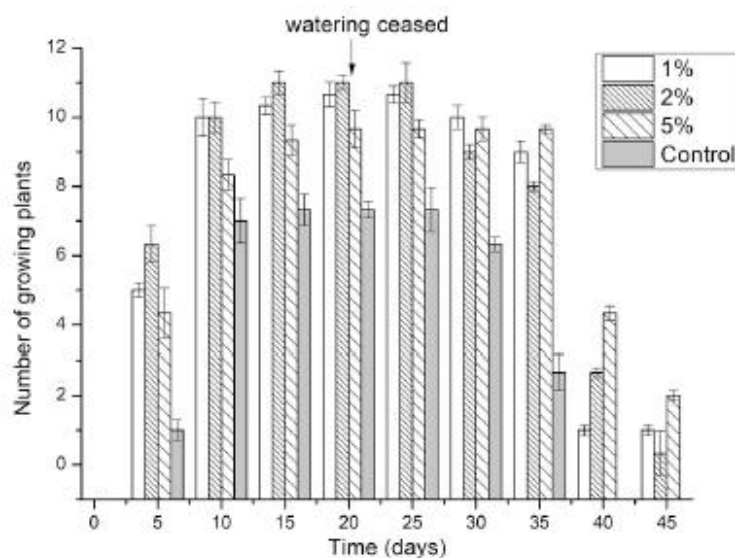
The course of biodegradation was monitored and quantified by CO<sub>2</sub> evolution in soil under aerobic conditions. Measuring the extent of carbon dioxide production in such an environment provided a higher level of control and objectivity for assessing biodegradation than usual determining loss in weight of hydrogel [49]. The CO<sub>2</sub> produced directly referred to the mineralization of the supplied carbon source by bacterial respiration, signifying ultimate degradation of the polymeric material by microorganisms [50]. The percentages for mineralization pertaining to the carbon content of the initial sample are displayed in **Fig. 11**. All the samples started to produce significant amounts of CO<sub>2</sub> in the first 3-5 days, potentially stemming from mineralization of the whey-polysaccharide material which was easily accessible to microorganisms. A slower rate of degradation was observed for the samples containing PLA, probably due to the hard and brittle nature of PLA, which is less susceptible to microbial attack and degradation in a natural environment than other biodegradable compounds of the hydrogel [51]. The trend recorded for the sample HPLA20 was one of extended biodegradation that reached almost 25%. By the close of a 60-day period, 73% of the sample had been mineralized compared to HPLA5 and HPLA0 (D=95% and 98%, respectively).

### 3.6. Effect of hydrogel application on plant growth

The influence exerted by the amount of hydrogel HPLA10 (1%, 2% and 5%) placed in the soil was monitored on the growth patterns of *Raphanus sativus* and *Phaseolus vulgaris* for 45 days. The number of germinated seeds in the pot (**Fig. 12**) and the average height of the plant (**Table 3**) were monitored for 25 days. After 20 days of the growing period, the plants were exposed to drought conditions. The data presented in **Fig. 12** show that the control group of *Raphanus sativus* exhibited 20% less growth than in soil supplemented with the hydrogels. The plants in the control group also showed significant signs of dehydration after 27 days of study (7 days without water). After 35 days of the planting (on the 15 th day without water), all the plants from the control group had completely withered. The hydrogel ability to absorb and retain water allowed the plants to absorb water for longer period during drought conditions. The best plant growth was observed for application of 1% and 2% of the hydrogel HPLA10.



**Fig. 11.** Mineralization curves for the hydrogel samples and cellulose (as a reference) in soil; data refer to mean values  $\pm$  SD ( $n = 3$ ).



**Fig. 12.** Effect of hydrogel application at concentrations of 1, 2 and 5% w/w of HPLA10 in the soil on seed germination and seedling growth of *Raphanus sativus* var. *Sativus*. Control represents soil sample without hydrogel.

The plants appeared to be more vital, and all plants in the hydrogel-supplemented soil samples showed higher growth of about 2 cm compared to the control (as present in **Table 3**). In addition, these plants grew almost 20% longer than the control plants during the period without water. Similar results were observed for plants of *Phaseolus vulgaris* (**Table 3** and Fig. S12, supplementary material). However, the raising the amount of hydrogel applied (5%) resulted in slight retardation in germination and plant growth of *R. sativus*, probably due to its higher sensitivity to soil condition (e.g. fertilization, acidification). A high concentration of hydrogel in soil can cause the consequent acidification of the soil due to the presence of acid whey which may affect the initial growth phase of the plant [31].

### 3.7. Effect of degraded products on soil quality

The impact of the degraded hydrogel HPLA20 on soil quality was investigated by macro-analysis of the soil before and after biodegradation of the hydrogel in relation to the pH of the soil and its content of organic carbon and nitrogen. Although acid whey caused the pH of the hydrogel to drop prior to the experiment, no extreme decrease in the pH of the soil was observed during the biodegradation of hydrogel. In fact, the pH level of the soil was slightly higher (rising from 5.8 to 6.4) once the hydrogel had degraded, caused by the presence of the decomposition products (C, N) of the whey-based material. Carbon is required in the photosynthesis process and serve as a limiting factor for plant growth [52]. Nitrate is also required to promote plant growth, since it is a primary constituent of numerous compounds that aid the structural development and metabolic processes of plants [43]. As **Table 4** shows, such essential nutrients increased as a consequence of the hydrogel degrading in the soil, thereby potentially enhancing the growth of the plants.

**Table 4** Effect of the degradation products of the hydrogel on carbon and nitrogen content (mg/l) and the pH of the soil.

Sample	C <sub>Tot</sub> (mg/l)	N (mg/l)	pH
Hydrogel	178.90	11.06	4.9
Pure garden soil	16.34	27.75	5.8–6.0
Soil with degraded hydrogel	88.02	35.08	6.4

## 4. Conclusions

The results of this study clearly reveal that incorporating low-molecular-weight PLA in the hydrogel made the material more stable in the soil environment, with the potential advantage of raising water retention in soil. The soil amended with the hydrogel exhibited almost 30% greater capacity for water retention compared to pure soil, while also having a positive effect on plant growth. Preliminary results indicated that the hydrogel is capable of the controlled release of fertilizers with the aim of optimizing their functionality. The increasing the amount of PLA led to a drop in the KNO<sub>3</sub> and urea loading capacity (from 76% to 69% for KNO<sub>3</sub> and from 66% to 51% for urea, respectively) but more of the fertilizer loaded was available for encapsulation and the hydrogels showed better entrapment efficiency (from 82% to 92% for KNO<sub>3</sub> and from 86 to 96% for urea, resp.). In addition, introducing PLA maintained the controlled release of agrochemicals from the hydrogel. The results of the biodegradation study in the soil revealed that hydrogels with the 20% wt PLA prolonged their degradation time in soil by almost 25%. The monitoring of CO<sub>2</sub> production during biodegradation by gas chromatography showed that almost 85% of the hydrogel in the soil was mineralized within 60

days of the study. Application of the hydrogel to the soil enhanced the growing and survival rate of *Raphanus sativus* and *Phaseolus vulgaris* by 20% during drought conditions, compared to control plants. Employing acid whey in the production of such hydrogels is a promising alternative that could advance fertilization practices. The whey-based hydrogel has the potential benefits of utilizing nutritional compounds from the whey more effectively and increasing their availability to plants.

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