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ORIGINAL PAPER

Natural Carrageenan/Psyllium Composite Hydrogels Embedded Montmorillonite and Investigation of Their Use in Agricultural Water Management

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Abstract

The carrageenan/psyllium composite hydrogels with embedded montmorillonite have been successfully prepared for the synthesis of a new hydrogel material that is natural, biodegradable and to be used as an absorbent in agriculture. Hydrogels with different composition ratios were found to have the water absorption capacities attaining 2893% and 775%, for free and under load conditions, respectively. The one-way compressional test results have yielded the module values reaching to 226 kPa and showed that they increase with the carrageenan and montmorillonite contents. The hydrogels exhibited different morphological structure depending on the composition ratios. On the other hand, the contribution of the gels to the water absorption and the water retention properties of the soil was investigated by applying various tests to the soil samples mixed with hydrogels. The results showed that including the hydrogels into soil at a ratio of 0.4% increased the water holding capacity of soil from 0.533 to 0.836 g/g and raised the water content % of the soil more than 60%. Additionally, biodegradation test results indicated that depending on the compositional ratios, the hydrogels exhibited a high biodegradation behavior with a weight loss of 39.88% at the end of 35th day. These all finding suggest that these new natural composite hydrogels would be an eco-friendly alternative to present synthetic soil conditioners.

Keywords Hydrogels · Carrageenan · Psyllium · Agriculture · Soil conditioner

Introduction

Agriculture is one of the areas where water is used the most, and it is known that more than 70% of the total water used is spent for irrigation [1].Various researches are being carried out to bring this high rate down, and new methods are introduced. One of these methods is the use of materials with water absorption feature to be placed in the soil. The main substances that increase the water holding capacity of the soil are: perlite [2], pumice [3], zeolite [4], montmorillonite [5] and superabsorbent polymers/hydrogels [6–11].

The use of hydrogels as water absorbents in this area is remarkable in recent years. Hydrogels, consisting of chemical or physical cross-linked hydrophilic polymers, have the ability to absorb water up to thousands of times their own weight thanks to the hydrophilic groups in their structure and their porous structure in various sizes. In particular, the use of acrylate-based synthetic superabsorbent hydrogels is common in the agricultural field. It is known that the most effective and most widely used super absorbent polymer (SAP) materials are polyacrylate derivatives. They present on the market shelves under different trademarks.

Although it has been stated that hydrogels have been used in agriculture since 1980s, it is seen that scientific studies in this field have gained speed especially in the last 10 years [12]. In one of the pioneering studies on the use of hydrogels in agriculture, it has been reported that it stores 95% of water in soil with the use of polyacrylamide gels [13]. In the following years, Woodhouse and its group have revealed that SAP materials increase plant growth and development in arid regions [14].

However, considering the synthetic and non-biodegradable structures of these substances, especially when approached from an environmental perspective, they are

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not very suitable for use because it is known that maximum 10% of non-renewable polyacrylates are biodegradable per year [15]. Moreover, it is worrying that toxic molecules are released into the soil during decomposition. For this reasons only a certain ratio of them is allowed to be used. Therefore, research has intensified especially on the production of new environmentally friendly SAP materials that can be an alternative to synthetic polyacrylate SAP. In this regard, various studies have been conducted with the hydrogels formed from combination of acrylate based polymer with different type of natural polymers such as chitosan, gelatin and starch [16–20]. Although the obtained gels have been semi-synthetic and it has been increased their biodegradability, they still consist of quite high amount of acrylate based polymer that hardly degrade. For this reason, recently investigations have focused on totaly natural biopolymers such as cellulose and starch derivatives and their hydrogels [10, 21, 22].

Nevertheless, in most of the abovementioned studies moderate values were obtained. For example, Nie et al synthesized carboxymethylcellulose hydrogels and found that their water adsorption capacity was 97%. In another study, Nnadi et al. prepared potato based SAP and they have seen that this natural superabsorbent increased the water holding capacity of soil 0.24% when used at a low ratio of 0.12. In another study carried out Franscesco et al. it was developed citric acid cross-linked hydrogel formed from carboxymethylcellulose (CMCNa) and hydroxyethylcellulose (HEC) and they investigated its potential by mixing with perlit. They found that addition of 1% hydrogel in perlite increased its water content from 28.3 to 36.2%.

The one of the best results obtained from the scientific studies may be belongs to Canazza et al. [23]. They prepared 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride crosslinked carboxymethylcellulose sodium salt (CMCNa) and hydroxyethylcellulose (HEC) hydrogels. They reported that these materials absorb 74 times distilled water and 40 times salt water of their own weights. However the effect of of SAP material on water retention capacity of soil was observed to be less than 5% in first 10 days.

In general, it is commonly known that SAP materials less absorb salt water than pure water and this ratio vary between 30 and 60 g water/g superabsorbent [24]. However, as seen in this study, this disadvantage in absorption becomes an advantage in desorption, salt water is released more slowly by superabsorbent—which is a very important point in agricultural use. What is expected from SAP in this field is to absorb as much water as possible and deliver it slowly. The decrease in the water desorption rate of the superabsorbent, which absorbed brine was explained with the formation of extra ion-dipol interactions between the ions and water molecules inside the hydrogel and it was stated that this makes the water molecules difficult to leave from hydrogel network.

The purpose of this study that we especially started by seeing that there are a limited number of studies on this subject, was to synthesis a new natural material that would exhibit better properties as soil conditioner than the those in the abovementioned studies.

According to the literature research, no studies on the use and synthesis of the proposed montmorillonite filled carrageenan/psyllium composite hydrogels have been found. With these natural hydrogel materials prepared in a completely new composition, it was aimed to develop an alternative natural hydrogel that can be used as a soil enhancer in agricultural field. With this aim, carrageenan was chosen as main component for preparation of the hydrogel. Carrageenan, which obtained from red seaweeds, is made up of repeating galactose units and both sulfated and nonsulfated 3,6-anhydrogalactose (3,6-AG) [25]. These sulfate groups bring extra water absorption capacity to carrageenan hydrogels. Because, these groups have the ability to totaly ionize, unlike various functional groups such as amine and carboxylic acid, which exist in chitosan, alginate, gelatin, carboxymethyl cellulose etc. In addition, their ionization is not affected by the ambient pH, which is very important when considering the pH variations in the soil. Most of the studies with carrageenan include the carrageenan hydrogels obtained by crosslinking with glutaraldehyde or the grafting with various synthetic polymers [26–28]. On the other hand, with the aim of obtaining totally natural material, they are being generally used with alginate and gelatin [29–31].

Psyllium, the second polysaccharide material used in hydrogel synthesis in this study, is a water-soluble fiber obtained from the grinding of the seeds of *Plantago ovata*, a plant grown in India. Psyllium, which is a polysaccharide mix consisting of arabinoxylan, arabinose and xylose, has a property that formes a gel structure when mixed with water, without need of extra crosslinker unlike various natural polymers. Psyllium has been the subject of several studies on hydrogel production. In most of these studies, acrylamide-derived hydrogels were synthesized in presence of psyllium and the properties of the new gels obtained were investigated [32–35]. In this study, it was estimated that psyllium would provide extra hydrophilic character, hence extra water absorption capacity to the hydrogels. And also, it was thought that because it has no contain any ionic groups, it would not interfere the effect of sulfonate groups in carrageenan.

Montmorillonite, the third and final component of hydrogel synthesis, is a member of the smectite clay family. Montmorilllonite clay itself has the ability to absorb water due to existence of high number of hydrophilic hydroxyl groups on its surface. Moreover, it has a property that increase the mechanical strength of various polymeric materials and used for this purpose [36, 37].

In this study, which aims to obtain a new natural absorbent material by combining these three components listed above montmorillonite filled carrageenan/psyllium composite hydrogels were prepared. It was estimated that psyllium chains in carrageenan hydrogel network would increase the water absorption of the gel network owing to their high amount of hydrophilic groups. At the same time, montmorillonite was expected to increase not only gel strength, but also water absorption. Additionally these two components were believed that they would have positively impact on the water holding and the water retention capacities of soil, which forms of the main purpose of this study. The gels were subjected to the following various tests after they were synthesized; swelling tests and absorbency water under load tests, mechanical test, morphological tests, water holding and water retention capacity of soil with hydrogel and finally biodegradation.

Experimental

Materials

The carrageenan that will form the main matrix was purchased from Aldrich Chemicals (Milwaukee, US), while the psyllium, which will be used as an additional polymer, was obtained from a functional food trading company. Sodium montmorillonite clay (MMT), used to increase mechanical strength, was purchased from Süd-Chemier-Germany. Potassium chloride, which is used to physically crosslink carrageenan polymer, was bought from Sigma Aldrich. Soil, on the other hand was supplied by a local market. In the hydrogel synthesis deionize water was used, while in swelling tests tap water of which pH was 7.4 and EC was 75 uμ.

Preparation of the Hydrogels

A certain amount of MMT was firstly dispersed in deionized water under ultrasonic homogenizer. Then, carrageenan, psyllium and potassium chloride were added in this mixture at different proportions in turn and a homogenous mixture was obtained. The compositional ratios of the hydrogels are seen in Table 1. The mixture was poured into the glass tubes in the water bath at 80 °C and allowed to gelation for 1 h. After gelation, the hydrogels were removed from the glass tubes and cut into 1 cm of thickness and dried at room temperature until constant weight. The all stages of the hydrogel synthesis were depicted in Fig. 1. The gels obtained were named as C-PX-MMTY. Here, X and Y represent the psyllium and MMT ratios respectively and their values are shown in Table 1 in detail. Additionally, gelation reaction was illustrated in Fig. 2.

Table 1 Chemical composition of hydrogels

Hydrogel composition ratios				
Hydrogel code	Carragenan (g/10 ml)	Psyllium (g/10 ml)	MMT (mg/10 ml)	KCl (g/10 ml)
C2MMT1	0.4	–	2	0.2
C2MMT2	0.4	–	4	0.2
C2P1MMT1	0.4	0.025	2	0.2
C2P3MMT1	0.4	0.075	2	0.2
C2P1MMT2	0.4	0.025	4	0.2
C2P3MMT2	0.4	0.075	4	0.2

Gel Fraction of the Hydrogels

The synthesized hydrogels were dried at room temperature until getting constant weight and their weights were recorded (W_1). Then they were immersed in deionize water to extract the unreacted soluble parts for 12 h. Afterwards, they were dried again by applying the same procedure and weighed (W_2). The gel fraction % values were calculated by using the following equation:

$$Gel\,Fraction\% = \frac{W_2}{W_1} \times 100. \qquad (1)$$

Free Swelling Test of the Hydrogels

In order to obtain swelling degrees of the hydrogels at free condition dry hydrogels with known weights were soaked in separately deionize water and tap water and it was monitored their weights against time by taking of them from the water at certain time intervals. The swelling degrees was calculated by using the following equation:

$$Sw\% = \frac{m_s - m_d}{m_d} \times 100 \qquad (2)$$

where m_s and m_d show the weights of the swollen and dry hydrogels respectively, while S_w % represents the swelling degree of the hydrogels.

Absorbency Under Load Tests of the Hydrogels

Dry hydrogels with known weight were placed in the swelling device under load and applied a load of 3 kPa. Then a suitable amount of tap water was added and left to swell for 24 h. At the end of 24 h, the hydrogels was removed from the environment, and the excess of water outside of the gels was taken with a filter paper and the

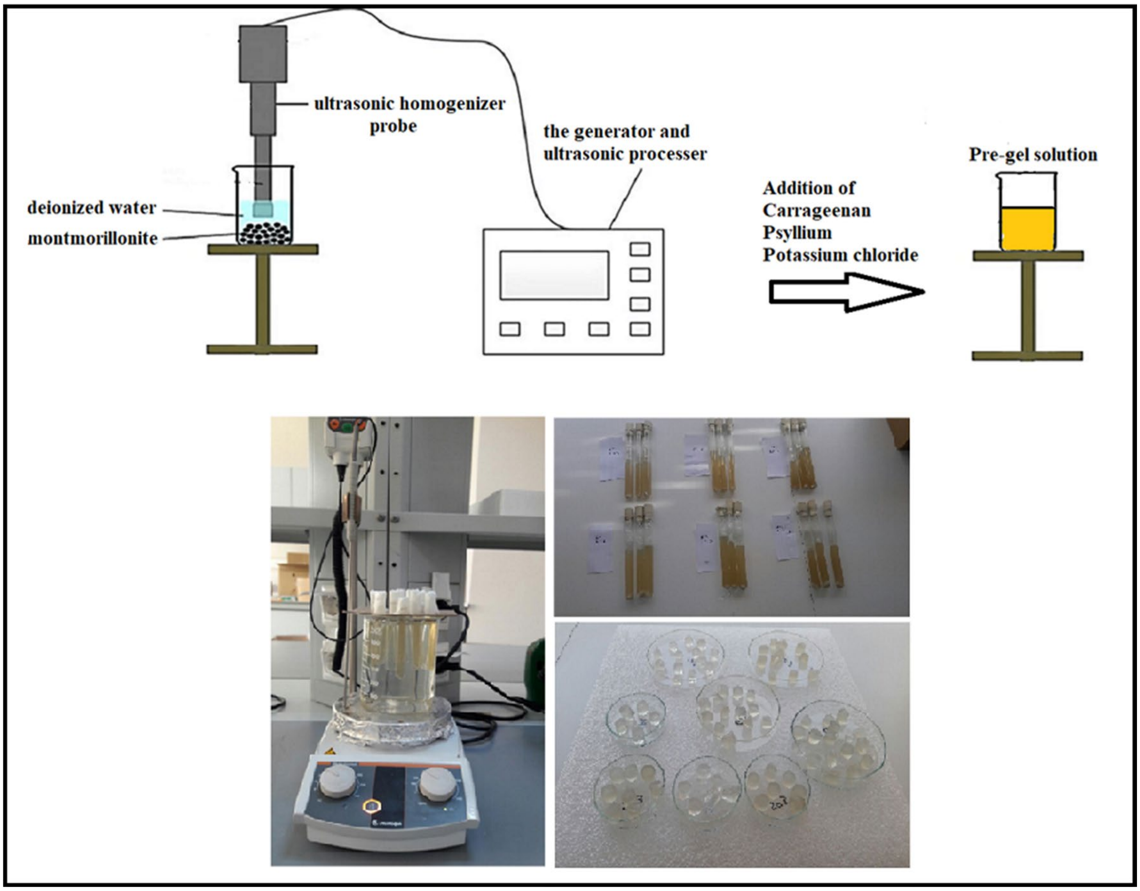

Fig. 1 Synthesis schema of the montmorillonite embedded carrageenan/psyllium hydrogels

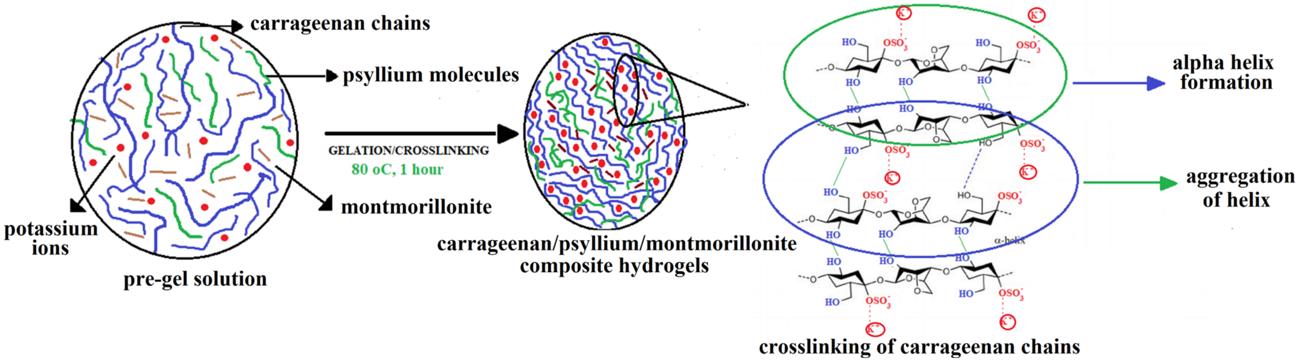

Fig. 2 Gelation/crosslinking of the montmorillonite embedded carrageenan/psyllium hydrogels

hydrogels were weighed. It was used following equation for calculation of the absorbency under load (AUL %):

$$AUL\% = \frac{m_s - m_d}{m_d} \times 100 \quad (3)$$

In the equation, ms and md show the weights of the swollen and dry hydrogels respectively, while AUL% represents the swelling degree of the hydrogels.

Mechanical Tests of the Hydrogels

The mechanical compression test of swollen hydrogels was carried out at the room temperature as single-axis with a compression speed of 2 mm/min. The tests were carried out with Zwick/Roell Z1.0 Universal Testing Machine (Zwick GmbH & Co.KG, Germany) with 50 N load cell and terminated when sample deformation reached 40%.

Morphological Tests of the Hydrogels

In order to investigate the morphology of the gels, SEM analysis of dry hydrogels was performed using FEI Inc., Inspect S50 model SEM device. Microscopic images of dry gel samples coated with gold were taken.

Water Holding Capacity Tests of the Soil with Hydrogel

The soil sample was thoroughly powdered by passing through a fine sieve and dried in the oven at 60° C. Then, 25 g of these soil samples were mixed with hydrogels to have hydrogel ratio 0.4% and placed into nylon filter bags. As control group, a sample of soil without any gel was placed in another filter. As done in the literature [38], nylon filter bags were immersed in beakers containing 100 ml of deionized water and waited for 20 min, allowing to water absorption. After 20 min, the increase in the weight of the filters taken from the medium was recorded and the water holding capacity (WHC) of soil samples with different composition ratios were determined (Eq. 4).

$$WHC = \frac{m_f - m_i}{m_i} \tag{4}$$

where mi and mf show the initial and the final weights of the soil samples, respectively, while WHC demonstrates the water holding capacity of the soil samples.

Water Retention Capacity Test of the Soil with Hydrogel

After the soil samples, which had absorbed water in the previous stage, were taken from the beaker full of water and hanged with a suitable device together with the filters they were in, and the decrement in the water content of soil were daily followed. The water retention percents, which means the percentage of the water content in the soil at t time with respect to the amount of water adsorbed by soil (WR%) were calculated by using following equation:

$$WR\% = \frac{W_t - \mathrm{W}}{W_0 - W} \times 100 \tag{5}$$

W and W_0 are the weights of the dry soil and the initial wet soil, respectively, whereas W_t represents the weight of the soil sample at certain time intervals.

Biodegradation Test of the Hydrogels

Soil burial test method was used for the biodegradation analysis of hydrogels [39]. The soil sample that powdered by passing through a fine sieve, was placed in a glass beaker and dried for 1 h in an oven at 60 °C. Dry hydrogel samples weighing approximately 0.1 g were then embedded in soil samples at a depth of 3 cm from the surface. Afterwards, enough tap to cover the soil water was added into the beakers and covered with aluminum foil, were kept at room temperature. Once every 7 days, the gels were removed from the soil, quickly washed with deionized water and dried to constant weight at room temperature. The hydrogels whose weights were measured, were burried into the same soil again. The weight loss of the hydrogels were calculated by using the following equation (Wi and Wf show the initial and the final weights of the hydrogel samples):

$$Weightloss\% = \frac{W_i - W_f}{W_i} \times 100. \tag{6}$$

Results and Discussion

Gel Fraction of the Hydrogels

The gel fraction % values of the hydrogels are seen in Table 2. The results ranged between 67.2 and 84.2% showed that both addition and rise in the psyllium content caused to an increment in the gel fraction. This increased values were observed most probably due to the increment in the polymer density in the hydrogel. This result is reasonable, because as the polymer concentration rises, the polymer chains more strongly interact with eachother, which makes them stable and indissoluble. On the other hand, it is seen that MMT ratio is effective in the gel fraction. However its effect seems to be less compared to psyllium content, possibly due to its low ratio in the hydrogel composition.

Table 2 Gel fraction % values of the hydrogels

Hydrogel code	Gel fraction %	Hydrogel code	Gel fraction %
C-MMT1	67.2 ± 2.05	C-MMT2	69.7 ± 2.78
C-P1-MMT1	73.8 ± 2.57	C-P1-MMT2	75.4 ± 2.91
C-P3-MMT1	79.5 ± 3.02	C-P3-MMT2	84.2 ± 3.19

Swelling Behaviour of the Hydrogels

Water Type Effect on the Swelling Behavior of the Hydrogels

The swelling curves of the hydrogels which immersed in deionize water and tap water separately are seen in Fig. 3. Generally, it is known that the hydrogels less swell in tap water due to various ions which enter to gel network. This effect is seen more pronounced in ionic hydrogels. Because these mentioned ions in tap water reduce the swelling degrees of the gels, by interacting with the ionic groups in the hydrogels. This situation, mentioned in the literature for chemical cross-linked gels, was not found in this study, which included a completely physical cross-linked gel composition. In this study, the swelling ratios in tap water were found close to those in deionize water. This fact can be explained by the fact that divalent cations that present in tap water, which cause to increment in physical cross-link density by interacting with the sulfate ions in carrageenan. Moreover also monovalent cations decrease the ionic character of these sulfate groups of carrageenan. Therefore the hydrogels become relatively more denser structure. Most probably in this situation psyllium interacts with carrageenan chains more, getting more stable structure and hence, contributing water absorption of the gels.

In fact, these swelling values in tap water, which do not decrease significantly, actually made gels more suitable for agricultural applications where tap water was used.

Hydrogel Composition Ratios Effect on the Swelling Behaviour of the Hydrogels

It is understood that insertion of psyllium into hydrogel increases the swelling ratios of the gels. However, as seen in the Table 3, psyllium had a different effect on swelling raios of the gels depending on MMT ratio. It was reported that in the C-MMT1 series, the addition of psyllium (C-P1-MMT1) increases the swelling degrees, as expected. Because psyllium has a high number of hydrophilic groups which would contribute to water absorption. On the other hand, the results showed that the triple ratio of psyllium (C-P3-MMT1) caused some reduction in swelling values. This negative effect can be attributed to fact that psyllium increases the polymer concentration in the hydrogel network and reduces the pore sizes, which are closely related to water absorption of the gels.

If one pay attention to the gels with higher MMT content; here, it is seen that the addition of psyllium (C-P1-MMT2) increases the swelling ratios of the gels, similar to C-MMT1 serie. However, unlike of this, increment in psyllium ratio

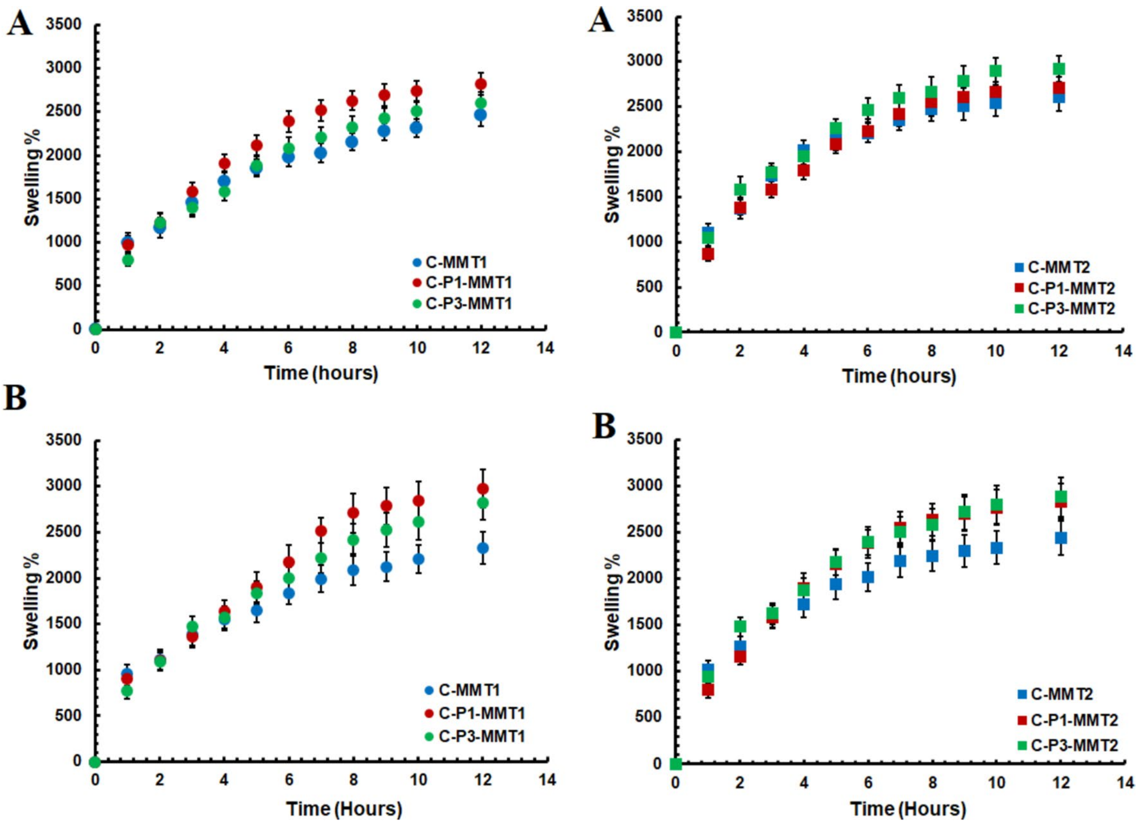

Fig. 3 Swelling curves of the montmorillonite embedded carrageenan/psyllium hydrogels in **a** deioneize water, **b** tap water

Table 3 Swelling kinetic constants and theorical equilibrium swelling degrees of the montmorillonite embedded carrageenan/psyllium hydrogels

Hydrogel	DW				TW			
Code	$S^{a}_{eq(exp)}$	$S_{eq(cal)}$	k_s	R^2	$S^{a}_{eq(exp)}$	$S_{eq(cal)}$	k_s	R^2
C-MMT1	2314	2865	1.33×10^{-4}	0.9884	2211	2762	1.31×10^{-4}	0.9819
C-P1-MMT1	2736	3788	7.09×10^{-5}	0.9847	2844	4525	3.69×10^{-5}	0.9139
C-P3-MMT1	2504	3448	7.36×10^{-5}	0.9837	2613	3802	5.41×10^{-5}	0.9721
C-MMT2	2537	3096	1.46×10^{-4}	0.9956	2338	2874	1.49×10^{-4}	0.9935
C-P1-MMT2	2659	3571	8.11×10^{-5}	0.9916	2773	4098	5.36×10^{-5}	0.9912
C-P3-MMT2	2893	3676	9.23×10^{-5}	0.9907	2804	3690	8.13×10^{-5}	0.9891

[a] S(exp) values are the average values obtained from triplicate measurements

caused the gel (C-P3-MMT2) to swell more. This interesting result can be ascribed to fact that high amount of MMT could not be homogenously dispersed in gel network due to greater psyllium content and it might interefere the formation of some physical crosslinks by accumulating on some regions of the hydrogel. Hence, they could be cause to decrease of crosslink density and thus, increase of swelling values. Presumably for this reason, although the gel density in C-P3-MMT2 gel composition is high, the swelling ratio in the C-MMT2 series was found to rise with increasing psyllium.

On the other hand, it can be seen from the table that also the MMT ratio was effective on the swelling percents. It was observed that the swelling degree increased from 2314% (C-MMT1) to 2537% (C-MMT2) with MMT content in gels without psyllium, as expected.

However, the situation in C-P1 was found to be different. For instance, it was noted that the gel swelled slightly less with MMT increase. This situation can be interpreted that the gel becomes denser with the addition of psyllium and MMT and they both filled the pores of the gels. This means to relatively low swelling extents. As to C-P3 gels, due to the presence of excess amount of psyllium the gel is denser. Hence, these high amount of MMT layers may have prevented formation of some physical crosslinks by entering between carrageenan chains, which means higher swelling degree.

Swelling Kinetic Constants of the Hydrogels

In addition to the maximum swelling ratios given above, the following second order kinetic equation, which is known to best explain the swelling process, was used to determine the swelling kinetic constants [40].

$$\frac{t}{S_t} = \frac{1}{S_{eq}}t + \frac{1}{k_s(S_{eq})^2} \tag{7}$$

In the equation, S_t and S_{eq} show the swelling degrees of gels in the predetermined t time intervals and equilibrium, respectively, and k_s the swelling rate constant. As can be seen in the Eq. 1, the swelling rate constant of the gels were calculated from the slope and intercept values of the graphs (Fig. 4) drawn between t/S_t and t with the help of swelling degrees taken at t time intervals. The obtained results were given in Table 3.

When Table 3 is examined, the correlation coefficients (R^2) were found very close to 1, indicating that the swelling process of the gels well fits to the second-order kinetic equation. However, interestingly, the theoretical equilibrium swelling values were found to be higher than the experimental ones. The big difference observed between these two parameters, which was more obvious in the gels containing psyllium, can be attributed to the fact that the gel consists entirely of physical cross-linked polymers. These interactions in physical crosslinked gels differ depending on whether the gel is more or less dense. In the low dense situation, these decrease of interactions between the psyllium molecules and carrageenan chains cause the psyllium molecules in the gel to hydrate, which leads these polymers to leave from the gel. Most probably for this reason at low dense medium, psyllium tends to dissolve. Unlike psyllium, carrageenan seems to be more stable since they are connected to each other strong ionic interactions that created by potassium chloride. It is suggested that the difference that observed especially for the gels with psyllium seems to be the reason is only psyllium.

Comparison of the swelling rate constants of the hydrogels indicated that for both the deionize and tap water environment, the hydrogels swelled faster with increasing MMT content. This result can be explained with the increment in hydrophilic character of the hydrogel with the addition of MMT. However, this increment was found to be lower in the gels without psyllium. Most probably in these gels, since there is only carrageenan chains exist, MMT had an opportunity for homogenously dispersed. An interesting point is that here there are possibly two opposite effects of MMT layers on the swelling rates. The first is that MMT has a high number of water absorbing hydrophilic groups which provides that the gel faster swell. The second is that increase of MMT cause to increment in gel

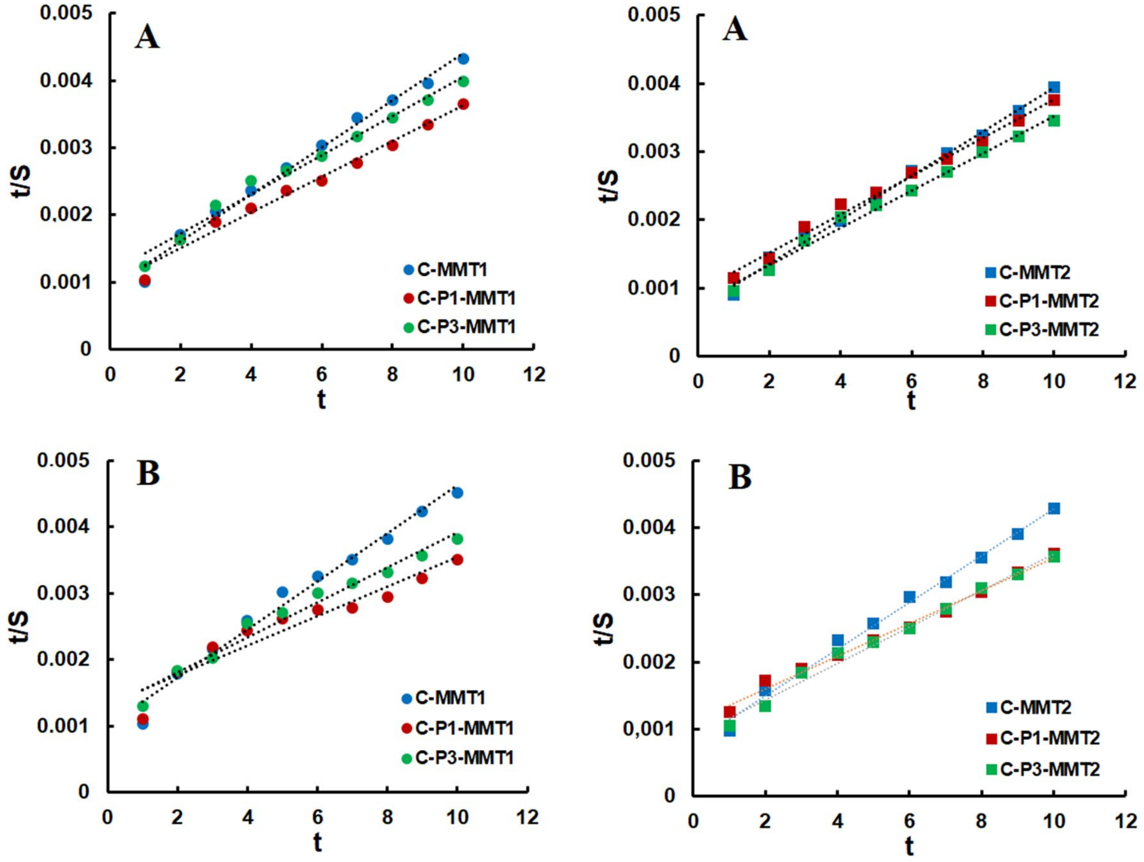

Fig. 4 Swelling kinetic relations of the montmorillonite embedded carrageenan/psyllium hydrogels in **a** deionize water, **b** tap water

density and thus, decrement in pore sizes of the gels. From the results, these two effects seem to be almost balanced.

On the other hand, it was revealed that the hydrogels swelled more slowly with the addition and increase of psyllium ratio. This is because the gels have denser structure with psyllium and hence, the amount of space, that the water will penetrate initially, decreases. The constant values varied between 7.09×10^{-5} and 9.23×10^{-5} showed that the hydrogel had the highest swelling rate constants was C-P3-MMT2 as seen from Table 3. This results is in a good agreement with the swelling degree values. Because the high swelling value of this gel was explained above with its possible low cross-link density due to heterogeneously dispersion of excess of MMT layers that interfere formation of some crosslinks. As is well known that lower crosslink density means bigger pore, which facilitates the water absorption.

Moreover, the swelling rate constant were found to be lower in tap water, which can be ascribed to fact that in the case of tap water some ions penetrate into hydrogel network along with water molecules and most of them make physically bonds with especially sulfonate groups in carrageenan which cause to increment the polymer density, which leads to slower water absorption.

Absorbency Under Load (AUL%) of the Hydrogels

The AUL % values of the gels, which were kept in tap water for 24 h under a load of 3 kPa, were given together with the equilibrium swelling degrees of the hydrogels under free condition in Table 4 for easy comparison. As expected, the swelling ratios of all gels under load, which found to be between 594 and 834%, significantly decreased compared

Table 4 Absorbency under load values and free swelling % of the montmorillonite embedded carrageenan/psyllium hydrogels in tap water

Hydrogel	Swelling % (24 h) (tap water)	AUL (%)[a]
C2-MMT1	2211	594
C2-MMT2	2338	834
C2P1-MMT1	2844	399
C2P3-MMT1	2613	607
C2P1-MMT2	2773	775
C2P3-MMT2	2804	775

[a] The measurements were done in triplicate and the AUL % values are the average values

to the free swelling degrees. This situation, which is well known in the literature, is mainly evaluated as the decrement in swelling values due to the reduction in the pore size of the gels under load. This explanation done for strong chemical crosslinked gels can also used for the physical cross-linked carrageenan gels in this study. In addition, the other reason can be proposed for explanation of this result. For instance the physically crosslinked hydrogels have a structure that easily disintegrated when applied a force. Apparently, these hydrogels lost of some physical bonds, which leads to especially dissolution of psyllium. Hence, as the hydrogels lost some of hydrophilic components its water absorbency declined.

According to the Table 4, it is seen that the AUL % values decrease with the presence of psyllium (0.25%) and increase then with the further addition (0.75%). This observed behavior can be evaluated by the fact that psyllium tends to dissolution and leave the gel, especially when being applied force to the gel. The fact that this decrease (from 594 to 399%) in C-MMT1 gels containing 0.02% MMT is higher than C-MMT2 gels containing 0.04% MMT supports this prediction. Additionally, it is understood that higher psyllium ratio had been positively effect on swelling. This can be attributed to the fact that the psyllium has strong interactions with the carrageenan due to the density of the medium in the gels in the C-MMT2 series, which were under load, and thus contributes to swelling by remaining stable in the gel.

When AUL% results are generally evaluated it was concluded that the biggest difference between the swelling ratios under load arises from the presence and amount of MMT as expected, and it was observed that the clay increases the swelling degrees of the gels under the load. This can be based on the mechanical forces of the gels expected to increase with MMT.

Mechanical Behaviour of the Hydrogels

The stress-deformation curves obtained as a result of compression tests applied to hydrogels at a speed of 3 mm/min are presented in Fig. 5, and elastic module values depending on the composition ratio are presented in Table 5.

As can be seen from the table, MMT content had a great impact on the gel strengths. This impact was found to be positive in the gels without psyllium. For instance, C-MMT1 was recorded to have the elastic module value of 73.52 kPa, while this extent was found to increase to 100.2 kPa for C-MMT2 gel.

On the other hand, according to the results the psyllium ratio in the gel was also found to have a significant effect on the mechanical strength of the gels. It is understood that the insertion of 0.25% of psyllium considerably increased mechanical strength of the gels with low MMT. For example, the modulus of C-MMT1 was found to increase from 73.52 to 226.17 kPa with the presence of psyllium. It can probably be mentioned here that MMT has a good dispersion property at a ratio of 0.02%. This good dispersion may

Table 5 The elastic module values and the equilibrium swelling degrees of the montmorillonite embedded carrageenan/psyllium hydrogels

Hydrogel code	Swelling %	Elastic modulus (kPa)[a]
C-MMT1	2211	73.52
C-MMT2	2338	100.20
C-P1-MMT1	2844	226.17
C-P3-MMT1	2613	198.24
C-P1-MMT2	2773	182.69
C-P3-MMT2	2804	130.41

[a] The elastic modulus are the average values obtained from triplicate measurements

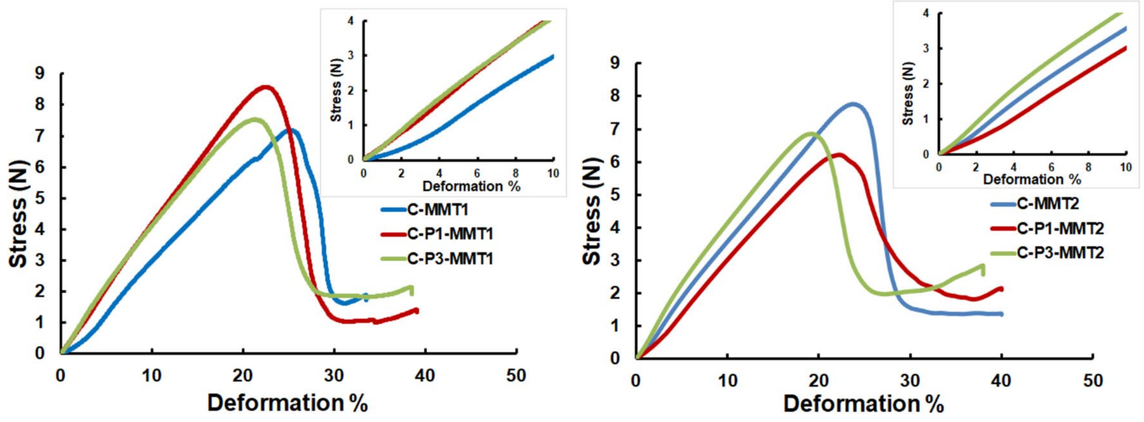

Fig. 5 Stress-deformation curves of the montmorillonite embedded carrageenan/psyllium hydrogels

also indicate that the psyllium also settles well in the gel and interacts well with carrageenan which is a good agreement with the increment in gel strength with psyllium content. Similar to these hydrogels, in the case of high MMT, it was also observed that insertion of psyllium into hydrogels caused to increment in the gel strengths. For example, it was found that C2-MM2 gels without psyllium had a module value of 100.20 kPa, while this value raised to 130.41 kPa with the psyllium ratio of 0.25%. However, tripling the ratio of psyllium was found to decrease the elastic modulus in gels. This mentioned effect was noticed to more obvious in the gels with high MMT content than those with low MMT content. It is understood that the presence of psyllium above a certain ratio in the gel with a high clay content may have prevented that carrageenan chains to form effective physical crosslinking. Presumably the reduction in this crosslink density reduced the mechanical strength of the gel. The high swelling degree of this hydrogel also proves this mechanical behaviour. In addition, another reason is that the clay layers are poorly dispersed in the gel due to the high rate of psyllium and MMT. This also cause psyllium molecules to be badly distributed, which psyllium had weaker interaction with carrageenan chains nd had a mechanically weak structure.

Morphological Behaviour of the Hydrogels

The morphological structures of the gels with different psyllium and MMT ratios are seen in Fig. 6. Comparison of the micrographs of C-MMT1 and C-MMT2 showed that increase of MMT causes the gels to have more denser structure, which may be ascribed to the fact that the extra MMT layers fill the pores in the gel network. However, for the hydrogels having 0.25% of psyllium, some lumps and holes were noticed on the surfaces of gels. The structure observed for the hydrogels with both MMT1 and MMT2 content was noticed to be different for further addition of psyllium depending on MMT ratio. In the case of the gels with low MMT, 0.75% of psyllium was found to decrease the pore size and cause the gels to have denser structure, on the contrary, in the case of the gels with high MMT content, bigger holes were observed, suggesting that the decrement in physical crosslink density with the reason of high dense media which cause them to prevent formation of some of crosslinks. This fact also well explains the swelling behaviour of the gels.

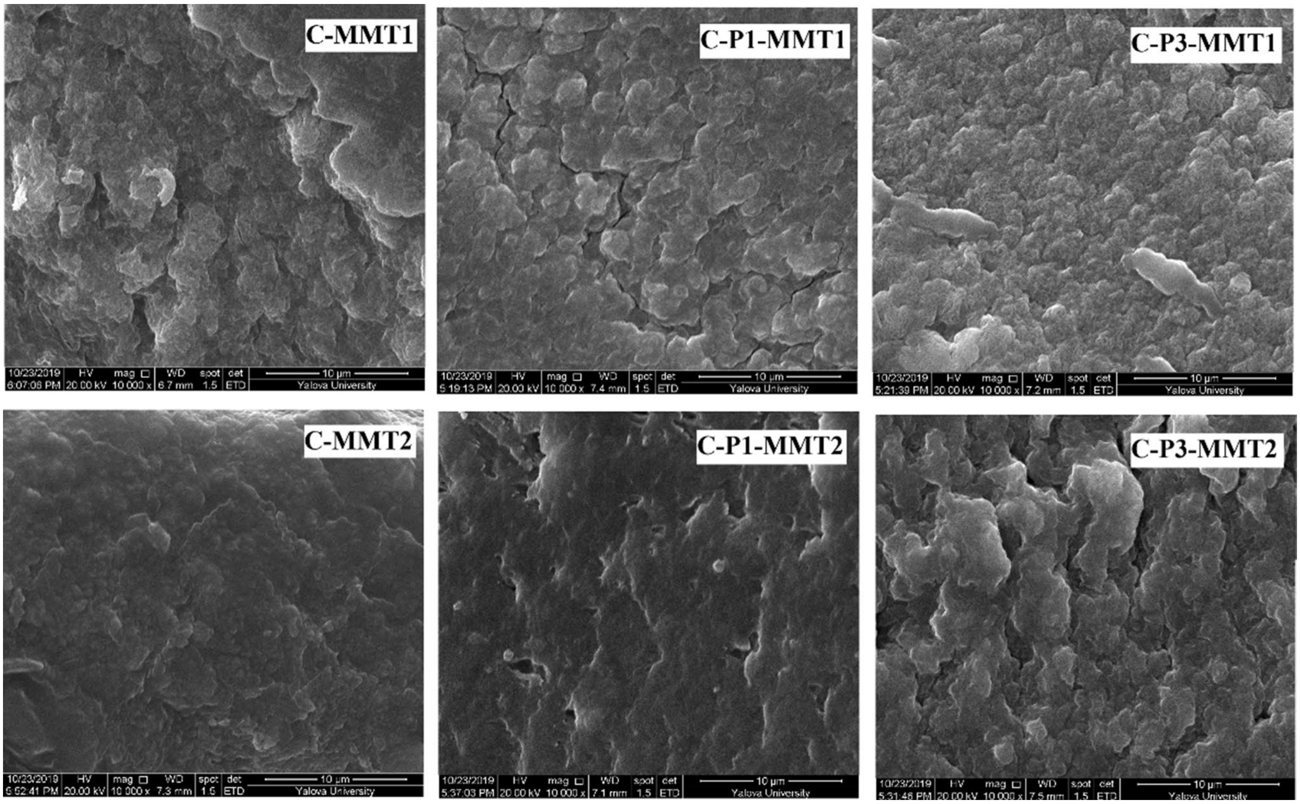

Fig. 6 SEM images of the montmorillonite embedded carrageenan/psyllium hydrogels. The scale bars are 10 µm

Water Holding Capacity of the Soils with Hydrogel

Water uptake capacities of soil samples, in which 0.4% hydrogel is included, are given in Table 6. As can be clearly seen from the table that the water holding capacity of the soil has increased significantly with the inclusion of gels. While the soil holding capacity per gram of water alone is 0.533 g, this value has increased up to 0.836 g with the addition of gels depending on the hydrogel composition. Although the component ratios in the hydrogel appear to be effective in soil absorption of water, it was understood that the differences between the values were probably not large due to the low hydrogel/soil ratio (0.4 g gel/100 g soil). The results in the table indicated that the insertion of psyllium in gels and increasing its ratio did not cause a significant change in water absorption values in the soil. This situation can mainly be explained as follows: Normally, psyllium is a substance that should contribute to water absorption with its hydrophilic property. However, as mentioned previously, unfortunately it is easily hydrolyzed and dissolved in aqueous medium especially when it presents in a certain hydrogel composition. Here, too, it is believed that it might have resolved quickly and left the gel.

As seen from the values in the table, it can be mentioned that the water holding capacity of the soil has increased with the addition and increase of clay in the gel. But the low ratio in the soil seems to prevent clear and very distinct differences from being seen here. However, this relatively higher ratio was found to vary depending on psyllium %. For example, in hydrogels with low psyllium content (C-P1), the water uptake capacity of the soil was recorded to increase from 0.611 to 0.836 g/g with the increase of MMT. But, in the hydrogels with high psyllium content (C-P3) this increment that realized from 0.562 up to 0.746 g/g, was seen that lower than those belongs to the hydrogels with low psyllium content. This small raise can be based on the high density of C-P3 gels, while the higher increment can be attributed to less denser structure of C-P1 gels.

Water Retention Capacity of the Soils with Hydrogel

Depending on the hydrogel composition, the water retention capacity % values of the soil are shown comparatively in Fig. 7 A. As it can be understood from the graph that all soil samples containing gel kept the water longer and more% than those without gel. The results showed that the soil samples without gel had a water retention capacity of 84.45%, whereas insertion of hydrogel at a ratio of 0.4% increased this value up to 92.84% depending on the hydrogel composition. This situation can be interpreted in two different ways: The first is that some of the high psyllium content may be dissolved and leave the gel matrix together with the water it holds. The second is that, with the increase of the psyllium content, the effective physical cross-link ratio of the carrageenan chains may have decreased and therefore the amount of space between the polymer chains has increased and hence, they easily give the water they hold.

Also MMT ratio was found to be effective on water retention % values. As seen from the figure, it is understood that increase of MMT ratio caused to decrement in WR%, suggesting that in MMT2 gels, this excess clay ratio probably does not distribute homogeneously, decreasing the physical crosslink density of carrageenan in certain areas of the gel, in other words, increasing the amount of space between the polymer chains by reducing gel density. These relatively large voids, which are mentioned for this very likely reason, seem to be the biggest reason for the easier delivery of water to the outside environment. SEM graphics also provided information that supports a similar possibility.

To observe the contribution of the hydrogels in the water retention capacities of the soil more detail, also the plots between the water content % and time were illustrated (Fig. 7b). Water content % values were determined with the below equation:

$$Water\ content\% = \frac{W_t - W}{W} \times 100 \tag{8}$$

where W shows the weight of dry soil and W_t refers to the weight of the soil, which absorbed water, at certain time. The results taken at the end of 7 days showed that insertion of

Table 6 Water holding capacity of the soils with the montmorillonite embedded carrageenan/psyllium hydrogels

Sample	Water holding capacity (g water/g soil)[a]	Sample	Water holding capacity (g water/g soil)[a]
Soil	0.533	Soil + C-MMT2	0.731
Soil + C-MMT1	0.725	Soil + C-P1-MMT2	0.836
Soil + C-P1-MMT1	0.611	Soil + C-P3-MMT2	0.746
Soil + C-P3-MMT1	0.562		

[a] The measurements were done in triplicate and the water holding capacities are the average values

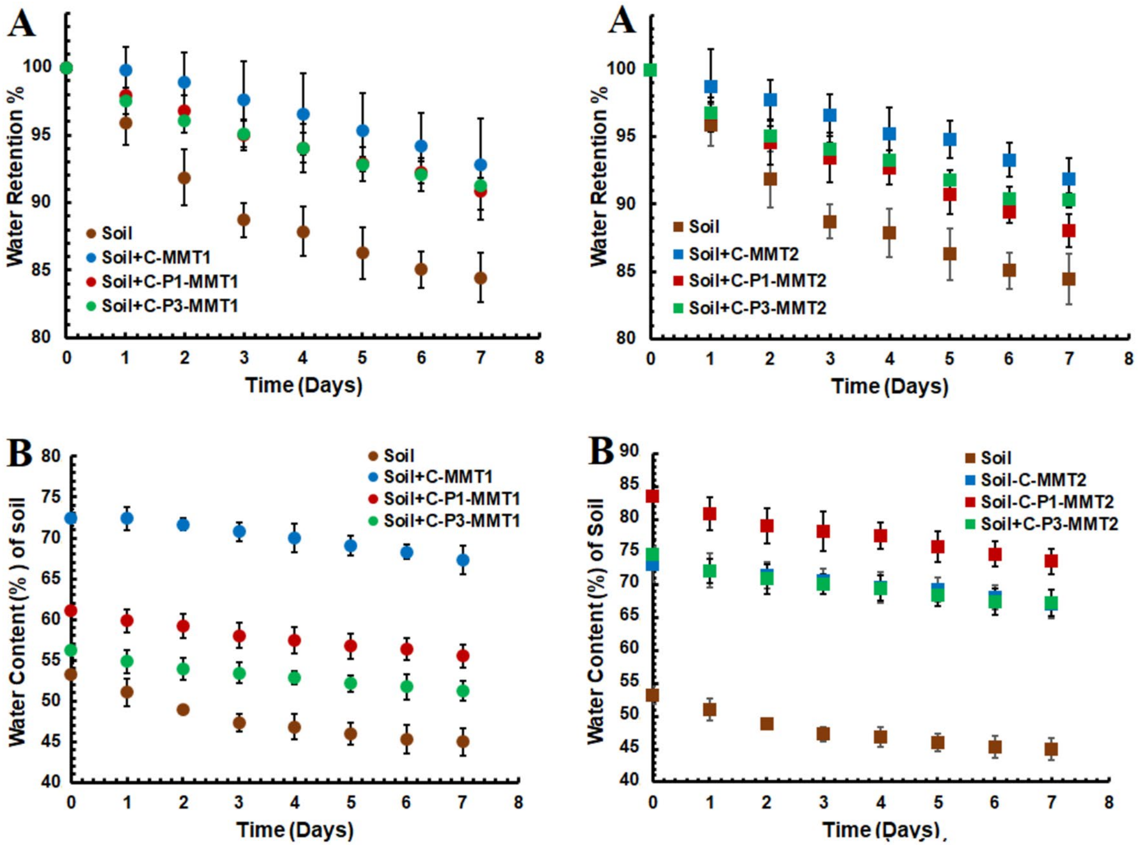

Fig. 7 **a** Water retention of soil with the montmorillonite embedded carrageenan/psyllium hydrogels as a function of time, **b** water content % of the soil

Table 7 Weight loss of the montmorillonite embedded carrageenan/psyllium hydrogels at 35th day

Hydrogel Code	Degradation % (35th day)[a]	Hydrogel Code	Degradation % (35th day)[a]
C-MMT1	14.68	C-MMT2	18.47
C-P1-MMT1	26.71	C-P1-MMT2	39.88
C-P3-MMT1	30.36	C-P3-MMT2	37.25

[a] The measurements were done in triplicate and the degradation percentages are the average values

C-P1-MMT2 hydrodels caused to an increment in the water content of the soil by the ratio of 66%.

Biodegradation Property of the Hydrogels

The weight losses % observed in the gels as a result of biodegradation tests carried out with soil-burial method and continued for 35 days were given in Table 7 and the weight losses % depending on time were shown in Fig. 8. From the test results, it was understood that at the end of the 35th day C-P1-MMT2 gel had the highest degradation ratio (39.88%) and C-MMT1 gel displayed the lowest degradation ratio (14.08%). It is seen from the figure that the gels containing psyllium undergo to biodegradation more and faster. The high biodegradability of the C-P1-MMT2 gel containing 0.04% MMT was not surprising. It has become the most and fastest-degrading gel due to its heterogeneous and poorly-interacted interaction with carrageenan, which is strongly interpreted by both swelling and mechanical properties.

From the results, it is understood that the clay content in the gel composition also has an effect on biodegradation. Especially high weight losses of gels with high MMT ratio are noteworthy. This situation can be interpreted as the high amount of MMT layers do not dispersed homogenously and accumulate excessively in some regions between the carrageenan chains, leading to decrement in the physical cross-link density. As it is known, as the cross-link density decreases, the polymer chains in the gel leave the structure more easily and increase the weight losses. This is probably the case observed here as well.

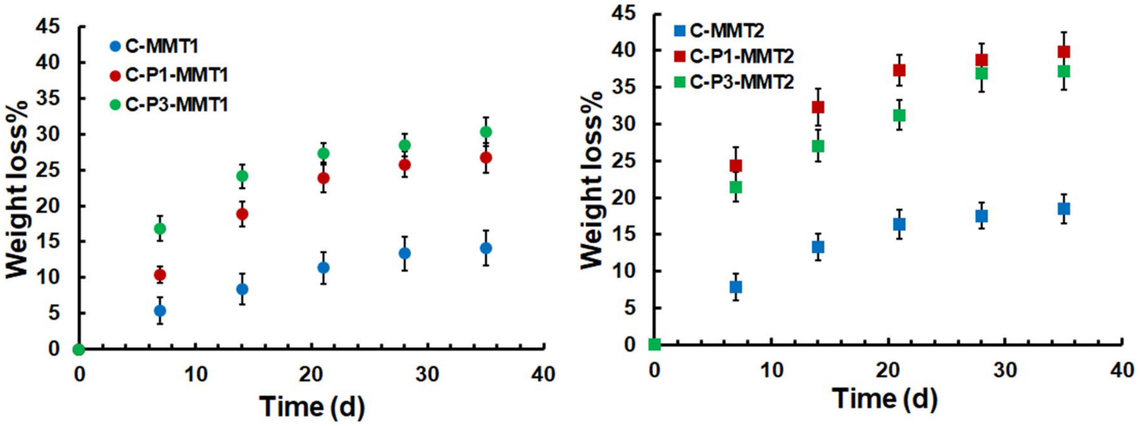

Fig. 8 Weight loss of the montmorillonite embedded carrageenan/psyllium hydrogels as a function of time

Conclusion

In present study, montmorillonite embedded carrageenan/psyllium composite hydrogels were successfully prepared to obtain a natural material to be used as soil conditioner in agriculture sector. The hydrogels formed from totally natural substances have subjected to various test. The swelling measurements showed that hydrogel composition had a great effect on the swelling degrees attaining 2893%. They especially increase with psyllium and montmorillonite contents. Moreover it was found that they also caused to increment in the gel strengths attaining 226 kPa, which is quite high when compared to other physical crosslinked natural hydrogels. However beyond a certain ratio this facts were reversed. Most probably due to the fact that montmorillonite layers do not dispersed homogenously in the gel network with the reason of high gel density, some of the physical crosslinks that would form between the carrageenan chains were blocked by the intervening excess montmorillonite molecules, which resulted in increased swelling degrees and decreased gel strengts.

The SEM analyses demonstrated that the hydrogels have a surface structure that consist of various holes and lumps especially in the case of high psyllium and MMT contents, suggesting that at high gel density, the gels begin to take a heterogenous structure which affect the whole properties of the hydrogels.

The test conducted in soil, on the other hand, showed that hydrogels were very effective on the water holding capacity of soil depending on hydrogel composition. The C-P1-MMT2 corresponding to 0.25% psyllium and 0.04% montmorillonite was determined to be the gel that increased the most the water absorption capacity of soil. While soil absorbs 0.533 g of water per g of it alone, after the insertion of this gel into the soil at a ratio of 0.04%, the water holding capacity of the soil was found to increase up to 0.825 g/g. Additionally, the results taken at the end of 7 days showed that insertion of C-P1-MMT2 hydrodels caused to an increment in the water content of the soil by the ratio of 66%.

On the other hand biodegradation tests carried out through 35 days showed that the hydrogels highly biodegradable. At the end of the 35th day, C-P1-MMT2 was found to be the most biodegraded gel with a weight loss ratio of 39%.

The overall results highlight the C-P1-MMT2 gel, showing that 2.5% psyllium and 0.4% MMT ratio were the optimum values for gels. With this new hydrogel composition it was recorded great properties, most of which exceed those of the similar hydrogel materials in the literature.

In conclusion, this study revealed that montmorillonite filled carrageenan/psyllium composite hydrogels have performed very well in terms of the purpose of increasing the water holding capacity of the soil and they are candidates for agricultural use. Moreover since psyllium is not very common among the polymer scientists and it has just begun to be recognized as a new material in hydrogels synthesis very recent years, it is believed that this study would also give some valuable information and a perspective to the researchers.

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