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Preparation of Sodium Carboxymethly Cellulose Hydrogel for Controlled Release of Manganese Micronutrient

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Abstract

In order to use potential in the development of wheatgrass plant (*Triticum Aestivum*), carboxymethyl cellulose sodium salt (NaCMC) hydrogels were prepared. The characterization of synthesized hydrogels was examined. Water absorbency and gel content properties were influenced the amount of crosslinker in hydrogels. The water absorbency was negatively affected with crosslinker on the contrary gel content. The application of hydrogels improved the water retention capacity of soil. The manganese release was examined in water and soil and the release slowed down with crosslinker. Manganese-loaded hydrogels were used for growing the wheatgrass plant. The growing of plant was positively affected with using manganese-loaded hydrogels. These results suggest that manganese-loaded hydrogels could be utilized as a controlled fertilizer system in agriculture areas.

Keywords: Sodium carboxymethly cellulose, manganese, micronutrient, hydrogel, wheatgrass

Kontrollü Mangan Mikro Besin Elementi Salımı için Sodyum Karboksimetil Selüloz Hidrojelinin Hazırlanması

Öz

Sodyum karboksimetil selüloz (NaCMC) hidrojelleri, buğday çimi bitkisinin (*Triticum Aestivum*) büyümesinde potansiyel kullanım için hazırlandı. Su absorpsiyon ve jel içeriği (yüzdesi) özellikleri test edildi. Jel içeriği sonuçlarının aksine çapraz bağlayıcı içeriğinin arttırılmasıyla su absorpsiyonu azaltılmıştır. Hidrojellerin toprak uygulaması, toprağın su tutma kapasitesini arttırdı. Su ve toprakta hidrojellerin mangan salım davranışı incelendi ve salım değerleri çapraz bağlanma yoğunluğu ile azaldı. Mangan yüklü hidrojelin buğday çimi bitkisinin performansı üzerindeki etkisi de saksı deneyleri yapılarak incelenmiştir. Buğday çimi büyümesi, mangan yüklü hidrojellerin kullanılmasıyla belirgin olarak artmıştır. Hidrojellerin kullanılmasıyla bitki performansındaki artış, hazırlanan hidrojellerin tarım alanlarında kontrollü bir gübre sistemi olarak kullanılabileceğini göstermektedir.

Anahtar Kelimeler: Sodyum karboksimetil selüloz, mangan, mikro besin elementi, hidrojel, buğday çimi

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1. Introduction

Plants require at least 17 plant nutrients in order to develop optimal growth. Macronutrients and micronutrients are known as plant nutrients. Carbon, hydrogen and oxygen (basic nutrient) are absorbed by plants from air and water. Plants take 14 other nutrient elements directly from the soil. Macronutrients are used more in quantity by plants, while micronutrients are used less in quantity by plants. The less usage of micronutrients by plants does not make them insignificant. One of the conditions limiting plant development is that the plant does not receive enough micronutrients. Manganese (Mn), nickel (Ni), zinc (Zn), molybdenum (Mo), copper (Cu), boron (B), chlorine (Cl) and iron (Fe) are acknowledged as microelements [1].

Manganese has a fundamental role in the activation of life-sustaining enzymes (dehydrogenase, decarboxylase, oxidase enzymes etc.). It plays a role in the disintegration of water in photosynthesis. It is effective in nitrogen metabolism and assimilation. It makes easy the absorption of magnesium, calcium and iron with iron in the formation of chlorophyll activity. It accelerates the germination and fruit ripening of the plant seed. In manganese deficiency, chloroplast formation is disrupted, and the cell becomes smaller. Manganese deficiency is often caused by calcareous, high pH soils is seen on. In the manganese excess, brown spots appear due to the accumulation of manganese dioxide (MnO_2) in leaves and chlorosis occurs around the spots. The toxicity range is 1000 mg kg^{-1}. Adequate concentrations of manganese change from 20 to 200 mg kg^{-1}[2].

The most effective method to make nutritional status equivalent to plant requirements is using controlled release fertilizer to control their release in soil. Compared to the traditional fertilizer type, controlled release fertilizers have many advantages such as (1) provide single easy application (2) minimize nutritional losses (3) no contamination in groundwater (4) minimum irrigation addiction and over dosage application. Controlled release fertilizers can be mainly separated into 3 categories based on their coating and nutrient composition: uncoated nitrogen-based fertilizers, coated nitrogen-based fertilizers and polymer-coated or polymer matrix multi-nutrient fertilizers [3,4].

Hydrogels are an important class of polymeric gel/materials known as insoluble in water. For a polymer to exhibit hydrogel properties when crosslinked, it must contain hydrophilic groups capable of forming hydrogen bonds such as hydroxyl, carboxyl, carbonyl, amine and amide in the main chain or its side branches [5].

Sodium carboxymethyl cellulose (NaCMC) is a biodegradable and biocompatible polysaccharide polymer. It is produced in alkaline medium by interacting cellulose with sodium monochloroacetate. It is a polyelectrolyte, so it is susceptible has to pH. NaCMC hydrogels can be synthesized easily because of their hydrophilic groups [6,7].

In this work, the controlled release fertilizer systems were prepared to block the pollution and restrain overabundant usage of fertilizers. NaCMC was used as a coating supplies to prepare controlled release fertilizer systems. The characterization of hydrogels was investigated. The manganese release experiments were used in soil and water medium. The influence of hydrogels contained micronutrient were investigated on plant growth.

2. Materials and Methods

2.1. Materials

NaCMC (nominal Mw 250 kg/mol), $MnSO_4.7H_2O$ and $FeCl_3.6H_2O$ (97%), were obtained from Sigma Aldrich.

2.2. Preparation of NaCMC hydrogel

Hydrogel were obtained using ionic crosslinker ($FeCl_3$). NaCMC solution (7%) was dropped into crosslinker by utilizing a 26-gauge needle [6]. The mixture was stirred with 200 rpm for 3 h. Hydrogels were ejected form medium and washed with distilled water to expelled unreacted chemicals and dried at 25°C. The amounts of components were summarized in Table 1.

Table 1. The amounts of components and gel content

Hydrogel	NaCMC (%)	$FeCl_3$ (%)	Gel content (%)
CMC-1	7	4	93.62 ± 0.52
CMC-2	7	6	95.52 ± 0.34
CMC-3	7	8	96.43 ± 0.82
CMC-4	7	10	97.36± 0.53

2.3. Gel content (%)

In order to specify the gel content of samples, the dried samples of determined weights were put into water at 100°C for 24 hours. Then, samples were washed, dried in oven and weighted. Equation (1) was used for determining the gel content:

$$\text{Gel content } (\%) = \frac{We}{Wi} x100 \qquad (1)$$

Where w_i and w_e are dry sample weights before and after extraction, respectively.

2.4. Water absorbency

Dry weights of hydrogels *(w_d)* were determined before starting the water absorbency test. Hydrogels placed in the water medium were weighed *(w_s)* at certain periods until the stabile value was determined. Equation (2) was utilized to measure water absorbency.

$$\text{Water absorbency } (\%) = \frac{(Ws-Wd)}{Wd} X100 \qquad (2)$$

2.5. Water retention

The hydrogel was buried in a plastic container with soil at a certain depth (5.0 cm). The initial weights (m_i) of the samples were determined. A constant volume of water was added to the sample every day. Samples were weighed daily (m_t). The equation (3) was utilized for obtaining the water retention rate (%) of the soil.

$$\text{Water retention } (\%) = \frac{(mi-mt)}{mt} x100 \qquad (3)$$

2.6. The loading of manganese in hydrogel

Classic entrapment method was applied for producing the manganese-loaded hydrogel. Manganese was entrapped in hydrogel during the synthesizing procedure (5 ppm per hydrogel). They dried firstly at room temperature and then, at 40°C.

2.7. Release test

Three release tests were applied for manganese loaded hydrogels:

- continuous releasing in water,
- intermittent releasing model in water
- releasing in soil

In first release procedure, the sample was taken into distilled water (100 mL) at room temperature. The aliquots of 100 µL was taken at certain period and measured by Atomic Absorption Spectrometer (AAS, Perkin Elmer A4000). The experimental was proceed until the constant release value was obtained.

In second release procedure, the sample was put into distilled water (100 ml). The sample was waited in room temperature for 15 min, then it was rejected and kept at room temperature to dry. AAS was utilized for detecting releasing rate and amount. After 1 day, sample was replaced into the same environment and the measurement was done again. The value was detected with Equation 3. The test was remade over again until the stable value was observed [1,6].

In the third release procedure, the permeable chiffon packages were used. The package contained hydrogel sample was buried at a certain depth in pots containing 5 L of soil. One package was taken from the environment before irrigation every day. The sample was kept in the release medium. The release rate and amount were obtained by AAS. The amount of micronutrient was measured until the stable value was reached.

2.8. Wheatgrass plant growth study

Pot experiment was carried out to determine the effect of manganese loaded hydrogel on wheatgrass plant. Wheatgrass seeds (*Triticum Aestivum*) were planted in soil of a certain depth (3 cm). An untreated sample is Control (CRL). Irrigation was done every day and plant heights were measured. After the growth of the wheatgrass plant remained constant, a fresh and dry sample mass of each plant was recorded.

3. Results and Discussion

3.1. Gel content (%)

NaCMC hydrogels were produced as described in the methods. Gel content (%) was measured with Equation 1 and the result was shown in Table 1. CMC-1 sample had lower gel content, while CMC-4 sample had higher value. While $FeCl_3$ percentage was changed from 4% to 10%, the values also increased. The crosslinker density enhanced the network linking strains of polymer, which caused the increment the value.

3.2. Water absorbency (%)

The water absorbency percentages were drawn as a function of time in Figure 1. The result of samples was given in Figure 1. The maximum water absorbency value was observed for CMC-1 sample, whereas the minimum value was obtained for CMC-4 sample. The water absorbency decreased with increasing $FeCl_3$ (Table 1). The electrostatic repulsion and osmatic pressure may have occurred by ionic groups in structure so, penetration enhanced as well. [8].

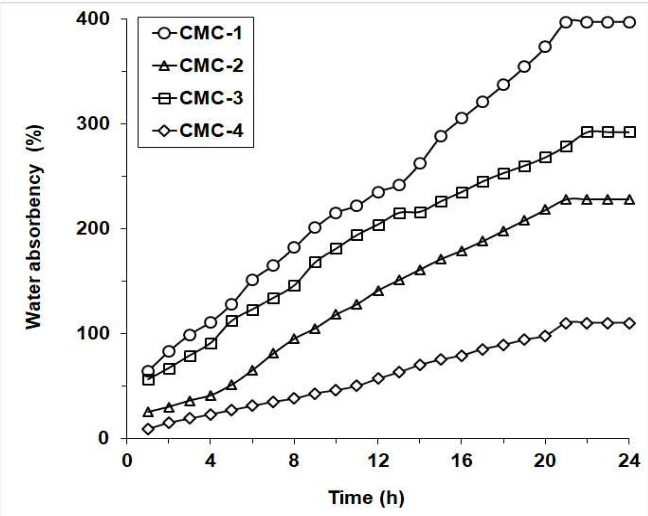

Figure 1. The water absorbency of samples

3.3. Water retention (%)

The existence of hydrogels increased the water retention as given in Figure 2. Control group contained only soil without hydrogel. The lowest percentages were obtained for control group. The maximum retention was found for the soil contained CMC-4 sample. The presence of hydrogel caused the increment of water retention. It can be clearly said that the water-holding ability of soil developed with using hydrogel [1,9].

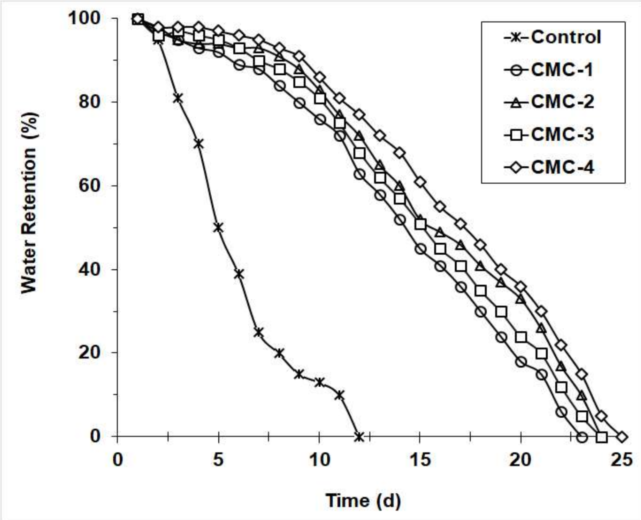

Figure 2. Water retention values of the soil treated with samples

3.4. Release studies

Figure 3 shows manganese release test in water at 25^{o}C. The sustainable manganese release continued during 30 h for NaCMC samples. The values are accordance with the water absorbency percentages. The cumulative release values decreased as $FeCl_3$ percentage was increased. The lower value was found for CMC-4 hydrogel due to its higher crosslinking [9,10].

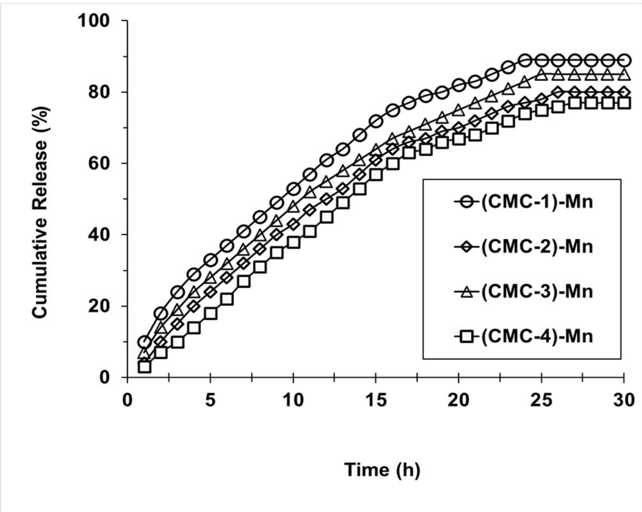

Figure 3. The continuous release degree of samples in water

A new intermittent release experiment was improved for soil experiment. Figure 4 displays manganese intermittent release properties of sample in soil at 25^{o}C. At the beginning, the rates were gradually increased, and stabled at the end of 14 days. The increasing of $FeCl_3$ (%) decelerated the release rate due to a rise hydrogel network density. There is an obvious difference in constant time contrasting to continuous procedure due to the using method [1,11].

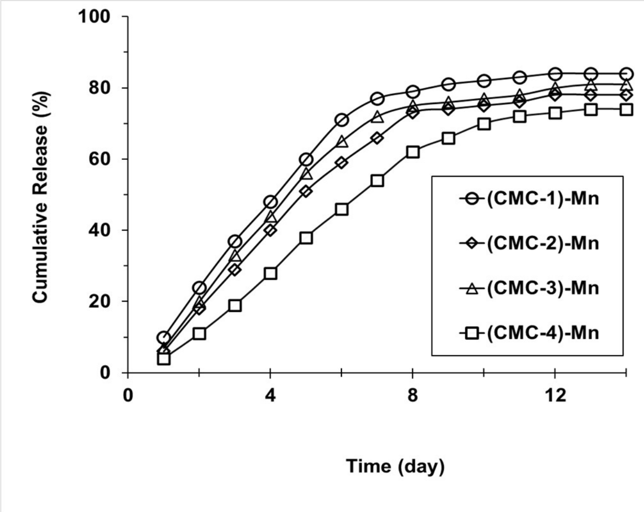

Figure 4. The manganese intermittent release degree of samples

Figure 5 displays the release degrees of samples in soil. The degrees are coherent with intermittent test values. The improved intermittent experiment is a practicable procedure to predict the stable release time in soil. The soil release degrees were slightly lower than in intermittent release degrees. It can be said that manganese release occurs by swelling of the samples in the soil. The plant nutrients diffuse easily through the pores of samples into water, while diffusion of nutrients get difficult in soil [1,12].

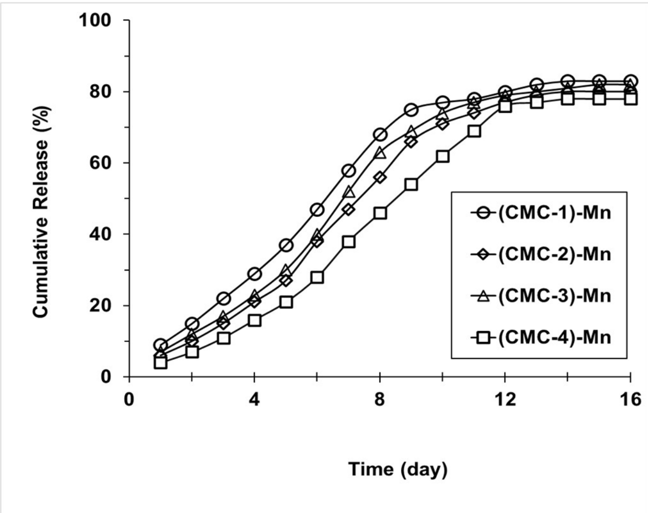

Figure 5. The manganese release degree of samples in soil

3.5. Effect of hydrogels on plant development

The pot experiment was determined by following the changes of plant growth. The height and total dry and fresh masses of plants were examined. The results display in Table 2 and Table 3 [1,13,14].

Table 2. The number of sample per pot, the average total fresh mass and the average total dry mass

Hydrogel	The number of hydrogel (per pot)	Average total fresh mass (g)	Average total dry mass (g)
CRL	-	17.6±0.7	4.4±0.5
CMC-Mn	15	23.3±0.4	6.8±0.5

Table 3. The average number of germinated seed at 14th days and the average plant height at 14th days of wheatgrass plant

Hydrogel	Average the number of germinated seed (per pot) at 14th days	Average plant height (cm) at 14th days
CRL	190±10	20.2±0.5
CMC-Mn	445±23	26.3±0.7

The photos of the plants at 4th and 10th day is given in Figure 6 and Figure 7. The existence of manganese-loaded samples positively affected the height of the wheatgrass plant, the number of germinated seeds, total fresh weight and total dry weight. It can be said that these prepared samples can be used in agricultural practices [13-15].

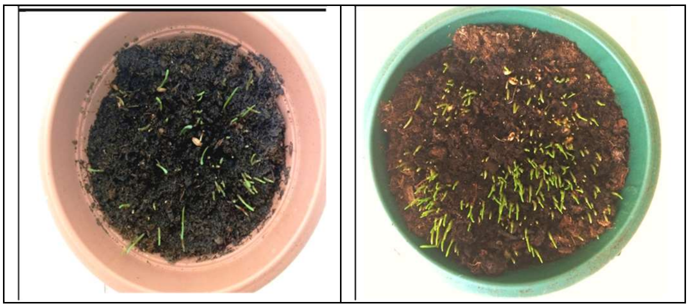

Figure 6. The wheatgrass germination in soil at 4th day after planting: (a) CRL, (b) CMC-Mn

Figure 7. The wheatgrass germination in soil at 10th day after planting: (a) CRL, (b) CMC-Mn

4. Conclusions

The aim of this study is to produce manganese loaded NaCMC hydrogels to investigate their usability in agricultural applications. The different amounts of crosslinker content directly affected the water absorption and gel content of hydrogels. Water retention rate was found higher in soils containing hydrogels. The release behavior of manganese-loaded samples was detected in water and soil. Manganese-loaded hydrogels improved the plant as compared to control group (without any treatment).

Acknowledgements

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