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Preparation of Sodium Carboxymethly Cellulose Hydrogels for Controlled Release of Copper Micronutrient

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Abstract: In this study, a series of nanoporous sodium carboxymethyl cellulose (NaCMC) hydrogels were synthesized using $FeCl_3$ ionic-crosslinker by changing the amounts of the components. Hydrogel formation percentages of the samples were determined and the highest value was obtained as 96% for the hydrogel containing the most amounts of polymer and crosslinker. Swelling/degradation behaviors of the hydrogels were studied by changing time, temperature and pH and it was determined that the swelling percentages regularly decreased with increasing the amounts of polymer and crossliker. S% values were determined to be 102% for the least swollen hydrogel. In general, NaCMC hydrogels much more swelled in basic medium than acidic medium. Releasing of copper micronutrient from NaCMC hydrogels were investigated by Atomic Absorption Spectrometer measurements. Kinetic in vitro release parameters, the release rate factor K and the release exponent n of micronutrients in hydrogel system were calculated. It can be concluded that the produced hydrogel system having controllable release values is useful for agricultural applications.

Keywords: Sodium carboxymethyl cellulose, Hydrogel, Micronutrient, Controlled-release

Introduction

Plant Nutrients

All plants must obtain a number of inorganic elements from their environment to ensure successful growth and development of both vegetative and reproductive tissues. At least 17 elements are known to be base nutrients for plants. There are four types of nutrients that fall into two broad categories: macronutrients and micronutrients. The nutrients which are required by plants in large quantities are called macronutrients. Macronutrients play a very important role in plant growth and development. Their functions range from being structural units to redox-sensitive agents.

Micronutrients are essential elements required by plant organisms in small quantities and play an important role in balanced crop nutrition. They are as important to plant nutrition as primary and secondary macronutrients, though plants don't require as much of them. A lack of any one of the micronutrients in the soil can limit growth, even when all other nutrients are present in adequate amounts. The classification of micro nutrients presented in Table 1.

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Table 1. Classification and some important properties of plant micro nutrients

Micronutrients	Mobility	Amount (aver., %)	Functions in the plant
Fe	Fe^{+2}, Fe^{+3}	2.10^{-2}	Component of many enzymes
Zn	Zn^{+2}	5.10^{-3}	High crop yields
Mn	Mn^{+2}	5.10^{-3}	Plays a direct role in photosynthesis
B	BO_3^{-3}, $B_4O_7^{-2}$	2.10^{-3}	Affecting membrane stability
Cu	Cu+2	6.10^{-4}	Activates enzymes and catalyzes reactions
Mo	MoO_4^{-2}	1.10^{-5}	Vital for the process of symbiotic N fixation

As a Micronutrient Copper

Copper is necessary for carbohydrate and nitrogen metabolism and, inadequate copper results in stunting of plants. Cu activates enzymes and catalyzes reactions in several plant-growth processes. The presence of copper is closely linked to Vitamin A production, and it helps ensure successful protein synthesis. Copper also is required for lignin synthesis which is needed for cell wall strength and prevention of wilting. Deficiency symptoms of copper are dieback of stems and twigs, yellowing of leaves, stunted growth and pale green leaves that wither easily. Copper uptake decreases as soil pH increases. Increased phosphorus and iron availability in soils decreases copper uptake by plants.

Controlled Release Fertilizers

The traditional fertilization methods cause serious environmental pollution, large economic and resource losses. In recent years, researchers and fertilizer producers have attempted to discover advanced techniques for fertilizer usage that can improve nutrient use efficiency and minimize environmental impacts (Trenkel, 2007) . One possible way to overcome this problem is controlled released fertilizer (CRF) usage. A literature review reveals that the history of CRFs development is based on 1960's. CRFs are broadly defined as products that release nutrients to soil for plant uptake at a pre-determined time and rate. Compared to the conventional type, CRFs have many advantages such as (1) decreasing fertilizer loss rate, (2) supplying nutrients sustainable, (3) lowering application frequency and (4) minimizing potential negative effects associated with over dosage.

CRFs can be divided into 3 categories based on their coating and nutrient composition. (1) Uncoated, nitrogen-based fertilizers are the oldest class of CRF that consist of chemically-bound urea and the release rate is determined by particle size, available water, and microbial decomposition e.g. (2) Coated, nitrogen-based fertilizers – Sulphur-coated urea is one of the first CRF. Thickness of sulphur coating controls the nitrogen discharge. (3) Polymer-coated or polymer matrix multi-nutrient fertilizers.

All principal classes of polymers, i.e. plastics, coatings, elastomers, fibers and soluble polymers are presently utilized in applications that include the controlled release of nutrients. In this type of CRF, thicknesses, porosities and swelling behaviors of polymers control the release of nutrients.

Hydrogels

Hydrogels are three dimensional crosslinked networks depend on hydrophilic polymers that can absorb or retain water without dissolution. The hydrophilic property is due to presence of chemical residues such as –OH, -COOH, $-NH_2$, $-CONH_2$, $-SO_3H$ and others with in molecular structure. Hydrogels have been extensively studied and preferred for a large number of applications in much kind of industrial fields (Pulat and Asıl, 2009). Because of their excellent characteristics, hydrogels can also be used for controlled release of agrochemicals and nutrients in agricultural and horticultural applications (Pulat and Yoltay, 2016).

Most of the synthetic polymers used to prepare hydrogels causes some problems because of their long degradation times and degradation products. Natural polymers are a good choice to overcome this issue (Pulat Uğurlu, 2016).

In recently hydrogels formed from natural polymers such as NaCMC, carrageenan, gelatin, chitosan etc. have been studied extensively due to biodegradable, biocompatible, nontoxic.

NaCMC

Sodium carboxymethyl cellulose (NaCMC) is a representative cellulose derivative, which is water soluble cellulose ether, manufactured by reacting sodium monochloroacetate with cellulose in alkaline medium. NaCMC is a polysaccharide polymer with excellent bioadhesive, biodegradability and biocompatibility.

It is also known that NaCMC is a polyelectrolyte, and thus this 'smart' cellulose derivative presents sensitivity to pH and ionic strength variations. It is easy to form NaCMC hydrogels because of the large number of reactive hydroxyl groups on the polymer chains (Rafaat, Eid M and El-Arnaouty, 2012).

Besides, the presence of carboxylate groups in the macromolecular chain enables to bond the chains to bond each other via multivalent ionic crosslinking. Several kinds of ions can be used to form ionic hydrogels. As an eco-friendly and nontoxic crosslinking agent, trivalent iron (Fe^{3+}) is a suitable ion to prepare NaCMC hydrogels. Indeed, the presence of NaCMC in a cellulose-based hydrogel enhances electrostatic charges in network, which have a double effect on the swelling capability.

NaCMC is widely used in several applications such as cosmetics, food and wound care industries, medicine and agriculture etc. for gelling, thickening agent, stabilizer and suspending agent (Barbucci, Magnani, and Consumi, 2000).

AIM: The aim of this study was to obtain a system that provides the controlled release of plant micronutrient. The matrices structure was prepared using NaCMC, a natural- biodegradable polymer and copper as micronutrient. Characterization of the synthesized fertilizer system was performed by investigating their swelling/degradation behaviors. Release studies were also carried out in water and soil.

Method

Preparation of NaCMC Hydrogel Beads

As schematically given in Figure 3, four different types of NaCMC hydrogel beads were prepared via ionic crosslinking reaction using $FeCl_3$ (Akalın and Pulat, 2018). 7% of NaCMC solution was drop-wisely added into 25.0 mL of $FeCl_3$ solution at different concentrations by using a 26-gauge needle. The obtained spherical hydrogel beads were mixed with a mechanical stirrer (200 rpm) for 3 h. They were filtered and washed several times with distilled water to remove unreacted $FeCl_3$ on the surface of beads and dried under room temperature for 24 h. The amounts of polymer (P) and crosslinker (C) and the relative ratios were summarized in Table 2.

Table 2. Preparation of hydrogels

Hydrogel	NaCMC (%)	$FeCl_3$ (%)	C/P	Mechanical properties
NaCMC-1	7	4	0.57	Brittle
NaCMC-2	7	6	0.86	Durable, steady
NaCMC-3	7	8	1.14	Durable, steady
NaCMC-4	7	10	1.43	Durable, steady

Hydrogel Formation

Gravimetric tests were carried out, and the formula given below was used to determine hydrogel formation (HF) percentage. Dried and weighed samples were placed in water for 48 h to extract the unreacted monomers and then dried (Chen *et al*., 2005).

$$HF\ (\%) = \frac{m}{m_0} \times 100 \qquad (1)$$

where m and mo are the weights of the dried hydrogel after and before extraction, respectively.

Swelling Behaviors

Swelling tests of hydrogel beads were gravimetrically carried out in three steps. In the first step, the weighed dried hydrogels were immersed in 100 mL of swelling medium Britton-Robinson buffer (BRB) solutions at pH=7.0, 30°C. Swollen gels removed from the swelling medium at regular intervals. Then, they were dried superficially with a filter paper, weighed, and placed into the same bath. The tests were performed until constant weight was reached. The swelling percentages of hydrogels were calculated from Equation 2:

$$Swelling\ (\%) = \frac{(W_2 - W_1)}{W_1} \times 100 \qquad (2)$$

Where W_1 is the dry weight of the sample before swelling, W_2 is the swollen mass of sample in every 24 h.
In second step, the dried hydrogels were swollen in BRB solution (pH= 7.0) at different temperatures ranging from 10 to 60°C to determine the effect of temperature on swelling behaviors. In the third step, dried hydrogels were immersed in different BRB solutions at various pH values (from 2.0 to 12.0) to investigate the effect of pH on the swelling behaviors. At the end of 24 h incubation, the swollen hydrogels were taken out from swelling medium, dried and weighed (Pulat and Asıl, 2009).

Degradation Test

Degradation test of hydrogel beads were performed at pH= 7.0, 30°C (Pulat and Akalın, 2013). Dried samples were left to swell in BRB. At the end of 24 h, swollen gels were removed from solution and weighed. This mass (Wm) recorded as the maximum swollen state of hydrogels. Then, they placed into the same medium and the weighing was continued at regular intervals until hydrogel completely degraded. The degradation was determined in terms of weight loss (%) from Equation 3:

$$Weight\ loss\ (\%) = \frac{(W_m - W_t)}{W_m} \times 100 \qquad (3)$$

where W_m is the weight of hydrogel at most swollen stage and W_t is the weight of hydrogel at time t.

SEM Observation

Depending on the swelling/degradation behaviors, NaCMC-4 hydrogel was chosen for release studies. Therefore, the morphological structure of NaCMC-4 was investigated via SEM observations. The hydrogel sample, swollen to equilibrium in water at room temperature, were removed and placed in a deep freezer at −20°C for 24 h and then transferred into a freeze dryer (Christ-Alfa 2–4 Model, Martin Christ GmbH, Germany) at −85°C for 1 week. The dried and swollen straps were coated with 200 Å Au. The surface micrographs of the samples were obtained with a scanning electron microscope (JEOL, JSM 6060A, Japan).

Preparation of the Copper Loaded Hydrogel

Copper loaded NaCMC-4 hydrogel was prepared by soaking method. 0.2 g of beads was left into copper solution (1.0 g/1 mL) for 4 h. Then, they were left to dry first in air and then in a vacuum oven at 40^{o}C. So, each bead contains 0.5 mg of Cu.

Release Studies

In vitro release studies were carried out by using Atomic Absorption Spectrometer (AAS, Perkin Elmer A4000). Cu-loaded hydrogels were transferred in 100 mL distilled water. 0,5 mL of aliquot distilled water was with drawn at different time intervals. This process continued until the equilibrium in vitro release degree was reached (Pulat, Akalın and Demirkol, 2014).

Reproducible results were obtained with triplicate measurements. The cumulative release (%) of the Cu^{+2} was calculated with the following equation:

$$\text{Cumulative release (\%)} = \frac{\text{Wt}}{\text{Wtotal}} \text{ X } 100 \qquad (4)$$

where Wt is the weight of the released Cu in the releasing medium at any time and Wtotal is the initial total weight of Cu^{+2} entrapped into the gel system.

A semi-empirical equation is introduced to represent the substance release process of the swelling polymer (Pulat, Tan and Onurdağ, 2011).

$$F = \frac{Mt}{M1} \times kt^n \quad (5)$$

where F is fractional solute release, Mt and M∞ are the amounts of u released at time t and the maximum released amount of MA, respectively. k is a characteristic constant related to the structure of the hydrogel network, and n is a swelling exponent.

Release Studies in Soil

Release studies were also performed in soil. 1of Cu-loaded bead was put into permeable chiffon package to preserve the sample from soil sticking. The packages were placed into the pots containing 5 L of dry torf at 2.0 cm depth. All pots were irrigated daily with 150 mL of water. Each day one package was removed from the pot and the bead was taken to be placed into 100 mL of distilled water. Cu^{+2} nutrient was extracted from the beads into the water and the Cu^{+2} diffusion was measured by AAS. So the amount of released Cu^{+2} into the soil had been calculated. This process was continued until the equilibrium soil release value was reached.

Results and Discussion

Hydrogel Formation

NaCMC hydrogel discs were produced as described in the methods. HF was calculated via Equation 1 and the result was given in Table 3. The lowest hydrogel formation was found as 94% for NaCMC-1 hydrogel. The gel content of NaCMC hydrogel beads that was given in Table 2 are verifying with HF, Ms and DT values. While the concentration of $FeCl_3$ was increased from 4% to 10%, the gel content of the samples also increased. The highest value was found 98% for NaCMC-4 hydrogel. The higher density improved the network binding forces of the polymers, which led to the increase of gel content. It is well known that polymer and crosslinker amounts promote the gel content, so the results are satisfying (Akalın and Pulat, 2018).

Table 3. HF, maximum swelling (MS) and time of 100% degradation (DT)

Hydrogel	HF (%)	MS (%)	DT (day)
NaCMC-1	94	292	36
NaCMC-2	96	213	37
NaCMC-3	97	135	36
NaCMC-4	98	102	38

Swelling results

All swelling percentages calculated from Equation 2. The photographs of dry and swollen hydrogels were presented in Figure 1.

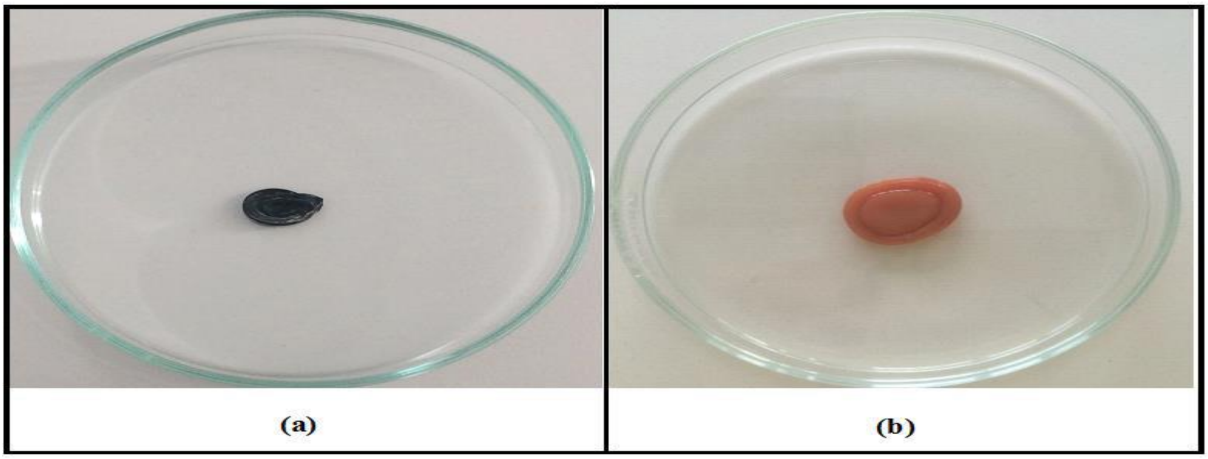

Figure 1. Dry and swollen NaCMC hydrogels

The variations of swelling values with time at pH 7.0 and 30°C were shown in Figure 2. The swelling increased with time initially and then remained constant at close to 24 h. S% values were determined to be 292% for the most swollen hydrogel NaCMC-1, and 102 % for the least swollen hydrogel NaCMC-4. Swelling values were directly connected with composition, monomer ratio, ionic charge content, polymerization route, type and density of cross-linker, and so forth (El-Sherbiny *et al.*, 2005). As C/P ratio increased, S% values decreased. This behavior is attributed to the fact that the network chains became inflexible at higher crosslinker density and thus, fewer amounts of water molecules penetrated the hydrogel structure.

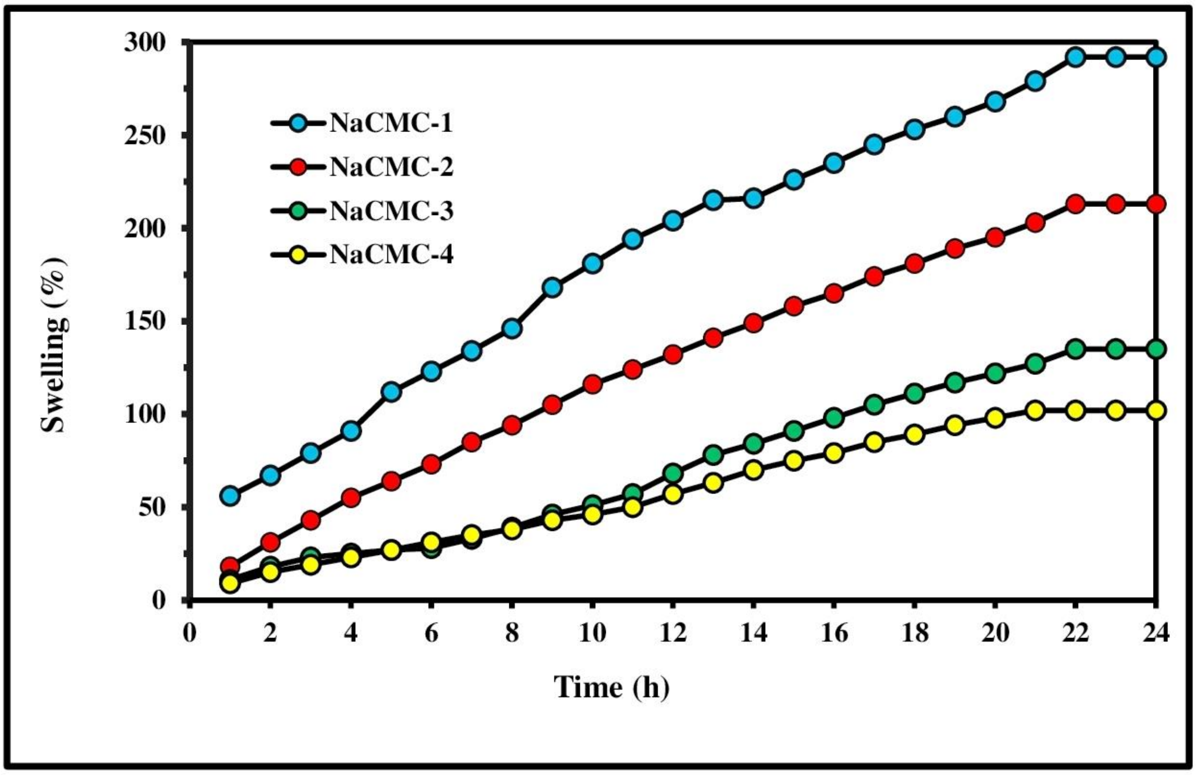

Figure 2. The variation of S% values with time at 30°C, pH = 7.0

The variations of swelling values with temperature at pH 7.0 and 24 h are presented in Figure 3. Swelling percentages slightly increased with temperature. As the temperature increases, thermal mobility of the polymer chains increases and H-bonds were broken, and hydrogels can easily swell. Because of their high stabilities, NaCMC hydrogels are suitable for using in wide temperature ranges.

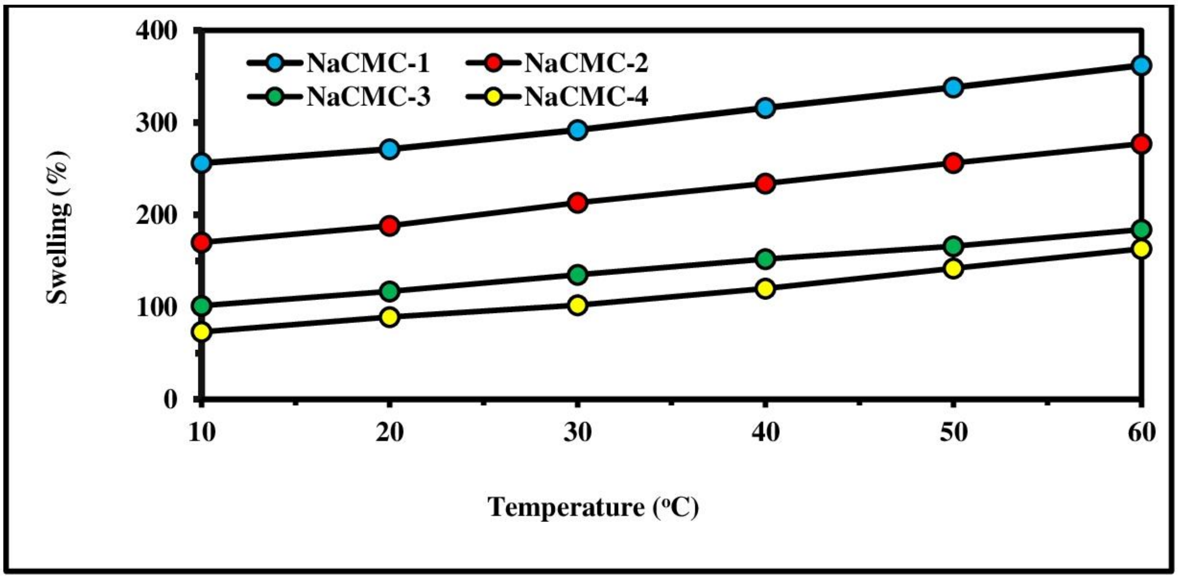

Figure 3. The variation of S% values with temperature at pH = 7.0 and 24 h

Figure 4 presents the variation of S% values of hydrogels with pH at 30°C and 24 h. As the pH is increased from 2 to 7, swelling values kept near constant and then a sharp increment was observed. . This result can be explained by the fact that the pKa of carboxylic acid groups containing in the polymer is about 4.5. These groups were ionized to the COO^- form since the pH of the environmental solution raised above its pKa value. The ionized negatively charged pendant groups on the polymer chains caused repulsion leading to swelling. As swelling pressure increased, hydrogel expanded and thereby maximizes the repulsion between the ionized groups.

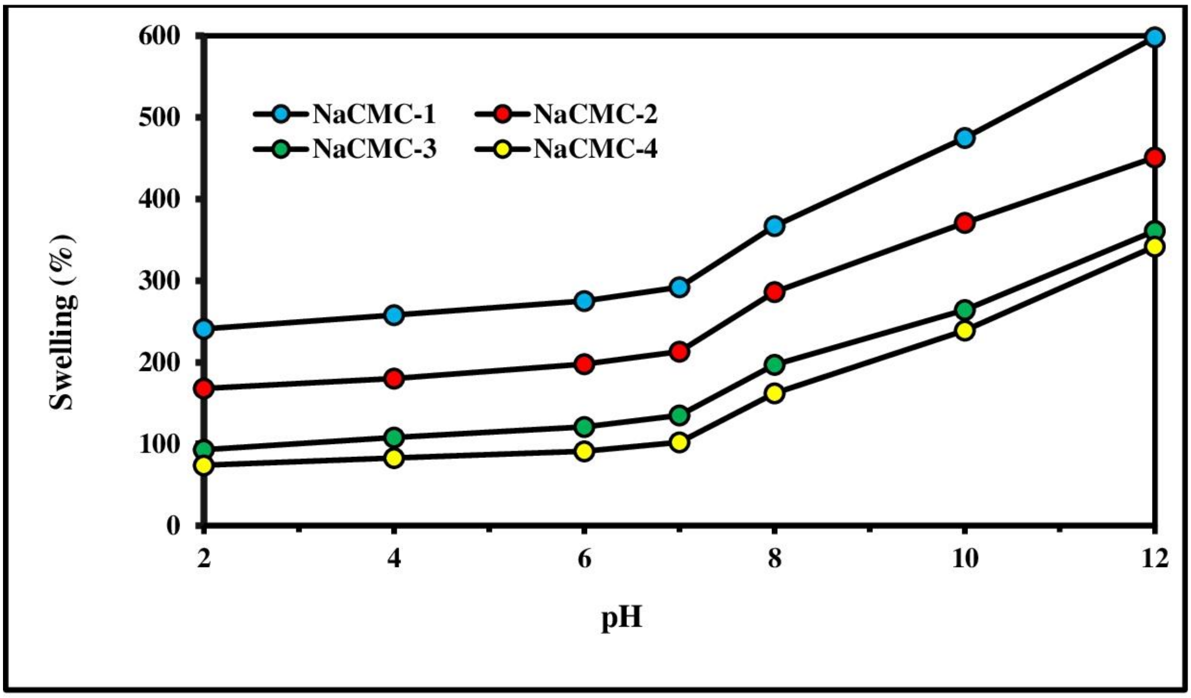

Figure 4. The variation of S% values with pH at 30°C, 24 h

Degradation

In this study, degradation values were calculated using Equation 3 and the degradation profiles were presented in Figure 5. All of the NaCMC hydrogels degraded in approximately 33-38 days. The fastest degradation was observed for NaCMC-1 hydrogel as 33 days. In general, crosslinking density is very effective on the degradations of the hydrogels. The high crosslinked hydrogel degraded slower than the lower crosslinked hydrogels, since the number of intermolecular bonds enhanced with increasing crosslinking density. NaCMC hydrogels can be suitable for long-term applications because of their good stabilities.

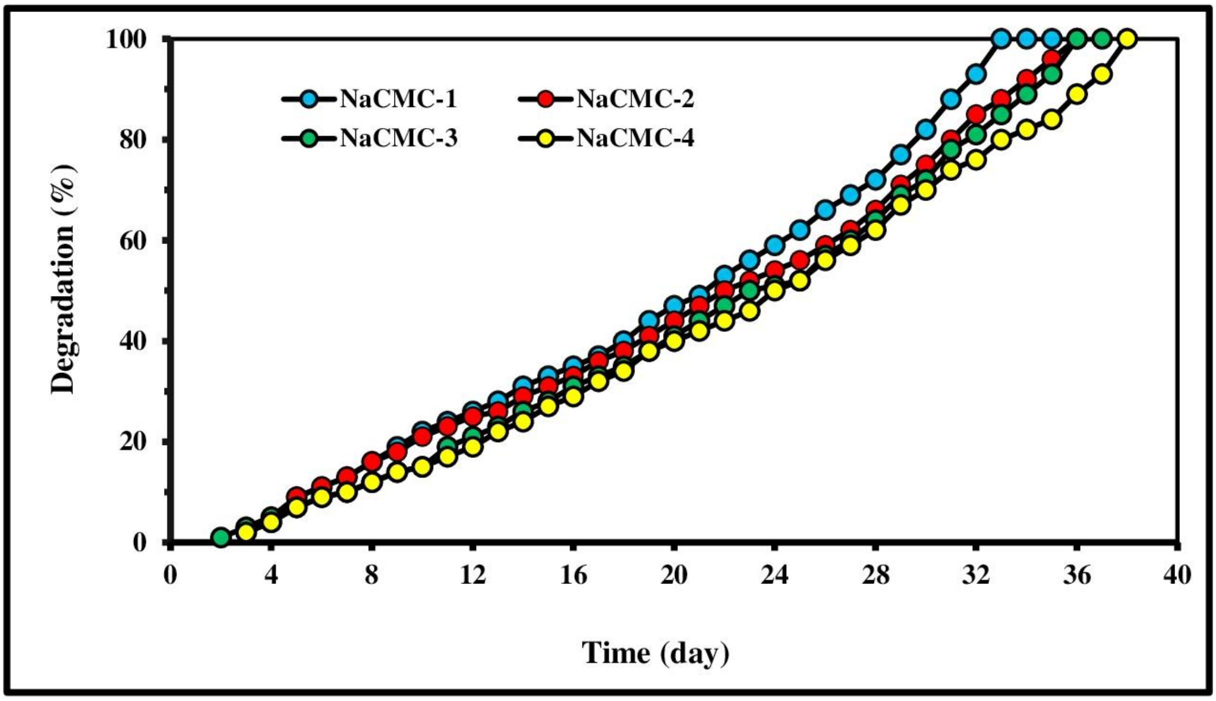

Figure 5. The degradation profiles of hydrogels at 30°C

SEM Analysis

The morphological differences between swollen hydrogels can be clearly observed from SEM micrographs given in Figure 10. The dried surface exhibited smooth and nonporous structure, in contrary the surface of swollen hydrogels had a granule structure. This situation can be explained that the ionic crosslinking occurred intensively on the surface. Polymer chains bound to crosslinker from large number of points, so a granulated view was appeared on the surface. The cross-section images of swollen hydrogels possessed a spongy structure with pores in different sizes from micro- to nano-scale, so this porosity enabled easy diffusion and absorption of water into the structure.

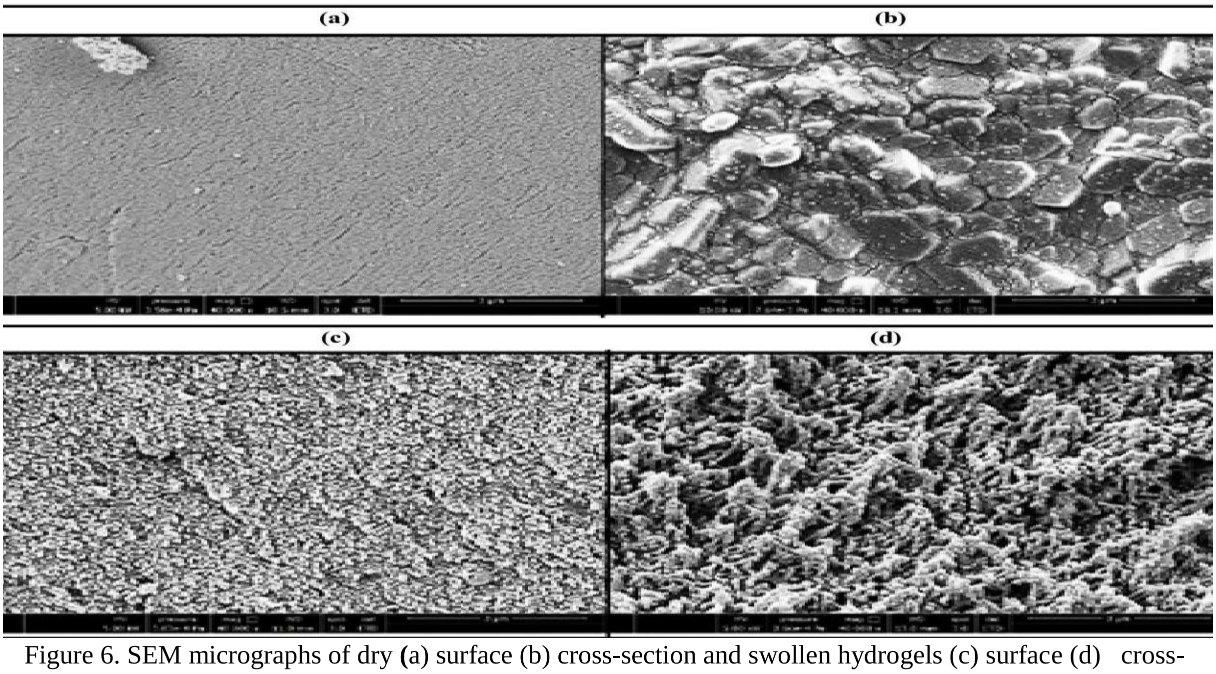

Figure 6. SEM micrographs of dry (a) surface (b) cross-section and swollen hydrogels (c) surface (d) cross-section (X 40000)

Micronutrient Release Kinetics

The release profile of copper micronutrients from NaCMC-4 is presented in Figure 7. The cumulative release (%) increased rapidly and then complied at near 25 h. Kinetic release parameters were calculated using Equation 4. 0.98 and 93,5 x 10^{-3} were found for n and k, respectively. As n value of the hydrogel was found close to 1.0, it can be mentioned about zero order kinetic for this hydrogel. The meaning of this is release rate of Cu are nearly constant during release.

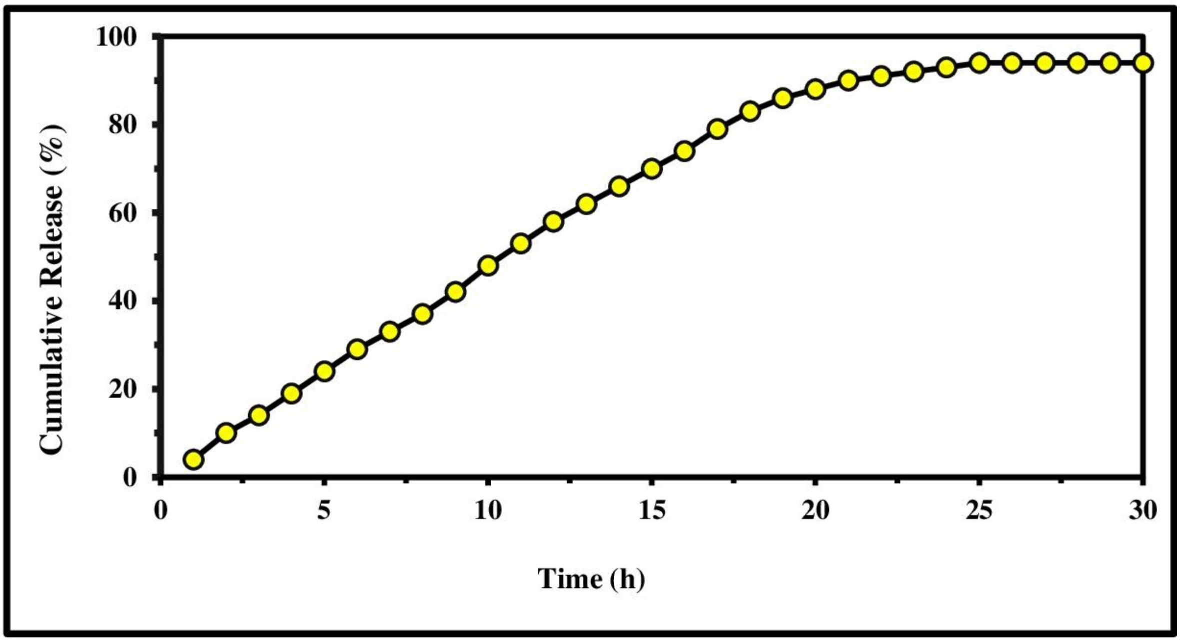

Figure 7. Cu+2 release in water from NaCMC-4 hydrogel

Soil Release

The Cu release through NaCMC-4 hydrogel in soil was also investigated and the profile was given in Figure 8. The maximum release value was reached as 83% at near about 16 days. Release in water 15 times faster than in soil. It could be concluded that this prepared micronutrient-loaded hydrogel system can be effective for a long time uses.

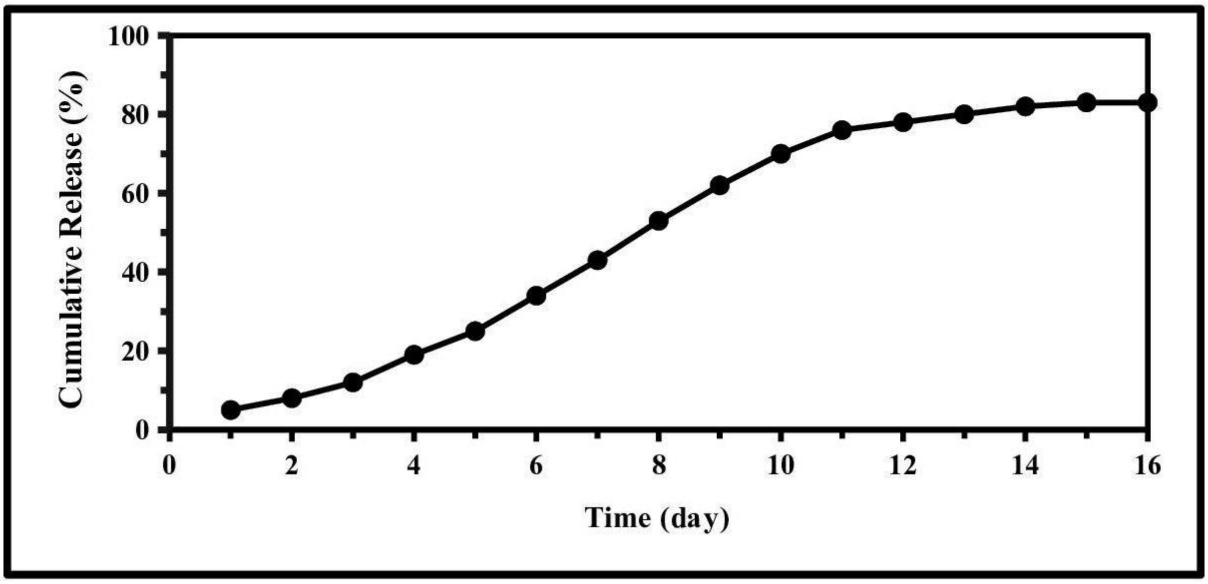

Figure 8. Cu+2 release in soil from NaCMC-4 hydrogel hydrogel

Conclusion

The results of the present work indicate that the NaCMC hydrogels are good support materials for controlled releasing Cu micronutrient with their excellent swelling/degradation capability. It can be concluded that the CRF system produced in this study is much promising in utilizing a natural resource like CMC in the production of matrix material which could significantly reduce the production costs and offering a quite environmental friendly alternative technique.

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