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SYNTHESIS, COLLOID-CHEMICAL PROPERTIES AND EFFICIENCY OF CARBOXYMETHYL STARCH DERIVATIVE HYDROGELS

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Abstract

New high-molecular sparsely cross-linked hydrogels based on carboxymethyl starch derivatives have been synthesized. The colloid-chemical properties and swelling abilities of new hydrogels in aqueous solutions, as well as their conformational transformations during the transition from one state to another have been investigated. The mutual influences of physic-chemical properties of aqueous solutions, including electrical conductivity, pH environment and swelling coefficient of hydrogels were studied. Based on the analysis of experimental results it has been established that during the ionization of new hydrogels in an aqueous environment, intramolecular associates were formed with the participation of protons and carboxylate anions, stabilized by hydrophobic interactions of the network structure of a sparsely cross-linked polyelectrolyte. It has been shown that this process was accompanied by a sharp change in pH values of the medium, increase in the electrical conductivity and the swelling coefficient of the hydrogels in water. The efficiency of new hydrogels for culturing plants on pebble-lands has been established by the field test results.

Keywords: Polymeric hydrogels, swelling coefficient, intramolecular associates, sparsely cross-linking, water-holding capacity, drought resistance.

1. Introduction

The impact of drought on the physiological state and productivity of plants are becoming significant as a result of global climate change. Water stress affects germination, growth, photosynthesis, protein synthesis, and lipid metabolism. The impact of drought on the physiological state and productivity of plants will become even more significant over the coming decades as a result of global climate change. The negative impact of water scarcity at the level of the whole plant leads to its death or a decrease in productivity. Water stress affects germination, growth, photosynthesis, protein and energy synthesis, lipid metabolism, causes an imbalance of nutrients and oxidative stress. To solve the problems caused by the action of abiotic stressors, it is important to find approaches that reduce their negative impact 1on plants. One of the innovative technologies for creating stress-resistant agrophytocenoses and increasing the yield of agricultural crops is the pre-sowing inlay of seeds with various protective and stimulating composite compositions. Together with the film-forming agent, various growth regulators are applied to the surface of the seed. Currently, more attention is being paid worldwide to the prospects for the development and using of new hydrogels [1-6]. In world practice, there is a growing interest in obtaining sparsely cross-linked polyelectrolyte hydrogels, and their use in agriculture for preserving moisture, improving soils water-holding capacity, drought resistance of plants and increasing productivity of agricultural fields [7-12]. The sparsely cross-linked polymer hydrogels are chemical compounds consisting of a hydrophilic polymer network with long interstitial chains and a water component, the amount of which can vary widely. One of the most unique properties of sparsely cross-linked polymer hydrogels is their ability to swell strongly in water and aqueous solutions. This is most pronounced in the case of polyelectrolyte hydrogels, the network of which can absorb and retain huge amounts of water. Another valuable property of sparsely cross-linked hydrogels is their high sensitivity to changes in environmental conditions, i.e. the ability to sharply change its volume in response to small changes in the composition of the solvent, temperature and a number of other parameters [13-18]. It is known that some synthetic polymers, such as acrylic acid derivatives, are polyelectrolytes. Identification of patterns connecting the physicochemical properties of chain molecules with their structure, as well as parameters characterizing the state of macromolecules in solution, can be useful when choosing a specific area of application of polymers and polyelectrolytes. A review of publications showed that the attention of many scientists is concentrated on the study of the physicochemical properties of synthetic polymers, but very little has been studied and discussed about the mutual influence of the obtained characteristics of polyelectrolytes [19-22]. In this regard, the study of the mutual influence of the physicochemical properties and characteristics of polyelectrolytes in aqueous solutionы is very relevant. The purpose of this work is to establish patterns of change and mutual influence of physicochemical properties and characteristics (electrical conductivity, pH environment, swelling and conformational transitions) of new polyelectrolytes and hydrogels based on sodium carboxymethyl starch in an aqueous solution, as well as to study the water-holding capacity and effectiveness of new hydrogels in agriculture farm for growing plants in peddle soils.

2. Materials and methods

Determination of swelling ability of CMS based hydrogels. The swelling ability of hydrogels in aqueous medium was determined by using a gravimetric method. The swelling coefficient (Ks) was calculated according to the formula $K_n = m_2 - m_1 / m_1$, where m_1 is the mass of the hydrogel used for swelling, m_2 is the mass of the hydrogel after swelling.

Determination of the electrical conductivity of hydrogels in aqueous solutions. The electrical conductivity of hydrogel aqueous solutions was measured using a digital stationary conductometer Bante 510-DH (Bante instruments).

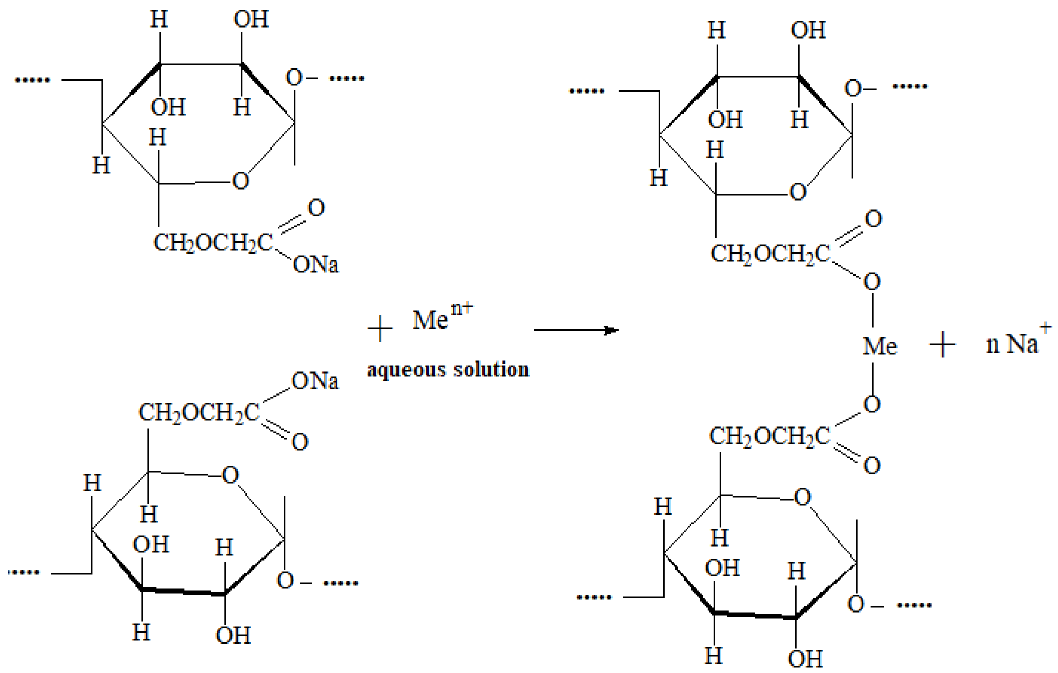
Determination of the pH of aqueous solutions. The pH of aqueous solutions of hydrogels was measured using a Metrohm 827 Lab pH meter (Switzerland).

The effectiveness of using hydrogels. The effectiveness of using hydrogels for growing almond plantations on pebble lands in mountain conditions was studied. The effectiveness of using hydrogels for growing almond plantations was evaluated by measuring height of the grown plants, diameter of root collars, linear increase in the heights depending on the hydrogels concentration.

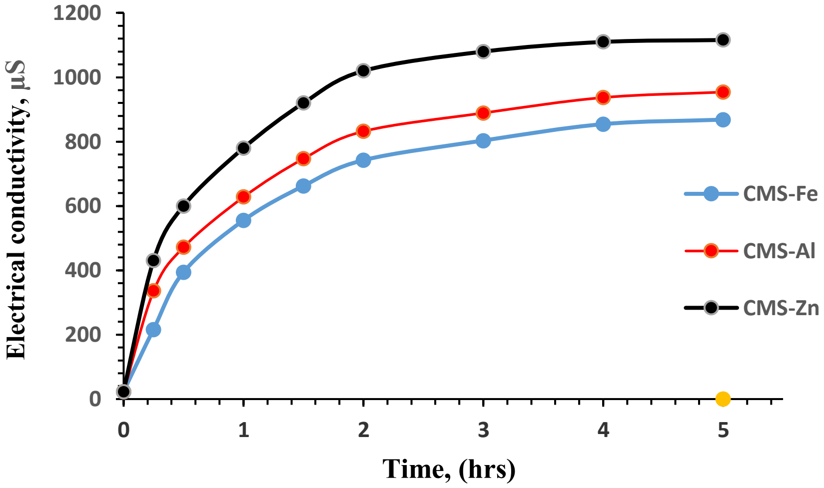
3. Results.

New hydrogels were obtained by the reaction of sodium carboxymethylstarch with aqueous solutions of polyvalent metal salts. In the first step we prepared water solutions of sodium carboxymethyl-starch (CMS-Na) with different concentrations. In order to prepare water solutions of different concentrations of sodium carboxymethyl-starch, the required amount of CMS-Na powder was weighed in exact mass and dissolved in water. The solution was stirred on a magnetic stirrer for 6 hours. Then a water solution of different concentrations of low molecular weight metal salts was added to the prepared CMS-Na solution and mixed at high speed. The formed hydrogel in the aqueous solution was cleaned by washing several times with anhydrous ethanol. The resulting hydrogel is placed in a thermostat at 50 °C for drying.

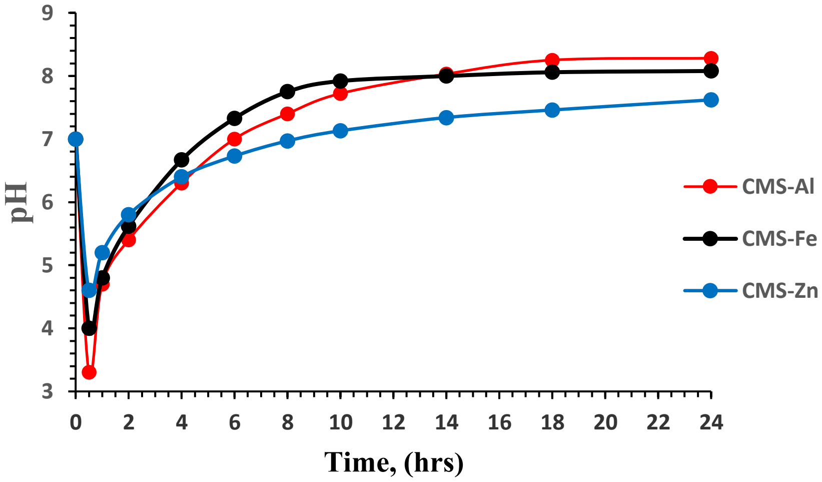
The hydrogel forming process of CMS-Na with different metal ions in water solutions was carried out according to the following general reaction:



Hydrogels obtained on the basis of carboxymethylstarch are polyelectrolytes capable of conformational changes due to flexibility of their chains and significant charge density in the ionized state. The specific electrical conductivity of new hydrogels in aqueous solutions and the time dependence of the pH environment of the solutions were studied. The obtained results of changes in the specific electrical conductivity of new hydrogels in an aqueous solution depending on time are shown in Figure 1a. The obtained results of changes in the pH-environment of the water solution of carboxymethylstarch based hydrogels are presented in Figure 1b.



a)



b)

Fig1. Changes in specific electrical conductivity (a) and pH environment (b) in the presence of carboxymethylstarch based hydrogels in aqueous solutions depending on time.

Obtained results in Fig.1 showed that due to the interaction between the hydrogel macromolecules with water molecules a sharp increase in specific electrical conductivity occurs. An increase in specific electrical conductivity indicates an increase in carboxylate anions in solution due to the dissociation of functional groups, which leads to an increase in the size of the cross-linked macromolecules. Potentially charged links of the polymer network repel each other, which leads to the straightening of the macromolecules, which were initially rolled into a ball. In this case, the hydrogel absorbs the solvent and swells, its volume increases significantly. Low molecular weight counterions move freely in the gel and acquire translational entropy during the quenching process. The electrical conductivity of CMS hydrogels is also affected by the pH values of the aqueous environment. The process of this effect can be confirmed by the change in the concentration of hydrogen ions in the aqueous solution of the hydrogel over time (Fig. 1b). The important factors affecting the electrical conductivity of CMS hydrogel are the concentration of charged ions and low molecular counterions and the atomic radius of metal ions. As a result of the ionization process of CMS hydrogel in an aqueous medium, charged groups repel each other, the cellular polymer macromolecule becomes a branched structure. As a result of the formation of molecular associations with the participation of stabilized metal cations and carboxylate anions, the electrical conductivity increases sharply due to their interaction. This process is also affected by differences in the pH values of the aqueous medium in the presence of the studied hydrogels. The established pattern of electrical conductivity was confirmed by the nature of the change in the concentration of hydrogen ions in the aqueous solution of the studied hydrogels depending on time (Fig. 1b). The result obtained in Fig. 1 can be divided into two stages: the first stage is a sharp transition of a weak acid macromolecule from a folded conformation to an unfolded macromolecular coil; in this case, a sharp increase in acidity was observed due to the dissociation of carboxyl groups, as a result of which the concentration of protons in the aquatic environment sharply increased. The second stage begins with an increase in the pH environment due to a decrease in the concentration of hydrogen (H^+) ions, associated with the destruction of previously formed intramolecular associates with the participation of two carboxylate anions and a proton. It should be noted that carboxyl groups are located on a three-dimensionally intertwined polymer chain, and for the abstraction of each subsequent proton it is necessary to expend additional work to overcome the forces of the electrostatic field created by neighboring, previously dissociated groups. This means that the dissociation process will depend on the number of previously dissociated groups, therefore the increase in pH values after 24 hours occurs insignificantly. Thus, our assumed nature of the conformational transformation of cross-linked CMS based hydrogel macromolecules in water is confirmed by a rather noticeable change in the hydrodynamic dimensions of the studied polyelectrolyte hydrogels network. Due to the increase in electrostatic repulsion between similarly charged chain links, the volume of cross-linked macromolecular coils increases.

The swelling of CMS based hydrogels in an aqueous medium was studied as a function of time. Figure 2 shows the swelling coefficient of studied hydrogels in aqueous media as a function of time. Carboxymethylstarch sodium salt is a linear polysaccharide,

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consisting of two main functional groups (-COOH and -OH). Carboxymethylstarch sodium salt binds other metal cations through carboxyl groups. The concentration of metal ions and crosslinking time are the most important variables affecting the swelling coefficient of hydrogels.

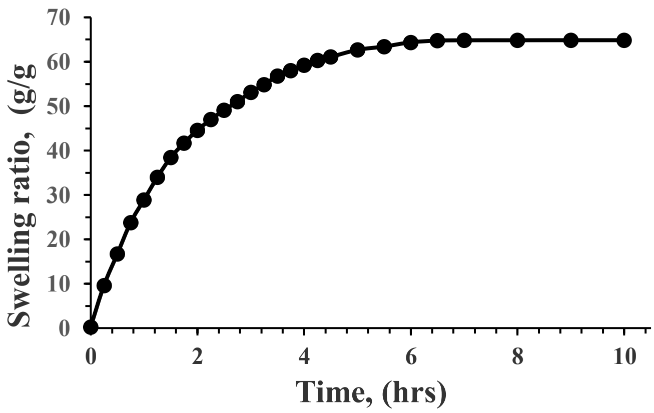

Figure 2. The correlation between time and swelling of the hydrogel obtained as a result of the reaction of CMS-Na with $FeCl_3$. A 1% solution of CMS-Na was used, the concentration of $FeCl_3$ solution was 0.1 mol/l.

As can be seen from Fig. 2, the results obtained reflect two processes that are different in nature, which can be divided into two sections that complement the results obtained from measuring specific electrical conductivity and pH environment. As follows from Fig. 2, the initial part of the curve up to 6 hours shows the concentration areas of the aqueous solution in the presence of CMS based hydrogel, in which polyelectrolyte properties are still weakly manifested. From Fig. 2, it is clear that the polyelectrolyte properties of CMS based hydrogel increase within 6 hours. In the time interval from 6 to 10 hours the swelling ratio increased very little and the curve showed the state of ionized cross-linked CMS based hydrogel macromolecules. At the maximum points of the resulting curve, the processes of dissociation and polyelectrolyte swelling of CMS based hydrogel are balanced. The maximum value of the swelling coefficient of the CMS based hydrogel was achieved after 6 hours. It was observed that the hydrogels obtained as a result of coagulation of CMS-Na with Fe^{3+} metal ions absorb water up to 300-350 times of their mass during 6 hours. Although these results are lower compared to synthetic polymers, they are higher for natural polymers. The swelling abilities of the hydrogels obtained as a result of reaction of CMS-Na macromolecules with different concentrations of Fe^{3+} ions were studied. The obtained results are presented in Fig. 3 below.

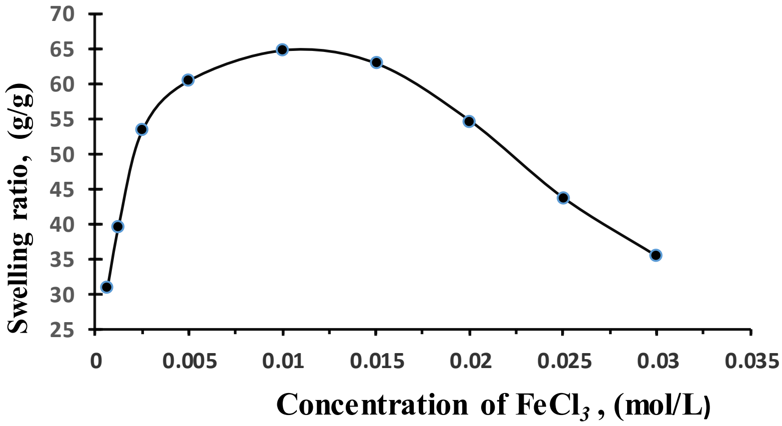

Figure 3. The correlation between $FeCl_3$ concentration and swelling of the hydrogel obtained by the reaction of CMS-Na with $FeCl_3$. A 1% water solution of CMS-Na was used. The concentrations of $FeCl_3$ in water solutions were 0.03 - 0.000625 mol/l.

5. Discussion

From the obtained results of studying the electrical conductivity of water solutions of CMS based polyelectrolyte hydrogels (Fig. 1a), it can be seen that their polyelectrolyte properties are weak due to the lack of swelling of hydrogels at the initial points of the graph. However, after 15 min, due to the beginning of the interaction of the macromolecule with water, the polyelectrolyte hydrogels swell and form charged groups and counterions of low molecular weight. In this case, the charged ions are connected to the chain and the opposite ions remain free, which increases the electrical conductivity. The almost unchanged electrical conductivity in the time interval from 3 to 5 hour can be explained by the fact that the quenching process slowed down and the concentration of low molecular counterions in the gel approached the equilibrium state. The results obtained on the basis of scientific investigations (Fig. 1b) showed that at the beginning of the process, the polyelectrolyte macromolecule changes from a cellular conformation to a spread conformation, and in this case, the dissociation of carboxyl groups is observed, resulting in a sharp increase in the concentration of protons in the aqueous medium. Then, due to the decrease in the concentration of hydrogen ions (H^+) in the process, the pH of the solution begins to rise. These results are related to the loss of previously formed molecular associations in the presence of carboxylate anion and proton. Due to the increase in electrostatic repulsion of similarly charged chain links, the volume of interconnected macromolecules increases. In an aqueous environment, an intensive increase in the pH of the solution is observed in the period from 0.5 to 10 hours, which is associated with the breakdown of associations in the macromolecule and the addition of protons to the resulting carboxylate anions. As showen in the graph in Figure 2, the degree of swelling of the hydrogel in aqueous medium increases with time. As the swelling coefficient of the hydrogel increases in the aqueous medium, the charge in the chain increases, and as a result of the opening of the pore state of the macromolecule, a state of equilibrium occurs in the hydrogel-water system. When CMS-Na macromolecules are ionized, they open from the pore state to the solvated helix. Therefore, the maximum value of the swelling coefficient of the hydrogel in an aqueous environment is reached after 6 hours. According to the results in Figure 3, in concentrations of $FeCl_3$ up to 0.015 mol/l the swelling of the hydrogel increased. Later, the swelling of the hydrogel decreased as the concentration of $FeCl_3$ increased. In this case, sodium (Na^+) ions contained in the carboxylate group (COONa) of CMS-Na are exchanged with iron (Fe^{3+}) ions, resulting in cross-linking of polymer macromolecules with the presence of Fe^{3+} ions. It can be seen that when the concentration of Fe^{3+} ions is low, the carboxylate anion forms less bonds with Fe^{3+} ions, and the hydrogel property of the obtained compound is much lower. At the same time, when the concentration of Fe^{3+} ions is high, the carboxylate anion creates many collisions with Fe^{3+} ions and restricts the entry of water molecules into the macromolecule. This greatly reduces the polielectrolite properties of the hydrogel.

The effectiveness of using CMS based hydrogel for growing almond plantations on pebble lands was studied. The results of the effectiveness of using CMS based hydrogel for growing almond plantations on pebble lands are presented in Table 1. As can be seen from the results obtained in Table 1, the use of the CMS based hydrogel for growing almonds in mountain conditions makes it possible to reduce the frequency of care in tree trunk circles by 6-8 times due to the prevention of the appearance of weeds and keeping the soil in tree trunk circles in an optimally loose state due to reducing moisture consumption for physical evaporation in the tree trunk circles. The frequency of watering was also reduced on average from 12 waterings per growing season to 4-5 waterings. From the data of taxation indicators of annual plants obtained at the end of the growing season, a more intensive increase in their height and diameter can be traced in the experimental variants with the application of CMS based hydrogel, in comparison with the control (without application of the hydrogel). On average, their height, stem diameter and current linear growth exceeded the control ones by 15-18% (Table 1). Observations of the intensity of almond transpiration in experimental variants with the addition of CMS based hydrogel showed, that in the first year after planting, young plants responded to improved moisture conditions by increasing their daily and seasonal indicators.

Table 1. Growth of annual almond seedlings in experimental variants using the CMS based hydrogel.

Hydrogel concentration, %	Annual seedlings		
	Height, cm	Diameter of root collar, mm	Current linear increase in height, cm
0.1	18.6-18,8	5.0-5.1	6.1-6.5
0.2	19.5-19,7	5.5-5.9	6.6-6.9
0.3	21.1-21,8	5.8-6.1	7.6-8.9
0.4	22.3-22,8	5.9-6.6	9.6-9.9
Control, 0%	11.9-12,1	3.1-3.3	3.6-3.9

Observations of the intensity of almond transpiration in experimental variants with the addition of CMS based hydrogel showed that in the first year after planting, young plants responded to improved moisture conditions by increasing their daily and seasonal indicators of transpiration intensity, compared with the control by 18-22%. Higher transpiration rates, compared to the control, in almond seedlings with the addition of CMS based hydrogel caused an increase in the saturation of leaves with water. In the experimental variants with the addition of CMS based hydrogel, the water deficit at a solution concentration of 0.2% was 6.72%, at a solution concentration of 0.4% the water deficit was 5.5%, and with the control variant the water deficit was 8.24%. Based on the results of field tests of CMS based hydrogel, it can be stated that the technology for its use is promising for growing almond plantations on pebble soils.

6. Conclusion

The specific electrical conductivity and pH environment in the presence of CMS based hydrogels in an aqueous solutions were studied depending on time. The swelling of CMS based hydrogels in an aqueous medium was studied as a function of time. It has been established that the state of the cross-linked polyelectrolyte structure of the new CMS based hydrogels was determined by the electrostatic interactions of charged groups. The presence of electrostatic repulsion forces between similarly charged groups of the studied hydrogels leads to a sharp change in the spatial arrangement of the chains between the cross-linking sites and a change in the conformation of the macromolecular coil. The mutual influence of physicochemical parameters (electrical conductivity, pH environment and swelling coefficient) in the presence of new CMS based hydrogels in an aqueous solution was established. In the process of ionization of the obtained hydrogels in an aqueous environment, intramolecular associations are formed with the participation of metal and carboxylate ions, and the pH values of the medium change dramatically due to the hydrophobic interaction of the network structure of the sparsely bound polyelectrolyte. It has been shown that during the ionization of studied hydrogels in an aqueous environment, intramolecular associates were formed with the participation of proton and carboxylate anions, stabilized by hydrophobic interactions of the network structure of the sparsely cross-linked polyelectrolyte molecules. This process was accompanied by a sharp change in the pH values of the medium, an increase in electrical conductivity and the swelling coefficient of the hydrogels in water. The high efficiency of using CMS based hydrogel when growing almond plantations on pebble soils has been established and recommended for application in agriculture. The maximum swelling coefficient of the polyelectrolyte hydrogel obtained as a result of sparse cross-linking of CMS macromolecules with metal ions increased up to 350 times for 6 hours.

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