

Absorption Characterization of Ca^{2+} , Na^+ , and K^+ on Irradiation Crosslinked Carboxymethyl Sago Pulp Hydrogel

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ABSTRACT: Hydrogel of carboxymethyl sago pulp (CMSP) of various degree of substitution (DS) was prepared by electron beam irradiation of various radiation doses. The CMSP hydrogels were subjected to swelling in different ionic strength solutions of KCl, NaCl, and CaCl_2 . The CMSP hydrogels, due to its polyelectrolyte nature, were found to be highly sensitive to ionic strength of the medium. All the CMSP hydrogels showed the absorption of K^+ and Ca^{2+} increases with the increase in the concentrations of the respective cation solutions. The cation absorption also decreases with DS and % gel fraction (%GF) of the CMSP hydrogels. Subjecting the CMSP hydrogels in NaCl results in deswelling and releases Na^+ to swelling medium where the Na^+ release increases with the increase of DS and %GF. The sorption capacity depends on the extent of crosslinking and decreases with the increase in the extent of crosslinking. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The swelling hydrogel study was developed based on the idea that solute transport is determined by the probability of the solute finding an opening between the polymer chains greater than the radius of the solute molecule. The properties of the hydrogels and the solute influence the solute transport through this hydrogels.¹ When a dry hydrogel is immersed in distilled water, the amount of the imbedded water determines the absorption and diffusion of the solutes through the hydrogel. The average pore size distribution and the pore interconnections are important factors in solute permeation into and out of the hydrogel. These factors are most influenced by the composition and crosslink density of the network. The solute size and shape, its relative hydrophilic and hydrophobic character, and the availability of water molecules to hydrate the solute molecules are also important factors governing solute permeation through any particular hydrogel.²

Radiation crosslinking has been proved to be a safe, clean, and effective method for hydrogel synthesis. Compared with conventional chemical routines, neither initiator nor crosslinker is

needed in most of the cases when using radiation methods and the products are free of toxic additives.^{3,4} Gamma radiation crosslinking of carboxymethylcelluloses with a degree of substitution (DS) from 0.7 to 2.2 in the solid-state and aqueous solutions at various irradiation doses was investigated.⁵ It was found that irradiation of carboxymethylcellulose with a relatively high DS (DS = 1.32) led to crosslinking and 20% (w/v) carboxymethylcellulose gave the highest gel fraction (GF). Carboxymethylcelluloses with a DS of 2.2 induced higher crosslinking than the carboxymethylcellulose with a DS 1.32 at lower irradiation doses with same concentration. It can be concluded that high DS and a high concentration in an aqueous solution were favorable for high crosslinking of carboxymethylcellulose. A preliminary enzymatic degradation study confirmed that carboxymethylcellulose hydrogel could be classified as a biodegradable polymer that is classified as environmentally friendly polymers. A further study of carboxymethylcelluloses with a DS of 2.2 was performed.⁶ It was found that in addition to concentration, the dose, dose rate, and the presence of oxygen in the surrounding have also important influence on the radiation crosslinking. Up to 95%

GF was obtained from 50 and 60% (w/v) carboxymethylcellulose solutions by gamma and electron beam radiation. carboxymethylcellulose hydrogels prepared at low dose swelled by absorbing 800 g of water per gram of dry gel. Swelling tests of carboxymethylcellulose hydrogels in salt solutions and in media of various pH showed that the swelling decreased with salt concentration and was lower at acidic pH values. Liu et al. used γ -radiation technique to form hydrogels from concentrations of carboxymethylcellulose solutions of more than 20% (w/v) and reported its swelling behavior at different conditions, such as acidic, basic, inorganic salt, and temperature led to a reduction in the swelling ratio.⁷

In fact, carboxymethylcellulose hydrogels are very sensitive to the presence of even a small amount of salt or a difference in the pH value.^{8,9} This can be explained by the fact that carboxymethylcellulose is a polyelectrolyte and the hydrogel maintains this feature. In accordance with the Donnan equilibrium theory, with rising ionic strength, the distinction in the concentration of mobile ions between the hydrogel and solution is reduced. Therefore, the osmotic swelling pressure of the mobile ions inside the hydrogel decreases and so the hydrogel collapses.⁸

A comparison of hydrogel swelling, as defined by the weight of water absorbed by 1 g of dried hydrogel, formed from carboxymethylcellulose aqueous solutions by electron beam radiation was studied.⁶ Swelling is highest just after the dose oversteps the gelation point and radically decreases with increasing absorbed energy at the early stages of hydrogel formation and then decreases slowly. At the beginning of gelation, the hydrogel is very weak but, because of a relatively low number of intermolecular bonds, is able to expand by absorbing and holding solvent in its voids. With a subsequently increasing dose, the hydrogel content increases, the crosslink density grows, and the hydrogel becomes more tightly packed and its ability to absorb water becomes less. The highest swelling was observed with a concentration of 50% (w/v) carboxymethylcellulose irradiated with electron beam radiation at a dose of 10 kGy with a 35% GF. The pattern exemplifies that not only is a high value of swelling important but also how much crosslinked material that only can absorb and keep a solvent is important.

The swelling of the hydrogels at pH values near neutral, 6.86 and 7.41, is much less than that in deionized water because buffers used in the experiments were based on acid–base salt solutions as proved before, carboxymethylcellulose hydrogels are very sensitive to salts. The equilibrium swelling ratios of ionic hydrogels are often an order of magnitude higher than those of neutral gels because of the presence of intermolecular interactions including coulombic, hydrogen-bonding, and polar forces. This means that drug or protein transport in ionic gels may be significantly faster than in neutral gels.¹⁰

Another study made on Na-Alg/carboxymethylcellulose superabsorbents is ionized hydrogels in which their swelling depends on both the characteristic of the chemical structure and the medium. The swelling of the absorbents in saline solutions decreased compared to the value measured in deionized water. The result shows that the swelling for the hydrogel in monovalent cations salt solutions is in order $\text{LiCl} > \text{NaCl} > \text{KCl}$. These results imply that

the smaller the cation radius, the stronger the hydration ability of the cation, that is, the binding ability to the carboxylate group is weakened and leads to the water absorbency increase.¹¹

To search for applications for carboxymethyl sago pulp (CMSP), electron beam irradiation-mediated synthesis of a novel polysaccharide-based superabsorbent CMSP hydrogels via radiation crosslinking were prepared. In this report, results of cation absorption and desorption in immersion of CMSP hydrogels in various cationic solutions are reported. It is expected that CMSP hydrogel can be used in promoting the plant growth.

EXPERIMENTAL

Isolation of Sago Pulp from Sago Waste

Sago waste was oven dried for 3 h, ground using a stainless-steel blender, and sieved through a 0.5 mm² test sieve. The ground sago waste was predried in the oven at 60°C for 1 h. About 5 g of sago waste was added into a 500 mL Erlenmeyer flask and suspended in hot distilled water (160 mL) together with glacial acetic acid (1 mL). Technical grade sodium chlorite (1.5 g) was then added. The conical flask was stoppered and heated in a water bath maintained at 70°C over a period of 3 h. The final residue was an almost white solid that retained the woody structure of the original sample. The mixture was filtered using a Buchner funnel and washed with cold distilled water until the pH of the filtrate was 7.0. The residue was dried in an oven at 60°C to constant weight.^{12,13}

Preparation of CMSP from Sago Pulp

CMSP was prepared by etherification of sago pulp with NaOH and sodium monochloroacetate, and the solvent used in this study was 2-propanol.^{12,13}

Preparation of CMSP of DS 0.4. Dried sago pulp (5.0 g, 30.9 mmol) was added into 2-propanol (100 mL) and sodium hydroxide (30% [w/v], 10 mL) was added in a drop-wise fashion. After stirring for 1 h, sodium monochloroacetate (3.0 g, 0.026 mol) was added and the reaction mixture was placed in thermostated water bath with horizontal shaker. The reaction mixture was heated to 45°C and shaken for 3 h. Once complete, the mixture was filtered and the residue was suspended in methanol (300 mL) overnight. The suspended methanol solution was then neutralized using glacial acetic acid and the resultant residue was washed with 300 mL ethanol, filtered, and dried to constant weight.

Preparation of CMSP of DS 0.6. The procedure was adopted as specified for DS 0.4 except using sodium monochloroacetate 6.0 g (0.052 mol) instead of 3.0 g with a reaction time of 2 h.

Preparation of CMSP of DS 0.8. The procedure was adopted as specified for DS 0.4 except for the basification process where NaOH was added (25% [w/v], 10 mL) instead of 30% (w/v) and the quantity of sodium monochloroacetate was 6.0 g (0.052 mol) instead of 3.0 g. The absolute values of DS were determined by potentiometric titration.^{12,13}

Preparation of CMSP Hydrogels from CMSP Solutions Preparation and Irradiation Procedures. Distilled water was added to CMSPs with DS 0.4, 0.6, and 0.8, which were then mixed until homogenous using a

glass rod. For preparing high concentrations of CMSP solutions (above 20% [w/v] CMSP), CMSPs were well kneaded and left for 24 h for complete dissolution. The CMSP mixtures were degassed before irradiation using a Henkovac vacuum. For free air irradiation, the CMSP mixtures were placed into polyethylene bags to make the process impermeable to air. After evacuation, 15 mL of the mixture is spread evenly in a plastic mold and covered with a plastic sheet. Then the covered plastic mold was placed in polyethylene plastic bag and sealed using sealer machine.

In the CMSP hydrogel preparation, the irradiation of the CMSP mixture was performed by electron beam generated from an electron beam machine (2 MeV; model EPS-3000) 10 mA current and various doses of irradiation were used.⁵

Determination of Gel Content in CMSP Hydrogel with Various DS. After electron beam irradiation, the CMSP hydrogels were accurately weighed (W_0), immersed in distilled water for 48 h, and then dried in oven at 60°C to a constant weight (W_1). The percentages of soluble fraction and GF were calculated according to the eqs. (1) and (2), respectively.¹⁴

$$\text{Sol fraction (\%)} = [(W_0 - W_1)/W_0] \times 100 \quad (1)$$

$$\text{GF (\%)} = 100 - \text{Sol fraction} \quad (2)$$

Swelling of the CMSP Hydrogels in Various Inorganic Salt Solutions

The CMSP hydrogels of DS 0.4, 0.6, and 0.8 with %GFs of 25%, 35%, and $\geq 40\%$ were immersed in various concentration (0.005–0.025 M) of 10 mL of inorganic aqueous solutions (NaCl, CaCl₂, and KCl) at room temperature for 48 h at room temperature. After swelling, the hydrogel was filtered by a stainless-steel net of 30 mesh. The percentage of metal uptake was calculated using eq. (3).^{8,15}

$$\text{Percent metal ion uptake } (P_u) = \frac{\text{Amount of metal ion sorbed}}{\text{Amount of metal ion in feed}} \times 100 \quad (3)$$

The amounts of sodium, calcium, and potassium were analyzed using atomic absorption spectroscopy (AAS) of model AAnalyst

Perkin 100. Sodium chloride solution was analyzed at wavelength 589 nm, CaCl₂ solution was analyzed at 422.7 nm, and KCl solution was analyzed at 766.5 nm. The measured absorbency was interpolated with the concentration on the standard curve of the respective cations.

RESULTS AND DISCUSSION

Swelling Behavior of Hydrogels

Swelling in different concentration of KCl, NaCl, and CaCl₂ solutions. CMSP hydrogels of DS 0.4, 0.6, and 0.8 with %GF 25, 35, and ≥ 40 were subjected to swelling in ionic solutions of KCl, NaCl, and CaCl₂ with concentrations from 0.005 to 0.025 M. These concentrations of KCl, NaCl, and CaCl₂ solutions were chosen referring to Liu et al. whereby they observed the sodium alginate/CMC hydrogels had a swelling activity in the range of 0.01–0.10 M and collapsed beyond 0.25 M concentration of the inorganic salt solutions.⁸ Figure 1 shows the replacement of the Na⁺ ion in the CMSP hydrogels with Ca²⁺ or K⁺ cations from the respective cation chloride solutions where the carboxylate groups form a salt bridge with the respective cations upon subjected to the cationic solutions.

In view of the fact that CMSP hydrogel is a polyelectrolyte, it is very sensitive to salt concentration. Figures 2 and 3 show all the nine types of carboxymethylcellulose hydrogels swelled in five different concentration of KCl and CaCl₂ solutions at room temperature (25°C) for 48 h and the amount of cations absorbed was determined using AAS. The sorption capacity depends on the extent of crosslinking and decreases with the increase in the extent of crosslinking.¹⁵ The CMSP hydrogel with %GF of 25, 35, and ≥ 40 studied showed that the absorption of the K⁺ and Ca²⁺ increased with the increase in the concentration of the KCl and CaCl₂ solutions. It is observed that the absorption of cations into the CMSP hydrogels increase with the decrease in the DS and %GF of the CMSP hydrogels. It could be due to the CMSP hydrogel with higher DS and higher %GF contributes to higher crosslinking density structures that decrease the absorption of the cations into the hydrogel.

The interaction between the counterions (K⁺ and Ca²⁺) in the inorganic salt solutions and the fixed ionic groups (COO⁻) on

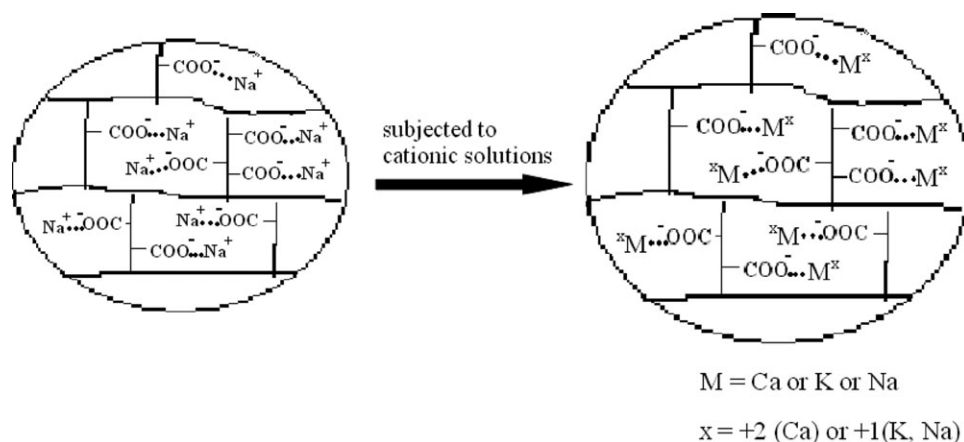


Figure 1. Schematic showing CMSP hydrogel and the salt bridge.

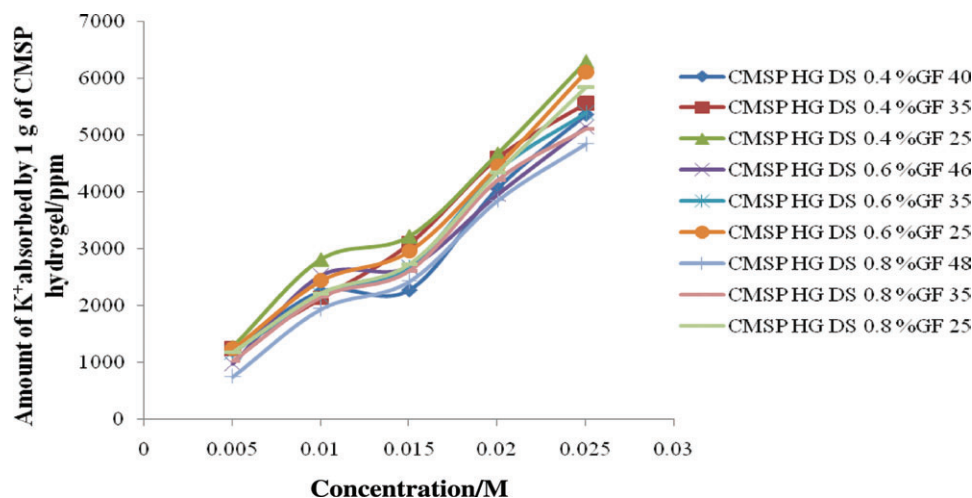


Figure 2. Amount of potassium absorbed by CMSP hydrogels of DS 0.4, 0.6, and 0.8 with %GF 25%, 35%, and ≥ 40 in KCl solutions with various concentrations (HG-Hydrogel). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the carboxymethylcellulose polymer in the hydrogels is not necessarily involved in the formation of covalent bonds. The counterion may be localized near the fixed ionic groups by the electrostatic attraction between two opposite charges. The counterions with higher valence are more strongly held because the electrostatic attraction is proportional to the ionic charges.²

Figure 4 shows that the absorption capacity decreases with an increase in charge of the metal cation ($\text{Ca}^{2+} < \text{K}^{+}$). This may be explained by the complexing ability arising from the coordination of the multivalent cations with carboxylate groups of the CMSP hydrogels. This ionic binding might occur at the surface of the particles and make them rubbery and very hard when that swells in Ca^{2+} solutions. Potassium ion has a smaller cationic radius (1.44 Å) compared to Ca^{2+} (2.0 Å) which

results in K^{+} having stronger hydration ability, which reduces the binding ability with the carboxylate group and leads to greater water absorbancy.^{11,16} An additional reason could be the increasing electrostatic attraction between anionic sites of the hydrogel chains and multivalent cations would lead to increased degree of “ionic cross-linking” and consequently loss of swelling.^{11,17}

A past study on superabsorbent hydrogel consisting of carboxymethylcellulose (DS 0.52) and sodium alginate was prepared using methylenebisacrylamide as a crosslinking agent. The swelling behavior was studied in chloride solutions of Na^{+} , Ca^{2+} , and Al^{3+} . The results showed that the swelling capacity is decreased with the increase in charge of the metal cations ($\text{Al}^{3+} < \text{Ca}^{2+} < \text{Na}^{+}$).¹¹

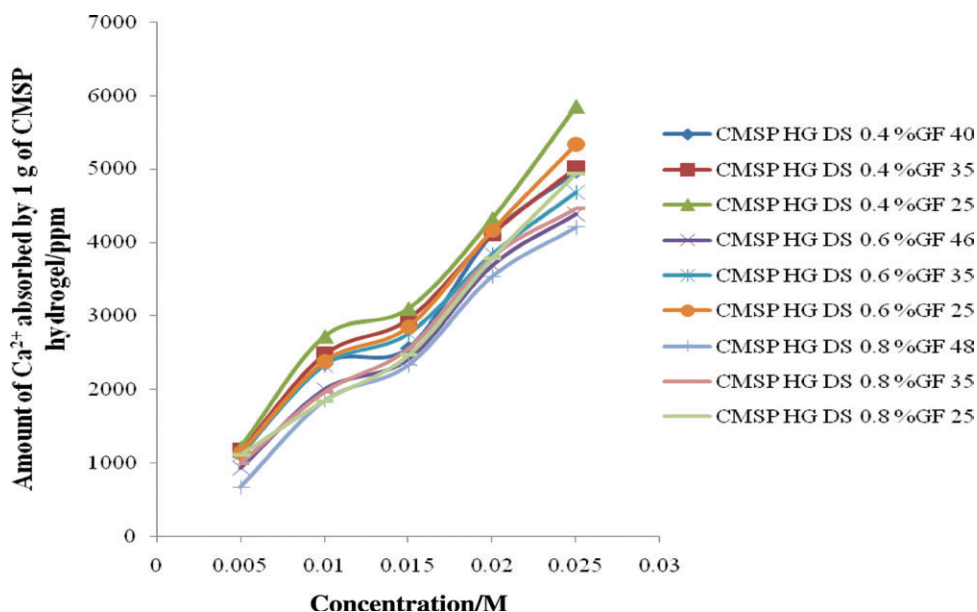


Figure 3. Amount of calcium absorbed by CMSP hydrogels of DS 0.4, 0.6, and 0.8 with %GF 25%, 35%, and ≥ 40 in CaCl_2 solutions with various concentrations (HG-Hydrogel). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

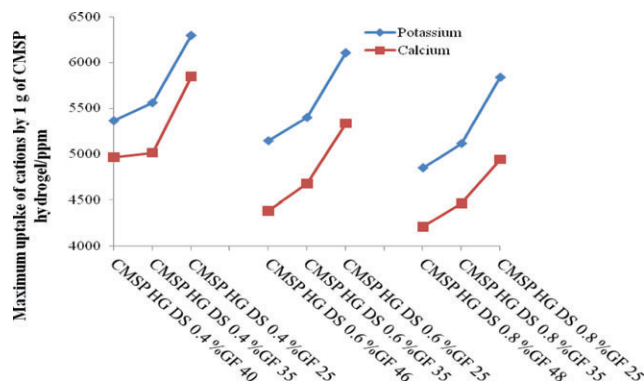


Figure 4. Maximum amounts of K^+ and Ca^{2+} absorbed by CMSP hydrogels of DS 0.4, 0.6, and 0.8 with %GF 25, 35, and ≥ 40 in KCl and $CaCl_2$ in 0.025 M concentrations of respective salt solutions (HG-Hydrogel). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The CMSP hydrogels are essentially ionized hydrogels and their absorption behavior depends on the both the characteristics of the chemical structure of the hydrogel and the medium. Upon using the NaOH in the formation of the CMSP so naturally, there will be a significant amount of Na^+ present and proportional to the %GF and DS. Figure 5 shows that the amount of Na^+ released to the medium increases with the increase in the ionic strength of the medium. The 0.1 g CMSP hydrogels of DS 0.8, 0.6, and 0.4 that have been used have 0.025, 0.02, and 0.015 g Na^+ , respectively. The NaCl mediums of concentrations 0.05, 0.01, 0.015, 0.02, and 0.025 M have 0.003, 0.006, 0.009, 0.012, and 0.015 g Na^+ , respectively. The concentration of the Na^+ in the CMSP hydrogels of DS 0.8, 0.6, and 0.4 is higher than in all the concentrations of NaCl medium. Thus, due to the difference in the concentration of Na^+ in the CMSP hydrogel and NaCl medium, diffusion of Na^+ from all the respective CMSP hydrogels into the medium occurs and increases the concentration of

Na^+ in the medium. These ionic diffusions resulted in the decrease of the osmotic pressure in the CMSP hydrogel and the collapse of the hydrogels (shrink).⁶

The Na^+ concentration released increased with the increase of DS and %GF of the CMSP hydrogels. This may be due to the release of Na^+ from the sodium CMSP hydrogel network and the number of Na^+ available in the CMSP hydrogel is increased with the increase in DS. As the CMSP hydrogels have the intrinsic Na^+ in the CMSP hydrogel network, they can be used as a source of Na^+ besides being used as a water retainer in the soil for agricultural industry. The CMSP hydrogels with DS 0.8 shows that a proportional release of Na^+ could be used to load fertilizers and then used as slow release fertilizer with extra benefit of the Na^+ release.

Wach et al. reported that the swelling of the carboxymethylcellulose hydrogels in the 5 mM and 1.0 mM NaCl solutions was decreased compared to the values measured in the distilled water.⁶ This well-known phenomenon commonly observed in the swelling of the ionic hydrogels is often attributed to charge screening effect of the additional cations, causing a nonperfect anion–anion electrostatic repulsion, leading to a decreased ionic osmotic pressure difference between the carboxymethylcellulose hydrogel network and the external solution.

Another study on a novel superabsorbent hydrogel composed of carboxymethylcellulose and sodium alginate was studied in various salt solutions. The tendency of the absorbency for these hydrogels in salt solutions is in the order $Na^+ > Ca^{2+} > Al^{3+}$ using NaCl, $CaCl_2$, and $AlCl_3$ aqueous salt solutions.^{11,18}

In another study on using the highly crosslinked polyacrylamide hydrogel as a superabsorbent on the salt resistance woody species, *Populus euphratica* were investigated under saline conditions. The results showed that the plant grown in hydrogel amended soils contained higher Ca^{2+} in both root and leaf relative to those grown in unamended saline soil. The amide group

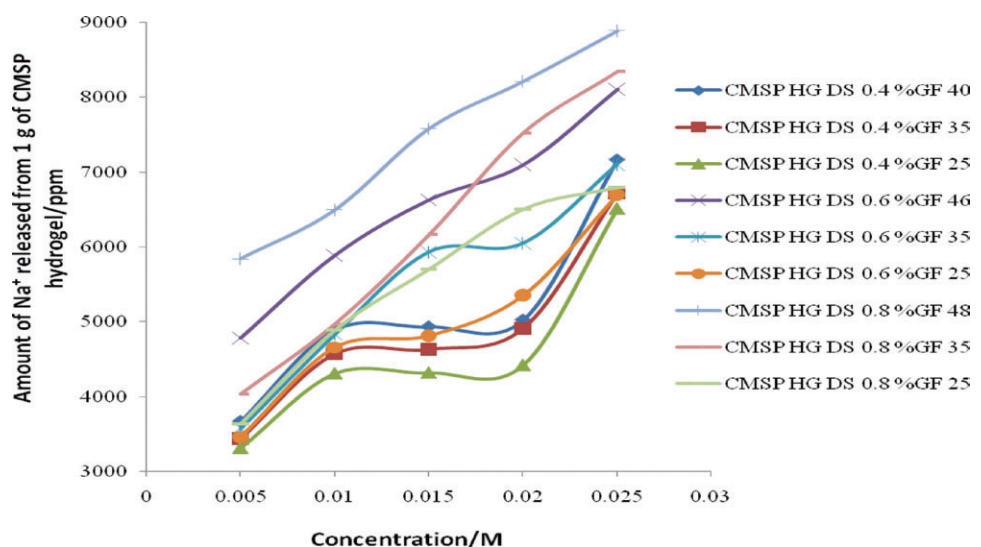


Figure 5. Amount of Na^+ released by CMSP hydrogels of DS 0.4, 0.6, and 0.8 with %GF 25, 35, and ≥ 40 in NaCl in various concentrations (HG-Hydrogel). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in the polyacrylamide hydrogel was hydrolyzed to carboxylic acid, which provides more oxygen atom for the formation of more stable bonds with Ca^{2+} instead of Na^+ . The hydrogels in the soil which were covered with roots allow good contact with Ca^{2+} and reduce the contact with Na^+ and Cl^- , thus playing a major role in improving salt tolerance. The hydrogel amendment in the saline soil enhanced Ca^{2+} uptake and increased salt exclusion capacity. As a result, the adverse effect of the salinity was reduced and the plant growth was ultimately improved.¹⁹

CONCLUSIONS

Subjecting the CMSP hydrogels in KCl and CaCl_2 resulted in swelling. The absorption of K^+ and Ca^{2+} increases with the increase of concentration of the respective cation solutions and decreases with DS and %GF of the all CMSP hydrogels. The CMSP hydrogels, due to its polyelectrolyte nature, was found to be highly sensitive to ionic strength of medium. Subjecting the CMSP hydrogels in NaCl results in deswelling and releases Na^+ to swelling medium where the Na^+ release increases with the increase of DS and %GF. So, the CMSP hydrogel may be used as a candidate to develop as an efficient biopolymer-based hydrogel for enhanced Ca^{2+} and K^+ uptake to promote plant growth and meeting the agricultural economy requirements.

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