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Effect of Salinity on Swelling Behaviors of Superwater Absorbent Hydrogel Prepared from Carboxymethyl cellulose/Acrylamide Blends by Gamma Radiation

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Abstract: Polysaccharide-based hydrogels act like smart materials and exhibit a wide range of properties that can be utilized for several applications. Polysaccharide-based super water absorbent (SWA) hydrogel was prepared from an aqueous solution of carboxymethylcellulose (CMC)/acrylamide (AAm) Using gamma radiation from a Co-60 gamma source at room temperature (~27°C). Functional groups of the prepared hydrogel were characterized in terms of Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR). The swelling of the SWA in water and the saline solutions (NaCl, $CaCl_2$, and $AlCl_3$) was examined. It was found that the swelling value of the SWA in water is higher (27900%) than those of in the saline solutions (2074% in NaCl, 1718% in $CaCl_2$ and 796% in $AlCl_3$). Results also indicated that the swelling capacity of SWA in saline solution decreases with an increased charge of cation in salt. Swelling ratio in NaCl solution was the highest which was 26, followed by 12.48 in $CaCl_2$ and 6.22 in $AlCl_3$ solution. A comparative swelling study was done by changing the cationic size of the same group elements (between KCl and NaCl). This study suggested that the swelling of the SWA depends upon the cationic size. Compared to the swelling of 2074% in NaCl solution, the swelling in KCl was found to be slightly higher (2442%). This behavior can be attributed to the charge screening effect for monovalent cations, as well as the ionic crosslinking of the SWA with the multivalent cations.

Keywords: Hydrogel, Carboxymethylcellulose, Swelling, Super Water Absorbent, Radiation

1. Introduction

Super water absorbent (SWA) polymers are under the broad category of hydrogels that can be defined as crosslinked macromolecular networks that are able to absorbe huge amount of water or physical fluids. However, during the absorption process, they retain their physical appearance by not getting dissolved when brought into contact with water [1]. These hydrogels are highly hydrophilic, non-toxic, biodegradable and biocompatible [1, 2].

Due to these excellent characteristics, SWA is being widely applied in many fields, such as agricultural, feminine napkins, disposable diapers, medical, and pharmaceuticals applications [3-6]. This huge amount of application accounts for the increase in the worldwide production of superabsorbent polymers (SAPs), that is now a million tons a year. Hence, synthesis and characterization of SWA is the prime goal of the several research groups in the world [7-10].

The various techniques adopted for the preparation of SWA include physical and chemical crosslinking, the grafting polymerization and the radiation crosslinking [11, 1]. However, Radiation crosslinking is the most convenient and sought for technique nowadays. This technique is a simple additive-free one-step process and the reactions such as polymerization, crosslinking and grafting can easily be controlled [12, 10].

Lately, attention has been focused on polysaccharide based SWA which are produced with monomer or polymer using gamma radiation for agricultural uses [4]. Polysaccharide-based hydrogels act like smart materials and exhibit a wide range of properties that can be utilized for several applications. [13, 14]. They can be highly useful in the biomaterial domain for their unique benefits such as abundance, non-toxicity, biodegradability and biological functions [2].

Carboxymethylcellulose, presently, is the most widely used polysaccharide for the fabrication of new engineered hydrogels [15, 16]. CMC is a biodegradable and biocompatible natural anionic polysaccharide, capable of being highly soluble in the water and thereby, increasing the viscosity of the water [3]. Because of the polyelectrolyte like behavior of CMC, it has been used in many fields e.g., environmental, biomedical, industrial applications etc. [17-19].

The study of swelling conditions is very important concerning the fact of the characterization of SWA. The properties of the swelling medium (e.g. pH, valency, ionic strength, and the counter ion) affect the swelling characteristics [20, 21, 13]. Among these conditions, the effects of salts or ions on the swelling properties of the hydrogels are of great interest and importance because salts are commonly present ubiquitously like in the case of biological systems [20, 22, 13].

Therefore, following a continuous research on the synthesis of natural-based SWA this work is an attempt on the synthesis, characterization and study of the effect of salts on the swelling characteristics of a polysaccharide-based super absorbing polymer prepared from CMC and Acrylamide by gamma radiation.

2. Experimental

2.1. Raw Materials

Acrylamide was purchased from Aldrich Chemical and purity of it was 97%. Low viscosity Carboxymethylcellulose was purchased from Sigma; NaCl, KCl, $CaCl_2$, and $AlCl_3$ were purchased from Fluka, Switzerland. Distilled water was used as the solvent.

2.2. Preparation of Acrylamide/CMC Co-Polymer Hydrogel

The hydrogel samples were prepared according to our previous work [5, 23]. Briefly, a homogeneous solution containing 5% of acrylamide was prepared in distilled water with 3% CMC concentration. The homogenous solution was poured into glass test tubes and sealed with a polyethylene bag. Then the test tubes with solutions were irradiated with 25 kGy gamma radiation dose from a Co-60 source situated at Institute of Food and Radiation Biology, Atomic Energy Research Establishment, Bangladesh Atomic Energy Commission, Dhaka, Bangladesh. The irradiated samples were cut into small pieces, dried at room temperature and then in an oven at 50°C till constant weight. The dried samples were used for the measurement of the swelling properties.

2.3. Measurement of Swelling Ratio

The gel sample dried to constant weight was dipped in distilled water for 48 hr at room temperature. The swollen hydrogel sample was then filtered using a stainless steel net of 30 meshes and weighed after the removal of the surface water by tissue paper. The swelling ratio was calculated as follows (equation 1):

$$\text{Swelling ratio} = [W_s - W_d)/W_d] \quad (1)$$

Where W_s is the weight of the swollen sample and W_d is the initial weight of the dry sample.

2.4. Measurement of Swelling Capacity

The gel sample dried to constant weight was immersed in distilled water at room temperature. Periodically, the weight of the samples was taken after the removal of surface water with a soft tissue paper. The swelling capacity/water absorption was calculated as follows (equation 2):

$$\text{Swelling Capacity (\%)} = (W_t - W_d)/W_d] \times 100 \quad (2)$$

Where W_t is the weight of the gel in swollen state at the time‘t’ and W_d is the initial weight of the dry gel.

2.5. Measurement of Swelling Behavior in Salt Solutions

Swelling behavior in different salt solutions (NaCl, CaCl2, and AlCl3) was investigated according to the procedure described in section 2.4.

2.6. Ftir Atr Spectrophotometric Analysis

The functional groups of CMC-AAm hydrogel, Acrylamide, and carboxymethylcellulose were determined using Perkin Elmer Spectrum-2 Ftir-Atr Spectrophotometer within 4000–450 cm^{-1} range from Institute of Radiation and Polymer Technology, Atomic Energy Research Establishment, Bangladesh Atomic Energy Commission, Dhaka, Bangladesh.

3. Results and Discussion

3.1. Swelling Behavior in Salt Solutions

The swelling capacity of super water absorbent hydrogel (SWA) could be significantly affected by various factors of the external solutions such as pH, temperature and salt concentration. The presence of ions in the swelling medium has a profound effect on the absorbency behavior of SWA. Many theories were formulated to understand the case of the swelling behavior of ionic hydrogels in saline solutions. One of the simplest theories is the Donnan equilibrium theory [24, 25]. According to this theory, the electrostatic interactions (ion swelling pressure) is due to the difference between the osmotic pressure of the free mobile ions in the gel and in the salt solutions. The osmotic pressure is the driving force for the swelling of SWA. Increasing the concentration difference of the mobile ions between the polymer gel and the external medium reduces the gel volume, i.e. the gel shrinks and the swelling capacity decreases. Figure 1 shows the effect of charges of cations on the swelling of SWA. It is found that the swelling ratio decreases with an increased charge of cation in the salt of the swelling medium. This result may be due to the formation of ionic bonds between cation of the swelling medium and carboxylate groups of CMC in the hydrogel; with increasing the charge of cation, more ionic bonds may be formed which decreases the number of the hydrophilic groups in SWA.

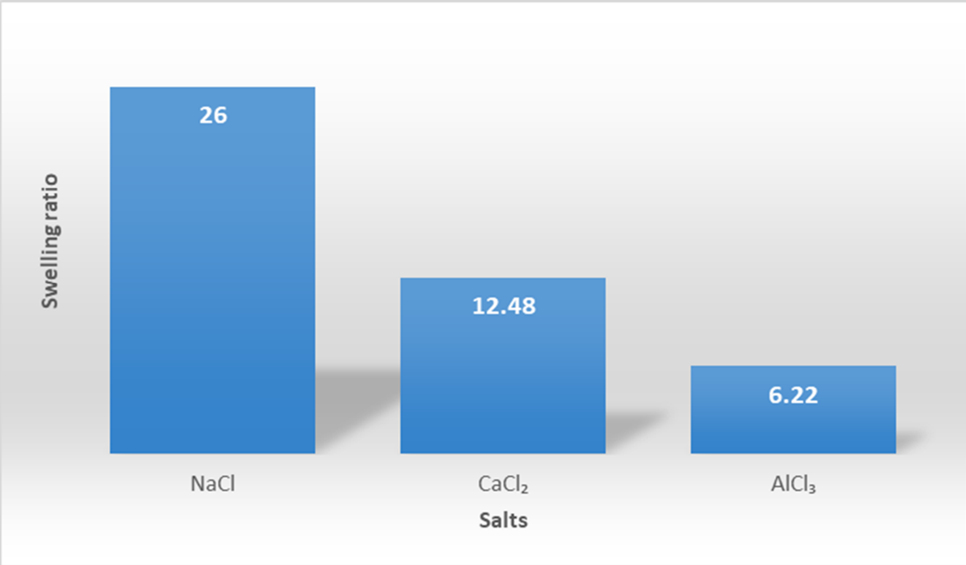

Figure 1. *Swelling Ratio of SWA in 0.1M mono-, di-, and trivalent salt solutions (radiation dose at 25 kGy).*

Figure 2 shows the effect of ionic strength of the swelling medium on swelling ratio of SWA. The results indicate that the swelling ratio of SWA decreases with an increase in the concentration of the salt i.e. ionic strength in the external solution. Bound charge concentration within the SWA exceeds the concentration of external salt solution at low ionic strength. Hydrogel swells and expands its network due to a large ion swelling pressure and thereby the swelling ratio is higher than those with a higher concentration of ions.

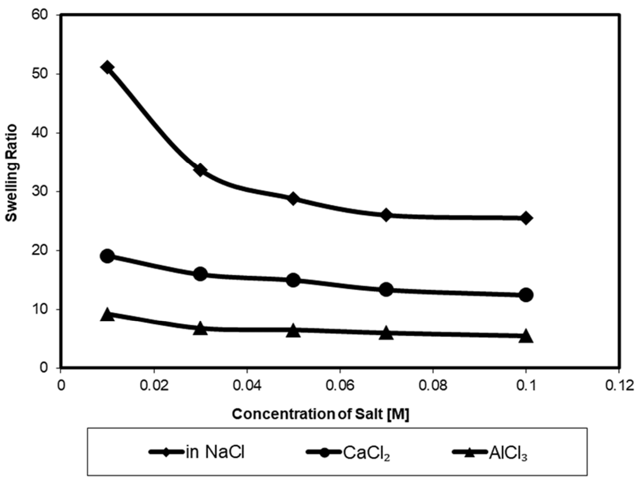

Figure 2. *Swelling of CMC-AAm blend hydrogel in mono-, di- and tri-valent salts at 25 kGy.*

With the rise in the external salt concentration, the difference between the external and internal ion concentration decreases and the SWA deswells. The hydrogel continues to deswell with increasing the concentration of the external salt until the mobile-ion concentrations inside and outside are approximately equal. The explanation of this phenomenon takes into account the repulsion between fixed charged groups on SWA.

The reduction in water absorption depends on the ionic state i.e., the oxidation state of the cation as shown in Table 1. The higher the oxidation states, the lower the water absorption. The existence of ions in the solution surrounding the polymer network can nullify the ions on the polymer by counteracting the mutual repulsion of the fixed ion on the network itself, and the decrease of the osmotic pressure difference between the external solution and the gel [26]. The salt type and concentration can be expressed in terms of ionic strength. The effect of the ionic strength on the water absorbency can be further understood by Flory's equation (equation 3) [27].

$$Q^{5/8} = [(i/2\nu_u S^{*1/2})^2 + (1/2 - \chi_1)/\nu_1]/(\nu_e/V_o) \quad (3)$$

Where Q is the degree of swelling, i/ν_u is the charge density of the polymer, S* is the ionic strength of the solution, $(\frac{1}{2} - \chi_1)/\nu_1$, is the polymer-solvent affinity, ν_e/V_O is the crosslinking density.

Equation 3 depicts that, increase in the ionic strength of the saline solution call upon the decrease in the water absorbency of the SWA. Mobile ions and their valence or oxidation state are both responsible for the ionic strength of the solution. A small amount of divalent or trivalent ions can dramatically reduce the swelling values. The decreases are more significant by trivalent ion Al3+ followed by divalent ion, Ca2+, and this trend is additionally due to the complex formation ability of carboxamide or carboxylate groups; or because one multivalent ion is able to nullify several charges inside the gel. Consequently, the crosslinking density of the network increases while water absorption capacity decreases [28].

Table 1. *Effect of salt solutions on water absorptiona.*

Solution	Ionic Strength (mol/L)	Water absorption (g/g)
Distilled water	-	279
0.1 M NaCl	0.1	20.74
0.1 M $CaCl_2$	0.3	17.18
0.1 M $AlCl_3$	0.6	7.96

[a]$I = \Sigma(C_iZ_iI^2)/2$ where I, Ci and Zi are the ionic strength, the ionic concentration, and charge on each individual ion, respectively.

3.2. Kinetics in Distilled Water and Saline Solutions

In practical application, a higher swelling rate is required along with a higher swelling capacity. The swelling behavior of SWA in distilled water and aqueous solutions of salts (0.1M NaCl, CaCl2 and AlCl3) are shown in Figure 3 & 4. From the figures, it is found that the swelling capacity of SWA in water is higher than those of SWA in the salt solutions. The maximum value of the water absorption of SWA is about 27900% in water, 2074% in 0.1 M NaCl, 1718% in 0.1 M CaCl2 and 796% in 0.1 M AlCl3 at 48 hours of standing time. These characteristics may be explained on the basis of osmotic pressure developed due to unequal distribution of ions in the swelling medium and polymer networks, as discussed in the previous section. When SWA is immersed in distilled water, there is a maximum osmotic pressure developed and thus a maximum swelling is obtained. But when SWA is kept in salt solutions the osmotic pressure developed becomes much lower because the external solution contains cation and anion. So the swelling is reduced significantly.

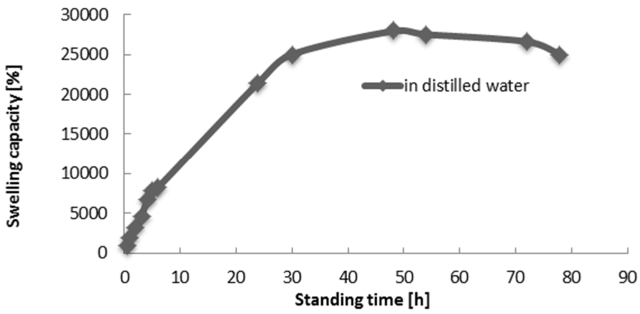

Figure 3. *Swelling kinetics of the CMC- AAm hydrogel in distilled water.*

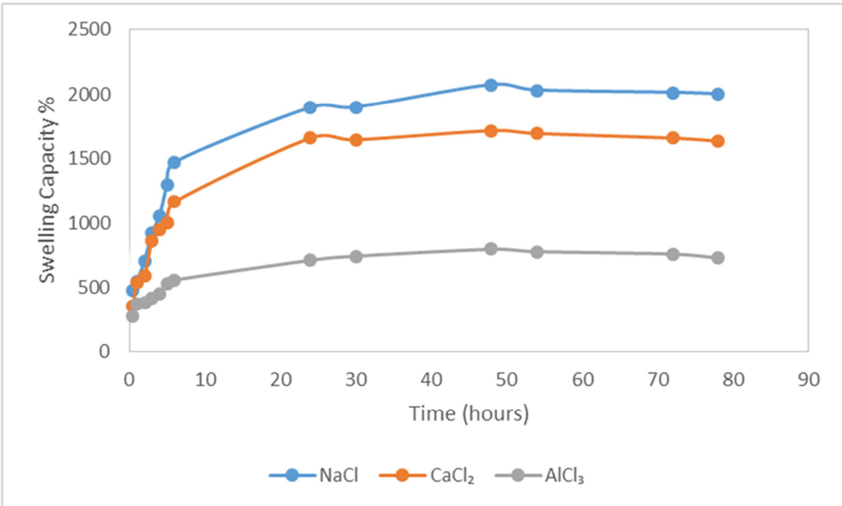

Figure 4. *Swelling kinetics of the CMC-AAm hydrogel in saline solutions.*

Figure 5 shows the swelling capacity of SWA in NaCl and KCl solution. From the figure 5, it is observed that the swelling capacity of SWA in KCl solution is higher than those of NaCl solution. The swelling of SWA in 0.1 M KCl is about 2442% and 0.1 M NaCl is about 2074% at 48 hours of standing time. The swelling of SWA may depend on the cationic size of the same group elements. Pass et al. has reported that the carboxylate anion more easily interacts with small cations, e.g. Na+, than with large cations, e.g. K+ [29]

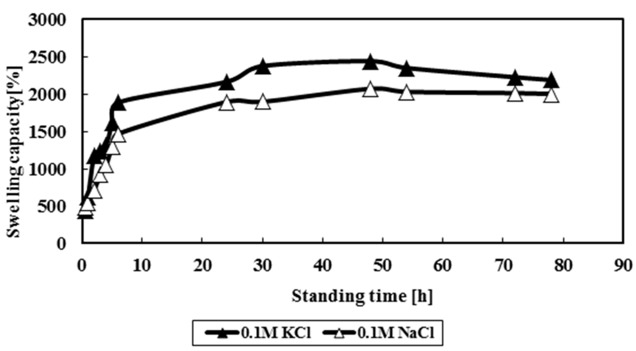

Figure 5. *Swelling kinetics of the CMC-AAm hydrogel in monovalent saline solutions.*

3.3. Ftir-Atr Analysis

Figure 6 (A) represents the infrared spectrum of raw acrylamide. The presence of band around 3341.8 cm^{-1} can be assigned to symmetrical and asymmetrical stretching of N–H group. The characteristic C=O stretching vibration bands of amide and acid groups are observed at 1597.65 cm^{-1} and 1663.07 cm^{-1} respectively [30].

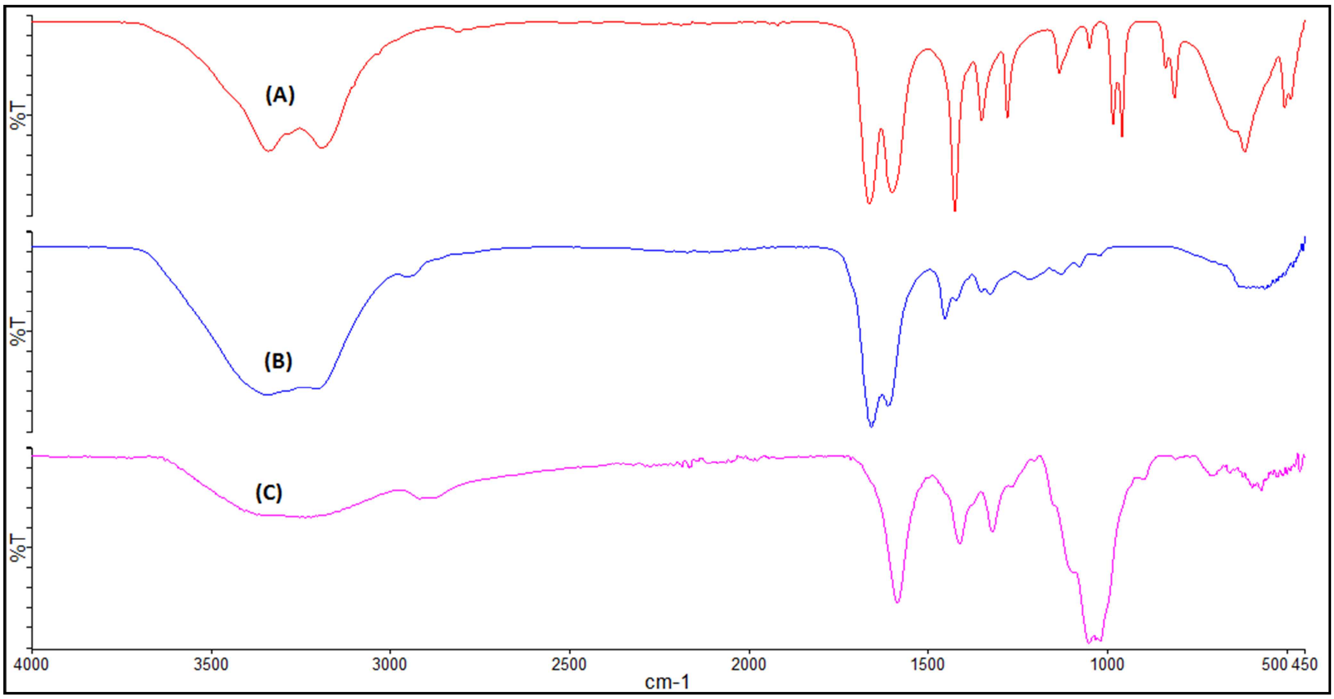

Figure 6. *Ftir-Atr spectra of (A) Acrylamide, (B) CMC-AAm hydrogel, (C) CMC.*

In the FT-IR spectrum of CMC as original material, in figure 6 (C); OH groups represent as a broad peak at around 3350 cm^{-1}. The peak around 2926.7 cm^{-1} represents the C-H asymmetric stretching in aliphatic methyl [31]. High intense band appearing at 1586.45 cm^{-1} and 1412.44 cm^{-1} may be attributed to stretching and bending vibrations of carboxylate anion groups (-COO-) in CMC. CMC sample showed a broad band at 1052 cm^{-1}, which dominates the spectrum of cellulose linkages and β-glycosidic linkage. [32].

The FTIR-ATR spectrum of CMC-AAm hydrogel in figure 6 (B) shows some peaks that are new compared to the spectra of Acrylamide and CMC. The emergence of peaks around 3350 and 3206 cm^{-1}, correspond to the –N-H stretching. The peaks at 2956.4 and 2930.8 cm^{-1} refer to the C-H stretching vibration. The peaks at 1659.71 and 1613.89 cm^{-1} (-NH bending) indicate amide I and amide II groups of the CMC-AAM hydrogel, respectively [33]. The peak around 1659.71 cm^{-1} can be attributed to the overlap of (-COO-) on the CMC backbone and the amide-II (-N-H) on the AAm chains. The peaks around 1454, 1423 and 1327.92 cm^{-1} are assigned to the scissoring of -CH2, symmetrical stretching of –COO- and the twisting of -CH2 units of the hydrogels [34, 35]. The peaks around 1200-1000 cm^{-1} are for the important (-CH-O-CH2) units of CMC-AAM hydrogel.

4. Conclusion

From this investigation, it can be concluded that the super water absorbent hydrogel (SWA) based on polysaccharide can be prepared from aqueous solution of carboxymethylcellulose (CMC)/acrylamide (AAm) with radiation processing technology using Co-60 gamma source at room temperature. Copolymer formation was evident from the FTIR-ATR spectrophotometric analysis of the raw acrylamide, Carboxymethylcellulose, and CMC acrylamide hydrogel. The swelling behaviors of the prepared SWA significantly depend on the swelling medium. The swelling ratio of SWA in water is higher than those of SWA in salt solutions. It is also depended on the cationic charge of salts. The swelling ratio of SWA in mono-valent solution is higher than those of SWA in multi-valent salt solutions. Swelling ratio decreases according to Na^{+1}<Ca^{+2}<Al^{+3}.

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