

Synthesis and Characterization of NaCMC/HEC/Activated Carbon Hydrogel Composites for the Desalination of Seawater*

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Abstract. Current available methods for water desalination are energy intensive, expensive, and not feasible for small-scale applications. As an alternative, hydrogels and hydrogel composites may be utilized both as draw agent and semi-permeable membrane to desalinate water via forward osmosis. In this study, a non-toxic, biodegradable, and low-cost hydrogel composite is prepared by adding activated carbon (AC) as filler to a 3:1 blend of sodium carboxymethyl cellulose (NaCMC) and hydroxyethyl cellulose (HEC), with citric acid as crosslinking agent. A one factor-at-a-time (OFAT) analysis was performed to correlate the crosslinker concentration, crosslinking duration, and AC content to the swelling and desalination efficiency of the CMC/HEC/AC hydrogel composite. Results showed that the swelling of the hydrogel varies directly with the crosslinking duration but varies inversely with the crosslinking concentration. The experiments also showed that the addition of AC as filler significantly improves the desalination efficiency of the hydrogel composite; however, it was also observed that efficiency is reduced if the AC content is excessive.

Index Terms: hydrogel, composite, desalination, activated carbon, cellulose

I. INTRODUCTION

Water desalination is achieved either by thermal processes or by membrane separation processes [1]. Between the two approaches, thermal processes are the most used method for water desalination. However, because heat is required to evaporate the saltwater, the main disadvantage of these processes is that they are energy-intensive; thus, more costly to operate, with approximately 55% of the operational costs are from evaporation and condensation alone [2].

On the other hand, membrane separation processes- such as reverse osmosis, ultrafiltration, and membrane distillation- can also be costly due to the high mechanical energy required as driving force, with 40-45% of the total cost being attributed to energy consumption [3]. Also, current available membrane filters are expensive and highly prone to fouling, making them not viable for use in small-scale desalination [4]. Thus, there is a need to develop a more economical method of generating drinking water on a smaller (i.e., household) scale for those residing in areas with easy access to seawater/brackish water but limited access to freshwater (e.g., small islands, low-income fishing communities).

One promising approach on small-scale desalination is the application of forward osmosis (FO) [5]. FO is a type of membrane separation process characterized by the

diffusion of water across a semi-permeable membrane in response to the difference in solute concentration of the feed solution and a drawing agent. The drawing agent is typically of high osmotic pressure and, thus, draws the water to the side of the membrane, which can afterwards be recovered by applying heat or pressure stimuli [6]. Unlike in reverse osmosis, FO is achieved at lower operating pressures and does not require a fluid motive device (i.e., pump)- thereby lowering the energy requirement and allowing for the use of thinner membranes.

For a low-capacity FO setup, it is desired to choose a material to serve as an ideal draw agent that provides a high osmotic gradient and substantial water flux [7]. One viable option is the use of hydrogels, which are superabsorbent, three-dimensional networks of polymer chains that are crosslinked by either physical or chemical bonds [6]. Depending on the existing hydrophilic groups, the hydrogel matrix itself can also serve as the semi-permeable membrane for salt ions, and water recovery from the swollen hydrogels can be accomplished repeatedly using light, heat, or pressure stimuli [6]. However, in order to address the aforementioned challenge, the desalination hydrogel to be used should also be non-toxic and inexpensive.

Bio-based hydrogels from cellulose derivatives such as sodium carboxymethyl cellulose (NaCMC) and hydroxyethyl cellulose (HEC) are among the potential candidates due to their non-toxicity, biodegradability, and economic viability [8]. NaCMC is a polyelectrolyte that is widely applied in drug delivery systems due to its pH-responsiveness and ease in synthesis [9], while HEC is another cellulose ether known to have excellent water-

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retention capability [8]. Based on previous studies, the combination of NaCMC and HEC have been shown to produce superabsorbent hydrogels [10]. In forming this hydrogel blend, citric acid is used as crosslinker since it is non-toxic and, thus, suitable for the objective of this desalination study [11].

Aside from the reduction of salt content, the removal of pathogens and other micro contaminants is also necessary to make the water potable. In a previous study, a NaCMC/HEC hydrogel composite was investigated using reduced graphene oxide (rGO) nanoparticles as filler [12]. However, rGO is very expensive to synthesize; therefore, a more viable alternative must be identified. One possible candidate is activated carbon (AC), which is a widely used adsorbent that is also utilized in point-of-use water purification devices because of its abundance and low cost [13].

II. OBJECTIVES

With the addition of AC filler, the properties of the hydrogel blend are expected to be significantly affected. Hence, the objective of the study is to synthesize the NaCMC/HEC/AC hydrogel composites and determine the effects of crosslinking duration, crosslinker concentration, and AC particle loading to their swelling and desalination behavior.

III. MATERIALS AND METHODS

3.1. Materials

The chemicals used in the synthesis of the hydrogels are deionized water, carboxymethyl cellulose powder (available as a sodium salt), hydroxyethyl cellulose powder, citric acid powder, and activated carbon powder. For the characterization of hydrogels, distilled water and sodium chloride powder are used.

3.2. Hydrogel Composite Synthesis

Figure 1 shows the general schematic procedure for synthesizing the hydrogel samples. AC powder was added to deionized water at a concentration of 10% (w/w) and was heated to 60°C while being stirred continuously using a magnetic stirrer. The hydrogel matrix was prepared following the 3:1 blend ratio of NaCMC-to-HEC. HEC was added to the solution first while still being heated to 60°C and while being stirred continuously. After the HEC-activated carbon solution became homogeneous, NaCMC was added and incorporated using an electric stirrer. The resulting homogeneous paste was then transferred to a beaker and was left to air-dry overnight. Then, three replicates per samples were prepared in circular observation dishes. The samples were then submerged in a 4 M citric acid solution half an inch above their height for 3 days to allow crosslinking. After crosslinking, the samples were immersed in deionized water for 2 days to remove any excess crosslinker and paste. Lastly, the hydrogel samples were strained and were dried using a convection oven at 40°C and 11 hours. Shown below is the image of a synthesized hydrogel.

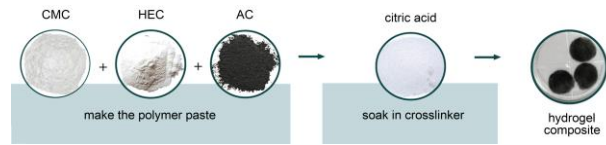


Figure 1. Schematic diagram of the synthesis of NaCMC/HEC/AC samples

3.3. Hydrogel Characterization and Testing

Table 1 below shows the three-level one-factor-at-a-time (OFAT) experimental design implemented by varying three parameters- namely, the crosslinking duration (X_1), crosslinker concentration (X_2), and AC filler loading (X_3). The sampling of hydrogels per trial was done in triplicate.

Table 1 : OFAT experimental design.

trial	X_1 (days)	X_2 (M)	X_3 (% w/w)
1	3	4	2.5
2	2	4	2.5
3	4	4	2.5
4	3	3.5	2.5
5	3	4.5	2.5
6	3	4	0
7	3	4	5

After drying, the initial weight (W_0) of each hydrogel composite sample was measured using a top loading balance. Then, the samples were immersed in a prepared 3.5% (w/v) NaCl solution. Twice a day, the hydrogels were strained and were patted with tissue paper until dry and then weighed to obtain the swollen weight (W_n). From this, the swelling ratio (SR) in percent was calculated using the following equation:

$$SR_n (\%) = \frac{W_n - W_0}{W_0} \times 100\% \quad (1)$$

To simulate the seawater, a 3.5% (w/v) aqueous NaCl solution was prepared. A plastic cup was filled with the saline solution until the mark where the hydrogel sample contained is submerged fully. Twice a day, the sample was strained from the set-up and the salinity of the strained water was determined using a salinity meter. After recording, the hydrogel was submerged back to the set-up until the next recording.

IV. RESULTS AND DISCUSSION

4.1. Swelling Test

Table 2 shows the effect of the crosslinking duration to the swelling ratio of the hydrogel composites. The increased exposure time of the polymer chains to the citric acid facilitates more hydrogen bonding between polymer chains, which then results to a higher crosslinking ratio. With the use of citric acid as crosslinker, the hydrogel is formed by the physical crosslinking between the cellulose derivative and citric acid via hydrogen bonding [8].

Table 2 : Swelling ratio of NaCMC/HEC hydrogels at different crosslinking duration.

crosslinking duration (days)	SR (%)
2	46.55
3	74.56
4	105.64

Table 3 shows the effect of the crosslinker concentration to the swelling ratio of the hydrogels. The hydrogen bonding is achieved during the acidification step where the hydrogel paste is immersed in the citric acid solution; thus, it is expected that an increased amount of citric acid also increases the crosslinking density of the hydrogel. However, hydrogels with high crosslinking ratio, consequently, have rigid structures with low polymer chain mobility and low free volume, hence, poor ability to absorb water [14]. This is in contrast with the observed effect of the crosslinking duration, despite both parameters being supposedly correlated with the number of citric acid molecules that are the available for crosslinking. It is hypothesized that the effect in swelling may be attributed to other factors such as the molecular transport of citric acid into the hydrogel blend: the increased duration allows for increased accumulation of crosslinking molecules within the NaCMC/HEC blend without an increase in diffusion rate, thereby increasing density without the sudden formation of rigid networks. On the other hand, the increase in citric acid concentration directly affects the concentration gradient that drives the transport of crosslinking molecules into the hydrogel blend, with the immediate introduction of hydrogel molecules to a larger number of crosslinking molecules resulting to formation of more crosslinking bonds.

Table 3 : Swelling ratio of NaCMC/HEC hydrogels at different crosslinker concentration.

crosslinking concentration (M)	SR (%)
3.5	13.29
4.0	74.56
4.5	67.12

Table 4 shows the effect of the activated carbon loading to the swelling ratio of the hydrogel composites. The activated carbon particles interact with the hydrophilic crosslinking bonds and increases network rigidity, thereby inhibiting the swelling of the hydrogels. On the other hand, if too much activated carbon is added, the hydrogel that is supposed to serve as the polymer matrix tends to behave more like a polymer binder, which favors the adhesion between the particle filler and the matrix and, consequently, reduces the formation of the rigid polymer network that restricts the swelling response of the sample.

Table 4 : Swelling ratio of NaCMC/HEC/AC composites at different activated carbon loading.

AC loading (% w/w)	SR (%)
0	158.58
2.5	74.56
5	92.21

4.2. Desalination Test

Table 5 shows the effect of the crosslinking duration to the desalination efficiency of the hydrogel composites. The desalination efficiency is expressed in terms of the percent change in the salinity of supernatant that has been collected from the washing of samples after they have been immersed in the simulated seawater bath. The desalination behavior may be attributed to the swelling behavior of the hydrogel blend: the increase in water content in the hydrogel increases salt migration by increasing its solubility within the hydrogel network, but also causes a reduction in concentration gradient (which may explain the decline in efficiency at longer duration).

Table 5 : Desalination efficiency of NaCMC/HEC hydrogels at different crosslinking duration.

crosslinking duration (days)	%increase in supernatant salinity
2	18.78
3	20.59
4	17.44

Table 6 shows the effect of the crosslinking concentration to the desalination efficiency of the hydrogel composites. The increased number of hydrophilic crosslinking bonds favors the migration of salt ions into the hydrogel; however, decrease in water sorption due to increased rigidity causes a reduction in solubility within the hydrogel.

Table 6 : Desalination efficiency of NaCMC/HEC hydrogels at different crosslinking concentration.

crosslinking concentration (M)	%increase in supernatant salinity
3.5	11.76
4.0	20.59
4.5	12.07

Lastly, Table 7 shows the effect of the activated carbon loading to the desalination of the hydrogel composites. The increase in AC loading increases the ion retention; however, the increased amount of particle fillers also reduces the swelling capacity of the hydrogel, thereby affecting its desalination efficiency [15]. Based on the observation, it is concluded that the desalination is more affected by the swelling behavior of the hydrogel matrix (i.e., presence of water) than the presence of the hydrophilic adsorbent.

Table 7 : Swelling ratio of NaCMC/HEC/AC composites at different activated carbon loading.

activated carbon loading (% w/w)	%increase in supernatant salinity
0	12.49
2.5	20.59
5	13.96

V. CONCLUSIONS

Based on the OFAT analysis, the swelling behavior of the NaCMC/HEC hydrogel blend varies directly with the crosslinking duration but varies inversely with the crosslinker concentration. On the other hand, the desalination efficiency of the blend varies directly with both parameters. For the NaCMC/HEC/AC hydrogel composite, the swelling behavior and desalination efficiency both increase with AC loading but only to an extent due to the conflicting effects of the presence of the AC particles to the swelling behavior of the hydrogel matrix. It is therefore recommended, for the purpose of material design, to further investigate the optimization of the NaCMC/HEC/AC blend formulation.

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