



Use of Polyacrylic Acid Hydrogel in The Desalination of Seawater of Haql Coast of Saudi Arabia



Mazen A. AlSolami

Department of Biology, Environmental Research Unit, College of Haql, University of Tabuk, Tabuk 71491, Saudi Arabia

DECREASING freshwater resources of the world has led to the use of seawater for human consumption. But availability of high concentration of salts in seawater makes it unsuitable for direct use, therefore, the seawater is desalinated by various techniques. The present investigation was carried out to test the efficacy of prepared polyacrylic acid hydrogel (PAA) in the desalination of seawater of Haql coast of Saudi Arabia. Hydrogels were prepared from PAA with different concentrations of *N, N*-methylene bisacrylamide cross-linker, ammonium persulfate and *N, N, N, N*-tetramethylethylenediamine. Free radical polymerization technique was used to proceed the reaction. The chemical structure was evaluated by infrared spectroscopy. The glass transition temperature was recorded by differential scanning calorimetry. Seawater of Haql coast was used to evaluate the swelling properties of hydrogels. The swelling and desalination of water were measured as a factor of time. The results of the study showed that prepared hydrogels were found helpful in the desalination of water samples. Highest desalination was observed in the gels with the largest pore size.

Keywords: Desalination, Hydrogel, Smart Polyacrylic Acid, Haql-Tabuk.

Introduction

Hydrogels can absorb massive amount of water and aqueous solutions and are often referred as “superabsorbers” [1]. Hydrogels possess the capacity to absorb a solvent 100 times of their own weight, the feature which has attracted scientists across a wide range of fields for this class of materials. The hydrogels have a cross-linked polymeric chain structure which usually carry charges attached to their backbones [2]. Hydrogels, with the affinity to water play multifaceted roles in the variety of applications on one side and on the other they are also used for specialised high-tech products. In the former category fall typically personal hygiene products and are used for the fast absorption of high quantities of bodily fluids [3]. Hydrogels are also used as underwater-cable insulations, the addition to agricultural soil to retain water close to the plants

or as a separating agent for water-oil slurries [4,5]. The category of high-tech applications include the stimuli responsive gels that switch their swelling state due to external stimuli such as salt [6], temperature [7], light [8], pH [9], electrical current [10], or the presence of certain small molecules [11]. Among the numerous practical applications of stimuli responsive hydrogels are the controlled release of drugs [11, 12], and the use as actuators in fluidics [13]. Moreover, various other materials have also been used in the purification and desalination of water which include activated lignin-chitosan extruded blends [14], Gum Arabic-crosslinked-poly(acrylamide)/Ni(OH)₂/FeOOH nanocomposites hydrogel [15], arginine based composite [16], and cobalt-zinc ferrite nanoadsorbents [17].

Natural freshwater resources are continuously draining by several drivers such as population growth, standard of living, climate change,

*Corresponding author: e-mail: m.alsolami@ut.edu.sa

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and depletion of the fossil aquifers [18,19]. Current assessments suggest that 40% of the global population is forced to live under severe water scarcity, which may rise to 60% by 2025 [20]. Moreover, 66% of the global population is compelled to survive under severe water scarcity conditions for at least one month in a year [21]. These estimates suggest that conventional water sources are no longer sufficient to meet the demand of increasing population in water-scarce areas. Therefore, it is highly desirable to find out alternate ways which could fulfil the ever-increasing demand of water for human consumption.

One of the possible solutions to the problem is the production of fresh water from the oceans by the removal of the contained salt (about 3.5 wt. %). Use of seawater after desalination became a common strategy in many parts of the world [22]. Seawater contains many different ions but mostly sodium chloride (87 wt. %) and several divalent ions [23]. Seawater desalination is already undertaken on a large scale by several countries such as Saudi Arabia, the United Arab Emirates, the USA, and Spain [18]. A study on desalination data exhibits that there are 15,906 operational desalination plants producing around 95 million m³/day of desalinated water for human use, of which 48% is produced in the Middle East and North Africa region [24]. All methods which separate salt from water require energy to overcome the osmotic pressure (seawater about 27 bar). Several technologies are in use to produce freshwater, the highest market shares are held by reverse osmosis and a number of distillation processes [25,26].

Haql city is located in Tabuk province, the northwest region of Saudi Arabia near the head of the Gulf of Aqaba, across the Jordanian border. The present study was carried out to test the desalination capacity of hydrogel of seawater of Haql coast. In the present study we focused on preparation of polyacrylic acid hydrogel (PAA) with different concentration of cross-linker. The influence of cross-linker concentration on the degree of swelling has been discussed. The present study will update the available outdated information on the state of desalination by providing novel methodology that considers the desalination efficacy of PAA.

Experimental

Chemicals

Acrylic acid (AA) (99% Merck, Germany), *N, N, N', N'*-tetramethylethylenediamine (TEMED) (99%, Acros, Germany), methylene bisacrylamide (MBA; 99%, Aldrich, Germany), ammonium persulfate (APS) (99% Merck, Germany). Other chemicals were used as and where required.

Instruments

Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer spectrophotometer at room temperature. The samples were milled with dry potassium bromide KBr (Merck 99%) and pressed to pellets. Perkin Elmer Differential Scanning Calorimeter (DSC) Pyris 1 was used for the determination of glass transition temperature (T_g) of solid polymers. The thermogram was recorded at heating and cooling rate of 5 °C/min. The morphology of the polymer was examined by Scanning Electron Microscopy (SEM) using a Zeiss NEON 40 instrument (USA); 2 kV (30 μm aperture). Sputter coater is a Bal-Tec SCD 500 with a film thickness monitor QSG 100. We applied approx. 4 nm of gold-palladium (Au: Pd = 80:20). Salinity/SG Refractometer 0 - 100ppt / 1-1.070SG ATC for measuring the salt concentration of water, the RSA0100A displays readings in parts per thousand (ppt) or specific gravity, while the RSA0028A display readings in % of salt.

Synthesis of PAA

To prepare PAA, in a test tube 0.05 mol AA and 0.001 mol MBA (cross-linker, 2 mol% over the total monomer concentration) were dissolved in 10 mL deionized water under stirring in water bath at 60 °C. After deoxygenation of the solution by N₂ bubbling for 30 min, 0.1 g APS (dissolved in 2 mL deionized water) and 3 drops of TEMED were added. Immediately the formation of gel was started. The gel was allowed to cool in a refrigerator for two hours then removed from test tube and pieces of 1 cm thickness were cut. Gel was dried overnight in an oven under reduced pressure.

IR (KBr): ν (cm⁻¹): 2990 (s) (CH₂, CH), 1720 (s) (C=O, carboxyl), 1610 (s) (C=O, amide).

Hydrogel Swelling

Dynamic swelling experiments were performed by placing the discs in seawater at 30 °C ± 0.1 °C (in a thermostatic bath) and measuring their weight gain as a function of time. The discs were removed from the water, dried quickly and

carefully with filter paper and weighted.

The degree of swelling at different times was calculated from the following equation:

$$W (\%) = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

Where m_0 and m are the weights of the initial dry sample (xerogel) and of the hydrogel, respectively.

Analysis of sea water desalination

The concentration of salt in the collected seawater samples was measured. Desalination of seawater with hydrogels was carried out in the three steps. First the dry hydrogel was immersed in 50 ml seawater. The swelling was determined as a function of time for each 1 h. for each swelling measurement the salinity of water was measured by refractometer. The polymer is subjected to an external stimulus, in this case hydrostatic pressure, to free the solution from it (step 3). The water received in the end was analysed for available salt concentration and was compared with the samples used initially.

Results and Discussion

The PAA was prepared using free radical polymerization. Three different hydrogels were prepared from three different molar concentrations of cross-linker MBA (10, 20, and 30). The effect of cross-linker concentration has sharply observed. Table 1 shows the amount of cross-linker, APS and TEMED.

FT-IR spectral analysis

KBr FT IR spectra showed characteristic bands we can observe an important sharp band at 1720 cm^{-1} (Figure 1). This band is assigned to the vibrations of the carbonyl group of the carboxylic group. Kim et al. [27] observed this band at 1709 cm^{-1} and correlated it with the intermolecular hydrogen bonds among the carbonyl groups of the polymer [18]. At 1610 cm^{-1} stretched band for CONH of cross-linker. CH and CH_2 polymer chain have appeared at 2990 cm^{-1} . Figure 1 indicates that that all the data were in accordance with the chemical structure.

Thermal analysis

Thermal gravimetric analysis

Figure 2 shows the thermal stability of hydrogels which recorded by thermal gravimetric analysis. Hydrogel A-10 showed one step decomposition while hydrogel B-20 and C-30 showed decomposition in two steps which can be due to increasing in cross-linker composition.

Differential scanning calorimetry

The glass transition temperature of dried samples was estimated by DSC at heating rate $5 \text{ }^\circ\text{C}/\text{min}$ as described above in the experimental part. The T_g value was taken as the midpoint inflection. The T_g values are given in Table 1 for hydrogel A-10, B-20 and C-30. Figure 3 shows a single T_g for each sample, which indicates the formation of random polymerization [1]. Hydrogel A-10 showed T_g at 100°C which is the lowest value. By increasing the concentration of cross-linker the T_g s were increased 130°C and 140°C for B-20 and C-30, respectively this due to increasing the cross-linking density which further increased crystallinity of hydrogel.

X-ray diffraction

The X-ray diffractograms (Figure 4) showed a broad peak at $2\theta = 20^\circ$. This peak is associated to the intra-chain segments distance of 0.45 nm (determined using the Bragg's law). Figure 4 shows significant increase in crystallinity of hydrogel C-30, B-20 and A-10 with increasing cross-linker density which affected the gel pore size and increases the intermolecular interaction.

Swelling and collapsed properties

Swelling is a typical process of polymeric networks and one of the most important features used in applications. By swelling, the network structure is extended as a suitable solvent is taken up into it and the previous liquid phase is solidified and immobilised. Swelling is used extensively for the characterisation of gels as the equilibrium swelling.

TABLE 1: The amounts used for preparation of PAA and the glass transition temperature (T_g).

Hydrogel	AA	MBA	APS	TEMED	T_g
	g/mol.	g/mol	(g)	(g)	($^\circ\text{C}$)
A-10	3/0.042	0.642/0.0042	0.2	0.02	100
B-20	3/0.042	1.295/0.0084	0.4	0.04	130
C-30	3/0.042	1.943/0.0126	0.6	0.06	140

AA acrylic acid; MBA methylene bisacrylamide; APS ammonium persulfate; TEMED N, N, N', N' -tetramethylethylenediamine; T_g glass transition temperature.

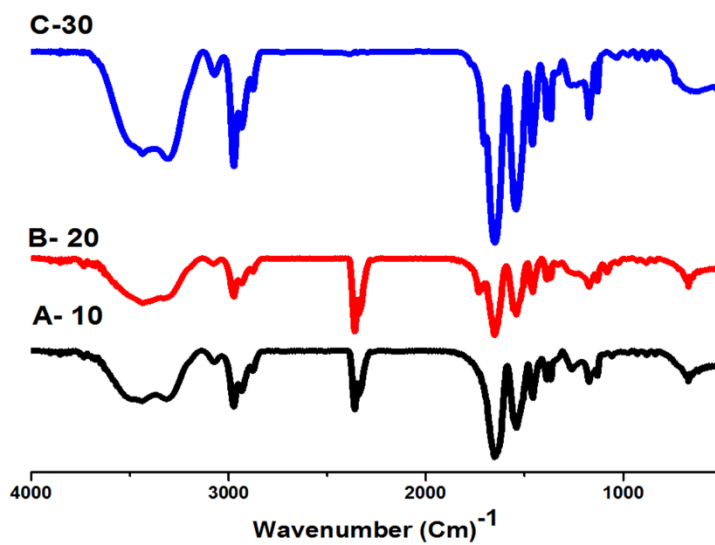


Fig. 1. FT-IR spectra KBr for hydrogels

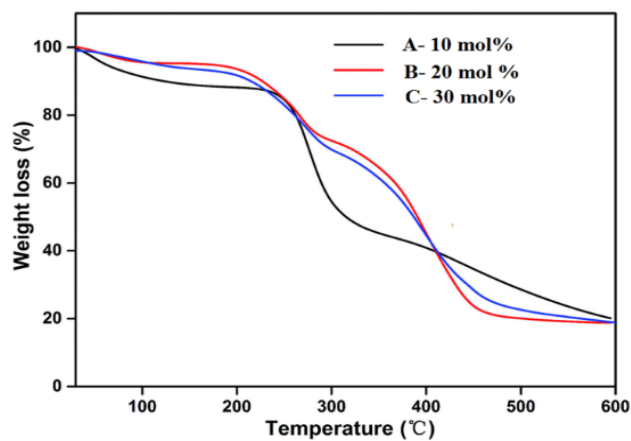
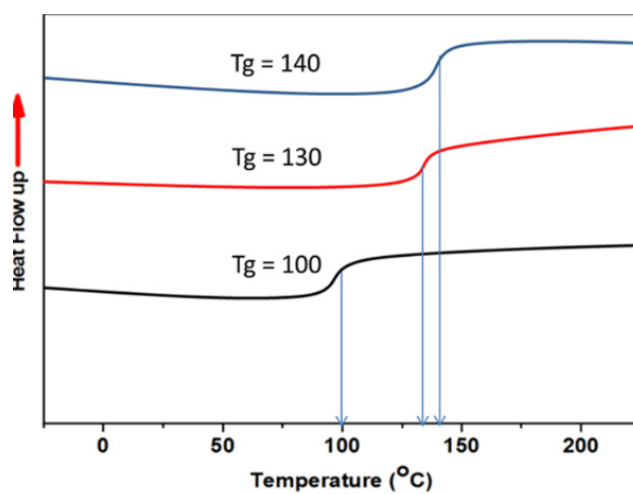


Fig. 2. TGA of Xerogel samples

Fig. 3. DSC shows the T_g of hydrogel

The degree of swelling of a network is quantified by the ratio of solvent to polymeric material. In the swollen gel this ratio can either be volume or mass. When placing dry polymer in contact with a solvent reservoir, it will take up solvent and swell. This is a time dependent process and therefore the swelling degree is time dependent. When dry polymer is in contact with a solution, in the beginning m_0 holds as no solvent is present in the polymer and m increases upon solvent. Table 2 exhibits the degree of swelling and desalination ratios of hydrogel with different mole ratios of cross-linker.

Figure 5 describes the relation of degree of swelling as a time function and demonstrated the highly swelling value with the lowest concentration of cross-linker. This might be attributed to the largest pore size in A-10 than B-20 and C-30 which allow to absorb much more water. From Table 2 and Figure 6 we observed the highest desalination occurred for A-10 with the largest pore size that might be due to lower density of cross-linker with intensively carboxylate ions charges for absorption much more amount of salt.

Morphological features

The SEM image of hydrogel A-10, B-20 and C-30 were obtained at a magnification of 1000 \times (Figure 7 A-C). The porosity of hydrogel

A-10 surface increases the whole surface looks like waxy with cross-linking. As increasing the concentration of cross-linker from B-20 to C-30 respectively we noticed decreased in pore size.

Conclusion

We synthesized new functional PAA with different mole ratio of cross-linker to study the effect of cross-linker in the degree of swelling and desalination of seawater. All polymer gels were evaluated by chemical methods and physical methods and showed significant results with their structure. The relation of degree of swelling as a time function demonstrated the higher swelling value with the lowest concentration of cross-linker which might be attributed to the largest pore size in A-10 than B-20 and C-30. This allowed increased absorption of water. We also observed the highest desalination occurred in A-10 with the largest pore size that might be due to lower density of cross-linker with intensively carboxylate ions charges which facilitated more absorption of salt.

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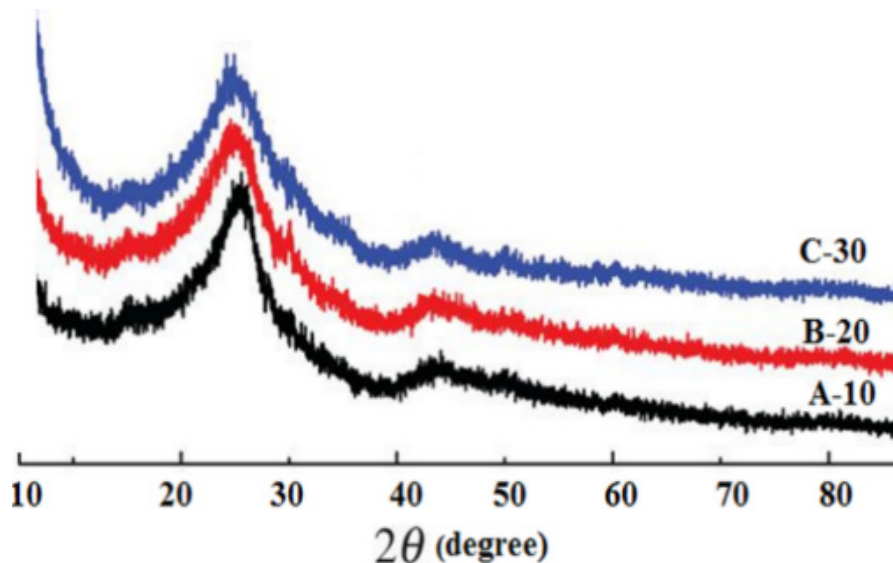


Fig. 4. X-ray diffraction of Xerogel (dry gel)

TABLE 2. The change of volume degree of swelling and salinity with time

time/h	Degree of swelling %			Salinity (ppt)		
	A-10	B-20	C-30	A-10	B-20	C-30
1	51	41	12	54	66	60
3	146	135	84	48	54	63
6	211	186	127	39	48	51
12	271	245	139	19	21	26
15	298	269	151	7.9	11.2	17
18	310	261	164	5.7	8.3	15
24	289	254	168	2.9	4.9	14.06

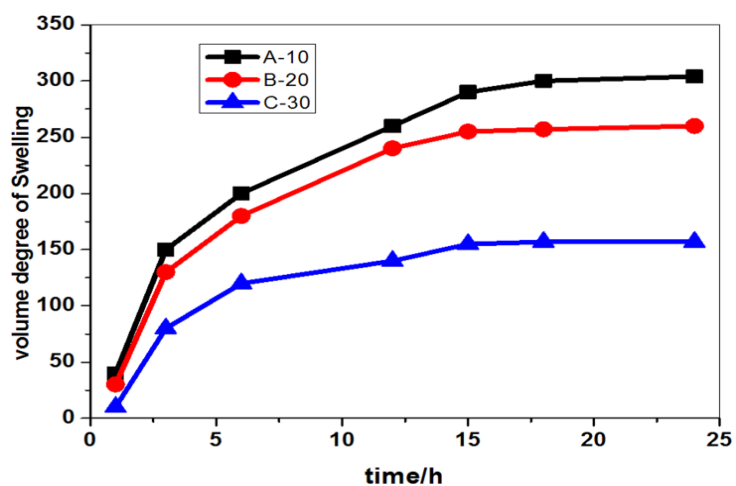


Fig. 5. The volume degree of swelling with time in hours

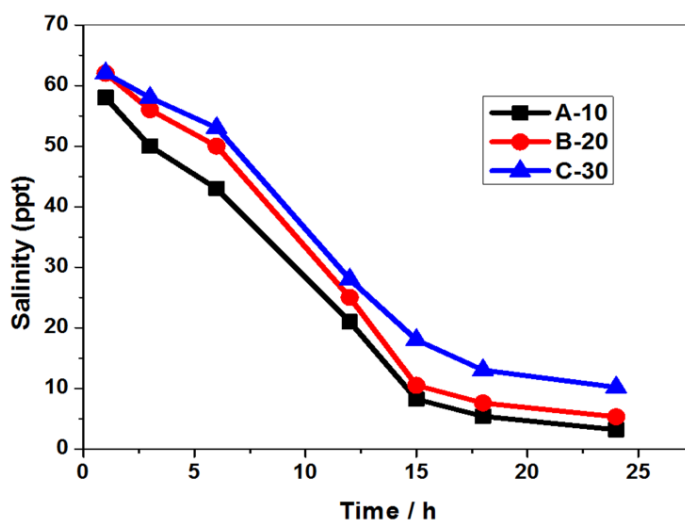


Fig. 6. The salinity (ppt) with time in hours

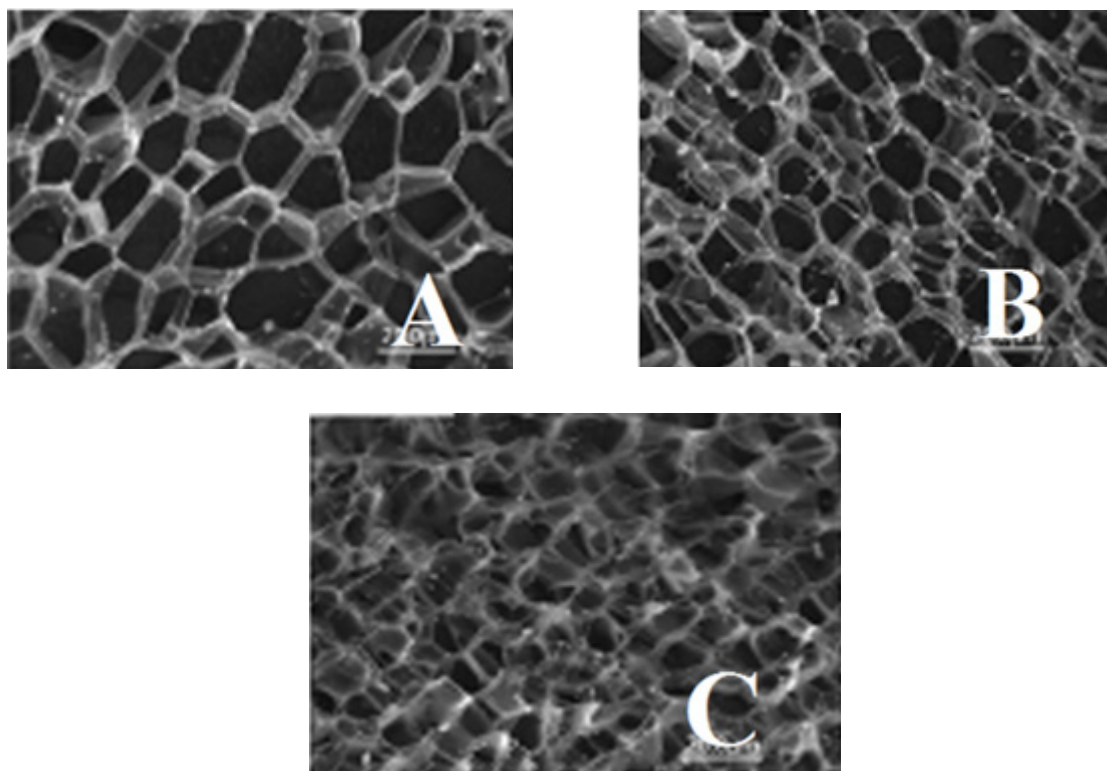


Fig. 7. SEM of hydrogels at 1000x magnification

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