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Softening of seawater and desalination brines using grafted polysaccharide hydrogels

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ABSTRACT

This paper investigates the potential of using polysaccharide hydrogels as softeners for saline solutions of seawater and reverse osmosis desalination brine. Grafting of acrylamide onto alginate and chitosan was conducted using microwave (MW) and ultraviolet (UV) irradiation techniques. The produced hydrogels: alginate (Alg-UV and Alg-MW) and chitosan (Ch-UV and Ch-MW) were characterized using X-ray diffraction and scanning electron microscopy. Hydrogel products were tested for their swelling behavior in distilled water and saline solutions, and their calcium and magnesium adsorption capacities in the pre-swollen and dry forms were measured in saline solutions. Swelling in distilled water was found to exceed that in saline solutions by 16.7–21-fold. Maximum attained swelling ratios in distilled water were 168 and 173 g/g for Alg-UV and Ch-MW grafted acrylamide hydrogels, respectively. Dry hydrogels had relative selectivity toward calcium adsorption in seawater and magnesium adsorption in brine. Furthermore, pre-swollen hydrogel manifested favorable adsorption for calcium and magnesium when compared to dry hydrogel at the same adsorbate volume. For both dry and pre-swollen hydrogels, maximum calcium adsorption capacities were 54 and 34 mg/g from seawater using Alg-MW and UV-prepared alginate and chitosan hydrogels, respectively. Maximum magnesium adsorption capacities from brine were 280 and 316 mg/g using dry alginate and chitosan hydrogels, respectively, prepared by MW technique. Magnesium adsorption capacities of the prepared hydrogels in brine were higher than those of tested commercial resins. It is concluded that alginate- and chitosan-grafted acrylamide hydrogels are promising softeners for saline solutions.

Keywords: Softening; Seawater; Brine; Hydrogel; Polysaccharide; Salt recovery

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1. Introduction

Attention has been recently drawn to recover valuable metals from seawater as well as reverse osmosis (RO) brine taking advantage of the high metal concentration present in brine, which when recovered can provide economic and environmental benefits. The most widely applied processes for removal or concentration of heavy metals from wastewater or saline solutions include: precipitation, evaporation, solvent extraction, coagulation, membrane separation, adsorption, and ion-exchange treatment [1–3]. Adsorption could be a promising process if the proper adsorbent was selected. Polymeric adsorbents are more effective due to their structure, cost effectiveness, ease of handling, reusability, and chemical and mechanical strength [4,5]. Separation and concentration of Ca and Mg from seawater and RO brine is important from the economic point of view. Muraviev et al. studied Ca and Mg separation from natural and seawater using carboxylic ion-exchange resins of acrylic and methacrylic types, and were able to achieve a separation factor of Ca/Mg (2.8–3.5) [6], while Yua et al. investigated the removal of Ca and Mg from potassium chromate wastewater using Amberlite IRC 748 and obtained adsorption capacities of 53 and 28 mg/g, respectively [7].

Nowadays, there is a growing interest in hydrogels due to their wide range of applications in the areas of biotechnology, water purification technologies, and metal ion recovery from water systems [8]. They are capable of undergoing volume phase transition in response to change in external parameters such as pH, temperature, and ionic strength [9]. These polymers separate metal ions by binding via adsorption, chelation, and ion-exchange processes [10,11]. Various copolymers have been synthesized by graft copolymerization of vinyl monomers onto natural polysaccharides using conventional heating, microwave (MW)-assisted or ultraviolet (UV) irradiation techniques in order to produce new hybrid polymer materials with desired properties [12–14].

Among all polysaccharides, chitosan and alginate were the most reported for metal sorption [15–17]. Several workers prepared synthetic hydrogels and investigated their potential for the removal of heavy metal ions and hardness from industrial effluents. Poly(N-vinyl-2-pyrrolidone), poly(N-vinyl-2-pyrrolidone/acrylic acid), acrylamide–maleic acid, poly(acrylamide-co-sodium methacrylate), and poly acrylic acid hydrogels were used for the removal of Zn, Pb, Cu, Zn, Mn, Fe, and Cd [18–20]. High adsorption capacities were achieved for some metals onto various copolymers such as 310 mg Ni/g chitosan-g-polyacrylic acid [16], 588 mg Cr/g polyacrylamide–guar gum graft copolymer hydrogel [21], and 190 mg Cu/g poly amidoxime chelating resin [22]. Saeed et al. studied the removal of up to 400 mg/l of each of the Ca and Mg hardness from synthetic solutions via adsorption of metal ions onto commercial polyacrylic acid hydrogel beads. The maximum attained adsorption capacities were 171.2 and 193.6 mg/g for Ca and Mg ions, respectively [23]. In a different study, adsorption of Ca and Mg metal ions separated from synthetic aqueous chloride solutions (100 mg/l) using chitosan-alginate membrane were 80 and 41 mg/g, respectively [17].

Scarce data is available on saline water softening using hydrogels. Therefore, this paper is concerned with the assessment of the adsorptive capacity of some chitosan and alginate acrylamide hydrogels regarding their potential for softening of seawater and RO desalination brine. This study should potentially open a window of opportunities for new hydrogel applications in the field of desalination and recovery of salts from seawater and RO brines.

2. Materials and methods

2.1. Materials

Chitosan with medium molecular weight (Sigma-Aldrich), alginic acid sodium salt (Routh, Germany), and acrylamide (Baker Chemical Co., USA) were used for hydrogel preparation. Potassium persulfate (KPS) (Merck, Germany) and methylene-bis-acrylamide (MBA) (Fluka, Germany) were used as initiator and cross-linker, respectively. The commercial resins Amberlite (IRC 120 H and 252 H) and DOWEX (50 WX2 (Na and H) and Marathon-C Na) were purchased from, Fluka, Sigma-Aldrich, and Dow Chemicals, respectively. The adsorption performance of these resins in saline solutions was tested against the prepared hydrogels.

Different saline solutions were investigated; natural seawater samples from the Mediterranean Sea (SW) and RO brine (B) samples from a desalination plant located in Egypt on the Red Sea. Chemical and physical characteristics of natural seawater and RO desalination brine are presented in Table 1 [24].

2.2. Methods

2.2.1. Preparation of hydrogels

Alginate and chitosan hydrogels were prepared by following the procedure of El-Sayed et al. [12] by applying higher molar ratios of chitosan/acrylamide and alginate/acrylamide of (1:4). Hydrogel samples were prepared through MW or UV techniques using a domestic MW apparatus with a temperature control

Table 1
Chemical and physical characteristics of Mediterranean seawater and RO brine

Parameter	Sea water Mediterranean (SW)	RO brine Red Sea (B)
Ca^{2+}, mg/l	400	690
Mg^{2+}, mg/l	1,460	2,600
Na^{+}, mg/l	11,000	24,000
Cl^{-} , mg/l	20,000	40,000
SO_4^{2-}, mg/l	2,700	5,400
K^{+}, mg/l	500	800
CO_3^{2-}, mg/l	20	43
HCO_3^{-}, mg/l	90	146
Alkalinity, mg/l	110	190
TDS, mg/l	36,320	73,870
Conductivity, µs	57,500	108,700
pH	7.6	7.87

unit (DAEWOO Electronics KOR-1A 6A, Korea) and a UV irradiation system comprised of a wooden box containing six UV lamps (15 W each) with a wavelength of 254 nm. The preparation steps are summarized as follows: (1) dissolution of chitosan or alginate followed by grafting of acrylamide onto chitosan or alginate solutions with the addition of KPS and MBA using MW or UV irradiation technique, (2) cooling the reaction product to room temperature, (3) adjusting the pH of the grafted hydrogels to pH 8 and removing the homopolymers using 70% ethanol, and (4) filtration, double washing with fresh ethanol, hydrolysis, and finally drying of the product at 70˚C [12]. Four hydrogel samples will thus be studied; Alg-MW, Alg-UV, Ch-MW, and Ch-UV.

2.2.2. Swelling studies

Swelling ratio (SWR) is generally used to describe the swelling behavior. Swelling characteristics of the prepared hydrogels have been conducted in distilled water (DW) and saline solutions (seawater and RO brine). First, the four prepared hydrogel samples were sieved to the desired particle size range (150–425 µm). Swelling was then performed by soaking 0.5 g of the prepared dry hydrogel in distilled water or saline solution for 24 h. Effect of salinity was studied by means of diluting the RO brine sample with DW by up to 16-fold, giving salinities ranging from 73,870 to 4,562 mg/l. Effect of time, on the other hand, was investigated by soaking Ch-MW hydrogel samples for 15 min to 48 h at room temperature. The swollen samples were allowed to drain using a plastic strainer for 5 min and were then weighed. SWR was calculated using the following equation [12].

$$\mathrm{SWR(g/g)} = \frac{W_s - W_d}{W_d} \tag{1}$$

where W_s and W_d are the weights of the swelled and dry hydrogel samples, respectively. SWR was calculated as grams of absorbed water per grams of dry hydrogel (g/g).

2.2.3. Adsorption studies

Metal ions adsorption capacities were measured by batch-mode technique at normal pH of the saline solutions (7.6–7.9). Adsorption was performed on dry or pre-swollen hydrogels in distilled water. Commercial resins have also been tested for comparison.

About 0.5 g of dry or pre-swollen hydrogels or commercial adsorbents with particle size range of 150–600 µm was added to a specific volume of saline solution, at the pre-mentioned pH range, in appropriate flasks. The flasks were sealed and constantly shaken using a water bath shaker (Julabo, SW-20C) with a constant agitation rate (150 rpm) and at room temperature for 24 h. The supernatant was decanted by filtration technique using a Whatman filter paper no. 4. The liquid supernatant was then analyzed to determine the equilibrium concentration of Ca and Mg in solution. The adsorption capacity (Q) was calculated by mass balance using the following equation [18]:

$$Q = \frac{C_o - C_e}{m} \times V \tag{2}$$

where Q is the amount of metal ions adsorbed in (mg/g of dry adsorbent), C_o and C_e are the initial and equilibrium ion concentrations (mg/l), respectively; V is the volume of metal ions solution used (l), and m is the weight of dry adsorbent (g).

2.2.4. Characterization and analysis

The prepared hydrogel samples were analyzed via X-ray diffraction (XRD) using a Philips XRD equipment PW/1710 with Monochrom TOR, Cu-radiation at 40 kV 35 mA, and scanning speed 0.02˚/s.

The surface morphology of the prepared hydrogel samples was characterized using a scanning electron microscope (SEM) (model JEOL: JXA-840A) of magnification power 50,000X and having an electron probe micro analyzer coupled with energy-dispersive X-ray spectrometer. Prior to measurement, hydrogel samples were hydrated with de-ionized water or tap water, and were frozen in liquid nitrogen overnight and then, finally, the dried samples were coated with 40 nm gold. Concentrations of Ca and Mg ions in saline solutions were measured by means of an atomic absorption flame spectrometer (GBC Avanta).

3. Results and discussion

3.1. SEM characterization of the prepared hydrogels

SEM images for the grafted alginate and chitosan hydrogel samples using both MW and UV irradiation techniques are shown in Figs. 1(a), (b) and 2(a), (b), respectively. The two grafted alginate samples show a rather smoother and more porous surface when compared to raw alginate which appears spherical in shape [12]. As for the grafted chitosan hydrogel samples in Fig. 2(a) and (b), it can be observed that the surface is different from raw chitosan which possesses a flaky nature with irregular shape and porous surface [12]. The flaky nature of chitosan is lost after grafting which seems to have taken place homogeneously.

3.2. XRD characterization of the prepared hydrogels

XRD spectra of the grafted alginate and chitosan hydrogel samples prepared using MW and UV graft-

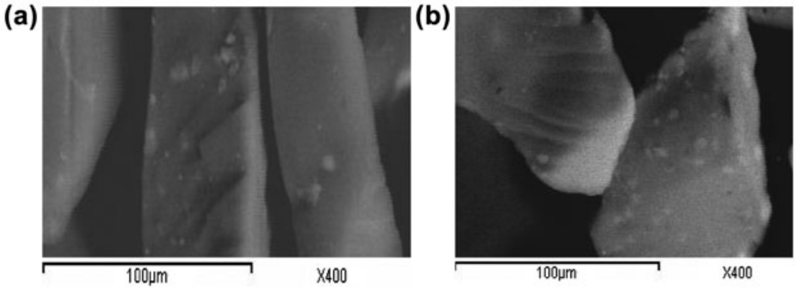

Fig. 1. SEM images for grafted alginate hydrogels using (a) UV and (b) MW techniques.

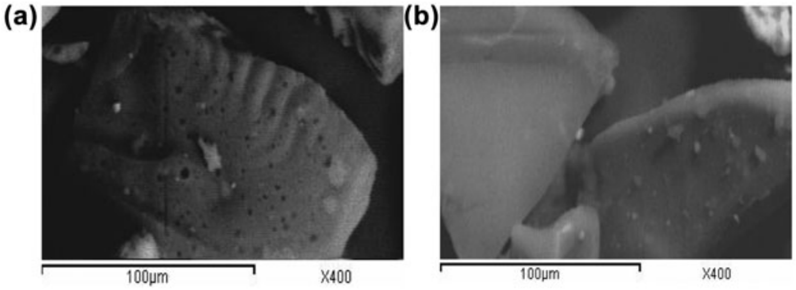

Fig. 2. SEM images for grafted chitosan hydrogels using (a) UV and (b) MW techniques.

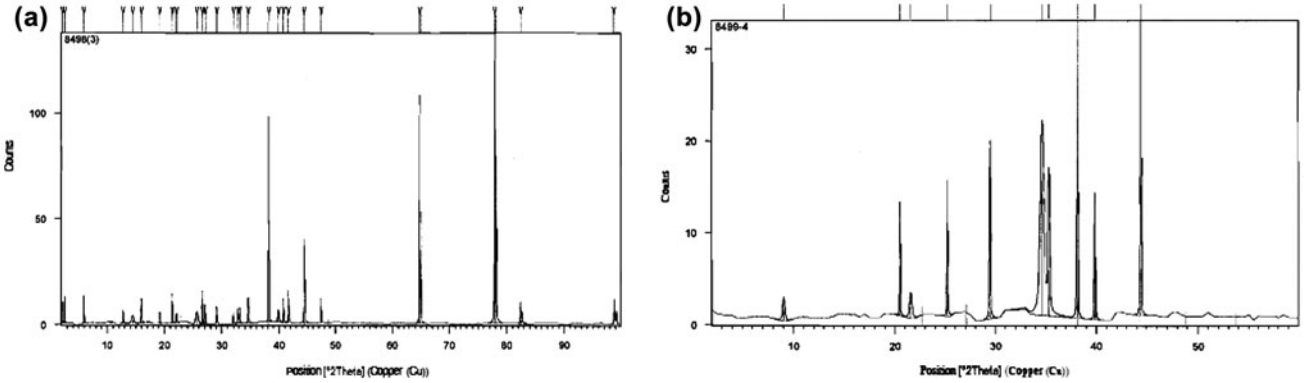

Fig. 3. XRD spectra for grafted alginate hydrogels using (a) UV and (b) MW techniques.

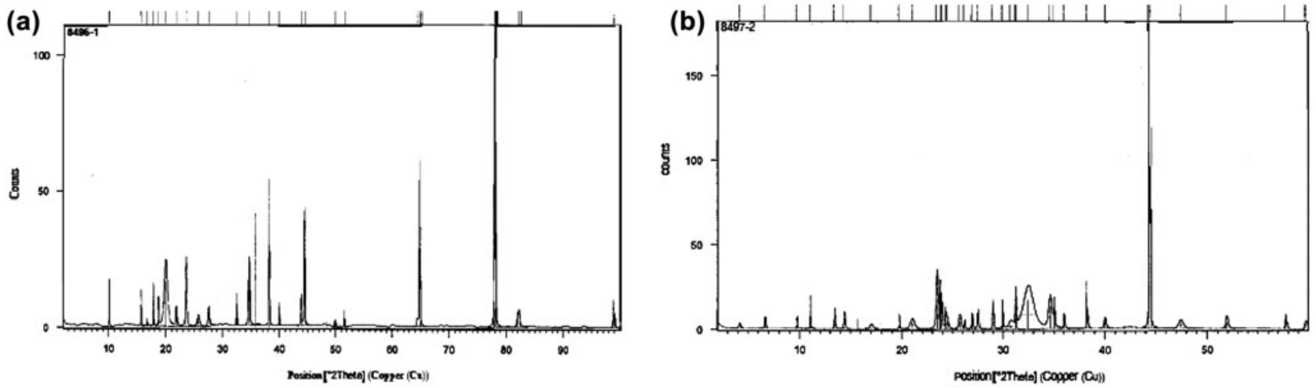

Fig. 4. XRD spectra for grafted chitosan hydrogels using (a) UV and (b) MW techniques.

ing techniques are presented in Figs. 3(a), (b) and 4(a), (b), respectively. XRD analysis for the grafted alginate hydrogel indicates crystallinity peaks at 2θ from 23° to 26° and from 32° to 36° due to presence of polyacrylamide grafted at alginate backbone, while no such peaks are visible in the XRD pattern of raw alginate [12,13] which exhibits very small crystallinity. In addition, XRD spectra of grafted chitosan hydrogel samples show many crystalline areas between 2θ from 19° to 22° and from 34° to 36°, which may be attributed to grafting of polyacrylamide onto chitosan backbone; again, no such peaks are visible in the XRD spectra of raw chitosan, and the crystalline peaks are reduced relative to the peaks present in raw chitosan [12,13].

3.3. Swelling characteristics

Figs. 5 and 6 illustrate the swelling properties of the prepared hydrogels in (DW) and saline solutions (seawater and RO brine), respectively. As shown in Fig. 5, comparable SWR values in DW (171.5 and 173 g/g) are observed for chitosan using MW and UV techniques, respectively. These values are higher than their counterparts pertaining to alginate. Comparing SWR values in DW for the different employed hydrogels to those in saline solutions, it can be deduced that the former is higher by 17–21-fold. The highest SWR obtained for hydrogels soaked in saline solutions is 10.36 g/g and this pertains to Ch-MW. This result is confirmed by the data in Fig. 7 in which SWR decreased by three-fold with increasing TDS by 16-fold (from 4,617 to 73,870 mg/l).

To study the effect of time on swelling characteristics, samples of Ch-MW hydrogel were soaked in RO brine for different time periods ranging from 15 min to 2 d and their SWR values were measured as shown in Fig. 8. Data revealed sharp increase in SWR up to 12 h followed by slow increase after 24 h.

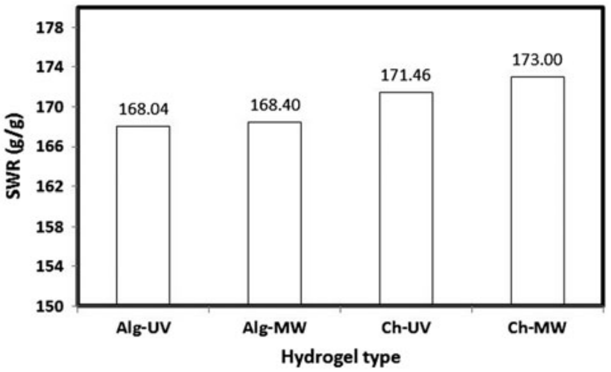

Fig. 5. Swelling ratios for hydrogels soaked in DW for 24 h at a concentration of 0.5 g/250 ml.

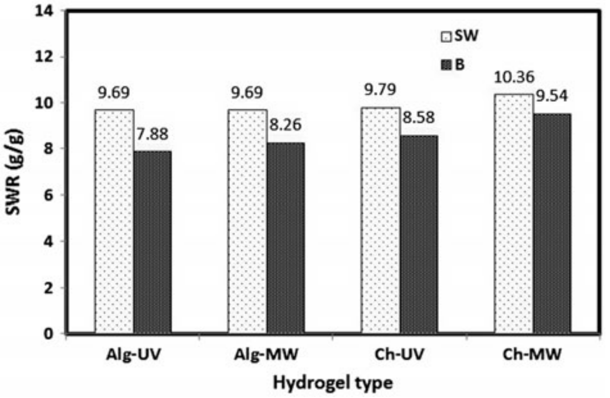

Fig. 6. Swelling ratios for hydrogels soaked in saline solutions for 24 h at a concentration of 0.5 g/250 ml.

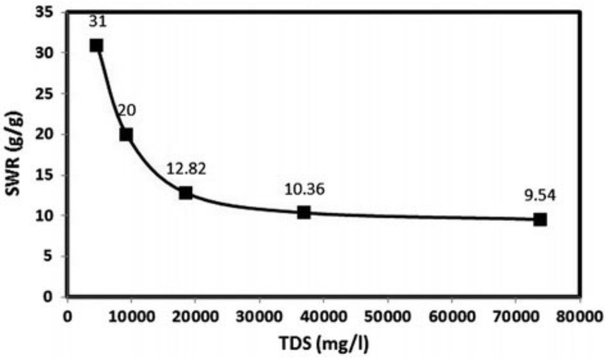

Fig. 7. Effect of salinity on swelling of Ch-MW soaked in brine for 24 h at a concentration of 0.5 g/250 ml.

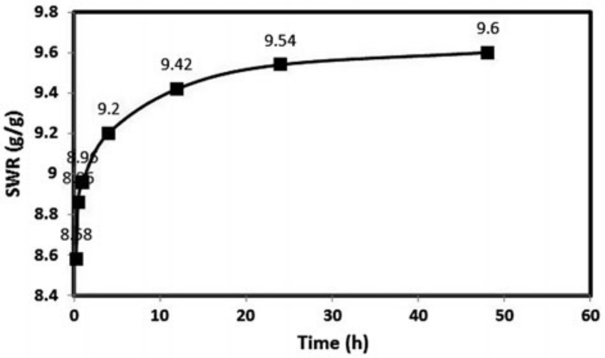

Fig. 8. Effect of time on swelling of Ch-MW soaked in brine for 24 h at a concentration of 0.5 g/250 ml.

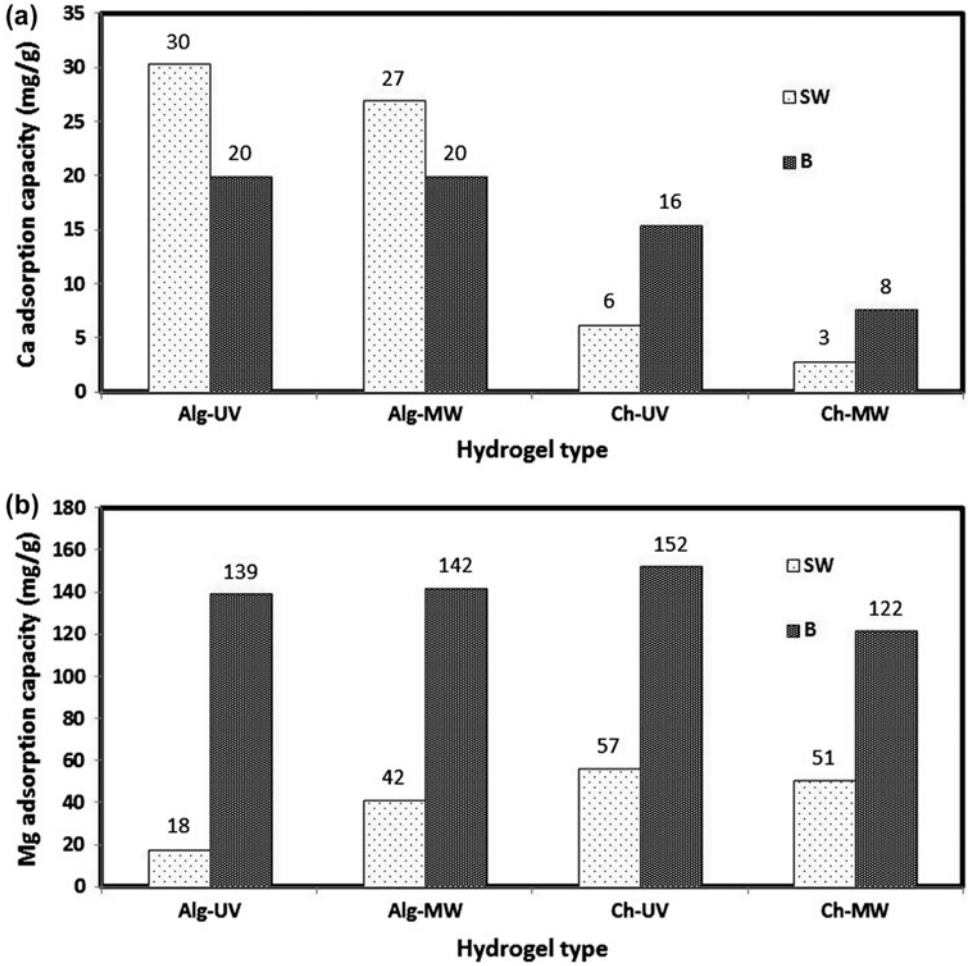

Fig. 9. Adsorption capacities of Ca (a) and Mg (b) from saline solutions using pre-swollen hydrogels soaked for 24 h at a concentration of 0.5 g/100 ml.

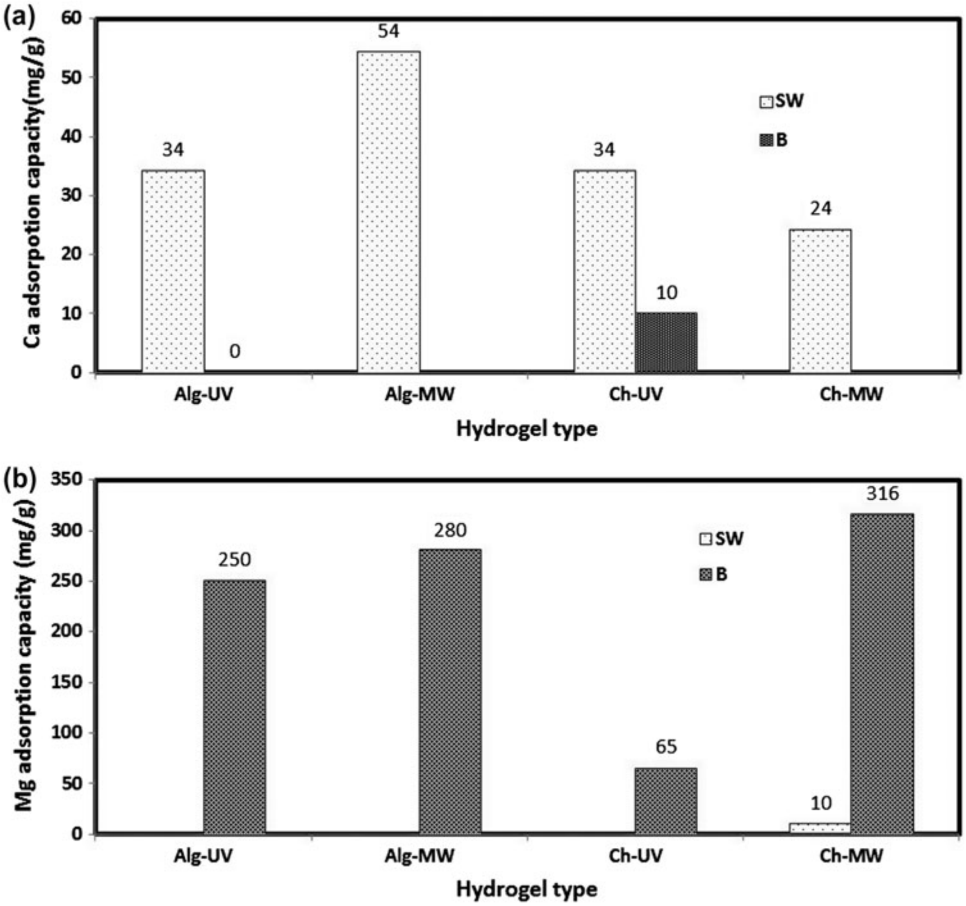

Fig. 10. Adsorption capacities of Ca (a) and Mg (b) from saline solutions using dry hydrogels soaked for 24 h at a concentration of 0.5 g/250 ml.

3.4. *Adsorption capacities of the prepared hydrogels*

3.4.1. *Pre-swollen hydrogels*

Fig. 9(a) and (b) presents the respective adsorption capacities (*Q*) of the pre-swollen hydrogels for Ca and Mg in different saline solutions. As shown in Fig. 9(a), maximum calcium adsorption in seawater (30 mg/g) is manifested by Alg-UV hydrogel, whereas both UV and MW alginate hydrogels show the highest calcium adsorption in RO brine (20 mg/g). The swollen hydrogels revealed relative selectivity in favor of magnesium in adsorption from seawater and brine where the highest adsorption capacities for magnesium were 57 and 152 mg/g as manifested by Ch-UV hydrogel in seawater and brine, respectively.

3.4.2. *Dry hydrogels*

Fig. 10(a) and (b) shows calcium and magnesium adsorption capacities using dry hydrogel samples. Calcium adsorption selectivity from seawater using the different hydrogel types was in the following descending order; Alg-MW, Alg-UV, Ch-UV, and Ch-MW, where the adsorption capacities were 54, 34, 34, and 24 mg/g, respectively. Very low calcium adsorption capacities were observed for the different hydrogels in brine, except for Ch-UV which adsorbed 10 m/g of calcium. As for magnesium, adsorption capacities from brine were promising. Comparable adsorption capacities of 316 and 280 mg/g were exhibited by Ch-MW and Alg-MW hydrogels, respectively.

3.4.3. *Effect of hydrogel pre-swelling on adsorption*

The pre-mentioned adsorption results revealed that the use of the prepared hydrogel samples for calcium and magnesium adsorption is affected by the wetting (pre-swelling) state, adsorbate volume, and salinity. Dry hydrogel is expected to manifest initial lower

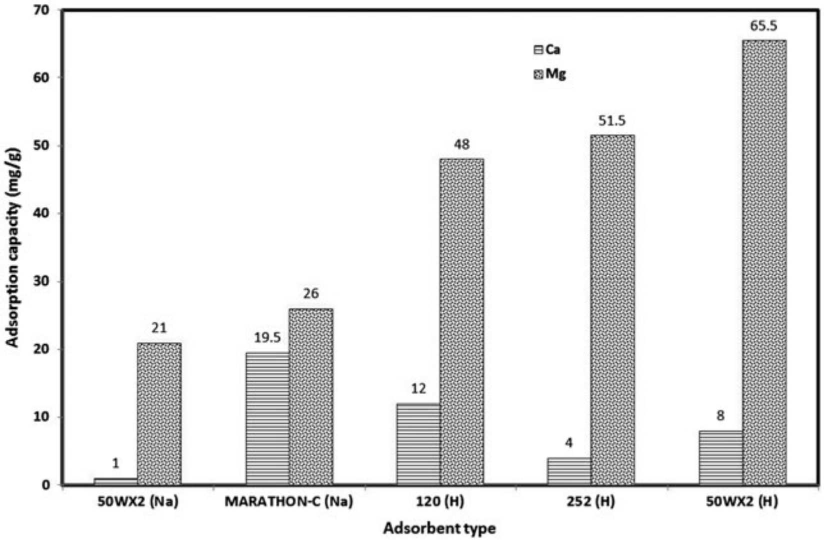

Fig. 11. Adsorption capacities of Ca and Mg from RO brine using different commercial resins soaked for 24 h at a concentration of 0.5 g/250 ml.

adsorbency when compared to the pre-swollen hydrogel since the active functional groups are totally or partially exposed to the adsorbate in the later case. This is clear from calcium adsorption capacities which recorded 20 and 2 mg/g for pre-swollen Alg-MW and dry Alg-MW hydrogels, respectively, from RO brine under the same adsorbate volume (100 ml). The corresponding magnesium adsorption capacities were 142 and 40 mg/g, respectively.

3.5. Comparative performance of commercial resins

Comparative assessment of the adsorption capacities of calcium and magnesium from RO desalination brine using some commercial resins is depicted in Fig. 11. It is shown that the maximum obtained calcium adsorption capacity was 19.5 mg/g using Dowex Marathon-C(Na), while that of magnesium was 65.5 mg/g using Dowex 50WX2 (H). These values are much lower than those obtained using the prepared hydrogel samples. The corresponding values for calcium and magnesium were 54 and 280 mg/g, respectively, using Alg-MW hydrogel as previously shown in Fig. 10.

4. Conclusions

Polysaccharide hydrogels comprising acrylamide-grafted alginate and chitosan have been prepared and tested for their swelling characteristics as well as their adsorption capacities for calcium and magnesium from saline solutions. Exploratory investigations revealed a lower swelling of the hydrogels in saline solutions when compared to distilled water by about 16–21-fold. Maximum adsorption capacities of calcium from seawater were 30 and 54 mg/g for pre-swollen Alg-UV and dry Alg-MW hydrogels, respectively. The corresponding values for RO brine were 20 mg/g for Alg-UV and Alg-MW and 10 mg/g for Ch-UV. Maximum capacities for magnesium adsorption were 57 and 152 mg/g from seawater and RO brine, respectively, by pre-swollen Ch-UV hydrogels. Their counterparts for dry hydrogels were 10 and 316 mg/g for Ch-MW. Furthermore, pre-swollen hydrogels manifested favorable adsorption of calcium and magnesium when compared to dry hydrogels at the same adsorbate volume, where adsorption capacity of magnesium from RO brine was about 142 and 40 mg/g in the pre-swollen and dry Alg-MW hydrogel forms, respectively. This could be attributed to enhanced swelling of the hydrogel as a result of the increase in adsorption loading (increasing volume of the solution/mass of adsorbent), which would consequently allow for exposure of more functional groups to the adsorbate ions.

The results of the present work tend to support the importance of high polymeric loading of the adsorbate for specified adsorbent weight. Comparing the exploratory values of the prepared hydrogels refers to competitiveness and the apparent advantages of MW-prepared hydrogels when compared to some commercial resins under the adopted experimental conditions.

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