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Full-Polysaccharide Superabsorbent Hydrogels Based on Carrageenan and Sodium Alginate

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Abstract: A new full-polysaccharide superabsorbent hydrogel was synthesized *via* chemical crosslinking of carrageenan (CG) and sodium alginate (Alg) using epichlorohydrine (ECH) as a cross-linker. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR spectroscopy. Scanning electron microscopy was also carried out to study the surface morphology of the hydrogel. The influence of ECH concentration, Alg/CG weight ratio and stirring speed as well as reaction time and temperature on water and saline (0.9 wt% NaCl) absorbency of the hydrogels were systematically investigated. Their swelling behavior was also measured gravimetrically in the *p*Hs ranging from 1 to 10. The hydrogels exhibited a *p*H-responsiveness character so that a swelling-deswelling pulsatile behavior was recorded at *p*Hs 2 and 8.

Key words: Hydrogel · Superabsorbent · Sodium alginate · Carrageenan · Swelling

INTRODUCTION

In recent years, much interest has been shown in the development of synthesis of natural-based superabsorbent hydrogels [1-8]. These biopolymer materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, saline or physiological solutions [9]. These crosslinked polymers have excellent characteristics, such as swelling, mechanical, permeation, surface and optical properties. Because of such unique properties, superabsorbent hydrogels are widely used in many fields, such as agricultural and horticultural, disposable diapers, feminine napkins, pharmaceuticals and medical applications [10-14]. Hence, syntheses and investigation of specific and new superabsorbent hydrogels with high absorbency, mechanical strength and initial absorption rate, has been the goal of several research groups in the past decades. A number of such biomaterials have been prepared by free radical graft copolymerization of vinyl monomers onto polysaccharides.

In some cases, full-polysaccharide-based hydrogels have been prepared from a single polysaccharide (e.g. carboxymethylcellulose sodium salt (CMC) [15] and sodium alginate [16-17], or a binary mixture (e.g. sodium alginate-chitosan) [18].

Alginate is a collective term for naturally derived polysaccharides, *i.e.* alginic acid, its salts and suitable substitutions for its derivatives. Alginates are composed of (1 4)-linked β-D-mannuronic acid and α-L-guluronic acid in a non-regular, block-wise pattern along the linear chain, which varied in amount and sequential distribution along the polymer chain depending principally upon the seaweed species [19, 20]. These polysaccharides are widely used in various applications such as chelating and thickening agents, emulsifiers, stabilizers, encapsulation, swelling and suspending agents, or used to form gels, films and membranes [21, 22].

Carrageenan is a collective term for linear sulfated polysaccharides prepared by alkaline extraction from red seaweeds. The types of carrageenans differ only in the position and number of ester sulfate groups which determine their physico-chemical properties, e.g. viscosity and gelation characteristics.

The present paper deals with the synthesis and investigation of swelling behavior of CG/CMC hydrogel in the presence of epichlorohydrine as a cross-linker in an aqueous medium.

MATERIALS AND METHODS

Hydrogel Preparation: The polysaccharides, *kappa-c*arrageenan (κC, from Condinson Co., Denmark) and

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sodium alginate (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Epichlorohydrine (ECH) was used as a crosslinking agent without any pretreatment. Sodium chloride and methanol as reagent grade were used without further purification. Distilled water was employed for the hydrogel preparation and swelling measurements.

Alg (0.0-2.0 g) and CG (0.0-2.0 g) were dissolved in 50 mL distilled water in a three-neck reactor equipped with mechanical stirrer (three blade propeller type, 600 rpm) and a reflux condenser. The reactor was immersed in a thermostated water bath preset at desired temperature (50-90°C). After complete dissolution of the polysaccharides, a definite amount of ECH (0.2-3.5 mL) was added into the mixture. After a prescribed time (30-120 min), the obtained hydrogel was poured into methanol (200 mL) to dewater for 24 h. Then, the product was filtered and dried in an oven at 60°C to reach a constant weight. The product was stored away from moisture, heat and light.

Swelling Measurements: The "tea bag" method was used for the measurement of swelling capacity of the dried gels. The sample particle size was 40 to 60 mesh (250-350μm). The tea bag (*i.e.* a 100 mesh nylon screen) containing the powdered superabsorbent sample (0.2 ± 0.001 g) was immersed entirely in distilled water (200 mL), salt solution (100 mL), or in solution with desired *p*H (100 mL) for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrium swelling (*ES*) was calculated according to the following equation:

$$ES9g/g) = \frac{Weight\ of\ swollen\ gel - Weight\ of\ dried\ gel}{Weight\ of\ dried\ gel} \quad (1)$$

Physical Measurements: The FTIR spectra of the produced hydrogel and physical mixture of the polysaccharides, CMC and Alg, were recorded in the form of potassium bromide pellets using an AAB Bomem MB -100 FTIR spectrophotometer.

In this work, the morphology of the hydrogels was observed by a scanning electron microscope (SEM; Leo, 1455 VP) operating at an accelerating voltage of 20 kV. All samples were mounted on a copper stub and sputter-coated with gold to minimize charging.

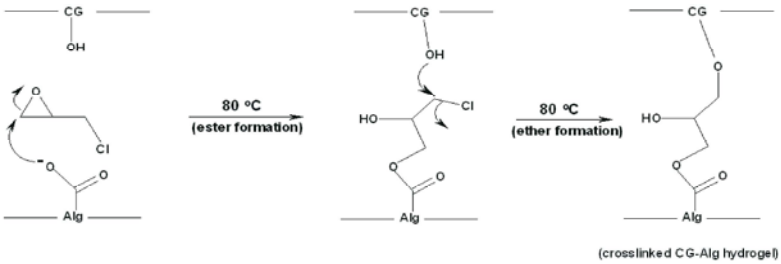
RESULTS AND DISCUSSION

Synthesis and Spectral Characterization: Scheme 1 shows a simple mechanism for chemically crosslinking of CG and Alg substrates in the presence of epichlorohydrine. According to the mechanism, under the neutral conditions (with a pH close to 7.0) of the reaction, carboxylate and hydroxyl groups of the both polysaccharides attack to either epoxide or CH_2Cl groups of ECH to form esteric linkages. These bonds can be confirmed by comparing the FTIR spectra of the Alg and CG mixture (Fig. 1a) and that of the crosslinked hydrogel synthesized (Fig. 1b). The bands observed at 841, 912, 1016 and 1220 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage and ester sulfate stretching of CG, respectively (Fig. 1a). The broad band at 3200-3400 cm^{-1} is due to stretching of $^{-1}$OH groups of CG and Alg (Fig. 1a and 1b). The additional bands at 1755 and 1062 cm^{-1} in the hydrogel spectra can be attributed to stretching modes of C=O and C^{-1}O bonds of the esteric groups, respectively.

One of the most important properties that must be considered is hydrogel microstructure morphologies. Fig. 2 shows the SEM image of the crosslinked Alg/CG hydrogel. This picture verifies that the herein synthesized polymer has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

Optimizing the Reaction Conditions

Effect of CG/Alg Weight Ratio: The swelling capacity in distilled water and 0.9 wt% NaCl solution as functions of CG/Alg weight percent was studied (Fig. 3). The maximum



Scheme 1: Proposed mechanistic pathway for the synthesis of crosslinked Alg/CG hydrogels in the presence of epichlorohydrine

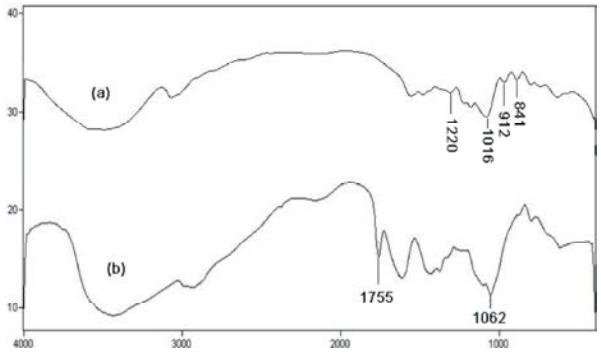


Fig. 1: FTIR spectra of the physical mixture of Alg and CG (a) and the crosslinked Alg/CG hydrogel (b)

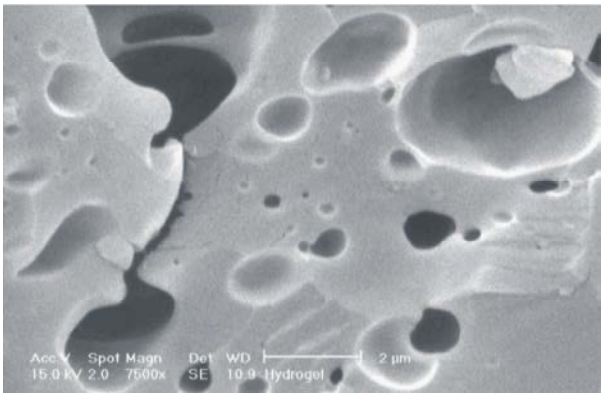


Fig. 2: SEM of the crosslinked Alg/CG hydrogel

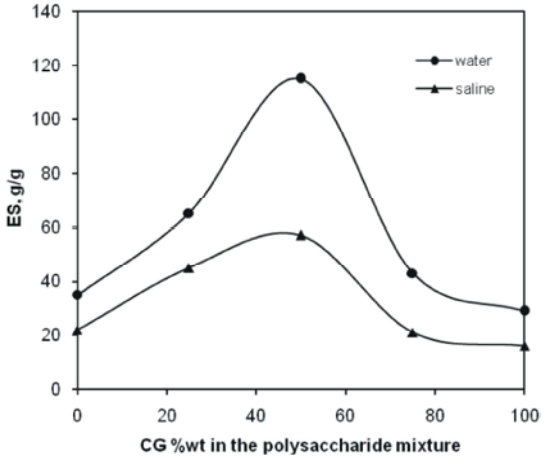


Fig. 3: Effect of CG content on swelling capacity

water and saline absorbencies (115 and 57 g/g, respectively) resulted in for 50% weight percent of CG/Alg. After this amount, the swelling capacity was decreased. This can be attributed to the increased viscosity of the reaction mixture with increasing of CG amount in the mixture, which hinders the movement of the reactants. This evidence was experimentally confirmed by the sol content values of the high CG hydrogel (*i.e.* 75% CG) comparing with that of the 50 % CG sample. The earlier was contained higher sol content (15 %) in comparison with the latter (sol content 4 %). In order to determine the sol content, the weighted powdered superabsorbent sample (0.50 g) was immersed in distilled water (200 mL) and allowed to swell for 24h at room temperature. Then, the filtered swollen hydrogel was dried in an oven at 60°C for 5h. The percent of sol content was measured by the difference between the initial and the final amount of hydrogel.

The swelling values of the hydrogels in saline solutions were decreased comparing to the values measured in deionized water. This well-known phenomenon commonly observed in the swelling of "ionic" hydrogels is often attributed to a "charge screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion, led to a decreased osmotic pressure difference between the hydrogel network and the external solution [23]. However, the swelling-loss in NaCl 0.9 wt% solution is not considerable and the hydrogels shown an "anti-salt" behavior. The reason for the behavior may be related to a small number of salt-sensitive carboxylate groups in these full-polysaccharide hydrogels comparing with those that are presence in the convenient fully synthetic superabsorbents. Also, carrageenan parts of the hydrogels contain lots of sulfate groups that can be dissociated in aqueous media more readily than the carboxylate groups of Alg part of hydrogel (in this regard, pKa of methane sulfonic acid, -2.0, may be compared with that of acetic acid, 4.8). Since the sulfate ions do not keep cations in their vicinity, the "charge screening effect" is not so effective. Thus, the resulting swelling loss is not appreciable.

The full-polysaccharide samples exhibit the lowest salt sensitivities. Meanwhile, the full-carrageenan hydrogel showed a higher swelling capacity comparing with the full-Alg hydrogel (Fig. 4). A similar conclusion is recently reported by Lim *et al*. [24] in the case of synthesis of sodium starch sulfate-g-polyacrylonitrile superabsorbent (SSS). They developed a method for synthesis of a superabsorbent with high water and saline absorbency. The maximum water and saline absorbencies of SSS were 1510 and 126.4 g/g, respectively, compared with 820 and 61.5 g/g for a hydrolyzed starch-g-polyacrylonitrile. They attributed the enhanced absorbency to increased charge density and ionization tendency brought about by the introduction of sulfate

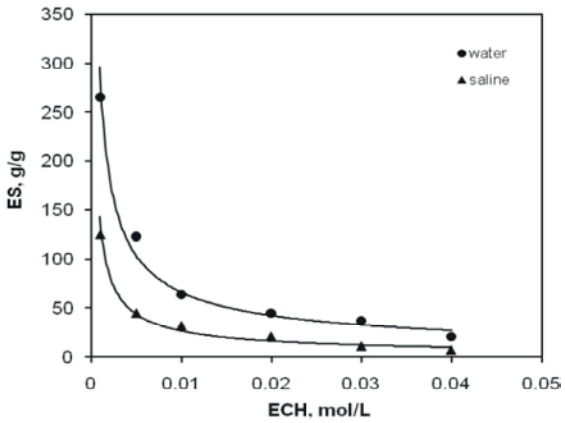


Fig. 4: Effect of ECH concentration on swelling capacity

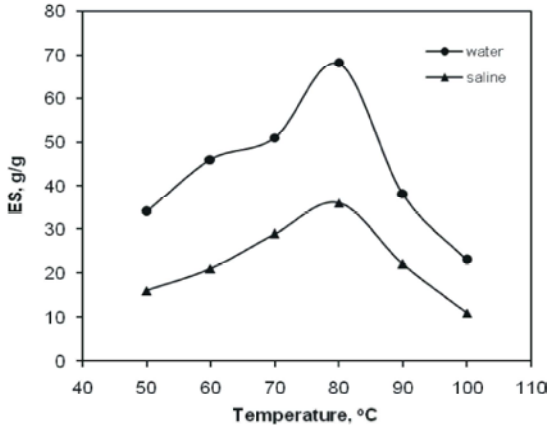


Fig. 5: Effect of reaction temperature on swelling capacity

anions, in addition to the carboxylic anion in SSS. In addition, Barbucci *et al*. [25] reported a sulfated carboxymethylcellulose hydrogel bearing considerable water absorbency. Therefore, the reason for high water and saline absorbency in our hydrogels certainly a result of the presence of sulfate groups in its CG parts.

It should be pointed out that the salt-sensitivity of a hydrogel means it's swelling-loss in salt solutions in comparsion to the swelling values in distilled water.

Effect of Cross-Linker Concentration: For studying the cross-linker concentration effect on absorbency, the amount of ECH was varied from 0.001 to 0.04 mol/L. Fig. 4 depicts the effect of epichlorohydrine (ECH) concentration on the swelling capacity of the hydrogels. As shown in the Fig. 4, the higher the cross-linker concentration, the lower water and saline absorbencies will be. This well-known relationship between the swelling ratio and concentration of the crosslinking agent is stated as Eq. (2):

$$Swelling\ capacity \cong k\,[ECH]^{-n} \quad (2)$$

Where k and n are constant for an individual hydrogel. Higher cross-linker concentration produces more crosslinked points in the polymeric chains and increases the crosslinking extent of the polymer network, which limits the swelling when it is brought into contact with the swelling medium. However, with epichlorohydrine concentrations lower than 0.001 mol/L, no hydrogel with good dimensional stability (swollen gel strength) was prepared. Therefore, maximum swelling capacity in distilled water (265 g/g) and saline solution (125 g/g) was achieved at 0.001 mol/L of epichlorohydrine.

Effect of Reaction Temperature: The effect of temperature on water absorbency was studied by varying temperature of the water bath from 50 to 100°C (Fig. 5). As it is obvious from the Fig., the temperature leading the hydrogel with highest absorbency (68 g/g) is around 80°C. More or less than this temperature give hydrogel with decreased swelling capacity. Increase in swelling values can be attributed to the rising of the epichlorohydrine diffusion rate into CG and Alg backbones, as well as the kinetic energy of the polysaccharide chains which led to lower soluble content of the produced hydrogel. As expected, the sol content of hydrogel A (15%, prepared at 50°C) was higher than that of the hydrogel B (7%, prepared at 80°C). This proves the higher reaction temperature results in higher reactant movement and effective collision. At the temperatures higher than 80°C, a possible "thermal crosslinking" of the polysaccharide backbones may act a major role to lead low-swelling hydrogels. In addition, the swelling loss may be related to the increasing of cross-linked bonding formation *via* completion of the ester and ether formations by further reaction of the possible mono-ester species with another polysaccharide chain (Scheme 1).

Effect of Reaction Time: Fig. 6 demonstrates the swelling and conversion variations in lieu of time of the crosslinking reaction. The data was also shown in Table 1. At the early minutes of the reaction, the conversion of the reaction is around 50%. It is gradually increased to about 70% after 50 min. Meanwhile, the swelling capacity of the hydrogel prepared after 10 min (*i.e.* 111 g/g) is appreciably decreased to 20-30 g/g in longer reaction time due to

Table 1: The values of conversion reaction percent and equilibrium swelling capacity in various reaction times

Reaction time	Equilibrium swelling (ES)	Conversion percent
10	111	51
30	47	63
50	31	71
70	21	83

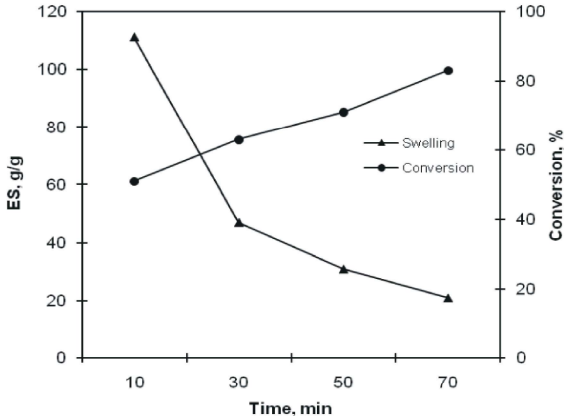


Fig. 6: Effect of reaction time on swelling capacity and conversion percent

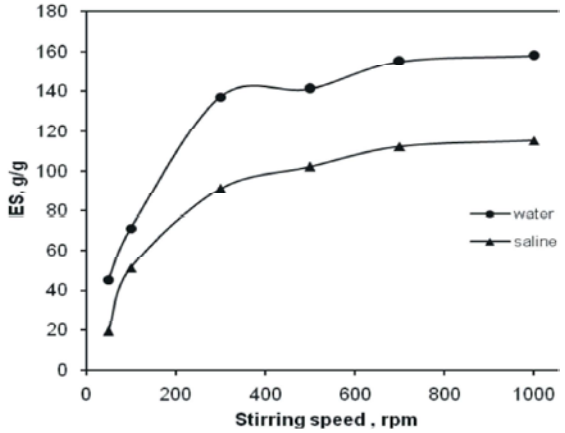


Fig. 7: Effect of mechanical stirrer speed on swelling capacity

enhancement of the crosslinking extent. No remarkable change of ES and conversion was observed in the case of longer time of the reaction.

Effect of Stirring Speed: The swelling behavior of hydrogel by varying the stirrer speed of sol solution in the 50 to 1000 rpm range has been studied (Figure 7). The water absorbency is considerably increased while the speed of the propeller-type stirrer from 50 to 300 rpm and then increased very gradually. The sudden swelling enhancement emphasizes on the remarkable effect of stirring efficiency on the final product properties. In such viscose heterogeneous media, effective stirring is required to achieve effective mixing and mass transfer. However, at high rpm values, shear forces may also act to degrade macromolecular chains leading to decreased molecular weight and subsequent loss of swelling. Therefore, at higher stirring rates, shear degradation neutralizes the enhancing effect of high speed of mixing.

Effect of pH Changing: To investigate the sensitivity of the hydrogels to pH, the equilibrium swelling (ultimate absorbency) of the 1:1 Alg/CG hydrogel was measured at various *p*Hs ranged from 1.0 to 10.0 (Fig. 8). No additional ions (through buffer solution) were added to medium for setting *p*H because absorbency of a superabsorbent is strongly affected by ionic strength. Therefore, stock NaOH (*p*H 10.0) and HCl (*p*H 1.0) solutions were diluted with distilled water to reach desired basic and acidic *p*Hs, respectively. The pK_a of sodium alginate and CG is around 3.3 [26]. Since the pK_a of the weak polyacids is about 3.0, their ionization occurs above these values and consequently swelling capacity is increased. According to Fig. 10, the high swelling capacity of the hydrogel at *p*H 6 can be attributed to high repulsion of COO^- groups. At very acidic conditions (*p*H≤3), most of carboxylate and sulfate groups are protonated and the low swelling values of hydrogels can be attributed to the presence of non-ionic hydrophilic COOH, SO_3H and -OH groups in the CG and Alg backbones. With further pH increase (*p*H>6), the swelling capacity is decreased. Again, the swelling loss is due to the counter ions, *i.e.* Na^+, that shield the charge of the carboxylate anions and prevents efficient anion-anion repulsion. As a result, a remarkable decrease in equilibrium swelling is observed.

pH-Responsiveness Behavior of the Hydrogel: Since the hydrogels show different swelling behaviors at various *p*Hs, their *p*H-reversibility was investigated in solutions buffered at *p*Hs 2.0 and 7.0 (Fig. 9). The Fig. shows a stepwise reproducible swelling changing of the hydrogel at 25°C with alternating *p*H between 2.0 and 7.0. At *p*H 7.0, the hydrogel swells up to 50 $g.g^{-1}$ due to anion^{-1}anion repulsive electrostatic forces, while at *p*H 2.0, it shrinks during few minutes due to protonation of carboxylate and sulfate groups. This sharp swelling-deswelling behavior of the hydrogels makes them suitable candidates for controlled drug delivery systems. This should be pointed out that this behavior must be investigated in two *p*Hs points in which hydrogels have maximum and minimum swelling capacity.

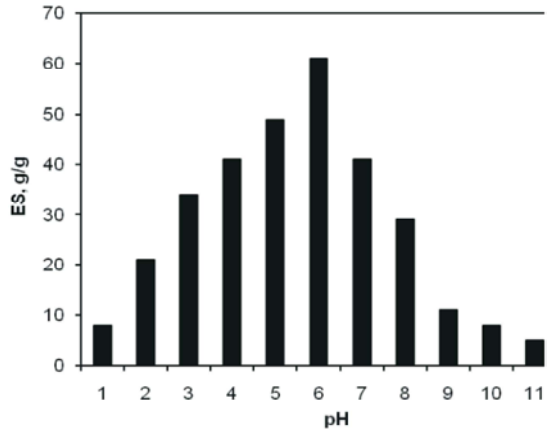


Fig. 8: Effect of *p*H of solutions on the swelling capacity of Alg/CG hydrogel

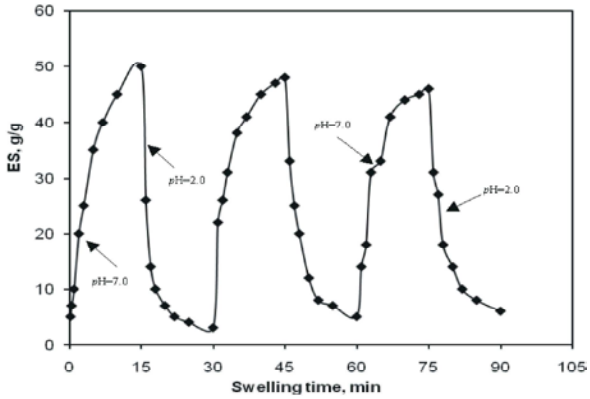


Fig. 9: On-off switching behavior as reversible pulsatile swelling (*p*H 7.0) and deswelling (*p*H 2.0) of the hydrogel

CONCLUSION

This article proposes a novel method to prepare full-polysaccharide hydrogels from epichlorohydrine crosslinking of carrageenan and sodium alginate. In this facile one-step method, no petrochemical monomer is needed. So, the process is not involved with several problems originated from a monomer (e.g., the monomer toxicity and the residual monomer). Also, very small amount of a petrochemical starting material, i.e. ECH, is employed. In addition, biopolymeric convenient materials, i.e. carrageenan and sodium alginate, are used to yield super-swelling biomaterials with potential bioactivity and biocompatibility.

The swelling of hydrogels in solutions with various *p*Hs exhibited a high sensitivity to *p*H. Ionic repulsion between charged groups incorporated in the gel matrix by an external *p*H modulation could be assumed as the main driving force responsible for such abrupt swelling changes. Furthermore, the reversible swelling-deswelling behavior in solutions with acidic and basic pH makes the hydrogels a suitable candidate for controlled drug delivery systems. Hence, as an extension of this work, the full-polysaccharide hydrogel is being subjected to further modification to prepare drug delivery carriers.

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