



ORIGINAL ARTICLE

Investigation Swelling Behavior of a Novel Alginate-based Composite Hydrogel in various Salinity solutions

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ABSTRACT

In this paper, swelling behavior of a novel alginate-based composite hydrogel in various salt solutions was investigated. Absorbency in aqueous chloride salt solutions indicated that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. The swelling of superabsorbing hydrogels was also measured in solutions with pH ranged from 1 to 13. The synthesized hydrogel exhibited a pH-responsiveness character so that a swelling-collapsing pulsatile behavior was recorded at pHs 2 and 8. This behavior makes the synthesized hydrogels as an excellent candidate for controlled delivery of bioactive agents.

Key words: alginate; composite hydrogels; salinity; swelling.

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INTRODUCTION

Synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world. These materials are defined as hydrophilic, three-dimensional networks with ability to absorb large values of water, saline solution, or physiological fluids. The absorbed fluids are hardly removable even under some pressure. They are widely used in various applications such as hygienics, foods, cosmetics, and agriculture [1-5]. This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996. Nowadays, the worldwide production of SAPs is more than one million tons in year. Hence, synthesis and investigation of specific and new superabsorbent hydrogels with high absorbency, mechanical strength and initial absorption rate, is important.

The properties of the swelling medium (e.g. pH, ionic strength and the counter ion and its valency) affect the swelling characteristics. SAPs responding to external stimuli such as heat, pH, electric field, chemical environments, etc, are often referred to as "intelligent" or "smart" polymers. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs. Therefore, these hydrogels have important applications in the field of medicine, pharmacy, and biotechnology [6-7].

Natural-based superabsorbent hydrogels have attracted much interest from the viewpoint of improving the tissue tolerance of synthetic polymers and the mechanical properties of natural polymers. The presence of the natural parts guarantees biodegradability of the superabsorbing materials. Because of their biocompatibility, biodegradability and non-toxicity, natural polymers, i.e. polysaccharides and proteins, are the main part of these biopolymers [9].

In the present report, to following synthesis of a novel alginate-based composite hydrogel via the grafting of acrylic acid onto alginate chains in the presence of a kaolin powder, the swelling behavior of the composite polymer in various salt solutions was investigated.

EXPERIMENTAL**Materials**

Sodium alginate (chemical grade, MW 50000), N, N'-methylene bisacrylamide (MBA, from Fluka), ammonium persulfate (APS, from Fluka), acrylic acid (AA, from Merck) with analytical grade were purchased and used without further purification. All other chemicals were also analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Superabsorbent Composite Synthesis

Synthesis of the hydrogel, H-alginate-g-PAA/kaolin, was carried out using APS as an initiator and MBA as a crosslinker in an aqueous medium. A general procedure for crosslinking graft copolymerization of AAc onto alginate was conducted as follows. alginate (0.50-1.50 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 40 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at desired temperature (35-70 °C). After complete dissolution of alginate, various amounts of kaolin powder (0.25-0.75 g) were added to the alginate solution and allowed to stir (300 rpm) for 15 min. Then the initiator solution (0.01-0.40 g APS in 5 mL H₂O) were added to the mixture. After stirring for 10 min, certain amounts of 70% neutralized AAc (2.0-8.0 g in 5 mL H₂O) and MBA (0.05-0.20 g in 5 mL H₂O) were simultaneously added to the reaction mixture. After 60 min, the produced hydrogel was poured to excess non-solvent ethanol (200 mL) and remained for 3 h to dewater. Then ethanol was decanted and the product scissored to small pieces (diameter ~5 mm). Again, 100 mL fresh ethanol was added and the composite hydrogel was remained for 24 h. Finally, the filtered composite is dried in oven at 60 °C for 10 h [22]. After grinding, the powdered superabsorbent was stored away from moisture, heat and light.

Swelling measurements using tea bag method

The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) with average particle sizes between 40–60 mesh (250-350 μm) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrated swelling (ES) was measured twice using the following equation [7]:

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

The accuracy of the measurements was ±3%.

Absorbency at various pHs

Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions (0.1 M) to achieve pH ≥ 6.0 and pH < 6.0, respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ±0.1). Then, 0.5 ± 0.001 g of the dried hydrogel was used for the swelling measurements according to Equation 1.

pH-sensitivity

pH-sensitivity of the hydrogel was investigated in terms of swelling and deswelling of the final product at two basic (pH 8.0) and acidic (pH 2.0) solutions, respectively. Swelling capacity of the hydrogels at each pH was measured according to Equation 1 at consecutive time intervals (30 min).

Swelling kinetics

For studying the absorbency rate of the hydrogels, certain amount of samples (0.5 ± 0.001 g) was poured into numbers of weighed tea bags and immersed in distilled water (200 mL) or salt solution (100 mL). At consecutive time intervals, the equilibrium swelling capacity of the hydrogels was measured according to the above-mentioned method.

RESULTS AND DISCUSSION**Equilibrium swelling at various pH solutions**

Ionic composite hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, equilibrium swelling for the synthesized hydrogels was measured in different pH solutions ranged from 1.0 to 13.0 (Figure 1). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 13.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (98 g/g) was obtained at pH 8. Under acidic pHs (≤4), most of the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling values are decreased. However, some sort of attractive interactions (H-O hydrogen bonding) lead to decreased absorbencies [11-14]. At higher pHs (5-8), some of carboxylate groups are ionized and the electrostatic repulsion between COO⁻ groups causes an

enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions (pH>8) is "charge screening effect" of excess Na⁺ in the swelling media, which shields the carboxylate anions and prevents effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems [17].

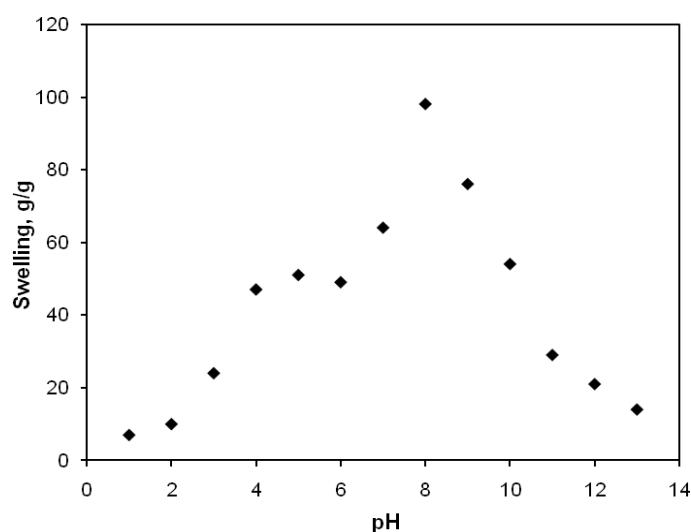


Figure 1. Effect of pH of solution on swelling of H-alginate-g-PACA/kaolin composite hydrogel.
pH-responsiveness behavior of composite hydrogel

Since the synthesized composite hydrogel, H-alginate-g-PACA/kaolin, shows different swelling behaviors in acidic and basic pH solutions, we investigated the reversible swelling-deswelling behavior of this hydrogel in solutions with pH 2.0 and 8.0 (Figure 2). At pH 8.0, the hydrogel swells due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to protonation of the sulfonate and carboxylate anions. This swelling-deswelling behavior of the hydrogels makes them as suitable candidate for designing drug delivery systems. Such on-off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels [16-19].

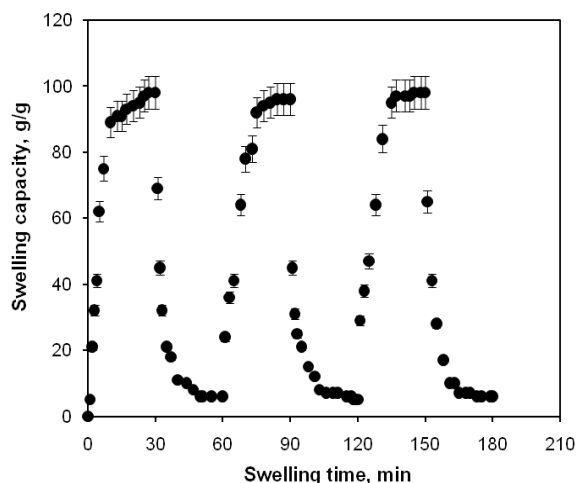


Figure 2. On-off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of the H-alginate-g-PACA/kaolin hydrogel.

Swelling in various salt solutions

The swelling ratio is mainly related to the characteristics of the external solution, i.e. the charge number and ionic strength, as well as the nature of polymer, i.e. the elasticity of the network, the presence of hydrophilic functional groups, and the extent of crosslinking density. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing to the swelling values in distilled water. This well-known undesired swelling-loss is often attributed to a "charge screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion [20-22]. Therefore, the osmotic pressure resulted from the mobile ion concentration difference between the gel and aqueous

phases decreased and consequently the absorbency amounts diminished. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciably decrease in swelling capacity [23].

In this series of experiments, the swelling capacity was measured in various salt solutions (Figures 3 and 4). It is obvious that swelling decrease is strongly depended on the "type" and "concentration" of salt added to the swelling medium. The effect of cation type (cations with different radius and charge) on swelling behavior is shown in Figure 3. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency for the hydrogel in the studied salt solutions is in the order of monovalent > divalent cations [24]. The effect of cation radius on swelling may also be observed from Figure 3.

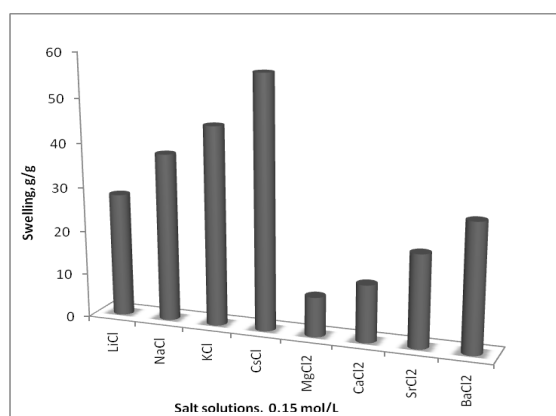


Figure 3. Swelling capacity of the hydrogel, H-alginate-g-PACA/kaolin, in different chloride salt solutions (0.15M).

As reported by Peppas *et al.* [10], the carboxylate anion interacts with small cations, e.g. Li^+ , stronger than with large cations, e.g. K^+ . The stronger interactions of carboxylate-small cation have been observed using measurement of activating coefficients of various cations in several salt solutions [25]. As a result, the absorbency in monovalent and divalent cation salt solutions is in the order of $\text{KCl} > \text{NaCl} > \text{LiCl}$ and $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, respectively.

Figure 4 illustrates a reverse and power law relationship between concentration of salt solutions (NaCl , CaCl_2 , and AlCl_3) and swelling capacity of the hydrogel. Again, charge screening effect and ionic crosslinking are the main explanations for the intense loss of swelling. The known relationship between swelling and concentration of salt solution is stated as following Equation [20]:

$$\text{Swelling} = k [\text{salt}]^{-n} \quad (4)$$

where k and n are constant values for an individual superabsorbent.

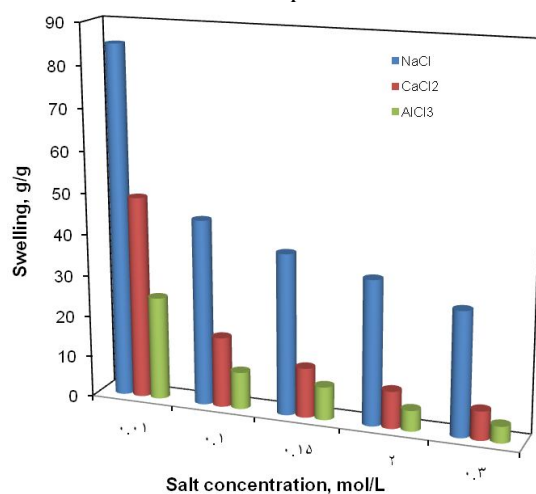


Figure 4. Swelling capacity variation of the H-alginate-g-PACA/kaolin in saline solutions with various concentrations.

CONCLUSION

In this paper, the swelling behavior of composite hydrogel, H-alginate-g-PACA/kaolin, in various salt solutions investigated. The swelling measurement of the synthesized composite hydrogels in different

salt solutions showed appreciable swelling capacity, especially in solutions with monovalent cations. However, swelling loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. The superabsorbent hydrogels exhibited also high sensitivity to pH, so that, several swelling changes of the hydrogel were observed in lieu of pH variations in a wide range (1-13). Ionic repulsion between charges groups incorporated in the gel matrix by an external pH 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 as a suitable candidate for controlled drug delivery systems.

REFERENCES

1. Krul, L. P., Narciko, E. I., Matusevich, Y. I., Yakimtova, L. B., Matusevich, V., Seeber, W. (2000). *Polym Bull*, 45, 159.
2. Dorkoosh, F. A., Brussee, J., Verhoef, J.C., Borchard, G., Rafeiee-Tehrani, M., Juninger, H.E. (2000). *Polymer*, 41, 8213.
3. Raju, K. M., Raju, M. P., Mohan, M. P. J. (2000). *Appl Polym Sci*, 85, 1795.
4. Lim, D. W., Yoon, K. J., KO, S. W. J. (2000). *Appl Polym Sci*, 78, 2525.
5. Buchholz, F. L., Graham, A. T. (1997). *Modern Superabsorbent Polymer Technology*, Wiley, New York.
6. Peppas, L. B., Harland, R.S. (1990). *Absorbent Polymer Technologie*; Elsevier, Amsterdam.
7. Po, R. J. *Macromol. Sci.-Rev.* (1994). *Macromol Chem Phys*, 34, 607.
8. Hoffman, A. S. (1996). *Polymeric Materials Encyclopedia*. J.C. Salamone (Ed.), CRC Press, Boca Raton, Florida, p. 3282.
9. Kost, J. (1999). *Encyclopedia of Controlled Drug Delivery*; E. Mathiowitz, Ed., Wiley, New York, p. 445.
10. Peppas, N. A. (1986). *Mikes, A.G. Hydrogels in Medicine and Pharmacy*; CRC Press, Boca Raton, Florida, Vol. 1.
11. Yazdani-Pedram, M., Retuert, J., Quijada, R., (2000). *Macromol Chem Phys*, 201, 923.
12. Sugahara, Y., Takahisa, O. J. (2001). *Appl Polym Sci*, 82, 1437.
13. Patel, G. M., Trivedi, H. C. (1999). *Eur Polym J*, 35, 201.
14. Silong, S., Rahman, L. J. (2000). *Appl Polym Sci*, 76, 516.
15. Flory, P.J. (1953). *Principles of polymer chemistry*. Ithaca, NY: Cornell University Press.
16. Chen, J., Zhao, Y. (2000). *J Appl Polym Sci*, 75, 808.
17. Lee, W. F., Lin, G.H. (2001). *J Appl Polym Sci*, 79, 1665.
18. Athawale, V. D., Lele, V. (1998). *Carbohydr Polym*, 35, 21.
19. Athawale, V. D., Lele, V. (1998). *Starch/Starke*, 50, 426.
20. Fanta, G. F. (1973). *Block and Graft Copolymerization*, R. J. Ceresa (Ed.), Wiley, London.
21. Branrup, J., Immergut, E.H., (1989). *Polymer Handbook*; 3rd Edn., Wiley: New York.
22. Hosseinzadeh, H., Pourjavadi, A., Zohouriaan-Mehr, M.J., Mahdavinia, G.R. (2005). *J Bioact Compat Polym*, 20, 475
23. Hsu, S. C., Don, T. M., Chiu, W. Y. (2002). *Polym Degrad Stab*, 75, 73.
24. Omidian, H., Hashemi, S.A., Sammes, P.G., Meldrum, I. (1998). *Polymer*, 39, 6697.
25. Pourjavadi, A., Sadeghi, M., Hosseinzadeh, H. (2004). *Polym Adv Technol*, 15, 645.

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