ISSN : 0974 - 7478 Volume 11 Issue 1

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 11(1), 2015 [024-029]

Imbibed salts and pH-responsive behaviours of sodium alginate based eco-friendly biopolymeric hydrogels- A solventless approach

S.Sudarsan[1], D.S.Franklin[1], S.Guhanathan[2]*

[1]Department of Chemistry, Periyar University, Salem, (INDIA)

[1]Department of Chemistry, C.Abdul Hakeem College of Engineering and Technology, Melvisharam-632509, (INDIA)

[2]PG & Research Department of Chemistry, Muthurangam Government Arts College, Vellore, Tamilnadu, 632002, (INDIA)

E-mail: sudarsan.sh@cahcet.edu.in, sai_gugan@yahoo.com

ABSTRACT

In this study, Sodium alginate was chosen to synthesis a series of pH-sensitive hydrogel due to naturally abundant, renewable, non-toxic, water-soluble, biodegradable and biocompatible. By virtue of these advantages, sodium alginate has attracted researchers in industrial and medical fields. The hydrogel was synthesised from Sodium alginate (SA), ethylene glycol and acrylic acid by using condensation followed by free radical polymerization in the presence of water. The formations of synthesised hydrogel were confirmed by FT-IR spectral analysis. The parameters of swelling equilibrium % were carried out in distilled water and various buffer solution of pH from 4.0 to 10.0. The surface morphology of the hydrogels was examined by SEM analysis which supported the swelling behavior of hydrogels. Furthermore, the salt responsive behaviour has also been studied with monovalent, divalent and trivalent salts viz., NaCl, $CaCl_2$ and $AlCl_3$. Swelling equilibrium was lower in multivalent anion salt solution than in monovalent anion salt solution, i.e., $Al^{3+} < Ca^{2+} < Na^{+}$. The synthesized biopolymeric hydrogels might be used in biomedical, agrochemical release, environmental application and also used to produce hygiene products such as diapers etc.,

KEYWORDS

Responsive biopolymer;
Swelling equilibrium;
Sodium alginate;
Diol;
Acrylic acid.

INTRODUCTION

Salts and metal ion causes series of problem to both environment and human health. The principal metal ion are sodium chloride (NaCl), Calcium chloride ($CaCl_2$) and Aluminum chloride ($AlCl_3$), which are most stable form of metal ion species present in water might be converted into toxic or important metal ions. The metal based compound were inorganic materials that dissolves easily in water and widely used in industry, company and other applications. In addition, excessive levels of metal ions in drinking water may leaded health problems, especially for infants. Adsorption using different polymeric material methods of choice in many waste-water treatment processes for the removal of metal

ions from chemical process industries and tanneries. Adsorption techniques have been applied primarily to the amputation of some metal ions, such as Al^{3+}, Ca^{2}, Na^{+}[1-2].

Hydrogels are hydrophilic, three-dimensional, expandable matrices that are produced through chemical or physical crosslinking of certain polymers. Hydrogels have been widely used as an excellent adsorbent on toxic metal ions. These biopolymeric hydrogels exhibited a determined response to volume change in certain environmental triggers such as the change in pH, temperature, time, concentration and electromagnetic fields[3]. Recently, there has been an increased interest in the utilization of hydrogels in toxic metal ions removal and dye industry effluent waste water field due to their biocompatibility, ease of metal ion adsorbed dispersion in a matrix, and high degree of control.

pH sensitive hydrogels are polymer networks that have pendant acidic and basic functional groups which either accept or release protons as a result of changing external pH. They are designed by acidic or basic functional groups which are present on the polymer network. These materials retain large amount of water due to the presence of hydrophilic functional groups, such as hydroxyl, carboxyl, amide, sulfonyl, and so forth, represented in the polymer network[4-5].

The percentage of water content of the hydrogels at equilibrium was one of their fundamental properties. A hydrogel with higher water content is generally more advantageous in increasing permeability, flexibility and biocompatibility. A lot of research already done to various aspects of swelling and shrinking of non-ionic and ionic gels in aqueous solution, phase transition in gels, the elastic properties of gels and the structure of solvents inside a gel[14-15]. Particularly, Sodium alginate based pH tuning hydrogels have been investigated by many research groups in the world.However, SEA biopolymeric hydrogels are permeable to oxygen and possess good biocompatibility due to imbibed a huge amount of water in itself.

Sodium alginate (SA) is an anionic natural macromolecule, which is composed of poly-b-1, 4-D-mannuronic acid (M units) and a 1, 4-L-glucuronic acid (G units) in varying proportions by1–4 linkages. SA could be extracted from marine algae or produced by bacteria, and so it is abundant, renewable, non-toxic, water-soluble, biodegradable and biocompatible[6]. However, the crosslinking hydrogel was broken due to the pKa characteristics of the carboxyl group and it leads to the swollen of the hydrogel, followed by uptake of water and metal ions. Due to the presence of ionized groups on a polymer network superimposes the effects of electrostatic interactions on the properties of the unionized polymer such as sodium alginate useful for increasing viscosity in solvents including water, and water treatment. By virtue of these advantages, SA has received considerable attention in industrial and medical fields[7]. Ethylene glycol (EG) was chosen as a difunctional monomer to improve the properties of hydrogels because of its flexibility and biocompatibility[8]. Zuber and coworkers prepared surface characteristics of biocompatible blends based on chitin/1, 4-butane diol[9]. Acrylic acid (AA) based polymeric hydrogels were also used to fabricate pH sensitive hydrogels[10]. AA based hydrogel for vital role in biomedical applications, due to the gels formation at different concentrations. Other materials can be incorporated into the AA prior to gel formation. Many investigations have shown that AA interactions enhanced the swelling behavior of hydrogels and there greater potential in medical field, particularly in site-specific drug delivery systems applications[11].

Based on above depiction a novel sodium alginate based biopolymeric pH-sensitive sodium alginate (SEA) hydrogels was synthesized by condensation followed by free-radical copolymerization. The structure and surface morphologies of the synthesized hydrogel were characterized by Fourier Transformation Infrared Spectra (FTIR) and Scanning Electron Microscope (SEM). The effects of different composition of monomer and polymer have also high water content properties of SEA hydrogel were investigated. In addition, water uptake, the swelling equilibrium, pH-sensitivity, and metal adsorption behaviors of the SEA hydrogels in various proportions were also evaluated systematically.

EXPERIMENTAL

Materials and Methods

Sodium alginate (SA) was purchased from Sigma- Aldrich Company (Bangalore, India). Ethylene glycol (EG) and acrylic acid (AA) were obtained from Merck. AA was vacuum distilled at 54ÚC/ 25 mm Hg to remove inhibitor hydroquinone. Demineralized water was used for polymerizations and the preparation of the buffer solutions.

Characterization

FT-IR spectra were recorded on a FT-IR spectrophotometer 8400 S. Shimadzu spectrophotometer. Prior to analysis, KBr pellets were prepared by mixing 1:10 of sample: KBr (w/w) followed by uniaxial pressing of the powder under vacuum. Spectra were recorded between 4000 and 400 cm^{-1} at 2 cm^{-1} resolution. SEM was performed on dried biopolymeric hydrogel samples were carried out using Hitachi, Model: S-3400. The samples were mounted on the base plate and gold-sputter coated to render them electrically conductive, the scanning was synchronized with a microscopic beam to maintain the small size over a large distance relative to the specimen.

Synthesis of novel SEA biopolymeric hydrogels

Synthesis of biopolymeric SEA hydrogel was the same as described in our earlier communication[12]. In brief, condensation followed by free radical polymerization was performed among sodium alginate (SA) and ethylene glycol (EG) in nitrogen atmosphere at 80ÚC resulted pre-polymer chains formation. Further, acrylic acid (AA) and $K_2S_2O_8$ initiator was also added to pre-polymer at 80 ^{0}C with constant stirring for 3 hrs. The yellowish dry hydrogel was obtained. The hydrogels are expressed as SEA biopolymeric hydrogels.

These hydrogel was equilibrated with distilled water for 2 days to remove unreacted monomer and other impurities. The resultant hydrogels were dried at room temperature and stored in sealed containers for further studies.

Equilibrium swelling behaviour of SEA biopolymeric hydrogels

Equilibrium swelling behavior of a series of biopolymeric hydrogel was studied in the solution of pH 4-10 at room temperature for 24 hr. Solution uptake with respect to time was observed by periodically and swollen gels were taken out and wiped with soft tissue paper to remove the water on the hydrogel surface, and then weighed. The equilibrium swelling (S_{eq}%) for each sample was calculated by using Equation (1)

$$S_{eq}\% = \frac{W_{eq} - W_d}{W_d} \times 100 \quad (1)$$

Where W_d and W_{eq} are the weights of the sample in dried state, swollen at equilibrium, respectively.

Salts responsive behaviours

One liter of 0.001, 0.01, 0.025 and 0.1M different (NaCl, $CaCl_2$ and $AlCl_3$) salt solution was prepared. 0.04 g of dried hydrogel was immersed 50 ml solution for 24 hr room temperature, the mixture was filtered. The (S_{eq}%) was calculated by using Equation (1).

RESULTS AND DISCUSSION

FT-IR spectral analysis

A comparative FT-IR spectrum of (a) sodium alginate (b) SEA biopolymeric hydrogel were presented in Fig 1. The–OH stretching band of EG overlapped with the -OH stretching band of the SA portion of the copolymer. As shown in Figure 1b, after formation of the products, most of the -OH groups in EG and acid groups in AA were converted to ester groups. Since the resulted product became insoluble in water, the cross links really formed between the SA, and other monomer. In was clearly indicated SA molecules presumably could be interacted with each other through hydrogen bonding. This fact practically proves that the SA involved in the crosslinking mechanism. It was obviously seen that there existed a characteristic strong broad absorption band at 3291.11 and 3341.99 cm^{-1} is due to a hydrogen bonded O-H groups[13]. The sharp intense band was found at 1738.55 cm^{-1} indicated the (C=O) stretching and C-O- stretching were observed at 1709.54 cm^{-1}[17], which confirmed the utilization of monomers in the polymerization by forming pre-polymer. The

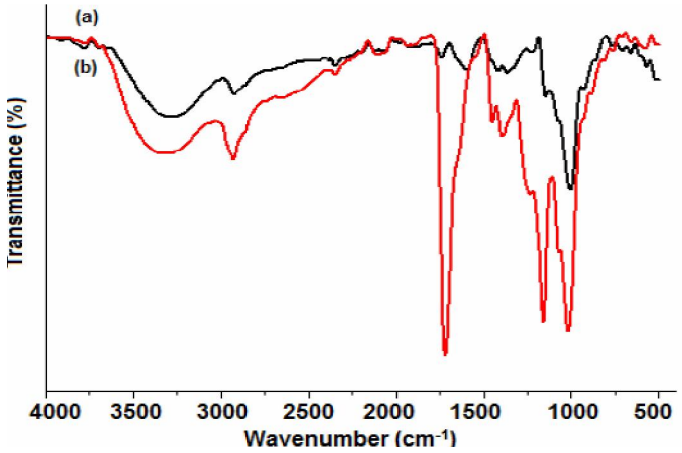

Figure 1 : Comparative FT-IR spectrum of (a) SA (b) SEA hydrogel

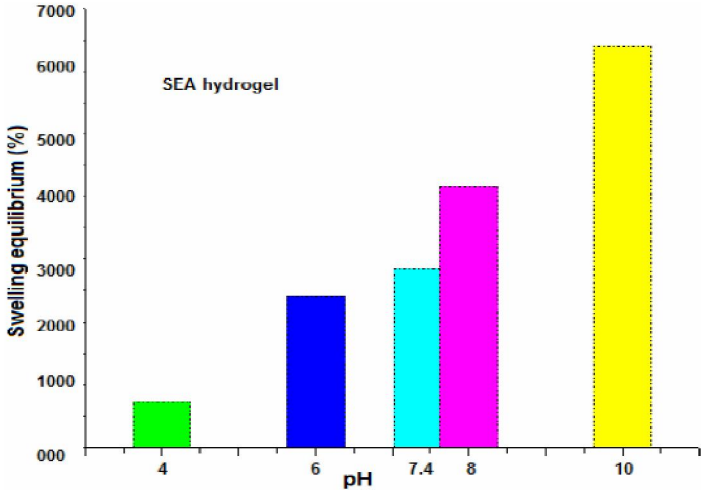

Figure 2 : Swelling equilibrium of SEA hydrogels at various pH

distinguish peaks were recorded at 1593.84 and 1414.12 cm^{-1} is due to the asymmetric and symmetric stretching vibration of carboxylate (COO-)[18]. The supportive results confirmed the synthesis of SA-EG-AA biopolymeric hydrogel. The absorption peaks have also been observed at 2922.42 and 2926.93 cm^{-1} were stretching vibration of $-CH_2-$ group.

Swelling equilibrium studies

The SEA biopolymeric hydrogels showed pH dependencies of equilibrium swelling revealed higher at pH 10.0 than acidic pH in Figure 2. The Seq% value of SEA at pH 4.0, 6.0, 7.4, 8.0, and 10.0 was corresponded to 733.00, 2425.00, 2833.00, 4150.00 and 6392.00% respectively. The enhanced swelling was observed due to poly-functionality of sodium alginate. This type of pH-sensitive hydrogels exhibited good swelling ability to adsorption of salt and other metal ions.

For the most part of the hydrogel systems are pH responsive[19] and, therefore the pH of the fascination medium has direct control over the degree of swelling of the network. The swelling equilibrium of SEA hydrogels have shown higher value at alkaline medium than in neutral and acidic medium. The results are depicted in Figure 2 which indicated that the pH increases, swelling also increases. The results could be attributed to the fact that with increasing pH of the external solution the COO^- groups of SA chains undergoes deprotanation, as the pH increases. This obviously produces anionically charged polymer chains which because of the mutual repulsion among carboxylate ions (COO-) results in an expansion of the network chains leading to an increase in swelling.

Effects of cationic salts

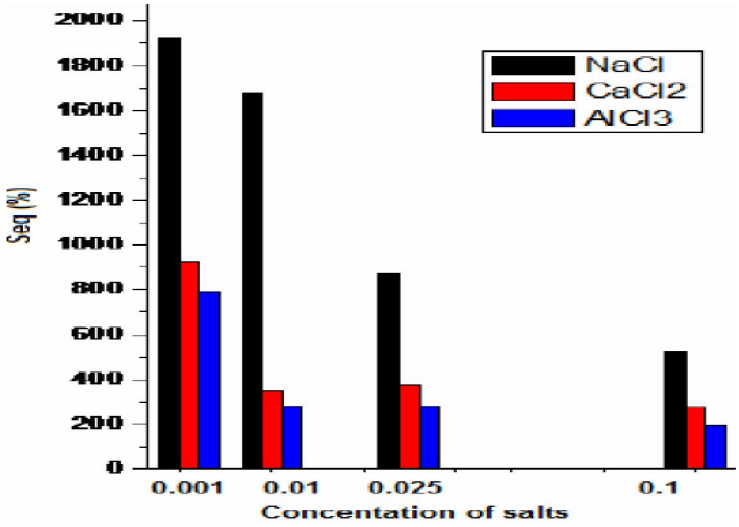

Figure 3 : Salt responsive behaviour of SEA hydrogel at (NaCl, $CaCl_2$, $AlCl_3$)

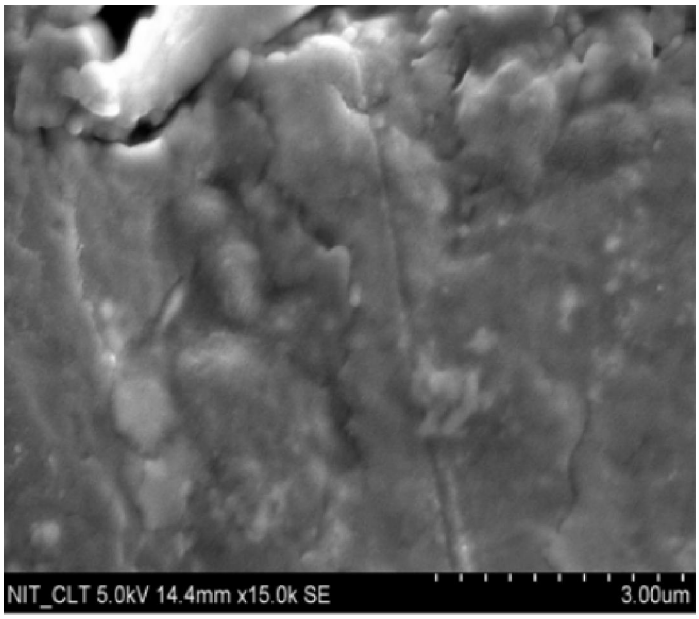

Figure 4 : SEM image of SEA hydrogel

In array to investigate the effect of cationic salts were imbibed SEA biopolymeric hydrogel was carried out the chlorides of sodium, calcium and aluminum were added into he suspension in the concentration at 0.001, 0.01, 0.025 and 0.1M. The results are shown in Figure 3, which revealed that adsorption decreases with increasing in the charge of the cationic salts. The order was found as follows,

Al^{3+}> Ca^{2+}> Na^{+}

The negative backbone of hydrogel network provides the active sites for the adsorption of ions. This obviously results in a preferential adsorption of positive ions like mono, di and tri valent ions, which resulted in a decreasing adsorption of ions. Ca^{2+} ions are bivalent they are held on a higher fraction of sites than Na^{+} ions and this justifies the observed order of effectiveness of the charged ions. A major significance also involved in a choice of purpose such as personal hygiene products, agrochemical and waste water release. The swelling ability of "anionic" hydrogels in various salt solutions was substantially decreased compared to the swelling values at various pH 4.0 -10.0 solutions. It was clearly indicated the undesired swelling-loss often attributed to a "charge screening effect". On the other hand cationic salts which causing a non-perfect anion–anion electrostatic repulsion inside the hydrogel.

Cationic salt solution the osmotic pressure consequential difference in the movable ion concentration between hydrogel and the cationic salt solution was decreased and as a result the absorbency amount of multivalent ions are diminished.

SEM morphologies of biopolymeric hydrogels

The morphological features of SEA polymeric hydrogel have been shown in Figure 4 In order to gain clear insights into the surface topography of the biopolymer hydrogel the images were recorded. The hydrogel has a uneven and rough surface structure. Some cracks and cavities also been observed on the surface could be due to the rupture of the surface. It is supposed that these pores are the regions of water penetration and interaction sites of external stimuli with the hydrophilic groups of the copolymers.

CONCLUSIONS

The present investigation was point out many outcomes in the key role of biopolymeric hydrogel materials for many recent applications.

The pH responsive sodium alginate based hydrogels was synthesized by simple method.

Eco friendly based hydrogels could be used as a template for solventless synthesis by green approach.

The FT-IR results were confirmed the formation of SEA hydrogels.

Swelling behaviors of hydrogels were also studied between pH 4.0 and 10.0 in phosphate buffer solution. The salts (cationic ions) responsive behaviours were also been observed with monovalent, divalent and trivalent salts viz., NaCl, $CaCl_2$ and $AlCl_3$.

Swelling equilibrium was lower in multivalent anion salt solution than in monovalent anion salt solution, i.e., $Al^{3+} < Ca^{2+} < Na^{+}$.

The surface morphologies of SEA hydrogels showed the perfect cavities and rough surface was enable the hydrogels for their enhanced swelling equilibrium.

SEA based Hydrogels could be employed in various aqueous environments like salts and waste water. The pH responsive behavior, salts and metal ion adsorbed hydrogels could be separated from the adsorption aqueous medium.

pH sensitive SEA biopolymeric hydrogels were also economically cheap and biocompatibility.

These kinds of biomaterials are tunable functional feature. Hence, the synthesized biocompatible eco friendly pH sensitive SEA based hydrogels may have an emergence for their utilization in salt removal, biomedical, agrochemical release and environmental remediation.

REFERENCES

[1] E.Salehi, S.S.Madaeni, S.Samiei Raad, A.A.Shirazi Manesh, V.Vatanpour; Desalination, **281**, 312–318 **(2011)**.

[2] S.S.Rahangdale, W.B.Gurnule, A.B.Zade; Ind.J.Chem., **48A**, 531–535 **(2009)**.

[3] D.Roy, J.N.Cambre, B.S.Sumerlin; Prog.Polym.sci, **35**, 278–301 **(2010)**.

[4] Y.Qiu, K.Park; Adv.Drug Deliv.Rev., **53**, 321 **(2001)**.

[5] H.Savas, O.Guven; Int.J.Pharm., **224**, 151 **(2001)**.

[6] H.V.Sather, H.K.Holme,G.Maurstad, O.Smidsrod, B.T Stokke; Carbohydrate Polymers, **74**, 813–821 **(2008)**.

[7] S.H.Yoo, Y.B.Song, P.S.Chang, H.G.Lee; Int.Journal of Biological Macromolecules, **38**, 25–30 **(2006)**.

[8] S.N.Dobic, J.M.Filipovic; S.L.Tomic; Chem.Eng.J, **179**, 372 **(2012)**.

[9] K.M.Zia, M.Zuber, I.A.Bhatti, M.Barikani, M.A.Sheikh, Int.J.Biol.Macromol., **44**, 18 **(2009)**.

[10] L.B.Peppas, N.A.Peppas; Biomaterials, **11**, 635–644 **(1990)**.

[11] Y.Huang H.Yu,C.Xiao; Carbohydr Polym, **69**,774–783 **(2007)**.

[12] S.Sudarsan.D.S.Franklin, S.Guhanathan; ITconference at tirucy, **(2014)**.

[13] E.Karada_g, D.Saraydýn, O.G€uven; Macromol.Mater.Eng., **286**, 34 **(2001)**.

[14] J.Theil, G.Maurer; Fluid Phase Equilibria, **165**, 225 **(1999)**.

[15] F.Horkay, I.Tasaki, P.J.Basser; Biomacromol, **1**, 8 **(2000)**.

[16] E.L.Simith, R.L.Hill, I.R.Lehran, R.J.Lefkowitz, P.Handler, A.White; in: Principles of Biochemistry, 7th Edtion, McGraw-Hill, Auckland, (**1985)**.

[17] Nuclear Instruments and Methods in Physics Research B, **187**,340–344 **(2002)**.

[18] J.Rosiak, K.Burczak, W.Pekala, N.Pislevski, S.Idziak, A.Charlesby; Radiat.Phys.Chem., **32**, 793 **(1988)**.

[19] D.S.Franklin, S.Guhanathan; J.Appl.Polym.Sci., **131**, 41403 **(2014)**.