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Swelling and salt responsive studies of biocomposite hydrogels via solventless green approach

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ABSTRACT

Hydrogels are three-dimensional, hydrophilic, water insoluble polymeric networks with interesting stimuli sensitive behavior (pH, temperature, light etc.,). pH sensitive biocomposite hydrogels were synthesized by using citric acid (CA) and acrylic acid (AA) with ethylene glycol (EG) stated as ACE-HA via a two- step condensation polymerization process towards a solvent-free green approach. Hydroxyapatite (HA) prepared from waste eggshells were added with the biopolymeric hydrogels of (ACE) resulted as biocomposite hydrogels. The formations of various hydrogels were confirmed using spectral techniques like FT-IR. The swelling experiments were achieved in different pH–buffer solutions at room temperature (4.0-10.0). SEM analysis further supported the morphology and the swelling behavior of synthesized biocomposite hydrogels. The swelling equilibrium for various hydrogen were also being accomplished. The swelling capability of hydrogels was also restrained in various salt solutions (NaCl, $CaCl_2$ and $AlCl_3$). Hence, the biocomposite hydrogels could also be an excellent candidate for drug delivery systems, hygienic products, agrochemical release etc.,

KEYWORDS

Biocomposite hydrogels;
pH sensitive;
Swelling equilibrium;
Spectral techniques.

INTRODUCTION

Hydrophilic polymers can swell and absorb water without dissolving, provided that chemical or physical crosslinks exist among the macromolecular chains. The polymer network resulting from the crosslinks swells in the aqueous solvent, until the thermodynamic force of swelling is totally counterbalanced by the elastic, retractive force exerted by the crosslinks. This 'solid-like solution' of polymer and water resulting at equilibrium is known as a hydrogel. The amount of water retained by the mesh of the hydrogel network depends on the structure of the polymer network itself and on the environmental conditions, such as the temperature, pH and ionic strength of the water solution in contact with the polymer[1].

Eggshells waste is a continuously growing problem at global, national and regional levels. Modernization and increasing population creating demands

on food and other essentials. Further, this can be utilized for the synthesis of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] which is a valuable biomaterial. Hydroxyapatite (HA), the inorganic constituent of bone and hard tissues is one of the most widely used biomaterials for reconstruction of the skeleton. Commercially available HA are expensive due to cost effective processing[2-3]. The combination of hydroxyapatite with smart polymeric architectures seems to be a promising route to the design of novel biomaterials. Composite of polymers with hydroxyapatite has long been an interesting subject of scientific research and industrial applications as the incorporation of hydroxyapatite can reduce production cost and improve the performance of material[4]. Attention towards eco-friendly biocomposite hydrogels have been increasingly studied due to their synergistic benefits offered by each of its ingredients. Hydrogels are class of polymers that can absorb water, biological fluids and swell several times as their volume based on various environmental conditions[5]. Such environment sensitive hydrogels were also called "smart" or "intelligent hydrogels". Citric acid (CA) is a renewable resource, mainly manufactured for fermentation of carbohydrate viz., starch or glucose. CA was chosen as a poly functional monomer because of its nutritionally harmless nature. Since, it is a nontoxic metabolic product of the body (Krebs or citric acid cycle) in all living cells that use oxygen as a part of cellular respiration; it is readily available and inexpensive monomer. Consequently, it has already been approved by FDA (Food and Drug Administration-US) for use in human[6]. Ethylene glycol (EG) was chosen as a difunctional monomer to improve the properties of hydrogels because of its flexibility and biocompatibility[7]. Acrylic acid (AA) were also used to synthesis pH sensitive hydrogels[8]. AA based material offers vast potential for biomedical applications as the gels formed from AA can be formulated at varying concentrations. They can be easily fabricated in a wide array of sizes and shapes. Other materials can be incorporated into the AA, prior to gel formation. Many investigation have shown that AA interactions exert strong influence on the swelling behavior of hydrogels and there is a great potential for their application in pharmaceutical preparations, particularly in drug delivery systems[9].

Based on careful analysis of literature, the present investigation is being focused on a new type of biocomposite hydrogels were prepared. The structure, thermal stability and morphologies of synthesized biocomposite hydrogels were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction studies (XRD), thermo gravimetric analysis (TGA), derivative thermo gravimetric analysis (DTG), and the scanning electron microscopy (SEM). In addition to this the swelling behaviors in various pH solutions were also investigated.

EXPERIMENTAL

Materials and physio-chemical characterisation

The monomer anhydrous citric acid (CA), acrylic acid were purchased from Sigma Aldrich Chemical Company (Bangalore, India). Ethylene glycol was purchased from Merck (India). Waste eggshells were collected from hotels in local town.

FT-IR spectra were recorded on a FTIR-8400 S, Shimadzu spectrophotometer. SEM was performed on dried biocomposite hydrogel samples were carried out using Hitachi, Model: S-3400. Swelling experiments were conducted in buffer solutions of various pH (4.0-10.0) at 37 °C. Dried biocomposite hydrogels were immersed in the swelling medium. Swollen biocomposite hydrogels were removed from the swelling medium at a regular time intervals and dried rapidly with filter paper, weighed and placed in the same bath. pH value (4.0–10.0) of swelling medium was adjusted by using aqueous HCl and NaOH solutions. The pH values were exactly checked with a pH meter (Systronics 3300, India).The swelling percentage and swelling equilibrium were calculated according to following Eq. 1.

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

W_d is the initial weight of the dried biocomposite hydrogel, W_t weight of the swollen sample at time t and W_{eq} weight of the swollen sample at equilibrium, respectively.

Swelling response in salt solutions were carried out according to the reported procedure, dried hydrogel sample was immersed in 50mL of saline solution (NaCl, $CaCl_2$ and $AlCl_3$) varying concentration at room temperature until the swelling equilibrium was attained (approximately for one day).

Synthesis of biocomposite hydrogels

The hydrogels (ACE) was synthesized according to our previous contribution[10-11]. Briefly, the citric acid (0.025 mol) dissolved in 1% solution of hydrochloric acid was taken in a round bottomed flask fitted with a mechanical stirrer and nitrogen inlet. Ethylene glycol (0.025 mol) was added drop wise using a dropping funnel. Acrylic acid (0.025 mol) was added to pre-polyester CE at 140 °C with constant stirring for 2 h in the nitrogen atmosphere. The formation of glassy gel (ACE) implies the completion of the reaction. After formation glassy gel, 0.2 g of HA was gradually added to ACE hydrogels. To ensure ACE and HA uniformly dispersed in the vessel, the mixture was stirred and heated at 140 °C for 6 h. The resultant composite hydrogel ACE-HA was dried by placing under lukewarm condition for 72 h. The dried biocomposite hydrogels were kept in air-tight container for further use[12].

RESULTS AND DISCUSSION

FT-IR Spectral studies of biocomposite hydrogels

The FT-IR spectra of hydroxyapatite prepared from egg shells has been shown in Figure 1. The strong absorption band observed at 1085.92, 1018.41 cm^{-1} and 833.25, 570.93 cm^{-1} corresponds to stretching and bending vibration of phosphate groups in hydroxyapatite respectively. The broad band at 2900-

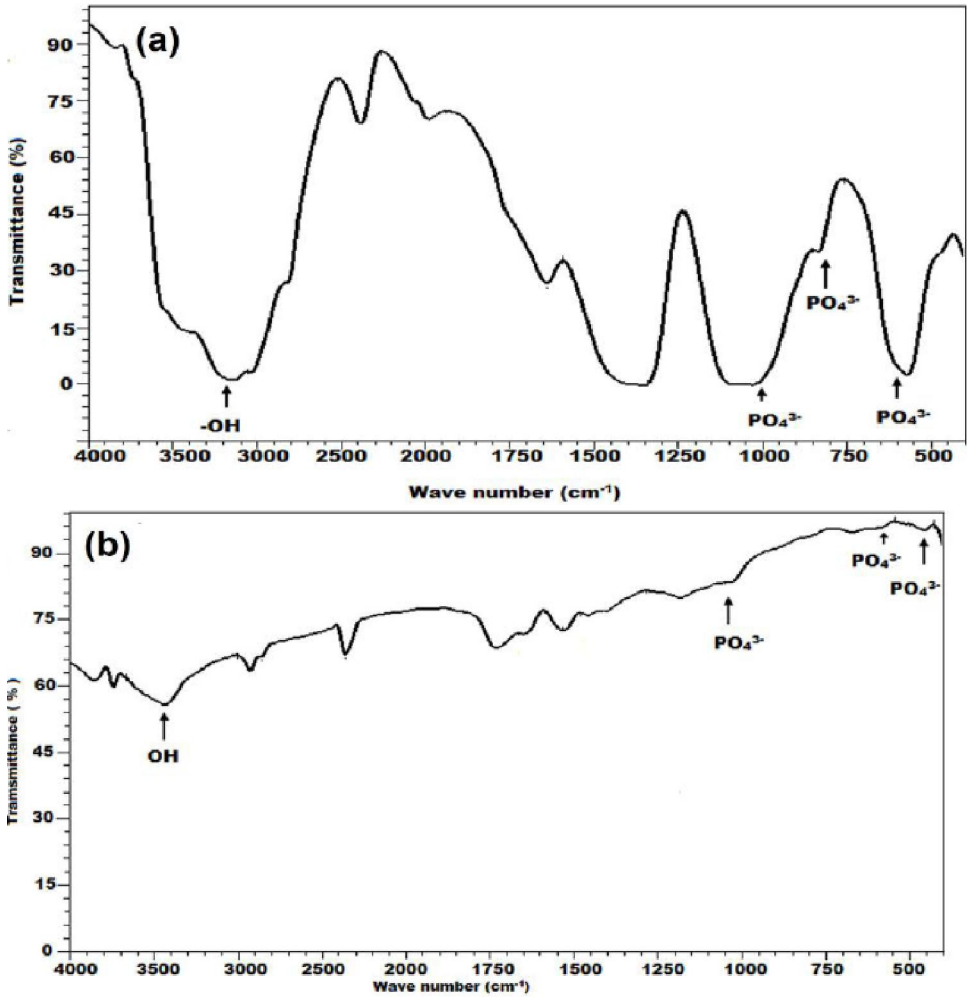

Figure 1 : FT-IR spectra of (a) Hydroxyapatite (b) ACE-HA

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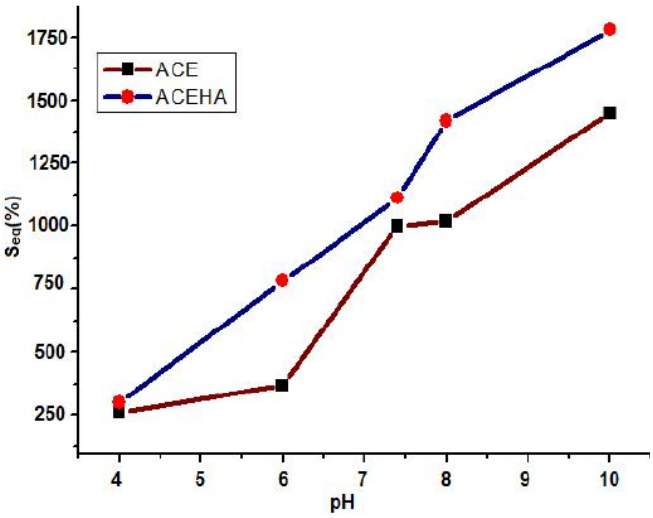

Figure 2 : pH sensitive equilibrium swelling of ACE hydrogel and ACE-HA biocomposite hydrogel

3700 cm^{-1} was assigned to OH stretching. Nikpour et al.[13] observed absorption bands at 1099, 952, 839, 563 cm^{-1} attributed to phosphate group in HA while the stretching band approximately between 2900-3700 cm^{-1}.

Samandari et al.[14] reported the intense absorption band of pure hydroxyapatite at 1029, 1092 and 961 cm^{-1} corresponding to the symmetric stretching and asymmetric stretching modes of PO_4^{3-} in HA respectively. The sharp and separated peaks 602 and 566 cm^{-1} were attributed to the bending group of HA. This clearly indicates the formation of hydroxyapatite from egg shells. The synthesized biopolymeric hydrogels and their composites were characterized by FT-IR spectroscopy. As per our earlier report, ACE hydrogels showed a strong absorption band at around 1732.08 cm^{-1}[10], which is a characteristic absorptions of C=O stretching vibration and C-O stretching was observed at 1188.15 cm^{-1} of ester groups indicating formation of polyesters. The spectra clearly marked broad stretching at 3439.09 cm^{-1} suggested the presence of hydrogen-bonded hydroxyl group. The peaks centered at around 2931.80 cm^{-1} exhibited methylene (-CH_2-) stretching contributed by diol. Similar to our observation, Yang et al.[15] was observed for citric acid and 1, 8 octane diol based systems.

Equilibrium swelling studies of biocomposite hydrogels

Equilibrium swelling studies were performed on a biocomposite hydrogel equilibrated in a buffer with pH value ranging from 4.0 to 10.0 at room temperature (Figure 2). The S_{eq}% value of ACE-HA hydrogel were 300.00, 783.00, 1112.00, 1420.00 and 1780.00%, ACD-HA hydrogels S_{eq}% values were found to have 385.00, 1180.00, 1257.00, 1533.00 and 1733.00 % and S_{eq}% value of ACT-HA hydrogel were 392.00, 1320.00, 1520.00, 1547.50 and 2400.00% at pH 4.0, 6.0, 7.4, 8.0 and 10.0 respectively[12].

It is clearly indicated that S_{eq}% of biocomposite hydrogels increases with respect to time and the swelling was strongly dependent on pH. It may be obvious that swelling % of synthesized hydrogels were significantly higher at higher pH, compared to the lower pH value. Hence, the ionization of all carboxylic groups in acid increases the S_{eq}% of hydrogels in the basic media than in acidic media. This type of pH sensitive biocomposite hydrogels could be a potential candidate in drug delivery applications.

Salt responsive behavior of hydrogel

The presence of an electrolyte in a saline medium has a greater influence in agriculture and biomedical fields, namely, for water reservoirs in agriculture and hydrogels as implants for drug release applications. The present investigation depicted on the effect of salts on the swelling of the hydrogel by the addition of various concentrations (viz., 0.025, 0.05, 0.075 and 0.10 M) of salts such as (NaCl, $CaCl_2$ and $AlCl_3$) solutions respectively.

Figure 3 shows the swelling data obtained from the chloride salt solutions of various cations with different ionic strengths. From the Figure 3, it was clear that swelling ratio decreased with increasing charge of the metal cation (Na^+>Ca^{2+}>Al^{3+}). Initially hydrogel showed good swelling behavior in each salt solution.

The swelling ability of anionic hydrogel in various salt solutions is appreciably decreased; it may be attributed to a charge screening effect of the additional cation. This might be due to the ionic charge increased; there was a proportionate increase in the cation-cation repulsion, which did not allow more entry of solution containing cation inside the

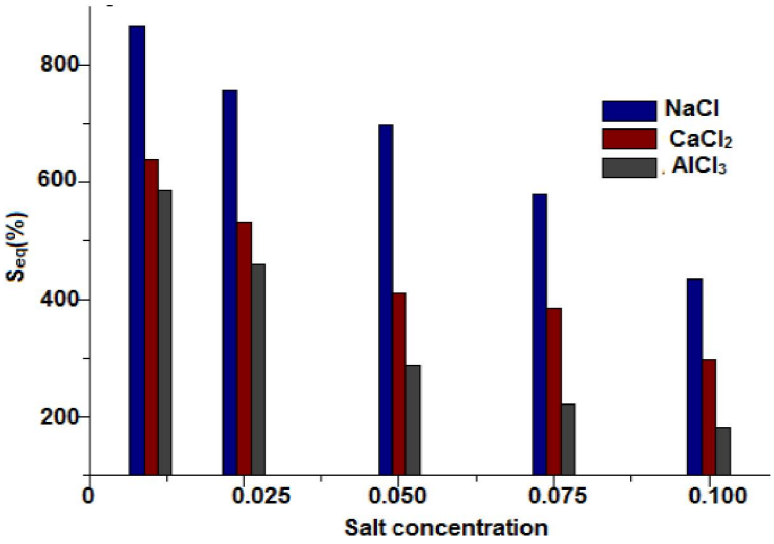

Figure 3 : Salt responsibility swelling in various salt solutions (NaCl, $CaCl_2$ and $AlCl_3$)

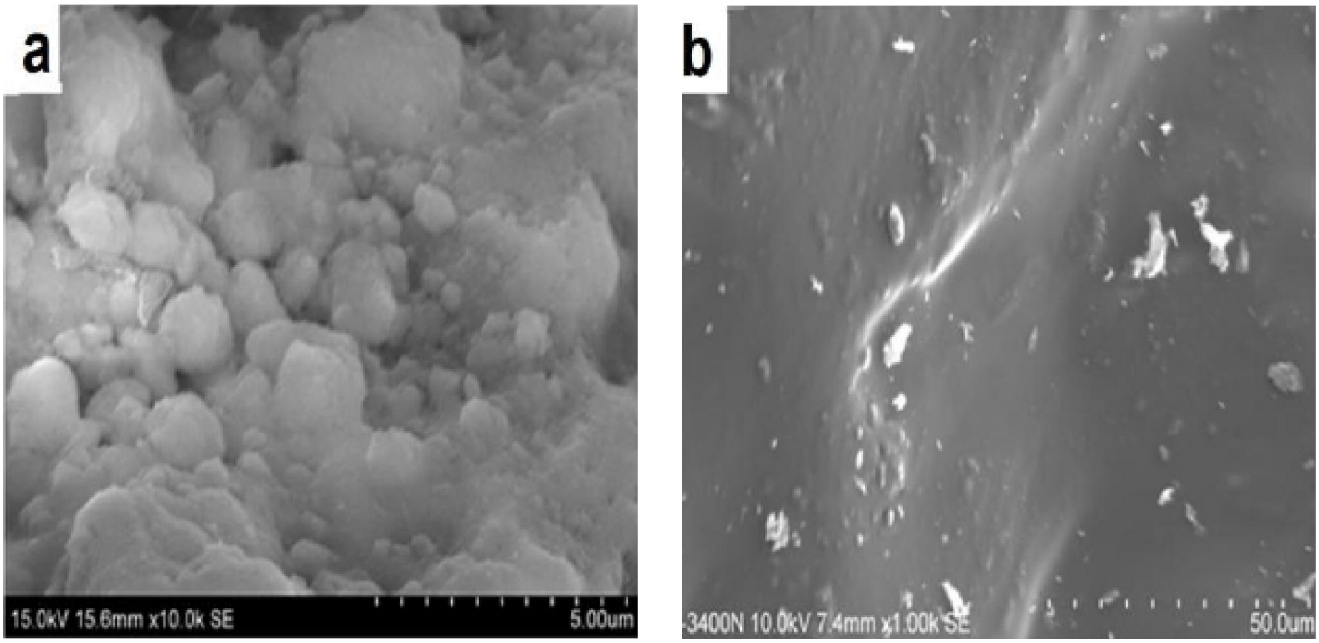

Figure 4 : SEM image of (a) HA (b) ACE-HA

crosslinked network. This ultimately leading to a decreasing trend in the swelling behavior of the polymeric hydrogel[16].

Morphologies of biocomposite hydrogels

Scanning electron microscopy (SEM) technique is useful to reveal the structure of hydrogels[11]. Figure 4 shows the SEM image of dried ACE-HA composite hydrogel and their hydrogels (ACE).

Figure 4 showed ACE-HA biocomposite hydrogel, which reveal the spherical shape and porous nature in their surfaces. The presence HA particles are scattered inside the polymer matrix. Incorporation of HA into the ACE polymer matrix reduces the crystallinity and alters the original polymer structure by increasing the swelling of biocomposite hydrogel. It encouraged the fluid to easily enter into the gaps, leading to substantially increase of the absorption rate than of ACE-HA biocomposite hydrogels.

CONCLUSIONS

Biocomposite hydrogels have been synthesized via condensation polymerization using along with

hydroxyapatite prepared from waste eggshells. Formation of biocomposite hydrogels were confirmed by FT-IR. Improved swelling behavior was noticed at alkaline medium. The enhanced swelling behavior was well supported by SEM studies. The results clearly suggests that the biocomposite hydrogels could also be an excellent candidate for polymeric drug delivery system. Hence, the synthesized biocomposite pH sensitive hydrogels may have a great opening for industrial and biological applications such as metal ion removal, cationic dye removal and controlled release of drugs to pH sensitive parts of human being.

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