



Synthesis of interpenetrating network hydrogel from poly(acrylic acid-co-hydroxyethyl methacrylate) and sodium alginate: Modeling and kinetics study for removal of synthetic dyes from water

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ABSTRACT

Several interpenetrating network (IPN) hydrogels were made by free radical *in situ* crosslink copolymerization of acrylic acid (AA) and hydroxy ethyl methacrylate in aqueous solution of sodium alginate. N,N'-methylenebisacrylamide (MBA) was used as comonomer crosslinker for making these crosslink hydrogels. All of these hydrogels were characterized by carboxylic content, FTIR, SEM, XRD, DTA-TGA and mechanical properties. Swelling, diffusion and network parameters of the hydrogels were studied. These hydrogels were used for adsorption of two important synthetic dyes, i.e. Congo red and methyl violet from water. Isotherms, kinetics and thermodynamics of dye adsorption by these hydrogels were also studied.

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1. Introduction

Hydrogels are crosslinked hydrophilic polymer capable of showing extensive swelling in water. Hydrogels are used as effective adsorbent for various applications including agriculture, horticulture, personal care products, drug delivery, separation of heavy metal ions and dye molecules from water, etc. (Wang, Zhang, & Wang, 2011). These superadsorbent polymers are prepared by crosslinking synthetic or natural polymers. Natural polymers are available in large quantities in nature and these biopolymers are also biodegradable and non toxic. Thus, much attention is being presently paid for making biopolymer based hydrogels. Cellulose, the most abundant renewable resource on earth, is the origin for most of the biopolymers (Chang, Duan, Cai, & Zhang, 2010; Peppas, Hilt, Ali, & Robert, 2006). Cellulose having abundant hydroxyl groups can be used to prepare hydrogels easily with fascinating structures and properties. Sodium alginate is a water soluble salt of alginic acid, a natural polysaccharide of brown algae. This non-toxic natural polysaccharide contains 1,4-linked-D-mannuronic acid and L-guluronic acid residues that are arranged in the polymer chain in blocks. These homogeneous blocks are separated by blocks made of random or alternating units

of mannuronic and guluronic acids (Peppas et al., 2006). The gelation and cross-linking of alginate is achieved by the exchange of sodium ions with multivalent cations. Such a cross-linked hydrogel is useful in controlled release of bioactive molecules. However, like most of the biopolymer based hydrogels, sodium alginate based hydrogels are also of poor mechanical strength (Jeon, Lei, & Kim, 2008). Properties of sodium alginate based hydrogel may be improved by physical or chemical modification. Jeon et al. incorporated polyaspartate in the matrix of sodium alginate and used this composite hydrogel for adsorption of malachite green and methyl orange from water (Jeon et al., 2008). Yin et al. grafted sodium alginate with acrylic acid and hydrogel was prepared by crosslinking this graft copolymer with MBA. This hydrogel showed excellent swelling characteristics in different buffer solutions (Yin, Ji, Dong, Ying, & Zheng, 2008). Hua et al. prepared hydrogel by freeze thawing blend of polyvinyl alcohol and sodium alginate. This hydrogel was investigated for controlled release of diclofenac sodium (Huua, Mac, Xun, Yanga, & Wang, 2010). IPN type hydrogel based on a natural polymer and a petrochemical based synthetic polymer could result in materials, which combine the mechanical properties of the synthetic polymer with the biological properties of the natural polymer. IPN polymers consist of two or more polymers where at least one polymer is crosslinked. Due to entanglement of the networks of the constituent polymers, IPN based hydrogels are of excellent mechanical strength. In recent times various IPN type hydrogels based on sodium alginate

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were synthesized for different applications. Solpan et al. prepared semi-IPN of sodium alginate and acrylamide and used this hydrogel for separation of several textile dyes from water (Dilek, Murat, & Guven, 2008). Kulkarni et al. synthesized IPN of polyvinyl alcohol and sodium alginate and used it for controlled release of prazosin hydrochloride from skin (Kulkarni, Sreedhara, Mutalikb, Setty, & Sa, 2010). Wang and Wang grafted sodium alginate with sodium acrylate and prepared semi-IPN with this grafted copolymer and polyvinyl pyrrolidone. This semi-IPN hydrogel was pH sensitive and showed good swelling properties (Wang & Wang, 2010). Horia et al. prepared IPN of sodium alginate and polyacrylic acid by gamma radiation. These hydrogels showed excellent sorption for heavy metal ions such as copper, cobalt and nickel (Horia et al., 2008).

It transpires from the above discussion that IPN of sodium alginate has been used as adsorbent for various applications. In the present work acrylic acid and hydroxy ethyl methacrylate monomers were copolymerized *in situ* in the matrix of water soluble sodium alginate by free radical polymerization. The copolymer was crosslinked with MBA. Accordingly, several semi-IPNs were made by varying crosslinker concentration, initiator concentration and % of sodium alginate in water. For these hydrogels molar ratio of acrylic acid and hydroxy ethyl methacrylate was fixed at 5:1. IPN were also made by copolymerizing sodium acrylate and hydroxy ethyl methacrylate in sodium alginate with same comonomer ratio (5:1). These semi-IPN hydrogels were characterized by carboxylic content, swelling characteristics, network parameters, FTIR, SEM, XRD, DTA–TGA and mechanical properties. These hydrogels were used for adsorption of two important synthetic dyes, i.e. Congo red and methyl violet from water. Both of these industrial dyes are extensively used for coloring products (Banat, Nigam, Singh, & Marchant, 1996; Li, Xu, Wang, Chen, & Feng, 2009). These dyes are highly soluble in water with high tinctorial values. Further, because of the presence of complex aromatic rings in its structures, these dyes are not biodegradable (Li et al., 2009). Thus, in the present work the semi-IPN hydrogels were used for adsorption of these industrially important synthetic dyes from water.

2. Materials and methods

2.1. Materials

Monomers i.e. acrylic acid (from Fluka), hydroxyethyl methacrylate (from Fluka), N,N'-methylenebisacrylamide (MBA, from Fluka), redox initiator pair i.e. ammonium persulfate (APS, from Fluka), sodium metabisulfite (SMBS, Merck), Congo red and methyl violet dye were of analytical grade and used without further purification. Natural polymer sodium alginate (average molecular weight 500,000 and degree of deacetylation 84%) was procured from Merck and used as it is without any further purification.

2.2. Methods

2.2.1. Preparation of hydrogel

Copolymer hydrogels were prepared by free radical cross-link copolymerization of acrylic acid and hydroxyl ethyl methacrylate in presence of crosslinker comonomer MBA. The polymerization reaction was carried out in a three necked glass reactor equipped with a mechanical stirrer, reflux condenser and thermometer. The dissolved oxygen of the reaction mixtures was removed by purging nitrogen gas for half an hour in the reaction mixtures before addition of the reacting monomers and crosslinker. After addition of the monomers and crosslinker the temperature of the reaction mixtures was raised to 60 °C with addition of required amounts of redox pair of initiator i.e. ammonium persulfate and sodium metabisulfite. The reaction was then continued at this temperature

till the reaction mixtures gelled. For synthesizing the IPN hydrogel, the hydrophilic natural polymer i.e. sodium alginate was first dissolved in water well for half an hour followed by addition of monomers to this viscous solution and stirring for another half an hour. Copolymerization of acrylic acid and hydroxy ethylmethacrylate were allowed in the solution of sodium alginate in a similar way as in the case of copolymerization of acrylic acid and hydroxy ethylmethacrylate in water. The gel obtained was disintegrated in a blender, washed with water and then isopropyl alcohol, followed by filtration and finally dried to constant weight at 30 °C in a vacuum oven. For synthesizing the IPN hydrogel of sodium salt, sodium acrylate was first made by drop wise addition of 1 M acrylic acid to 1 M sodium hydroxide solution in water kept on an ice bath till complete neutralization occurs. Four kinds of hydrogels as obtained by the above reaction i.e. the hydrogel obtained from copolymer of acrylic acid and hydroxy ethylmethacrylate, sodium acrylate and hydroxy ethyl methacrylate, IPN of copolymer of acrylic acid and hydroxy ethylmethacrylate with sodium alginate and IPN of copolymer of sodium acrylate and hydroxy ethyl methacrylate with sodium alginate were designated as CP, SCP, CPSA_x and SCPSA_x, respectively where *x* is % of sodium alginate in the IPN.

2.2.1.1. Gel content of the hydrogel. The hydrogels as synthesized above were dried in a vacuum oven at ambient temperature to a constant weight (W_i). The dried sample was then kept in deionized water for a week with occasional shaking to remove the water soluble uncrosslink and low molecular weight substances from the gel. It was then taken out from water. This water insoluble gel sample was further dried in vacuum oven to a constant weight (W_d). The percent gelation of IPN gels were obtained as

$$\text{Gel\%} = \frac{W_d}{W_i} \times 100 \quad (1)$$

2.2.2. Characterization of the hydrogels

The synthesized hydrogels were characterized by the following methods.

2.2.2.1. Determination of carboxylic groups present in the hydrogels.

Total amount of free carboxylic groups (COOH, mass% of hydrogel) present in the hydrogels were determined by a method reported elsewhere (Mall, Srivastava, Kumar, & Mishra, 2006; Mandal, Ray, & Bhattacharyya, 2012). Around 0.5 g of hydrogel sample (*w*) was taken in 25 mL 0.1 M NaOH solution and after mixing under magnetic stirring for 2 h it was titrated with 0.1 M HCl solutions. The amount of carboxylic groups (mass%) in the hydrogel was calculated as

$$C = [(C_{\text{NaOH}} \times V_{\text{NaOH}} - C_{\text{HCl}} \times V_{\text{HCl}}) \times 45 \times 10^{-3} \times 100] \quad (2)$$

2.2.2.2. Fourier transform infrared spectroscopy (FTIR).

FTIR spectra of the copolymer hydrogels were recorded on a FTIR spectrometer (Perkin Elmer, model-Spectrum-2, Singapore) using KBr pellet made by mixing KBr with fine powder of the polymer gel samples (10:1 mass ratio of KBr to polymer).

2.2.2.3. Scanning electron microscopy (SEM).

The copolymer and IPN gel samples were coated with gold (Au). The morphology of the gels were observed by using SEM (scanning electron microscope, model no. S3400N, VP SEM, Type-II, made by Hitachi, Japan) with the accelerating voltage set to 15 kV.

2.2.2.4. X-ray diffraction (XRD).

The change of crystallinity of sodium alginate by IPN formation was characterized by X-ray diffraction (XRD). Wide angle X-ray diffraction profile of the hydrogel samples were studied at 25 °C with a diffractometer (model:

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