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Macroporous composite IPN hydrogels based on poly(acrylamide) and chitosan with tuned swelling and sorption of cationic dyes

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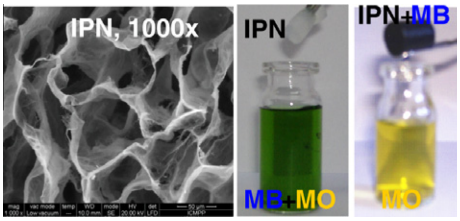
HIGHLIGHTS

- ▶ Macroporous hydrogels by cryopolymerization of acrylamide in presence of chitosan.
- ▶ Anionic full-IPN cryogels by cross-linking of chitosan chains in alkaline medium.
- ▶ Cryogels with high sorption capacity of cationic dyes and high reusability.
- ▶ High selectivity in separation of cationic dyes from the mixture with anionic dyes.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of macroporous ionic composite cryogels consisting of two independently cross-linked and oppositely charged networks is reported in the paper. Semi-interpenetrating network cryogels were prepared first by cross-linking polymerization of acrylamide (AAm) with N,N′-methylenebisacrylamide (BAAm) in the presence of chitosan (CS), under freezing conditions, the main parameters varied being cross-linker ratio (*X*), pH of the CS solution, and CS molar mass. The fraction of CS trapped in the semi-IPN cryogels increased with the increase of both *X* and pH of CS solution. The CS chains trapped in the semi-IPN cryogels have been cross-linked with epichlorohydrin under alkaline conditions, to generate the second network, when a partial hydrolysis of the amide groups in the PAAm matrix simultaneously occurred. Examination of scanning electron microscope images showed inter-connected macropores, in both semi-IPN and full-IPN cryogels. The generation of an anionic matrix during the formation of the second network led to a high sorption capacity of a model cationic dye, methylene blue (MB), by the full-IPN cryogel, around 750 mg dye/g gel, at 25 °C. The benefits of the full-IPN cryogels consist of their high reusability and in the high selectivity in separation of MB from the mixture with methyl orange.

1. Introduction

Hydrogels, by their high water content, are similar to a variety of natural living tissues, and therefore have found large applicability in medicine as artificial organs, cartilage, muscles, immunoinsulation membranes, drug delivery systems [1–5], etc. For many applications, like artificial implants and controlled release systems, multicomponent hydrogels as semi- or full-interpenetrating polymer networks (IPNs) showed improved response rate and diffusion of solutes [6–9]. Considerable interest has been lately focused on the macroporous hydrogels, characterized by a faster response rate at small changes of the external stimuli than the conventional hydrogels. Macroporous hydrogels can be mainly achieved by: cross-linking polymerization in the presence of a pore-forming agent, when a microphase separation occurs [10], porogen leaching [11–14], cross-linking in the presence of substances releasing porogen gases [15], lyophilization of the hydrogel swollen in water [16,17], and cryogelation [18–20]. By cryogelation, the cross-linking polymerization reactions are conducted below the freezing point of the reaction solutions, when the most part of the solvent (water) forms crystals, the bound water and the soluble substances

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(monomers, initiator, polymers) being concentrated in a non-frozen liquid microphase, where the gel is formed. Cryogelation technique has been also used to produce scaffolds with controlled internal microarchitecture by the cross-linking of two polysaccharides under freezing conditions [21]. Advantages of cryogelation in the preparation of hydrogels consist of the absence of any organic porogen, the ice crystals playing the role of inert template, the microstructure of the gel being the negative replica of the ice crystals [18–27]. Thus cryogelation is a low cost and very friendly technique for the fabrication of supermacroporous gels. Not only hydrogels have been prepared by this technique, but also organogels [28].

Cryogels, by their inter-connected pore structure, allow the unhindered diffusion of solutes or even colloidal particles, making them very attractive in biomedicine and biotechnology including chromatographic materials, carriers for the immobilization of molecules and cells, matrices for cell separations, and cell culture [24–28]. Cryogels can withstand high levels of deformations, being also characterized by superfast responsiveness at water absorption [22,29–33]. Ionic cryogels would have potential applications in controlled delivery of drugs and separation processes of small ionic species [34–36].

Poly(acrylamide) (PAAm) is a widely used polymer due to its affinity for proteins and other biomolecules, the presence of amide groups making this polymer susceptible for further reactions [6,8,37]. By their accessibility, biocompatibility, and biodegradability, PAAm hydrogels constitute one of the most investigated matrix in the preparation of semi-IPN hydrogels, achieved by cross-linking polymerization of acrylamide in the presence of synthetic or natural polymers. Such hydrogels have numerous applications, such as drug delivery systems [38,39], soil conditioners, and wastewaters remediation [40]. Chitosan (CS) is a copolymer of N-acetyl-glucosamine and N-glucosamine units distributed randomly or in blocks throughout the biopolymer chain, depending on the processing method used to obtain the biopolymer. By its outstanding properties, such as gel and film forming ability, bioadhesion, biodegradability and biocompatibility, chitosan has received a great deal of attention in the pharmaceutical field [1,3,41]. Due to the high content of amino and hydroxyl functional groups, CS has also drawn attention as a sorbent showing high potential for the adsorption of proteins, dyes, and metal ions [6,37,40].

Last decades, several works have explored the feasibility of PAAm/CS IPN composites for various applications [27,37–39,42–45]. The most part of them refer to the conventional hydrogels [37–39,43,44]. Porous PAAm/CS IPN composite hydrogels have been prepared either in the presence of substances releasing porogen gases during the synthesis [42] or by freeze-drying of the equilibrium swollen gels [45]. Jain et al. reported on the synthesis of PAAm/CS based cryogel matrix in different formats, namely, monolith, disks, and beads used for the cell immobilization in packed-bed bioreactors [27].

Recently we have reported the preparation of conventional ionic hydrogels, using poly(acrylamide) (PAAm) as a matrix and CS as trapped polycation [9]. Preliminary tests on the capacity of these composite gels to adsorb model ionic dyes evidenced some shortcomings consisting of their limited mechanical resistance, which also diminished their applicability in separation processes. Therefore, in this study, cryogelation technique has been adopted to prepare first macroporous composite semi-IPN ionic cryogels based on PAAm as a matrix and CS as trapped polycation. In the second step, full-IPN macroporous composite gels have been generated by the cross-linking with epichlorohydrin (ECH) of the CS chains trapped in the semi-IPN PAAm/CS cryogels, under alkaline conditions, when a partial hydrolysis of the amide groups in the PAAm matrix occurred. A remarkable enhancement of the equilibrium swelling ratio in basic range has been observed in the case of full-IPN cryogel. To demonstrate that negative charges are predominant in the full-IPN, the adsorption/desorption of a model cationic dye, methylene blue (MB), has been investigated as a function of contact duration and initial concentration of the dye. It was also shown that the full-IPN composite cryogels have a selective sorption for MB from its mixture with methyl orange (MO).

2. Experimental

2.1. Materials

The CS as powder, with molar mass of 235 kDa (CS1), purchased from Fluka, and CS with molar mass of 467 kDa (CS2), purchased from Sigma–Aldrich, were used as received. The viscometric average molar mass has been measured in 0.3 M CH_3COOH–0.2 M CH_3COONa (1:1, v/v), at 25 ± 0.1 °C according to the method previously described [46]. Degree of acetylation (DA) of CS has been evaluated by infrared spectroscopy in KBr pellets, using a Vertex 70 Bruker FTIR spectrometer as previously shown [46]. An average value of DA = 15%, resulted from three measurements, has been taken into account for both samples. Acrylamide (AAm, Fluka), N,N′-methylenebisacrylamide (BAAm), ammonium persulfate (APS), N,N,N′,N′-tetramethylethylenediamine (TEMED), all purchased from Sigma–Aldrich, were used as received. ECH purchased from Sigma–Aldrich, has been double distilled on KOH before using. Stock solutions of APS and TEMED were prepared by dissolving 0.2 g of APS and 0.625 mL of TEMED, each in 25 mL of double distilled water. Stock solutions of BAAm were prepared by dissolving BAAm, calculated for a certain cross-linker ratio defined as the mole ratio of the cross-linker BAAm to the monomer AAm, X, in 25 mL of double distilled water, at 30 °C, under magnetic stirring. Methyl orange (MO) was used after three times recrystallization from a 8 wt.% solution in a mixed solvent of water and methanol (1:1 v/v). Methylene blue (MB) from Sigma–Aldrich was used without purification.

2.2. Preparation of PAAm/CS composite cryogels

For the preparation of PAAm/CS composite cryogels, the free radical cross-linking copolymerization of AAm has been performed in the presence of CS, in aqueous medium, at −18 °C. This temperature has been chosen because the previous studies concerning the formation of PAAm cryogels showed that cryogels with enhanced mechanical properties and with large pores of sizes about 70 μm could be obtained [22,29,31]. Also, it was found that the lower the gel preparation temperature, the shorter the time period until the freezing temperature of the reaction solution is reached [22]. This freezing temperature has been also adopted as appropriate in the preparation of other cryogels, both hydrogels [30] and organogels [28]. The redox initiator system used consisted of APS and TEMED. The cross-linker ratio varied in the range 1/80–1/20. The feed composition and the samples code of the composite gels are summarized in Table 1.

The general code of the semi-IPN composite hydrogels consists of the term s-IPN followed by three numbers separated by dots: the first one represents CS1 or CS2, respectively, used as trapped polymer, the second one represents the mole number of AAm per one mole of BAAm, and the third one represents the pH of the CS solution. The general code of full-IPN consists of the term IPN followed by the same numbers like the semi-IPN used for their preparation.

In the synthesis of semi-IPN, the initial concentration of monomers (AAm + BAAm), C_o (5 w/v%), and the concentration of APS and TEMED have been kept constant in all experiments. The synthesis procedure is briefly presented below, taking the sample