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Preparation of cellulose aerogels from ionic liquid solutions for supercritical impregnation of phytol

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ABSTRACT

The use of natural polysaccharides is especially attractive to the pharmaceutical industry because of their stability, availability, renewability and low toxicity. In this study, cellulose aerogels obtained from cellulose/ionic liquid solutions were prepared by supercritical drying with surface areas ranged from 154 to 434 $m^2 g^{-1}$, pore volume from 0.3 to 2.4 $cm^3 g^{-1}$ and pore diameter from 7.9 to 34 nm. Drug loading capacity was investigated by impregnating phytol as model compound into the aerogels, using supercritical CO_2 at 100 bar, 40 °C and mass ratio of phytol per gram of aerogel 10:1. The quantity of drug present is consistent in each aerogel. The aerogel prepared from 2 wt% cellulose in [Emim][DEP] solution showed the highest loading capacity. The high amount of drug loaded (approx 50% w/w) in the cellulose aerogels prepared from ionic liquid solutions shows their potential uses in the pharmaceutical or medical industry.

1. Introduction

Natural polymers are promising materials for preparing polysaccharide-based aerogels with high surface area (70–680 m^2/g) [1]. Among them, cellulose extensively used for the preparation of aerogels [2] namely cellulose aerogels [3–7]. Different applications of cellulose aerogels have been proposed: as carriers of bioactive compounds [8], for protein adsorption [9], oil absorption [4], lightweight shielding material [10] or as food additives [11]. In general, their applications depend on the material properties which can vary with the type of biomass, IL and drying technique. The production of cellulose-based aerogels consists of three main steps:

1) Dissolving cellulose in non-derivatizing solvents such as lithium chloride/dimethylacetamide (LiCl/DMAc), *N*-methylmorpholine-*N*-oxide (NMMO) or ionic liquids (ILs), among other solvents. ILs are a group of salts that are fluid below or around 100 °C. An important advantage of working with ILs is their low vapor pressure: ILs do not evaporate like organic solvents. The most studied cations in cellulose processing are those derived from imidazolium. ILs with alkylmethylimidazolium-based cations combined with chloride, acetate and phosphate anions are known to be good solvents of cellulose [12–17]. There are a number of works in which cellulose aerogels are prepared from ILs. Some works include the study of the different preparation parameters (biopolymer concentration, dissolution time, coagulation temperature) of the cellulose solution and coagulation process on the properties of these aerogels [18,19].
2) The second step in the preparation of the aerogel is the formation of a gel. A cellulose hydrogel can be obtained by soaking homogeneous mixtures of cellulose with ionic liquid into water [20] to cause the coagulation of cellulose. If the solution is soaked into an alcohol (e.g. ethanol) the gel obtained is known as alcogel. The morphology of coagulated microcrystalline cellulose (MCC) in water is similar to the morphology in ethanol as showed by FTIR spectra of regenerated cellulose from the IL 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) [21].
3) After the formation of the hydrogel/alcogel the last step is the removal of the coagulation solvent by drying. Different drying

Abbreviations: [Amim][Cl], 1-allyl-3-methylimidazolium chloride; BET, Brunauer-Emmet-Teller; BJH, Barret-Joyner-Halenda; [Bmim][Cl], 1-butyl-3-methylimidazolium chloride; DSC, differential scanning calorimetry; [Emim][Ac], 1-ethyl-3-methylimidazolium acetate; [Emim][DEP], 1-ethyl-3-methylimidazolium diethyl phosphate; [HOemim][Cl], 1-(2-hydroxyethyl)-3-methylimidazolium chloride; ILs, ionic liquids; LiCl/DMAc, lithium chloride/dimethylacetamide; MCC, microcrystalline cellulose; NMMO, *N*-methylmorpholine-*N*-oxide; SC-CO_2, supercritical carbon dioxide; SEM, scanning electron microscopy

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methods can be used in order to obtain materials with different properties for different applications. These methods include air drying, oven drying, nitrogen freeze drying, regular freeze drying, reduced pressure and supercritical carbon dioxide (SC-CO_2) drying. To obtain cellulose as aerogels, freeze drying and SC-CO_2 drying have been used. As water is not compatible with CO_2, the aerogel's pore structure can collapse, thus the water present in the coagulation solvent media has to be exchanged with an alcohol (usually ethanol) prior drying. To avoid damages to the hydrogel, water replacement is usually performed stepwise using water-ethanol solutions of increasing ethanol concentration.

In this work the influence of different operational parameters on the properties of cellulose aerogels produced using ILs is studied: various alkylmethylimidazolium-based ILs are employed, at low dissolution temperature, and with several cellulose concentrations. In the second part of this work, an impregnation study was performed to determine the loading capacity of the cellulose aerogels with the bioactive compound phytol. Phytol is an acyclic diterpene alcohol, present in green plants and, which is claimed to have antibacterial and anti-inflammatory properties [22–24]. Recently an investigation on SC impregnation of phytol in silica and alginate aerogels resulted in a method to obtain higher loading capacity without the use of organic solvent [25]. The method consists on the adsorption of the active compound to it into a SC-CO_2 saturated with the active compound. The impregnation of cellulose aerogel with phytol has not been described in the literature, but a study has been reported on cellulose acetate aerogels loading capacity with thymol which showed morphology changes with high impregnation yields [26]. In this second part, the cellulose aerogels morphology was analysed before and after the SC impregnation with phytol for possible swelling and/or plasticizing effect of SC-CO_2 and excess of solute on the biopolymer.

2. Experimental section

2.1. Materials

Microcrystalline cellulose was supplied by Alfa Aesar and dried for 5 h at 60 °C under vacuum before the dissolution. Ionic liquids 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) with purity > 99% and moisture of 0.140 wt%, 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([HOemim][Cl]) with purity of > 99% and moisture of 0.214 wt%, 1-ethyl-3-methylimidzolium acetate ([Emim][Ac]) with purity of > 95% and moisture of 0.385 wt% and 1-ethyl-3-methylimidazolium diethyl phosphate ([Emim][DEP]) with purity of 98% and moisture of 0.067 wt%, were provided by Iolitec (Germany). 1-allyl-3-methylimidazolium chloride ([Amim][Cl]) was purchased from Alfa Aesar with purity of 98% and moisture content of 0.247 wt%. The water content was measured by Karl-Fischer titration (Mettler Toledo C20 Coulometric KF titrator).

2.2. Methods

The complete procedure for aerogels preparation is summarized in Fig. 1. Each step is described in following sections.

2.2.1. Preparation of cellulose alcogel

The cellulose solution was prepared by dissolving MCC in IL at 80 °C. Samples were handled under N_2 atmosphere to avoid water absorption. After heating and stirring a clear solution was obtained indicating the total dissolution of cellulose. Then the cellulose/IL solution was transferred to cylindrical moulds (15 mm of diameter and 3 mm high) and washed with an aqueous solution of ethanol at room temperature to extract the IL. The volume of the solution employed was 10 times higher than the IL volume in order to remove the most of it. As a sudden change of the solvent composition can damage the gel structure,

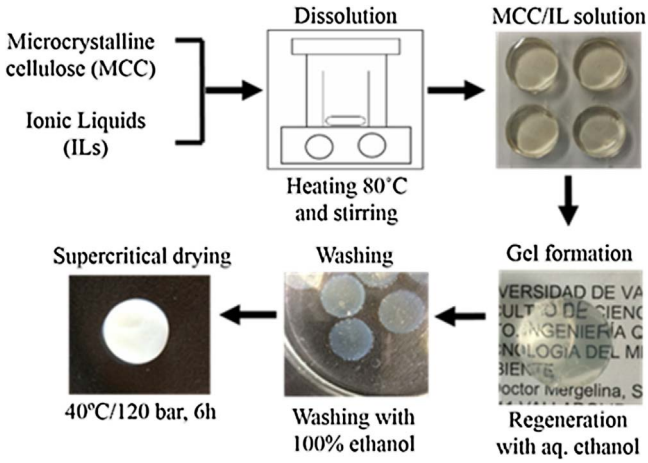

Fig. 1. Scheme of cellulose aerogel preparation in ionic liquid and supercritical drying.

the gels were successively soaked in solutions of increasing ethanol concentration: 10, 30, 50, 90 and 100%, in 2 h cycles. The exchanges with 100% ethanol were done twice to ensure that there is no water residuals left in the alcogel.

2.2.2. Supercritical drying

Cellulose aerogels were produced by SC-CO_2 drying at 120 ± 5 bar and 40 °C. The procedure employed is similar to the method described elsewhere [25,27] where the drying was done in 3 cycles of CO_2 flow, each one lasting 2 h. At the end of each cycle, the extracted ethanol was collected and fresh CO_2 was introduced. After completing the total period of 6 h of SC drying, the system was depressurized at rate of 2 bar/min to avoid shrinkage of cellulose aerogels.

2.2.3. Supercritical impregnation

The impregnation study was performed to determine the loading capacity of the cellulose aerogels with bioactive compounds. A 70 mL stainless steel high pressure autoclave (inner diameter 32 mm and length 80 mm) with a maximum working pressure a temperature of 150 bar and 200 °C respectively, was used. The equipment was manufactured by Eurotechnica GmbH (Hamburg, Germany). A known mass of pure phytol with respect to mass of aerogel was placed at the bottom of the autoclave (10 g of phytol per 1 g of aerogel). Meanwhile a known mass of dried cellulose aerogels was wrapped in metal filters and separated from the phytol by lifting them up from the bottom of the autoclave applying a cylindrical metal platform. The autoclave was heated to 40 °C and pressurized with CO_2 to 100 bar at rate of 2 bar/min. The pressure was maintained for 24 h to ensure that adsorption equilibrium was reached. Magnetic stirrer was employed to additionally enhance the dissolution of phytol. After that time, the system was slowly depressurized at a rate of 2 bar/min to avoid aerogels shrinkage or collapse of the mesoporous structure of the aerogels. The impregnated aerogels were recovered from the autoclave and the loading of compounds was determined gravimetrically and calculated as indicated in the following equation:

$$\frac{w_a\,(g) \;-\; w_b\,(g)}{w_b(g)} \;\times\; 100\%$$

where w_a is the mass of cellulose aerogels after impregnation, w_b is the mass of cellulose aerogels before impregnation (g). This is a common method to determine the weight of such amounts of non volatile compound impregnated in aerogels. Thus, the measurement is precise as phytol does not evaporate after impregnation and before the weight was recorded the impregnated aerogels were placed in a dessicator to let the CO_2 to be properly release from the pores and avoid absorbing moisture from the ambient. The measurement was repeated three times and reported as means ± SD.

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