



Hydroxypropyl methylcellulose based aerogels: Synthesis, characterization and application as adsorbents for wastewater pollutants

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ABSTRACT

Hydroxypropyl methylcellulose (HPMC) E4M and J5MS samples with degrees of substitution of methyl groups (DS) 1.9 and 1.5, respectively, and molar substitutions of hydroxypropyl groups (MS) 0.25 and 0.75, respectively, were used to create aerogels in the presence of citric (cit), oxalic (oxa) or terephthalic (ter) acids, as crosslinkers. E4M-cit, J5MS-cit and J5MS-oxa aerogels presented outstanding stability in water, acid media, alcohols, acetone and hydrocarbons, density values of $\sim(0.020 \pm 0.002) \text{ g/cm}^3$, compressive modulus ranging from $(111 \pm 9) \text{ kPa}$ to $(133 \pm 11) \text{ kPa}$. On the other hand, E4M-oxa, E4M-ter and J5MS-ter aerogels were not adequate adsorbents because they collapsed in water. The adsorption behavior of 17 α -ethinyl estradiol (EE) and methylene blue (MB) onto E4M-cit, J5MS-cit and J5MS-oxa aerogels were fitted to Freundlich model, indicating higher affinity of EE for J5MS-cit and J5MS-oxa and higher affinity of MB for E4M-cit aerogels. HPMC aerogels could be successfully reused.

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1. Introduction

Dyes, drugs (hormones, anti-inflammatories, antibiotics) and phenolic compounds are examples of emerging organic contaminants found in wastewater, rivers and ground water, as result of human and industrial activities. Advanced oxidation process, nanofiltration, reverse osmosis, and adsorption are some strategies for the removal of organic pollutants (Rashed, 2013). Adsorption is one of the most popular of them due to the efficiency, selectivity, low cost, simplicity and possibility of adsorbent recycling. The adsorbent choice should meet some criteria such as large surface area, mechanical stability, possibility of recycling and biodegradability. Grassi and co-workers (Grassi, Kaykioglu, Belgiorno, & Lofrano, 2012; and references therein) showcased an overview about the advantages and disadvantages of natural materials, agricultural waste and minerals (activated carbon, clays) as adsorbents. Among the natural materials, cellulose and cellulose derivatives are attractive due to their large adsorption capacity, renewable origins and biodegradability. Particularly, aerogels made of renewable materials constitute an interesting class of adsorbents

because they present a combination of low density, large surface area and resilience (García-González, Alnaief, & Smirnova, 2011). The physical properties of aerogels depend on the method used for their preparation, solvent used, and presence of reinforcing particles (Siqueira, Bras, & Dufresne, 2010). The aerogel is produced by extracting the solvent of a gel, while keeping the structure of the gel network. Freeze-drying and supercritical drying are the most common methods; in the former the polymer solution is frozen and the solvent is subsequently sublimated under reduced pressure, while in the latter, the solvent used for the polymer dissolution is first exchanged by CO₂ under supercritical conditions and then CO₂ evaporates upon bringing the system back to environmental conditions (Martins et al., 2015).

The application of cellulose based aerogels for solving environmental issues has received much attention due to their low density, low cost, nontoxic and biodegradable properties. For instance, aerogels made of cellulose nanofibrils extracted from rice straw cellulose behaved as super-adsorbents for water and organic solvents; after hydrophobization they served as selective adsorbents for oils (Jiang & Hsieh, 2014). Hydrophobically modified cellulose aerogels prepared in the absence (Feng, Nguyen, Fan, & Duong, 2015; Jin, Han, Li, & Sun, 2015; Wang, Xu, Du, & Wang, 2016) or in the presence of poly(ethylene glycol) of high molecular weight (Wan & Li, 2015a) presented high affinity for oil. Hybrid aerogels composed of cellulose and maghemite particles presented excellent ability

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for Cr(VI) removal from contaminated water (Wan & Li, 2015b). Hybrid aerogels composed of wheat straw cellulose, polypyrrole and silver nanoparticles presented antibacterial properties upon contact with microorganisms (Wan & Li, 2016). Cellulose aerogels are materials with outstanding mechanical properties and large sorption capacities, but scarce literature about aerogels made of cellulose ethers (He, Sui, He, & Li, 2015), such as hydroxypropyl methylcellulose (HPMC), was found. HPMCs are interesting materials because their hydrophobic/hydrophilic character can be controlled by the degree of substitution (DS) of methyl groups and molar substitution (MS) of hydroxypropyl groups in the cellulose chains. Moreover, HPMCs nontoxicity and physicochemical properties allow their application in food and drug formulations (<http://www.fda.gov/Food/IngredientsPackagingLabeling/GRAS/NoticeInventory/ucm153856.htm>). In the present work, aerogels were prepared with two HPMC samples with different DS and MS, in the presence of three different crosslinkers, by slow freeze-drying. Oxalic, terephthalic and citric acids were used as crosslinkers. Oxalic and terephthalic acids are hydrophilic and hydrophobic diprotic acids, respectively, and citric acid is a triprotic hydrophilic acid. Thus, one aim of the present study was to investigate how the chemical nature of crosslinkers would affect the properties of the resulting aerogels made of HPMC chains with different hydrophobic/hydrophilic characters. The physicochemical and mechanical properties of HPMC aerogels and their efficiencies to remove 17α -ethinyl estradiol, a hormone, and methylene blue, a dye, from contaminated water were evaluated, as well as the possibility of aerogels recycling. The choice of contaminants was based on their relevance for environmental issues. One major environmental problem related to 17α -ethinyl estradiol, which is the principal component in contraceptive pills, is that its release to ground water and rivers in concentration as low as 2 ng/L causes alterations in reproduction or development of fishes because it acts in their endocrinal systems (Snyder, Westerhoff, Yoon, & Sedlak, 2003; Ankley et al., 2009). Although methylene blue is not an US FDA-approved drug due to the limited data about serotonergic effects, it has been used for medical purposes, as for instance, for treatment of methemoglobinemia, encephalopathy or cyanide poisoning, with doses smaller than 10 mg/kg (<http://www.fda.gov/Drugs/DrugSafety/ucm276119.htm>). On the other hand, the use of methylene blue as a dye for textiles might cause ground water and rivers contamination; depending on the level of contamination, water consumers and species living in the contaminated medium might suffer toxicological effects (Vutskits et al., 2008).

The present study considers the hypothesis that structural aspects of HPMC chains, distinct DS and MS values, in combination with different crosslinkers as di- or triprotic acids yield aerogels with different physical chemical properties and affinities for 17α -ethinyl estradiol and methylene blue.

2. Experimental

2.1. Materials

Commercial HPMC samples coded as E4M and J5MS were kindly supplied by The Dow Chemical Company (Brazil); their characteristics are presented in Table 1. Citric acid (Labsynth, Brazil, 192.12 g/mol), oxalic acid (Labsynth, Brazil, 90.03 g/mol), terephthalic acid (Labsynth, Brazil, 166.13 g/mol), sodium hypophosphite (Labsynth, Brazil, 87.98 g/mol), methylene blue (MB, M9140 Sigma Aldrich, 319.85 g/mol) and 17α -ethinyl estradiol (EE, E4876 Sigma Aldrich, 296.40 g/mol) were used without further purification. MilliQ water was used in all experiments. The chemical structures of HPMC, citric acid, oxalic acid, terephthalic acid, MB and EE are schematically represented in Fig. 1.

2.2. HPMC aerogels preparation

First HPMC aqueous solutions at 20 g L^{-1} (2 wt%) in the presence of crosslinker (citric acid or oxalic acid or terephthalic acid) at 1.0 g L^{-1} and sodium hypophosphite at 0.5 g L^{-1} were prepared. One should note that using cold water ($\sim 10^\circ\text{C}$) as solvent and vigorous stirring favor the HPMC dissolution. At lower temperature the dispersive forces among the HPMC chains are weaker, favoring the contact among water molecules and polymer chains and, thus the mixture enthalpy. At 25°C the solubilities of terephthalic acid, oxalic acid and citric acid in water are 0.015 g/L, 98.1 g/L and 383 g/L, respectively (<http://pubchem.ncbi.nlm.nih.gov/compound/311#section=Computed-Properties>). In the case of terephthalic acid, it was first dissolved in a small volume (typically 0.5 mL/L) of NH_4OH 10% v/v, then it was added dropwise to the HPMC solution and then the medium pH was adjusted to pH 7 with HCl 10% v/v, without any visible aggregation or phase separation.

The concentrations of crosslinker and sodium hypophosphite were chosen based on previous reports (Bueno, Bentini, Catalani, & Petri, 2013; Bueno & Petri, 2014; Marani, Bloisi, & Petri, 2015; Reddy and Yang, 2010;). The solutions were poured into molds made of polypropylene with dimensions of $2.5\text{ cm} \times 1.7\text{ cm} \times 1.3\text{ cm}$ (height) and frozen at -18°C , during 4 h (slow freezing). After that, the frozen samples were freeze-dried in a LT600 Terroni (Terroni, São Carlos, Brazil) equipment for 24 h. After freeze-drying, crosslinking of HPMC chains with the acid was achieved by heating the aerogels at 165°C for 7 min (Bueno et al., 2013). The crosslinking results from esterification reactions between crosslinker acid groups and HPMC hydroxyl groups, catalyzed by sodium hypophosphite, with release of water molecules (Xinhao et al., 2014; Marani et al., 2015). The temperature used is sufficient to promote the esterification reaction and it is far below the polymer decomposition temperature (Table 1). The unreacted sodium phosphite, crosslinker and HPMC molecules were removed by dialysis against MilliQ water. The conductivity of the external medium was measured periodically. The external MilliQ water was exchanged by fresh MilliQ water until the conductivity achieved $\sim 5\ \mu\text{S/cm}$. After that, the aerogels were freeze-dried again and characterized. Considering that two types of HPMC and three types of crosslinkers were used, six different types of aerogels were prepared at all. They were coded as E4M-cit, E4M-oxa, E4M-ter, J5MS-cit, J5MS-oxa and J5MS-ter, where cit, oxa and ter stand for the crosslinkers citric acid, oxalic acid and terephthalic acid, respectively.

2.3. HPMC aerogels characterization

The apparent density of aerogels was determined at $(24 \pm 1)^\circ\text{C}$ by dividing the mass of freeze-dried aerogels by the corresponding volume, which was estimated by their dimensions. The mean apparent density values correspond to the average of at least 25 aerogels samples of same type. The chemical stability of HPMC aerogels was tested by immersing them in methanol, ethanol, isopropanol, cyclohexane, chloroform, HNO_3 2.0 M, NaOH 0.01 M and water. All organic solvents were supplied by LabSynth (Brazil) with 99.9% purity. SEM analyses were performed in a Jeol microscope FEG7401F equipped with a Field-Emission Gun. Samples were prepared by cryo-fracturing freeze-dried aerogels. The cryo-fractured surfaces were analyzed after gold coating (sputtering) with the equipment operating at voltage of 5 kV. The compressive tests were performed for 50 aerogels samples of same type using an Impac, Digital Dynamometer IP-90DI, with a 10 N load cell, at strain rate of 0.01 s^{-1} and at room temperature. The capillary constant (C_w) was determined with a Krüss K100 precision tensiometer (Krüss, Hamburg Germany), in the sorption mode, at 20°C , using *n*-hexane as test liquid, and the Washburn equation (Eq. (1)) (Galet Patry, &

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