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A facile approach to fabricate porous nanocomposite gels based on partially hydrolyzed polyacrylamide and cellulose nanocrystals for adsorbing methylene blue at low concentrations

Chengjun Zhou [a], Sunyoung Lee [b], Kerry Dooley [c], Qinglin Wu [a,*]

[a] School of Renewable Natural Resource, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA
[b] Department of Forest Products, Korea Forest Research Institute, Seoul, Republic of Korea
[c] Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

HIGHLIGHTS

- Nanocomposite gels were fabricated using electrospinning and thermal treatment.
- Partially hydrolyzed polyacrylamide and cellulose nanocrystals were used in the gels.
- The electrospun nanofibers comprised 3D porous gels with a porosity of more than 50%.
- The gels displayed a rapid swelling rate and an efficient adsorption capacity.

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ABSTRACT

Porous nanocomposite gels were fabricated by a facile method consisting of the electrospinning and subsequent heat treatment based on partially hydrolyzed polyacrylamide (HPAM) of ultra-high molecular weight, with cellulose nanocrystals (CNCs) as crosslinker. The effects of three electrospinning parameters (i.e., solution concentration, composition of solvent mixture, and CNC loading level) on morphology and diameter of electrospun fibers were systematically investigated. The swelling properties of porous gels and their application in the removal of methylene blue dye (as a compound representative of contaminants) were evaluated. Electrospun fiber morphologies without beads, branches, and ribbons were achieved by optimizing the electrospinning solutions. The thermal crosslinking between HPAM and CNCs was realized through esterification, rendering the product nanocomposite membranes insoluble in water. Electrospun fibers of approximately 220 nm in diameter comprised the 3D porous nanocomposite gels, with porosity greater than 50%. The porous nanocomposite gels displayed a rapid swelling rate and an efficient adsorption capacity in removing methylene blue at low concentrations from aqueous solutions.

1. Introduction

Polyacrylamide (PAM) gels have been widely used in various fields including the petroleum industry for enhanced oil recovery [1,2], agriculture for agrochemical controlled release [3], and biomedicine for tissue engineering [4,5]. Particular attention has been paid to the utilization of PAM gels as superadsorbents in water and wastewater treatments for the removal of organic and inorganic pollutants from aqueous solutions [6,7]. Because of PAM's unusual chemistry and structure, PAM gels have become among the most versatile adsorption materials for water purification. The amide ($-CONH_2$) side groups in PAM are active sites to remove soluble heavy metal species from water by coordination and chelation [8]. In addition, when the amide groups are partly converted to carboxylates by hydrolysis [9], the anionic PAM gels obtained can adsorb and trap cationic dyes, such as methylene blue (MB) and methyl violet, from wastewater.

In recent years, many adsorbents based on PAM gels have been developed exhibiting high adsorption capacity, fast adsorption rate, and excellent mechanical strength. Almost all investigations have focused on the formation of hybrids, blends, and composites of PAM gels combined with other functional components such as clay [10,11], poly(2-acrylamido-2-methylpropanesulfonic acid) [12], methylcellulose [13], and chitosan [14]. Most adsorbents made use of the conventional gels, modifying the other component, but other strategies, such as adjusting the microstructure of

* Corresponding author. Tel.: +1 225 578 8369; fax: +1 225 578 4251.
E-mail address: wuqing@lsu.edu (Q. Wu).

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the composite adsorbents, were seldom exploited [15,16]. Recently, Dragan et al. [17] reported macroporous composite cryogels based on polyacrylamide and chitosan had a fast adsorption rate for cationic dyes, attributed to the high porosity of the cryogels.

Electrospinning is one of the most popular and facile methods to produce 3D porous membranes for various applications. PAM of high molecular weight has been electrospun to membranes with a variety of morphologies, including beads, beaded fibers, smooth fibers, and ribbons [18], and were crosslinked into fibrous gels by glutaraldehyde with a complex procedure [19].

Our approach in this study was to produce the porous PAM-based gels by the electrospinning technique and the subsequent crosslinking. The specific objective of this research was to develop a facile fabrication method for porous PAM-based nanocomposite hydrogels by using partially hydrolyzed polyacrylamide (HPAM) with ultra-high molecular weight (more than 10^7 Da) as matrix and cellulose nanocrystals (CNCs) as crosslinker. Considering that the cellulose hydroxyl groups on the CNC surfaces are capable of reacting with the carboxyl side groups of HPAM to form ester linkages by heat treatment [20], it was anticipated that the crosslinking of CNCs and HPAM could render the composite gels water-soluble. Moreover, using HPAM with ultra-high molecular weight could easily generate an effective density of network junctions even at a low of crosslinking density [21].

In this work, porous HPAM/CNC nanocomposite membranes were prepared by investigating the effect of three electrospinning parameters (i.e., concentration of HPAM, solvent system, and CNC loading level) on morphology and diameter of electrospun fibers. The membranes fabricated were heat-treated to form gels. The crosslinking reaction and swelling properties of the gels, as well as their application in the removal of the cationic dye MB, used as a model compound for contaminants, were evaluated. MB is a typical dye with a heterocyclic aromatic molecular structure, and has been used in many industries such as textiles and paper. However, its direct discharging may lead to environmental problems because MB is stable and difficult to biodegrade in natural conditions [22]. To reduce the harmful impacts of MB on receiving waters, it is necessary to treat effluent containing such dye.

2. Experimental

2.1. Materials

Anionic HPAM with anionicity (the fraction of units in HPAM which have been hydrolyzed) of 10% and a molecular weight of 12–13 × 10^6 Da was supplied by SNF Inc. (Andrezieux, France) under the trade name FLOPAM AN 910 SH. HPAM is a white granular solid with a bulk density of approximately 0.8 g mL^{-1} and a solid content of 92–94%, and was dried under vacuum at 80 °C for 24 h before use. CNCs derived from cotton fabrics were prepared by a combined process of acid hydrolysis with 64% H_2SO_4 and high-pressure homogenization according to our previous report [23]. The product CNCs had length ranging from 40 to 120 nm and an average diameter of approximately 10 nm. The aqueous solutions and suspensions in all experiments were prepared with deionized water. Ethanol of A.C.S. grade and MB were purchased from Sigma–Aldrich Inc. (St. Louis, MO, United States).

2.2. Preparation of solutions for electrospinning

Pure HPAM solutions were prepared at 25 °C under constant magnetic stirring for at least 12 h. For HPAM/CNC suspensions, a certain amount of HPAM was added into CNC suspension with or without ethanol followed by stirring for more than 12 h. Ethanol was used to reduce the viscosity and to increase the evaporation rate of electrospinning solutions. Table 1 presents the preparation conditions of solutions or suspensions for electrospinning.

2.3. Fabrication of fibrous membranes

Three variables in electrospinning PAM solutions and PAM/CNC suspensions, i.e., PAM concentration, solvent system, and solid content of CNCs, were investigated, as shown in Table 1. The electrospinning solutions or suspensions were transferred to a plastic syringe of 5 mL with a 20 gauge (inner diameter = 0.584 mm) needle. The needle was connected to a high voltage power supply (Gamma High Voltage Research, Inc., Ormond Beach, FL, United States), which generates a positive DC voltage of 15 kV. The flow rate of the solutions or suspensions was controlled at 0.4 mL h^{-1} by a Chemyx Fusion 100 syringe pump (Stafford, TX, United States). The distance between the needle and the collector plate was 20 cm. A circular plate of aluminum with a diameter of 15 cm was used as the collector. To obtain the test samples with structures controlled as much as possible, all electrospun fibrous membranes were produced from 2 mL of the corresponding electrospinning solutions or suspensions with the spinning conditions stated above, at 60% relative humidity and 25 °C. The membranes obtained were vacuum-dried at 60 °C for 12 h, and then stored in a desiccator prior to characterization. The membranes were designated as HPAM*x* or HPAM*x*/C*y*-*MA*, where *x* (wt.%) is the concentration of HPAM (C_{HPAM}) in the solution, *y* (wt.%) is the content of CNCs (C_{CNC}) based on the weight of HPAM, and *MA* is the mass ratio of water to ethanol in the mixture solvent. For example, HPAM2/C10-4/1 refers to a membrane electrospun from a suspension of 2 wt.% HPAM and 10 wt.% CNCs (i.e., 0.1 times the weight of HPAM), where the solvent is a mixture of water and ethanol with a mass ratio of 4 to 1.

To perform the crosslinking of electrospun HPAM/CNC fibrous membranes, the samples were heat-treated in a GSL-1100X tube furnace (MTI Corporation, Richmond, CA, United States) at 150 °C for 1 h under nitrogen atmosphere [20].

2.4. Characterization

Electrical conductivities of the electrospinning solutions were measured at room temperature by using a Jenway Model 4330 conductivity & PH meter (Bath, United Kingdom). The electrospun fibrous membranes was sputter coated with gold for 2 min and examined using a field emission scanning electron microscopy (FESEM, a FEI Quanta 3D FEG dual beam SEM/FIB system, Hillsboro, OR, United States) at a 5 kV accelerating voltage. The average fiber diameters were calculated from 100 measurements of individual fibers by the analysis of SEM images using ImageJ 1.46 software (http://rsb.info.nih.gov/ij/). ImageJ was also used to calculate an approximate pore diameter of membrane based on SEM micrographs. Fourier transform infrared (FTIR) spectra of electrospun membranes were measured using a Bruker FTIR analyzer (Tensor-27, Bruker Optics Inc., Billerica, MA, United States) in attenuated total reflectance (ATR) mode. Each spectrum was acquired in a transmittance mode on a Zn/Se ATR crystal cell by accumulation of 64 scans with a resolution of 4 cm^{-1} and a spectral range of 4000–600 cm^{-1}.

The porosity of the gels was calculated according to the following equation [24]:

$$\text{Porosity } \% = \left(1 - \frac{\rho}{\rho_0}\right) \times 100 \quad (1)$$

where ρ and ρ_0 (g mL^{-1}) are densities of fibrous membrane and casting film samples, respectively. Density was calculated as weight divided by volume. HPAM/CNC films were prepared by casting suspensions into a Petri dish followed by drying in open air at 45 °C.

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