



Evaluation of thermally crosslinkable chitosan-based nanofibrous mats for the removal of metal ions



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ABSTRACT

Environmentally sensitive composite nanofibrous mats capable of metal ion adsorption were successfully prepared via electrospinning. The composite nanofibers were fabricated with different ratios of chitosan to thermo-responsive polymer, poly(*N*-isopropylacrylamide-*co*-*N*-methylolacrylamide) (poly(NIPAAm-*co*-NMA), PNN). NMA provided the function of thermal crosslinking of the nanofibrous mats to form water-stable nanofibers in aqueous solution. Subsequently, glutaraldehyde was used as a secondary crosslinking agent to increase the gel fraction of the nanofibrous mats. The morphology changes of the nanofibers in different environments were studied. Comparing the nanofibrous mats and films of the same material, the fibrous mats showed significantly increased adsorption of Cu(II). The adsorption amount of Cu(II) on the chitosan/PNN (50/50) nanofibrous mats could reach 79 ± 2 mg/g-mats, and its desorption was relatively effective. The incorporation of poly(NIPAAm-*co*-NMA) significantly improved the desorption of Cu(II) from the nanofibrous mats. The chitosan/PNN fibrous mats maintained the capacity of Cu(II) adsorption for 4-time regeneration.

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1. Introduction

Heavy metals are highly toxic and exist in the aqueous waste streams of many industries. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Of all the heavy metal ions, copper (Cu) and nickel (Ni) ions are usually considered as the model ions (Bailey, Olin, Bricka, & Adrian, 1999). Treatment processes for waste streams include chemical precipitation, membrane filtration, ion exchange, and carbon adsorption (Babel & Kurniawan, 2003). Recently, cheap agricultural wastes such as rice straw, bark, wool, and coconut husks have been highlighted as potential adsorbents for metal ion removal from wastewater (Crini, 2005). Minamisawa, Minamisawa, Yoshida, and Takai (2004) used chitin and chitosan for the adsorption of metal ions such as Cu(II), Cd(II), and Pb(II). Chitin is universally present in the exoskeletons of arthropods and is manufactured on a large scale from crab and shrimp shell wastes. Chitin and chitosan are nontoxic and readily biodegradable and hence are environmentally acceptable.

Chitosan is one of the most extensively studied polysaccharides. It is generally derived from chitin by alkaline deacetylation. Chitosan is a random copolymer composed of (1 → 4) linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose units. It is a pH-responsive polymer because of its amino groups along the chain. It can be dissolved in acidic solution due to the protonation of its amino group on the C-2 position of pyranose, and it then becomes a cationic pH-sensitive polyelectrolyte. It is also a low-cost biosorbent with a high adsorption capacity for metal ions (Ngh, Teong, & Hanafiah, 2011).

Electrospinning is a technique for manufacturing nanofibrous mats from a variety of synthetic or natural polymers (Sill & von Recum, 2008). The process begins with a polymer solution in a syringe, held at the end of the needle by its surface tension. A high-voltage charge is then induced on the needle by an external electric field. As the applied electric field is increased, the created charges directly oppose the surface tension. At a critical value, these forces cause the formation of a protruding conical shape known as the Taylor cone at the tip of the needle (Reneker & Yarin, 2008). Beyond this critical value, the electric field causes the charges to overcome the surface tension, and a charged jet of solution is formed. As this jet travels in the air, it experiences instabilities and follows a spiral path as the solvent evaporates, leaving behind a charged polymer fiber that is deposited onto the collector.

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Poly(*N*-isopropylacrylamide) (PNIPAAm) is a thermo-responsive polymer; it has a phase transition temperature, also known as the lower critical solution temperature (LCST), at approximately 32 °C (Binkert, Oberreich, Meewes, Nyffenegger, & Ricka, 1991). The transition from a hydrophilic to a hydrophobic structure occurs dramatically at the phase transition temperature (Schild, 1992). However, the application of polymer nanofibers of PNIPAAm and chitosan has been hindered by their relatively rapid dissolution in water at room temperature. *N*-(methylol acrylamide) (NMA) is a bifunctional monomer containing a self-condensable methylol group and a reactive double bond (Huglin & Radwan, 1991). Therefore, it could be copolymerized with NIPAAm and provided the function of thermal crosslinking.

The aim of this study was to develop water-stable chitosan/poly(NIPAAm-co-NMA) (PNN) nanofibrous mats as adsorbents for the removal of metal ions. First, the thermally crosslinkable copolymer PNN was synthesized. Subsequently, chitosan/PNN nanofibers were fabricated via electrospinning. The morphologies of the chitosan/PNN nanofibers were observed by SEM. Additionally, Cu(II) and Ni(II) were used as model ions, and the adsorption and desorption of metal ions on the chitosan/PNN nanofibrous mats were studied in aqueous solution.

2. Experimental

2.1. Material

Chitosan (degree of deacetylation 83% (Desai, Kit, Li, & Zivanovic, 2008), molecular weight (*M_w*) 223 kDa) and *N*-methylol acrylamide (NMA; 48 wt% in water) were obtained from Sigma-Aldrich (St. Louis, MO, USA). *N*-isopropylacrylamide (NIPAAm), 2,2'-azobisisobutyronitrile (AIBN), trifluoroacetic acid (TFA), dichloromethane (DCM), glutaraldehyde solution (GA; 25 wt%), CuSO₄·5H₂O, NiSO₄·6H₂O, and nitric acid (70%, trace metals basis) were acquired from Acros Organic (Geel, Belgium). AIBN was recrystallized from ethanol. All other chemicals were at least of analytical grade and were used without the need of further purification.

2.2. Synthesis of poly(NIPAAm-co-NMA) (PNN)

To maintain the nanofibrous structure of the soaked nanofibers, a thermally crosslinkable monomer, NMA, was introduced into the copolymer. NIPAAm (30.55 g) and NMA solution (48 wt%; 6.32 g) were dissolved in 118 mL of methanol; the molar ratio of NMA to NIPAAm was 10:90. The solution was purged with nitrogen and heated to 60 °C. AIBN (0.0616 g) was dissolved in 2 mL of methanol and poured into the solution. Polymerization was carried out at 60 °C for 24 h. The resulting solution was subjected to dialysis (3000 Da molecular weight cut-off) at room temperature for 72 h in a series of methanol/deionized (DI) water mixtures (100%, 70%, 50%, and pure water for 3 times, 12 h for each step) to remove the residual initiator and unreacted monomer. The final dialyzed product was dried by lyophilization. The total monomer conversion (*X*, %) was calculated by gravimetric analysis using the following equation:

$$X = \frac{W_{\text{dry}}}{W_{\text{NIPAAm}} + (0.48 \times W_{\text{NMA}})} \quad (1)$$

where *W_{NIPAAm}* and *W_{NMA}* are the weights of NIPAAm monomer and NMA solution in the feed, respectively. The number of 0.48 is the weight concentration of the NMA solution. *W_{dry}* is the weight of the PNN polymer after lyophilizing for 72 h.

2.3. Preparation of the chitosan/PNN nanofibrous mats

The chitosan/PNN nanofibers were fabricated via electrospinning using TFA/DCM as a cosolvent, in which the weight ratio of TFA to DCM was 73 to 27. First, PNN and chitosan were separately dissolved in the cosolvent at equal concentrations of 2.5 wt%. The two solutions were blended at different weight ratios (CS/PNN = 100/0; 75/25; 50/50; 25/75; 0/100). The viscosities of the electrospun solutions were measured by viscometer (Brookfield DV-E, USA). The solution was filled in a syringe and pumped into a needle at a rate of 1 mL/h by a syringe pump (KD Scientific Model 100, USA). A high-voltage charge (14 kV) was then induced on the needle via a high voltage supply (Chargemaster CH30P, SIMCO, USA). As the applied electric field was increased, a charged jet of solution was formed. As this jet traveled in the air, it experienced instabilities and followed a spiral path while the solvent evaporated, leaving behind a charged polymer nanofiber that was deposited onto the collector. The distance from the needle tip to the collector was 12 cm. All electrospinning was carried out at room temperature.

2.4. Crosslinking of the nanofibers

In this study, two crosslinking reactions were carried on: thermal crosslinking for the PNN copolymer and the crosslinking of chitosan chains by glutaraldehyde vapor. PNN is a thermally crosslinkable copolymer, which led to the formation of a bis(methylene ether) and then of a methylene bridge by eliminating water and formaldehyde, respectively. First, the chitosan/PNN nanofibrous mats were baked at 110 °C for 48 h. Second, the chitosan/PNN nanofibrous mats were crosslinked via GA vapor. The nanofibrous mats were placed in a vacuum chamber with a bottle containing 10 mL of 25 wt% glutaraldehyde solution, and then the chamber was evacuated until the first bubble was present in the solution at 25 °C. After 7 h, the weights of the crosslinked nanofibrous mats were measured and noted as *W₀*. Sequentially, the mats were washed and brought to a pH of 4 for 2 days; the weights of the swollen mats were noted as *W_s*. Finally, the chitosan/PNN nanofibrous mats were dried by lyophilization and made ready for the adsorption studies; the weights of the dried mats were noted as *W_d*. The swelling ratio and gel fraction were calculated by Eqs. (2) and (3).

$$\text{Swelling ratio} = \frac{W_s}{W_d} \quad (2)$$

$$\text{Gel fraction} = \frac{W_d}{W_0} \quad (3)$$

2.5. Morphology

The morphologies of the crosslinked nanofibrous mats were observed by scanning electron microscopy (SEM; JOEL JSM-6700F). A small section of the fibrous mats was placed on the SEM sample holder and sputter-coated with platinum. Furthermore, morphology changes of the mats which were soaked at various pH values and temperatures were studied. The mats were immersed in various environments (25 °C pH 2, 70 °C pH 2, and 25 °C pH 10) for 24 h. Then, the mats soaked at 25 °C were dried by lyophilization, and those soaked at 70 °C were dried by vacuum oven at 70 °C.

2.6. Phase transition temperature

The phase transition temperature was measured by differential scanning calorimetry DSC (TA Q20 System, USA). The PNN copolymer was dissolved in deionized water adjusted to pH 4 by HCl at

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