Characterization of cellulose-based electrospun nanofiber membrane and its adsorptive behaviours using Cu(II), Cd(II), Pb(II) as models

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Nanofiber membranes from the composite of cellulose acetate/polyvinylpyrrolidone were prepared using electrospinning technique. After treated with water and alcoholic KOH to remove partially polyvinylpyrrolidone and deacetylate the cellulose acetate, the membranes were further functionalized with thiol groups using thioglycolic acid. Related materials were characterized using infrared and thermogravimetric analysis. And the results showed that the membranes were success of functionalisation. Then the nanofiber membranes were used in the sorption-desorption process. The effects of pH, contacting time and adsorption capacity of nanofiber membranes were studied against Cu(II), Cd(II) and Pb(II) ions. And the maximum adsorption capacities of Pb (II), Cu (II), and Cd (II) ions were estimated at 30.96, 19.63, 34.70 mg g⁻¹. Our results suggested that the adsorption behaviour of metal ions could be described using Langmuir model. Their adsorption kinetics was in agreement with the model of pseudo-second order, suggesting chemical adsorption as the rate-limiting step of the adsorption mechanism. The durability of the thiol-functionalized cellulose nanofiber membranes was also evaluated by repetitive adsorption-desorption.

electrospinning nanofiber, characterization, thioglycolic acid, heavy metal ions, adsorption

1 Introduction

Heavy metals and their compounds are widely involved in industries and it is inevitable that metal-contaminated materials are released into our environment, which has posed a great threat on environmental safety and human health. Therefore, the removal of heavy metal ions from contaminated water has attracted particular attention. Recent research has been focused on the application of materials for adsorption and separation of heavy metal ions in addition to electroplating, ion exchange and membrane separation [1–4] since adsorption is regarded as one of the most effective and cost-efficient approaches in this regard. A variety of adsorbents, for example, activated carbons [5], natural zeolites [6, 7], biosorbents [8, 9], and chelating materials [10], have been employed for the adsorption of metal ions. Among the factors which affect the adsorption capacity, efficiency and durability, surface area is the most important one. To this end, nanomaterial is of great interest because of their high specific area.

Electrospinning is a technology for preparation of ultralong one-dimensional fibre materials with diameters in the scale of nanometer, which exhibits high specific area. Therefore, electrospinning membrane may have a great potential for the adsorption of metal ions. It is well known that electrospinning nanofibers have found applications in biomedicine [11–13], tissue engineering [14, 15] and armored fabric materials [16]. Introduction of functional groups onto the surface of electrospinning nanofibers could further improve their utilization as adsorbents to remove heavy metal
ions. Indeed, sulfanyl group [17], carboxyl [18, 19], amino [20, 21], thiol group [22, 23], and thioether group [24] have been used and resultant materials showed excellent adsorption capacity towards metal ions, for example, Cu(II) [25], Cr(VI) [26], Cr(III) [27, 28].

Cellulose acetate (CA) is a useful material in industry with applications in the fields of coating, film and membrane separation. Through electrospinning, CA can also be transformed into nanofiber materials. In electrospinning, choosing appropriate solvent is vital because the solvent dictates not only whether a material can be electrospun into nanofibers, but also the quality of the nanofibers. It was reported that a mixed solvents of acetone/dimethyl acetylamide (DMAc) (2/1) was the most versatile solvent for the electrospinning of CA [29]. CA can also be mixed with other polymers to produce nanofibers, for example, CA/Polyvinylpyrrolidone (PVP) fibres were successfully prepared using electrospinning [30].

In this work, we further explore the composite of CA/PVP by functionalizing with thiol groups. Nanofiber membranes were prepared using a mixture of CA/PVP via an electrospinning technique. Subsequently, the PVP of the membranes was partially removed and the CA was further deacetylated before functionalization with thiol groups. Characterization of the obtained nanofibers was completed using infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis. The adsorption behaviors and kinetics of the materials towards selected metal ions, Cu(II), Cd(II) and Pb(II), were investigated. The durability of the material was estimated using repetitive adsorption-desorption.

In our work, nanofiber membranes were prepared using an electrospinning technique, and then the membranes were treated with water and alcoholic KOH to partially remove polyvinylpyrrolidone and deacetylate the cellulose acetate in order to increase binding site when further being functionalized with thiol groups using thioglycolic acid. And in any other references, the membranes were modified directly with water or other solvent. The advantage of the proposed thiol-functionalized cellulose nanofibers is greater adsorption capacity and faster adsorption speed.

2 Experimental

2.1 Chemicals

CA (Degree of substitution, DSacetyl = 2.45) was purchased from Wuhan Yuancheng Technology Development Co. Ltd (China). PVP (Mw = 1,300,000g mol\(^{-1}\)), dimethyl acetylamide (DMAc), thioglycolic acid and tetrahydrofuran (THF) were all supplied by Aladdin Reagent. Copper powder (99.999%), lead powder (99.999%) and cadmium powder (99.999%) (Shanghai Chemical Reagent Co., Ltd, China) were used to prepare the heavy metal ion stock solutions (1 g L\(^{-1}\)) for adsorption investigations. Acetone, hydrochloric acid and nitric acid were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Distilled water was used throughout this work. All the reagents were used as received without further purification.

2.2 Instrumentation and general procedures

Infrared spectral data was collected using NEXUS470 (Thermo Nicolet, USA). The surface morphologies of the nanofiber membranes were studied using scanning electron microscopy (S-4800, Hitachi, Japan). TGA was carried out with a DSC-200PC (NETZSCH, Germany). pH values were measured on a pH-meter (Mettler Toledo, Switzerland). The concentration of M(II) was analysed using an atomic absorption spectrophotometer (AAS) (PerkinElmer, USA).

A solution of 10% (w/w) CA in aceton/DMAc (v/v = 2/1) was prepared at room temperature. A mixture of the CA solution and PVP (mass ratio of CA and PVP = 25/10, 25/9, 25/8, 25/7 and 25/6, respectively) was stirred at room temperature for one day to achieve a homogeneous mixture. The above solution (4 mL) was placed in a syringe (10 mL) with a stainless steel needle (Φ = 0.6 mm) which was docked to a direct current high-voltage generator (JG50-1, Shanghai Shenfa Detecting Instrument Factory, China). The syringe was connected to a syringe pump (KDS-200, KD Scientific, USA) to control the flowing rate at 1.5 mL h\(^{-1}\). The nanofibers were collected on a disk of aluminium foil in the form of non-woven mat. The applied voltage between the tip of the needle and the collector was 10 kV and the distance from the tip to the collector was 13 cm. The electrospinning experiments were performed at room temperature (23–30 °C) under the humidity between 73%–82%. The CA/PVP nanofiber membranes were dried under vacuum at 80 °C to remove as much solvents as possible.

2.3 Preparation of the cellulose nanofiber membranes

2.3.1 Deacetylation

The CA/PVP nanofiber membranes were immersed in de-ionized water to partially remove the PVP component under supersonification for 3 h. After being dried at 80 °C under vacuum for 24 h, the membranes were deacetylated in alcoholic KOH solution (0.5 mol L\(^{-1}\)) for 3 h. The regenerated cellulose membranes (RCM) were then rinsed with distilled water for several times and dried under vacuum at 80 °C.

2.3.2 DS_{thiol} of RCM

RCM (0.1 g) was added to a solution of NaOH (0.2 mol L\(^{-1}\)) in a mixed solvents (EtOH/H\(_2\)O = 5/4, 10 mL) at ambient temperature for 72 h under stirring. The excessive base was titrated with HCl (0.1 mol L\(^{-1}\)) using phenolphthalein as an indicator.