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Preparation and dye filtration property of electrospun polyhydroxybutyrate–calcium alginate/carbon nanotubes composite nanofibrous filtration membrane

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ABSTRACT

Polyhydroxybutyrate–calcium alginate/carboxyl multi-walled carbon nanotubes composite nanofibrous filtration membranes (PHB–CaAlg/CMWCNT) were prepared by electrospinning technique combined with redissolving the top hydrogel nanofibrous layer to form dense thin film as barrier layer on PHB nanofibrous substrate through suitable water mist wetting process and Ca^{2+} cross-linking. The obtained PHB/CaAlg nanofibrous membrane by synchronization electrospinning could improve the hydrophilic property as middle layer and closely integrate with the top hydrogel layer. The morphology of the membranes was observed by SEM. The hydrophilic property, tensile mechanical property, dye adsorption and filtration properties were characterized. The results showed that the tensile mechanical property and hydrophilic property of PHB–CaAlg/CMWCNT membrane were significantly improved, and the dye Brilliant blue adsorption capacity was twice higher than PHB–CaAlg membrane. The flux and rejection rate of PHB–CaAlg/CMWCNT membrane for Brilliant blue were 32.95 L/m^2 h and 98.20%, respectively. The thickness of PHB–CaAlg/CMWCNT membrane was about 40–50 μm and the membrane consisted of 20 μm PHB nanofibrous substrate, 10 μm PHB/CaAlg membrane and 10–20 μm CaAlg/CMWCNT membrane. The optimum time of water mist wetting process and Ca^{2+} cross-linking was 5 min and 8 h, respectively. This PHB–CaAlg/CMWCNT membrane has promising applications as nano-filtration membrane with high flux and rejection rate for small organic molecules in wastewater under low operating pressure.

1. Introduction

With the rapid development of dye industry, the production of dyes wastewater has become a major source of water pollution [1]. The potential toxicity and resist degradation of organic dyes and their post-processing pose a serious threat to the environment. There have been made many efforts for removing dyes from dye-containing effluents or dyes polluted water bodies, such as electrochemical method, adsorption method, membrane separation method, and the combination of above methods [2–5]. Compared with other methods, membrane separation technology is a simple design, efficient and low cost method which widely used in dye removal from water [6–8].

The separation membranes for dye wastewater treatment belong to nano-filtration membrane technology due to the average molecular weights of the majority dyes in the range of 100–1000 Da and the nano-filtration membrane has high rejection rate for organics with the average molecular weights in this range [9–11]. However, the flux of nano-filtration membrane is very low under low operating pressure. Li et al. [12] prepared poly(vinyl alcohol) (PVA)/poly (vinylidene fluoride) (PVDF) hollow fiber composite membranes modified with TiO_2 nanoparticles by a dip-coating method and used for dye desalination and wastewater treatment. The flux and rejection rate of composite membrane with three PVA layers for Congo red dye solution under the operating pressure of 0.3 MPa were 5.10 L/m^2 h and 92.20%, respectively. The flux of composite nano-filtration membrane was low at low operating pressure and glutaraldehyde as the cross-linker of PVA hydrogel could cause environmental pollution. Xu et al. [13] prepared polyamide/polysulfone nano-filtration membrane coupling with electrolytic oxidation in treating simulated dye wastewater and the flux reached to 55 L/m^2 h under the operating pressure of 1 MPa. Zhao et al. [14] prepared a free-standing calcium alginate hydrogel membrane with the flux of 15 L/m^2 h for Brilliant blue dye solution under the

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operating pressure 0.1 MPa. Although the flux is higher than other nano-filtration membranes, it also can't satisfy the rapid pollution of water bodies by dye. Therefore, research on high flux nano-filtration membrane has been caused widespread attention.

Electrospinning technology is an effective method to prepare nanofibers membrane with diameter in the range of tens nanometers to several micrometers and high specific surface areas. The electrospun nanofibrous membrane possesses three-dimensional network completely interconnected pore structures, the qualitatively controlled pore size distribution from sub-micron levels to a few micrometers, and high porosity [15,16], and it have been widely used for wastewater treatment [17–19]. However, the irreversible fouling of traditional electrospun filtration membrane materials with poor hydrophilic property results in the membrane pores blocking and flux significantly decreasing [20]. Many efforts have been exerted to modify the hydrophilic property of membranes, including polymer blending [21], surface coating [22], and surface grafting [23].

Some studies have been reported that the hydrogel membranes can be used to water filtration and possess excellent hydrophilic and anti-fouling property [24,25]. The electrospun hydrogel membranes also have been investigated. Wang et al. [26] prepared the high flux thin film nanofibrous composite ultrafiltration membrane containing a hydrophilic PVA hydrogel barrier layer and a polyacrylonitrile (PAN) nanofibrous substrate by electrospinning technique and followed by remelting the hydrophilic top layer to form a barrier film with several micrometers thickness on the supporting layer by suitable solvent vapor exposure and chemical cross-linking. The highest permeate flux of 210 L/m^2 h was achieved with the rejection rate of 99.5% for oil–water separation by the composite membrane under the operating pressure of 0.3 MPa. However, the cross-linking agent of glutaraldehyde water/acetone solution possesses irritation and toxicity which easily caused environmental pollution and the ultra-filtration membrane had low rejection for small molecule organic dyes.

Sodium alginate (NaAlg), a polysaccharide extracted from seaweed, has shown excellent water solubility and can create an ionic cross-linked hydrogel under mild conditions [27]. Due to the rigid molecular chain of NaAlg, the pure NaAlg aqueous solution could not form fibers by electrospinning [28]. However, many efforts have been exerted to improve the spinnability of NaAlg by adding other flexible polymer, such as PVA, polyoxyethylene (PEO) and chitosan [29–31]. The nanofibers could improve the performance and expand the applications of NaAlg, especially in the biomedical field. The study of electrospun calcium alginate/carbon nanotubes hydrogel coating on nanofibrous substrate composite membrane has not been reported in the filtration field.

In this paper, polyhydroxybutyrate–calcium alginate/carboxyl multi-walled carbon nanotubes three layer composite nanofibrous filtration membranes (PHB–CaAlg/CMWCNT) with the thickness of 40–50 μm were prepared by electrospinning combined with redissolving and Ca^{2+} cross-linking of the top hydrogel nanofibrous layer as barrier layer on PHB nanofibrous substrate. The obtained PHB/CaAlg nanofibrous membrane by synchronization electrospinning could improve the hydrophilic property as middle transitional layer and closely integrate with the top hydrogel layer. The morphology and structure of the membranes were studied by SEM. The hydrophilic property, tensile mechanical property, dye adsorption and filtration properties were investigated.

2. Experimental

2.1. Materials

Polyhydroxybutyrate (PHB) was purchased from Tianjin Rhyme Biological Technology Co., Ltd. Carboxyl multi-walled carbon nanotubes (CMWCNT) were purchased from Nanjing XFNANO Materials Technology Co., Ltd. Chloroform, dimethylformamide (DMF), tween-80 and 0# diesel were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Sodium alginate (NaAlg) and calcium chloride anhydrous ($CaCl_2$) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. Poly(ethylene oxide) (PEO) was purchased from Scientific Research Special. Brilliant blue was purchased from Tianjin Umbrella Science & Technology Co. Ltd.

2.2. Electrospinning of PHB, PEO/NaAlg and PEO/NaAlg/CMWCNT nanofibers

The preparation of PHB nanofibers by electrospinning is as follows. The PHB powder was dissolved in the mixed solvent of chloroform/DMF (90/10, w/w) and stirred at 40 °C for 8 h to obtain 2.5 wt% homogeneous spinning solution. The applied voltage was 16 kV and the polymer-flow-rate was 2 mL/h. A grounded stainless steel drum with a rotating speed of 200 rpm was used to collect the deposited nanofibers. The diameter of the spinneret was 0.6 mm and the distance between the spinneret and the grounded drum was 20 cm. The prepared PHB nanofibrous membrane was used as the nanofibrous substrate with the thickness about 20 μm.

The preparation of PEO/NaAlg and PEO/NaAlg/CMWCNT nanofibers by electrospinning is as follows. A homogenously mixed spinning solution was obtained by dissolving 1.5 wt% PEO, 1.5 wt% NaAlg in deionized water with or without CMWCNT through ultrasonic dispersing (the proportion of CMWCNT was 5 wt% in NaAlg), and stirred for 12 h. Perfect fibers were produced for an optimum electrospinning condition: an applied voltage of 18 kV, a polymer-flow-rate of 2 mL/h, a spinneret to collect drum distance of 16 cm, and spinneret diameter of 0.6 mm. The thickness of the PEO/NaAlg and PEO/NaAlg/CMWCNT nanofibrous layer as the top layer can be controlled in the range of 10–20 μm by adjusting the depositing time.

The transitional layer of PHB/PEO/NaAlg nanofibers was prepared by the synchronously electrospun PHB and PEO/NaAlg nanofibers and deposited on the PHB nanofibrous substrate as shown in Fig. 1. The spinning parameters were consistent with the preparation of PHB and PEO/NaAlg nanofibers in the above.

2.3. Preparation of the PHB–CaAlg and PHB–CaAlg/CMWCNT composite nanofibrous filtration membranes

For preparation of the PHB–CaAlg and PHB–CaAlg/CMWCNT three-layer composite nanofibrous filtration membranes containing CaAlg or CaAlg/CMWCNT barrier layer, PHB/CaAlg transitional layer and PHB nanofibrous substrate, a new and simple fabrication route was developed as shown in Fig. 2. Firstly, the PEO/NaAlg and PEO/NaAlg/CMWCNT nanofibers were deposited on the electrospun PHB/PEO/NaAlg transitional layer with PHB nanofibrous substrate to form three-layer nanofibrous membrane. Then the three-layer nanofibrous membrane was treated by water mist wetting for about 5 min at room temperature and redissolved the PEO/NaAlg and PEO/NaAlg/CMWCNT nanofibers to form hydrosol. After that, the membrane was immersed in 2.5 wt% $CaCl_2$ aqueous solution for ionic cross-linking of NaAlg for 8 h. Finally, the PHB–CaAlg and PHB–CaAlg/CMWCNT composite nanofibrous filtration membranes were prepared.

2.4. Characterization

Digital camera and scanning electron microscope (SEM, HITACHI, Japan) were used to observe the morphology of PHB–CaAlg and PHB–CaAlg/CMWCNT composite nanofibrous filtration membrane. All the membrane samples were freeze–dried and sputter-coated with an ultrathin layer of gold before SEM examination.