



Fabrication of poly(ether sulfone)/poly(zinc acrylate) ultrafiltration membrane with anti-biofouling properties



Juan Zhang, Manying Zhang, Kaisong Zhang*

Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

ARTICLE INFO

Article history:

Received 10 December 2013

Received in revised form

18 February 2014

Accepted 20 February 2014

Available online 28 February 2014

Keywords:

Anti-biofouling

Zinc immobilization

Ultrafiltration

Regenerable membrane

ABSTRACT

Biofouling is a severe problem for membrane process. Incorporating biocides such as heavy metals into polymer membranes have been demonstrated for their effectiveness in anti-bacterial performance; however, the metal ion leaches due to the poor compatibility of the metal ions and the polymer. The bactericidal effect will be disappeared and the unexpected pores will be formed when all the metal ions leach out. To overcome this problem, an anti-biofouling poly(ether sulfone)/poly(zinc acrylate) (PES/PZA) ultrafiltration composite membrane was investigated by immobilizing Zn ions onto polymer chains. The PES/PZA composite membrane has a good anti-biofouling property during a 3 months test in an aerobic bioreactor treating municipal wastewater. The higher the PZA content, the better anti-biofouling ability the membrane has. The Zn^{2+} content can be restored by incubating the membrane in a solution containing Zn^{2+} (even after the Zn^{2+} has been replaced by other cations during the water treatment), which secures the long time anti-biofouling properties of the membranes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The separation membrane technology has become a well known method over the past decades for water treatment and desalination. However, biofouling is a severe problem in long term operation membrane process, especially in the wastewater treatment containing high biological components [1–6].

Biofouling has serious impacts on membrane performance, for example, reducing the permeate flux, increasing energy costs and shorting the life of the membrane [7–9]. Membrane biofouling is often considered irreversible and is very difficult to handle due to the self-replicating nature of microbes [10,11]. Thus, efforts have been aimed at preventing it happening. Biocides such as heavy metals, including copper, zinc or silver, have been proved effective in anti-bacterial performance [12–14]. However, most of the works conducted on incorporating heavy metal ions into polymers reported leaching problems due to the poor compatibility of the metal ions and the polymer [14–16]. Furthermore, with the metal ions leaching out, the bactericidal effect will disappear. Some unwanted voids will be existed in the membrane and on the membrane surface, which will bring negative effects on the membrane performance.

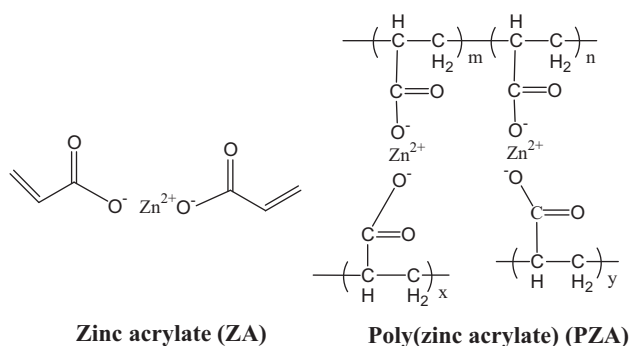
To overcome this problem, immobilizing the metal ions onto polymer chains, and recovering the metal ions to regenerate the

bactericidal effect would be a good strategy. Zhu et al. [17] chelated ionic silver or metallic silver onto the chitosan based membrane as there is a high content of amino groups in chitosan which can easily chelate with transitional metals. The membrane has great anti-biofouling properties, but this method could not be easily applied to other commercially available membranes like poly(ether sulfone) (PES), poly(vinylidene fluoride) (PVDF), polypropylene (PP), polyacrylonitrile (PAN) etc. So, they [18] explored another method to immobilize the silver ions onto PP membrane surface by grafting thiol groups on PP membrane first and then immobilize the silver ions with thiol groups. However, grafting of thiol groups on PP membrane involves immersing the membrane in saturated bromine water solution which requires to be sealed in transparent facilities for lighting that cannot be easily commercialized.

Previous research reported that polymers with heavy metal ions immobilized on the polymer chains have good antimicrobial properties [19–25]. However, most of them were not applied to membrane materials. Poly(zinc acrylate) (PZA) is one of the polymers incorporate the zinc ions onto the polymer chains. Because of its substantial antimicrobial activities, it is used in biopharmacy [23,24]. Its monomer, zinc acrylate, is commercially available and the polymerization condition is mild. So adding PZA into membrane materials would be an easy way to improve the anti-biofouling properties of membranes. Furthermore, if Zn^{2+} is ion exchanged by other ions during the water treatment, it is assumed that the zinc ions (Zn^{2+}) can be easily re-loaded onto the

* Corresponding author. Tel./fax: +86 592 6190 782.

E-mail address: kszhang@iue.ac.cn (K. Zhang).



Scheme 1. Chemical structure of zinc acrylate (ZA) and cross-linked poly(zinc acrylate) (PZA).

polymer chains and the bactericidal effect will be regenerated by simply immerse the membrane in zinc salt solutions, e.g. zinc sulfate (ZnSO_4) and zinc nitrate (ZnNO_3) solutions.

A new anti-biofouling PES/PZA ultrafiltration composite membrane with metal ions immobilized onto polymer chains will be prepared. Commercially available PES membranes are widely used in water and wastewater treatment because of their high void volume, well-controlled porosity, good thermal and chemical stabilities and low cost. The zinc acrylate (ZA) will be thermally polymerized into PZA in the casting solution before the membrane casting. Scheme 1 shows the chemical structure of ZA monomer and PZA cross-linked polymer. The effects of different contents of PZA on the membrane morphology, hydrophilicity, and thermal stability etc. will be investigated. The water flux of the obtained membranes and their anti-adhesion and formation of biofilm properties will be discussed. The recover ability of zinc ions onto polymer chains after ion exchange by magnesium will be evaluated.

2. Experimental part

2.1. Materials

Polyethersulfone (PES Ultrason E6020P, $M_n=52,000$ g/mol) was purchased from BASF, Germany. PES was dried at 110°C overnight in an oven prior to dope preparation. Zinc acrylate (ZA, 98%) was purchased from Sigma and used as received. Azobisisobutyronitrile (AIBN, 99%) was purchased from Aladdin and used as received. Dimethyl sulfoxide (DMSO), bovine serum albumin (BSA), Na_2HPO_4 , and NaH_2PO_4 were obtained from Guoyao Group, China. De-ionized water was used to prepare all solutions needed in the study.

2.2. Preparation of composite membranes

All casting solutions were conducted with the weight ratio of (PES+ZA): DMSO=18:72. The concentration of the initiator AIBN was 0.025% (wt/vol). And different weight ratios of PES and ZA were used, as listed in Table 1. The polymerization of ZA was carried out under nitrogen in a dried flask equipped with a magnetic stirring bar. The flask was charged with DMSO and ZA, sealed with a rubber septum, and stirred at 80°C for 5 min. Then PES was added and stirred until dissolved completely. The AIBN was then added and the solution was stirred for another 2 h for zinc acrylate to be polymerized. Finally, the solution was degassed for 10 h.

All membranes were prepared using the wet phase-inversion process. The casting solution was spread uniformly on a non-woven support with a casting knife gap setting of $250\ \mu\text{m}$ at an

Table 1
Weight ratios of PES and ZA, and Zn^{2+} contents in membranes determine by ICP-OES.

Sample	Weight ratio of PES and ZA	ZA loading ^a (%)	Theoretical Zn^{2+} content ($\mu\text{g}/\text{cm}^2$)	Zn^{2+} content ^b ($\mu\text{g}/\text{cm}^2$)
M0	100:0	0	–	–
M1	95:5	5	36	34 ± 1
M2	90:10	10	72	58 ± 5
M3	85:15	15	107	119 ± 8
M4	80:20	20	143	168 ± 1

^a Based on the weight of PES and ZA.

^b Determined by ICP-OES.

appropriate casting shear. The thickness of the non-woven support layer was $110\ \mu\text{m}$. The initial thickness of the composite membrane was around $140\ \mu\text{m}$. The fresh membrane was immersed into the deionized water bath at room temperature for the remainder of the phase-inversion process and for removing any residual solvent before all the characterization.

2.3. Membrane characterizations

In order to study the effect of poly(zinc acrylate) (PZA) on the microstructure of the membranes, field emission scanning electron microscopy (FESEM) (JSM-6300F, JEOL) equipped with an X-ray energy dispersive spectroscopy (X-EDS) system was employed to analyze the surfaces and cross-sections of PZA/PES membranes. All the samples were sputter-coated with platinum prior to the FESEM imaging observation.

Inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 7000DV) was used to determine the Zn^{2+} contents in membrane samples with different ZA loading and confirm that ZA was successfully polymerized. The obtained membrane samples were dissolved in 98% concentrated sulfuric acid (H_2SO_4), and then diluted with deionized water and filtered with $0.45\ \mu\text{m}$ filter. The Zn^{2+} contents were then analyzed by ICP-OES.

The contact angle-measuring instrument (DSA100, German KRUSS) was used to determine the hydrophilicity of the prepared membranes. To reduce the experimental error, the contact angle was measured at four random locations for each sample and the average value was reported.

The filtration performances of membranes were evaluated by a dead-end filtration system (Sterlitech HP4750). The membrane effective area was $4.1\ \text{cm}^2$. The pure water flux of the membrane was recorded at 0.1 MPa. The membrane selectivity was evaluated by filtering 200 ppm BSA feed solution, and the concentration of the first 30 ml permeate solution was measured by UV–vis spectrophotometer (DR5000) at 280 nm.

The porosity of different membranes was calculated using Eq. (1) [26],

$$\varepsilon = \frac{(W_w - W_d)/D_w}{(W_w - W_d)/D_w + (W_d/D_p)} \times 100\% \quad (1)$$

where ε is the porosity of the membrane (%), W_w is the wet sample weight (g), W_d is the dry sample weight (g), D_w and D_p is the density of the water and polymer respectively. Three samples for each membrane were calculated and the average value was reported.

Thermal gravimetric analysis (TGA, Perkin Elmer) was used to evaluate the thermal stability of membranes. TGA measurements were carried out under nitrogen atmosphere over a temperature range of $40\text{--}800^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$.

Download English Version:

<https://daneshyari.com/en/article/633641>

Download Persian Version:

<https://daneshyari.com/article/633641>

[Daneshyari.com](https://daneshyari.com)