Journal of Hazardous Materials 187 (2011) 311–317

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Polyrhodanine modified anodic aluminum oxide membrane for heavy metal ions removal

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ARTICLE INFO

Article history:
Received 16 August 2010
Received in revised form 5 January 2011
Accepted 6 January 2011
Available online 14 January 2011

Keywords:
Anodic aluminum oxide
Polyrhodanine
Nano filter
Heavy metal ions
Heavy metal removal

ABSTRACT

Polyrhodanine was immobilized onto the inner surface of anodic aluminum oxide (AAO) membrane *via* vapor deposition polymerization method. The polyrhodanine modified membrane was applied to remove heavy metal ions from aqueous solution because polyrhodanine could be coordinated with specific metal ions. Several parameters such as initial metal concentration, contact time and metal species were evaluated systematically for uptake efficiencies of the fabricated membrane under continuous flow condition. Adsorption isotherms of Hg(II) ion on the AAO-polyrhodanine membrane were analyzed with Langmuir and Freundlich isotherm models. The adsorption rate of Hg(II) ion on the membrane was obeyed by a pseudo-second order equation, indicating the chemical adsorption. The maximum removal capacity of Hg(II) ion onto the fabricated membrane was measured to be 4.2 mmol/g polymer. The AAO-polyrhodanine membrane had also remarkable uptake performance toward Ag(I) and Pb(II) ions. Furthermore, the polyrhodanine modified membrane could be recycled after recovery process. These results demonstrated that the polyrhodanine modified AAO membrane provided potential applications for removing the hazardous heavy metal ions from wastewater.

1. Introduction

The water pollution by heavy metal ions is one of the worldwide environmental problems due to the bioaccumulation tendency of these toxic materials [1,2]. The heavy metal can cause various fatal diseases [3,4]. For example, mercury is well-known as neurotoxin that can induce insanity, paralysis, and death [3]. Thus, the removal step of heavy metal ions from wastewater is regarded as the important process before discharging it into ecosystem. There are various heavy metal removal technologies such as chemical precipitation [5], electrolysis [6], adsorption [7–10] and membrane separation [11–13]. Among these removal techniques, membrane application has cost competitiveness in the water purification industry because it filters out the pollutants from water without additional electric power supply or gathering procedure of adsorbents [11,12].

The anodic aluminum oxide (AAO) membrane has been widely used as a template for the fabrication of carbon, metal and polymer nanofibers or nanotubes due to its well-defined nano-size channels [14–17]. Recently, several studies have been reported that the AAO membrane could be used as a membrane itself (without etching process) [18,19]. As a filter, the AAO membrane provides uniform channels, facile controllable pore size and large surface area. Especially, it is expected that the adsorbent-modified AAO membrane can remove the heavy metal ions effectively from aqueous solutions due to the enhanced inner surface area.

Our previous research demonstrated that vapor deposition polymerization (VDP) applied for effective way in order to fabricate polymer nanomaterials [16,20,21]. The uniform and nano-sized polymer shell can be formed onto the specific surface *via* the polymerization of vaporized monomer [16,20,21]. Herein, we report the fabrication of polyrhodanine nanotubes immobilized AAO membrane by VDP method. In general, polyrhodanine has been used for antibacterial [22,23] and anticorrosion applications [24]. In addition, the polyrhodanine has strong metal binding sites such as oxygen and sulfur group in its monomeric unit [25,26]. Based on this metal binding property of polyrhodanine, the polyrhodanine modified membrane can be used as the filter for the removal of heavy metal ions. In this study, the effects of initial metal ion concentration, contact time and species of metal ions on the uptake capacity were evaluated to analyze the adsorption propety of the prepared membrane. In addition, the adsorption isotherm of Hg(II) ion on the AAO-polyrhodanine membrane was analyzed using Langmuir and Freundlich isotherm models. The recyclability of the prepared membrane was also studied for heavy metal removal.

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doi:10.1016/j.jhazmat.2011.01.026

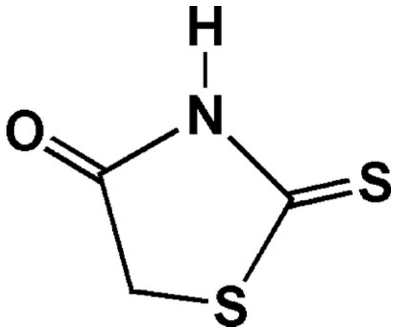

Fig. 1. Molecular formula of the rhodanine monomer.

2. Experimental

2.1. Materials

The AAO membrane was obtained from Whatman Co. (UK) Rhodanine monomer (Fig. 1) and ferric chloride were purchased from Aldrich chemical Co. (Milwaukee, WI, USA). The n-methyl-2-pyrrolidinone (NMP) solvent was purchased from Junsei chemical Co., Ltd. (Japan). For heavy metal ion removal test, cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$), mercury nitrate monohydrate ($Hg(NO_3)_2{\cdot}H_2O$), and lead nitrate ($Pb(NO_3)_2$) were purchased from Aldrich chemical Co. (Milwaukee, WI, USA). Nitric acid and ammonia solution were also bought from Aldrich chemical Co. (Milwaukee, WI, USA) for adjusting solution pH. The membrane cartridge (Model KS-13, Advantec.) was used to load the membrane and the peristaltic pump (Model 323E/D, Watson-Marlow) was used for the feeding of metal ion containing solution.

2.2. Fabrication of AAO-polyrhodanine membrane and bulk polyrhodanine

First, the AAO membrane was immersed in the ferric chloride solution (0.15 mol/L) for 5 min. Then, solution was evaporated in the vacuum oven at 25 °C. The Fe ion as oxidant was impregnated into the inner surface of AAO membrane channels *via* the evaporation step. After removal of the solution, the oxidant impregnated AAO membrane was placed into a closed vessel. The 0.75 mmol of rhodanine monomer was introduced into the vessel separated with AAO membrane, and evacuated until the inner pressure reached up to 10^{-2} Torr. Then, the vapor deposition polymerization was proceeded for 6 h at 160 °C. After polymerization, the AAO membrane was washed several times with distilled water to remove the residual reagents. After the polymerization, the increased weight of the membrane was measured. The average weight of polyrhodanine which was immobilized on AAO membrane was *ca.* 0.8 mg. As a control material for metal removal, the bulk polyrhodanine was synthesized through dispersion polymerization at 60 °C for 24 h. The 0.25 g of rhodanine monomer was dispersed in aqueous solution (100 mL) and 0.5 g of $FeCl_3$ was added to initiate the polymerization. After 24 h, the bulk polyrhodanine was precipitated by centrifugal precipitation and washed with distilled water to remove residual reagents.

2.3. Adsorption studies of the AAO-polyrhodanine membrane

The studies which were related to the metal uptake and adsorptivity using different initial concentrations, kinetic, and recycling have been only performed with Hg(II) ion. In order to investigate the effect of initial metal ion concentration to uptake capability, the Hg(II) ion solutions with various initial concentrations (from 10 mg/L to 200 mg/L) were prepared. The kinetic study and the recycling study were performed with Hg(II) ion at 100 mg/L and 200 mg/L of initial concentration, respectively. On the other hand, the comparative study was performed employing the three following metal ions: Hg(II), Pb(II) and Ag(I) ions. All of the above mentioned metal removal studies performed under continuous flow condition. In order to investigate the metal removal capability of the AAO-polyrhodanine membrane, the prepared AAO-polyrhodanine membrane was equipped with membrane cartridge. The 10 mL of heavy metal ion solution was passed through the membrane (Fig. 2). The residual amounts of metal ion were measured. The flow rate of solution was 2 mL/h, the pH value of solutions was adjusted to 6.0 and tests were proceeded at room temperature. In kinetic study, the aliquots of filtered solution were taken as a function of time (from 60 min to 300 min), and the concentrations of residual metal ion were measured. The uptake amount of metal ions on the AAO-polyrhodanine membrane was calculated according to the following equations.

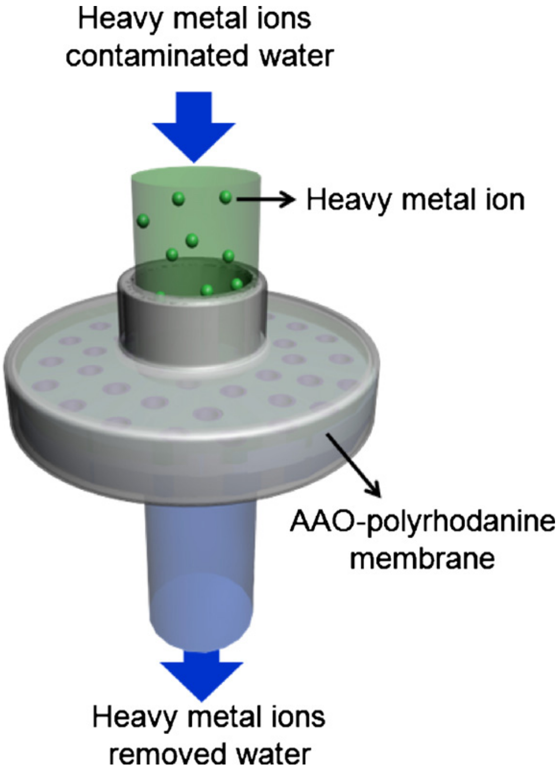

Fig. 2. Schematic diagram of removal procedure of heavy metal ions from wastewater using the fabricated AAO-polyrhodanine membrane as a filter.

$$q = \frac{C_0 - C}{C_0} \times 100 \quad (\%) \qquad (1)$$

$$Q = \frac{(C_0 - C_e) \times V}{W} \qquad (2)$$

where q is the adsorptivity (%), Q is the uptake of adsorbent in mmol (metal)/g (adsorbent), C_0 and C is the concentration of metal ions before and after metal removal experiment in mmol/L, C_e is the equilibrium concentration of metal ions in mmol/L, V is the volume of metal ions solution in liter, and W is the weight of the adsorbent in gram scale. The fabricated membrane exhibited almost similar metal uptake performance when the passing metal ion solution increased from 10 mL to 15 mL. Therefore, we assumed that the concentration of residual metal ion reached equilibrium value (which means C_e) sufficiently after passing the 10 mL of metal ion solution.