



Polyrhodanine modified anodic aluminum oxide membrane for heavy metal ions removal

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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.

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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 property 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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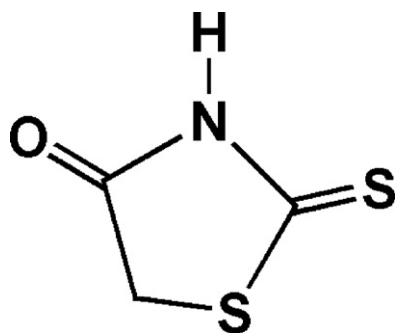


Fig. 1. Molecular formula of the rhodanine monomer.

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 ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), mercury nitrate monohydrate ($\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$), and lead nitrate ($\text{Pb}(\text{NO}_3)_2$) 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

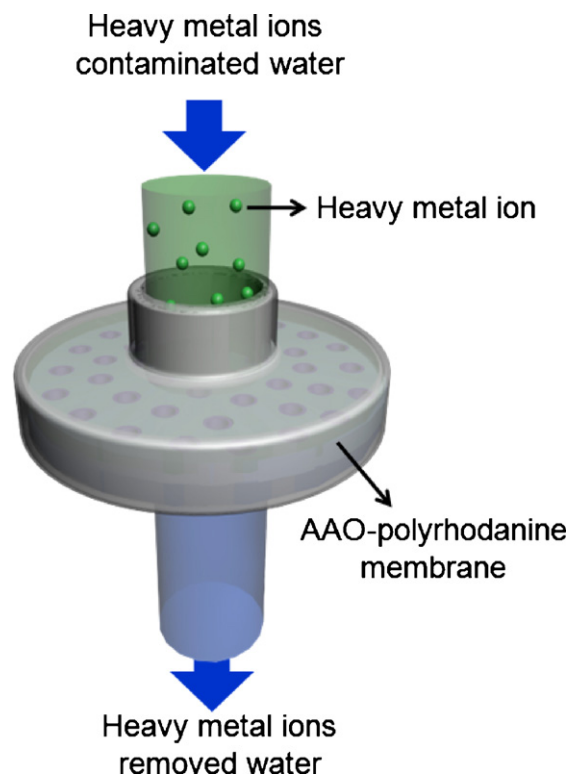


Fig. 2. Schematic diagram of removal procedure of heavy metal ions from wastewater using the fabricated AAO-polyrhodanine membrane as a filter.

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.

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

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

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.

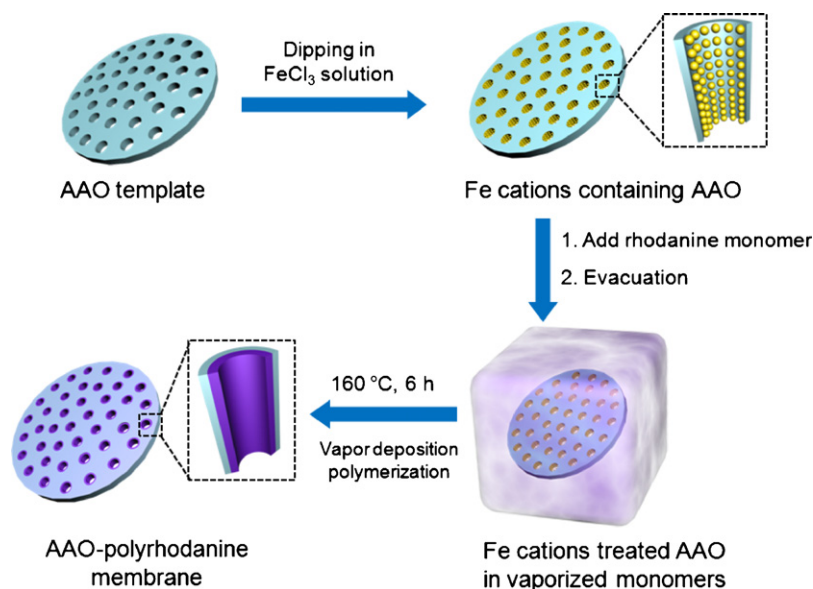


Fig. 3. Schematic illustration of synthetic procedure of the AAO-polyrhodanine membrane.

2.4. Adsorption studies of bulk polyrhodanine

The bulk polyrhodanine powder was prepared as a control material for heavy metal uptake. By contrast with AAO-polyrhodanine membrane, the heavy metal removal experiment of the bulk polymer was performed under batch condition. The bulk polyrhodanine powder was added to 10 mL of heavy metal solution (200 mg/L) and shaken using mechanical shaker for 5 h. After then, the concentration of residual metal ion was measured.

2.5. The recycling of the synthesized membrane

In order to wash out the metal ion from the used membrane, the 10 mL of nitric acid solution (pH 4.0) was passed through the used membrane at a rate of 2 mL/h. After then, the membrane was sufficiently washed with deionized water for neutralization and recondition. In order to confirm the recovered metal uptake property, the 10 mL of Hg(II) ion solution was passed through the refreshed AAO-polyrhodanine membrane at a flow rate of 2 mL/h. The pH value of solutions was adjusted to 6.0 and the test was performed at room temperature. The recovery rate was calculated according to the following equations.

$$RE = \frac{Q_c}{Q_0} \times 100 \quad (\%) \quad (3)$$

where RE is the recovery rate (%), Q_0 is the uptake of metal ions by the fresh membrane in mmol (metal)/g (polymer) and Q_c is the uptake of metal ions after recovery procedure in mmol (metal)/g (polymer).

2.6. Characterization method of synthesized AAO-polyrhodanine membrane

The image of transmission electron microscopy (TEM) was obtained with a JEM-200CX (JEOL, Japan). Acceleration voltage for TEM was 200 kV. The AAO membrane was etched with hydrochloric acid (3 mol/L) for 24 h, at 60 °C and then, fully washed with distilled water in order to obtain the TEM image of polyrhodanine tube. Field-emission scanning electron microscopy (FE-SEM) images were obtained using a JSM-6701F (JEOL, Japan) at an acceleration voltage of 10 kV. Energy dispersive X-ray (EDX) analysis was performed using INCA energy (Oxford Instruments Analytical Ltd.,

UK) coupled with an EDX facility. Fourier transform infrared (FT-IR) spectra were obtained using a Bomem MB 100 spectrometer (Quebec, Canada) in the absorption modes at resolution of 4 cm^{-1} and 64 scans. The UV-vis spectra were taken with a UV-vis spectrometer Lambda-20 (Perkin-Elmer, USA). The synthesized polyrhodanine was dissolved in NMP solvent to obtain the UV-vis spectra. The metal ion concentrations were measured by inductively coupled plasma ICPS-7500 (Shimadzu, Japan). For accuracy of the results, all of the concentration values were analyzed three times and averaged. The standard deviation was less than 5%.

3. Results and discussion

3.1. Characterization of synthesized AAO-polyrhodanine membrane

The overall synthetic procedure of AAO-polyrhodanine membrane is illustrated in Fig. 3. The Fe(III) ions as initiator were deposited onto the wall of AAO channel by dipping the membrane in the ferric chloride aqueous solution. The Fe(III) ions can be preferentially attached onto the negative charged wall of AAO membrane due to a charge-charge interaction [27]. The initiator impregnated AAO membrane and rhodanine monomer were placed in a closed vessel separately. During the VDP process, the vaporized rhodanine monomers reacted with Fe cations on the inner wall of AAO membrane and the polyrhodanine modified AAO membrane was obtained.

Fig. 4a represents TEM image of synthesized polyrhodanine. The AAO template was etched with hydrochloric acid in order to observe the morphology of fabricated polymer. As shown in the TEM image, the polyrhodanine had hollow tubular structure; an average diameter and a shell thickness of the polymer nanotube were ca. 180 nm and ca. 15 nm, respectively. In addition, the polymer modified membrane was also characterized by FE-SEM analysis. As displayed in the FE-SEM image of frontal membrane surface (Fig. 4b), the prepared membrane had the pores with the average diameter of ca. 150 nm. From the cross-sectional FE-SEM image, the thickness of polyrhodanine membrane was measured to be ca. 60 μm (Fig. 4c). Judging from these data, it could be concluded that the polyrhodanine nanotubes were successfully synthesized on the inner wall of AAO membrane by VDP method.

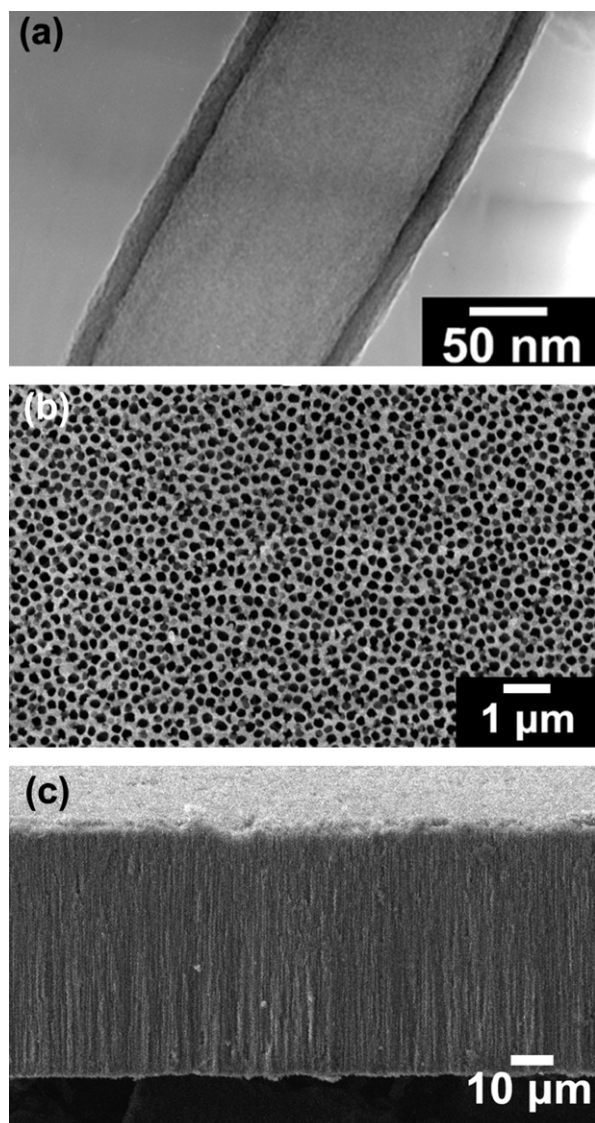


Fig. 4. (a) TEM image of the polyrhodanine nanotube and FE-SEM images of (b) the frontal surface and (c) cross-section of the fabricated AAO-polyrhodanine membrane. To obtain the TEM image, the membrane was immersed in 3 M of hydrochloric acid to etch the AAO template.

The composition of polymer modified membranes was also investigated by the EDX analysis (Table 1). Compared to the pristine AAO, the atomic % C and % S values of the AAO-polyrhodanine membrane increased and % Al value relatively decreased due to the polyrhodanine nanotubes onto the AAO membrane surface. Notably, the drastically increased % S value proves the existence of polyrhodanine in the AAO membrane because the polyrhodanine has sulfur groups in its chemical structure. The detected carbon of pristine AAO sample could be originated from carbon-tape used for fixing the samples on EDX specimen mount.

Table 1
Atomic percentage of pristine AAO and AAO-polyrhodanine membrane using EDX analysis.

Atomic percentage	Pristine AAO	AAO-polyrhodanine membrane
% C	9.89	26.6
% O	64.9	62.8
% S	0.04	1.07
% Al	25.2	9.54

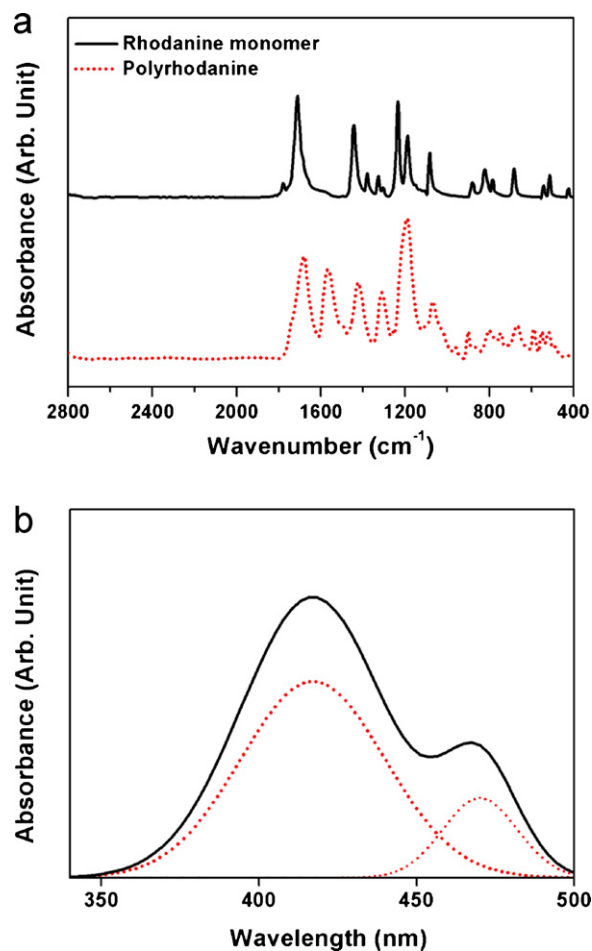


Fig. 5. (a) FT-IR spectra of rhodanine monomer (black solid line) and polyrhodanine nanotubes (red dotted line); (b) UV-vis spectra of the fabricated polyrhodanine in NMP solvent. In the UV-vis spectra, red dotted lines are obtained by the peak deconvolution.

FT-IR and UV-vis spectroscopy analysis was performed to verify the polymerization of rhodanine (Fig. 5). The absorption peaks of polyrhodanine were observed after etching the AAO template by acidic solution. Fig. 5a exhibits the FT-IR spectra of rhodanine monomer and synthesized polyrhodanine nanotube. In the FT-IR spectrum of the polyrhodanine, the strong C=O stretching vibration peak at 1710 cm^{-1} disappeared and new peaks at 1680 and 1575 cm^{-1} were observed compared with that of rhodanine monomer. The peak of 1680 cm^{-1} could be assigned to C=C stretching vibration and the absorbance at 1575 cm^{-1} was ascribed to C=N stretching vibration of synthesized polyrhodanine. Furthermore, the C–O stretching peak at 1180 cm^{-1} intensively increased relative to the peak of rhodanine monomer. Based on the FT-IR spectra, it could be concluded that the chemical oxidation polymerization of rhodanine proceeded via the formation of C=C, C=N, and C–O bonding [28]. The UV-vis spectrum data also demonstrated that the polymerization was successfully performed (Fig. 5b). The absorption peaks at 415 nm and 470 nm were obtained by peak deconvolution in the UV-vis spectroscopy. The $n\text{-}\pi^*$ transition of metal-binding rhodanine structures was observed at 415 nm [22,23] and the $\pi\text{-}\pi^*$ transition of the conjugated polyrhodanine backbone was displayed at 470 nm [28]. Therefore, the polyrhodanine modified AAO membrane was successfully fabricated by VDP process.

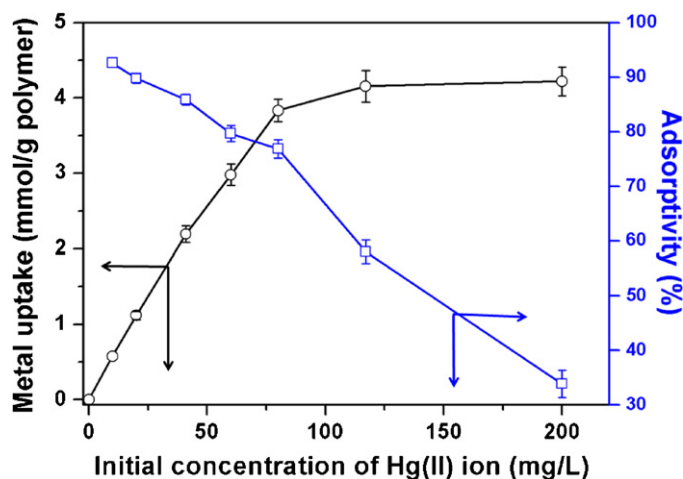


Fig. 6. Effect of initial Hg(II) ion concentration on the metal uptake (black circle) and adsorptivity (blue square) of AAO-polyrhodanine membrane (the pH value was adjusted as 6.0 and flow rate was 2 mL/h).

3.2. Effect of initial Hg(II) ion concentration on metal uptake

The fabricated AAO-polyrhodanine membrane was applied for removal of heavy metal ion and Hg(II) ion was selected as testing metal ions. The experimental procedure of metal ion removal by the polyrhodanine modified membrane is schematically illustrated in Fig. 2. The Hg(II) ion removal performance was evaluated as a function of the initial Hg(II) ion concentration (from 10 mg/L to 200 mg/L). Fig. 6 displays the effect of the initial mercury ion concentration to the adsorption capability. It was clearly observed that the metal uptake of AAO-polyrhodanine membrane increased with increasing initial Hg(II) ion concentration. In particular, at low initial concentration region (below 80 mg/L), the metal ion uptake (which represents the uptake amount and obtained from Eq. (2)) increased rapidly as the initial Hg(II) ion concentration increased. At this region, the heavy metal ions are bound with the plentiful adsorption sites in the channels of AAO-polyrhodanine membrane, resulting in high metal ion uptake performance. Above the 80 mg/L, the increase rate of Hg(II) ion uptake declined and finally it reaches an asymptotic value around 4 mmol/g polymer at 120 mg/L of initial Hg(II) ion concentration. This plateau phenomenon can be interpreted that the active binding sites (which are available for metal ions binding) of the fabricated membrane are nearly occupied with mercury ions. In this study, the maximum uptake of the AAO-polyrhodanine membrane for Hg(II) ions is obtained to be 4.2 mmol/g polymer. On the other hand, the adsorptivity (which indicates the ratio of removed metal ion) decreases with increasing the initial Hg(II) ion concentration. The highest adsorptivity value was obtained to be 92.6% at 10.1 mg/L of initial mercury ion concentration. The Hg(II) ion uptake data were analyzed according to the linear form of Langmuir and Freundlich adsorption isotherm models (Supporting information). As a result, it is revealed that the Hg(II) ions on the AAO-polyrhodanine membrane obey the Freundlich adsorption isotherm than Langmuir isotherm.

3.3. Adsorption kinetics of Hg(II) ion onto the AAO-polyrhodanine membrane

The time dependence of Hg(II) ion uptake of the polyrhodanine modified AAO membrane was investigated for the kinetic study. As shown in Fig. 7, the increase rate of metal uptake decreases as the filtering time passes. It could be described as follows. At the initial stage, the metal ions can interact easily with the abundant metal binding sites of the AAO-polyrhodanine membrane. The

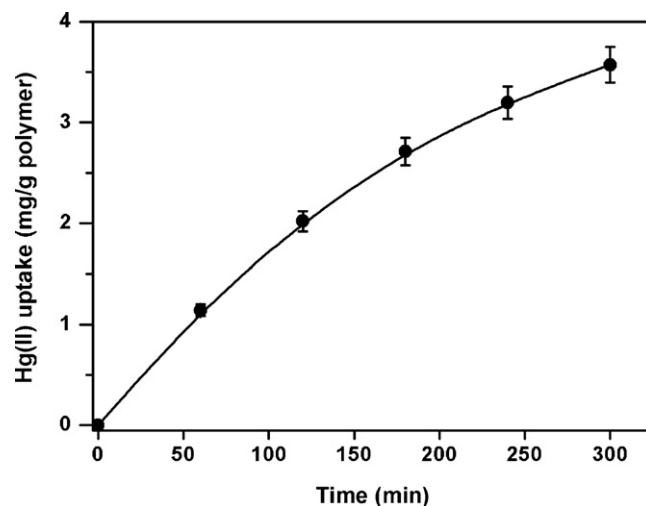


Fig. 7. Time dependence of adsorption capacity of Hg(II) ion onto the polyrhodanine modified AAO membrane. The initial concentration of Hg(II) ion was 100 mg/L, pH value was 6.0 and the flow rate of solution was 2 mL/h.

binding sites were gradually occupied with metal ions and the adsorption process became slow as the contact time increased. In order to investigate the mechanisms of metal adsorption process, the linear form of pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data (Supporting information). As a result, the metal ion uptake process of the AAO-polyrhodanine membrane can be well described by the pseudo-second-order model which assumes that the determining adsorption rate depends on chemical adsorptions. It can be considered that the adsorption of the heavy metal ions onto the polyrhodanine modified AAO is mainly performed by chemical process involving valence forces *via* sharing or exchanging electrons.

3.4. Adsorption study on metal ion species

In addition to Hg(II) ions, the adsorption performances of Pb(II) and Ag(I) ions onto the AAO-polyrhodanine membrane were investigated. Bulk polyrhodanine powder was fabricated *via* dispersion polymerization for control test. As a result of metal uptake test under batch condition, the metal ion uptake values of the bulk polyrhodanine powder are at least five times lower than that of the polyrhodanine modified AAO membrane (Fig. 8). It can be thought that the enhanced metal uptake performance of the AAO-polyrhodanine membrane is attributed to the enlarged surface area which provides more metal binding sites compared to bulk polymer. In our study, the uptake capacities of the fabricated membrane were as follow: Ag(I) > Hg(II) > Pb(II). It has been reported that silver ions readily coordinate with the thioamide and sulfide functional groups of polyrhodanine [26,29]. The sulfur groups of polyrhodanine also have strong affinity to mercury [29]. Consequently, the polyrhodanine-modified AAO membrane shown excellent removal performance to Ag(I) ions (7.0 mmol/g polymer) and Hg(II) ions (4.2 mmol/g polymer) from aqueous solution. It can be thought that the different affinity of binding site of polyrhodanine to Ag(I) and Hg(II) ions affect the different uptake capacity. On the other hand, it was reported that the Pb(II) ions preferably bind to amide groups than sulfur groups [29]. In this study, the uptake of the AAO-polyrhodanine membrane for Pb(II) ions was obtained as 2.3 mmol/g polymer. The fabricated membrane preferentially uptake Ag(I) and Hg(II) ions than Pb(II) ion because the number of sulfur groups is two times more than that of amide groups in polyrhodanine. Therefore, it can be suggested that the different binding sites of Ag(I), Hg(II), and Pb(II) ions cause the dif-

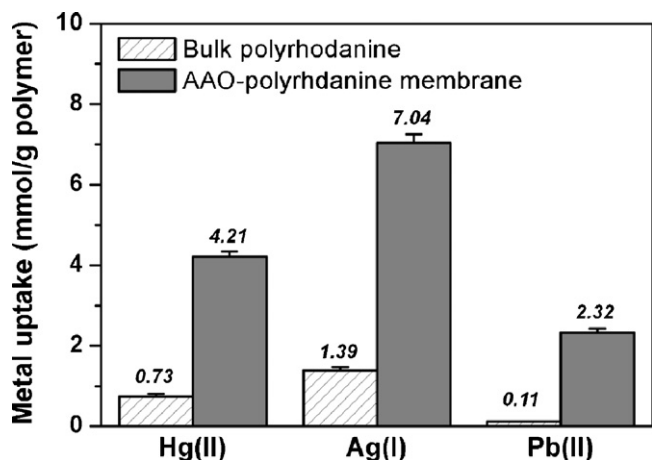


Fig. 8. Hg(II), Ag(I) and Pb(II) ions uptake capacity of the bulk polyrhodanine and AAO-polyrhodanine membrane. The initial concentrations of metal ions were adjusted as 200 mg/L and pH value was 6.0. The AAO membrane was tested under continuous flow condition at 2 mL/h of flow rate and the bulk polymer was tested under batch condition.

ferent uptake capability of these metal ions onto the polyrhodanine modified AAO membrane. In addition, the disparity in cation radius and interaction energy of the heavy metal ions can also affect the different uptake capability [8]. These results suggest that the AAO-polyrhodanine can be used for filtration of various heavy metal ions from water.

3.5. Recycle of the AAO-polyrhodanine membrane

Recyclability is regarded as a crucial property in the filter systems. Among the metal ions, Hg(II) ion was selected for the recycling study of polyrhodanine modified AAO because mercury is well-known for toxic and harmful metal. In order to recover the metal binding property, the used polyrhodanine membrane was washed with nitric acid solution at pH 4.0. When the acid solution passed through the membrane, the adsorbed metal ions were substituted with abundant H^+ ions. In order to neutralize the acid-treated membrane, it was washed several times with deionized water. After the regeneration process, the metal ion uptake of the membrane was evaluated. As a result, the metal removal capability of the recovered membrane was similar to that of the fresh one. After five times of recycling, the polyrhodanine membrane shown above 94.5% of Hg(II) ion uptake efficiency (Fig. 9). G. Kardas and

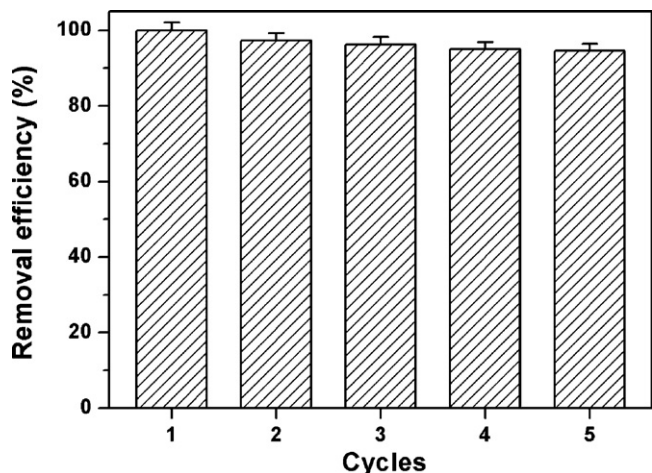


Fig. 9. Removal efficiency of Hg(II) ions in serial recycle tests by the AAO-polyrhodanine membrane.

R. Solmaz reported that the polyrhodanine well dissolved in NMP solution turned dark purple from optically transparent [28]. The acid solution used for recovery process was mixed with NMP solvent in order to confirm the existence of the polyrhodanine in the solution. As a result, the mixed solution maintained optically transparent state. Therefore, it was concluded that the polyrhodanine was not washed out from inner wall of AAO during acid treatment. According to these data, it is confirmed that the used membranes readily recover their metal-binding properties by acid treatment and washing process. Therefore the AAO-polyrhodanine membrane can be re-used in heavy metal ion removal studies.

4. Conclusion

The AAO-polyrhodanine membrane was synthesized by the VDP method and applied for heavy metal ion adsorption. As a result, the fabricated membrane exhibited enhanced metal uptake performance compared with bulk polyrhodanine powder. The improved metal adsorption capability could be originated from the large inner-surface area of the AAO membrane. The kinetics of adsorption of Hg(II) ion on polyrhodanine membrane followed a pseudo-second order equation, indicating that the metal ions are chemically adsorbed. The maximum uptake capacities of Ag(I), Hg(II) and Pb(II) ions onto the AAO-polyrhodanine membrane were 7.0 mmol/g polymer, 4.2 mmol/g polymer, and 2.3 mmol/g polymer, respectively. In addition, the fabricated membrane could be recycled after regeneration process. According to these results, the AAO-polyrhodanine membranes can be used as the potential filter for heavy metal removal from water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.01.026.

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