

Hyperbranched Poly(amidoamine)–Anchored Membrane for Heavy Metal Ions Removal from Wastewater

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1. Introduction

The discharge of heavy metal ions into water causes a serious environmental problem due to their toxicity and the potential of bio-accumulation.¹ Herein, we prepared a hyperbranched poly(amidoamine)–anchored membrane in which hyperbranched poly(amidoamine) (HYPAM) can be used as a potential sorbent for the removal of heavy metal ions from wastewater. HYPAM was attached to a polysulfone (PSf) membrane by 1) modifying HYPAM to be amphiphilic, 2) blending it with PSf solution and then 3) solidifying the blend by phase inversion. It was revealed by XPS and ATR-IR that HYPAM was located at the membrane surface. The morphology of the membrane and the amount of the introduced HYPAM were investigated by FE-SEM and TGA, respectively. The HYPAM–anchored membrane can be reusable since not only does HYPAM fix onto the surface but also binds and releases heavy metal ions in water under varied pH conditions. Therefore, HYPAM–anchored membrane is one of promising candidates as a highly efficient and reusable membrane for removal of heavy metal ions in water treatment.

2. Experimental

HYPAM was synthesized by a simple one-pot method.²

To modify the HYPAM to be amphiphilic, 0.76 mL of palmitoyl chloride dissolved in 10 mL chloroform solution was slowly added to a solution of 14.5 wt% HYPAM in chloroform and 0.70 mL of triethylamine. The mixture was stirred at 35 °C for 24 h, and then washed with deionized water several times. The lower phase was separated and dried with anhydrous magnesium sulfate (MgSO₄) and then filtrated. Subsequently, the

filtrate was precipitated in methanol. After the precipitate was dried under vacuum at 50°C for 24 h, the amphiphilic HYPAM (a-HYPAM) was obtained.

To fabricate HYPAM-anchored membrane, polysulfone (PSf) was dissolved in N-methyl-2-pyrrolidinone (NMP) to make 15 wt% polymer solutions. The PSf solution and the a-HYPAM were mixed together in a given composition (1, 4, 8 wt% a-HYPAM vs. PSf solution) to make dope solutions. The dope solutions were cast on a glass substrate with a 120 μm applicator and immersed in the bath (5 wt% NMP aqueous solution) immediately. After peeling from the substrate, the membranes were rinsed with deionized water several times and stored in water before use.³

3. Results and discussion

The chemical structure of the HYPAM was characterized by FT-IR, ¹H-NMR, ¹³C-NMR. The IR absorptions at 3300 (NH₂ stretch) and 1557 cm⁻¹ (NH₂ bend) were observed. In addition, a relatively weak peak at 1730 (ester C=O stretch) and a strong peak at 1650 cm⁻¹ (amide C=O stretch) were observed.

The analysis of the a-HYPAM was conducted by FT-IR and ¹H-NMR spectra. In FT-IR spectra, a long alkyl chain peak was observed in the range of 2850–3000 cm⁻¹. In ¹H-NMR (CDCl₃) spectra, 0.88 (-CH₃) and 1.25 [-(CH₂)₁₃-] peaks appeared.

PSf and 1, 4, 8 wt% HYPAM-anchored membranes (PSf-M, HYP-M1, HYP-M4, HYP-M8) were characterized by XPS, ATR-IR to confirm the presence of a-HYPAM on the membrane surface. Figure 1 shows XPS curves of the membrane surface. In the case of HYP-M series, signal observed at 530.1 eV was attributed to the oxygen of carbonyl

group which was not observed in PSf-M.

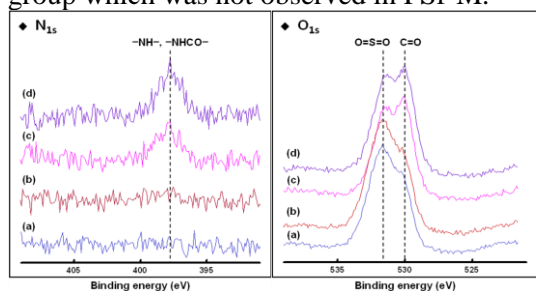


Figure 1. XPS curves of a) PSf-M, b) HYP-M1, c) HYP-M4, d) HYP-M8 surfaces.

The signal observed at 397.9 eV was attributed to the nitrogen of amine and amide which were larger in order of the greater content of a-HYPAM.

ATR-IR spectra of the membranes displayed the characteristic peaks of a-HYPAM. The peak at 3300 cm^{-1} (N-H stretch) and 1650 cm^{-1} (amide C=O stretch) became larger in accordance of the content of a-HYPAM. Moreover, the peak in the range of $2850\text{--}3000\text{ cm}^{-1}$ (C-H stretch) became larger due to the increase in the contents.

The contents of a-HYPAM anchored on membranes were measured from TGA curves. Figure 2 shows the weight loss of the four membranes when heated from 50 to $700\text{ }^{\circ}\text{C}$. The a-HYPAM contents, estimated from comparing the residual weight of (b), (c), and (d) with that of (a) at $500\text{ }^{\circ}\text{C}$, are 5, 19, and 34 wt%.

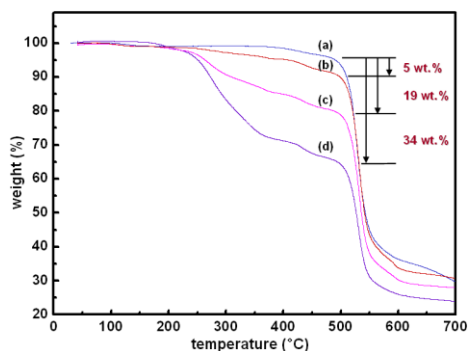


Figure 2. TGA curves of a) PSf-M, b) HYP-M1, c) HYP-M4, d) HYP-M8.

Fig. 3 shows FE-SEM images of both surfaces and the cross-section of the membrane. The water-contacting (front) surface had cracks, and the glass-contacting (back) surface had pores. The pore size observed on the back surface of the four

membranes was in the range of 10–100 nm. No significant change of morphology was observed with an increase in the content of a-HYPAM.

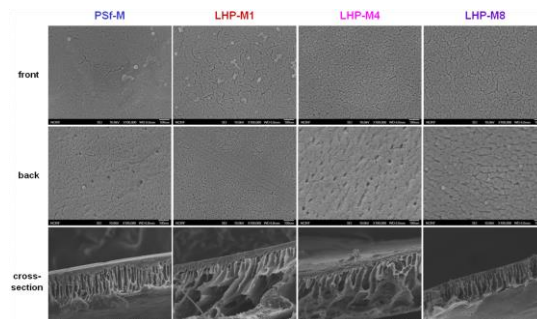


Figure 3. FE-SEM images of PSf-M, HYP-M1, HYP-M4, and HYP-M8.

4. Conclusions

In this study, we focused on the preparation of HYPAM-anchored membrane which is a promising candidate for removal of heavy metal ions from wastewater. The HYPAM-anchored membrane has been fabricated and confirmed by ATR-IR and XPS. The contents of a-HYPAM present on membranes have been measured by TGA and have been 5, 19, and 34 wt% in order of HYP-M1, HYP-M4, and HYP-M8. No significant change of the membrane morphology has been observed by FE-SEM images. Consequently, the results of this study indicate that HYPAM-anchored membrane can be successfully fabricated for removal of heavy metal ions in water treatment.

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