Hyperbranched poly(amidoamine)/polysulfone composite membranes for Cd(II) removal from water

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A B S T R A C T

A composite membrane composed of hyperbranched poly(amidoamine) (HYPAM) and polysulfone (PSf) was successfully prepared to enable the removal of heavy metal ions from contaminated aqueous media. HYPAM was prepared by a one-pot reaction followed by modification with palmitoyl chloride, which included a long aliphatic chain that improved the compatibility with the hydrophobic PSf. The dendritic chelating agent HYPAM was incorporated into PSf via a phase inversion process to produce a HYPAM/PSf membrane. The resulting membrane was characterized by thermogravimetric analysis, X-ray photoelectron spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy, and field-emission scanning electron microscopy. The binding capacity of the HYPAM/PSf membrane toward heavy metal ions [Cd(II)] was investigated by inductively coupled plasma atomic emission spectroscopy. The efficiency of Cd(II) removal was 51% and resulted from metal ion complexation by a tertiary amine of HYPAM, and primary amine and amide groups grafted onto the PSf membrane surface. Moreover, the water permeability and the bovine serum albumin (BSA) retention of the HYPAM/PSf composite membrane were as high as 18 L m⁻² h⁻¹ at 1 bar and 85%, respectively. Under acidic conditions, the composite membrane recovered 86% of the Cd(II) ions. The findings of the present study highlight the potential for using HYPAM/PSf composite membranes as effective recyclable materials for the removal of heavy metal ions in the context of water treatment.

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1. Introduction

Water contamination by heavy metals is a grave environmental issue [1]. Heavy metals are discharged from a variety of sources in daily life and can be readily oxidized into ions when dissolved in water [2]. They do not degrade naturally and pose significant risks to human health and the environment. Among the heavy metals, cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), copper (Cu), and zinc (Zn) are the most hazardous and are included on the U.S. Environmental Protection Agency’s (EPA) list of priority pollutants. To date, three major strategies are used to approach the problem of metal ion removal from water: chemical precipitation, reverse osmosis processes, and adsorbents, such as activated carbon or ion exchangers [3]. Although these methods are effective in removing metal ions, they are expensive to operate, non-reusable, or they cause membrane fouling or secondary contamination.

Poly(amidoamine) (PAMAM) dendrimers have been proposed as promising sorbents for the removal of heavy metal ions because they contain numerous cavities and are amenable to functionalization with a range of chemical groups that selectively chelate a target metal ion [4,5]. The high density of nitrogen ligands and the potential for attaching functional groups, such as amines and amidites, to the PAMAM dendrimers can substantially increase the binding capacity toward a variety of toxic metal ions. However, the use of PAMAM dendrimers in the field of water treatment has been limited. They are expensive and time-consuming to synthesize due to a tedious and iterative synthetic reaction sequence. Moreover, chelating agents, such as PAMAM dendrimers, must be filtered through an ultrafiltration (UF) or nanofiltration (NF) membrane to separate and recover the polymer from the aqueous solutions [4,6]. This requirement imposes an additional cost on the removal of heavy metal ions from water.

Recently, several studies have attempted to remove metal ions from water using a combination of technologies and membranes. The use of membranes rather than separation or purification processes during metal ion removal can reduce the operating costs and the net energy consumption requirements. Several studies have tested UF membranes and have shown considerable improvements upon addition of chelating polymers that form complexes with metal ions. These complexes are subsequently retained by the UF membrane. This method is called polymer-assisted UF or polymer-enhanced UF (PEUF). Diallo et al. carried out an extensive study of PEUF for the removal of metal ions from aqueous solutions using EDA core PAMAM dendrimers [4,7,8]. Lebrun et al. combined...
poly(ethyleneimine) (PEI) with a poly(vinyl alcohol) matrix to produce a novel membrane [3,9]. The PEI was used for the removal of Pb(II), Cd(II), and Cu(II). Natural polymers, such as chitosan [10–12] and alginate [13], or synthetic polymers, such as poly(acrylic acid) (PAA) [14,15], have also been used for PEUF. PEUF yields a filtrate containing purified water and a retentate containing metal ion–polymer complexes. The retentate may be regenerated at low pH to recover the metals and recycle the polymers. Despite these advantages, the tedious and costly synthesis of chelating polymers limits their applicability.

The goal of this work was to simplify PEUF by using polysulfone (PSf) membranes, in which chelating polymers, hyperbranched poly(amidoamine) (HYPAM), were integrated in a single operation to produce a HYPAM/PSf composite membrane. HYPAM was selected in view of its low cost of synthesis via a one-pot reaction [16,17], its good binding capacity toward various metal ions, and its reusability [5], all of which qualities are more favorable than the PAMAM dendrimer. Moreover, the immobilization of HYPAM in membranes was expected to lower the loss of the chelating polymer and to reduce the operating costs by simplifying the metal ion removal process. PSf was selected for its excellent characteristics, such as its solubility over a large range of aprotic polar solvents, high thermal resistance, high chemical resistance over the entire pH range, resistance to oxidation in solution, high mechanical resistance of films, and moderate reactivity in a variety of chemical treatments [18,19]. The structural features of the HYPAM/PSf composite membrane were characterized by X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The morphology was characterized by field-emission scanning electron microscopy (FE-SEM). The weight percentage of the chelating polymer incorporated into the PSf membrane was measured by thermogravimetric analysis (TGA). Finally, and most importantly, the binding capacity of the membrane toward heavy metal ions [Cd(II)] was investigated by filtering metal ion solutions at pH 7. The concentrations of the solution before and after filtration were evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES). ICP-AES results were compared with the results of the HYPAM-free membrane to analyze the efficiency of metal ion removal. In addition, the recovery efficiency of the composite membrane was measured by regenerating the metal ion-loaded membrane.

2. Experimental

2.1. Materials

Reagent-grade ethylenediamine (EDA) and N-methyl-2-pyrrolidone (NMP) were supplied by Tokyo Chemical Industry Co. and were used as received. Methyl acrylate (MA) was purchased from Alfa Aesar and purified by vacuum distillation. PSf (Ultraspin S 6010) was obtained from BASF and dried in a vacuum oven at 80 °C for 24 h prior to use. Bovine serum albumin (BSA, Mw: 67 kDa) and cadmium nitrate tetrahydrate (Cd(NO3)2·4H2O) were purchased from Sigma–Aldrich. Water used in all experiments was distilled and deionized.

2.2. Preparation and modification of hyperbranched poly(amidoamine)

Hyperbranched poly(amidoamine) (HYPAM) was synthesized by a one-pot method (see Fig. S1). To prepare the tetra-ester (MA4–EDA), 17.22 g (0.2 mol) methyl acrylate (MA) and 30 mL methanol were placed in a round-bottomed flask, and 3.01 g (0.05 mol) ethylenediamine (EDA) was added drop-wise to the flask at 3 °C for 2 h. The system was allowed to react at room temperature for 24 h [20]. The flask was fixed onto a rotary evaporator to remove the methanol under vacuum at room temperature. Further additions of 21.04 g (0.35 mol) EDA to the flask, and the reaction were conducted over 24 h at 50 °C. After reacting for 1 h at 60 °C, 2 h at 100 °C, 2 h at 120 °C, and 2 h at 140 °C under reduced pressure, the final product, a yellow gum, was obtained [16]. The product was modified with palmitoyl chloride (PC) to yield amphiphilic HYPAM (a-HYPAM). A 5.62 g (20.4 mmol) sample of PC dissolved in 12 mL chloroform was slowly added to a mixture containing 22.96 g HYPAM in 50 mL chloroform and 4.13 g (40.9 mmol) triethylamine. The system was stirred at 35 °C for 24 h and washed with deionized water several times. The lower phase was separated and dried over anhydrous magnesium sulfate (MgSO4), followed by filtration. The filtrate was subsequently precipitated in cold methanol. The precipitate was dried under vacuum at 50 °C for 24 h to yield the modified HYPAM.

2.3. Preparation of HYPAM/PSf composite membrane

PSf was dissolved in N-methyl-2-pyrrolidone (NMP) to make 15 wt% polymer solutions. The PSf solution and a-HYPAM were mixed together in a given composition (weight percentages of a-HYPAM to PSf solution: 1, 3, 5 wt%) and stirred for 24 h at 40 °C to prepare the casting solutions. The composite membranes were prepared using a phase inversion process, in which the solutions were cast on a glass substrate using a 150 μm applicator, followed immediately by immersion in a coagulant bath (5 wt% NMP in water). After peeling from the substrate, the membranes were rinsed with water several times and stored in water prior to use. The fabricated flat membranes were denoted neat-F, HYP1-F, HYP3-F, and HYP5-F, respectively, according to the composition of the a-HYPAM in the casting solution. Hollow fiber composite membranes were fabricated using a spinning apparatus. A casting solution was prepared by adding the modified HYPAM to the PSf solution. The mixture was spun to fabricate the hollow fiber membranes. The spinning conditions are described in detail in Table 1. The HYPAM-free and the HYPAM-incorporated hollow fiber membranes are denoted neat-H and HYP-H, respectively.

Table 1

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting solution 1 (neat-H)</td>
<td>PSf/NMP = 75/425 (g)</td>
</tr>
<tr>
<td>Casting solution 2 (HYP-H)</td>
<td>PSf/NMP/a-HYPAM = 75/425/26 (g)</td>
</tr>
<tr>
<td>Bore solution</td>
<td>Water/ethylene glycol = 25/75 (g)</td>
</tr>
<tr>
<td>Coagulant</td>
<td>Water/NMP = 95/5 (g)</td>
</tr>
<tr>
<td>Air gap</td>
<td>2 cm</td>
</tr>
<tr>
<td>Spinnernet diameter</td>
<td>Outer diameter/inner diameter = 1.4/0.7 (mm)</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>30%</td>
</tr>
</tbody>
</table>

2.4. Characterization

2.4.1. Instrumentation

1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 NMR spectrometer (600 MHz for proton) in CDCl3 using TMS as the internal standard. Quantitative 13C NMR measurements (150 MHz for carbon) were conducted in D2O as the solvent with a delay between pulses of 55 s. The quantitative response was verified using a test solution of known Me4NOH concentration. The conditions for the multi-angle light scattering (MALS) measurements are as follows: the measurements were performed using a Wyatt Technology miniDAWN Tristar photometer with a laser operated at 690 nm to evaluate the weight-average molecular weight (Mw) of HYPAM in acetate buffer solution at pH 5. The solution (50 °C, flow rate 0.5 mL min−1) was injected into the
apparatus equipped with a refractive index detector (Wyatt Optilab DSP), a column pack (Waters Ultraspheryd gel 250), and a MALS detector. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra in the range 4000–650 cm⁻¹ were recorded using a Thermo Scientific Nicolet 6700 IR spectrometer with 128 scans and a spectral resolution of 8 cm⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG SIGMA PEBE spectrometer using a mono-chromatic Al Kα (1486.6 eV) as the X-ray source. Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q-5000 IR Analyzer over the temperature range 50–700 °C with a scan rate of 10 °C min⁻¹ under nitrogen stream. The morphology of the top surface (coagulant-contacting surface) and the cross-section of the membrane were examined using a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM). Prior to FE-SEM measurements, the samples used to gather cross-sectional images were immersed in liquid nitrogen for 5 min and fractured. All samples tested were coated with gold under vacuum prior to observation.

2.4.2. Permeation with pure water and bovine serum albumin (BSA)

Filtration experiments were performed using two systems, as described previously [4,21]. Flat membrane experiments were performed using a 50 mL stirred cell (Amicon, model 8050) with an effective membrane area of 13.4 cm². Hollow fiber membranes were prepared using small hollow fiber modules. Each module consisted of 4 pieces of hollow fibers 8.5 cm in length (see Fig. S2). The water permeability of the membrane was measured under the following conditions. The trans-membrane pressure was kept constant at 1 bar by applying pressure from N₂ gas, and the filtration cell was stirred at 200 rpm min⁻¹ using a stirrer plate. The filtration was pre-run for 30 min before measuring the water permeability. The permeation data were collected at fixed time intervals to determine the water flux (Jw) until the flux remained constant for at least three successive readings.

\[
J_w \text{ (L m}^{-2}\text{h}^{-1}) = \frac{\text{permeate volume}}{\text{membrane area} \times \text{filtration time}}
\]  

(1)

Bovine serum albumin (BSA) was used as a standard for evaluating the membrane retention performance. A standard BSA solution (15, 25, 50, 75, 100, 200 ppm) was prepared at room temperature by dissolving a pre-weighed amount of BSA powder in phosphate buffer at pH 7.2 [22]. The absorbance values of the feed and permeate were measured by UV–vis absorption spectroscopy at 280 nm. The average of three replicates was reported. Rejection of the membranes for BSA (R_{BSA}) was expressed as follows:

\[
R_{BSA} \% = \left(1 - \frac{\text{permeate concentration}}{\text{initial concentration}}\right) \times 100
\]  

(2)

where C_P and C_I are the permeate and feed concentrations, respectively.

2.4.3. Heavy metal ions removal and membrane recovery

Filtration tests were conducted on the same system used previously to test water and BSA permeation. Cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O) was used as a source for the heavy metal ion [Cd(II)]. Prior to the experiment, Cd(NO₃)₂·4H₂O was dissolved in water, and the pH of the solution was adjusted with 0.1 M NaOH to pH 7.0. The concentration of the solution was 25 ppm. During the experiment, the system was operated at a steady flow rate of 0.1 mL min⁻¹. The filtrate was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The membrane recovering efficiency was measured after desorbing the metal ions retained by the membrane. Recovery experiments were performed using a 0.1 M HCl solution (pH 1.2) filtered through the metal ion-loaded membrane. The recovery rate of the membrane was calculated by comparing the concentrations of the retained metal ions and the filtrate. Additional experiments were conducted using the hollow fiber membranes to test the possibilities for industrial applications because hollow fibers have been widely used in industry for water purification. The experimental procedure was as described above.

3. Results and discussion

3.1. HYPAM and modified HYPAM

The preparation of HYPAM was confirmed by ¹H NMR spectroscopy. Fig. S3 shows the 600 MHz ¹H NMR spectra of MA₄–EDA, EDA, and HYPAM in CDCl₃ in support of the synthesis of HYPAM. The spectrum in Fig. S3(a), MA₄–EDA, contained peaks assigned to (a) –COOCH₃ at 3.67 ppm; (b) N–CH₂–CH₃–COOCH₃ at 2.77 ppm, triplet; (c) N–CH₂CH₂–N at 2.49 ppm, singlet; and (d) N–CH₂–CH₃–COOCH₃ at 2.44 ppm, triplet. The spectrum of EDA was readily assigned due to the simple chemical structure, with (e) –CH₂CH₂– at 2.74 ppm and (f) –NH₂ at 1.20 ppm (Fig. S3(b)). Significant differences were observed in the spectrum of HYPAM, which displayed (g) –CO–NH– at 7.41–8.24 ppm and (i and j) –CONH–CH₂– at 3.23–3.44 ppm peaks (Fig. S3(c)). The broad peak of the primary amine groups k (–NH₂) was observed at 1.48 ppm. Because the ¹H NMR results were insufficient to reveal the chemical structure of HYPAM, quantitative ¹³C NMR measurements were conducted using a calibrated product (Me₄NOH, 2.56 mmol). Fig. S4 shows ¹³C NMR spectrum of HYPAM and assigned peaks of the functional groups of HYPAM. The integral ratios relative to the calibrated HYPAM are presented along with the structural units in Table S1. The quantities of each functional group were obtained by comparison with the Me₄NOH peak at 55.22 ppm, as follows:

\[
\text{Quantity of functional group (mmol g}^{-1}) = \frac{\text{integral ratio to calibration product}}{\text{mass of the sample}}
\]  

(3)

where the integral of the calibration product (Me₄NOH) was 2.56 mmol, and the mass of the sample (HYPAM) was 0.14 g. The weight average molecular weight (Mw) of HYPAM was 3600 g mol⁻¹, determined by multi-angle light scattering (MALS) analysis. The refractive index increment (dn/dc) for HYPAM was 0.250 (ml/g⁻¹). Quantitative analysis of the chemical structure was conducted by MALSS, along with quantitative ¹³C NMR spectroscopy. The chemical structure of the polymer is described in detail in Tables S1 and S2. Adding palmitoyl groups to HYPAM endows a hydrophobic character that is compatible with the hydrophobic PSF. Fig. S5 shows three ¹H NMR spectra of (a) HYPAM, (b) palmitoyl chloride, and (c) modified HYPAM (a-HYPAM). Each characteristic peak was assigned, as shown in Fig. S5, to provide the substitution degree of the terminal group by comparing the integral values of a (–NH₂ at 1.60 ppm) and k (–COOCH₂–CH₂–(CH₂)₁₃CH₃ at 1.88 ppm). The substitution degree of the terminal group was found to be 8.67, which was relatively close to the theoretical value of 7.00. Overall, the HYPAM modification process was successful.

3.2. HYPAM/PSf composite membrane

ATR-FTIR spectral analyses were performed to verify the incorporation of modified HYPAM into the membrane. Significant differences between the spectra of the as-prepared flat membranes were observed in the ATR-FTIR results, as shown in Fig. 1. An absorption peaks at 1640 cm⁻¹ appeared in the spectra of the HYP-F series due to the presence of carbonyl groups in the a-HYPAM. The N–H stretching peaks also appeared at 3299 cm⁻¹ due to the
presence of amino groups in the α-HYPAM. The relative intensities of the observed peaks gradually increased as the modified HYPAM content in the membrane increased. Introduction of modified HYPAM into the membrane was qualitatively demonstrated. XPS was used to analyze the chemical composition of the membrane. The XPS spectra of the neat-F and HYP-F series did not display any signals in the N1s region of the former membrane, whereas signals appeared at 399.6 eV in the latter membrane series. These signals were attributed to the amide [–NH(C=O)–] and amino groups [–NH–] of the α-HYPAM molecule (see Fig. 2). The intensity of the signal increased with the α-HYPAM content of the membrane. In the O1s spectra of all membranes, the signals at 533 eV
Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>neat-F (%)</th>
<th>HYP1-F (%)</th>
<th>HYP3-F (%)</th>
<th>HYP5-F (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.77</td>
<td>83.91</td>
<td>83.50</td>
<td>83.39</td>
</tr>
<tr>
<td>O</td>
<td>10.44</td>
<td>12.22</td>
<td>11.96</td>
<td>11.97</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>0.48</td>
<td>1.16</td>
<td>1.82</td>
</tr>
<tr>
<td>S</td>
<td>3.48</td>
<td>3.39</td>
<td>3.38</td>
<td>2.82</td>
</tr>
<tr>
<td>N/S</td>
<td>0</td>
<td>0.14</td>
<td>0.34</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 2 shows the composition of the membranes.

corresponded to the sulfonyl groups [O=SiO] of PSf, whereas strong signals at 531.8 eV were observed only in the spectra of the composite membranes. This indicated that the signals were attributed to the carbonyl groups [C=O] of a-HYPAM. The molecular composition of the membrane, listed in Table 2, agreed with the XPS results. For example, the N/S ratio indicated the relative a-HYPAM content of the membrane. Table 2 shows that the nitrogen concentration increased with the a-HYPAM content. In summary, the ATR-FTIR and XPS results provided clear evidence that the modified HYPAM was successfully introduced into the membrane. The weight percentage of a-HYPAM in the membrane was measured by TGA. The TGA spectra shown in Fig. 3 provide a starting point for the weight loss behavior and the percentage weight loss. In the spectra, all three HYP-F membranes showed similar behavior, in which the first change occurred at 210 °C and the second at 480 °C. The changes were attributed to the loss of a-HYPAM and PSf, respectively. The weight percentage of a-HYPAM incorporated into the membrane was investigated by comparing the weights at 210 °C and 480 °C. As a result, the measured values were 2.60 wt%, 12.98 wt%, and 25.02 wt% a-HYPAM in the HYP1-F, HYP3-F, and HYP5-F, respectively. Table 3 shows the mass of a-HYPAM in the casting solution and the weight percentage of a-HYPAM in the fabricated membrane. There is a large difference between calculated composition and measured composition for a-HYPAM content of HYP1-F. Since a-HYPAM is amphiphilic, small amount of a-HYPAM can leak out to the aqueous coagulant when phase inversion takes place. The loss of small a-HYPAM content from HYP1-F casting solution results in a large discrepancy between the calculated and the measured whereas the small loss from HYP5-F casting solution does not lead to a strong difference between two values. The calculated percentage of HYP5-F was quite similar to the calculated value. The FE-SEM images of the four membranes are shown in Fig. 4, which shows the top surface and cross-sectional images. All membranes were 70 μm thick. The membranes had a relatively dense top layer and a porous sub-layer. No significant defects were found on the surfaces of the composite or neat membranes. The cross-sectional images varied significantly according to the a-HYPAM content. Typical finger-like macrovoids were observed in the cross-sections of the neat-F membrane. However, as the a-HYPAM content increased, the finger-like voids became less numerous and more sponge-like structures were observed. These results confirmed that the a-HYPAM included in the polymer solution was closely related to the morphological changes. Macrovoid formation requires the presence of a dense layer in the membrane that limits the penetration of bulk solvent, such as water, into the sub-layer and additionally prevents formation of more than a few nuclei, which initiate macrovoid formation [23]. Because the modified HYPAM used in this study was amphiphilic, the hydrophilic region of a-HYPAM could leach out of the membrane surface during phase inversion. This can result in formation of sponge-like structures, rather than macrovoids, upon addition of a-HYPAM. The outer surface and the cross section images of the hollow fiber are presented in Fig. 5. It is seen that the cross-sectional morphologies of neat-H and HYP-H have completely different structures. A number of finger-like macrovoids are observed in the cross-section of neat-H as seen in that of the flat membrane, neat-F. On the other hand, many sponge-like structures are observed in the HYP-H. This phenomenon may correspond to the sponge-like structure formation principle mentioned above.

3.3. Pure water permeability and BSA retention

The water permeability of a membrane is an important factor for membrane performance, and was measured for the membranes prepared here. Deionized water was used as a feed solution. The volume collected was quantified using an electronic balance. The average permeabilities (J_w) were 4.0, 5.4, 6.7, and 18.4 L m⁻² h⁻¹, respectively, for neat-F, HYP1-F, HYP3-F, and HYP5-F. The permeabilities and error ranges are plotted in Fig. 6. The four membranes had relatively low permeabilities when compared to commercial UF membranes, such as Amicon YM5 regenerated cellulose membranes (ca. 30 L m⁻² h⁻¹) supplied from Millipore [4,25]. This result can be due to the hydrophobicity of PSf and having no additives like non-solvent or pore-forming agent to the casting solution, but it is beyond the scope of this study and will not be discussed in detail. The permeabilities gradually increased with the a-HYPAM content in the membrane, possibly due to formation of the sponge-like structures shown in the FE-SEM cross-sectional images. Porous structures (sponge-like structures) usually reduce the trans-membrane resistance to water flow, resulting in a higher membrane flux [21]. Membrane retention is another important factor for membrane performance. BSA was used as a retention test substance in these experiments. A calibration curve was constructed by plotting the absorbance of BSA as a function of the concentration of an internal standard (15, 25, 50, 75, 100, 200 ppm) using a least squares approximation. The retention rate (R_{BSA}) was calculated using Eq. (2) mentioned above. The average retention values were 94.0%, 91.9%, 85.5%, and 84.5%, respectively, for neat-F, HYP1-F, HYP3-F, and HYP5-F. The retentions and error ranges are plotted in Fig. 6. The retentions decreased slightly as the a-HYPAM content in the membrane increased, but all membranes tested yielded high retentions (above 85%). These properties may

![Figure 3](Image)

**Fig. 3.** TGA curves of (a) neat-F, (b) HYP1-F, (c) HYP3-F, and (d) HYP5-F.

![Figure 3](Image)

**Table 3**

<table>
<thead>
<tr>
<th></th>
<th>HYP1-F (%)</th>
<th>HYP3-F (%)</th>
<th>HYP5-F (%)</th>
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</thead>
<tbody>
<tr>
<td>PSf (g)</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>a-HYPAM (g)</td>
<td>0.05</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>Calculated (wt%)</td>
<td>6.25</td>
<td>16.67</td>
<td>25.74</td>
</tr>
<tr>
<td>Measured (wt%)</td>
<td>2.60</td>
<td>12.98</td>
<td>25.02</td>
</tr>
</tbody>
</table>

* (mass of a-HYPAM/mass of PSf) × 100.
be attributed to the structure of the membrane skin layer. Generally, the membrane retention depends on the structure of the membrane top layer but seldom depends on the structure of the membrane sub-layers [21]. Because all membranes tested had similar surface structures, even though more porous structures were present in the sub-layers, as observed in the FE-SEM images, they exhibited high levels of retention. The hollow fiber membrane behavior was similar to that of the flat membrane in terms of water permeability and BSA retention. The water permeabilities were 3.7 and 18.1 L m⁻² h⁻¹, respectively, for neat-H and HYP-H. The BSA retention values were 94.3% and 87.2%, respectively, for neat-H and HYP-H.
3.4. Cd(II) removal and membrane recovery

The Cd(II) removal and recovery capacities of the flat membranes were evaluated. Changes in the concentration of Cd(II) were analyzed by ICP-AES. The changes in the quantity of Cd(II) retained by the membranes were analyzed with increasing time. The accumulated uptake based on time was graphed as shown in Fig. S6. The total quantity of Cd(II) penetrated into each membrane was 450.7 µg (the amount of 25 ppm Cd(II) present in 18 mL aqueous solution) for 180 min. 5.04, 6.49, 185.58 and 227.88 µg were finally retained, respectively by neat-F, HYP1-F, HYP3-F and HYP5-F. As presented in Table 4, the HYPAM-free membrane, that is, the neat-F membrane, barely captured Cd(II), whereas the amounts of Cd(II) taken up by the composite membranes were proportional to the a-HYPAM content. Based on the dimension of membrane, the amount of Cd(II) ion uptake for neat-F, HYP1-F, HYP3-F, and HYP5-F were 0.38, 4.89, 13.85, and 17.06 µg cm⁻², respectively. In particular, the removal efficiency for the HYP5-F sample is significantly higher than HYP1-F and HYP3-F, with a value of approximately 50%, which is a significant reduction of heavy metal ion. The removal efficiency, R, was defined as the percentage of the quantity of retained metal ion (i−f) by the initial quantity of metal ion (i):

\[
R (\%) = \left(1 - \frac{f}{i}\right) \times 100
\]

where f is the quantity of filtrated metal ion. The membrane recovery process was complex, although the metal ions were successfully recovered to investigate the reusability of the membrane. The Cd(II) retained could be removed from the membrane using an aqueous HCl solution (0.1 M). To our knowledge, the detailed mechanism of Cd(II)-PAMAM complex has yet to be reported. However, the adsorption–desorption mechanism whereby Cu(II) bind to the poly(amidoamine) has been studied previously [24] (see Fig. S7). Herein, the Cd compound used as a metal ion source is dissolved into a divalent cation [Cd(II)] in water just as the Cu compound used in ref. [24]. The oxidation state of Cu and Cd used is +2. In addition, the counter ion coordinated to both metal ions is identical (nitrate anion, NO₃⁻). Therefore, it is assumed that absorption–desorption mechanism of Cd(II) with the dendrimer is almost identical to that of Cu(II) with the dendrimer. After the HCl solution had been sufficiently filtered through the membrane, the filtrate was analyzed by ICP-AES. The recovering efficiency, Rₑ, was defined as the ratio of the quantity of recovered metal ion (nₑ) by the quantity of metal ion (nᵢ) retained in the membrane:

\[
Rₑ (\%) = \left(\frac{nₑ}{nᵢ}\right) \times 100
\]

The membrane recovery rates were 87.0%, 84.7%, and 86.7%, corresponding to HYP1-F, HYP3-F, and HYP5-F, respectively. The composite membranes showed high recovery efficiencies. Subsequent experiments were carried out to confirm whether the loss of the HYPAM takes place during recovery process. Each of the flat membranes was weighed and analyzed by FT-IR before and after use for Cd(II) removal and recovery. The mass of as-prepared membrane with area of 13.4 cm² was 0.072 g, 0.072 g, and 0.068 g, respectively for HYP1-F, HYP3-F, and HYP5-F. After the filtration experiments, the used-membranes (denoted u-HYPF-F)
were washed several times with deionized water and dried under vacuum followed by weighing: 0.073 g, 0.071 g, and 0.067 g, respectively. In addition, the FT-IR results in Fig. S8 showed the identical peaks to those of the unused-membranes. These results confirm that does not have the release of HYPAM in membrane during the whole washing process.

The hollow fiber membranes were tested to examine their binding capacity toward Cd(II) and to evaluate the feasibility of their re-use. The accumulated uptake based on increasing time was represented in Fig. S9. The total quantity of Cd(II) flowed through the membranes was 793.8 μg (the amount of 25 ppm Cd(II) in 30 mL) for 300 min. In case of the hollow fiber membrane, the amount of Cd(II) removed by the neat-H membrane was only 43.7 μg, whereas the HYP-H membrane retained 408.0 μg Cd(II). As shown in Table 4, HYP-H showed a binding capacity (27.29 μg·cm^{-2}) toward Cd(II) that was much higher than that of the neat-H membrane, which captured low quantities (2.92 μg·cm^{-2}) of the metal ions. Cd(II) was removed up to 51% after 300 min. The retained Cd(II) was separated from the used membranes using an aqueous HCl solution (0.1 M). The HYP-H membrane exhibited a high recovery efficiency of 85.7% for Cd(II). Both the flat and hollow fiber HYPAM-containing membranes yielded high recovery efficiencies as well as relatively high binding capacities toward heavy metal ions when compared to the HYPAM-free membrane. HYPAM/Psf composite membrane was applied as highly efficient recoverable and reusable material for heavy metal ion removal.

Table 4
Cd(II) removal efficiency (R) and recovering efficiency (R_e) of the membranes.

<table>
<thead>
<tr>
<th>Flat type</th>
<th>HYP1-F</th>
<th>HYP2-F</th>
<th>HYP5-F</th>
<th>Hollow fiber type</th>
<th>HYP-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>i (μg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f (μg)</td>
<td>445.6</td>
<td>385.2</td>
<td>450.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R (%)</td>
<td>1.1</td>
<td>14.4</td>
<td>42.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (μg/cm^2)</td>
<td>0.38</td>
<td>4.89</td>
<td>13.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n_e (μg)</td>
<td>0</td>
<td>56.5</td>
<td>157.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_e (%)</td>
<td>0</td>
<td>87.0</td>
<td>84.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>86.7</td>
<td>86.7</td>
<td></td>
<td>793.8</td>
</tr>
</tbody>
</table>

4. Conclusion

In this study, the high density branched polymers containing a number of cavities and functional groups were combined to an UF membrane, with the aim of discussing: the feasibility of using the composite membrane to remove heavy metal ions from water and the possibility of re-use of the membrane. HYPAM was synthesized by the one-pot reaction that is time- and cost-effective. The combination of HYPAM with a Psf membrane was successfully achieved by phase inversion process after modifying HYPAM into amphiphilic HYPAM, producing flat and hollow fiber membranes. Filtration test showed that both of these types of HYPAM/Psf composite membranes have higher water fluxes with maintaining high BSA retentions of more than ca. 85% when compared with Psf alone. In addition, these membranes had much higher removal ratios toward Cd(II) than the HYPAM-free membrane which seldom removed the metal ions. They also showed the possibility of re-use with high recovering efficiencies of 85–87%. Thus, this work provides useful insights into the use of HYPAM/Psf composite membranes as efficient materials for the removal of heavy metal ions 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.memsci.2011.12.048.

References


