

Novel Polyamide Bilayer Membranes With Improved Desalination Performance

Young-Hye Na,^{*} Jacquana Diep,^{**} Radwan Al-Rasheed,^{***} Blake Davis,^{*} Geoff Geise,^{****} Ankit Vora,^{*} Majed Nassar,^{**} Melanie McNeil,^{**} Benny Freeman,^{****} Geraud Dubois^{*}

^{*}IBM Almaden Research Center, 650 Harry Road, San Jose, CA95120, yna@us.ibm.com

^{**}Department of Chemical and Materials Engineering, San Jose State University, San Jose, CA95192

^{**}King Abdulaziz City for Science and Technology (KACST), Kingdom of Saudi Arabia, P.O Box 6086, Riyadh 11442.

^{***}Department of Chemical Engineering, University of Texas at Austin, TX 78758.

ABSTRACT

A polyamide bi-layer membrane consisting of conventional non-substituted aromatic polyamide under-layer (REFPA) and HFA-substituted aromatic polyamide top-layer (HFAPA) was prepared by sequential interfacial polymerization of MPD (1st aqueous sol), TMP (organic sol), and HFA-MDA (2nd aqueous sol). The polyamide bilayer membrane showed significant improvement in salt rejection (ca. 50 % reduction in salt passage) with very minor loss in water flux (ca. 8 % reduction) compared to underlying REFPA, resulting in excellent combination of salt rejection and water flux. Efficient removal of toxic substances such as arsenic and boron was also demonstrated.

Keywords: reverse osmosis, desalination, polyamide bilayer, sequential interfacial polymerization

1 INTRODUCTION

Thin film composite (TFC) membranes comprised of ultra-thin active layers upon porous supports have been widely used for water desalination.¹⁻³ For the last few decades, many materials have been investigated as the active layer to enhance separation performance of TFC membranes, and a cross-linked aromatic polyamide prepared by interfacial polymerization of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) has exhibited the best performance (e.g. water flux and salt rejection) so far.⁴ However, the crosslinked aromatic polyamide is easily attacked by chlorine, which is generally added upstream of desalination membranes to kill bacteria and other microorganisms, resulting in significant loss in salt rejection.⁵

Recently, we developed a new chlorine tolerant polyamide TFC membrane containing hexafluoroalcohol (HFA) moieties (Figure 1).⁶ Both the electron withdrawing nature and the steric bulkiness of the HFA groups were shown to be advantageous in protecting the polyamide membranes from chlorine attack. The membranes are relatively hydrophobic at neutral conditions but become hydrophilic at basic conditions due to ionization of the HFA

groups, so we refer to HFA functionality as an “ionizable hydrophobe” and the resulting membrane as “*i-phobe*”.

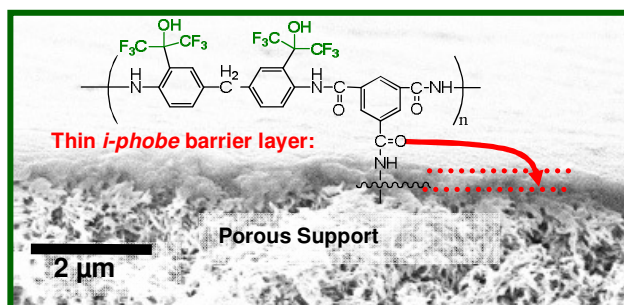


Figure 1. Chemical structure and cross-sectional SEM image of HFA-containing polyamide (*i-phobe*) membrane.

The *i-phobe* membranes show strongly pH-dependent reverse osmosis behavior with enhanced performance (high water flux and high salt rejection) at high pH (ca. pH = 10). However, the maximum salt rejection rate (96 %) obtained with *i-phobe* membranes was lower than the values reported with conventional polyamide desalination membranes (in general, higher than 99.0 % for commercial RO desalination membranes).

In order to further improve the performance of *i-phobe* membranes, specifically in salt rejection, here we have developed a polyamide bilayer membrane consisting of conventional aromatic polyamide under-layer (REFPA) and HFA-substituted aromatic polyamide top-layer (HFAPA).

2 EXPERIMENTAL

General Information: 3,3'-Bis(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)-4,4'-methylene-dianiline (HFA-MDA) was provided by Central Glass, Inc. (Japan) and used as received. m-Phenylene diamine (MPD flakes, > 99 %) and trimesoyl chloride (TMC, 98 %), sodium arsenate (Na₂HAsO₄·7H₂O, 99 %), and arsenic (III) oxide (As₂O₃, > 99.5 %) were purchased from Sigma-Aldrich, and TMC was distilled before use. Sodium chloride (NaCl), sodium hydroxide (NaOH, pellets) and sodium carbonate

(Na₂CO₃) were purchased from J. T. Baker. Hexane was purchased from OmniSolv. Deionized water was used for all experiments. Polysulfone (PSF) ultrafiltration (UF) membranes were purchased from Sepro Membranes, Inc.

2.1 Fabrication of Reference Polyamide Membrane (REFPA)

A PSF UF membrane was placed in an aqueous solution of 2% (w/v) MPD for 2 min, and the membrane was rolled with a rubber roller to remove excess solution. The MPD-saturated PSF membrane was then immersed in a solution of 0.1% (w/v) TMC in hexane. After 1 min of reaction, the TMC solution was decanted and the resulting membrane was rinsed with an aqueous solution of 0.2% (w/v) sodium carbonate and stored in pure water.

2.2 Fabrication of Polyamide Bilayer (HFAPA-on-REFPA)

A Polyamide bilayer membrane, HFAPA-on-REFPA, was synthesized on a pre-formed polysulfone(PSF) ultrafiltration membrane by sequential interfacial polymerization. The PSF membrane was placed in an aqueous solution of 2 % (w/v) MPD for 2 min, and the MPD soaked support membrane was then rolled with a rubber roller to remove excess solution. MPD saturated membrane was then immersed in a solution of 0.1 % (w/v) trimesoyl chlorure (TMC) in hexane. After 1 min of reaction, the resulting membrane was dried and placed in an aqueous basic solution of 2 % (w/v) HFA-MDA diamine for 5 min (2 eq. of NaOH per HFA-MDA molecule was added to completely dissolve HFA-MDA monomer in water). The resulting membrane was then dried for 5 min, followed by rinsing with an aqueous solution of 0.2 % (w/v) sodium carbonate for 5 min and stored in D. I. water until the membrane was evaluated.

2.3 Evaluation of Desalination Performance

Membrane performance was evaluated using a crossflow filtration system. The pure water flux was measured at room temperature (25 °C) after the membrane was compressed for 3 hours at 400 psi (crossflow rate 3.8 L min⁻¹). The salt rejection was performed using an aqueous feed containing 2000 ppm NaCl at the same pressure, and the rejection (R) was calculated as follows:

$$R (\%) = 100 \times (1 - C_p/C_f),$$

where C_p and C_f were the salt concentrations of permeate and feed, respectively.

2.4 Evaluation of Arsenic Removal Efficiency

Arsenate (As(V)) Filtration: 4 mg of Na₂HAsO₄ (As(V)) was dissolved in 14mL of pure water. 12.5 mL of this

solution was added to 4 gallons of water (this produced an As(V) ion concentration of approximately 200 µg/L). 8.8 grams of NaCl was added to this solution (200 µg As(V)/L, 10mM NaCl, pH = 7.3). As(V) rejection was measured with this feed solution by using cross-flow filtration system at 400 psi. pH of feed solution was adjusted using 1M NaOH. 15 mL of permeate was collected for each test and As(V) concentration of permeate samples was analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

Arsenite (As(III)) Filtration: 10 mg of As₂O₃ (As(III)) was dissolved in approximately 10 mL of 0.2 M HCl solution under sonication for approximately two hours. 4 mL of this solution was added to 4 gallons of feed water to get an As(III) concentration of 200 µg/L. Everything else was done exactly the same here as with the As(V) filtration experiments.

2.5 Evaluation of Boron Arsenic Removal Efficiency

75.5 mg of H₃BO₃ (B(III)) was dissolved in 100 mL of D.I water, and this solution was added to 4 gallons of water to form a feed solution with (B(III) concentration: 5 mg/L). Boron rejection was measured with this feed solution by using cross-flow filtration system at 400 psi. pH of the feed solution was adjusted using 1M NaOH. 15 mL of permeate was collected for each test and boron concentration of permeate samples was analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

3 RESULT AND DISCUSSION

A polyamide bilayer membrane was synthesized by sequential interfacial polymerization as shown in Figure 2.

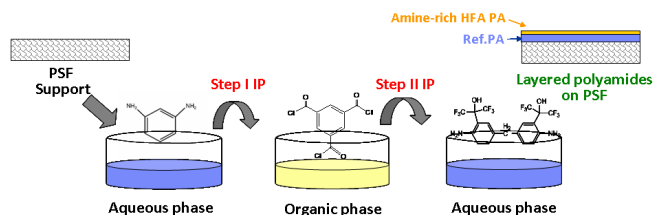


Figure 2. Procedure to fabricate polyamide bilayer membrane by sequential interfacial polymerization

The traditional interfacial polymerization of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) was first performed to form a dense-, crosslinked-aromatic polyamide (REFPA) underlayer on a porous PSF support (step 1 IP in Figure 2). The surface of the resulting REFPA layer always contains free acid chloride groups which did not react with amines in the first interfacial polymerization step. These unreacted acid chlorides are hydrolyzed to carboxylic acid groups as normally observed at the surface

of conventional aromatic polyamide RO membranes. But the hydrolysis reaction is relatively slow so that the acid chlorides can further react with different diamine compounds before the hydrolysis occurs. Thus, the REFPA membrane was directly immersed into an aqueous basic solution of HFA-containing diamine monomer to form HFA-bearing polyamide onto the REFPA (step 2 IP in Figure 2). For comparison, non-substituted reference polyamide (REFPA) membrane was also fabricated by single-step interfacial polymerization of MPD and TMC.

XPS survey spectra showed newly generated-F(1s) peak at 688.4 eV after 2nd step IP, confirming that the HFAPA layer formed successfully on REFPA although cross-sectional SEM/TEM images didn't show a significant enhancement in the film thickness. Water contact angle (θ_w) measurement indicated that the surface of membrane becomes much more hydrophobic ($\theta_w \cong 140^\circ$) after forming a HFAPA layer on REFPA ($\theta_w \cong 78^\circ$).

The separation performance of HFAPA-on-REFPA membrane was evaluated by cross-flow filtration system with 2000 ppm NaCl feed solution and was directly compared with that of REFPA membranes. Table 1 shows the water flux and salt rejection rates obtained with both HFAPA-on-REFPA and REFPA.

	REFPA (A)	HFAPA-on-REFPA (B)	Perforamcne change (ratio)
Water Flux ($L m^{-2} h^{-1}$)	66.7	61.5	-5.2 (7.8 % Red.)
NaCl Rejection(%)	99.4	99.7	+ 0.3
NaCl Passage (%)	0.6	0.3	- 0.3 (50 % Red.)

Table 1. Water flux and salt rejection rates of REFPA and HFAPA-on-REFPA. The filtration experiment was performed with 2000 ppm NaCl solution at 400 psi.

Compared to REFPA, HFAPA-on-REFPA membrane showed about 0.3 % improvement in salt rejection, which corresponds to almost 50 % reduction in salt passage. Since the thickness of the 2nd HFAPA layer was relatively thin as confirmed by SEM/TEM (no noticeable thickness increment), water flux loss caused by this additional layer was not that significant (almost 5 LMH decrement, 7.8 % reduction), in result, the HFAPA-on-REFPA membrane showed very nice combination of salt rejection and water flux. Enhanced performance of the HFAPA-on-REFPA bilayer membrane, specifically in salt rejection is likely due to effective repelling of ionic species by the hydrophobic HFA groups existing on the membrane surface. Relatively weak interaction between ionic salts and hydrophobic HFAPA-REFPA membrane surface was also proved by

concentration polarization modulus value (CPM), which is defined as the ratio of salt concentration at the membrane surface to the bulk feed concentration.⁷ In most cases, HFAPA-REFPA showed lower CPM value ($M = 1.78$) than REFPA ($M = 2.82$) when all membranes were evaluated at the exactly same conditions. (*Two specific membrane coupons, one form HFAPA-on-REFPA and the other from REFPA, with same water flux were also tested to eliminate the effect of the transmembrane flux on CPM, but HFAPA-on-REFPA still showed slightly lower CPM value than REFPA). Relatively lower concentration polarization modulus observed with the HFAPA-on-REFPA bilayer membrane confirms that the hydrophobic HFA groups play an important role in minimizing the accumulation of ions on the membrane surface under the given cross-flow filtration conditions.

The HFAPA-on-REFPA also showed outstanding efficiency in removing harmful substances such as boron and arsenic from water. In general, boron and arsenic (specifically arsenite: As(III)) rejection rates depend on the pH of feed water because some of these compounds are non-ionic at neutral conditions and become ionic at basic conditions ($pH \geq 9.0$). It is reported that 30 ~ 60 % of boron can be removed by commercial brackish water RO membranes at neutral pHs and the rejection rate increases upto 90 ~ 95 % at basic pHs ($pH 10 \sim 11$). One of the commercial RO membranes (ES-10 from Nitto Denko) showed 85 % of arsenate (As(V)) and 50 % of arsenite (As(III)) rejection rates at acidic conditions, but the rejection rates reached almost 90 % for both species at basic condition.⁸

Figure 3 and Figure 4 shows boron and arsenic (As(V) and As(III)) rejection rates measured with the HFAPA-on-REFPA bilayer membrane described in this work at various pHs, respectively.

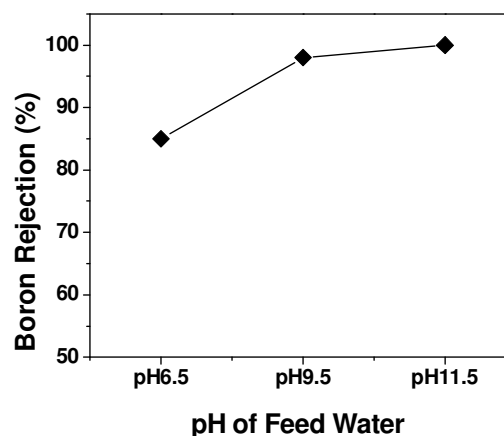


Figure 3. Boron rejection rates of HFAPA-on-REFPA membrane at various pHs

The HFAPA-on-REFPA membrane filtered more than 85.5 % of boron from water at neutral conditions (pH 6.5) and nearly 100 % of boron at high pH (boron content in the permeate was less than the detection limit of ICP-MS spectroscopy), whereas REFPA showed almost 2 ~ 5 % lower boron rejection at the same pH conditions (data for REFPA were not shown in the Figure).

The HFAPA-on-REFPA also effectively filtered predominant arsenic species. As(V) rejection was very high at both neutral and basic conditions (more than 99.5 %), while As(III) rejection increased from 92.5 % to 98.3 % by increasing pH of feed water from 6.5 to 11.5.

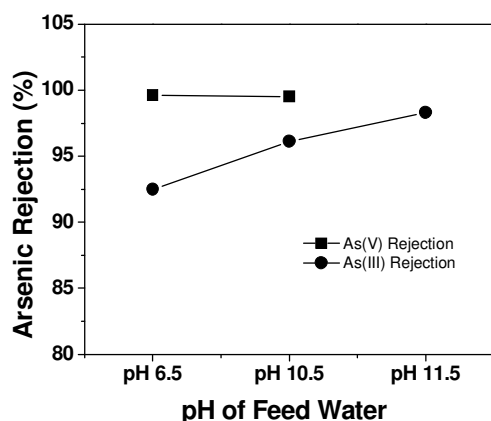


Figure 4. Arsenic (As(V) and As(III) rejection rates of HFAPA-on-REFPA membrane at various pHs

4 CONCLUSION

A novel thin film composite (TFC) membrane having polyamide bilayer on a porous polysulfone support was prepared by a process we call sequential interfacial polymerization. The polyamide bi-layer membranes (HFAPA-on-REFPA) consist of conventional non-substituted aromatic polyamide under-layer (REFPA) and HFA-substituted aromatic polyamide top-layer (HFAPA). Water contact angle (θ_w) measurement indicated that the surface of HFAPA-on-REFPA membrane becomes much more hydrophobic ($\theta_w \cong 140^\circ$) after forming the second layer, HFAPA, onto REFPA ($\theta_w \cong 78^\circ$) although cross-sectional SEM/TEM images showed no noticeable enhancement in the film thickness. The HFAPA-REFPA bilayer membrane with hydrophobic surface has showed significant improvement in RO performance, specifically in salt and toxic substance removal (ca. 50 % reduction in salt passage compared to REFPA).

This new approach to fabricate layered polyamide membranes enables easy modification of membrane surface and results in the synergy of the characteristic properties of

two layers, thus we think it has promise as a new design strategy for improving membrane performance.

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