Hg removal and the effects of coexisting metals in forward osmosis and membrane distillation

Chia-Yu Wu, Shiao-Shing Chen, Dai-Zhou Zhang and Jun Kobayashi

ABSTRACT

In this study, we investigate the rejection of Hg, Cd, and Pb and the effect of coexisting metals on Hg removal through forward osmosis (FO) and membrane distillation (MD) in order to establish a more effective water treatment process. The results of our laboratory experiment indicate that more than 97% of the rejection for each metal is achieved through the FO system, and this rejection is the highest among previous studies using membrane filtrations. Moreover, we examine the matrix effect of the coexisting Cd and Pb on the rejection of Hg in the FO system. Hg^{2+} rejection increases with increase in the concentration of the coexisting metals. Furthermore, we study the effect of the Hg concentration and the water temperature on rejection of Hg^{2+}. Indeed, the rejection of Hg^{2+} is achieved above 95% under any condition. However, approximately 1–10 ppb Hg from the feed solution remains in the draw solution due to permeation. Therefore, we use a FO–MD hybrid system. Approximately 100% rejection of Hg^{2+} and a stable water flux are achieved. Thus, the FO–MD hybrid system is considered an important alternative to previous studies using membrane filtration for heavy metals removal.

Key words | forward osmosis, Hg removal, membrane distillation, multi-metal coexistence

INTRODUCTION

In recent years, the heavy metals present in industrial wastewater and effluents have attracted significant attention worldwide due to the more stringent discharge standards, their increased usage, and their high-toxicity cumulative adverse impact (Hutton 1987; Urgun-Demirtas et al. 2012; Jaishankar et al. 2014). Hg is one of the most toxic metals in the environment and produces severe adverse neurological and other health effects on humans and animals (Risher 2003; Zhang & Wong 2007; Liu et al. 2011). Pb and Cd are commonly used in mining, electroplating, and metal surface treatment processes (e.g., CRT, LCD, fluorescent lamps, and batteries). Both the metals and Hg are categorized as the ‘priority hazardous substances’ by the agency for toxic substances and disease registry because of their high toxicity, mobility, and long residence time in the biosphere (ATSDR 2013). Wastewater and leachate from waste incineration generally include many heavy metals. Therefore, development of more effective treatments for mixtures of harmful compounds is required.

In previous studies, the removal behavior of heavy metals in several traditional treatments was examined, and advanced technologies were developed (Otto & Bajpai 2007). Membrane technology has been identified as one of the most effective approaches to address polluted water sources. The most widely used membrane techniques include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, which are pressure-driven and require external energy to pressurize water through the membranes. Among them, nanofiltration (NF) and reverse osmosis (RO) have proved their effectiveness in removing heavy metals from polluted water (Al-Rashdi et al. 2013; Alzahrani et al. 2015). However, both processes are operated at high pressures and have relatively low water-recovery rates. Therefore, comparatively high costs are incurred, and there is a high risk of severe membrane fouling. Forward osmosis (FO), an osmotic process that uses a semi-permeable membrane to achieve separation, has several advantages such as being operated without adding hydraulic pressure and having fewer membrane fouling problems. Previous studies have been conducted to investigate the FO processes utilized in heavy metal-polluted wastewater treatment (Butler et al. 2013; Cui et al. 2014; Mondal et al. 2014;
Zhao et al. 2016). However, the widespread application of FO as a stand-alone process for water treatment is limited by the lack of a suitable draw solution (DS) that can generate high osmotic pressure, while the draw solutes are recovered efficiently from the diluted DS (Shafer et al. 2015). Membrane distillation (MD) is a thermally driven separation process through which water vapor is transported through a hydrophobic microporous membrane via temperature-gradient-induced vapor pressure (Husnain et al. 2015b). Because the partial vapor pressure of water is only minimally affected by an increase in the concentration of dissolved salts, MD is an ideal process for re-concentrating the FO DS, which contains a relatively high salt concentration even after being diluted. Besides, the water flux in MD is nearly constant, and very pure product water is generated in the MD process by almost completely rejecting all nonvolatile compounds (Husnain et al. 2015a). The FO–MD combination has been previously proposed as a promising and effective method of recovering the DS (Camacho et al. 2015; Zhang et al. 2014; Nguyen et al. 2016). However, this hybrid system has not been applied for the treatment of wastewater contaminated by heavy metals, especially Hg.

In the present study, we aim to reveal the rejection of Hg, Cd, and Pb and the effect of coexisting metals on Hg removal using a FO system. We conducted the following three experiments. First, to reveal the rejection of each heavy metal and the influence of the coexisting metals on the rejection of Hg in the FO system, the rejection of Hg, Cd, and Pb was examined individually. Then, we investigated the rejection of Hg under coexisting Cd and Pb. Second, the influence of the differences in the influent Hg concentrations and that of water temperature on the rejection of Hg in the FO system was examined. Finally, to reveal the complementary role of the MD system for enhancing the Hg rejection and establishing sustainable operation, the rejection of Hg in the FO–MD hybrid system was examined.

MATERIAL AND METHODS

Membrane, FO, and MD bench-scale apparatus

A commercial flat thin-film composite (TFC) FO membrane (Hydration Technology Innovations (HTI), OR, USA) was used in the experiments. The FO membrane cell was made of natural acetal copolymer (Delrin®) (CF042 FO, Sterlitech Corporation, WA, USA). The FO membrane module comprised a cross-flow membrane cell with two channels for the feed and DS. The channel has dimensions of 9.2 cm length, 4.6 cm width, and 0.2 cm height, providing an effective membrane area of 42 cm².

In the MD process, a hydrophobic, microporous polytetrafluoroethylene membrane (Teflux®–PTFEM–220, Ray–E Creative Co., LTD, Taiwan) was used. The membrane comprised a thin PTFE active layer on top of a polypropylene support layer. The MD membrane cell was made of POM material (Ray–E Creative Co., LTD, Taiwan), suitable for use at 110 °C. The channel dimensions were 15.6 cm long, 15.6 cm wide, and 6.1 cm high, providing an effective membrane area of 100 cm². The solution reservoirs used in the MD were made of double glazing insulation to minimize heat loss. The physicochemical properties of the FO and MD membranes are listed in Table S1, in the Supplementary material (available with the online version of this paper).

A peristaltic pump was used to recirculate the feed and DS. A constant cross-flow rate of 0.1 L/min was maintained between the two closed loops for the feed and DS in the FO system, and a 1.5 L/min cross-flow rate was maintained in the MD system. Reservoirs were digitally weighed, and their weight changes were recorded at regular time intervals. A thermostatic water bath was used to regulate and maintain the water temperature. pH and conductivity meters were used to monitor the quality variation of the solutions at 30 min intervals. Details are offered in the Supplementary material.

We constructed an FO–MD hybrid system by combining the FO system with the MD system, and its structure is shown in Figure 1.

Experiment procedure

In the feed side, the inorganic metals salts HgCl₂, Pb(NO₃)₂, and CdCl₂ were diluted in distilled water to simulate contaminated water. In the draw side, 1 M NaCl solution was used. The details are available in the Supplemental information.

Experiment I: Influence of coexisting metals on the rejection of Hg in the FO system

Individual rejection of Hg, Cd, and Pb in the FO system was investigated to confirm the performance of this system. The solution of each metal (10 ppb) was prepared and examined individually. Then, to investigate the Cd–Pb matrix effect on the rejection of Hg (these are all divalent metals), a mixture solution of these three metals (each metal concentration was 15 ppb) was prepared and examined. The water temperature in both feed and DS was
Moreover, 0.4 mL of the samples was collected from the reservoir of both feed and DS, at 60 min intervals to quantify the total concentration of the tested metals. The conductivity and pH were measured at 30 min intervals.

Experiment II: Influence of concentration and water temperature on rejection of Hg in the FO system

To investigate the influence of concentration and water temperature on the rejection of Hg in the FO system, the present experiment was conducted under different Hg concentrations (15 and 1,000 ppb) and water temperatures (25°C and 40°C). The FO system and the measured procedure of this experiment were as well as Experiment I.

Experiment III: Rejection of Hg$^{2+}$ in the FO–MD hybrid system

The MD process was conducted using simulated diluted DS with three different initial concentrations (0.1, 0.3, and 0.5 M NaCl) by adding 1 ppb Hg as the feed solution. The appropriate dilution degree of the FO process was investigated to optimize the DS recovery efficiency.

After the FO process, the diluted DS was collected and used as the feed solution in the MD process. The feed was operated at an elevated temperature of 55 ± 1°C, and deionized water, which was used as the initial distillate stream, was maintained at room temperature (20 ± 1°C). The remaining volumes of the solutions were measured, and the performance parameters were calculated after each test.

Analytical methods

The Hg concentration was measured using an Hg analyzer (MA–3000, Nippon Instruments Corporation, Tokyo, Japan), and the detection limit is 1 ng/L (sample amount was 5 mL). The concentration of Hg in the solution and the residual amount on the membrane surface were measured by the reducing–vaporization–atomic absorption method and the thermal decomposition atomic absorption spectroscopy, respectively. Pb and Cd were measured with an atomic absorption spectrophotometer (Z–2000, Hitachi High-Technologies Co., Tokyo, Japan). The average and standard deviation (SD) of the performance parameters were obtained experimentally in parallel with collecting the above measurements. The error bar for each experiment represents the mean SD obtained after the three tests. Details are offered in the Supplementary material.

Data analysis

The experimental water flux, $J_W$ (L/m² h), was calculated by measuring the mass change in the DS container versus time as follows:

$$J_W = \frac{\Delta V}{A \times \Delta t},$$

where $\Delta V$ is the total increased volume of permeate water (L) collected over a predetermined time interval $\Delta t$ (h), and $A$ is the effective FO membrane area (m²). The reverse solute flux, $J_S$ (g/m² h), of the chosen draw solute was determined by converting its electrical conductivity.
measured by a conductivity meter when the draw solute dissociates in its aqueous solution as follows:

\[ J_S = \frac{C_t V_t - C_0 V_0}{A \times \Delta t} \]  

(2)

where \( C_t \) and \( V_t \) are the permeated salt concentration (g/L) and the volume (L) of the feed solution measured at time \( t \) (h), respectively. \( C_0 \) and \( V_0 \) are the initial concentration and the volume of the feed solution, respectively. In addition, the specific reverse salt flux and the permeated water flux (\( J_S/J_W \), g/L) are defined as the respective amounts in the draw solute lost per litre of water.

Taking the initial concentration as the 1 M DS, the salt rejection was determined from the conductivity measurements of the feed and DS. Similarly, the metals' rejection was determined from the metal concentration difference between the bulk feed (\( C_f \)) and permeate (\( C_p \), which refers to the DS). Consistent with this definition, the contaminant rejection in FO processes is defined as:

Salt rejection (\( \% \)) = \( \left[ 1 - \frac{C_p}{C_f} \right] \times 100 \)  

(3)

where \( C_p \) and \( C_f \) are the salt concentrations of the permeate and feed streams, respectively. The permeate concentration was calculated based on the following equation by considering the dilution effect:

\[ C_p = \frac{C_f m_1 - C_0 m_0}{m_1 - m_0} \]  

(4)

where \( m_0 \) and \( m_1 \) are the initial and final masses of the permeate stream, respectively. \( C_0 \) and \( C_f \) are the initial and final salt concentrations of the permeate stream that could be determined based on the conductivity, respectively. The investigated target is present at relatively low levels in permeate, and at higher concentrations in the bulk feed.

The percentage of flux recovery for the MD experiment was calculated using the following equation:

Recovery (\( \% \)) = \( \frac{\Delta V_d}{V_f} \times 100 \)  

(5)

where \( \Delta V_d \) is the total increased volume of distillate (L) collected within the predetermined time, and \( V_f \) is the initial feed volume (L) of the diluted DS.

The average and the SD of the performance parameters were obtained experimentally. The error bars for each experiment represent the mean SD obtained after three tests.

The metals' ionic properties were predicted using MINEQL\(^+\) (Environmental Research Software, USA), which simulates the dominant metal species and the equilibrium constant (\( \log K \)).

**RESULTS AND DISCUSSION**

**Influence of coexisting metals on the rejection of Hg in the FO system**

**Individual rejection of Hg, Cd, and Pb in the FO system**

More than 97% of the rejection of each metal is achieved with the proposed process (within 5 h of the system’s operation) (Figure 2). The rejection of each metal in this study is higher compared to previous studies using membrane filtrations such as RO, NF, and UF (Table 1). Therefore, the proposed method demonstrates reliable metal removal with an osmotic gradient generated by a 1 M NaCl solution. The high rejection of the heavy metals ions under the FO system could be attributed to several reasons. (1) Because no pressure is applied in the FO process, the effect of convective flow on the metal ion transport is insignificant.
Compared to other pressure driving membranes, the dominant mechanism for heavy metal transport across the TFC FO membrane is the solution–diffusion mechanism. Because diffusivity decreases with increasing hydrated radius, heavy metal ions with larger radii of hydration can be rejected easily. (2) The Donnan equilibrium effect may also contribute to the high rejections under the FO process. Due to the presence of highly concentrated robust draw solute ions, the relatively lower amounts of feed ions may not diffuse easily from the feed side to the draw side (Hancock et al. 2011). Hence, high rejection of metals ions can be expected under such circumstances. The result is consistent with a previous investigation (Cui et al. 2014).

The maximum rejections in increasing order are Hg$^{2+}$ (99.4%) > Pb$^{2+}$ (98.3%) > Cd$^{2+}$ (97.6%). This could be attributed to physicochemical properties such as the hydrated radius (Table S2, available with the online version of this paper). In addition, as shown in the specific reverse salt flux, the chloride ion in the DS (NaCl solution, 1 M) permeates to the feed solution including metals (ppb level), and the chloride ion concentration is significantly higher than the concentration of the metal ion. Therefore, other forms of the metal such as a metal complex with the chloride ion could also be incorporated. Especially, the equilibrium distribution between mercuric chloride complexes (univalent and divalent anion complexes) as a function of the chloride content can be calculated using the two reactions shown below (Caban & Chapman 1972):

$$\text{HgCl}_2 + \text{Cl}^- \rightarrow \text{HgCl}_3^+ \quad K_1 = 7.1,$$

$$\text{HgCl}_3^+ + \text{Cl}^- \rightarrow \text{HgCl}_4^{2-} \quad K_2 = 10.$$  

The values for $K_1$ and $K_2$ are obtained from Caban & Chapman (1972).

According to the results of the simulation, under the present experimental conditions, the dominant species of Hg is HgCl$^2_+$, which is easily excluded using the negatively charged membrane due to electrostatic repulsion (Xie et al. 2012). On the other hand, the dominant species of Pb and Cd present in the aqueous phase are uncharged hydrated compounds (Figure S1, available with the online version of this paper). Therefore, size exclusion has a greater influence on the separation for these metals, which means that ions with a smaller hydrated radius are more likely to pass through the semi-membrane. However, Cd, with a relatively large hydrated radius (4.26 Å), has relatively low removal compared to other metals. It was previously hypothesized that the reason for this is that ions with weak hydration bonds can lose some or all their water and fit through the membrane pores (Tansel et al. 2006). In addition, comparing the three metals, Cd exhibits the smallest ion radius (0.97 Å). Thus, the permeability is slightly improved by the small size of the uncharged metal.

The water flux and the specific reverse salt flux show a similar increasing order of the three target metals as follow: Pb$^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+}$.

The Cd–Pb matrix effect on the rejection of Hg in the FO system

Coexisting solutes increase the Hg removal capacity. However, the degree of the increase depends on co-metal ions present in the system (Figure 3). The order of Hg rejection is as follows: [Hg$^{2+} + \text{Pb}^{2+} + \text{Cd}^{2+}$]
(99.8 ± 0.1%) > [Hg$^{2+}$ + Cd$^{2+}$] (99.3 ± 0.4%) > [Hg$^{2+}$ + Pb$^{2+}$] (98.8 ± 0.3%) > [Hg$^{2+}$] (95.9 ± 2.0%). It is speculated that the coexisting solutes enhance the selectivity of the membrane surface. When an increased amount of counter-ions (i.e., Cl$^-$ and NO$_3^-$) is incorporated by adding metal compounds, the membrane separates HgCl$_4^{2-}$ more easily due to the Donnan effect (Wang et al. 2009). Moreover, the hydrated metal Cd, which has the maximum hydrated radius, has a more significant screening effect on the surface and the pores than Pb does, leading to higher removal of the Hg ion. When Hg and Pb coexist, a higher water flux (6.12 ± 0.04 L/m$^2$ h) and a specific reverse salt flux (0.53 g/L) are observed, due to the relatively higher affinity of Pb in the aqueous phase (Bessbousse et al. 2008). It is speculated that the hydrated Pb ion easily adheres to negatively charged surfaces, and increases the polarity of the membrane. The higher hydrophilicity caused by the polar surface improved the diffusibility of water molecules as well as the free ions in the solution. In addition, the internal concentration polarization effect observed in this study is negligible, due to the low ion concentration in the feed solution. The speculation is proven by the experiment results: we had observed a slight mass loss of the investigated metal ions, but insignificant water flux variation in the FO process.

**Influence of concentration and water temperature on the rejection of Hg in the FO system**

Rejection of Hg above 95% is achieved within 24 h of operation, under all tested conditions (Figure 4), and the influence of the Hg concentration and the water temperature on the rejection of Hg may be small. However, approximately 1–10 ppb Hg are observed in the DS owing to permeation from the feed solution after the long-term experiment, despite rejection of over 95% of the Hg. Therefore, a further suitable removal process such as the MD would be required to remove the heavy metal completely.

The specific DS concentration, which is defined as the ratio of the DS initial total dissolved solids (TDS) concentration (i.e., 1 M NaCl) to the concentration, which varies

---

**Figure 3** | Comparison between the Hg rejection under coexisting Cd and Pb and the water flux and specific reverse salt flux in the FO system. (a) Rejection of Hg. (b) Water flux (left axis) and specific reverse salt flux (right axis).

**Figure 4** | Comparison of the Hg rejection under different concentrations and water temperatures in the FO system. (a) Rejection of Hg. (b) Time trend of the Hg concentration in the DS.
with operating time (Figure 5), can be used to estimate the degree of dilution of the DS. A similar decreased trend of the water flux is observed, under the three operational conditions examined here, due to the decreased osmolality of the DS (from 1 M to 0.5 M). Moreover, a relatively rapid speed of recovery (nearly 65.1% recovery within 24 h) is found at 40 °C because the osmotic pressure increases proportionally with the solution temperature (Zhao & Zou 2014), and further provides a stable driving force to promote the water permeate steadily through the membrane.

### Rejection of Hg in the FO–MD hybrid system

Higher water flux and recovery rate are observed for a relatively low initial concentration in the feed stream (Table 2). This suggests that the higher recovery achieved (i.e., above 70%) in the FO system is more appropriate to recovery in the DS in the MD system. Furthermore, nearly 100% rejection of Hg$^{2+}$ is achieved in the FO–MD system, and the Hg$^{2+}$ concentration is not detected in the distillate, under all the present experimental conditions.

In the present approach, we allow the MD process to operate continually with the 0.1 M initial NaCl concentration until 80% recovery is achieved (Figure 6). Within 24 h of operation, although the distillate water flux decreases from 9.04 to 6.73 (LMH), the NaCl concentration increases steadily to nearly 0.7 M, and the final NaCl concentration in the concentrated stream is 41,700 mg/L. In addition, the total dissolved solids and the conductivity of the distillate are as low as 4.7 mg/L and 6.8 μS/cm, respectively, which allow the reuse of the water (Todd & Mays 1980).

### CONCLUSIONS

We examined the rejection of Hg, Cd, and Pb and the effect of coexisting metals on Hg removal using FO. In the FO system, more than 97% rejection for each metal was observed, suggesting that FO is one of the most effective water treatment processes. The Cd–Pb matrix effect on Hg rejection in the FO system was slightly observed, and the rejection was attributed to the combined effects of the Donnan exclusion, the size exclusion, and the diffusion of the solutes. Furthermore, although the Hg concentration and the water temperature had only a small effect on the rejection of Hg in this study, approximately 1–10 ppb Hg was recorded in the DS due to permeation from the feed solution under long-term operation. Therefore, we attempted to enhance the rejection of Hg and to establish a sustainable

### Table 2 | The DS recovery performance of the MD processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Inflow</th>
<th>Water flux (LMH)</th>
<th>Salt rejection (%)</th>
<th>Recovery (%)</th>
<th>Hg in perm. (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD 55 °C (FS) with 20 °C (DS)</td>
<td>0.1 M NaCl + 1 ppb Hg</td>
<td>8.0 ± 1.6$^a$</td>
<td>100.0 ± 0.0$^a$</td>
<td>21.3 ± 4.6$^a$</td>
<td>ND$^b$</td>
</tr>
<tr>
<td></td>
<td>0.3 M NaCl + 1 ppb Hg</td>
<td>8.2 ± 0.6$^a$</td>
<td>100.0 ± 0.0$^a$</td>
<td>22.7 ± 1.5$^a$</td>
<td>ND$^b$</td>
</tr>
<tr>
<td></td>
<td>0.5 M NaCl + 1 ppb Hg</td>
<td>7.7 ± 0.4$^a$</td>
<td>100.0 ± 0.0$^a$</td>
<td>20.7 ± 2.7$^a$</td>
<td>ND$^b$</td>
</tr>
</tbody>
</table>

$^a$Mean ± SD. The mean and SD for each experiment was obtained after the three replications.

$^b$ND, Not detected.
operation using a FO–MD hybrid system. As a result, approximately 100% rejection of Hg and a stable water flux were observed. This result indicates that the FO–MD hybrid system could be considered as an important alternative for heavy metal removal.

ACKNOWLEDGEMENTS

The authors are grateful to the Prefectural University of Kumamoto International Postgraduate Scholarship for Research on Hg and Kumamoto Prefecture, Japan. The authors would especially like to thank the Water Laboratory in TAIPEI TECH and Dr Jeffrey Stewart Morrow of the Prefectural University of Kumamoto (PUK) for their suggestions and great help on this work. The authors are grateful to Hinano Mouri and Yukiko Uchiyama of PUK for their kind instructions and great help on this work. The authors are grateful to the Prefectural University of Kumamoto (PUK) for their suggestions on TAIPEI TECH and Dr Jeffrey Stewart Morrow of the USA.

REFERENCES


First received 23 November 2016; accepted in revised form 20 February 2017. Available online 6 March 2017.