Domestic wastewater treatment by forward osmosis-membrane distillation (FO-MD) integrated system

Jie Li, Deyin Hou, Kuiling Li, Yong Zhang, Jun Wang and Xiwang Zhang

ABSTRACT

In this study, real domestic wastewater treatment by forward osmosis-membrane distillation (FO-MD) integrated system was investigated in laboratory scale. The integrated membrane system presented a good separation performance and the removal efficiency of most contaminants in the domestic wastewater was higher than 90%. High molecular weight contaminants were completely removed, while a few low molecular weight contaminants permeated through the membrane. The FO membrane fouling layer mainly consisted of organic substances like polysaccharides and proteins, and was very loose and could be effectively removed by rinsing the membrane surface with tap water. By comparison, the MD membrane fouling was mainly induced by inorganic salts and was not as severe as that of the FO membrane. During 120 h continuous operation, the FO-MD integrated system exhibited satisfying performance stability and maintained a high water yield and high product water quality. The results indicated the potential of the FO-MD integrated system for municipal wastewater treatment in coastal cities, water purification and desalination.

Key words | domestic wastewater, forward osmosis, membrane distillation, membrane fouling

INTRODUCTION

The finite fresh water and energy supply in the world poses a need to identify alternative strategies in order to meet the increasing demand (Elimelech & Phillip 2011). Intensive research on wastewater treatment and reclamation through low energy consumption and low cost ways has been carried out (Ge et al. 2015). Among many potential solutions, membrane separation technologies such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) have found their overwhelming applications in the field of water treatment (Su et al. 2012; Goh et al. 2016). However, these processes are hydraulic pressure driven, thus are prohibitively expensive due to substantial chemical and energy consumptions as well as high fouling propensity, which leads to efficiency decrease. Advancements to current desalination technology have aimed at low energy consumption, high separation efficiency, environmental-friendliness and utilization of clean energy such as solar energy, wind energy, tidal energy etc., which encourages the progress in membrane preparation technology and the development and application of innovative integrated membrane systems (Al-Obaidani et al. 2009; Park et al. 2009; Lin 2014; Gude 2015; Shenvi et al. 2015). Among those innovative membrane technologies, forward osmosis (FO) and membrane distillation (MD), with the advantages of low energy consumption and low environmental impact load, are representative (Shirazi et al. 2012; Zhang et al. 2014; Darwish et al. 2016).

Both FO and MD are contact membrane separation processes, and the main difference between them is their driving force for separation (Reverberi et al. 2014). FO uses a semi-permeable membrane to separate water from the feed solution (FS) (Cath et al. 2006). The driving force for this separation process is the osmotic pressure gradient between the draw solution of high osmotic pressure and the FS of a relatively low osmotic pressure (McCutcheon et al. 2006; Jin et al. 2011; Qin et al. 2012; Zhao et al. 2012a, 2012b). Comparatively, MD is a thermally driven separation process that uses a hydrophobic membrane as the barrier to isolate the liquid phase (El-Bourawi et al. 2006; Alkhudhiri et al. 2012; Pangarkar et al. 2014). The driving force of this process is the difference in vapor pressure between different sides of the membrane (Al-Obaidani et al. 2008; Khayet 2011).

Some common advantages of FO and MD are as follows. (1) The processes are conducted at a normal pressure, which...
leads to a low investment in equipment and a convenient operation (Martinetti et al. 2009; Xie et al. 2013; Husnain et al. 2015). (2) The membrane fouling of the two technologies is alleviated due to the contact separation process, which reduces the membrane cleaning expense as well as the pollution resulting from the use of chemical cleaning agents (Blandin et al. 2016; Jang et al. 2016). (3) The operating costs are low. During the separation process of FO, water molecules in the FS permeate through the semi-permeable membrane spontaneously, and the draw solution is easily recycled (Zhao et al. 2012a, 2012b; Luo et al. 2014). Thus the energy consumption of the wastewater concentration process can be significantly reduced (Li et al. 2014; Mazlan et al. 2016). As for the MD process, it can utilize heat pumps, solar energy and low grade waste heat from the system to reach a high removal efficiency (Al-Obaidani et al. 2008; Lin et al. 2014; Dow et al. 2016). (4) The water yield is high. By choosing a suitable draw solution, the water yield of FO can be greater than 90% (Garcia-Castello et al. 2009; Wu et al. 2016). For the MD process, only a vapor phase such as water vapor can pass through the membrane pores. The product water quality is better than the water quality from RO desalination, and the water yield of MD can be up to 100% theoretically (Chen et al. 2014; Luo & Lior 2016).

In recent years, more attention has been drawn to developing novel integrated membrane processes to exploit the advantages of the FO process. Good-quality product water, as well as higher water flux, have been obtained by hybrid FO systems such as FO-NF (Tan & Ng 2010), FO-RO (Choi et al. 2009), osmotic membrane bioreactor (OMBR) (Cornelissen et al. 2011) and FO/microbial fuel cell (FO-MFC) (Zhang et al. 2011). Furthermore, the hybrid FO systems showed superiority in energy efficiency. The model-based specific energy consumption of FO-RO decreased by 20% compared with the conventional two stage RO process at a system recovery of 50% (Shaffer et al. 2012). For typical conditions of 1,000 m³/d product flow, 40% overall recovery, the total specific energy consumption of seawater reverse osmosis (SWRO)/dual media filtration (DMF)/FO was 5.89 kWh/m³, which is lower than that of SWRO/DMF (6.39 kWh/m³) (Darwish et al. 2016). The application of an FO-RO integrated system for concentration of protein solutions (Wang et al. 2011) and dye wastewater treatment (Ge et al. 2012) has also been studied and thus indicated the feasibility of FO-MD technology for solution concentration and water treatment.

The integration of FO and MD process combines the advantages of both processes, including high product water quality, low fouling tendency, and potential utilization of industrial waste heat (Liu et al. 2016). In the FO-MD integrated system, FO technology serves as a low-cost and high-efficiency pretreatment and is able to remove some organic contaminants from the FS that may lead to the membrane wetting of MD, while the MD process continuously re-concentrates the diluted draw solution for the FO process and simultaneously produces high-purity water from its permeate side. Since MD is only used to concentrate the sole draw solutes, both the membrane fouling and membrane wetting of MD are reduced. In addition, MD technology can realize the low-cost but high-efficiency recovery of draw solutes of high osmotic pressure by applying the low grade heat resource from this integrated system or clean energy like solar energy. Consequently, the FO-MD integrated system has important potential for scientific research.

With increasing fresh water demands and higher water prices in many coastal cities, seawater and reclaimed wastewater are considered as main sources to alleviate short water supplies. In view of the above-mentioned advantages, the FO-MD integrated system may be a promising alternative for simultaneous treatment of domestic wastewater and seawater desalination, in which seawater can be utilized as a satisfactory natural draw solution due to its high osmotic pressure. By using this hybrid process, seawater can be diluted before desalination, hence reducing the energy cost of desalination, and simultaneously, contaminants in the wastewater are prevented from migrating into the product water. This research investigated the application of an FO-MD integrated system in real domestic wastewater treatment using saline water as the draw solution. During the process, concentrated sewage and desalted water were simultaneously obtained. The performance of the FO-MD integrated system including the permeate flux as well as rejection and transportation of typical contaminants among the FS, interface of membranes and product water of MD were studied. Besides, the membrane fouling in both the FO and MD processes, which is critical for an integrated process dealing with wastewater reclamation, is also investigated. The purpose of this work is to provide technology support for the municipal wastewater treatment in coastal cities, and to obtain a high-efficiency and energy-saving process for water purification and desalination.

**MATERIALS AND METHODS**

**Materials**

The cellulose triacetate (CTA) FO membrane was provided by Hydration Technology Innovations (HTI) (Albany, OR);
it was constituted of cellulose-based polymers with an embedded polyester mesh as the supporting layer, and the thickness and effective area of the membrane were 50 μm and 61.6 cm², respectively. The MD membrane used in the experiments was polyvinylidene fluoride (PVDF) hydrophobic hollow fiber membrane fabricated in our own laboratory. The thickness of the MD membrane was 186 ± 5 μm, average pore size was 0.073 μm, and the effective area of the MD module was 150 cm². The draw solute for FO was NaCl aqueous solution.

The wastewater samples were taken from the effluent of the fine screens of Xiaohongmen wastewater treatment plant, Beijing. Table 1 presents the water quality of the raw wastewater.

### Experimental set-up

The FO-MD integrated system is schematically shown in Figure 1. This hybrid system was designed to conduct FO and MD studies independently or jointly. The FO apparatus consists of a flat-sheet membrane cell, an FS tank and a draw solution (DS) tank, and peristaltic pumps are used to recirculate fluids in separate closed loops. Rotameters are used to monitor the flow rates of both solutions. Two constant temperature water baths are used to maintain the FS and DS temperature separately. Both the FS and DS temperature are monitored by thermometers. The FS tank is continuously weighed on an analytical balance linked to a computer. The change of weight is recorded and then used for flux calculations. The MD unit is very familiar to FO apparatus, except for the hollow fiber membrane module.

#### FO-MD experimental procedure

The FO unit used real domestic wastewater as FS and 35 g/L NaCl solution as DS. The FS and DS formed a circular flow by peristaltic pump at 0.28 m/s, and operated with counter-current flow. The liquid temperature for both sides (FS: 20 °C, DS: 53 °C) of the membrane was controlled by thermostatic water bath and cooling circulating pump and measured by thermometer. The FS tank was placed on the electronic balance, which connected to the computer to measure the mass change continuously for calculation of membrane flux. The conductivity of the FS and the Cl⁻ concentration of the DS were measured by the multi-parameter controller. The diluted DS from the FO unit was pumped into the hot side of the MD unit directly for condensation.

The direct contact membrane distillation (DCMD) unit was operated with co-current flow. Draw water heated in the water bath was pumped into the hot side of the MD module by the pump, and the product water outflowed from the cold side of the module. Temperature of the cold side of the module was kept by the cooling system at 20 °C, and the temperature of the hot side of the module was kept at 53 °C. Thermometers were used for measuring the temperature of both sides of the module, and rotameters

### Table 1 | Water quality of raw wastewater

<table>
<thead>
<tr>
<th>Water quality index</th>
<th>TOC</th>
<th>NH₃-N</th>
<th>TN</th>
<th>TP</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>PO₄³⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/L)</td>
<td>24.38</td>
<td>52.16</td>
<td>59.60</td>
<td>17.42</td>
<td>227.55</td>
<td>6.82</td>
<td>244.48</td>
<td>15.10</td>
</tr>
</tbody>
</table>

### Figure 1 | Schematic diagram of the FO-MD integrated system.
were used for measuring the flow rate of both sides. The flow rate of the hot side and cold side were maintained at 0.50 m/s and 0.15 m/s, respectively. The quantity change of the product water was measured to calculate the membrane flux of MD, and the conductivity of the product water was measured by conductivity meter all the time.

**Methods of analysis**

According to the Water and Wastewater Monitoring and Analysis Methods, parameters such as total organic carbon (TOC), NH$_3$-N, total nitrogen (TN) and total phosphorus (TP) of the water sample were measured using a TOC analyzer (Torch, Tekmar Dohrmann Corporation, USA) and ultraviolet spectrophotometer (DR-5000, Hach Company, USA).

The fluorescence excitation-emission matrix (FEEM) spectra of the water samples were recorded by the fluorometer (F-7000, Hitachi Ltd, Japan). FEEM were collected every 5 nm over an excitation (Ex) range of 200–400 nm, with an emission (Em) range of 280–550 nm by 5 nm. High performance liquid chromatography-size exclusion chromatography (HPLC-SEC) (LC-20AD, Shimadzu Co. Ltd, Japan) was used to characterize the molecular weight of the water sample, and the chromatographic column (TSK-GEL G3000PWx1, Tosoh Corporation, Japan) measured the molecular weight between 100 and 500,000. A field emission scanning electron microscope (FE-SEM) (SU8020, Hitachi Ltd, Japan) was used for the morphology observation of the membrane surface, and the composition of membrane fouling was analyzed by its energy disperse spectroscopy. A Fourier transform infrared (FTIR) spectrometer (Nicolet 8700, Thermo Nicolet Corporation, USA) was used to analyze the structure of deposits on the membrane surface.

**RESULTS AND DISCUSSION**

**Treatment efficiency of the FO-MD integrated system**

The treatment efficiency of the FO-MD integrated system can be found in Figure 2. Overall, the FO-MD integrated system showed a good separation performance, where the removal efficiency of most contaminants in the real domestic wastewater was more than 90%. The FO process had a relatively low removal efficiency for NO$_3^-$, mainly because the retention rate of the FO membrane for monovalent ions was lower than that for multivalent ions. The FO process also presented a low removal efficiency for NH$_3$-N and TN. A possible reason is that ammonium is a monovalent cation which has a low molecular weight, but the FO membrane has negative charges, which leads to its low retention rate. The removal efficiency of the FO-MD integrated system was obviously higher than a single FO unit, since it had two treatment units (FO and MD) and the MD membrane can separate almost all non-volatile substances. The integrated system showed an excellent treatment performance with a high product water quality.

**Water quality variation analysis**

Different organic substances have specific fluorescence characteristics, and different peak positions and intensities can be presented in the fluorescence spectra. In general, the fluorescence spectra can be divided into five regions, which represent tyrosine proteins, tryptophan proteins, soluble microbial products, humic acid and fulvic acid substances, respectively (as listed in Table 2).
Figure 3 shows the three-dimensional fluorescence spectra of the raw water, concentrated FS and product water. As shown in Figure 3(a), the main organic matters in the raw water are aromatic proteins like tyrosine, tryptophan and soluble microbial products. After FO-MD treatment, the intensity of the corresponding fluorescence peaks is enhanced (Figure 3(b)), which represents the raw water being concentrated. The fluorescence intensity of product water decreased (Figure 3(c)), which means that tryptophan proteins were almost removed, and only low concentrations of tyrosine proteins remained. Moreover, the removal rate of soluble microbial products was relatively lower.

The separation principle of HPLC-SEC is that components with different molecular weight in the sample interact slightly differently with the adsorbent material of the column, causing different flow rates for the different components and leading to the separation of the components as they flow out of the column. In general, the organics with larger molecular weight flow more quickly than the smaller.

Figure 4 shows the HPLC-SEC spectra of raw wastewater, concentrated FS and product water. The peak appearance time at 5.570 min, 6.390 min, 9.173 min, 9.798 min corresponds to the molecular weight of 315,789 Da, 29,425 Da, 691 Da and 147 Da, respectively. In the raw wastewater, the molecular weight of the organic substances was from 147 to 315,789 Da. After FO-MD treatment, organic matters greater than 500 Da were trapped by the FO membrane, while there were still organic substances smaller than 100 Da in the product, which indicates that higher molecular weight organics can be removed by the FO-MD integrated process, whereas a few small molecule organic matters remain.

Membrane fouling and cleaning

After operation, the surfaces of the FO and MD membranes were observed by FE-SEM, and the elements and their relative contents on the membrane surface were analyzed by the energy disperse spectroscopy.

As shown in Figure 5, the FO membrane surface was covered by foulants after operation. Element analysis

<table>
<thead>
<tr>
<th>Organic matters</th>
<th>Tyrosine proteins</th>
<th>Tryptophan proteins</th>
<th>Fulvic acids</th>
<th>Soluble microbial products</th>
<th>Humic acids</th>
</tr>
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</table>

Figure 3 | FEEM spectra of raw wastewater (a), concentrated FS (b) and product water (c).
indicates that there were C, O, Na, Mg, Si, S, Cl, Ca, and Fe on the membrane surface. Hence, the deposits on the membrane surface were complex foulants containing organic matters, calcium salts, magnesium salts, sodium salts, silicates, etc. The specific content of each element showed that C and O made up the majority of the foulants, indicating that the FO membrane surface is prone to fouling by organic substances. During domestic wastewater treatment, due to the retention effect of the FO membrane, inorganic ions were accumulated at the FS side, thus the concentration process enhanced the inorganic deposit formation. In Figure 5, it can be found that Si had a high relative content in the membrane foulants compared with other inorganic elements. In general, silicate exists in wastewater as a colloid. With the water permeate moving through the FO membrane from the FS side to DS, the component concentrations of the FS would increase. Due to the charge neutralization and compression of the double charged layer induced by Ca$^{2+}$ and Mg$^{2+}$ ions, the silica colloids stability was eliminated and the colloids aggregated (Sheikholeslami et al. 2001). For this reason, silica scaling would gradually deposit on the membrane surface. The hydroxyl groups of the silica colloids are prone to combining with the organic substances in the wastewater, which aggravated membrane fouling (Neofotistou & Demadis 2004). Compared with the FO membrane, the MD membrane fouling was depressed greatly, and there were only a few foulant aggregates scattered on the membrane surface. According to the results of element analysis, the MD membrane foulants primarily consisted of NaCl salt crystals. Since the FO membrane retained most contaminants of the FS, the MD membrane fouling was mainly induced by the draw solution concentration.

**Figure 4** | HPLC-SEC spectra of raw wastewater, concentrated FS and product water.

**Figure 5** | FE-SEM images of fouled FO and MD membrane and the microanalysis report of the foulants deposited on the membrane surface: (a) FO membrane and (b) MD membrane.
FTIR spectra can provide some information about functional groups of the deposits on the membrane surface. Figure 6 presents the FTIR spectra of the virgin, fouled and cleaned FO membrane. For the virgin membrane, there existed the C=O stretching vibration band (at 1,733 cm⁻¹), C=C skeletal stretching vibration band (at 1432.1 cm⁻¹), the C-H in plane stretching vibration band (at 1367.9 cm⁻¹) and the C-H in plane deformation band of the p-substituted aromatics (at 1,216.2 cm⁻¹). For the fouled membrane, some of the original peaks disappeared, and there appeared some other characteristic peaks of polysaccharides and proteins, such as the OH stretching vibration band of the C-OH bond of polysaccharides (at 3,050–3,570 cm⁻¹), carboxylate -COO asymmetric stretching vibration band (at 1,540–1,620 cm⁻¹), carboxylate symmetric stretching vibration band (at 1,390–1,420 cm⁻¹) and aromatic ring =C-H in plane bending vibration band (at 990–1,300 cm⁻¹). The peak pattern indicated that polysaccharides and proteins were the main organic substances deposited on the membrane surface. The FTIR spectra of the cleaned membrane (the fouled membrane rinsed 5 min under the tap) was consistent with the virgin membrane, which means that the polysaccharides and proteins deposited on the membrane surface can be effectively removed using only the hydrodynamic shear forces.

FO membrane samples (both fouled membrane and cleaned membrane) were taken for 4 cm² and immersed into 15 mL deionized water, respectively. After 30 min sonication, the water samples were taken and analyzed by HPLC-SEC. The HPLC-SEC spectra shown in Figure 7 indicate that the small molecular weight organic substances were the major foulants deposited on the FO membrane surface. On the other hand, the results also demonstrated that almost all the membrane foulants can be removed by only the hydrodynamic shear forces due to the loose structure of the membrane foulants.

**Operation stability of the FO-MD integrated system**

From an industrial application perspective, it is important to maintain the membrane permeability, keep the permeate flux and solute rejection of the FO-MD integrated system for long-time operation. To investigate the operation performance stability of the integrated system, a 120 h continuous experiment for real domestic wastewater treatment was conducted, and all the operating parameters were in accordance with the previous experiments. The experimental result can be found in Figure 8. During the 120 h continuous operation, the water flux of the FO-MD integrated system remained at 17.60 LMH, suggesting that the integrated system exhibited satisfying performance stability and maintained a high water yield. With operation time...
prolonging, the conductivity of the product water decreased gradually and stabilized at 7.5 μS/cm.

However, it was found that after operation for 120 h, the draw solution reduced, indicating that the water yield of the FO process became less than that of the MD process. This is mainly because the FO membrane directly contacted with the real domestic wastewater, and the contaminants in the FS gradually accumulated on the FO membrane surface and blocked the membrane pores with the operation time prolonging. But, in contrast, the MD membrane fouling was not as severe as that of the FO membrane due to the MD membrane directly contacting with draw water (salt aqueous solution).

CONCLUSIONS

This study demonstrated the applicability of an FO-MD integrated membrane system for treatment of domestic wastewater for sustainable water recovery; the product water quality and membrane fouling of the integrated process were investigated.

The FO-MD integrated system presented a better separation performance in comparison with the single FO or MD unit. The removal efficiency of most contaminants in the domestic wastewater was higher than 90%, which is comparable to some other technologies such as OMBR, FO-NF and FO-RO reported by other studies. After treatment by FO-MD process, the high molecular weight contaminants were completely removed while a few low molecular weight contaminants permeated through the membrane.

The main foulants deposited on the FO membrane surface were organic substances like polysaccharides and proteins, which was the main reason for the decrease of the permeate flux. Silicate was the main inorganic pollutant aggravating membrane fouling. However, the FO membrane fouling layer was very loose and could be effectively removed by rinsing the membrane surface with tap water. By comparison, the MD membrane fouling mainly consisted of inorganic salts and was not as severe as that of the FO membrane.

During 120 h continuous operation, the FO-MD integrated system exhibited satisfying performance stability and maintained a high water yield and high product water quality. The results indicated the potential of the FO-MD integrated system for municipal wastewater treatment in coastal cities, and water purification and desalination.

ACKNOWLEDGEMENTS

Financial support provided by the National Natural Science Foundation of China (grant numbers 51478454 and 51678555) and the National Key R&D Program of China (No. 2016YFC0400500) are gratefully acknowledged.

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First received 4 September 2017; accepted in revised form 9 January 2018. Available online 23 January 2018