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Bangxi Zhang

China Agricultural University, Guizhou Institute of Agricultural Resources and Environment

Xiaoye Song

University of Wollongong, xs245@uowmail.edu.au

Long D. Nghiem

University of Wollongong, longn@uow.edu.au

Guoxue Li

China Agricultural University

Wenhai Luo

China Agricultural University, wl344@uowmail.edu.au

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Disciplines

Engineering | Science and Technology Studies

Publication Details

Zhang, B., Song, X., Nghiem, L. D., Li, G. & Luo, W. (2017). Osmotic membrane bioreactors for wastewater reuse: Performance comparison between cellulose triacetate and polyamide thin film composite membranes. *Journal of Membrane Science*, 539 383-391.

**Osmotic membrane bioreactors for wastewater reuse: Performance
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Journal of Membrane Science (2017) 539: 383 – 391

Bangxi Zhang ^{a,b}, Xiaoye Song ^c, Long D. Nghiem ^c, Guoxue Li ^a, Wenhai Luo ^{a*}

^a Beijing Key Laboratory of Farmland Soil Pollution Prevention and Remediation,
College of Resources and Environmental Sciences, China Agricultural University,
Beijing, 100193, China

^b Guizhou Institute of Agricultural Resources and Environment, Guiyang, Guizhou,
550001, China

^c Strategic Water Infrastructure Laboratory, School of Civil, Mining and
Environmental Engineering, University of Wollongong, Wollongong, NSW 2522,
Australia

* Corresponding author: luowenhai@cau.edu.cn; Ph: +86 18311430503.

Abstract

This study compared the performance between the asymmetric cellulose triacetate (CTA) and polyamide thin film composite (TFC) forward osmosis (FO) membranes in an osmotic membrane bioreactor (OMBR). A reverse osmosis (RO) system was integrated with OMBR to regenerate the draw solution and produce clean water. Results show that the TFC membrane exhibited a higher initial water flux but more dramatic flux decline compared to the CTA membrane when they were used for OMBR. The CTA and TFC membranes also resulted in discernible difference in salinity build-up in the bioreactor and thus biomass characteristics during OMBR operation. All 30 trace organic contaminants (TrOCs) selected in this study were effectively removed by the OMBR-RO hybrid system regardless of the FO membrane type. Compared to the CTA membrane, the TFC membrane contributed more significantly toward the removal of hydrophilic and biologically persistent compounds and thus reduced their accumulation in the draw solution during OMBR-RO operation. In addition, CTA and TFC FO membranes also resulted in considerable differences in TrOC residuals in the sludge during OMBR operation.

Keywords: Osmotic membrane bioreactor; trace organic contaminants; forward osmosis; cellulose triacetate; polyamide.

1. Introduction

Water reuse is a pragmatic strategy to ensure adequate water supplies and alleviate water scarcity, which is a key issue hindering the sustainable development of our society [1]. However, the ubiquitous presence of trace organic contaminants (TrOCs) in reclaimed wastewater is often a major obstacle to water reuse. TrOCs, such as endocrine disrupting and pharmaceutically active compounds, are derived from either anthropogenic or natural activities. Although TrOCs are present in the environment at trace concentrations, only ranging from a few nanograms per liter to several micrograms per liter, they would cause health risks to humans and other living organisms [2]. Thus, recent efforts have been dedicated to develop new or improve current technologies to increase TrOC removal and thereby advance wastewater treatment and reuse.

Osmotic membrane bioreactor (OMBR), which integrates forward osmosis (FO) with biological treatment, has recently been developed for advanced wastewater treatment and reuse [3-8]. OMBR applications for nutrient recovery from waste streams have also been demonstrated in several recent studies [9, 10]. In OMBR, treated water is transported from the mixed liquor, through a semi-permeable FO membrane, into a highly concentrated draw solution (e.g. NaCl and seawater), with the osmotic pressure difference between these two solutions as the driving force. By using the osmotically driven FO process, OMBR also has lower membrane fouling propensity and higher fouling reversibility than conventional MBR that utilizes hydraulically driven membrane processes, such as microfiltration and ultrafiltration [3, 4]. Compared to conventional MBR that is widely deployed for non-potable water reuse, OMBR can produce higher quality effluent due to the high rejection capacity of the FO membrane [11-13]. In particular, an additional desalination process, such as reverse osmosis (RO) or membrane distillation, is usually coupled with OMBR to regenerate the draw solution and further purify treated water suitable for potable reuse [14, 15].

Recent studies have demonstrated the effective removal of TrOCs by OMBR. Lay et

al. [16] reported that OMBR removed three pharmaceuticals, including naproxen, diclofenac, and ibuprofen, by more than 96%. This result was consistent with that reported by Alturki et al. [17] who found that over 80% removal by OMBR was achieved for TrOCs with molecular weight larger than 266 g/mol; while the removal of smaller compounds varied significantly depending on their intrinsic biodegradability. Moreover, Holloway et al. [14] reported that 15 of 20 TrOCs detected in domestic wastewater were removed to below detection limit by OMBR and other five non-ionic hydrophobic chemicals (that were not highly removed) could be effectively retained by the subsequent RO process, which was used for draw solution regeneration and clean water production. It is noteworthy that all these studies utilized the asymmetric cellulose triacetate (CTA) FO membrane, which is featured with high water permeability and excellent fouling resistance due to the hydrophilic nature of cellulose [18].

With the development of new membrane materials and fabrication technologies, the polyamide thin film composite (TFC) FO membrane has been commercialized [19, 20]. The polyamide TFC FO membrane has higher water permeability, lower salt permeability, and better solute rejection in comparison with its CTA counterpart [21, 22]. The robust performance of OMBR using the TFC FO membrane for TrOC removal has been demonstrated by Luo et al. [23]. Since the CTA and TFC FO membranes are structurally and chemically different [24], it is necessary to compare comprehensively their performance in the biological reactor and thus provide important insight into membrane development for industrial OMBR applications. Wang et al. [25] recently reported that biofouling was more significant to the CTA membrane; while inorganic fouling was more severe to the TFC membrane due to its higher salt rejection during OMBR operation. Nevertheless, the effect of these two widely used FO membranes on the removal of TrOCs in OMBR is still unknown.

This study aimed to compare the performance between the CTA and TFC FO membranes for OMBR application. A cross-flow RO process was integrated with each OMBR system to regenerate the draw solution and produce treated water. The

integrated system was evaluated in terms of water production, salinity build-up in the bioreactor, biological stability, and contaminant (particularly TrOCs) removal. In addition, TrOC residuals in the sludge were examined in both OMBR systems. Results from this study provide important implications to the development of FO membranes for OMBR applications.

2. Materials and methods

2.1 Synthetic wastewater and trace organic contaminants

A synthetic wastewater, consisting of 100 mg/L glucose, 100 mg/L peptone, 17.5 mg/L KH_2PO_4 , 17.5 mg/L MgSO_4 , 10 mg/L FeSO_4 , 225 mg/L CH_3COONa , and 35 mg/L urea, was used in this study. Basic characteristics of the synthetic wastewater are shown in Table S1, Supplementary Data.

A set of 30 TrOCs were selected to represent emerging chemicals of significant concern. These compounds can be categorized as endocrine disrupting compounds, pharmaceutical and personal care products, industrial chemicals, and pesticides, which are ubiquitously present in municipal wastewater. Basic properties of the 30 TrOCs, including molecular weight, hydrophobicity, acid dissociation constant (pKa), and chemical structure, are shown in Table S2, Supplementary Data. A stock solution containing 25 $\mu\text{g/mL}$ of each of TrOCs was prepared in pure methanol and stored at $-18\text{ }^\circ\text{C}$ in the dark. The stock solution was added to the synthetic wastewater to obtain a concentration of 5 $\mu\text{g/L}$ of each compound.

2.2 Membranes

Flat-sheet CTA and TFC FO membranes used for OMBR were supplied by Hydration Technology Innovations (HTI, Albany, OR). The CTA FO membrane consisted of an active layer made of cellulose triacetate and a polyester mesh for mechanical support. The TFC FO membrane comprised a polyamide active layer and a porous polysulfone supporting layer. A flat-sheet LFC3 membrane (Hydranautics, Oceanside, CA) made of polyamide was used in the RO system to re-concentrate the OMBR draw solution

and produce treated water. Basic properties of these membranes are summarized in Table S3, Supplementary Data.

2.3 Experimental system

Two identical, lab-scale OMBR-RO systems using different FO membranes were operated in parallel (Figure S1, Supplementary Data). Detail description of the OMBR-RO hybrid system has been reported in our previous study [26]. Briefly, this system was consisted of a wastewater reservoir, a biological reactor made of glass and housed a plate-and-frame FO membrane module, a draw solution tank, a cross-flow RO cell, and several pumps. The wastewater reservoir was placed on a digital balance, which was connected with a data logger to determine the OMBR water flux.

The FO membrane module was made of acrylic plastic and engraved a flow channel for the draw solution with a length, width, and height of 20 cm, 15 cm, and 0.4 cm, respectively. The FO membrane was sealed on the module surface with the active layer facing the mixed liquor (i.e. FO mode) and an effective area of 300 cm². The RO membrane cell was made of stainless steel with a flow channel of 10 cm long, 4 cm wide, and 0.2 cm high. A temperature controller (Neslab RTE7, Waltham, MA) with a stainless steel heat exchanger coil was used to maintain the draw solution temperature. A digital flow meter (Optiflow, Palo Alto, CA) was connected to another data logger to record the RO water flux.

2.4 Experimental protocol

Each OMBR-RO system was inoculated with activated sludge collected from a conventional MBR, which had acclimatized to the synthetic wastewater and laboratory conditions for over 3 months and exhibited stable performance in terms of organic and nutrient removal. The mixed liquor suspended solid concentration (MLSS) was adjusted to approximately 5 g/L. Each bioreactor had an effective volume of 6 L and was continuously aerated to provide a dissolved oxygen (DO) concentration of above 2 mg/L. The sludge retention time (SRT) was maintained at 20 days by daily withdrawing 300 mL mixed liquor.

A 0.5 M NaCl solution was used as the OMBR draw solution and was circulated to the FO membrane cell at a cross-flow velocity of 2.8 cm/s. At the same time, the draw solution was pumped to the RO system with a cross-flow velocity of 41.7 cm/s. The hydraulic pressure was adjusted daily to balance the water flux between the OMBR and RO units, thereby maintaining the effective volume of the draw solution at 10 L. The draw solution temperature was maintained at 21 ± 1 °C, which was also the controlled laboratory temperature. The two OMBR-RO systems were operated continuously for 30 days without any membrane cleaning.

2.5 Analytical methods

2.5.1 Basic water quality parameters

Dissolved organic carbon in aqueous samples was quantified by total organic carbon (TOC) measurement. TOC and total nitrogen (TN) were analyzed using a TOC/TN analyzer (TOC-V_{CSH}, Shimadzu, Kyoto). Ammonium (NH₄⁺) and orthophosphate (PO₄³⁻) were measured by a Flow Injection Analysis system (QuikChem 8500, Lachat, CO). An Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Waltham, MA) was used to measure solution pH and electrical conductivity.

2.5.2 Analysis of trace organic contaminants

TrOC concentrations in aqueous samples were analyzed every six days based on the method reported previously by Hai et al. [27]. This method included solid phase extraction (SPE), derivatization, and measurement by a gas chromatography – mass spectrometry system (QP5000 GC-MS, Shimadzu, Kyoto). During OMBR-RO operation, TrOC removal by the bioreactor (R_{Bio}), OMBR (R_{OMBR}), and the overall OMBR-RO system was defined as follow:

$$R_{Bio} = (1 - \frac{C_{Sup} V_{Bio} + C_{Draw}^* \Delta V_{FO}}{C_{Feed} \Delta V}) \times 100\% \quad (1)$$

$$R_{OMBR} = (1 - \frac{C_{Draw}^*}{C_{Feed}}) \times 100\% \quad (2)$$

$$R_{Overall} = (1 - \frac{C_{Permeate}}{C_{Feed}}) \times 100\% \quad (3)$$

where C_{Feed} , C_{Sup} , and $C_{Permeate}$ was the measured TrOC concentration in wastewater, mixed liquor supernatant, and RO permeate, respectively; C_{Draw}^* was the TrOC concentration in the FO permeate; V_{Bio} was the effective bioreactor volume; and ΔV_{FO} was the volume of water produced by FO between time t and $t+\Delta t$. Some TrOCs could accumulate in the draw solution if they passed through the FO but not the RO membrane. Thus, C_{Draw}^* was calculated based on the mass balance:

$$C_{Draw}^* = \frac{M_{FO}}{Q_{FO}} \quad (4)$$

$$M_{FO} = \frac{V_{Draw}(C_{Draw(t+\Delta t)} - C_{Draw(t)})}{\Delta t} + \frac{(C_{RO(t+\Delta t)} + C_{RO(t)})}{2} \Delta V \quad (5)$$

$$\Delta V = Q_{RO} \Delta t \quad (6)$$

where M_{FO} was the mass flow rate of TrOCs that passed through the FO membrane; $C_{Draw(t)}$ and $C_{Draw(t+\Delta t)}$ was the measured TrOC concentration in the draw solution at time t and $t+\Delta t$, respectively; $C_{RO(t)}$ and $C_{RO(t+\Delta t)}$ was the measured TrOC concentration in the RO permeate at time t and $t+\Delta t$, respectively; and Q_{FO} and Q_{RO} was the FO and RO water flux, respectively, which was adjusted to be equal as described in Section 2.4. Based on eqs. (4) – (6), C_{Draw}^* was calculated as follows:

$$C_{Draw}^* = \frac{V_{Draw}(C_{Draw(t+\Delta t)} - C_{Draw(t)})}{\Delta V_{FO}} + \frac{(C_{RO(t+\Delta t)} + C_{RO(t)})}{2} \quad (7)$$

To quantify the contribution of the FO and RO membranes toward TrOC removal in the OMBR-RO hybrid system, their observed rejections were calculated according to eqs. (1) – (3):

$$R_{Ob\ FO} = R_{OMBR} - R_{Bio} \quad (8)$$

$$R_{Ob\ RO} = R_{Overall} - R_{OMBR} \quad (9)$$

where $R_{Ob\ FO}$ and $R_{Ob\ RO}$ was the observed TrOC rejection by the FO and RO membrane, respectively.

TrOC residuals in the sludge phase were also measured after being extracted according to a solvent extraction method previously reported by Wijekoon et al. [28]. Briefly, this method involved sludge drying by a Freeze Dryer (Alpha 1-2 LD, Christ GmbH, Germany), ultrasonic solvent extraction using methanol and its blend with dichloromethane (1:1, v/v), respectively, following by SPE and subsequent quantification using GC-MS as described for aqueous samples.

2.5.3 Biomass and membrane fouling characterization

Sludge concentration was examined by measuring the MLSS and mixed liquor volatile suspended solids (MLVSS) contents in the two bioreactors based on the Standard Method 2540. Biomass activity was indicated by the specific oxygen uptake rate (SOUR) of activated sludge, which was determined by the Standard Method 1683. Extracellular polymeric substance (EPS) in the sludge was extracted using a method described by Zhang et al. [29]. EPS and soluble microbial products (SMP) in the mixed liquor were measured by quantifying their protein and polysaccharide contents, which were determined by the Folin method with bovine serum albumin as the standard and the phenol-sulfuric acid method with glucose as the standard, respectively [30].

The morphology and composition of both FO membrane surfaces were characterized by a scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) (JCM-6000, JEOL, Tokyo, Japan) at the end of OMBR operation. Membrane samples were air-dried in a desiccator and then coated with an ultra-thin gold layer with a sputter coater (SPI Module, West Chester, PA) for SEM imaging.

3. Results and discussion

3.1 Water flux and salinity build-up

A higher initial water flux was observed for OMBR using the polyamide TFC membrane in comparison with that using the CTA membrane under the same operating condition (Figure 1A). This result can be attributed to the different water permeability coefficients (i.e. A values) of the two FO membranes. Based on the standard protocol established by Cath et al. [21] to characterize FO membranes, the water permeability of the TFC membrane was approximately three times higher than that of the CTA membrane (Table S3, Supplementary Data).

Figure 1: Water flux (A) and mixed liquor conductivity (B) during OMBR-RO operation using the CTA and polyamide TFC FO membrane. Experimental conditions: DO = 5 mg/L; initial MLSS = 5.5 g/L; SRT = 20 d; temperature = 22 ± 1 °C; draw solution = 0.5 M NaCl; draw cross-flow velocity = 2.8 cm/s; RO cross-flow velocity = 41.5 cm/s.

Water flux of the OMBR system decreased continuously when using either TFC or CTA FO membrane (Figure 1A). Since the draw solution salinity only decreased slightly (Figure S2, Supplementary Data), the observed flux decline was mainly attributed to salinity build-up in the bioreactor (Figure 1B) and membrane fouling (Figure S3, Supplementary Data). Salinity build-up in the bioreactor is inherent to OMBR due to the high salt rejection by the FO membrane and the reverse draw solute flux [31]. The elevated salinity could increase the osmotic pressure in the mixed liquor side and thus reduce the effective driving force (i.e. transmembrane osmotic pressure) for water transport. On the other hand, despite the low fouling propensity of

the FO membrane due to the absence of hydraulic pressure, a cake layer, mainly consisting of carbon, oxygen, phosphorus, sodium, magnesium, and calcium, was formed on both CTA and TFC membrane surfaces (Figure S3, Supplementary Data), thereby reducing the water flux (Figure 1A).

The TFC membrane encountered a more dramatic flux decline compared to its CTA counterpart (Figure 1A). This result can be attributed to the higher initial water flux and the more significant increase in the bioreactor salinity when using the TFC membrane (Figure 1). There is evidence that foulants accumulated on the FO membrane surface could transition from a sparse and loose fouling layer at a low initial permeate flux to a more compact and cohesive fouling layer at a high initial permeate flux [32]. In addition, Mazlan et al. [24] also reported that the TFC FO membrane was more susceptible to organic fouling than its CTA counterpart at the same initial water flux, due to its relatively higher surface roughness and prominent ridge-and-valley structure on the membrane surface. Foulants deposited on a rough membrane surface could be shielded from air scouring or cross-flow shear force by positive asperities and thus facilitate the development of a cohesive fouling layer [24, 33]. Indeed, a more homogenous and thick cake layer was observed on the TFC membrane surface in comparison with that on the CTA membrane in this study (Figure S3, Supplementary Data).

Salinity build-up in the bioreactor was more significant for the TFC membrane within the first 10 days (Figure 1B), although it exhibited a lower salt permeability and thus a smaller reverse salt flux than the CTA membrane (Table S3, Supplementary Data). This observation was caused by the higher salt rejection of the TFC membrane (Table S3, Supplementary Data). The higher bioreactor salinity encountered by the TFC membrane could not only reduce the effective driving force for water transport, but also lead to more severe membrane scaling and thus flux decline in comparison with when the CTA membrane was used for OMBR. Although there were different hydrodynamic conditions adjacent to the membrane surface, a higher salinity build-up and more dramatic flux decline was also observed for the TFC membrane when these

two FO membranes were compared in a side-stream OMBR system [25]. Nevertheless, the significant flux decline associated with the TFC membrane reduced salinity build-up in the bioreactor, which was even lower than when the CTA membrane was used from day 14 onward (Figure 1B).

3.2 Biomass characteristics

Different salinity profiles accompanied with the CTA and TFC membranes resulted in discernible differences in biomass characteristics during OMBR operation (Figure 2). It has been reported that the elevated salinity could inhibit microbial growth and activity by causing cell plasmolysis before biological acclimatization to the saline condition was achieved during OMBR operation [34, 35]. Indeed, an initial decrease but subsequent increase in the biomass concentration (indicated by the MLSS and MLVSS contents) and biological activity (suggested by the sludge SOUR) was observed for both OMBR systems in this study (Figure 2A-C). Although the TFC membrane resulted in more significant salinity build-up in the bioreactor than the CTA membrane within the first two weeks (Figure 1B), there was no significant difference between the two OMBR systems in terms of biomass concentration and sludge activity. However, the MLVSS concentration decreased continuously in OMBR using the CTA membrane (Figure 2B), possibly due to inadequate microbial adaptation to the elevated saline condition, which was more severe than that using the TFC membrane from day 14 onward (Figure 1B).

Figure 2: Biomass characteristics during OMBR operation using the CTA and polyamide TFC FO membrane. Experimental conditions are shown in the caption of Figure 1.

The saline condition can also increase the endogenous respiration of bacteria and thus drive the secretion of organic cellular substances [34]. As mentioned above, the TFC membrane caused more considerably saline condition to biomass than its CTA counterpart within the first two weeks (Figure 1B). Thus, a more notable increase in the SMP and EPS concentrations was observed for OMBR using the TFC membrane (Figure 2D and E). With salinity build-up becoming less significant, the SMP and EPS concentrations in the mixed liquor decreased gradually during OMBR operation with the TFC membrane, and then stabilized at approximately 20 mg/L and 60 mg/g MLVSS, respectively, from day 14 onward. By contrast, the bioreactor salinity

increased continuously for OMBR using the CTA membrane (Figure 1B), remaining a significant increase in the SMP concentration in the mixed liquor (Figure 2D). Nevertheless, the EPS concentration was relatively stable along with salinity increase in the bioreactor (Figure 2E), possibly due to its transition to SMP under saline conditions [34].

3.3 Removal of bulk organic matter and nutrients

During OMBR-RO operation, no significant difference in TOC removal was observed between the CTA and TFC FO membranes (Figure 3A and B). It has been well established that the removal of organic matter in OMBR was driven by both biological degradation and the rejection of the FO membrane [3]. Despite the observed salinity build-up in the bioreactor, the two OMBR systems using different FO membranes exhibited effective biodegradation of organic substances as indicated by low TOC concentrations in both bioreactors. Nevertheless, compared to the CTA membrane, a slightly higher TOC concentration in the bioreactor was observed when using the TFC membrane (Figure 3A and B), possibly due to its higher rejection of biologically persistent organic substances.

Although there was no significant difference in the overall TN removal by OMBR-RO, its distribution in the hybrid system varied considerably when using different FO membranes (Figure 3C and D). Compared to the CTA membrane, the higher rejection capacity of the TFC membrane resulted in more significant TN accumulation in the bioreactor, since TN removal was only dependent on the biological assimilation with the absence of denitrification in the aerobic bioreactor [36]. As a result, TN accumulation in the draw solution was more remarkable for OMBR-RO using the CTA membrane, because some nitrogen species, mainly nitrate, could permeate through the FO but was retained by the RO membrane [14]. Regardless of the FO membrane type, TN accumulation in the draw solution consequently reduced its overall removal by OMBR-RO and thus deteriorated the product water quality.

Figure 3: Distribution and removal of total organic carbon (TOC) (A and B) and total nitrogen (TN) (C and D) in the OMBR-RO hybrid system using the CTA and polyamide TFC FO membrane. Experimental conditions are given in the caption of Figure 1.

Almost complete removal of nutrients was observed for OMBR-RO using either CTA or TFC FO membrane (Figure 4). Negligible NH_4^+ was detected in the two bioreactors, indicating effective nitrification during OMBR operation regardless of the FO membrane type (Figure 4A and B). However, PO_4^{3-} accumulated considerably in the two bioreactors (Figure 4C and D), due to its high rejection by both FO membranes and low biological removal. It has been well established that PO_4^{3-} removal by activated sludge was only through microbial assimilation, particularly by polyphosphate accumulating organisms, which are susceptible to the saline condition [37]. On the other hand, the FO membrane can effectively reject phosphate ions since they are negatively charged and have large hydrated radius [38]. Given its higher rejection capacity and more negatively charged surface (Table S2, Supplementary Data), the TFC membrane resulted in more PO_4^{3-} accumulation in the bioreactor than

the CTA membrane (Figure 4C and D). Nevertheless, both CTA and TFC membranes enabled negligible nutrient accumulation in the draw solution during OMBR-RO operation (Figure 4).

Figure 4: Distribution and overall removal of ammonia nitrogen (NH_4^+) (A and B) and orthophosphate (PO_4^{3-}) (C and D) in the OMBR-RO hybrid system using the CTA and polyamide TFC membrane. Experimental conditions are given in the caption of Figure 1.

3.4 Removal of trace organic contaminants

Based on their effective octanol – water partition coefficient (i.e. Log D) at the mixed liquor pH of 8, TrOCs selected in this study could be classified as hydrophilic (Log D < 3.2) and hydrophobic (Log D > 3.2) [39]. Generally, almost complete removal of all 30 TrOCs by the OMBR-RO hybrid system was achieved when using either the CTA or TFC FO membrane (Figure 5). This effective removal can be attributed to the complementarity of the biological treatment and the dual high retention barriers created by the FO and RO membranes.

Figure 5: TrOC removal by the OMBR-RO hybrid system using the (A) CTA and (B) polyamide TFC FO membrane. Average removal data obtained from five measurements (once every six days) were demonstrated with standard deviation in the range of 0 to 20% (not shown in the Figure). TrOCs were ordered based on their hydrophobicity indicated by the effective octanol – water partition coefficient (i.e. Log D) at pH 8. Observed TrOC rejection rates do not reflect the real separation capacity of the membranes, but can quantify their contributions toward TrOC removal in the hybrid system. Experimental conditions are as described in the caption of Figure 1.

Of the 30 TrOCs investigated in this study, all 12 hydrophobic compounds (with Log D > 3.2) were effectively removed from the two bioreactors (Figure 5). This result is consistent with previous studies, where the effective removal of hydrophobic TrOCs by activated sludge was attributed to their high adsorption onto biomass, which therefore facilitated their biodegradation [28, 39]. As a result, the FO and RO membranes did not significantly contribute toward the removal of these hydrophobic TrOCs, as indicated by their negligible observed rejection rates (Figure 5). In other words, the difference between the CTA and TFC FO membranes was insignificant regarding the removal of these hydrophobic TrOCs in OMBR.

Effective removal from the two bioreactors (>95%) was also observed for some hydrophilic TrOCs (Figure 5). They were salicylic acid, ketoprofen, naproxen, metronidazole, ibuprofen, gemfibrozil, enterolactone, pentachlorophenol, DEET, and estriol. These 10 hydrophilic TrOCs were readily biodegradable, due to the presence of strong electron donating functional groups (e.g. amine and hydroxyl) in the molecular structure (Table S2, Supplementary Data) for enzymatic hydrolysis [39]. Therefore, there was also no discernible difference between the two OMBR systems for the removal of these hydrophilic and readily biodegraded TrOCs (Figure 5).

Several hydrophilic TrOCs were not well removed (<80%) from the two bioreactors (Figure 5). These compounds included clofibric acid, fenoprop, primidone, diclofenac, propoxur, carbamazepine, atrazine, and ametryn. They have been referred

to as biologically persistent chemicals due to their low removal by activated sludge, which could be further related to the presence of strong electron withdrawing functional groups (e.g. chloro, amide, and nitro) in the molecular structure [28, 39]. Nevertheless, the high retention barriers created by the FO (either CTA or TFC) and subsequent RO membranes ensured more than 98% removal of these hydrophilic and biologically persistent TrOCs by OMBR-RO (Figure 5).

Compared to the CTA membrane, the TFC membrane exhibited more contribution toward the removal of hydrophilic and biologically persistent TrOCs in OMBR (Figure 5). This result could be attributed to the higher rejection of these compounds by the TFC membrane. The TFC membrane with polyamide active layer was more negatively charged than the CTA membrane (Table S1, Supplementary Data). Thus, the TFC membrane could enhance the rejection of negatively charged hydrophilic TrOCs (e.g. clofibric acid and fenoprop) with $pK_a < 8$ (i.e. the mixed liquor pH) by electrostatic repulsion (Figure 5). In addition, pore hydration induced by membrane surface charge could also result in higher TrOC rejection by the TFC membrane. Pore hydration is caused by the permanent attachment of a layer of water molecules to the negatively charged membrane surface via hydrogen bonding and thus could narrow the effective membrane pore size [40]. It has been reported that the TFC membrane encountered more pore hydration than the CTA membrane due to its more surface charge and less reverse salt flux [22], since the higher reverse salt flux could increase the ionic strength within the membrane pores and thereby suppress pore hydration [41]. Therefore, although the TFC membrane had a larger pore size and molecular weight cut-off (Table S2, Supplementary Data), it exhibited a higher rejection of TrOCs (either ionic or non-ionic) by steric hindrance than the CTA membrane. Steric hindrance could be more notable for the rejection of ionic TrOCs ($pK_a < \text{mixed liquor pH}$) (Table S2, Supplementary Data), because they were hydrated and their hydrated radii were significantly larger than their apparent radii in the mixed liquor [41].

The higher rejection capacity of the TFC membrane led to almost complete removal of all hydrophilic and recalcitrant TrOCs in OMBR and thus reduced the rejection

stress of the downstream RO membrane when compared to the CTA membrane (Figure 5). It has been reported that TrOCs could accumulate in the draw solution and consequently deteriorate the product water quality if they could pass through the FO membrane, but was retained by the RO membrane in FO-RO applications [42]. Indeed, a much more considerable accumulation of TrOCs in the draw solution was observed in this study when the CTA membrane was used for OMBR-RO in comparison with that using the TFC membrane (Figure S4, Supplementary Data). This result suggests that the deployment of highly selective FO membranes in the OMBR-RO hybrid system would reduce the purification of the draw solution (e.g. by advanced oxidization process and activated carbon adsorption) to secure the high product water quality and system sustainability.

3.5 Residues of trace organic contaminants in the sludge

TrOC residuals in the sludge varied considerably at the end of OMBR operation using either the CTA or TFC FO membrane (Figure 6). Of the 30 TrOCs selected in this study, relatively low accumulation in the sludge was observed for most hydrophilic compounds ($\text{Log } D < 3.2$), given their weak hydrophobic interaction with biosolids [43]. Some hydrophilic TrOCs, such as carbamazepine and pentachlorophenol, resided significantly in the sludge in both bioreactors. Similar results were also observed during conventional MBR operation and could be attributed to their moderate hydrophobicity and relatively low biodegradability [28, 44]. Although hydrophobic TrOCs absorbed easily on biosolids, their residuals in the sludge was insignificant with amitriptyline as the only exception (Figure 6). This result was caused by the high biodegradability of these hydrophobic TrOCs and their favorable adsorption onto biosolids, which in turn facilitated their biodegradation [43]. The high content of amitriptyline in the sludge was observed, because of both the hydrophobic and electrostatic interactions between this positively charged compound and negatively charged biosolids [45].

Of the 30 TrOCs selected in this study, 14 compounds accumulated more significantly

455 in the sludge when the CTA membrane was used in comparison with the TFC
456 membrane (Figure 6). This observation was possibly due to the higher bioreactor
457 salinity at the end of OMBR operation when the CTA membrane was used (Figure
458 1B). The elevated salinity could increase the sludge hydrophobicity [34] and thus
459 enhance the hydrophobic interaction with TrOCs. By contrast, six TrOCs exhibited
460 considerably higher accumulation in the sludge when the TFC membrane was used
461 (Figure 6). They were carbamazepine, pentachlorophenol, atrazine, ametryn,
462 amitriptyline, 4-tert-octylphenol, and octocrylene. These compounds were moderately
463 or highly hydrophobic and could be effectively rejected by the TFC FO membrane,
464 thereby increasing adsorption onto biosolids. Thus, further attention should be paid on
465 the removal of these TrOCs, especially these that are biologically persistent, in the
466 management of waste sludge from OMBR using highly selective FO membranes.

Figure 6: TrOC residues in the sludge phase at the end of OMBR-RO operation using the CTA and polyamide TFC FO membrane. Error bars represent standard deviation from two sludge samples taken from each bioreactor. Experimental conditions are as described in the caption of Figure 1.

4. Conclusion

Results reported here show that the TFC membrane produced higher initial water flux but more significant flux decline than the CTA membrane in OMBR operation. A higher but subsequently lower salinity build-up in the bioreactor was observed for OMBR using the TFC membrane compared to its CTA counterpart, which thereby caused considerable differences in sludge characteristics. All 30 TrOCs selected in this study were effectively removed by the hybrid OMBR-RO system using either the CTA or TFC membrane. Nevertheless, the TFC membrane contributed more contribution toward the removal of hydrophilic and biologically persistent TrOCs than the CTA membrane and thus reduced their accumulation in the draw solution in OMBR-RO. In addition, these two FO membrane types also resulted in different TrOC accumulation in the sludge during OMBR operation.

5. Acknowledgements

This research was supported under Australian Research Council's Discovery Project funding scheme (project DP140103864) and Science & Technology Planning Project of Guizhou Academy of Agricultural Science (project 2014-014). Dr. Jinguo Kang is thanked for TrOC analysis.

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**Osmotic membrane bioreactors for wastewater reuse: Performance
comparison between cellulose triacetate and polyamide thin film
composite membranes**

Supplementary Data

Bangxi Zhang ^{a,b}, Xiaoye Song ^c, Long D. Nghiem ^c, Guoxue Li ^a, Wenhai Luo ^{a*}

^a *Beijing Key Laboratory of Farmland Soil Pollution Prevention and Remediation,
College of Resources and Environmental Sciences, China Agricultural University,
Beijing, 100193, China*

^b *Guizhou Institute of Agricultural Resources and Environment, Guiyang, Guizhou,
550001, China*

^c *Strategic Water Infrastructure Laboratory, School of Civil, Mining and
Environmental Engineering, University of Wollongong, Wollongong, NSW 2522,
Australia*

* Corresponding author: luowenhai@cau.edu.cn; Ph: +86 18311430503.

Figure S1: Schematic diagram of the OMBR-RO system used in this study.

Figure S2: Electrical conductivity of the draw solutions during OMBR operation using the CTA and polyamide TFC FO membranes. Experimental conditions: DO = 5 mg/L; initial MLSS = 5.5 g/L; SRT = 20 d; temperature = 22 ± 1 °C; draw solution = 0.5 M NaCl; draw cross-flow velocity = 2.8 cm/s; RO cross-flow velocity = 41.5 cm/s.

Figure S3: Photos, SEM images, and EDS measurements of the CTA and polyamide TFC FO membranes after 30 days of OMBR-RO operation. Experimental conditions are shown in the caption of Figure S2.

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667 **Figure S4:** TrOC concentrations in the draw solution on day 10 and 30 during OMBR-RO operation using the CTA and TFC FO membrane.

668 Experimental conditions are shown in the caption of Figure S2.

Table S1: Key physicochemical properties of the synthetic wastewater (average $\pm$ standard deviation from 18 measurements during the two OMBR-RO operation)

Parameters	Synthetic Wastewater
Conductivity ($\mu\text{S}/\text{cm}$)	321 ± 15
pH	6.2 ± 0.3
Total Organic Carbon (mg/L)	141.9 ± 11.2
Total Nitrogen (mg/L)	23.5 ± 3.2
Ammonium (mg/L)	10.6 ± 1.0
Phosphate (mg/L)	11.1 ± 1.8

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Table S2: Physicochemical properties of 30 TrOCs investigated in this study.

Compounds	Chemical Formula	Log D (pH8)	MW (g/mol)	pKa	Chemical Structure
Clofibric acid	$\text{C}_{10}\text{H}_{11}\text{ClO}_3$	-1.29	214.6	3.18
Salicylic acid	$\text{C}_7\text{H}_6\text{O}_3$	-1.14	138.1	3.01
Ketoprofen	$\text{C}_{16}\text{H}_{14}\text{O}_3$	-0.55	254.3	4.23
Fenoprop	$\text{C}_9\text{H}_7\text{Cl}_3\text{O}_3$	-0.28	269.5	2.93
Naproxen	$\text{C}_{14}\text{H}_{14}\text{O}_3$	-0.18	230.3	4.84
Metronidazole	$\text{C}_6\text{H}_9\text{N}_3\text{O}_3$	-0.14	171.2	14.44
Ibuprofen	$\text{C}_{13}\text{H}_{18}\text{O}_2$	0.14	206.3	4.41

Primidone	$C_{12}H_{14}N_2O_2$	0.83	218.3	12.26
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	1.06	296.2	4.18
Gemfibrozil	$C_{15}H_{22}O_3$	1.18	250.3	4.75
Propoxur	$C_{11}H_{15}NO_3$	1.54	209.2	12.28
Enterolactone	$C_{18}H_{18}O_4$	1.88	298.33	9.93
Carbamazepine	$C_{15}H_{12}N_2O$	1.89	236.3	13.94
Pentachlorophenol	C_6HCl_5O	2.19	266.4	4.68
DEET	$C_{12}H_{17}NO$	2.42	191.3	-1.37
Estriol	$C_{18}H_{24}O_3$	2.53	288.4	10.25
Atrazine	$C_8H_{14}ClN_5$	2.64	215.7	2.27
Ametryn	$C_9H_{17}N_5S$	2.97	227.3	3.71
Amitriptyline	$C_{20}H_{23}N$	3.21	277.4	9.18
Benzophenone	$C_{13}H_{10}O$	3.21	182.2	-7.5
4-tert-Butylphenol	$C_{10}H_{14}O$	3.39	150.2	10.13

Oxybenzone	$C_{14}H_{12}O_3$	3.42	228.2	7.56
Estrone	$C_{18}H_{22}O_2$	3.62	270.4	10.25
Bisphenol A	$C_{15}H_{16}O_2$	3.64	228.3	10.29
17 α -ethynylestradiol	$C_{20}H_{24}O_2$	4.11	296.4	10.24
17 β -estradiol	$C_{18}H_{24}O_2$	4.14	272.4	10.27
Triclosan	$C_{12}H_7Cl_3O_2$	4.93	289.5	7.8
β -Estradiol-17-acetate	$C_{20}H_{26}O_3$	5.11	314.4	10.26
4-tert-Octylphenol	$C_{14}H_{22}O$	5.18	206.3	10.15
Octocrylene	$C_{24}H_{27}NO_2$	6.89	361.5	--

673 *Note:* Information in this table was obtained from SciFinder Scholar (ACS) database.

Table S3: Key properties of the FO and RO membranes used in this study (average values $\pm$ standard deviation from duplicate measurements).

Parameter	CTA FO	TFC FO	RO
Active layer	Cellulose Triacetate	Polyamide	Polyamide
Pure water permeability (L/m ² h-bar) ^a	0.84 $\pm$ 0.03	2.50 $\pm$ 0.25	2.65 $\pm$ 0.07
Salt (NaCl) permeability (L/m ² h) ^b	0.32 $\pm$ 0.06	0.19 $\pm$ 0.03	--
Observed NaCl rejection (%) ^b	92 $\pm$ 1.4	98 $\pm$ 0.2	98 $\pm$ 0.3
Contact angle (°) ^c	60 $\pm$ 5	42 $\pm$ 3	35 $\pm$ 5
Zeta potential at pH 8 (mV) ^d	-4.5 $\pm$ 0.4	-14.2 $\pm$ 0.5	-20 $\pm$ 0.5
Estimated pore size (nm) ^e	0.37	0.42	--
Estimated molecular weight cut-offs (g/mol)	196 ^f	250 ^g	--

^a determined in a cross-flow RO system described in the manuscript with deionized water as the feed, an applied hydraulic pressure of 10 bar, a cross-flow velocity of 25 cm/s, temperature of 22 $\pm$ 1 °C.

^b measured under the same conditions for pure water permeability, but with a 2,000 mg/L NaCl solution as the feed.

^c tested using a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) based on the standard sessile drop method.

^d analyzed using a SurPASS electrokinetic analyser (Anton Paar CmbH, Graz, Austria).

^e obtained from Xie et al. (2014).

^f calculated by translating the estimated membrane pore size to an approximate Stokes radius (radius of equivalent sphere) and molecular weight using the Wilke and Chang and the Stokes-Einstein equation based on the method reported previously by Xie et al. (2016).

^g obtained from Xie et al. (2016).

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