Microbial Electrochemical Nutrient Recovery in Anaerobic Osmotic Membrane Bioreactors

by

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Abstract

This study demonstrates that by incorporating a microbial electrochemical unit into an anaerobic osmotic membrane bioreactor (OMBR), the system addressed several challenges faced by traditional anaerobic membrane bioreactors and recovered biogas, nitrogen, and phosphorus while maintaining high effluent quality with low dissolved methane. The microbial recovery cell (MRC)-OMBR system showed excellent organic (>93%) and phosphorus removal (>99%) and maintained effluent COD below 20 mg/L. Furthermore, the reactor effectively recovered up to 65% PO_4^{3-} and 45% NH_4^+ from the influent, which can be further improved if membranes with higher selectivity are used. Nutrients removal from bulk solution mitigated NH_4^+ penetration to the draw solution and reduced scaling potential caused by PO_4^{3-} . The maximum methane yield was 0.19 L $\text{CH}_4/\text{g COD}$, and low methane (<2.5 mL CH_4/L) was detected in the effluent. Further improvement can be made by increasing charge efficiency for better nutrient and energy recovery.

Keywords: forward osmosis, anaerobic osmotic membrane bioreactor, nutrient recovery, microbial electrochemical technology, dissolved methane

1. Introduction

Osmotic membrane bioreactors (OMBRs) have been gaining great interests for wastewater treatment and reuse. An OMBR integrates biological degradation of wastewater substrates and a semi-permeable forward osmosis (FO) membrane for physiochemical separation (Achilli et al. 2009, Cath et al. 2006, Chen et al. 2014, Gu et al. 2015, Holloway et al. 2014, Holloway et al. 2015b, Lay et al. 2010). Water flows from a low-salinity feed solution (FS) to a high-salinity draw solution (DS) through the non-porous FO membrane, which acts as a barrier to the contaminants so the effluent quality can be satisfactory. Most OMBR studies have focused on wastewater treatment under aerobic conditions while only a few studies so far paid attention on anaerobic OMBR process, which carries good potential for energy and resource recovery in addition of high quality treatment (Chen et al. 2014, Gu et al. 2015, Liu et al. 2017).

Anaerobic osmotic membrane bioreactor (AnOMBR) reduces energy demand and recovers biogas or other renewable energy, and it can achieve high treatment efficiency in low-strength wastewater while promoting anaerobic degradation in the reactor by concentrating organic substrates (Chen et al. 2014). AnOMBR has several advantages over conventional pressure-driven anaerobic membrane bioreactors (AnMBRs) that use MF or UF membranes. Firstly, AnOMBR has shown lower fouling propensity due to the absence of hydraulic pressures, which could compact the foulant layers and reduce water permeation (Chen et al. 2014, Gu et al. 2015, Holloway et al. 2015a, Holloway et al. 2014, Holloway et al. 2015b, Lay et al. 2010). In addition, AnOMBR utilizes non-porous semi-permeable FO membranes, which have the potential to alleviate several

major problems faced by traditional AnMBRs, such as dissolved methane in the effluent and low removal of soluble carbon, nitrogen, and phosphorus (Martinez-Sosa et al. 2011, Smith et al. 2013, Smith et al. 2012).

However, AnOMBRs still face challenges such as membrane fouling, bidirectional solute diffusion, and effective approaches of nutrient recovery. Because anaerobic reactors contain high concentrations of foulants, membrane fouling can be more severe compared to aerobic processes. Previous studies demonstrate that membrane fouling can be alleviated by coupling OMBRs with microbial fuel cells (MFCs) pretreatment. MFCs are anaerobic bioelectrochemical reactors that generate very small amount of biomass while producing electricity during biodegradation, so they can be complementary to OMBRs as they help decrease foulants concentration and condition sludge property thus reduce fouling (Hou et al. 2016, Tian et al. 2014). On the other hand, OMBR helps increase electrolyte conductivity which facilitates MFC electrochemical reaction kinetics and increases power generation (Hou et al. 2016).

In this study, we developed an integrated AnOMBR system that attempted to resolve several major challenges aforementioned such as effective nutrient (N, P) recovery, biogas recovery, and reduce dissolved methane concentration in the effluent. We introduced a microbial electrochemical nutrient recovery unit into the OMBR, which we call a microbial recovery cell (MRC). The central hypothesis is that by taking advantage of the electrical potential generated across the anode and cathode in the MRC, charged ions such as $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$ and salts can be extracted from the OMBR bulk solution

and recovered in a separated recovery solution (Chen et al. 2015). Final product such as struvite can be obtained (Qiu et al. 2016). This integration will minimize the penetration of NH_4^+ through the FO membrane thus improve effluent quality. In addition, PO_4^{3-} in the OMBR bulk is recovered, which reduces the scaling potential lead by PO_4^{3-} . Presumably, incorporating MRC into OMBR may also recover SO_4^{2-} from OMBR bulk solution thus reduce methane loss due to sulfate reduction and improve methane yield. Moreover, MRC not only recovers nutrients from OMBR but also desalinates OMBR bulk solution, which reduces osmotic pressure loss and maintains FO membrane flux. In the MRC-OMBR system, OMBR concentrates organics and solutes in the bulk and increases buffer capacity. Such changes improve MRC current density, which in turn increases the driving force of nutrient recovery and biogas production when a balance is maintained between solute accumulation and removal. In addition, the produced biogas could balance energy consumption needed for draw solution recovery. We also investigated the dissolved methane in the bulk solution and draw solution (DS) and characterized membrane fouling behavior.

2. Material and methods

2.1 Membranes and Chemicals

A commercial CTA FO membrane (Hydration Technology Innovations, Albany, OR) was used in this study. The membrane has a water permeability of 2.08×10^{-12} m/s.Pa, a NaCl permeability of 1.76×10^{-7} m/s, and a structure parameter of 0.48 mm (She et al. 2013, Zhang et al. 2014). Membrane coupons were soaked in MilliQ water (18.2 M Ω .cm) at room temperature for over 24 h before use (She et al. 2013, Zhang et al. 2014).

Glucose-based defined medium was used as the synthetic feed wastewater, so degradation and current production mechanisms can be quantified (Gu et al. 2015, Hou et al. 2016, Lu et al. 2014). The medium contained (mg/L): glucose, 200; yeast extract, 50; NaHCO₃, 150; NH₄Cl, 80; KH₂PO₄, 50; Na₂SO₄, 40; MgCl₂•6H₂O, 5; and CaCl₂, 10. The total soluble chemical oxygen demand (COD), NH₃-N, PO₄-P, electric conductivity and pH of the feed solution were 275 ± 10 mg/L, 21.6 ± 0.5 mg/L, 13.0 ± 0.2 mg/L, 0.57 ± 0.05 mS/cm and 7.20 ± 0.05, respectively (Hou et al. 2016, Lu et al. 2014).

2.2 Reactor Configuration and Operation

The schematic diagram of the reactor system is shown in Figure 1. A microbial electrochemical module and a FO membrane module (effective membrane area, A_m : 272 cm²) with active layer facing feed orientation were fully submerged into a bioreactor (effective volume, V_R : 4.5 L). The microbial electrochemical module was firstly constructed in microbial electrolysis cell (MEC) configuration that consisted of two carbon felt anodes (136 cm² each) and a NiFe layered double hydroxide Ni foam cathode (136 cm²), which was placed between the anodes (Lu et al. 2016a, Lu et al. 2016b). The MEC module was operated for biogas production for more than 30 days after stabilization and then was switched to microbial recovery cell (MRC) mode for nutrient recovery by adding two recovery chambers (total volume: 200 mL) between the anodes and cathodes with hydraulic connection. The recovery chamber was formed by a cation exchange membrane (CEM, Excellion MI-100, SnowPure, 136 cm²) and an anion exchange membrane (AEM, Excellion MI-200, SnowPure, 136 cm²), facing the anode and cathode, respectively (Forrestal et al. 2012). The glucose-based medium

was directly fed into the bulk solution of the bioreactor. Nutrients were recovered via MRC recovery chambers and clean water was recovered via FO draw solution. Biogas was collected from bulk solution headspace. The anodes were inoculated with the anaerobic digested sludge collected from Boulder Wastewater Treatment Plant and fed with the synthetic wastewater. A voltage of 0.8 V was applied between the anode and cathode with an external resistor (R , 1 Ω) inserted into the circuit for current monitoring every 10 minutes using a data acquisition system (Keithley Instruments, Inc., OH) (Chookaew et al. 2014). A higher voltage of 1.0V was applied at the end batch of MRC operation to investigate the effects of voltage. An air pump was used to recirculate the produced biogas through a gas diffuser in order to mix the solution and scour the FO membrane for fouling control, and the recirculation rate was controlled at 2 L/min. The whole reactor was maintained at anaerobic condition and 25.0 ± 0.5 °C.

During operation, the solution volume of the system was monitored by a digital balance. When the weight of the reactor dropped below the designated value, fresh feed wastewater was transferred into the reactor using a peristaltic pump. Conductivity, temperature, pH, oxidation–reduction potential (ORP) values in the reactor were monitored and logged using LabVIEW. In the meanwhile, draw solution (DS, 0.5 M NaCl) and/or nutrients recovery solution (NS, initial: 10 mM NaCl, 3.0 L) were recirculated at a flow rate of 560 mL/min (equivalent to a cross flow velocity of 7.0 cm/s) and 50 mL/min, respectively. The concentration of DS was monitored by conductivity measurements and maintained constant through dosing a 5 M NaCl stock solution. The water flux was determined gravimetrically by weighing the mass of permeate water collected at predetermined time intervals with a digital balance (Ohaus, Parsippany, NJ). The

membrane module was cleaned after each run by tap water flush and reused for next operation; and after the final run, the membrane was taken out and characterized.

2.3. Water and Solute Flux Modeling

In order to simulate water flux and solute accumulation in OMBR, a water flux model accounting concentration polarization was developed in our previous research.(Hou et al. 2016) Based on the model, the theoretical ratio of the accumulated solute flux from wastewater to the total solute accumulation ($\eta_s = 22.6\%$ in this study) can be determined using:

$$\eta_s = \frac{J_{s_FS}}{J_{s_FS} + J_{s_DS}} \quad \text{Eq. (1)}$$

where J_{s_DS} is the reverse solute flux from draw solution, J_{s_FS} the accumulated solute flux from wastewater. Experimentally, the contributions of solutes from wastewater to the total solute accumulation (η_s') in OMBR can be estimated using:

$$\eta_s' = \frac{EC_0 \left(\frac{\int J_w A_m dt}{V_R} + 1 \right)}{EC_t + \sum_1^t \frac{V_S}{V_R} (EC_t - EC_0)} \quad \text{Eq. (2)}$$

where EC_0 is the solution conductivity of fresh wastewater, $\int J_w A_m dt$ the cumulative volume of water transport to the draw solution from the OMBR bulk solution at time t, V_R the OMBR reactor volume, EC_t the solution conductivity in OMBR at time t, and V_S the sampling volume at time t. The biological COD removal efficiency (R_{COD}), and the overall removal efficiency (R) and recovery efficiency (η_R) of nutrients in the whole MEC/MRC-OMBR system were calculated using Eq. (3), Eq. (4) and Eq. (5), respectively.

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$$R_{COD} = 1 - \frac{\Delta C_{COD,R}V_R + C_{COD,DS}V_{DS}}{C_{COD,FS}V_{FS}} \quad \text{Eq. (3)}$$

$$R = 1 - \frac{C_{DS}}{C_{FS}} \quad \text{Eq. (4)}$$

$$\eta_R = \frac{\Delta C_{NS}V_{NS}}{C_{FS}V_{FS}} \quad \text{Eq. (5)}$$

198 where C_R , C_{DS} , C_{FS} and C_{NS} are the solutes and/or contaminants concentrations in the
 199 reactor bulk, draw solution, feed solution and nutrient recovery solution, respectively;
 200 and V_R , V_{DS} , V_{FS} , and V_{NS} are the volume of OMBR reactor, draw solution, feed solution
 201 and nutrient solution; ΔC_R and ΔC_{NS} are the concentration changes of solutes and/or
 202 contaminants in the bulk reactor and nutrient recovery solution. Detailed descriptions of
 203 R and η_R can be found elsewhere (Gu et al. 2015, Hou et al. 2016).

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205 **2.4. Analyses**

206 All samples for COD, N and P measurements were centrifuged (5000 RPM for 5 min)
 207 and then filtered through 0.45 μm cellulose membranes (Millipore). COD was measured
 208 according to standard methods described in detail by American Public Health
 209 Association (APHA 1998). $\text{NH}_3\text{-N}$ (TNT 832/831/830) and $\text{PO}_4\text{-P}$ (TNT 846) were
 210 measured with HACH test tubes (HACH, Loveland, CO). All samples were collected and
 211 analyzed in triplicate. (Wang et al. 2011) The current and Coulombic efficiency (%) of the
 212 MEC/MRC were calculated according to previous studies (Luo et al. 2012b). In order to
 213 determine the current utilization efficiency of certain nutrient ions, charge efficiency was
 214 defined as ratio of the electric charge of the recovered ion to the total charge introduced
 215 by the current (Chen et al. 2015).

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Biogas (250 μ L samples) in the reactor headspace was sampled using a gastight syringe (500 μ L; Hamilton Samplelock Syringe) and analyzed using a gas chromatograph (8610C, SRI Instruments) for H₂, CH₄ and CO₂. Dissolved methane was also measured by transferring a liquid sample (10 mL) from OMBR or DS tank into a serum bottle (12.5 mL, HACH, Loveland, CO), leaving a headspace of 2.5 mL; the headspace air was replaced by N₂ gas and the bottle was sealed with a thick butyl rubber stopper (20 mm diameter, Chemglass Inc.). After establishing gas–liquid equilibrium by shaking the serum bottle for 24 hours at room temperature, the amount of dissolved methane was back-calculated from the measured methane amount in the headspace according to Henry's Law (Ren et al. 2014). All serum bottles were autoclaved, and all liquid samples were collected in triplicate and filtered using 0.2 μ m cellulose membranes (Millipore) to prevent biological activities. Paired two-sample *t*-test was performed to study the significance of methane yield improvement.

3. Results and discussion

3.1. Reactor Water Flux Change, Salinity Accumulation, and Membrane Fouling

Figure 2 shows the time-course change of water flux and solution conductivity in the OMBR. Varied in different operations, within one stage (~11 days) the solution conductivity could increase dramatically from 0.7 ± 0.05 to 17.0 ± 0.2 mS/cm during MEC-OMBR operation or to 12.7 ± 0.2 mS/cm during MRC-OMBR operation. The increase of solution conductivity was partially due to solutes accumulation from wastewater (i.e., NaCl, NaHCO₃, KH₂PO₄, Na₂SO₄) during FO water extraction. Our previous study quantified that salt accumulation in the wastewater FS contributed $82.1 \pm 4.0\%$ (η_s') of

the salinity build-up in an OMBR with TFC membranes (Hou et al. 2016). However, we found in this study that when CTA membrane was used, such contribution of salt accumulation only accounted for $\eta_s'' = 25.1 \pm 3.0\%$ (Figure S2), which is much smaller than the contribution from reversely diffused solutes (i.e., NaCl). Such difference is due to the intrinsic low-rejection property of CTA membranes (Chen et al. 2014, Gu et al. 2015, Xiao et al. 2011). The lower salinity buildup in MRC-OMBR than the MEC-OMBR operation was due to ion migration across the ion exchange membranes into the recovery solution (Chen et al. 2015, Luo et al. 2011). This is confirmed by the conductivity change of the recovered nutrient solution, which increased from 1.10 ± 0.05 mS/cm to 11.25 ± 0.25 mS/cm under 0.8 V or 12.86 mS/cm under 1.0 V, respectively. Previous studies demonstrated that the alleviation of salinity reduces its potential toxicity on microbial activities, and it also alleviates membrane fouling by decreasing protein concentration in the soluble microbial products (SMPs), as well as affecting the charge interactions between foulant-foulant and/or foulant-membrane (Chen et al. 2014, Hong and Elimelech 1997).

Corresponding to salinity build up in the OMBR bulk, water flux decreased from 8.7 ± 0.3 to 4.0 ± 0.2 LMH in 13 days. The experimental flux profile matches the modeled flux, which simulates the flux under solute conductivity build-up without considering membrane fouling. This is attributed to the low fouling property of CTA membrane as well as fouling mitigation carried by MEC/MRC. The flux decline was also slower than that in an MFC-OMBR system equated with thin-film composite (TFC) membrane. (Hou et al. 2016) All these reveal that CTA membrane is less prone to fouling than TFC

membrane, which can be attributed to CTA membrane's smoother surface and less binding properties with the fouling precursors (e.g., divalent ions) (Gu et al. 2013, Mi and Elimelech 2008, Mi and Elimelech 2010). The less fouling property of CTA was also supported by the fact that almost a full recovery of flux ($97.3 \pm 0.7\%$) was obtained after each cleaning using tap water.

Visual inspection and electron microscopy were performed on FO membrane coupons. Visual examinations of virgin and fouled membrane samples after one cycle are illustrated in Figure S3. The observed foulant layer is thin and loose, which can be easily removed from membrane surface by water rinsing. More importantly, the SEM images (Figure S3) indicate that biofouling/organic fouling contributed higher to membrane flux decline than inorganic scaling. This is different from results obtained in other studies, in which crystal deposition was abundantly observed in the foulant layer (Gu et al. 2015). Further research will be conducted in order to reveal the inorganic scaling behavior in the MEC/MRC-OMBR systems.

3.2. Organic Removal and Nutrients Recovery

Figure 3 shows the changes of COD concentration in the bulk solution and draw solution of OMBR. High COD removal ($>93\%$) was accomplished in both stages of operation, and the COD in the OMBR draw solution maintained below 20 mg/L due to the good rejection performance ($>90\%$) by the CTA membrane. One interesting finding is that different from many studies where continued COD decrease was observed, COD in the bulk solution increased first during each batch till it reached to a peak then it started to drop till the end of the batch. This bell shaped profile is presumably related to

the interaction between FO concentration and biological degradation of organics. Initially, COD in the bulk solution increased because the concentration factor of FO overweighed the biodegradation of COD in the bulk solution, which resulted in the accumulation of COD. However, overtime the flux declined due to slower mass transfer and membrane fouling (Figure 2), while biodegradation rate increased, therefore COD removal became dominant after the peak (Brown et al. 2015, Hou et al. 2016). This can also be observed in Figure 5B, in which the relationships among COD, conductivity and current are illustrated. Smaller peaks were observed in MRC-OMBR operation, which is likely due to the removal of charged organics such as volatile fatty acids during nutrient recovery.

Figure 4 shows the changes of nutrients ($\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$) in the OMBR bulk solution, draw solution and nutrient recovery solution. During the MEC-OMBR stage, $\text{NH}_3\text{-N}$ concentration in OMBR bulk solution initially increased due to accumulation then dropped due to the migration of $\text{NH}_3\text{-N}$ to the DS. The limited removal of $\text{NH}_3\text{-N}$ in AnOMBR is widely observed in previous studies, which is partially due to the lack of biological degradation in anaerobic condition but also the low rejection of $\text{NH}_3\text{-N}$ by CTA membrane (Chen et al. 2014, Gu et al. 2015). The pH increase in bulk solution (6.7 ± 0.2 to 7.8 ± 0.2 , Figure S4) also played a role as it affects $\text{NH}_4^+/\text{NH}_3$ distribution and lead to higher flux of $\text{NH}_3\text{-N}$ in the form of NH_3 toward the draw solution. Because MEC does not have nutrient recovery function, the majority of nitrogen in bulk solution migrated to FO draw solution, but the performance of CTA in $\text{NH}_3\text{-N}$ rejection was actually better than that of TFC membrane reported in previous studies, because the deprotonation of carboxylic groups on TFC membranes leads a negatively charged surface, which

promotes diffusion of cations (e.g., NH_4^+) from OMBR bulk solution to DS (Hou et al. 2016, Lu et al. 2014, Xue et al. 2015). In contrast, the MRC-OMBR stage showed much better $\text{NH}_3\text{-N}$ removal with its concentration in bulk solution dropped from ~75 mg/L to ~50 mg/L and the concentration in DS dropped from ~21 mg/L to ~16 mg/L. The removed nitrogen was recovered in the MRC recovery solution, in which $\text{NH}_3\text{-N}$ increased from 0 up to 80 mg/L, representing a nitrogen recovery efficiency between 28-45%.

In contrast to the low rejection and removal of $\text{NH}_3\text{-N}$ due to membrane limitation, the MEC/MRC-OMBR showed almost perfect rejection (> 99%) and removal (> 99%) of $\text{PO}_4\text{-P}$ (Figure 4B). $\text{PO}_4\text{-P}$ in DS cannot be detected, and the concentration of $\text{PO}_4\text{-P}$ increased from 13.0 up to 280 mg/L for MEC-OMBR in one batch. The high PO_4^{3-} may react with other cations (NH_4^+ , Mg^{2+} , and Ca^{2+}) to form $\text{Ca}_3(\text{PO}_4)_2$ and/or struvite (i.e., $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) (Gu et al. 2015). The MRC-OMBR recovered 41-65% $\text{PO}_4\text{-P}$ from the bulk solution to the recover solution by the end of each stage, which enables nutrients recovery and alleviates scaling potential. Mass balance calculation details can be found in Supporting Information.

It is interesting to note that $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentration in the OMBR bulk solution tended to stabilize after 6 days. This might be due to electroosmosis as well as the competitive effects between the potential gradient and the concentration gradient across the ion exchange membranes, which drive the diffusion of $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ in reverse directions (Pronk et al. 2006). Another reason can be revealed using charge efficiency

(Figure S5), which is defined as the electric charges of those recovered ions to the total electric charges induced by the current (Chen et al. 2015). The initial charge efficiencies for NH_4^+ and PO_4^{3-} in MRC-OMBR were ~10% and 6% (Figure S5A), respectively, which were comparable to the results reported in previous studies (NH_4^+ : 15.5% and PO_4^{3-} : 6.3%) (Chen et al. 2015). However, the charge efficiencies decreased to low level along with operation. Previous research showed that ion migration across the membrane can be affected by the mobility, concentration of ions, and the electrical field intensity and membrane selectivity (Luo et al. 2012a). Accordingly, the loss of charge efficiency for NH_4^+ and PO_4^{3-} might be majorly caused by the accumulation and competition of other ions, especially Na^+ and Cl^- , which are the predominant ions in the OMBR bulk solution (Figure S2 and Figure S5B). It is interesting that owing to the increased current, the recovery ratios of NH_4^+ and PO_4^{3-} remained stable (~40%, Figure 4B) in the first 6-8 days, and increased up to 60%, respectively. While this demonstrates that MRC and OMBR has mutual benefits for more efficient nutrients recovery, further studies can be conducted to better understand the competitive migration characteristics, and more efficient MRC (e.g., higher current and higher $\text{NH}_3\text{-N}$ selectivity) can be configured for enhanced $\text{NH}_3\text{-N}$ recovery.

3.3. Current and Biogas Production

Figure 5A shows the current and Coulombic efficiency of the system. For both stages, the current increased in the first few days due to the increase in solution conductivity (Figure 2), COD (Figure 3), and buffer capacity (Figure 4A and Figure S4) (Hou et al. 2016, Nam et al. 2010). Because MRC has higher internal resistance than MEC due to the presence of membranes and increased distance between electrodes, MRC-OMBR

showed smaller current. Increasing the applied voltage in MRC boosted the current (Figure 5A). Similar to the bell curve shaped COD profiles in Figure 3, the current profiles also showed initial increase then decline. This is mainly caused by the depletion of substrates, below which the COD level was not enough to support high current production (Hou et al. 2016, Zhang et al. 2015). Similar trends were observed in Coulombic efficiency, which increased from $20\pm1\%$ up to $60\pm2\%$ and then decreased and stabilized around $40\pm1\%$. Such changes can also be related to the interactions of solution conductivity, buffer capacity, substrate availability, and microbial competition (Hou et al. 2016, Zhang et al. 2015). Nevertheless, the Coulombic efficiency in this research is much higher than that in our previously reported MFC-OMBR system in which air-cathode was used. Figure 5B shows the interactive effects of COD and solution conductivity on the current production of MEC-OMBR. It can be seen that in the concentration range used in this study (COD < 500 mg/L, E.C. < 20mS/cm), increasing COD and solution conductivity boosted current production.

In addition to organic removal and nutrient recovery, the anaerobic system also generated biogas as a renewable energy source. It can be seen from Figure 6 that methane yield (volume of methane produced per gram COD removed) increased during MEC-OMBR operation as methanogens started to acclimate. The highest methane yield was about 0.15 L CH₄ /g COD, representing 50% of the maximal theoretical value. The methane yield is comparable to the values reported in previous literature on anaerobic OMBRs or MBRs, in which methane yields ranged from 0.15 to 0.25 L CH₄ /g COD when treating municipal wastewater at 20-35 °C (Chen et al. 2014, Martinez-Sosa et al.

2011). H₂ production was negligible during the operation so its production was not accounted into biogas production. It was reported previously that methane losses (28% to 39%) in MBRs can be due to the activity sulfate reducing bacteria, dissolved oversaturation, and the loss of dissolved methane in the effluent (Smith et al. 2013, Smith et al. 2012). However, methane oversaturation was not observed in this study, and dissolved methane in the reactor was consistently below 8 mL CH₄/L (Figure 6). This can be attributed to the use of biogas sparging to reduce mass-transfer limitations between the gas and liquid-phases (Gimenez et al. 2012). More importantly, the dissolved methane in the DS was always below 2.5 mL CH₄/L, which is much lower than reported dissolved methane in conventional MBRs (Gimenez et al. 2012, Martinez-Sosa et al. 2011, Smith et al. 2013, Smith et al. 2012). The low methane permeation can be attributed to the rejection by the CTA FO membrane (Donohue et al. 1989). Moreover, low fouling propensity of FO membrane reduces biofilm attachment including methanogens on the membrane, which reduced the in situ methane oversaturation on the membrane surface thus methane permeation. Therefore, it is believed that FO membrane processes advantages over conventional pressure driven porous membranes, such as MF and UF, in mitigating methane loss. It is interesting that compiling MRC into OMBR showed improved methane yield ($P < 0.05$). This is likely due to sulfate recovery from OMBR bulk by MRC, which mitigated methane loss due to sulfate reduction (Figure 6). Though the recovered sulfate was not characterized in this research, previous research reported the recovery of sulfate by MRC (Chen et al. 2015). In addition, desalination of OMBR bulk solution by MRC might also mitigate methanogen inhibition from salinity build-up, which reduced the conversion of substrate

to extracellular polysaccharides under high osmotic conditions (Chen et al. 2014). Further optimization needs to be performed to improve gas production and collection. Nevertheless, MEC/MRC-OMBR showed superiorities over the conventional MBR in treating low-strength wastewater, in which no measurable biogas production was observed at influent COD <225 mg/L (Smith et al. 2013, Smith et al. 2012).

4. Conclusions

The incorporation of electrochemical nutrient recovery process in anaerobic osmotic membrane reactor improved effluent quality, energy production, and resource recovery compared to traditional membrane processes. The removal of charged ions from OMBR bulk solution also alleviated osmotic pressure drop and improved water flux, as well as reduced scaling potential. In addition, different from conventional AnMBR reactors, methane oversaturation was not observed in the MEC/MRC-OMBR, and the dissolved methane in the draw solution was maintained at low level.

While the study demonstrates the feasibility and benefits of integrating nutrient recovery with OMBR, more works are needed to optimize system configuration and performance. Similar to most OMBR reactors, the limited rejection of ammonium by FO membranes leads to the presence of ammonium in draw solution effluent. The integration of MRC in FO reduced such migration by approximately 50%, but new membrane and solute development are needed in order to reduce $\text{NH}_3\text{-N}$ penetration through the membrane (Lu et al. 2014, Devia et al. 2015). Also, draw solution can be further processed with post treatment using reverse osmosis or membrane distillation to generate pure water. The geometry of MRC-OMBR (e.g., submerged or in series) can be adjusted to improve

charge efficiency of nutrient ions, and the recovered nutrients can be processed for struvite precipitation (Qiu et al. 2016, Xie et al. 2014, Xie et al. 2016) or biochar adsorption (Huggins et al. 2016). Different operational conditions need to be tested such as low temperature, high organic loading, and different retention times (Heidrich et al. 2014, Lettinga et al. 1999). Optimizations can also be optimized by modeling membrane flux, solute accumulation, and solute recovery/desalination of the system, all of which are key factors affecting reactor treatment performance.

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List of Figures

Figure 1. Schematic diagram of the MEC/MRC-OMBR system. The microbial electrochemical module was firstly operated in MEC mode followed by MRC mode with the addition of nutrient recovery chambers. Detailed schematics of MEC and MRC modules are available in Figure S1 (Supporting Information).

Figure 2. Time-course changes of membrane water flux (top) and solution conductivity (bottom) of the bulk or nutrient recovery solution during two-stage operation (MEC/MRC-OMBR).

Figure 3. Time-course changes of COD concentration in the OMBR bulk solution and draw solution, as well as COD removal during two stage operation (MEC/MRC-OMBR).

Figure 4. (A) Time-course changes of $\text{NH}_3\text{-N}$ (top) and $\text{PO}_4\text{-P}$ (bottom) concentrations in the OMBR bulk, draw solution and nutrient recovery solution, respectively. (B) $\text{NH}_3\text{-N}$ (top) and $\text{PO}_4\text{-P}$ (bottom) removal from the bulk solution and recovery in the nutrient recovery solution.

Figure 5. (A) Time-course changes of current and Coulombic efficiency in the MEC/MRC-OMBR system; (B) Interactive effects of COD and solution conductivity on current production.

Figure 6. Time-course changes of dissolved CH_4 in the OMBR bulk and draw solution and CH_4 yield during two-stage operation (MEC/MRC-OMBR).

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1) Boosted Current Density

2) Lower Fouling

3) Biogas Production

= 4) Nutrients Recovery

5) Improved Effluent Quality

6) Enhanced Methane Yield

MRC-OMBR
Mutual Benefits