Nutrient-Energy-Water Recovery from Synthetic Sidestream Centrate Using a Microbial Electrolysis Cell - Forward Osmosis Hybrid System

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Abstract

Recovery of nutrients, water, and energy from high-strength sidestream centrate offers benefits such as reusable resource, minimized discharge and cost-savings in mainstream treatment. Herein, a microbial electrolysis cell - forward osmosis (MEC-FO) hybrid system has been investigated for integrated nutrient-energy-water (NEW) recovery with emphasis on quantified mass balance and energy evaluation. In a closed-loop mode, the hybrid system achieved recovery of 54.2 ± 1.9 % of water (70.4 ± 2.4 mL), 99.7 ± 13.0 % of net ammonium nitrogen (8.99 ± 0.75 mmol, with extended N₂ stripping), and 79.5 ± 0.5 % of phosphorus (as struvite, 0.16 ± 0.01 mmol). Ammonium loss primarily from reverse solute flux was fully compensated by the reclaimed ammonium under 6-h extended N₂ stripping to achieve self-sustained FO process. The generated hydrogen gas could potentially cover up to 28.7 ± 1.5 % of total energy input, rendering a specific energy consumption rate of 1.73 ± 0.08 kWh m⁻³ treated centrate, 0.57 ± 0.04 kWh kg⁻¹ COD, 1.10 ± 0.05 kWh kg⁻¹ removed NH₄⁺-N, 1.17 ± 0.06 kWh kg⁻¹ recovered NH₄⁺-N, or 5.75 ± 0.54 kWh kg⁻¹ struvite. Recycling of excess Mg²⁺ reduced its dosage to 0.08 kg Mg²⁺/kg struvite. These results have demonstrated the successful synergy between MEC and FO to achieve multi-resource recovery, and encouraged further investigation to address the challenges such as enhanced hydrogen production, reducing nutrient loss, and optimizing MEC-FO coordination towards an energy-efficient NEW recovery process.

Keywords: Resource recovery; Forward osmosis; Microbial electrolysis cell; Nitrogen and phosphorus; Mass and energy balance.

1. Introduction

Wastewater has been considered as a resource rather than a waste in the 21st century to sustainably address some major challenges, i.e. water scarcity, nutrient depletion with increasing food demands, and energy shortage (McCarty et al. 2011). Conventional wastewater treatment generates a considerable amount of treated water while producing excess mixed liquor (high sludge content) as a sidestream. Subsequent sidestream treatment by anaerobic digestion (AD) enables degradation and stabilization of sludge featuring significant reduction of solid volume (up to 77%) (Kim et al. 2012). The concomitant resource recovery accredits to anaerobic conversion to biogas and nutrients reclamation (N and P) from digested sludge centrate (referred as “centrate” unless otherwise stated) as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) (De-Bashan and Bashan 2004, Qiu et al. 2015). However, the resource recovery capabilities of AD are greatly impaired by its incomplete organics removal ($1000 \sim 2000 \text{ mg L}^{-1}$ remaining COD) (Arango et al. 2016, Uggetti et al. 2014) and unsatisfying struvite crystallization under an imbalanced N/P ratio with a low P level ($\sim 56 \text{ mg L}^{-1}$) as a major limiting factor (Xie et al. 2016), rendering an abundant amount of $\text{NH}_4^+\text{-N}$ ($>1000 \text{ mg L}^{-1}$) that is not recovered. Recycling the nutrient-rich centrate back to the mainstream, though contributing less than 1% of total wastewater flow, leads to notable increase of nutrient loading rate (up to 30%), additional energy investment, and elevated environmental footprint of mainstream treatment facilities (Lackner et al. 2008).

Insufficient resource recovery from sidestream centrate urges substantial process reformation with emphasis on comprehensive reclamation of nutrients (both N and P), bioenergy derived from remaining organics, and high-quality water towards zero-liquid discharge (Tong and Elimelech 2016). Physicochemical approaches deliver unique advantages for simultaneous

nutrient concentration and centrate desalination. For example, clean water could be extracted from centrate in an electrodialysis-reverse osmosis (ED-RO) coupled system (Mondor et al. 2008), with ammonium being separated through air stripping (Ippersiel et al. 2012). The concentrate with an elevated P level ($> 100 \text{ mg L}^{-1}$) could facilitate subsequent struvite precipitation (recovery rate $> 95\%$) (Xie et al. 2016). RO could be replaced by microfiltration (MF) for enrichment of volatile fatty acids (VFAs) towards biogas fermentation (Tao et al. 2016), or membrane distillation (MD) for generating contaminant-free fresh water (Kim et al. 2016). However, these electricity-, pressure-, and thermal-driven membrane processes require substantial energy investment, weakening their potential for broader applications.

The path forward lies in energy-efficient innovations for integrated nutrient-energy-water (NEW) recovery from sidestream centrate, such as bioelectrochemical systems (BES) powered by bioenergy and osmotically-driven membrane processes (OMDPs). BES has been deemed as an attractive treatment method due to continuous nutrient enrichment and energy recovery as electricity (microbial fuel cell, MFC) (Logan et al. 2006) or value-added products such as hydrogen gas (microbial electrolysis cell, MEC) (Kelly and He 2014). OMDPs, especially forward osmosis (FO), take advantage of osmotic pressure gradient across a semi-permeable membrane to spontaneously harvest high-quality product water (Lutchmiah et al. 2014). Integrating BES with OMDP may accomplish multiple tasks including nutrient recovery, bioenergy conversion, and wastewater treatment towards further reuse (Hou et al. 2016, Lu et al. 2014).

Our previous study has demonstrated the feasibility of a hybrid MEC-FO system using recovered ammonium as a draw solute for subsequent water recovery (Qin and He 2014). However, phosphorus recovery was not addressed, and this warranted synergistic coordination between MEC and FO towards multi-nutrient reclamation. Exact energy performance (i.e. energy output and recovery efficiency) was not quantified to enable better comparison with existing technologies aiming at similar targets. In addition, lacking thorough mass/energy balance on a system level would jeopardize the scaling-up potential of this hybrid system. Herein, we have comprehensively evaluated the feasibility of the aforementioned NEW recovery from synthetic centrate by using this hybrid MEC-FO system (linked to a struvite precipitation process). The specific objectives of this study were to (1) enhance the effectiveness of phosphorus recovery via struvite from low-P synthetic centrate; (2) analyze NEW mass balance on a system level with emphasis on NH_4^+ -N loss and self-compensation, closed-loop struvite precipitation yield, continuous water extraction capability, and bioenergy recovery as hydrogen gas; and (3) quantify specific energy consumption of the hybrid system to identify the challenges for future development.

2. Materials and methods

2.1 MEC-FO Hybrid System

The MEC-FO hybrid system was operated either in an open-loop mode for start-up or in a closed-loop mode to minimize liquid discharge (Fig. 1). In the open-loop mode, a synthetic centrate was continuously pumped into the MEC anode chamber, where exoelectrogens (electrochemically active microorganisms) converted the organics into electricity to power ammonium migration across the cation exchange membrane (CEM, 12 cm × 6 cm), rendering

continuous enrichment of ammonium and energy recovery as hydrogen gas in the cathode. Upon utilization of biodegradable COD (indicated by diminished electricity), the anolyte was replaced by fresh synthetic centrate (for next batch cycle), and the discharged anolyte was transferred to the FO feed chamber for water recovery and phosphorus concentration. Finally, the concentrated feed solution was filtered, and the phosphorus was reclaimed from filtrate as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) via chemical precipitation. In a closed-loop mode, in addition to the above processes, the supernatant was then recycled back to the anode of the MEC mixing with fresh synthetic centrate as the influent. For example, the struvite precipitation supernatant from the cycle 1 was mixed with fresh synthetic digestate to serve as the MEC anode influent in the cycle 3 with a mixing ratio shown in Table S1 (Appendix A. Supplementary Materials). The whole system was operated in a temperature-controlled lab (20 ± 2 °C).

2.2 MEC Setup and Operation

A flat-plate MEC (20 cm $\times$ 10 cm) was constructed with two identical chambers (90 mL each). A 12-cm carbon brush was inserted into the anode chamber as an anode electrode. Two pieces of carbon cloth (12 cm $\times$ 4 cm) coated with Pt/C as catalyst ($0.5 \text{ mg Pt cm}^{-2}$) were bound on two sides of a stainless-steel mesh (12 cm $\times$ 4 cm) and served as the cathode electrode. The synthetic centrate contained (per liter DI water): 2.60 g NaAc (2000 mg L^{-1} COD), 3.82 g NH_4Cl ($1000 \text{ mg L}^{-1} \text{ NH}_4^+\text{-N}$), 0.31 g KH_2PO_4 ($70 \text{ mg L}^{-1} \text{ PO}_4^{3-}\text{-P}$), 0.10 g MgSO_4 , 0.05 g CaCl_2 , and 1.0 mL trace elements, to mimic digestion centrate without any buffer agents (Münch and Barr 2001). Each of the anolyte and the catholyte (0.01 M NaCl) was connected with a 200-mL reservoir bottle (Table S1), and recirculated at 10 mL min^{-1} (0.85 cm s^{-1} for 0.5 cm pipe). The MEC was first operated in an MFC mode (detailed information in Supplementary Materials) for two weeks

and then switched to the MEC mode with 0.8 V external voltage. The MEC was operated in a batch mode with its voltage monitored (2-min interval) over an external resistor of 10 Ω . The generated hydrogen gas in the cathode was collected and measured by using a water replacement method. One MEC operation cycle was terminated if the generated current was decreased to around 1.0 mA, and both reservoir bottles were replenished with new anolyte/catholyte. Samples (5 mL) were taken directly from the reservoir bottles at the 0 h of each cycle with a 24-h interval thereafter for water quality analysis.

2.3 FO Setup and Operation

In the cross-flow FO cell, one piece of Aquaporin InsideTM membrane (Aquaporin A/S, Denmark) with an effective working area of 15 cm² was installed with its active layer facing the feed side (FO mode), creating an identical volume of 10 mL for each chamber. During operation, 100 mL 1-M NH₄HCO₃ (conductivity 64.9-65.4 mS cm⁻¹, pH 7.65-7.76) was used as draw solution while the effluent of the MEC anolyte served as the feed. The recirculation flow rate for both draw and feed solution was 10 mL min⁻¹ (0.85 cm s⁻¹ for 0.5 cm pipe). The FO was operated in a batch mode with each cycle for 24 h. Membrane fouling was well-controlled by 6-h *in-situ* physical flushing with ~500 mL DI water (reused, 100-150 mL min⁻¹, or 8.49-12.74 cm s⁻¹) after each cycle. The FO cell was sealed without membrane replacement throughout the whole experiment. Samples were taken at the initial and the end of each cycle for analysis.

2.4 Struvite Precipitation

The concentrated feed solution from the FO was filtered by 0.45 μ m filter paper to remove biomass. The filtrate pH was adjusted by HCl (37%, ~33 μ L) to around 2.0, followed by N₂

stripping (0.5 h) for removal of carbonate and bicarbonate. Stripping system was connected to an absorption bottle filled with 1 mol L⁻¹ sulfuric acid to collect ammonia. A certain amount of MgCl₂•6H₂O was then added (Mg:P=2:1) before pH adjustment to around 9.0 with 10-M NaOH (~40 µL) (Nelson et al. 2003). It should be noted that the volume of each chemical solution for pH adjustment was less than 0.1% of total concentrated feed volume, resulting in very small material expense in the operating cost of the proposed system. The mixed liquor was stirred at 30 rpm for 5 min to achieve complete struvite precipitation before the second filtration. The generated white crystals were washed twice with DI water, and the final products were air dried in fume hood (RT) overnight. The remaining supernatant was sent back to the MEC anode and mixed with fresh synthetic centrate as the anolyte (closed-loop mode, starting from cycle 3).

2.5 Analytical Methods

Detailed methods for water quality analysis, water flux, and Coulombic efficiency (CE) were provided in the Supplementary Materials. Collected hydrogen gas was analyzed by gas chromatograph coupled with thermal conductivity detector (GC-TCD, Shimadzu, Japan). The obtained solids from chemical precipitation were coated with Au/Pd (6:4, wt%) and then characterized using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Powder X-ray diffraction (XRD) measurements were performed using a Rigaku MiniFlex 600. In the closed-loop mode (starting from cycle 3, Table S1), the initial nutrient concentration in the MEC anode influent (C_{inf} , mol L⁻¹) was calculated based on mass balance (Eq. S1, Supplementary Materials). In the FO, quantification of water flux (e.g. average water flux, J_a) was based on Eq. S2-S4. The solute build-up (SBU) at the feed side was quantified by Eq. S5 with a unit of mmol m⁻² h⁻¹ (Zou and He 2016). SBU is typically resulted

from the concentrating effect in the feed (due to membrane rejection of the feed solute) and reverse solute flux (RSF, $\text{mmol m}^{-2} \text{h}^{-1}$) from the draw solution. Specific RSF (g L^{-1} , Eq. S6) was also calculated as the ratio of RSF and maximum water flux (J_w , $\text{L m}^{-2} \text{h}^{-1}$, LMH).

The yield (γ , %) for phosphorus recovery as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MW} = 245 \text{ g mol}^{-1}$) was defined as the ratio of recovered struvite mass to theoretical struvite amount (Eq. S7). The substrate energy recovery efficiency (η_s) was described as the ratio of reclaimed energy (collected hydrogen gas) to intrinsic chemical energy originated from organic substrates (Call and Logan 2008).

$$\eta_s = \frac{W_{H_2}}{W_s} = \frac{n_{H_2} \times \Delta H_{H_2}}{n_s \times \Delta H_s} = \frac{V_{H_2} \times \frac{1 \text{ mol}}{24 \text{ L}} \times \Delta H_{H_2}}{m_s \times \frac{1 \text{ mol}}{82 \text{ g}} \times \Delta H_s} = \frac{V_{H_2} \times \frac{1 \text{ mol}}{24 \text{ L}} \times \Delta H_{H_2}}{\Delta \text{COD} \times \frac{1 \text{ g NaAc}}{0.78 \text{ g COD}} \times \frac{1 \text{ mol}}{82 \text{ g NaAc}} \times \Delta H_s}$$

where W_{H_2} (kJ) is the recovered energy based on heat combustion of H_2 , $\Delta H_{H_2} = 285.83 \text{ kJ mol}^{-1}$. The mole amount of H_2 (n_{H_2}) was estimated according to ideal gas law (1 mol H_2 equals to 24 L, 293 K). W_s (kJ) is the originated chemical energy from substrate (NaAc, $\Delta H_s = 870.28 \text{ kJ mol}^{-1}$). The amount of consumed substrate was estimated from the degraded COD (ΔCOD , g) divided by a conversion factor ($0.78 \text{ g COD g}^{-1} \text{ NaAc}$).

The energy consumption was evaluated on the whole system level (MEC-FO), and the consumption rate was normalized by unit treated wastewater (kWh m^{-3}), unit reduced COD (kWh kg COD^{-1}), unit removed or recovered $\text{NH}_4^+\text{-N}$ (kWh kg N^{-1}), or unit obtained struvite (kWh kg^{-1}). The energy consumption rate of the FO was normalized by unit extracted clean water (kWh m^{-3}) (Xiang et al. 2017). The abovementioned specific energy consumptions (SEC),

based on total energy input of major energy consumers (power supply and/or recirculation pumps) and output hydrogen gas, were provided in Supplementary Materials (Eqs. S8-S13).

3. Results and discussion

3.1 Hydrogen Energy Recovery

Chemical energy in the remaining organics (expressed as COD) of centrate could partially be converted to hydrogen gas through microbial electrolysis, accompanying with current generation induced by an external voltage. When being operated in an open-loop mode (the MEC received only freshly prepared synthetic centrate), the MEC exhibited a typical batch profile of electricity production. With an applied voltage of 0.8 V, the MEC generated a maximum current of 5.52 ± 0.06 mA and a CE of 21.8 ± 1.5 % (Fig. 2A). The decrease in current generation was due to decreased organic concentration and anolyte pH (from 6.75 to 4.54, Fig. 2B) by oxidative H^+ generation, and concurrent increase of the catholyte pH (from 8.05 to 10.06) by reductive OH^- release, leading to elevated pH gradient over CEM and deteriorated potential loss (Rozendal et al. 2007). The MEC achieved a COD removal efficiency of 79.8 ± 0.6 % and COD removal rate of 0.322 ± 0.001 kg $m^{-3}d^{-1}$. In a closed-loop mode (the residue left from the struvite process was mixed with fresh anolyte, cycles 3-5), the MEC achieved a higher CE of 26.7 ± 1.8 % than that under the open-loop mode; this was likely benefited from a higher initial anolyte pH (8.58 vs. 6.75 in open-loop mode, Fig. 2B) with more alkalinity for buffering the pH during the following reaction. Increased current generation extended the operation length of each cycle to 6 days (originally 5 days), rendering a more desired organic removal efficiency of 88.5 ± 2.7 % but a relatively lower COD removal rate of 0.266 ± 0.008 kg $m^{-3}d^{-1}$. Cross-CEM COD migration was

low throughout the whole experiment ($24.67 \pm 4.19 \text{ mg L}^{-1}$ in the catholyte), and no biofouling was with significant effects on ammonia recovery was observed in the cathode chamber.

Hydrogen gas production was observed under both modes, and because of a higher CE, the closed-loop mode produced $27.3 \pm 1.2 \text{ mL}$ of hydrogen gas per cycle, higher than $17.8 \pm 0.9 \text{ mL}$ per cycle in the open-loop mode. An average specific production rate of $18.2 \pm 0.8 \text{ L H}_2 \text{ m}^{-3} \text{d}^{-1}$ could be achieved for closed-loop operation, much higher than $11.8 \pm 0.6 \text{ L H}_2 \text{ m}^{-3} \text{d}^{-1}$ in the open-loop mode (Fig. 2C). The hydrogen production performance was comparable to stand-alone MECs treating domestic wastewater ($15 \text{ L H}_2 \text{ m}^{-3} \text{d}^{-1}$) (Heidrich et al. 2013) or winery wastewater ($\sim 25 \text{ L H}_2 \text{ m}^{-3} \text{d}^{-1}$ on average) (Cusick et al. 2011). The quantified substrate energy recovery (SER) efficiency in the closed-loop mode ($6.4 \pm 0.5 \%$) outcompeted that in the open-loop mode ($4.1 \pm 0.2 \%$, Fig. 2C inset), which was consistent with CE tendency. It should be noted that methane was not detected during gas collection, suggesting an absence of methanogens in the MEC cathode.

3.2 Water Recovery

Recovering reusable water from the MEC anolyte effluent was successfully achieved by the FO process. In the open-loop mode, $73.3 \pm 0.3 \text{ mL}$ water was extracted with a maximum water flux of $6.25 \pm 0.15 \text{ LMH}$ (Fig. 3), rendering a $63.0 \pm 1.6 \%$ of volume reduction. The generated water flux using Aquaporin InsideTM membrane was at least 2 times larger than that using cellulose triacetate (CTA) membrane ($2.0\sim 3.0 \text{ LMH}$) by using $1 \text{ mol L}^{-1} \text{ NH}_4\text{HCO}_3$ as the draw (Chanukya et al. 2013, Qin and He 2014). In the closed-loop mode, a slightly lower amount of the reclaimed water ($70.4 \pm 2.4 \text{ mL}$, Fig. 3 inset) was collected due to the increased salinity of

the feed solution (MEC anolyte effluent) ($8.25 \pm 0.13 \text{ mS cm}^{-1}$ vs. $6.98 \pm 0.28 \text{ mS cm}^{-1}$ in the open-loop mode) and thus reduced osmotic gradient (i.e. driving force). No significant difference in the maximum water flux was observed between two operation modes ($5.9 \pm 1.2 \text{ LMH}$ in closed-loop vs. $6.0 \pm 0.3 \text{ LMH}$ in open-loop, $p > 0.05$, Fig. 3). Considering that 130 mL of fresh synthetic centrate was added in each closed-loop cycle, the hybrid system achieved a water recovery rate of $54.2 \pm 1.9 \%$. The final diluted draw solution would then go through a heat-driven solute regeneration process (typically 60°C , not investigated in the present study) (McGinnis and Elimelech 2007), where NH_4HCO_3 dissociates to NH_3 and CO_2 gas. Both NH_3 and CO_2 gas emit from the liquid phase and are absorbed in condenser for regeneration (NH_4HCO_3), avoiding gradual organic and nutrient build-up issues emerged in most RO regeneration processes (McGinnis et al. 2013a). The content of organics ($49.00 \pm 11.52 \text{ mg L}^{-1}$) and P ($7.49 \pm 0.63 \text{ mg L}^{-1}$) in the remaining product water (liquid phase) should not be a major concern for agricultural and industrial reuse (Agency 2012).

3.3 Nitrogen Recovery

Ammonium, as the dominant form of nitrogen in AD centrate, effectively migrated across the CEM with the aid of an electric field and was enriched in the MEC catholyte towards further recovery. In the open-loop mode, the $\text{NH}_4^+\text{-N}$ concentration of the MEC anolyte decreased from 699.3 ± 2.7 to $186.5 \pm 14.2 \text{ mg L}^{-1}$ ($73.3 \pm 1.9 \%$ removal efficiency), resulting in a total removal amount of $9.66 \pm 0.20 \text{ mmol}$ (Fig. 4A). There was $8.96 \pm 0.10 \text{ mmol}$ of $\text{NH}_4^+\text{-N}$ accumulated in the MEC catholyte. Though effectively decreased in the MEC module, the ammonium concentration in the centrate would inevitably increase when passing the following FO module, owing to the concentrating effect and reverse NH_4HCO_3 leakage. The $\text{NH}_4^+\text{-N}$ amount at the FO

feed side was increased from 1.56 ± 0.17 mmol (186.5 ± 14.2 mg L⁻¹) to 14.34 ± 1.58 mmol (4633.3 ± 166.7 mg L⁻¹) in an open-loop mode (Fig. 4B), indicating a specific RSF of 0.85 ± 0.16 g L⁻¹ (Fig. 4C), which was 57.5% lower than that of CTA membrane (2.01 g L⁻¹) under similar operation conditions (Achilli et al. 2010). The NH₄⁺-N concentration increment in the concentrated feed was mainly attributed to concentrating effect (10.9%) induced by membrane rejection and RSF (89.1%, Fig. 4C).

In the closed-loop operation mode, additional NH₄⁺-N was introduced to the MEC anolyte by the remaining supernatant from the struvite precipitation, leading to increased ammonium loading of 19.87 ± 0.92 mmol (nearly 60% higher than 12.48 ± 0.05 mmol in the open-loop mode) and doubled concentration (341.3 ± 47.3 mg L⁻¹) in the anode effluent. However, ammonium migration in MEC was greatly enhanced due to elevated current generation in the closed-loop mode, rendering a superior ammonium recovery rate of 13.74 ± 0.28 mmol (vs. 8.96 ± 0.10 mmol in the open-loop mode, Fig. 4A). The ammonium recovery performance outcompeted lab-scale bipolar bioelectrodialysis in previous study (~ 4 mmol for 5-day operation, 0.8 V) (Zhang and Angelidaki 2015a), and could be further enhanced if buffer solution is applied in MEC system (Zhang and Angelidaki 2015b). Reverse ammonium leakage in the subsequent FO process was comparable among cycles 3-5, but slightly higher than that in open-loop mode (15.56 ± 0.45 mmol, Fig. 4B). It should be noted that specific RSF of NH₄⁺-N reached its maximum value of 1.22 g L⁻¹ in cycle 3, owing to accumulated fouling and corresponding reduced water flux (Fig. 3). With proper increase of post-cycle flushing rate from 100 mL min⁻¹ to 150 mL min⁻¹, reversible fouling was well controlled with restored water recovery and reduced specific RSF in subsequent cycles. The average NH₄⁺-N concentration in the

concentrated feed was $5111.1 \pm 175.0 \text{ mg L}^{-1}$ with an increased contribution of the concentrating effect ($16.4 \pm 2.5 \%$, Fig. 4C).

3.4 Phosphorus Recovery

The hybrid MEC-FO system effectively concentrated the phosphorus in low-P centrate to achieve a more desirable recovery rate. In MEC process, phosphorus removal/recovery was rather limited due to negligible biological consumption and high rejection of CEM, leading to a consistent $\text{PO}_4^{3-}\text{-P}$ concentration in the anode effluent at both modes (Fig. 5A). It should be noted that the lower $\text{PO}_4^{3-}\text{-P}$ concentration in the closed-loop mode was attributed to dilution effect from the recycled P-free struvite supernatant. In the FO process, the $\text{PO}_4^{3-}\text{-P}$ level was elevated from 71.5 ± 0.5 to $153.5 \pm 4.5 \text{ mg L}^{-1}$ in the open-loop mode, or from 57.0 ± 0.7 to $116.8 \pm 5.3 \text{ mg L}^{-1}$ in the closed-loop mode (Fig. 5B). During this concentration process, part of P would inevitably diffuse through FO membrane to the draw side, i.e. forward solute flux (FSF) due to its same direction with water flux. Hence, the total $\text{PO}_4^{3-}\text{-P}$ amount was decreased from 0.268 ± 0.010 to $0.213 \pm 0.009 \text{ mmol}$ in the open-loop mode ($20.5 \pm 0.5 \%$ loss rate, Fig. 5B), indicating a specific FSF of $0.008 \pm 0.001 \text{ g L}^{-1}$. The $\text{PO}_4^{3-}\text{-P}$ loss was alleviated (down to $0.042 \pm 0.004 \text{ mmol}$, Fig. 5B) in the following closed-loop cycles because of reduced concentration gradient (i.e. lower initial P level) and lower FSF ($0.006 \pm 0.001 \text{ g L}^{-1}$). The struvite precipitation efficiency was 100% (no P detected in the supernatant), rendering an overall phosphorus recovery efficiency of $79.5 \pm 0.5 \%$ due to FSF $\text{PO}_4^{3-}\text{-P}$ loss in FO process. Owing to recycling of excess Mg^{2+} in the supernatant, Mg^{2+} dosage was significantly reduced from $0.17 \text{ g Mg}^{2+} \text{ g}^{-1}$ stuvite (open-loop) to $0.08 \text{ g Mg}^{2+} \text{ g}^{-1}$ stuvite (closed-loop), though slightly higher than that of a previous study ($0.06 \text{ g Mg}^{2+} \text{ g}^{-1}$ stuvite) (Xie et al. 2014).

The obtained struvite crystals were examined by using SEM-EDS and powder XRD. The SEM image of standard struvite sample (Fig. S2A) presented an orthorhombic structure with an average size of $\sim 60\ \mu\text{m}$, whereas the recovered struvite (Fig. S2B and S2C) showed amorphous structure owing to filtration/grinding treatment. The coupled EDS analysis confirmed three major elements (Mg, P and O) composing struvite in the recovered powders (Fig. 5C). Absence of N peak was due to its light weight, and hence could not be detected in EDS (Xie et al. 2014). The mass percentage of Mg ($12.65 \pm 0.61\ \%$) and P ($15.17 \pm 0.61\ \%$) in recovered struvite were close to that of the standard struvite ($9.79 \pm 0.17\ \%$ for Mg and $13.41 \pm 1.66\ \%$ for P, Table S2). Further XRD analysis indicated that the obtained solids had identical peak positions to that of standard struvite samples (Fig. 5D). All these results confirmed that phosphorus recovery from the low-P synthetic centrate was desirably enhanced by the MEC-FO hybrid system, compared to that of direct precipitation (Fig. S3, detailed experiment process in Supplementary Materials).

3.5 Mass Balance

The mass balance for both N and P (in the closed-loop mode) is presented in Fig. 6. Within one cycle (on average), a total of $16.91 \pm 0.43\ \text{mmol NH}_4^+\text{-N}$ could be reclaimed, including $13.74 \pm 0.28\ \text{mmol}$ in the MEC (81.3%), $3.01 \pm 0.30\ \text{mmol}$ by N_2 stripping (17.8%), and $0.16 \pm 0.01\ \text{mmol}$ by struvite recovery (0.9%) (the latter two were presented together in struvite precipitation process, Fig. 6A). Thus, the MEC acted as a major process for ammonium recovery with negligible loss ($0.01 \pm 0.00\ \text{mmol}$). In the FO, RSF ($15.56 \pm 0.45\ \text{mmol}$) and evaporation ($0.75 \pm 0.05\ \text{mmol}$) were demonstrated to be the primary source of ammonium loss (Fig. 6A), resulting from undesired cross-membrane diffusion and NH_4HCO_3 decomposition into NH_3/CO_2 at a

relatively higher concentration (1.0 mol L^{-1} in draw solution). It should be noted that ammonium loss by RSF ($15.56 \pm 0.45 \text{ mmol}$, Fig. 6A) and system operation ($0.76 \pm 0.05 \text{ mmol}$) could be fully compensated because of supernatant recycling and MEC ammonium recovery (detailed approach illustrated in our previous study (Qin and He 2014)) in the subsequent cycle, leading to self-supplied and continuous-replenished FO draw solutes that will notably reduce operational cost. Other processes, such as regeneration of thermolytic NH_4HCO_3 and $\text{NH}_4^+\text{-N}$ isolation from the MEC catholyte, could cause additional ammonium loss and will warrant further assessment. Nonetheless, based on current data, the MEC-FO could achieve self-compensated ammonium recovery. To further enhance net ammonium recovery in current MEC-FO system, an extended N_2 stripping (25 mL min^{-1}) could be performed followed by filtered feed concentrate (Fig. S4, detailed experiment process in Supplementary Materials). As a result, 53.8% of ammonium ($\sim 8.4 \text{ mmol}$) in the FO concentrate ($15.57 \pm 0.17 \text{ mmol}$, Fig. 6A) could be stripped out and recovered as $(\text{NH}_4)_2\text{SO}_4$ in the absorption tank, rendering a net ammonium recovery amount (operation loss and ammonium self-compensation excluded) and efficiency of $8.99 \pm 0.75 \text{ mmol}$ and $99.7 \pm 13.0 \%$, respectively.

Phosphorus was efficiently precipitated from the centrate in the form of struvite. Though phosphorus recovery was negligible in the MEC (rejected by CEM), the centrate was desirably enriched in phosphorus by the FO to secure a phosphorus recovery of $0.16 \pm 0.01 \text{ mol}$ via struvite, rendering 100% struvite precipitation yield and 80% overall phosphorus recovery efficiency. The only loss was through FSF in the FO ($0.042 \pm 0.004 \text{ mmol}$, Fig. 6B), which could be reduced with further advancement of membrane fabrication and alleviated fouling-induced concentration polarization (She et al. 2012). Complete removal of carbonate and bicarbonate

through stripping was a key to ensure struvite purity. With less sampling points and corresponding loss, higher phosphorus recovery efficiency (0.267 mmol total recovery with 0.042 mmol loss in FO, up to 86%, Fig. 6B) can be expected. It was observed that gradual ammonium increment (0.60 ± 0.12 mmol per cycle) and phosphorus decrement (0.015 ± 0.009 mmol per cycle) occurred in the MEC anode, owing to recycling of ammonium-rich and phosphorus-free supernatant. Our calculation indicated that the initial phosphorus input could reach a stable amount of 0.452 mmol in long-term operation, leading to a fixed initial anolyte concentration of 55 mg L^{-1} . However, ammonium input would continuously increase, and to maintain a balanced system performance, enhanced ammonium recovery via extended N_2 stripping time should be encouraged.

3.6 Energy Consumption

The information of energy input is often missing in many prior studies of resource recovery (Zou et al., 2016). Although estimate of energy consumption from a bench-scale system would not reflect actual conditions of pilot- or full-scale applications, it will give us a rough picture of energy consumption with guiding next-step optimization. In the closed-loop mode, 27.3 ± 1.2 mL hydrogen gas (per cycle) could provide a maximum of 0.33 ± 0.01 kJ through combustion, accounting for up to 28.9 ± 1.6 % of total energy input in the MEC (1.13 ± 0.04 kJ, 5.3% pump and 94.7% power supply) and 28.7 ± 1.5 % of total energy input in MEC-FO system (1.14 ± 0.04 kJ, 99.1% from the MEC and 0.9% from the FO, Fig. 7A). It should be noted that an energy consumption rate of 0.73 kWh m^{-3} would be expected for draw solute regeneration (0.50 ± 0.01 mol L^{-1} initial diluted draw concentration, low-pressure single distillation column) (McGinnis and Elimelech 2007). Recent research confirmed that this part of energy consumption could be

compensated by waste heat, and hence it was not counted in the evaluation in this study (Zhou et al. 2015).

Specific energy consumption was subsequently quantified on a system level (MEC-FO). Net energy consumption, with recovered hydrogen energy deducted, was normalized by unit treated water, unit degraded COD, unit removed or recovered NH_4^+ -N (Fig. 7B, detailed calculation in Supplementary Materials). The MEC-FO system consumed $1.73 \pm 0.08 \text{ kWh m}^{-3}$ treated centrate, $0.57 \pm 0.04 \text{ kWh kg}^{-1}$ eliminated COD, $1.10 \pm 0.05 \text{ kWh kg}^{-1}$ removed NH_4^+ -N, $1.17 \pm 0.06 \text{ kWh kg}^{-1}$ recovered NH_4^+ -N, or $5.75 \pm 0.54 \text{ kWh kg}^{-1}$ struvite. The proposed hybrid system could be more energy-efficient than other lab-scale nutrient recovery processes, such as a single chamber MEC for struvite production ($1.8 \pm 0.2 \text{ kWh kg}^{-1} \text{ COD}$) (Cusick and Logan 2012) and electrochemical ammonium recovery from digestate (down to $5.0 \text{ kWh kg N}^{-1}$ recovered) (Desloover et al. 2012). Although struvite precipitation from separated urine had a much lower energy requirement of 0.76 kWh kg^{-1} struvite (Maurer et al. 2003), the hybrid system could accomplish multiple goals (i.e. integrated NEW recovery). It should be noted that ammonium regeneration from the MEC catholyte and FO diluted draw solution was not studied here but would require an additional amount of energy input (Desloover et al. 2012). The energy consumption could be offset by reduced electricity consumption from mainstream treatment due to minimized nutrient and hydraulic loading rate (i.e. minimized sidestream discharging). The FO process alone consumed merely $0.14 \pm 0.01 \text{ kWh m}^{-3}$ recovered fresh water, outcompeting other lab-scaling emerging water recovery technologies such as microbial desalination cell (MDC, as low as 1.3 kWh m^{-3}) (Ping et al. 2015), bench-scale ED (7.0 kWh m^{-3}) (Walker et al. 2014), air gap membrane distillation (AGMD, $2.5\text{-}3.0 \text{ kWh m}^{-3}$) (Alkhudhiri et al. 2013).

3.7 Perspectives

The MEC-FO hybrid system has offered attractive merits of simultaneous multi-nutrient recovery, water extraction and hydrogen production. The quantified mass balance and energy consumption enable better understanding of competing challenges within this system and warrant further investigations for process optimization in the aspects of draw solute, system coordination, and system scaling up. First, the present system adopted thermolytic NH_4HCO_3 as a draw solute, which can relatively easier to regenerate and has been applied in pilot test of desalination (McGinnis et al. 2013b). However, NH_4HCO_3 exhibits relatively larger specific RSF compared to other inorganic salts with same osmotic pressure, such as Na_2SO_4 , NaCl , and MgCl_2 (Achilli et al. 2010). Though the lost ammonium is fully recovered and reused in the closed-loop operation, it gradually elevates the influent ammonium concentration in the subsequent cycle. Extended N_2 stripping followed by FO offers a promising solution to mitigate ammonium build-up with enhanced ammonium recovery. However, to truly reduce RSF and strengthen long-term performance, membrane advancements, for example emerging fabrication materials with specialized salt rejection, and operation strategies (e.g. electrolysis-assisted solute capture) (Zou and He 2017) should be encouraged. Second, the MEC and FO exhibits different treatment capacity and should be well-coordinated for maximized resource recovery output (Lu et al. 2014). For example, one cycle of MEC lasts for 6 days while FO only takes 1 day in the present hybrid system. To solve this, the volume ratio of MEC to FO can be designed as 6:1. Alternatively, six parallel MECs can be linked to one FO module with stagger discharging. As a result, increased membrane fouling propensity should be expected while more phosphorus may be lost by FSF resulting from intensified fouling-induced concentration polarization. Third, further scaling-up of

the proposed system will be necessary with long-term operation of treating actual centrate. Given the fact that struvite process has been commercialized (Prasad et al. 2007), the challenge of scaling up the proposed hybrid system will lie in FO and MECs. FO has been successfully scaled up to a pilot scale for treating different waters and examining draw solutes and membrane fouling (Hancock et al. 2011, Hancock et al. 2013, Phuntsho et al. 2016). Because of relatively simple structure, an FO system could be scaling up without much difficulty. Once the key problems such as draw solute regeneration and membrane cost/durability are solved, we believe that FO systems could be quickly developed to a full scale. MECs or relevant bioelectrochemical systems such as MFCs and MDCs have also been scaled up to the scale of pilot systems or significantly beyond a bench scale (e.g., a few hundred liters) (Cusick et al. 2011, Ge and He 2016, Heidrich et al. 2014, Zhang et al. 2013), and those prior efforts will provide valuable experiences to scaling up the proposed system. The key issues for MEC scaling up include the optimization of reactor design for maximal hydrogen production and reduction of electrode/membrane cost.

4. Conclusions

In this study, an innovative MEC-FO hybrid system has been investigated for integrated NEW recovery from synthetic sidestream centrate. Under a closed-loop mode, a desirable recovery of fresh water, ammonium nitrogen, phosphorus and hydrogen gas was observed with notable advantages of reduced Mg^{2+} dosage, buffered anolyte with better MEC performance, and most importantly minimized liquid discharge for further treatment. Ammonium loss primarily from RSF in the FO system was fully compensated by the reclaimed ammonium under extended N_2 stripping to achieve self-sustained osmotic water recovery. Detailed energy performance (i.e.

energy output and recovery efficiency) was analyzed to enable better comparison with existing technologies, and the generated hydrogen gas could potentially support up to 28.7 ± 1.5 % of total energy input. Mass balance was quantified on the system level for performance optimization towards maximized resource output. The results of this study warrants further investigation on solute leakage reduction via RSF mitigation, long-term performance evaluation with actual sidestream centrate, and system scaling up and coordination between modules.

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Figure Captions

Figure 1. Schematic of the hybrid MEC-FO system for nutrient-energy-water (NEW) recovery.

Figure 2. Energy recovery in the MEC: (A) current generation; (B) anolyte COD removal with anode/cathode pH variations; and (C) specific H₂ production rate and collected H₂ volume with substrate energy recovery (SER) efficiency (inset).

Figure 3. Water recovery in the FO in terms of average water flux and extracted water volume (inset).

Figure 4. Nitrogen recovery: (A) anolyte/catholyte NH₄⁺-N distribution (column) and corresponding removal/recovery amount; (B) NH₄⁺-N distribution in draw/feed together with draw solute loss; and (C) RSF of NH₄⁺-N with composition of NH₄⁺-N build-up in final feed solution. The “I” and “E” in Fig. 4A and 4B stand for the initial and ending amount of NH₄⁺-N in each cycle, and the total column height represents the overall amount on system level (either MEC or FO).

Figure 5. Phosphorus recovery: (A) PO₄³⁻-P concentration in anode/cathode effluent; (B) PO₄³⁻-P distribution in draw/feed together with initial/end concentration in feed solution; (C) EDS peaks of standard/recovered struvite; and (D) XRD spectrum of standard/recovered struvite. The “I” and “E” in Fig. 5B stand for the initial and ending amount of PO₄³⁻-P in each cycle, and the total column height represents the sum of feed and draw amount.

Figure 6. Mass balance of nutrients in the proposed system: (A) NH₄⁺-N; and (B) PO₄³⁻-P. The ammonium reclamation amount in struvite recovery of Fig. 6A is the sum of normal N₂ stripping (to remove HCO₃⁻/CO₂) and struvite precipitation. Ammonium percentage in Fig. 6A is based on total recovery amount per cycle (16.91 mmol, extended N₂ stripping excluded). The yellow-

orange line, green line and blue line stand for centrate flow, nutrient recovery, and draw solution (with ammonium regeneration).

Figure 7. Profiles of energy consumption in MEC-FO hybrid system: (A) total energy input on system level; and (B) specific energy consumption (SEC) normalized by unit treated wastewater (kWh m^{-3}), unit reduced COD (kWh kg COD^{-1}), unit removed or recovered $\text{NH}_4^+\text{-N}$ (kWh kg N^{-1}), or unit obtained struvite (kWh kg^{-1}).

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