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# Phosphorus and water recovery by a novel osmotic membrane bioreactor - reverse osmosis system

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## **Abstract**

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# Phosphorus and water recovery by a novel osmotic membrane bioreactor – reverse osmosis system

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## **Abstract**

An osmotic membrane bioreactor – reverse osmosis (OMBR-RO) hybrid system integrated with periodic microfiltration (MF) extraction was evaluated for simultaneous phosphorus and clean water recovery from raw sewage. In this hybrid system, the forward osmosis membrane effectively retained inorganic salts and phosphate in the bioreactor, while the MF membrane periodically bled them out for phosphorus recovery with pH adjustment. The RO process was used for draw solute recovery and clean water production. Results show that phosphorus recuperation from the MF permeate was most effective when the solution pH was adjusted to 10, whereby the recovered precipitate contained 15 – 20% (wt/wt) of phosphorus. Periodic MF extraction also limited salinity build-up in the bioreactor, resulting in a stable biological performance and an increase in water flux during OMBR operation. Despite the build-up of organic matter and ammonia in the draw solution, OMBR-RO allowed for the recovery of high quality reused water.

*Key words:* Phosphorus recovery; osmotic membrane bioreactor (OMBR); forward osmosis (FO); reverse osmosis (RO); microfiltration (MF).

## 1. Introduction

Phosphorus is a finite resource and an essential nutrient for agriculture production. In the environment, phosphorus is also a contaminant that can result in severe eutrophication of natural waterways (Conley et al., 2009). In addition, during wastewater treatment, phosphorus (in the form of phosphate) can react with ammonium and magnesium to form crystalline precipitate known as struvite, which causes blockage and scaling of plant equipment (Doyle et al., 2002). Thus, phosphorus recovery from wastewater is strategically important to secure a continuous and sustainable supply of this essential nutrient, reduce environmental discharge, and avoid struvite scaling.

A novel osmotic membrane bioreactor (OMBR) system has been recently recognised as a promising technology in wastewater treatment and reuse (Achilli et al., 2009; Cornelissen et al., 2011; Luo et al., 2014; Nguyen et al., 2015). OMBR utilizes forward osmosis (FO) to extract treated water from the bioreactor mixed liquor into a draw solution. This system can be used as a stand-alone process to extract treated water for osmotic dilution or integrated with other processes, such as reverse osmosis (RO) or membrane distillation (MD), to produce clean water and recover the draw solute. Compared to conventional MBR systems that employ pressure-driven membrane processes, such as microfiltration (MF) and ultrafiltration (UF), OMBR has several advantages, including higher contaminant removal and lower fouling propensity (Cornelissen et al., 2008; Achilli et al., 2009; Alturki et al., 2012).

A major technical challenge to OMBR application is the build-up of salinity in the bioreactor (Yap et al., 2012; Luo et al., 2014). This occurs due to the high salt rejection by the FO membrane and, more importantly, reverse solute flux from the draw solution. The increased bioreactor salinity can severely affect the microbial viability and membrane performance (Nawaz et al., 2013). Thus, several approaches have been recently proposed to prevent salinity build-up in the bioreactor during OMBR operation. A promising control strategy is to integrate an MF or UF membrane with OMBR to form a hybrid MF/UF-OMBR system to bleed out dissolved inorganic salts accumulated in the bioreactor. By applying this strategy, Wang et al. (2014) demonstrated a stable operation of OMBR integrated with continuous MF extraction and concluded that the integration of MF could increase OMBR water flux and improve the biological treatment. Similar observations were subsequently reported by Holloway et al. (2015) who combined an UF membrane with OMBR.

The hybrid MF/UF-OMBR system has the potential to simultaneously recover phosphorus and clean water during wastewater treatment. In this hybrid system, the FO membrane can effectively retain phosphate and magnesium/calcium based salts in the bioreactor, while the MF/UF membrane allows them to be bled out for phosphorus recovery by pH adjustment. Based on this rationale, Qiu et al. (2015) showed that phosphorus could be directly recovered from municipal wastewater mostly in the form of calcium phosphate by a hybrid MF-OMBR system, where the FO and MF membranes were operated continuously in parallel. In their study, phosphate concentration in the bioreactor was in the range of 10 to 70 mg/L over 98 days of operation and decreased with an increase in the MF permeate flux (Qiu et al., 2015). It is noteworthy that phosphate enrichment in the bioreactor can be further enhanced by operating the MF membrane at low permeate flux or in periodic extraction mode, thereby increasing the economics of phosphorus recovery from the OMBR mixed liquor, preventing the hydraulically pressure-driven MF membrane from fouling, and reducing its energy consumption.

This study aimed to investigate the potential of a hybrid OMBR-RO system integrated with periodic MF extraction to simultaneously recover phosphorus and clean water from raw sewage. The RO process was used for draw solute recovery and clean water production. Phosphorus was directly recovered from the MF permeate, extracted periodically from the OMBR mixed liquor, in the form of phosphorus precipitates by pH adjustment. Performance of the hybrid OMBR-RO system was systematically assessed in terms of water production, product water quality, membrane fouling, and biological stability.

## **2. Materials and methods**

### *2.1 Wastewater and membranes*

Raw sewage was collected from the Wollongong Wastewater Treatment Plant (New South Wales, Australia) and stored at 4 °C. Over the experimental period of 60 days, 18 measurements were conducted to determine key water quality parameters of this sewage. The composition of raw sewage was relatively stable. The concentrations of orthophosphate, ammonia, calcium, magnesium, and potassium were  $24 \pm 4$ ,  $45 \pm 4$ ,  $23 \pm 5$ ,  $33 \pm 3$  and  $15 \pm 1$  mg/L, respectively (average  $\pm$  standard deviation). Conductivity, pH, total organic carbon concentration of this sewage were  $1130 \pm 53$   $\mu$ S/cm,  $7.3 \pm 0.2$ , and  $28 \pm 5$  mg/L, respectively (average  $\pm$  standard deviation).

A flat-sheet, cellulose-based FO membrane from Hydration Technology Innovations (Albany, OR) was used for the OMBR process. The FO membrane comprised a cellulose triacetate layer embedded with a polyester mesh for mechanical support. A flat-sheet, ESPA2 membrane supplied by Hydranautics (Oceanside, CA) was used for the RO process. The RO membrane was composed of a thin polyamide layer with a porous polysulfone support layer.

A hollow fibre MF membrane module (Mitsubishi Rayon Engineering, Tokyo, Japan) was also used in this study. The MF membrane was made of polyvinylidene fluoride. The effective surface area and nominal pore size of this membrane module were 740 cm<sup>2</sup> and 0.4 µm, respectively.

## 2.2 OMBR-RO system and operation

The lab-scale OMBR-RO hybrid system used in this study comprised a feed reservoir, an aerobic bioreactor, and a submerged FO and a cross-flow RO unit (Fig. 1). A Masterflex peristaltic pump (Cole-Parmer, Vernon Hills, IL) controlled by a water level sensor was used to feed the bioreactor with an effective volume of 6 L. The feed reservoir was placed on a digital balance (Mettler-Toledo, Hightstown, IL) connected to a computer to determine the OMBR water flux.

### [FIGURE 1]

The FO component comprised a submerged, plate-and-frame membrane cell, a gear pump (Micropump, Vancouver, WA), and a stainless steel draw solution reservoir with a working volume of 8 L. The membrane cell was made of acrylic plastic with a draw solution flow channel 20 cm long, 15 cm wide, and 0.4 cm high. The FO membrane was mounted on the cell with the support layer in contact with the draw solution (i.e. FO mode). A 0.5 M NaCl draw solution (corresponding to osmotic pressure of 23 bar determined by the OLI Stream Analyzer software) was circulated from the draw solution reservoir to the membrane cell at a cross-flow velocity of 2.8 cm/s.

The RO process was used to recover the draw solute and extract clean water. A Hydra-Cell pump (Wanner Engineering, Minneapolis, MN) was used to feed the draw solution to a stainless steel RO membrane cell, which had a flow channel 10 cm long, 4 cm wide and 0.2 cm deep. The hydraulic pressure and retentate cross-flow velocity were regulated by a back-pressure regulator and a bypass valve. A digital flow meter (Optiflow, Palo Alto, CA) was connected to a computer to monitor the permeate flux. The draw solution temperature was

maintained at  $22 \pm 1$  °C by a temperature control unit (Neslab RTE7, Waltham, MA) equipped with a stainless steel heat exchanger coil.

Prior to the OMBR-RO operation, activated sludge collected from the Wollongong Wastewater Treatment Plant (New South Wales, Australia) was seeded to the bioreactor integrated with an MF membrane module to form a standard MBR to pre-condition the biomass under laboratory conditions. Once acclimatized in terms of the bulk organic removal (i.e. 95% total organic carbon (TOC) removal), the MF module was replaced by the FO module and the RO unit was integrated to form the hybrid OMBR-RO system.

The hybrid OMBR-RO system was run for 60 days in a temperature-controlled room ( $22 \pm 1$  °C), following a cycle of 8 days 'on' (continuous operation) and 2 days 'off' (cease of feeding and FO-RO extraction). The MF membrane was operated to extract water from the bioreactor mixed liquor for subsequent phosphorus recovery when the FO and RO membranes were kept 'off' (section 2.3). The initial mixed liquor suspended solids (MLSS) concentration was adjusted to approximately 10 g/L. The sludge retention time (SRT) was maintained at 50 days by regularly wasting a small amount of mixed liquor every two days. The hydraulic retention time (HRT) was determined by the OMBR water flux and was in the range of 30 to 80 hours. The mixed liquor pH was maintained between 6 and 7 by periodically dosing small volumes of concentrated HCl solution to reduce the spontaneous precipitation of phosphate minerals in the bioreactor. The bioreactor was continuously aerated to obtain dissolved oxygen (DO) concentration of approximately 5 mg/L throughout the experiment. The RO permeate flux was adjusted daily to match that from the OMBR by regulating the hydraulic pressure while maintaining the retentate cross-flow velocity at 41.7 cm/s. On day 30 of the experiment, 50 g NaCl was added to the draw solution to compensate for the draw solute loss. This value was calculated based on the reduction in the concentration of the draw solution (due to reverse draw solute flux and its permeation through the RO membrane), which was determined by its electrical conductivity and a NaCl calibration curve.

### *2.3 Phosphorus recovery protocol*

During OMBR-RO off time, the MF membrane was operated for 24 hours to extract 3 L water from the bioreactor mixed liquor at a constant permeate flux of  $1.7 \text{ L/m}^2\text{h}$ . The bioreactor mixed liquor was subsequently replenished with 3 L sewage and aerated for 24 hours before a new OMBR-RO operating recycle. Periodic MF extraction was employed here

to ensure high phosphate enrichment in the bioreactor during OMBR-RO operation, thereby increasing the efficiency of subsequent phosphorus recovery. In addition, the intermittent operation mode could also reduce the MF membrane fouling and energy consumption.

Phosphorus in the MF permeate was directly recovered by pH adjustment using a 3 M NaOH solution. The MF permeate extracted after the first 8 days of OMBR-RO operation (denoted as “MF-1”) was used to evaluate the efficiency of phosphorus recovery as a function of pH (between pH 8 and 13). The optimal pH was applied to recover phosphorus from the MF permeate extracted in the subsequent OMBR-RO operating cycles. The pH-adjusted permeate was gently mixed using a magnetic stirrer, and then filtered through 0.7  $\mu\text{m}$  glass filters to recover precipitates. Recovered solids were air-dried in a desiccator at room temperature ( $22 \pm 1$  °C) and filtrates were stored at 4 °C for later analysis.

## 2.4 Analytical methods

### 2.4.1 Water quality analysis

TOC and total nitrogen (TN) were assessed by a TOC/TN analyser (TOC-V<sub>CSH</sub>, Shimadzu, Kyoto, Japan). Ammonium ( $\text{NH}_4^+$ -N) and orthophosphate ( $\text{PO}_4^{3-}$ -P) ions were measured using a Flow Injection Analysis system (QuikChem 8500, Lachat, CO). Calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), and potassium ( $\text{K}^+$ ) ions were determined using an inductively coupled plasma-optical emission spectrometer (710 ICP-OES, Agilent Technologies, CA). Solution pH and conductivity were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Waltham, MA).

### 2.4.2 Precipitate characterization

Precipitates obtained were air-dried and characterized using X-ray diffraction (GBC MMA, Hampshire, IL). The morphology and elemental composition of precipitates were examined using a scanning electron microscopy (SEM) coupled to energy dispersive spectroscopy (EDS) (JEOL JCM-6000, Tokyo, Japan). In addition, the dried precipitates were dissolved with 5% nitric acid to determine major elemental concentrations using ICP-OES.

### 2.4.3 Membrane autopsy

At the conclusion of the experiment, the surface morphology of both FO and RO membranes was analysed by SEM-EDS. Prior to SEM measurement, membrane samples were air-dried in a desiccator and then coated with an ultra-thin layer of gold using a sputter coater (SPI Module, West Chester, PA).

#### 2.4.4 Biomass characterization

MLSS and mixed liquor volatile suspended solid (MLVSS) concentrations were measured following the Standard Method 2540. Biomass activity was assessed by measuring the specific oxygen uptake rate (SOUR) of the activated sludge based on the Standard Method 1683. Extracellular polymeric substances (EPS) and soluble microbial products (SMP) in the mixed liquor were quantified by measuring the protein and polysaccharide concentrations. EPS was extracted using a thermal method previously reported by Zhang et al. (1999). Protein concentration was measured by the Folin method using bovine serum albumin as the standard (Lowry et al., 1951). Polysaccharide concentration was determined using the phenol-sulfuric acid method with a glucose standard (Dubois et al., 1956).

### 3. Results and discussion

#### 3.1 Bioreactor salinity and phosphate enrichment

During OMBR operation, reverse solute (NaCl) flux from the draw solution and high salt rejection by the FO membrane resulted in an increase in the mixed liquor conductivity (Fig. 2a). By periodically bleeding out dissolved salts via the MF membrane, salinity build-up in the bioreactor could be effectively controlled. During the entire experiment, the mixed liquor conductivity was in the range of 7 to 14 mS/cm (corresponding to approximately 3.5 and 7 g/L NaCl, respectively). This salinity range is higher than that reported in previous studies where a stable mixed liquor conductivity of approximately 5 mS/cm was observed during OMBR operation with continuous MF extraction (Wang et al., 2014; Qiu et al., 2015). Nevertheless, following a small and brief disturbance at the beginning of the experiment (section 3.3), stable biological performance could be obtained. The observed stable operation can be attributed to the acclimatization of the biomass in the activated sludge to the saline condition (Lay et al., 2010; Jang et al., 2013).

FO membrane rejection resulted in the enrichment of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{PO}_4^{3-}\text{-P}$  in the bioreactor (Fig. 2b). Their high concentrations could induce spontaneous phosphate precipitation in the bioreactor, particularly under alkaline conditions (Qiu and Ting, 2014), thereby reducing soluble phosphate ions extractable by the MF membrane for subsequent recovery. Chen et al. (2014) observed an initial increase but then a subsequent decrease in phosphorus concentration in an anaerobic OMBR when the mixed liquor pH increased from 6.9 to 7.6. The pH increase was driven by forward proton diffusion from the bioreactor to the draw solution associated with reverse draw solute flux to maintain the mixed liquor

electroneutrality (Hancock and Cath, 2009). Thus, in this study, to reduce spontaneous phosphate precipitation in the bioreactor, the mixed liquor pH was maintained between 6 and 7 by periodically adding small amounts of concentrated HCl solution. Although a lower mixed liquor pH could maximize dissolved phosphate ions in the bioreactor for subsequent MF extraction (Qiu et al., 2015), it may adversely affect the microbial viability (Tadkaew et al., 2010) and the FO membrane performance (Xie et al., 2012).

## [FIGURE 2]

### 3.2 Phosphorous recovery from the MF permeate

Dissolved inorganic salts and phosphate enriched in the bioreactor during OMBR operation were readily permeable through the MF membrane (Fig.2b). Inorganic salts may facilitate phosphorus recovery by enhancing ionic strength and precipitation potentials (Song et al., 2002). Therefore, phosphorus in the MF permeate could be directly captured in the form of phosphate minerals by pH adjustment without any inorganic salt addition.

#### 3.2.1 pH adjustment of the MF permeate

By increasing the MF permeate pH, phosphorus precipitate could be obtained. As shown in Fig. 3, soluble  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}\text{-P}$  in the MF permeate decreased considerably when pH increased from 8 to 10. The increase in pH resulted in the deprotonation of phosphate species (i.e. from  $\text{H}_2\text{PO}_4^-$  to  $\text{HPO}_4^{2-}$  and then  $\text{PO}_4^{3-}$ ) and thus enhanced their reactivity as inorganic ligands or ion pairs with calcium (Reddy and DeLaune, 2008). Elemental analysis also revealed an increase in calcium and phosphorus contents in the recovered precipitate as the MF permeate pH increased from 8 to 10. Further pH increase from 10 to 13 resulted in nearly complete capture of  $\text{PO}_4^{3-}\text{-P}$  from the MF permeate (Fig. 3). At the same time, the high pH also induce the formation of other calcium/magnesium-based precipitates without phosphorus, as indicated by the significant decline in soluble  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the MF permeate at pH above 10. As a result, phosphorus content in the obtained precipitate decreased when pH increased from 10 to 13. Thus, a solution pH of up to 10 would assist in maximizing phosphorus content in the recovered precipitate from the MF permeate. This result is consistent with that previously reported by Song et al. (2002) who modelled that an increase in solution pH up to 10 significantly promoted phosphorus recovery by the precipitation of calcium phosphate.

Both  $\text{NH}_4^+\text{-N}$  and  $\text{K}^+$  can react with  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}\text{-P}$  to form struvite or its analogues for phosphorus recovery (Xu et al., 2011). In this study, despite the high  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}\text{-P}$

concentrations, no significant decrease in either  $\text{NH}_4^+\text{-N}$  or  $\text{K}^+$  concentrations was observed in the MF permeate after recovering the precipitate at pH of 8 – 13 (Fig. 3). This observation suggests that the crystallization of struvite and its analogues was not a major pathway for phosphorus recovery. Indeed, as shown in the next section, the obtained phosphorus was mostly in the form of amorphous calcium phosphates.

### [FIGURE 3]

#### 3.2.2 *Precipitate composition and characteristics*

The precipitate recovered from the MF-1 permeate at pH 10 was characterized to identify the solid morphology, elemental composition, and structure. The recovered precipitate demonstrated a distinctive amorphous structure. The EDS spectrum of the recovered solids showed that the three major peaks were oxygen, phosphorus, and calcium, which are key elements of calcium phosphate. In addition, a low nevertheless discernible peak was also detected for carbon, sodium, magnesium, silicon, chloride, and potassium, possibly due to their considerable accumulation in the bioreactor during OMBR operation. The XRD spectrum showed a broad peak between the diffraction angles of  $25^\circ$  and  $35^\circ$ , suggesting that the obtained precipitate was mostly amorphous calcium phosphates (Cao and Harris, 2008), rather than the more thermodynamically stable hydroxyapatite. This observation is consistent with that reported by Qiu et al. (2015) who attributed it to the high activation energy required for hydroxyapatite formation. In addition, the presence of  $\text{Mg}^{2+}$  and organic matter (e.g. humic-like substances) could inhibit the conversion of amorphous calcium phosphate to hydroxyapatite (Alvarez et al., 2004; Cao and Harris, 2008).

#### 3.2.3 *Phosphorus recovery*

Phosphorus content in the precipitates obtained from the MF permeate at pH 10 was in the range of 15 to 20% throughout the experiment (Fig. 4). This range is higher than that previously reported (11 – 13%) by Qiu et al. (2015), possibly due to a more significant phosphate enrichment in the bioreactor with periodic MF extraction and a higher operational pH (pH 10 versus 9). The calcium/phosphorus molar ratio in the recovered precipitate was in range of 0.9 – 1.4, which was slightly lower than the theoretical ratio (1.5) of amorphous calcium phosphate. This result could be attributed to the co-precipitation of amorphous magnesium phosphate, as evidenced by the high magnesium content (12 – 17%) in the precipitate (Fig. 4). [Nevertheless, beneficial reuse or environmental discharge of the MF](#)

permeate after phosphorus recovery must be carefully considered given its high salinity and pH. A potential strategy is to blend it with the RO permeate.

**[FIGURE 4]**

### 3.3 OMBR-RO performance

#### 3.3.1 Water production and membrane fouling

A small and steady water flux decline was observed during OMBR operation (Fig. 5). The observed flux decline can be attributed to membrane fouling, salinity build-up in the bioreactor (Fig. 2a), and a decrease in the draw solution concentration. The last two factors could lower the overall driving force (i.e. osmotic pressure difference) for water transport. Thus, a reduction in bioreactor salinity due to periodic MF extraction and subsequent wastewater replenishment increased the water flux of OMBR at the beginning of each operating cycle (Fig. 5).

**[FIGURE 5]**

Reverse draw solute (NaCl) flux and to a lesser extent its permeation through the RO membrane (rejection > 98%) resulted in a decrease in the draw solution concentration. As noted in section 2.2, 50 g NaCl was added on day 30 to replenish the draw solute loss. However, NaCl replenishment did not significantly enhance the OMBR water flux compared to that obtained from the previous cycle (Fig. 5). In addition, the role of bioreactor salinity reduction in flux increase was less significant from day 30 onward. These observations indicate that membrane fouling gradually played a much more important role in OMBR flux decline as the experiment progressed. The FO membrane autopsy at the conclusion of the experiment suggests the formation of cake layer, which was mainly composed of carbon, oxygen, sodium, phosphorus, calcium, aluminium, and iron.

RO membrane permeability exhibited a similar profile to the OMBR water flux over the entire experiment (Fig. 5). As the hybrid system operated, the RO membrane permeability decreased due to membrane fouling caused by the build-up of contaminants in the draw solution (Fig. 6). A notable increase in the RO membrane permeability was observed at the beginning of each operating cycle (Fig. 5), likely due to fouling mitigation by membrane relaxation when the RO filtration was ceased.

#### 3.3.2 Removal of organic matter and nutrients

In the OMBR-RO hybrid system, the synergy between biological treatment and high-retention membrane processes (i.e. FO and RO) secured the production of high quality recycled water (Fig. 6). During OMBR operation, TOC concentration in the bioreactor increased within the first 30 days (Fig. 6a). This observation could be attributed to the adverse impacts of the elevated bioreactor salinity and the high rejection of organic matter by the FO membrane. The high bioreactor salinity could severely affect the microbial metabolism and thus limit the biological treatment (Lay et al., 2010). As the experiment progressed, TOC concentration in the bioreactor gradually decreased and then stabilized at approximately 10 mg/L from day 35 onward, probably due to microbial adaption to saline conditions (Jang et al., 2013).

#### [FIGURE 6]

The elevated bioreactor salinity also inhibited the nitrification process, thus increasing  $\text{NH}_4^+$ -N concentration in the bioreactor (Fig. 6b). In aerobic bioreactors, the nitrification process drives the conversion of  $\text{NH}_4^+$ -N to  $\text{NO}_2^-$ -N and then  $\text{NO}_3^-$ -N. These nitrogen species could be effectively retained by the FO membrane (Holloway et al., 2007; Cath et al., 2010). As a result, the incomplete nitrification process under a highly saline condition induced the build-up of  $\text{NH}_4^+$ -N and  $\text{NO}_x^-$ -N in the bioreactor, and thereby increasing TN concentration (Fig. 6c). Nevertheless, both  $\text{NH}_4^+$ -N and TN concentrations in the bioreactor gradually decreased from day 30 onward. Once again, this observation could be ascribed to microbial acclimatization to the saline environment of the bioreactor.

Biological phosphorus removal in the aerobic bioreactors occurs mainly through microbial assimilation, particularly by polyphosphate accumulating organisms (Zuthi et al., 2013). These organisms are susceptible to saline conditions, and the increased osmotic pressure within their cells due to salt accumulation could diminish their phosphate accumulating capacity (Lay et al., 2010). Thus, phosphorus removal in OMBR relies largely on the physical rejection by the FO membrane (Yap et al., 2012). In this study, a considerable build-up of  $\text{PO}_4^{3-}$ -P in the bioreactor was observed, but its concentration in both the draw solution and the product water (i.e. RO permeate) was negligible (Fig. 6d). Holloway et al. (2007) also showed that near complete rejection of phosphate by an FO membrane could be attained during concentration of anaerobically digested sludge centrate. The high phosphate rejection by FO membranes can be ascribed to the negative charge and large hydrated radius of hydrogen phosphate and dihydrogen phosphate ions, which are the dominant phosphate species in the pH range of 5 to 10 (Holloway et al., 2007; Reddy and DeLaune, 2008).

A notable build-up of organic matters (indicated by elevated concentrations of TOC, TN, and  $\text{NH}_4^+\text{-N}$ ) in the draw solution was observed as the experiment progressed (Fig. 6). It has been previously reported that contaminants that were permeable through the FO but not the RO membrane could accumulate in the draw solution and subsequently reduce the product water quality in closed-loop FO-RO hybrid systems (Cath et al., 2010; D'Haese et al., 2013). In this study, a small but discernible decrease in the overall removal of organic matter and  $\text{NH}_4^+\text{-N}$  by the hybrid OMBR-RO system was observed (Fig. 6). In addition, as discussed above, contaminant accumulation in the draw solution also reduced the permeability of the RO membrane (Fig. 5). Therefore, an additional process (e.g. granular activated carbon adsorption) should be implemented to minimize contaminant build-up in the draw solution (Xie et al., 2013), to secure the product water quality in the hybrid OMBR-RO system and enhance the system sustainability in practical application.

### 3.3.3 Biomass characteristics

Water extraction by the MF membrane from OMBR mixed liquor for phosphorus recovery did not significantly impact biomass characteristics (Table 1). The MLSS and MLVSS concentrations in the bioreactor decreased within the first 28 days. A similar decrease over time was also observed for the sludge SOUR value. These observations were likely due to the inhibition on the biological growth and activity caused by the elevated bioreactor salinity (Reid et al., 2006; Lay et al., 2010). Nevertheless, stable biomass concentration and sludge SOUR value were observed from day 28 onward due to microbial adaptation to the saline bioreactor condition.

#### [TABLE 1]

Sludge response to the elevated bioreactor salinity also caused an increase in SMP concentration in the mixed liquor, especially within the first 8 days (i.e. the first OMBR-RO operating cycle). The increased SMP concentration was contributed by cell lysis, EPS release, and the production of unmetabolised and intermediate substances under the increased salinity condition (Reid et al., 2006). On the other hand, an increase in salinity could enhance the EPS solubility in the bioreactor (Laspidou and Rittmann, 2002). Thus, there was not significant variation in EPS concentration in the mixed liquor throughout the experiment (Table 1). This observation is consistent with that previously reported by Chen et al. (2014).

## 4. Conclusion

Results reported here show the potential of OMBR-RO with periodic MF extraction to simultaneously recover phosphorus and clean water from wastewater. Phosphorus was captured from the MF permeate, extracted periodically from OMBR mixed liquor, mainly in the form of amorphous calcium phosphates with phosphorus content of 15 – 20% at pH 10. Periodic MF extraction also effectively controlled salinity build-up in the bioreactor, ensuring stable biological performance and increasing OMBR water production. Although OMBR-RO allowed for the recovery of high quality water, further investigation is required to address the build-up of organic matter and ammonia in the draw solution.

## Supplementary data

Supplementary data associated with this article can be found in the online version.

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**LIST OF FIGURE**

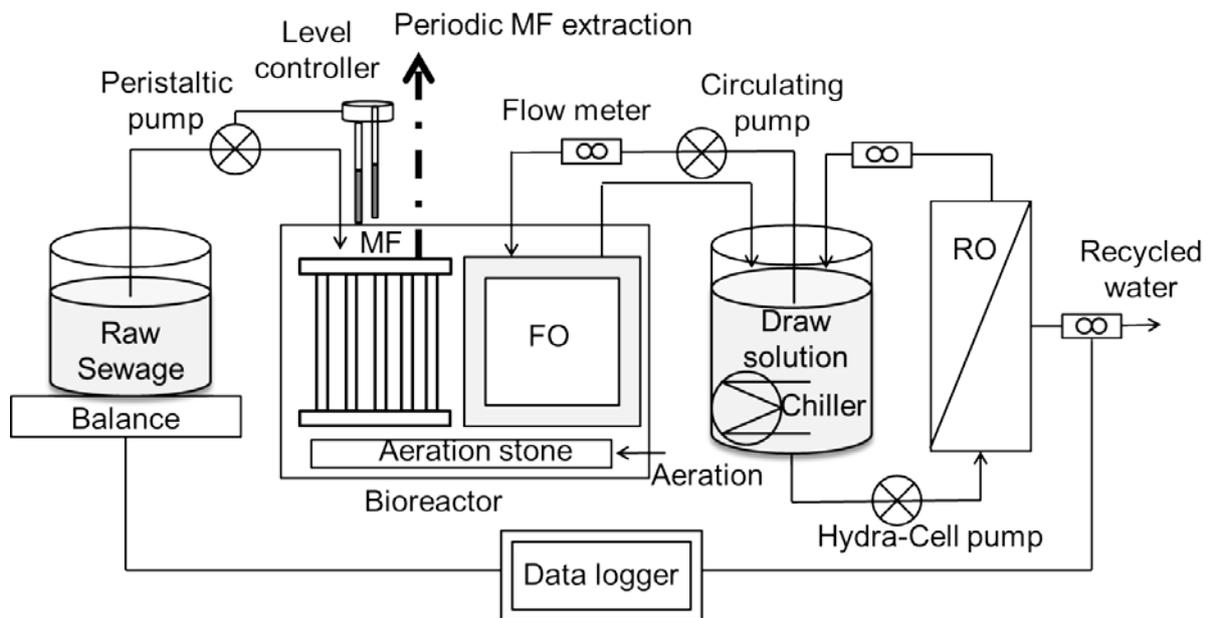


Fig. 1: Schematic diagram of a lab-scale OMBR-RO hybrid system integrated with periodic MF extraction.

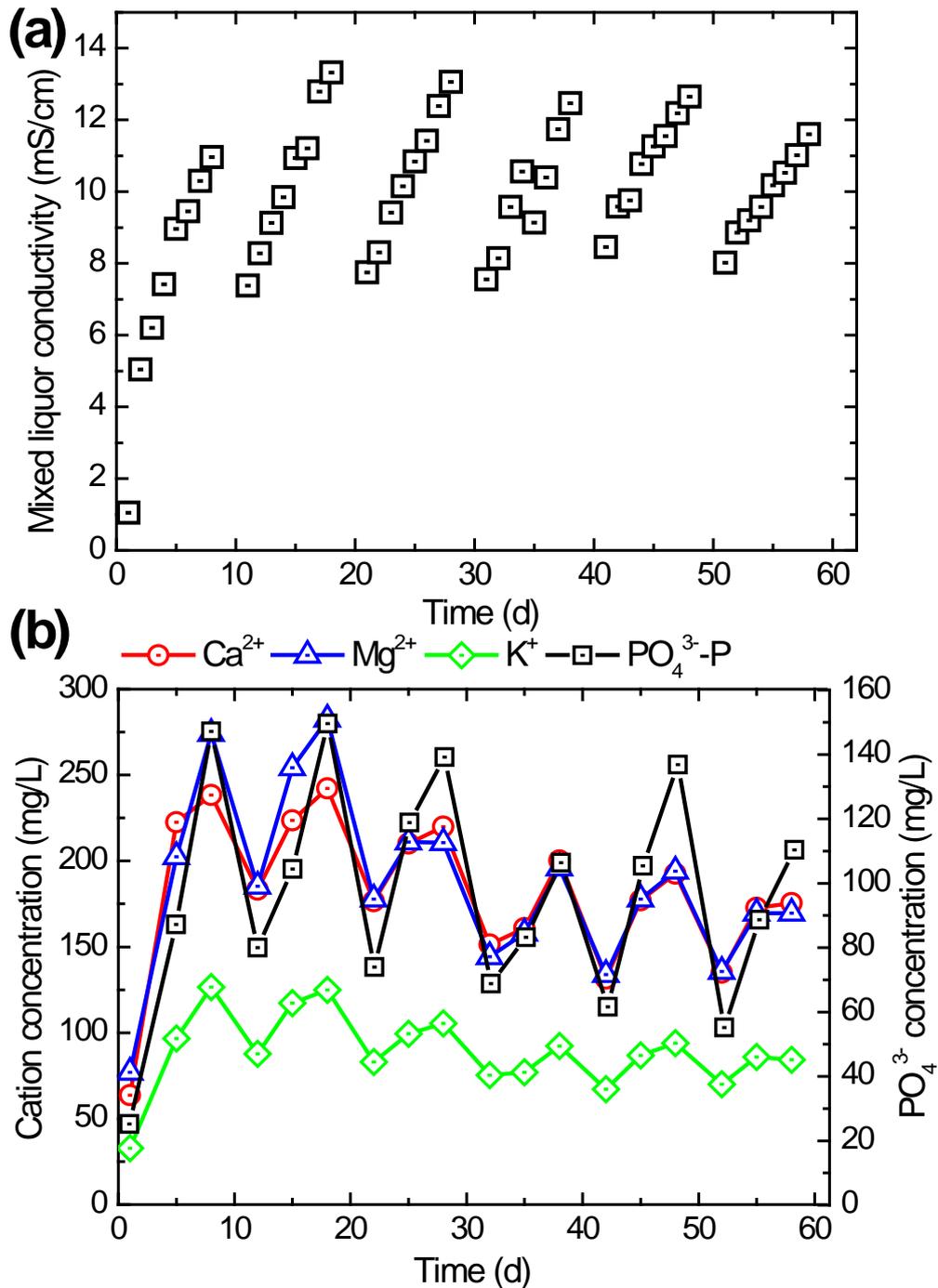


Fig. 2: (a) Mixed liquor conductivity and (b) major cation and PO<sub>4</sub><sup>3-</sup>-P concentrations in the bioreactor. OMBR-RO was run in a cycle of 8 d on and 2 d off. MF was operated for 24 h to extract 3 L water from the bioreactor for phosphorus recovery during OMBR-RO off time. The bioreactor was then replenished with 3 L sewage and aerated for 24 h. On day 30, 50 g NaCl was added to the draw solution. Experimental conditions: draw solution = 0.5 M NaCl; cross-flow velocity = 2.8 cm/s; initial MLSS concentration = 10 g/L; mixed liquor pH = 6 – 7; SRT = 50 d; HRT = 30 – 80 h; DO = 5 mg/L; temperature = 22 ± 1 °C.

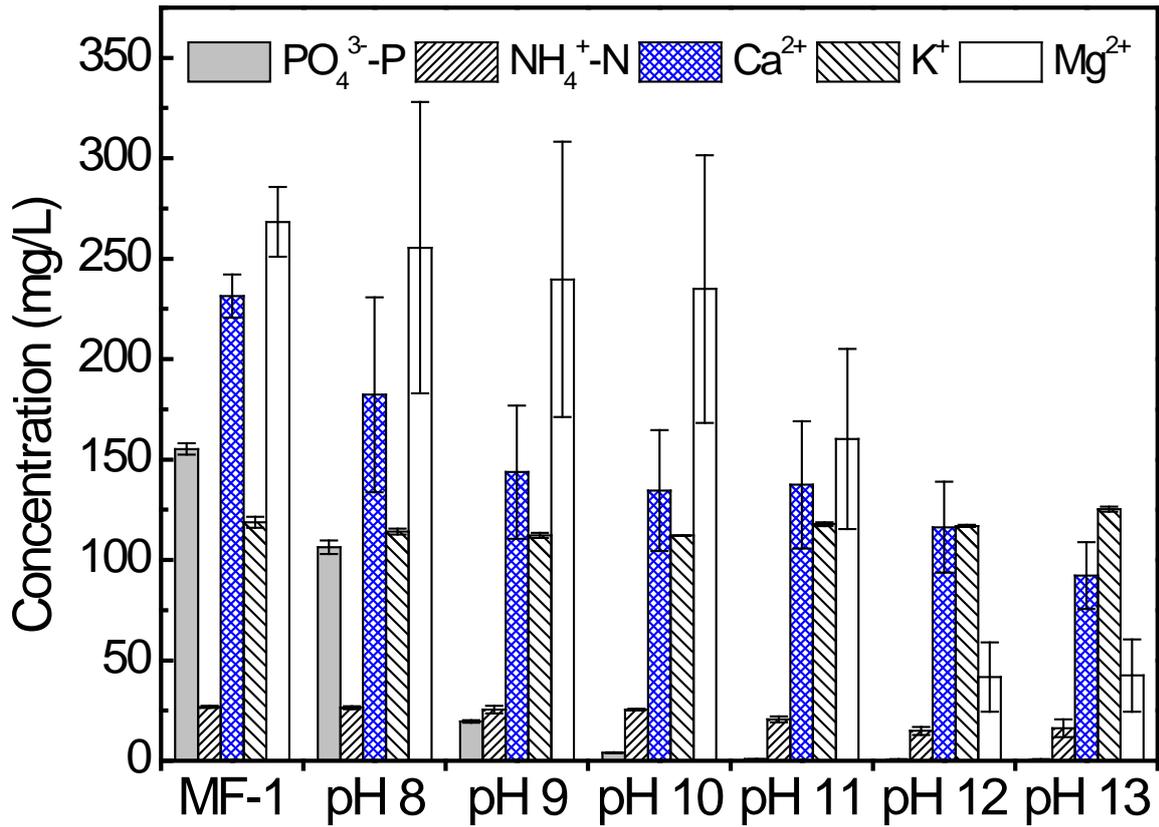


Fig. 3: Orthophosphate, ammonium, and major cation concentrations in MF-1 permeate before and after phosphorus recovery by pH adjustment. MF-1 permeate was extracted from OMBR mixed liquor in the first operating cycle. MF permeate pH was adjusted using 3 M NaOH solution and then gently mixed, followed by filtering through 0.7  $\mu\text{m}$  glass filters. Error bars represent standard deviation from duplicate measurements.

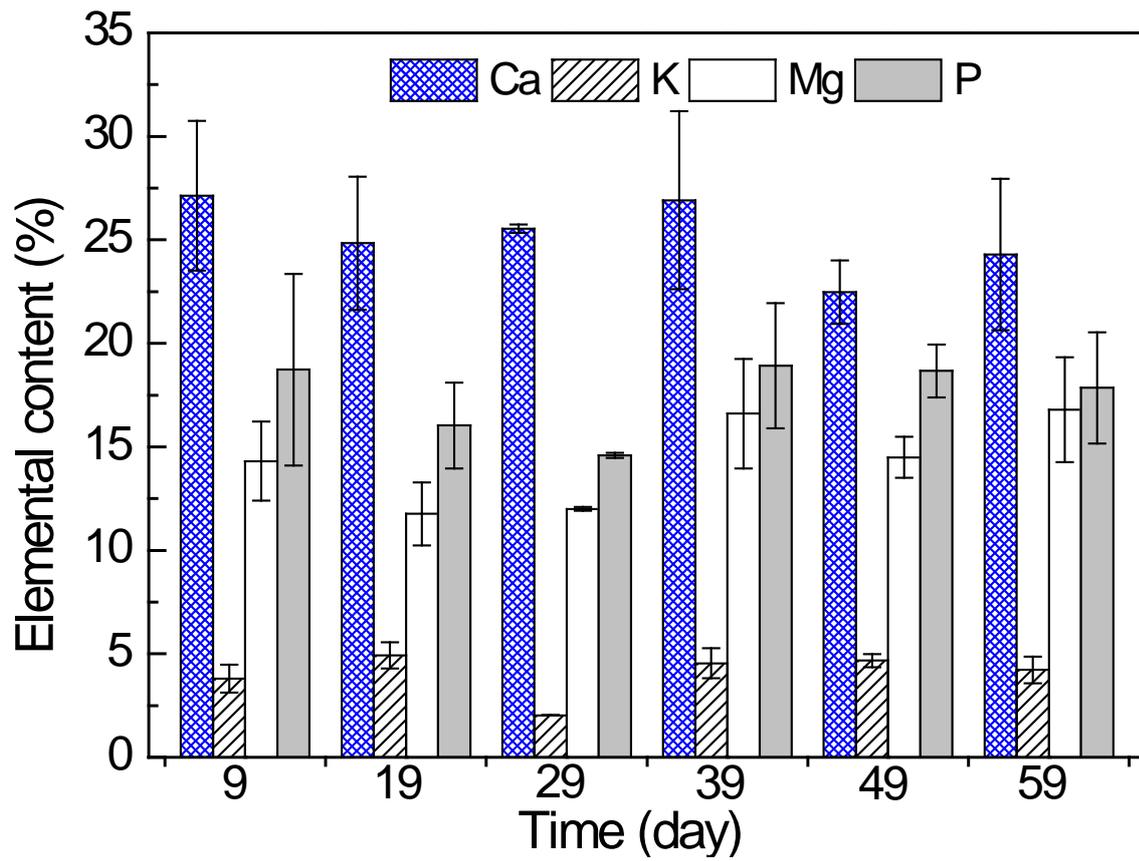


Fig. 4: Major elements in the precipitate recovered from the MF permeate (extracted periodically from OMBR mixed liquor) at pH 10. Error bars represent standard deviation from duplicate measurements.

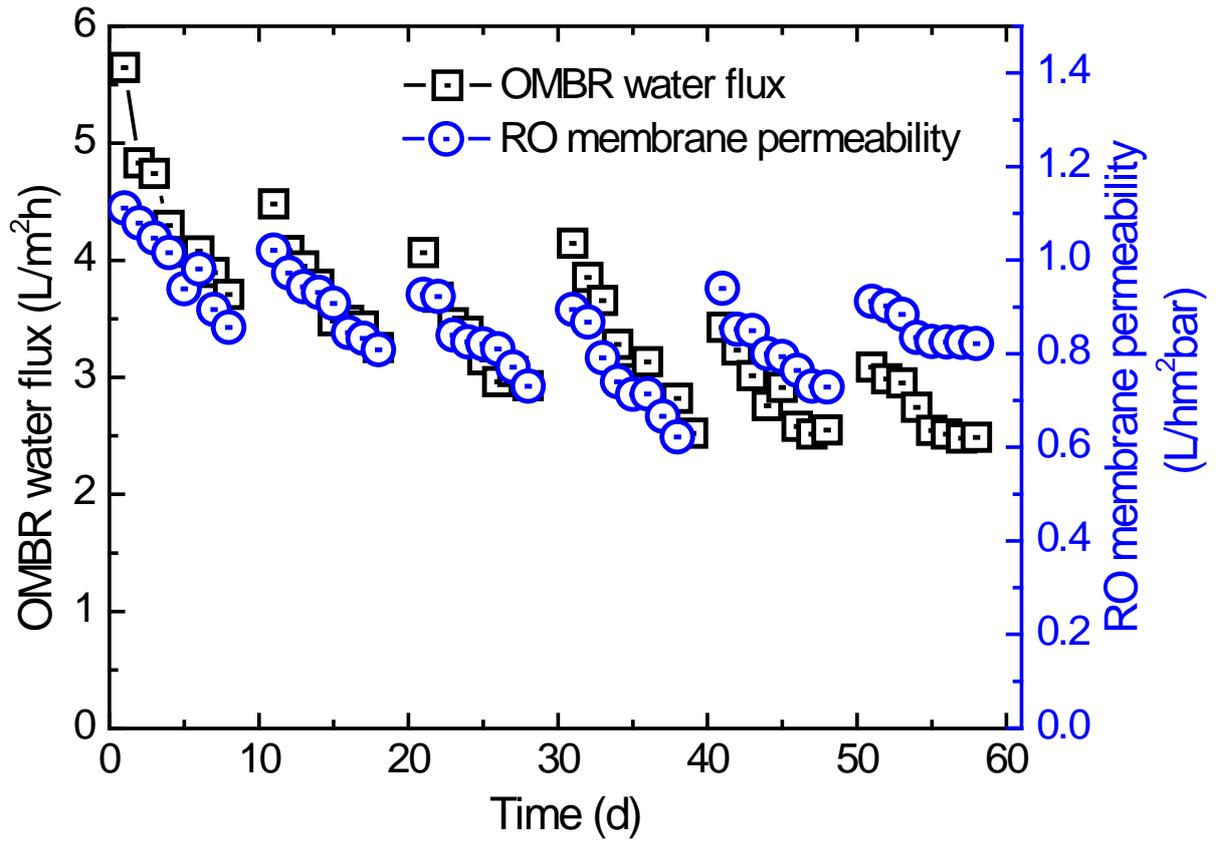


Fig. 5: OMBR water flux and RO membrane permeability over time. Operational protocol and conditions of OMBR-RO are as detailed in the caption of Fig. 1. RO permeate flux was adjusted daily to match that from OMBR by changing the hydraulic pressure while maintaining the retentate cross-flow velocity at 41.7 cm/s.

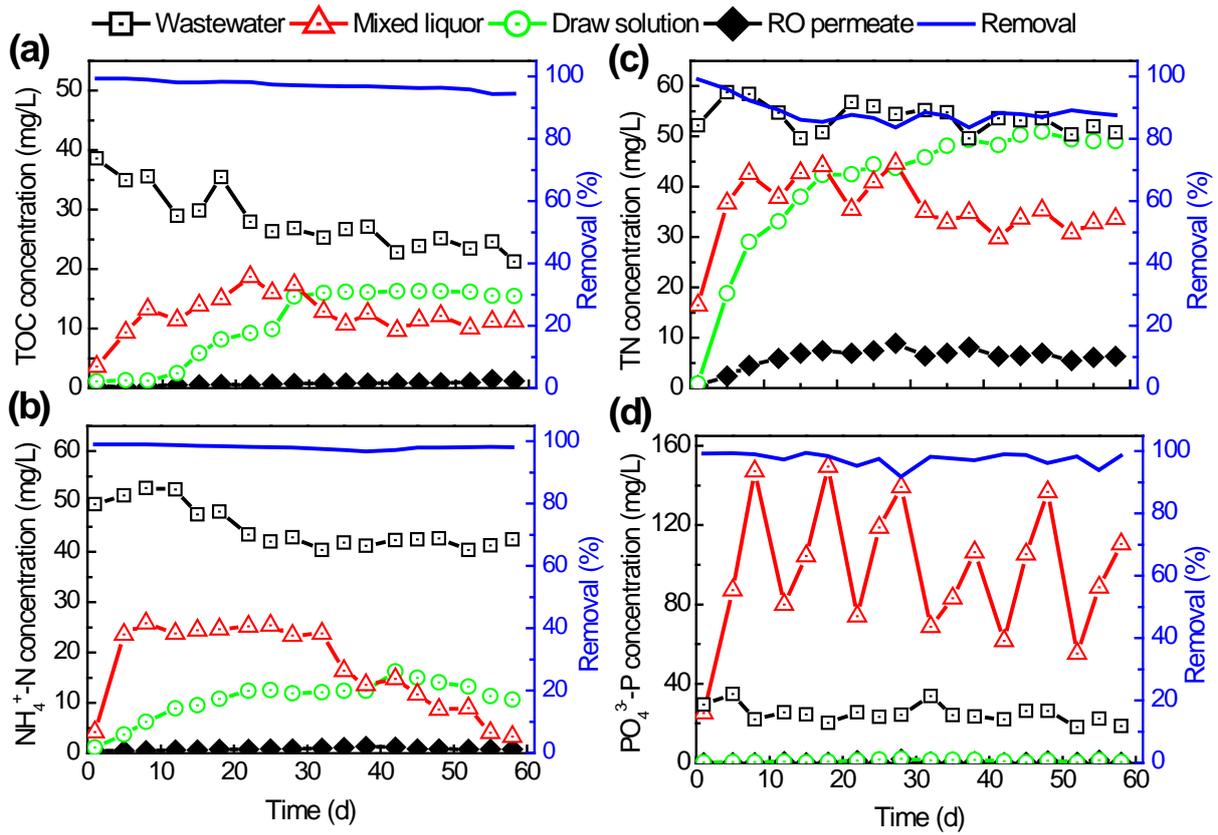


Fig. 6: (a) TOC, (b)  $\text{NH}_4^+\text{-N}$ , (c) TN, and (d)  $\text{PO}_4^{3-}\text{-P}$  concentrations and their overall removal by the hybrid OMBR-RO system. Experimental conditions are as described in the caption of Fig. 1.

## LIST OF TABLE

Table 1: Biomass characteristics during OMBR-RO operation.

Time (d)	MLSS (g/L)	MLVSS (g/L)	SOUR (mg O <sub>2</sub> /g MLVSS h)	SMP (mg/L)	EPS (mg/g MLVSS)
1	9.7	5.9	4.6	81	31
8	8.3	5.5	3.3	147	25
18	6.7	4.4	2.8	128	34
28	6.1	3.6	2.9	123	23
38	6.2	4.2	2.7	108	35
48	6.2	4.0	2.8	100	21
58	6.1	3.8	3.0	107	27

# Phosphorus and water recovery by a novel osmotic membrane bioreactor – reverse osmosis system

## SUPPLEMENTARY INFORMATION

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**Table S1:** Operational protocol of the hybrid OMBR-RO system integrated with periodic MF extraction.

Time (d)	Procedure
1 – 8 11 – 18 21 – 28 31 – 38 41 – 48 51 – 58	Continuously operating the hybrid OMBR-RO system
9, 19, 29, 39, 49, 59	<p>Ceasing feeding and the FO-RO extraction;            Operating MF for 24 h to extract 3 L water from OMBR mixed liquor</p>
10, 20, 30, 40, 50	<p>Ceasing feeding and the FO-RO extraction;            Removing the MF membrane module;            Replenishing 3 L sewage to OMBR mixed liquor and aerating for 24 h</p>

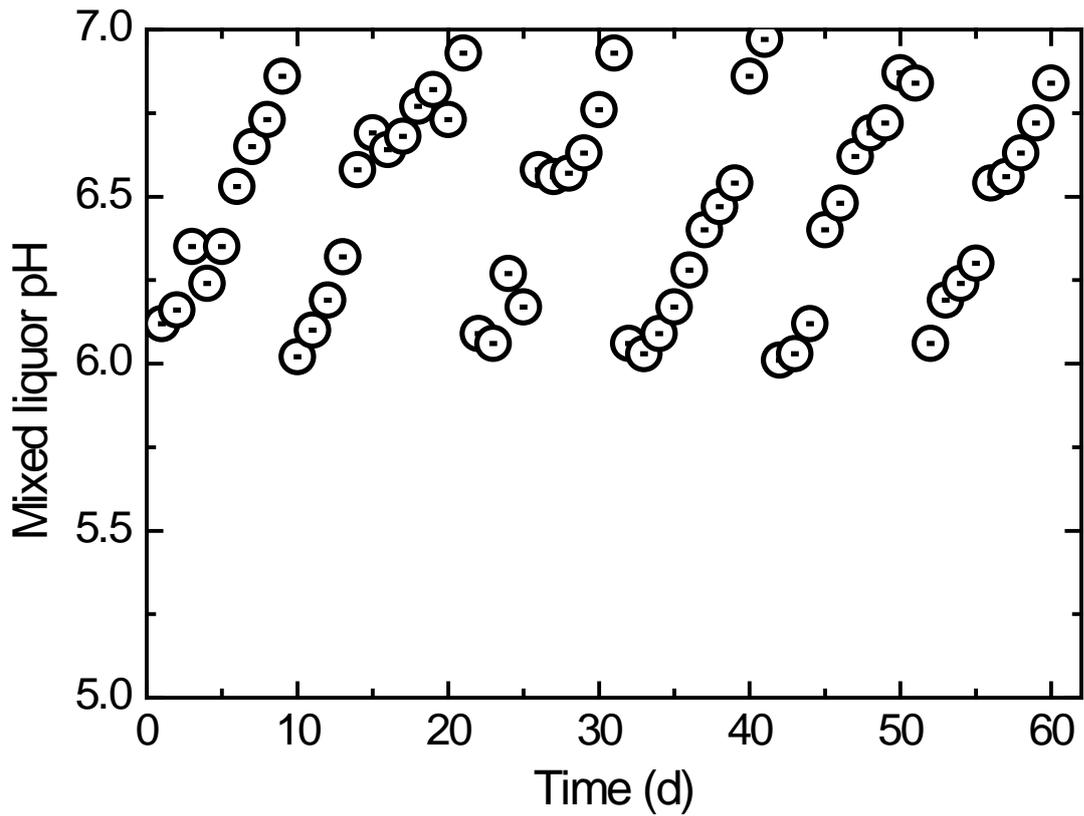


Fig. S1: Mixed liquor pH over the entire experiment. Mixed liquor pH was maintained between 6 and 7 by periodic addition of concentrated HCl solution. Experimental conditions: draw solution = 0.5 M NaCl; cross-flow rate velocity = 2.8 cm/s; initial MLSS concentration = 10 g/L; SRT = 50 d; HRT = 30 – 80 h; DO = 5 mg/L; temperature =  $22 \pm 1$  °C; RO retentate cross-flow velocity = 41.7 cm/s.

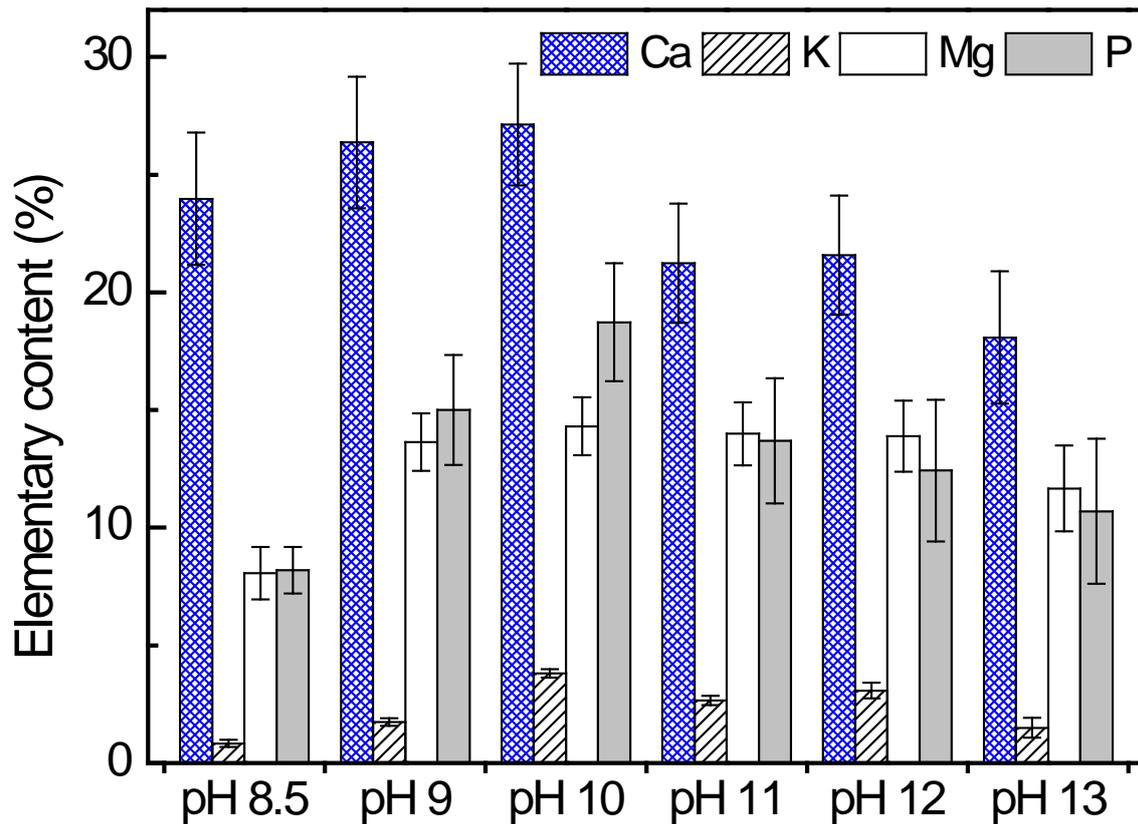


Fig. S2: Major elements in the precipitate recovered from MF-1 permeate (extracted after the first 8 days of OMBR-RO operation). MF permeate pH was adjusted using 3 M NaOH solution and then gently mixed, followed by filtering through 0.7  $\mu\text{m}$  glass filters. Error bars represent standard deviation from duplicate measurements.

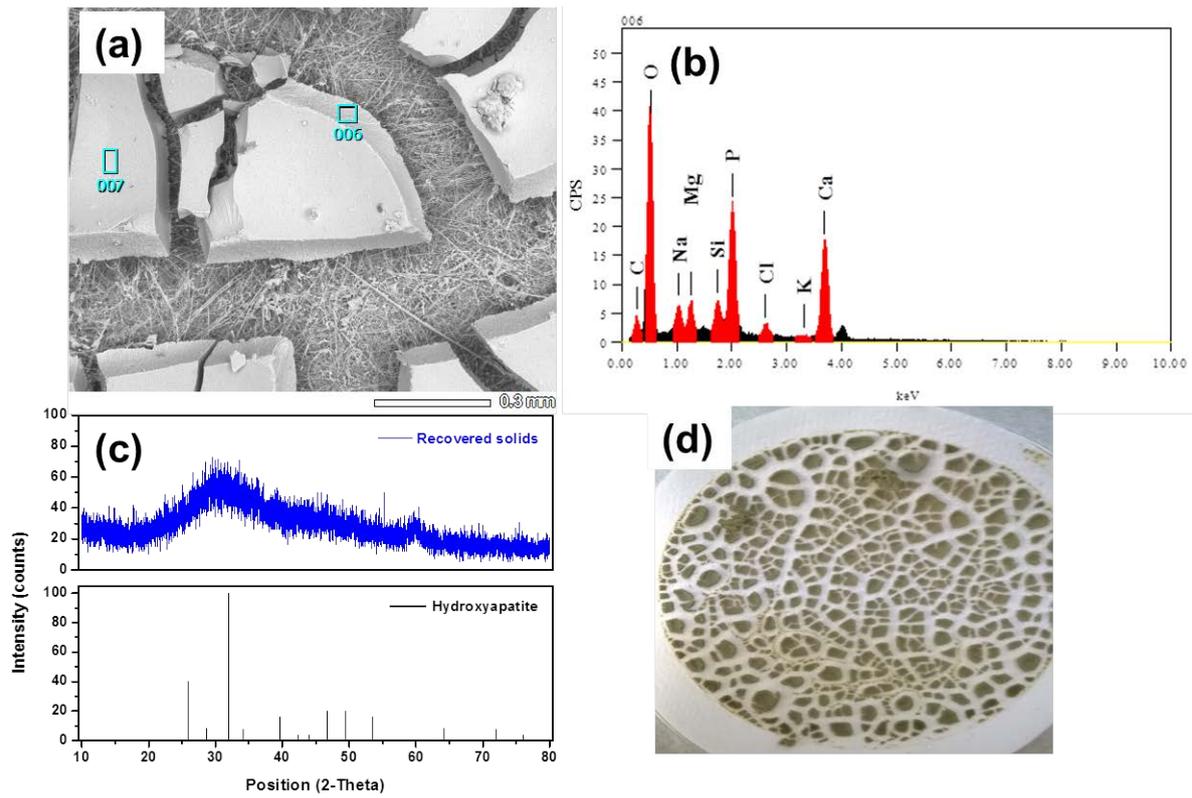


Fig. S3: (a) SEM image, (b) EDS measurement, and (c) XRD analysis, (d) visible observation of precipitates recovered from MF-1 permeate (extracted after the first 8 days of OMBR-RO operation) at pH 10.

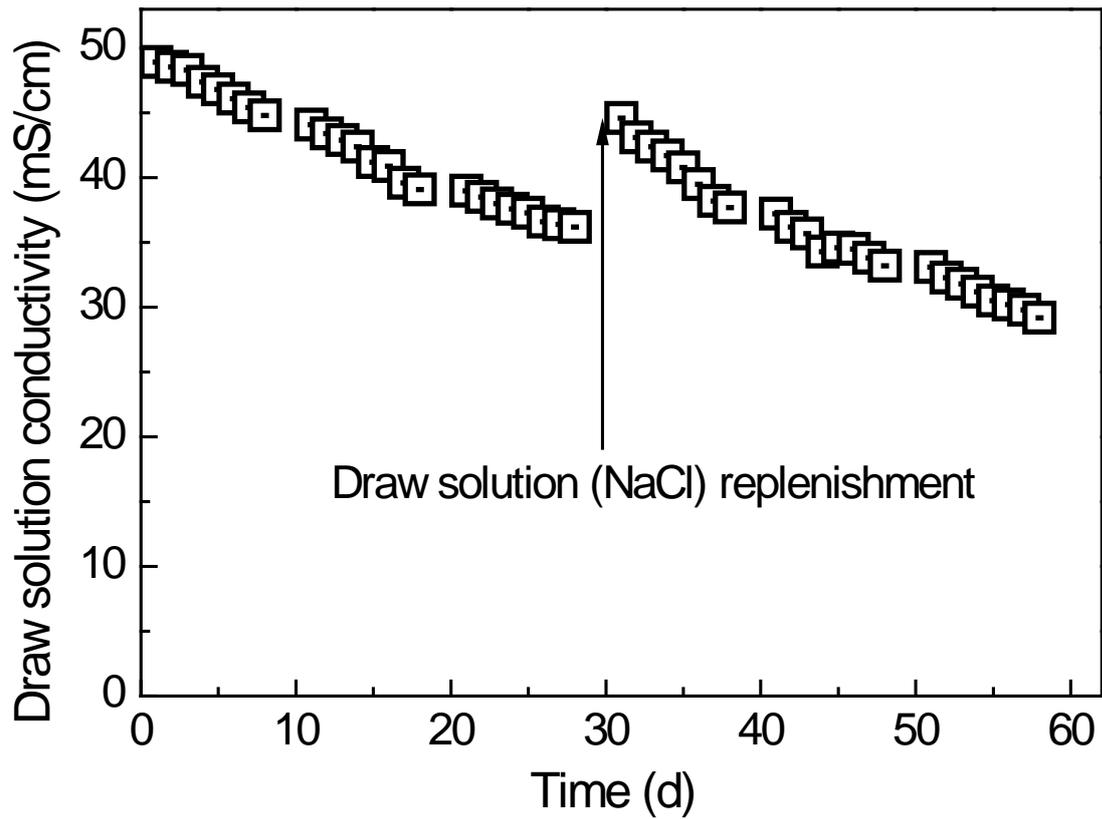


Fig. S4: Draw solution (NaCl) conductivity during OMBR-RO operation. Experimental conditions are as given in the caption of Fig. S1. On day 30, 50 g NaCl was added to replenish the draw solute loss.

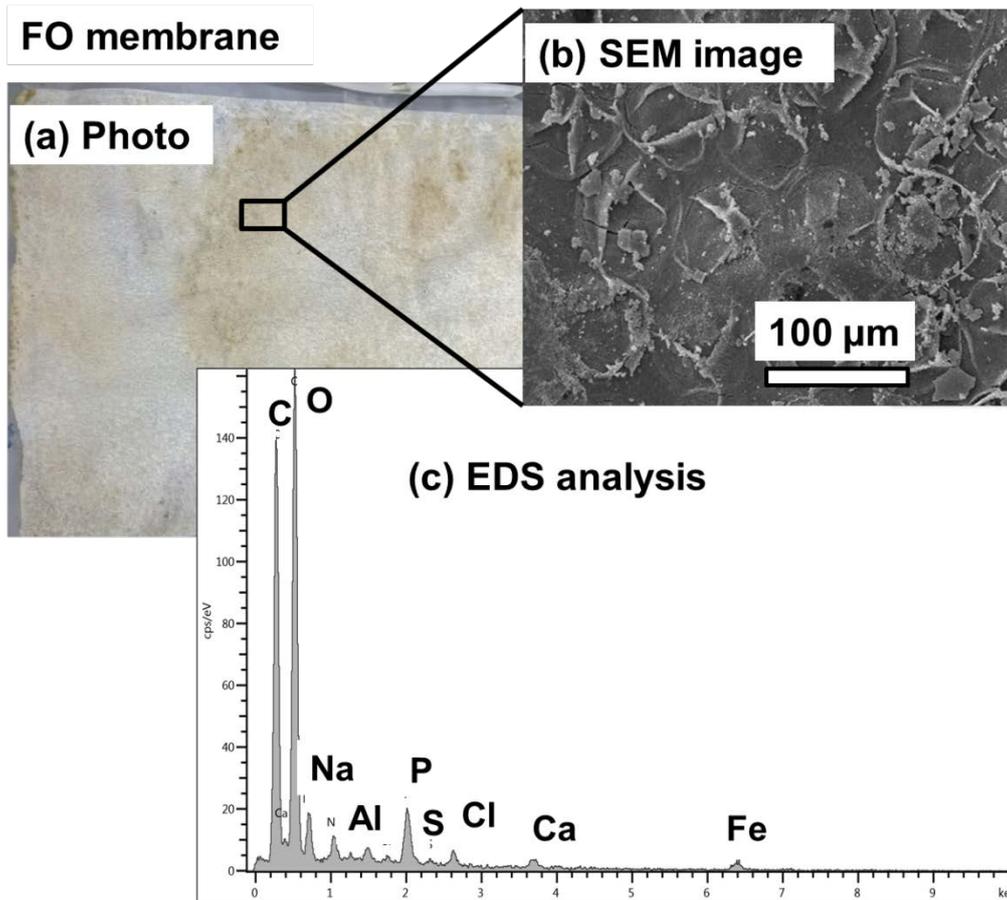


Fig. S5: FO membrane autopsy at the conclusion of the experiment: (a) photo of the fouled FO membrane; (b) SEM micrograph; and (c) EDS analysis for foulant elemental composition. Experimental conditions are as described in the caption of Fig. S1.