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Toward resource recovery from wastewater: phosphorus extraction from digested sludge using hybrid forward osmosis - membrane distillation process

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Abstract

We demonstrate the simultaneous extraction of phosphorus and clean water from digested sludge centrate using a forward osmosis (FO)-membrane distillation (MD) hybrid process. In this FO-MD hybrid process, FO concentrates orthophosphate and ammonium for subsequent phosphorus recovery in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), while MD is used to recover the draw solution and extract clean water from the digested sludge centrate. A decline in water flux was observed during the FO process, but fouling was largely reversible after a brief, simple membrane flushing using deionized water. The FO process also provides an effective pretreatment capacity to the subsequent MD process, which exhibited stable water flux. The use of MgCl_2 as the draw solute for the FO process is another novel aspect of the system. The reverse salt flux of magnesium to the concentrated digested sludge across the FO membrane and the diffusion of protons away from the digested sludge create favorable conditions for the formation of struvite crystals. The precipitates obtained in the hybrid process were verified to be struvite crystals by examining the crystal morphology, element composition, and crystal structure. Results reported here highlight the potential and robustness of the FO-MD hybrid process for extracting phosphorus from wastewater.

Keywords

distillation, process, recovery, wastewater, toward, phosphorus, resource, extraction, digested, sludge, hybrid, forward, osmosis, membrane

Disciplines

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Toward Resource Recovery from Wastewater: Phosphorus Extraction from Digested Sludge using Hybrid Forward Osmosis – Membrane Distillation Process

Environmental Science & Technology Letters

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ABSTRACT

We demonstrate the simultaneous extraction of phosphorus and clean water from digested sludge centrate using a forward osmosis (FO) – membrane distillation (MD) hybrid process. In this FO-MD hybrid process, FO concentrates orthophosphate and ammonium for subsequent phosphorus recovery in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), while MD is used to recover the draw solution and extract clean water from the digested sludge centrate. The FO process experienced water flux decline during operation, but fouling was largely reversible after a brief, simple membrane flushing using deionized water. The FO process also provides an effective pretreatment capacity to the subsequent MD process, which exhibited stable water flux. The use of MgCl_2 as the draw solute for the FO process is another novel aspect of the system. The reverse salt flux of magnesium to the concentrated digested sludge across the FO membrane and the diffusion of protons away from the digested sludge create favorable conditions for the formation of struvite crystals. The precipitates obtained in the hybrid process were verified to be struvite crystals by examining crystal morphology, element composition, and crystal structure. Results reported here highlight the potential and robustness of the FO-MD hybrid process for extracting phosphorus from wastewater.

Introduction

Phosphorus is an essential nutrient for plants. The flow of phosphorus from minable phosphate rocks to farm land and ultimately the natural waterway has accelerated in the last few decades due to the industrialization of agricultural production¹. Thus, the global phosphorus reserve is being depleted at a rate that could seriously threaten food security². Phosphorus is also a major contaminant and its release to the aquatic environment is responsible for algal bloom and other severe ecological impacts³. A promising approach to ensure a renewable supply of phosphorus and protect the environment is to extract phosphate ions from livestock and human wastes in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) mineral⁴, which is an excellent slow release fertilizer⁵.

Previous studies have demonstrated the extraction of phosphorus as struvite from wastewater^{6,7}, anaerobically digested sludge⁸⁻¹², and urine^{13,14}. Several innovative techniques to recover struvite from wastewater have also been proposed. Cusick and Logan¹⁵ reported the recovery of struvite and simultaneously produced valuable hydrogen gas using a microbial electrolysis cell. Zhang et al.¹⁶ employed an electrodialysis process to fractionate phosphate for

subsequent struvite precipitation. The formation of struvite requires the addition of magnesium, which is a high value commodity. However, the demand for magnesium can be reduced if phosphate and ammonium can be enriched from source solution.

Forward osmosis (FO) has the potential to concentrate phosphate, ammonium, and magnesium in the source solution to facilitate struvite recovery. High rejections of phosphate and ammonium from activated sludge¹⁷ and wastewater¹⁸ by FO membranes have been reported. At the same time, the use of magnesium-based salts (e.g., MgCl_2) as the draw solute can enhance struvite formation due to the inherent bidirectional diffusion of ions in the FO process¹⁹. Reverse diffusion of magnesium into the feed solution will elevate the magnesium ion concentration of the feed side, while the coupled diffusion of protons from the feed to the draw solution will increase in the feed solution pH,²⁰ with both conditions favoring struvite precipitation. FO can not only be a standalone process in osmotic dilution to extract clean water^{21, 22}, but also be integrated with other processes to recover clean water and to concentrate and recycle the draw solute²³. In a recent study, Xie et al.²⁴ coupled FO with membrane distillation (MD) for direct sewer mining, demonstrating stable water flux and high quality product water by this hybrid FO-MD system.

In this study, we demonstrate for the first time the extraction of phosphorus from anaerobically digested sludge by an FO-MD hybrid system with MgCl_2 draw solution. System efficiency was examined in terms of nutrient concentration and product water recovery. The bidirectional diffusion of magnesium and protons, which facilitates struvite precipitation, was also quantified.

Materials and Methods

FO – MD System. A lab-scale FO-MD system was employed to extract water and phosphorus from digested sludge. The FO-MD system comprised two identical membrane cells (for the FO and direct contact MD process, respectively), four circulation pumps, and a temperature control unit (Figure S1 of the Supporting Information (SI)).

Digested Sludge and Membranes. Anaerobically digested sludge was collected from an anaerobic digester of a sewage treatment plant with biological nutrient removal (BNR) in Wollongong (New South Wales, Australia). The centrate was obtained by screening the sludge through a 0.5 mm sieve then centrifuging at 3,750 rpm for 20 min (Allegra X-12R, Beckman

Coulter, Fullerton, CA). Key physicochemical properties of the digested sludge centrate are summarized in Table 1.

A flat-sheet, cellulose triacetate membrane from Hydration Technology Innovations (Albany, OR) was used for the FO process. A microporous, hydrophobic membrane from Porous Membrane Technology (Ningbo, China) was used for the MD process. Key properties of the FO and MD membranes are summarized in Table S1 of the SI.

TABLE 1

Experimental Protocol for Water and Phosphorus Recovery. Digested sludge centrate was processed continuously by the FO-MD hybrid system until 1 L of permeate had been produced. Initial volumes for digested sludge centrate, draw, and distillate solutions were 1.5, 2, and 1 L, respectively. For the FO process, 1.5 M MgCl_2 draw solution at 40 °C generated a water flux of 9 $\text{L/m}^2\text{h}$. In the MD process, the same water flux was obtained at draw and distillate temperatures of 40 and 20 °C, respectively. Water fluxes for the FO and MD processes were recorded continuously. Digested sludge centrate, draw, and distillate samples were taken at specific time intervals for further analysis. All experiments with the FO-MD hybrid system were conducted in duplicate.

To mitigate FO membrane fouling and balance the water fluxes of the FO and MD processes, the FO system was flushed using deionized water for 15 min at a cross-flow velocity of 18 cm/s (twice the value used in the FO-MD process) when the FO water flux decreased to 50% of its initial value. After 500 mL of distillate has been obtained, the distillate temperature was also increased from 20 to 30 °C to reduce the MD water flux to match that of the FO process.

Digested sludge centrate was also treated directly by the MD process alone, where feed and distillate temperatures were 40 and 20 °C, respectively. Initial volumes for feed and distillate solutions were 1.5 and 1 L, respectively. Membrane flushing was also conducted in the MD only process. The fouled MD membrane was flushed by deionized water using the aforementioned protocol for the FO process (i.e., cross-flow velocity of 18 cm/s at 40 °C for 15 min).

Phosphorus recovery from digested sludge centrate as struvite was performed at the conclusion of each FO-MD experiment. The concentrated digested sludge centrate was first filtered by a 0.45 μm filter paper (GC50, Advantec, Japan), and then was adjusted to obtain a

molar ratio of magnesium (Mg^{2+}) and orthophosphate (PO_4^{3-}) of 2:1 by adding appropriate volumes of 1 M MgCl_2 stock solution to the concentrated centrate. Next, the pH of the concentrated centrate was increased to 9.5 by adding a small volume of 1 M NaOH to form struvite crystals. The solution was mixed by a magnetic stirrer and the pH was continuously monitored until no further crystal formation was observed. The obtained crystals were washed with deionized water twice and dried in a desiccator at room temperature (approximately 22 °C).

Analytical Methods. Key water quality parameters for digested sludge centrate, draw, and distillate samples were measured according to standard methods. Specifically, ammonium (NH_4^+) and orthophosphate (PO_4^{3-}) were determined using a Flow Injection Analysis system (QuickChem 8500, Lachat, Loveland, CO). Total organic carbon (TOC) and total nitrogen (TN) were measured by a TOC/TN analyzer (TOC-V_{CSH}, Shimadzu, Kyoto, Japan). Magnesium (Mg^{2+}) concentration was determined by atomic absorption spectrometry (SpectrAA-220, Varian, Australia). Solution pH and electrical conductivity were measured by an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Waltham, MA).

The crystals obtained were characterized using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) (JEOL JCM-6000, Tokyo, Japan) and X-ray diffraction (GBC MMA, Hampshire, IL). An X-ray diffraction (XRD) spectrum of struvite crystal standard with purity of 99.998% (Alfa Aesar, Lancashire, UK) was also obtained and used as reference to verify the struvite crystals obtained from our study.

Results and Discussion

FO-MD Produces High Quality Water from Digested Sludge Centrate. FO pre-treatment ensures a stable water production by the MD process (Figure 1). Particularly, organic fouling of the hydrophobic MD membrane was effectively suppressed²⁵. By contrast, when the digested sludge centrate was directly applied to the MD process, the water flux decreased from 10 to 2 L/m²h due to severe membrane fouling. Fouling of the MD membrane with the digested sludge centrate was irreversible as membrane flushing with deionized water was not able to recover the water flux (Figure S2, SI). Given the very high total solids content (1,800 mg/L) and TOC (647 mg/L) of the digested sludge centrate (Table 1), significant water flux decline was also observed for the FO process. However, in the case of FO, membrane fouling was largely reversible following a simple, brief flushing with deionized water, which resulted in 82 and 68%

water flux recovery for the first and second membrane flushing cycles, respectively (Figure 1A). The results confirm the low propensity of membrane fouling in FO, which is mostly reversible, particularly at relatively low initial water flux^{26,27}. Water flux decline in FO could be attributed to both feed salinity build-up and membrane fouling. Reverse diffusion of MgCl₂ draw solute elevated feed salinity, thereby reducing the overall driving force (i.e., effective osmotic pressure difference) in FO. In addition, FO membrane autopsy suggested the formation of a dark fouling layer, whose major element compositions were phosphorus, sulfur, oxygen, and magnesium (Figure S3, SI).

FIGURE 1

The FO-MD hybrid system effectively rejected inorganic salts (indicated by electrical conductivity, ammonium, and orthophosphate) and organic matter (indicated by TOC and TN measurements), thereby leading to high quality product water (Table S2, SI). This high product water quality was mainly attributed to the near complete rejection by the MD process where only water vapor is transported through the membrane pores²⁸. However, such high MD rejection also resulted in the accumulation of contaminants (e.g., ammonium and orthophosphate) in the draw solution during the operation of the FO-MD system (Figure S4, SI)²⁴. Mitigation strategies to reduce the accumulation of contaminants in the draw solution have been proposed in our recent work^{24,29}.

FO Concentrates Ammonium and Phosphate. FO exhibited high rejection of ammonium (>90%) and orthophosphate (>97%) (Figure S5, SI), thereby effectively concentrating these nutrients in the digested sludge centrate (Figure 2A). This is consistent with previous FO studies^{17,30}. The enrichment of ammonium and orthophosphate, which are two key constituents for struvite, substantially elevated the precipitation potential and product yield of struvite.

FIGURE 2

Bidirectional Diffusion of Magnesium and Protons Facilitates Phosphorus Extraction as Struvite. An appropriate magnesium concentration and an alkaline solution are two key factors for the extraction of phosphorus as struvite from the nutrient-concentrated digested sludge centrate³¹. Here, the bidirectional ion diffusion, which is a unique mass transfer phenomenon in FO^{19,32-34}, can be utilized to facilitate phosphorus extraction. Specifically,

forward proton diffusion elevated feed solution pH and, at the same time, reverse magnesium diffusion enhanced the feed magnesium concentration (Figure 2B). The increase in feed pH was mainly driven by maintaining solution electroneutrality³⁵. Similar pH variation was observed by Hancock et al.²⁰ who examined the bidirectional ion diffusion in an FO process. More importantly, reverse magnesium permeation (reverse magnesium flux of 12 mmol/m²h) substantially increased the feed magnesium concentration, thereby supplementing magnesium for struvite formation.

The ionic product of ammonium, orthophosphate, and magnesium at the conclusion of the FO-MD experiment was $10^{-5.77} \text{ M}^3$, which was above the struvite conditional solubility product of $10^{-7.54} \text{ M}^3$ (Figure 2)³⁶. The molar ratio of magnesium to orthophosphate was further increased from 1:1.43 to 2:1 by addition of a small amount of magnesium (0.06 g Mg²⁺ per gram struvite produced), thereby promoting struvite precipitation. Indeed, struvite formation was indicated by the continuous decrease in solution pH (Figure S6, SI). The solution pH variation also revealed that the struvite induction time was less than two minutes.

The precipitate was analyzed to identify the crystal morphology, element composition, and structure (Figure 3). The precipitated crystals showed a distinctive orthorhombic structure, with an average size of 40 μm (Figures 3A and B). The XRD spectrum obtained of the precipitate was identical to that of the reference pure struvite crystal standard (Figure 3C). The EDS spectrum showed that the three major peaks were for magnesium, phosphorus, and oxygen, which are the key elements of struvite. Apart from carbon (which was used to coat the sample), no other elements were detected. Thus, the results shown in Figure 3D confirm the purity of the obtained struvite crystal. It is noteworthy that struvite also contains nitrogen. However, nitrogen is a light element and cannot be detected by EDS analysis. The high struvite purity observed here could be attributed to the enrichment of phosphate and ammonium by the FO-MD hybrid system.

FIGURE 3

In summary, our results demonstrate the potential of the FO-MD hybrid system for simultaneously extracting phosphorus and clean water from digested sludge centrate. The fouling resistant FO process provides an effective pre-treatment for MD to enable a stable water flux. In addition, the bidirectional transport of magnesium (the draw solute) and protons across the FO

membrane creates favorable conditions for phosphorus extraction in the form of struvite precipitate.

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Notes

The authors declare no competing financial interest.

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Associated Materials

Supporting Information

Details on description of lab-scale FO-MD system and the schematic diagram (Figure S1); key properties of FO and MD membranes (Table S1); water production by MD-only process (Figure S2); FO membrane autopsy (Figure S3); product water quality by FO-MD hybrid system (Table S2); rejection of ammonium and orthophosphate by FO process (Figure S4); accumulation of ammonium and orthophosphate in draw solution (Figure S5); solution pH variation as a function of time in struvite formation (Figure S6). This information is available free of charge via the Internet at <http://pubs.acs.org/journal/estlcv>.

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Table 1: Key physicochemical properties of digested sludge centrate (average \pm standard deviation from duplicate measurements)

Parameter	Value
Solids Content (mg/L)	1,800 \pm 100
Turbidity (NTU)	524 \pm 9
Electrical Conductivity (mS/cm)	6.72 \pm 0.12
pH (-)	7.72 \pm 0.02
Total Organic Carbon (mg/L)	647 \pm 20
Total Nitrogen (mg/L)	783 \pm 11
Ammonium (mg/L)	538 \pm 25
Phosphate (mg/L)	223 \pm 12
Magnesium (mg/L)	10.5 \pm 2.1

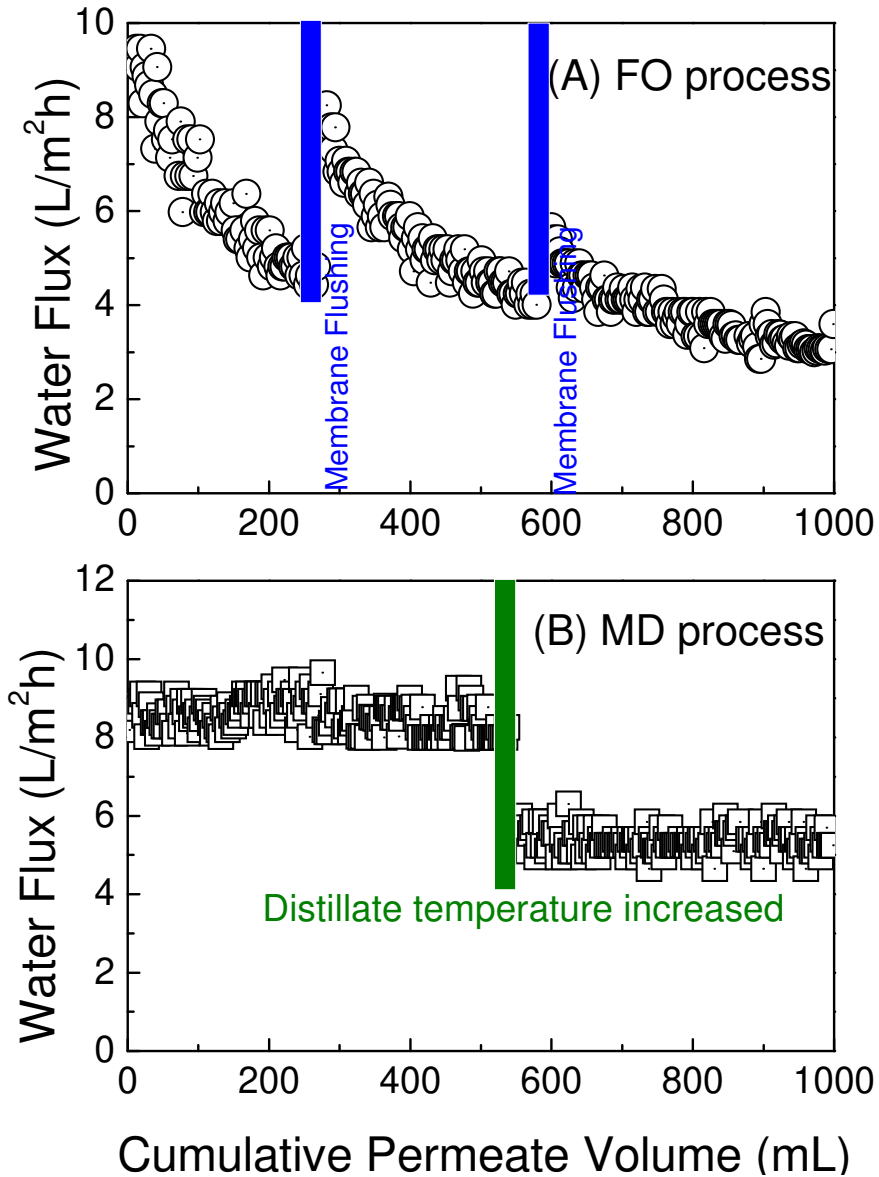


Figure 1: Water production by the FO – MD system: (A) FO and (B) MD process. Experimental conditions: digested sludge centrate feed (Table 1); draw solution of 1.5 M MgCl₂; temperatures of feed, draw, and distillate of 20, 40, and 20 °C, respectively; and cross-flow rates of 1 L/min (corresponding to cross-flow velocity of 9 cm/s) for the feed, draw, and distillate. FO membrane flushing was conducted when water flux decreased to 50% of its initial value. Deionized water was used to flush the fouled FO membrane for 15 min at a cross-flow velocity of 18 cm/s. Distillate temperature was increased from 20 to 30 °C, after 500 mL permeate had produced, to reduce MD water flux in order to maintain similar water fluxes for the FO and MD processes.

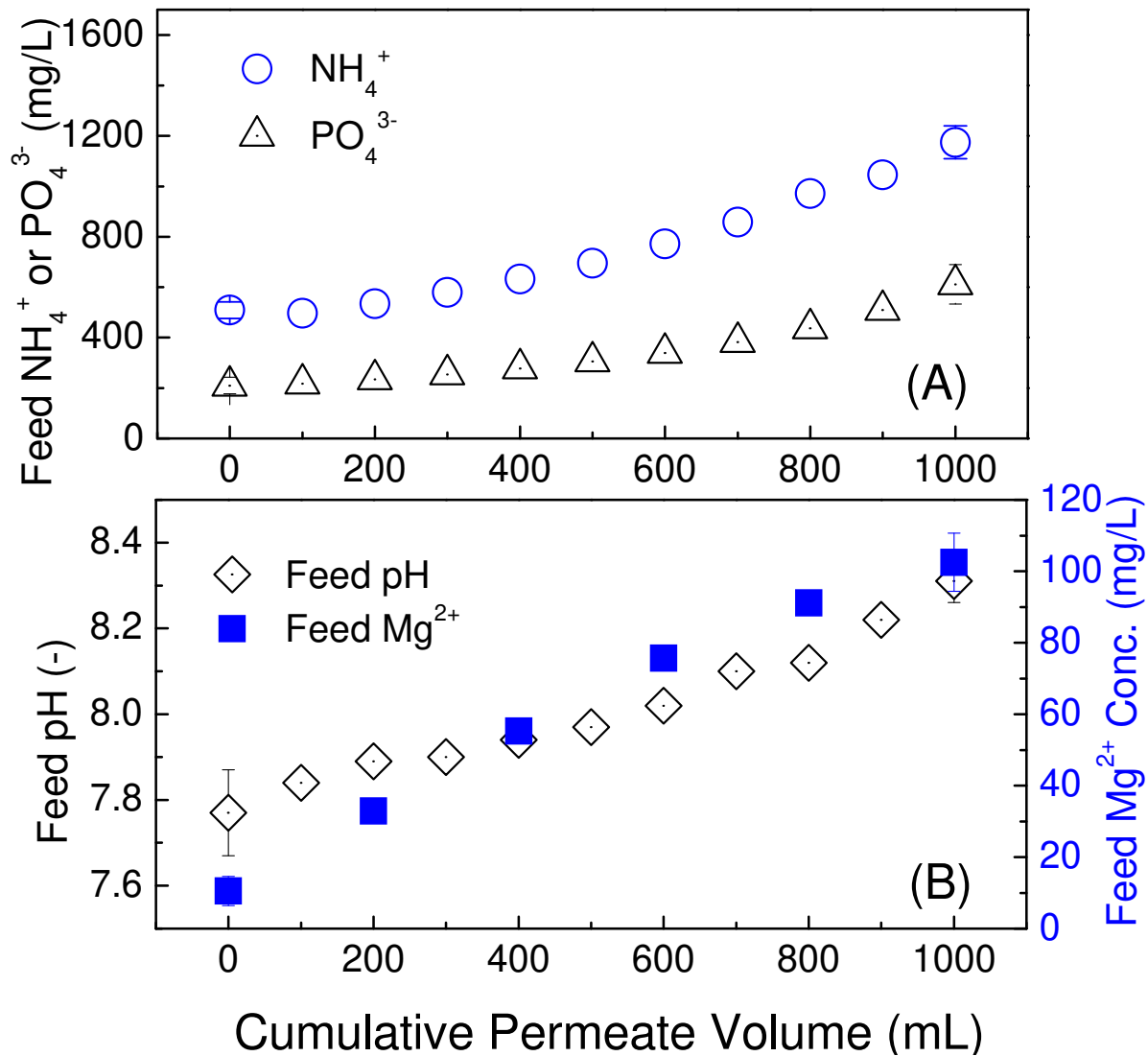


Figure 2: (A) concentration of feed NH_4^+ and PO_4^{3-} by the FO-MD process; (B) concentration of feed Mg^{2+} and increase in pH as a function of cumulative permeate volume. Experimental conditions are described in Figure 1.

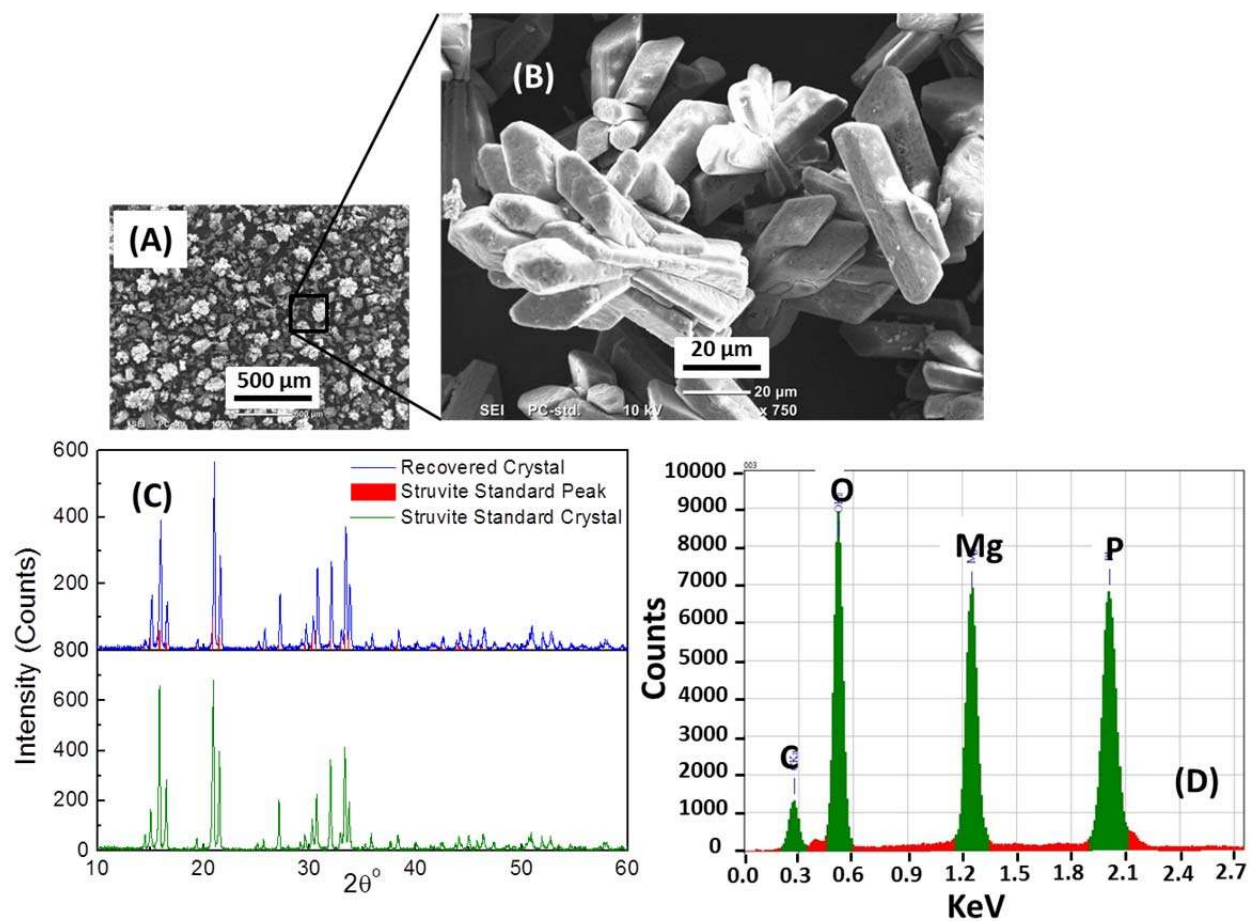


Figure 3: Struvite crystal recovered by the FO-MD process: (A) and (B) SEM images, (C) EDS analysis, and (D) XRD analysis. Solution pH was further increased to 9.5 by addition of base (NaOH). Continuous stirring was applied for two hours, and crystals were recovered and dried in a desiccator at room temperature.

Supporting Information

Toward Resource Recovery from Wastewater: Phosphorus Extraction from Digested Sludge using Hybrid Forward Osmosis – Membrane Distillation Process

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SUPPLEMENTARY MATERIALS AND METHODS

FO – MD System. Each membrane cell was constructed with symmetric flow channels (145 mm long, 95 mm wide, and 3 mm deep) on both sides of the membrane that facilitated concurrent flow along the 140 cm² effective membrane area. In the FO-MD hybrid system, the draw solution reservoir of the FO process was also the feed reservoir for the MD process. Variable speed gear pumps (Micropump, Vancouver, WA) were used to circulate the feed, draw, and distillate solutions at a cross-flow velocity of 9 cm/s. A temperature sensor and a heating element were connected to a temperature control unit that maintained the draw solution temperature; a water bath (Neslab RTE 7, Thermo Scientific, Waltham, MA) controlled the distillate temperature that was monitored continuously using a digital thermometer. Weight changes of the feed and distillate reservoirs were recorded by digital balances (Mettler Toledo, Hightstown, NJ) connected to a computer.

Table S1: Key properties of the FO and MD membranes used in this study

Parameter	FO membrane	MD membrane
Active layer	Cellulose triacetate	Polytetrafluoroethylene (PTFE)
Air permeability (L/m ² -s)	N.A.	6 – 8 ^a
Pure water permeability (L/m ² -h-bar)	0.65 ± 0.027 ^b	N.A.
Salt (NaCl) permeability (L/m ² -h)	0.25 ± 0.07 ^b	N.A.
Membrane structural parameter (mm)	0.67 ± 0.13 ^b	N.A.
Pore size (nm)	0.37 ^c	30 ^d
Contact angle (°)	60 ± 3 ^e	135 ± 15 ^f
Zeta potential at pH 7 (mV)	-4.6 ^g	N.A.

^a provided by the manufacturer; membrane sample (70 mm in diameter) was measured at 127 Pa

^b determined using standard protocol proposed by Cath et al. ¹; data reported by Xie et al. ²

^c reference ³

^d provided by the manufacturer

^e reference ⁴

^f determined by standard sessile drop method

^g reference ⁴

Table S2: Key parameters of the feed, draw, and product water for the FO-MD system (average \pm standard deviation from duplicate experiments). Experimental conditions were described in Figure 1 in the paper.

Parameter	Feed	Draw	Product Water
TOC (mg/L)	647 \pm 20	95.7 \pm 3.8	4.7 \pm 1.2
TN (mg/L)	783 \pm 11	65.2 \pm 2.8	2.1 \pm 0.5
Electric Conductivity (μ S/cm)	6720 \pm 120	N.A.	14.2 \pm 2.1
Ammonium (mg/L)	538 \pm 25	48.7 \pm 4.8	0.33 \pm 0.11
Orthophosphate (mg/L)	223 \pm 12	19.7 \pm 1.5	0.15 \pm 0.15

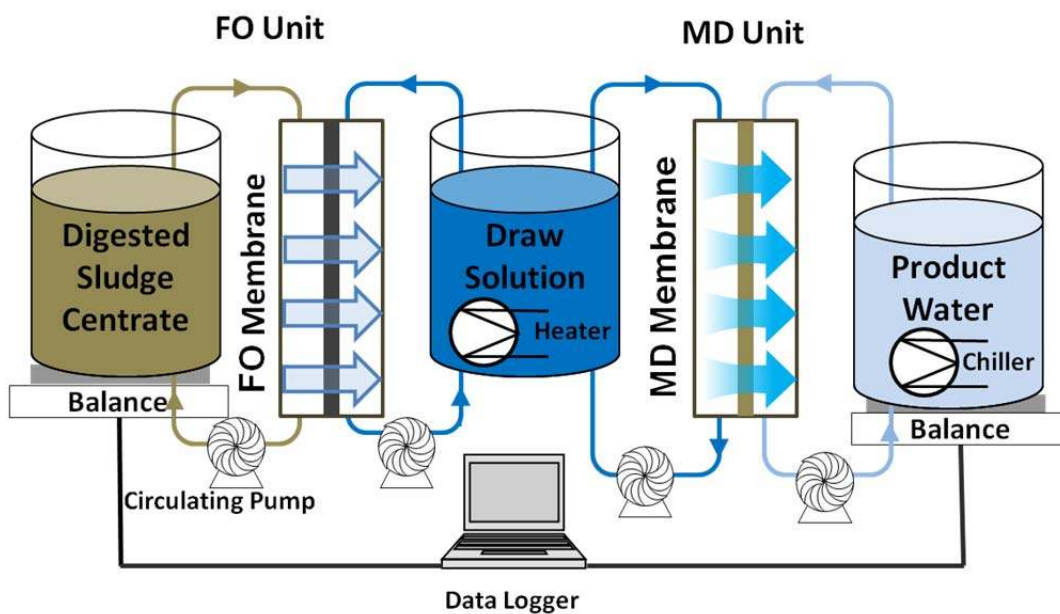


Figure S1: Schematic diagram of the lab-scale FO-MD experimental setup for phosphorous extraction from digested sludge centrate.

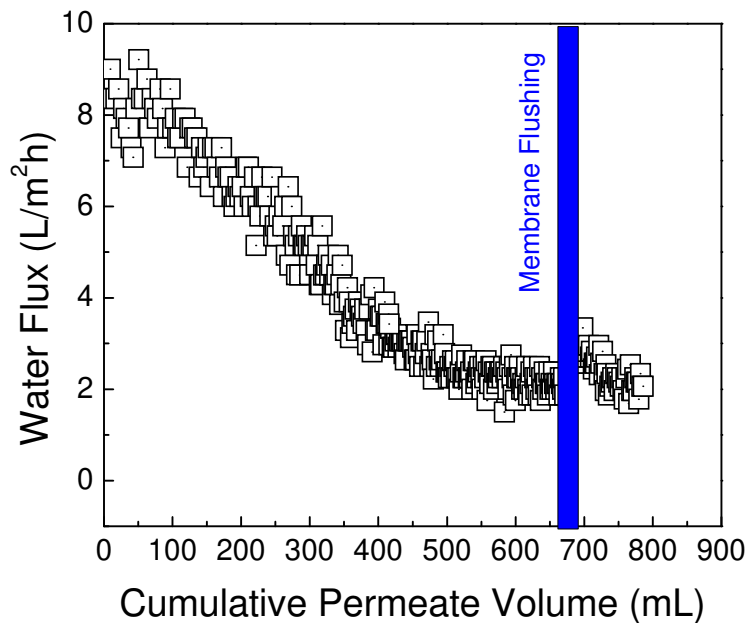


Figure S2: Water flux of the MD-only process using digested sludge centrate feed. Experimental conditions: initial volumes of both the feed and distillate were 1 L; feed and distillate temperatures were 40 and 20 °C, respectively; and cross-flow rates were 1 L/min (corresponding to cross-flow velocity of 9 cm/s) for both the feed and distillate. A brief, simple membrane flushing was conducted after producing 650 mL permeate, in which Milli-Q water was used to flush the fouled MD membrane at a cross-flow velocity of 18 cm/s at 40 °C.

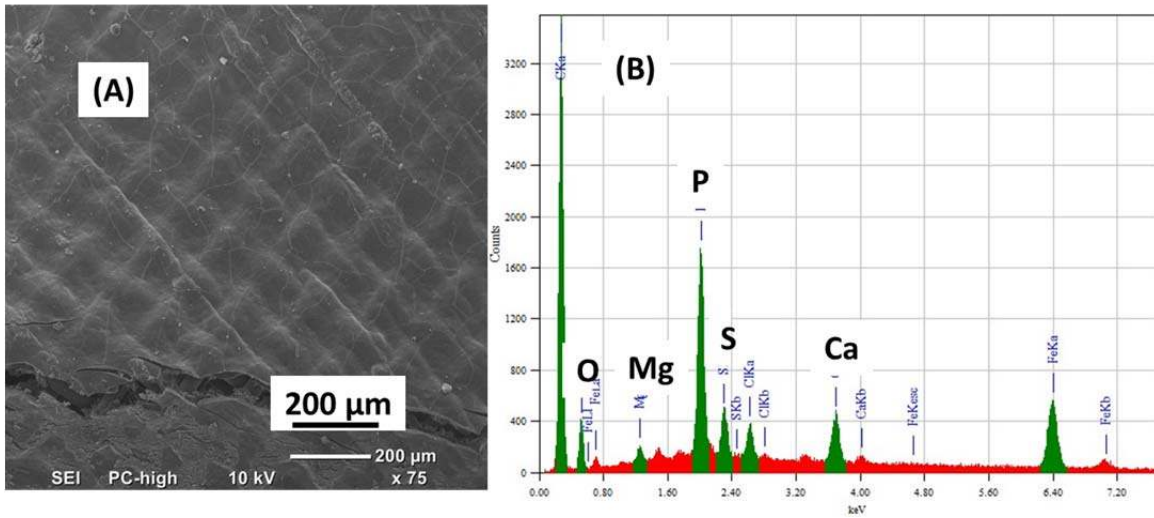


Figure S3: FO membrane autopsy: (A) SEM image and (B) EDS analysis for element composition of the fouling layer. Experimental conditions were described in Figure 1 in the paper.

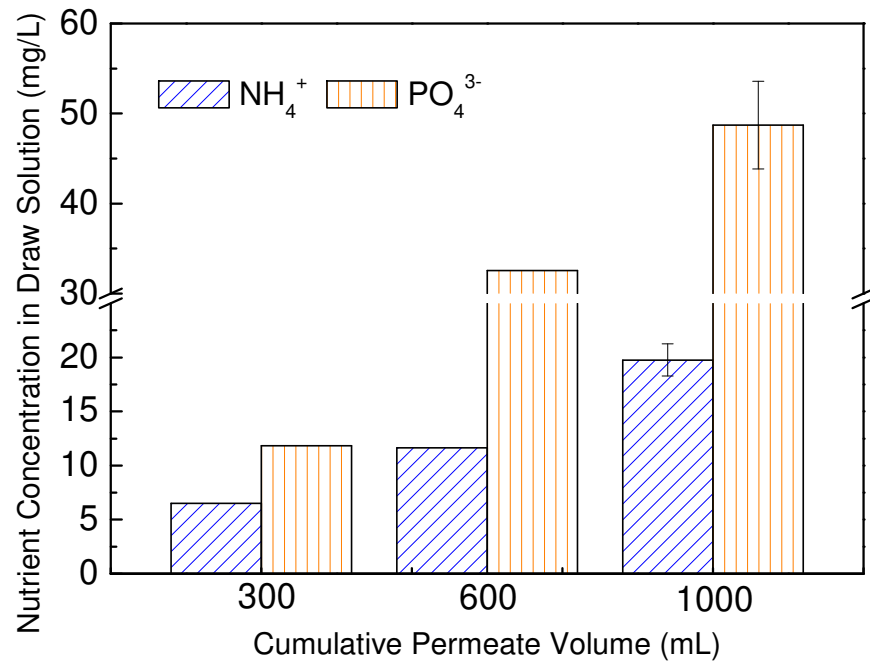


Figure S4: Accumulation of ammonium and orthophosphate in the draw solution as a function of cumulative permeate volume. Experimental conditions were described in Figure 1 in the paper.

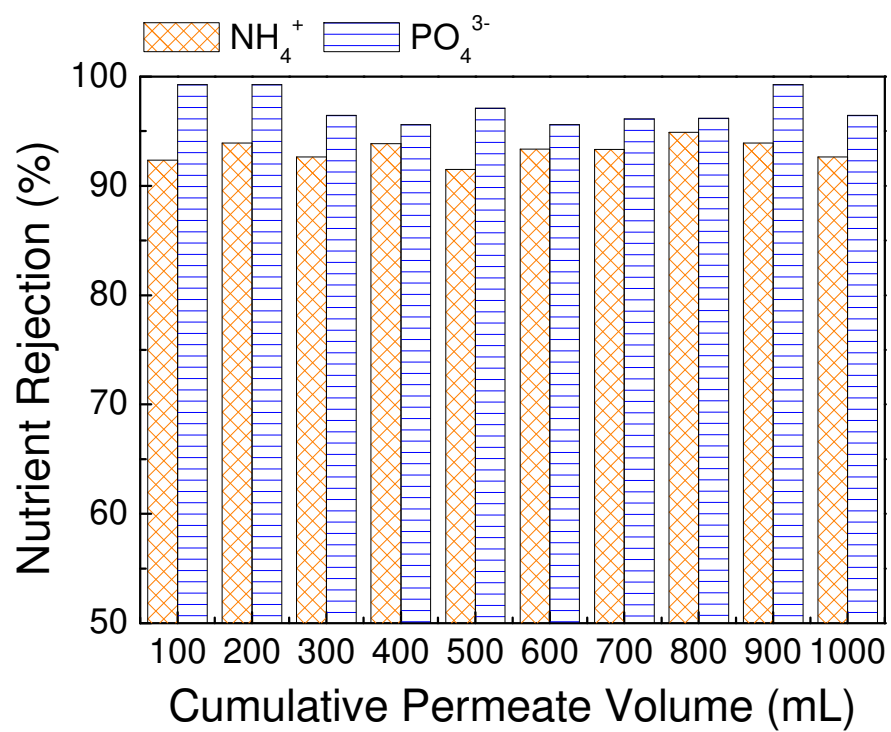


Figure S5: Rejection of ammonium and orthophosphate by the FO process as a function of cumulative permeate volume. Experimental conditions were described in Figure 1 in the paper.

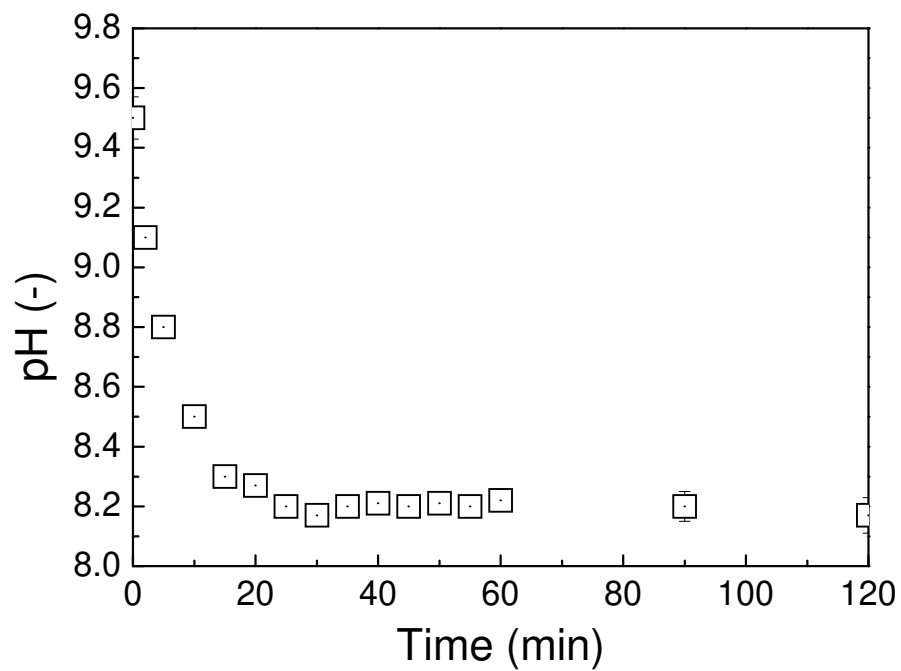


Figure S6: pH variation as a function of time during struvite formation. Experimental conditions were described in Figure 3 in the paper.

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TOC Graphic

