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Phosphorus recovery from digested sludge centrate using seawater-driven forward osmosis

Ashley J. Ansari

University of Wollongong, ashleyz@uow.edu.au

Faisal I. Hai

University of Wollongong, faisal@uow.edu.au

William E. Price

University of Wollongong, wprice@uow.edu.au

Long D. Nghiem

University of Wollongong, longn@uow.edu.au

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Abstract

In this study, we demonstrate a novel seawater-driven forward osmosis (FO) process to recover calcium phosphate precipitates from digested sludge centrate without any chemical addition and draw solute regeneration. The FO process effectively pre-concentrated phosphate and calcium in the digested sludge centrate. Spontaneous precipitation of calcium phosphate minerals in the digested sludge centrate was achieved by the sustained concentrative action of the FO process and the gradual pH increase due to the diffusion of protons to the draw solution. Pre-concentrating digested sludge centrate by three-fold resulted in a 92% recovery of phosphate via precipitation. The phosphate precipitate only constituted 3% of the total inorganic solids recovered, therefore subsequent treatment steps would be required to recover phosphorus in a useable form. A water flux decline of 30% from the initial value was observed as the digested sludge was concentrated by three-fold. This observed water flux decline was mostly attributed to the decrease in the effective osmotic driving force due to the increasingly concentrated feed solution and diluted draw solution. It is also noteworthy that membrane fouling was readily reversible. By flushing the membrane with deionised water and subjecting the membrane to feed and draw solutions with the same osmotic pressure as the initial conditions, complete water flux recovery could be achieved.

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**Phosphorus recovery from digested sludge centrate using seawater-driven
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Ashley J. Ansari¹, Faisal I. Hai¹, William E. Price², and Long D. Nghiem^{1,*}

¹ Strategic Water Infrastructure Laboratory, School of Civil, Mining and Environmental
Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

² Strategic Water Infrastructure Laboratory, School of Chemistry, University of Wollongong,
Wollongong NSW 2522, Australia

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* Corresponding author: Long Duc Nghiem, Email longn@uow.edu.au; Tel: +61 2 4221 4590

Abstract: In this study, we demonstrate a novel seawater-driven forward osmosis (FO) process to recover phosphorus in the form of calcium phosphate precipitates from digested sludge centrate without any chemical addition and draw solute regeneration. The FO process effectively pre-concentrated phosphate and calcium in the digested sludge centrate. Spontaneous precipitation of calcium phosphate minerals in the digested sludge centrate was achieved by the sustained concentrative action of the FO process and the gradual pH increase due to the diffusion of protons to the draw solution. Pre-concentrating digested sludge centrate by three-fold resulted in a 92% recovery of phosphate via precipitation. [The phosphate precipitate only constituted 3% of the total inorganic solids recovered, therefore subsequent treatment steps would be required to recover phosphorus in a useable form.](#) A water flux decline of 30% from the initial value was observed as the digested sludge was concentrated by three-fold. This observed water flux decline was mostly attributed to the decrease in the effective osmotic driving force due to the increasingly concentrated feed solution and diluted draw solution. It is also noteworthy that membrane fouling was readily reversible. By flushing the membrane with deionised water and subjecting the membrane to feed and draw solutions with the same osmotic pressure as the initial conditions, complete water flux recovery could be achieved.

Keywords: forward osmosis (FO); phosphorus recovery; digested sludge centrate; seawater; calcium phosphates.

1. Introduction

Phosphorus is a key element for all life on earth. Without the phosphorus in biological molecules such as ATP (or adenosine triphosphate) and DNA (or deoxyribonucleic acid), life would not be possible. Phosphorus can also be found in the minerals in bones and teeth. Thus, phosphorus is an essential part of the human diet and a vital element for plants. Indeed, food security is increasingly dependent on the availability of phosphate fertilisers. As natural phosphorus reserves continue to deplete, it is necessary to improve resource efficiency by investing in the recycling and recovery of phosphorus [1]. A considerable proportion of the phosphorus consumed by society ends up in municipal wastewater. In wastewater, phosphorus is a pollutant. When discharged to the environment, phosphorus can cause the widespread eutrophication of receiving waters. This has motivated the implementation of regulatory standards for phosphorus removal at wastewater treatment plants. Overall, the environmental and regulatory need for phosphorus removal, together with the non-renewable nature of phosphorus, give significant incentive for the wastewater treatment sector to recover phosphorus from wastewater [2-4].

A pragmatic option to supplement phosphorus resources is to recover it from wastewater, or more precisely from anaerobically digested sludge centrate. In a typical wastewater treatment plant, influent phosphorus is biologically accumulated in sludge. When sludge is anaerobically digested, orthophosphate is released and remains dissolved in the sludge centrate (i.e. supernatant). Digested sludge centrate can contain phosphate concentrations in the range of 75 – 300 mg/L, compared with about 8 mg/L present in influent wastewater [2]. The elevated phosphate concentration in digested sludge centrate presents significant opportunities for phosphorus recovery techniques to be readily integrated into current wastewater treatment infrastructure. Implementing phosphorus recovery can improve nutrient management at wastewater treatment plants. Nutrient rich digested sludge centrate is commonly returned to the head of the treatment plant, leading to the gradual build-up of phosphorus in the plant, decreasing the efficiency of wastewater treatment with respect to phosphorus removal [5]. More importantly, the build-up of phosphorus can also result in gradual struvite precipitation causing blockages and equipment scaling [6]. Thus, by recovering phosphorus from digested sludge centrate, phosphorus removal to comply with effluent discharge standards can be improved and costly maintenance due to blockages can be avoided. At the same time, phosphorus fertilisers can be produced.

Despite the benefits of phosphorus recovery from digested sludge centrate, there are several challenges to developing techniques that are both economically viable and environmentally friendly. Conventional techniques to precipitate agronomically suitable phosphate minerals are expensive and chemically intensive. For example, controlled precipitation of the slow-release fertiliser struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) requires the addition of magnesium in a significant quantity to exceed the stoichiometric ratio. The high cost of magnesium salts makes the conventional

struvite recovery process uneconomical and consumes more resources than are produced [7]. Indeed, primary drivers for most recently installed plants are to prevent struvite blockages and to enhance phosphorus removal. Calcium phosphate precipitates have gained recent attention as an alternative phosphate mineral to be recovered from wastewater, attributed to the simplicity, lower cost and easy acceptance into industrial fertiliser production [8]. Additionally, the initial phosphate concentration is the most important parameter that dictates the efficiency, thus cost effectiveness of a phosphorus recovery process. Therefore, phosphorus recovery can also be enhanced by firstly pre-concentrating the phosphate in digested sludge centrate [9, 10].

Pre-concentrating phosphate in digested sludge centrate can increase the precipitation kinetics of phosphorus mineral recovery. There have been several membrane-based techniques (e.g. membrane distillation and reverse osmosis) for mineral pre-concentration and subsequent recovery from saline industrial wastewaters [11, 12]. However, most of them are not suitable for digested sludge centrate given its high fouling propensity. One key technology with significant potential to perform this function is the osmotically driven membrane filtration process forward osmosis (FO). FO has a number of advantages when applied for the treatment of complex solutions including digested sludge centrate [10, 13], fracking fluid [14, 15], reverse osmosis brine [16], and landfill leachate [14]. FO membranes can retain more than 97% phosphate in digested sludge centrate [10, 13]. Furthermore, fouling in FO is mostly reversible, even with complex feed solutions [17]. The bi-directional transport phenomenon of FO is another important advantage. This leads to an increase in pH of the feed solution [10, 18], which is optimal for phosphate mineral precipitation. Additionally, the back diffusion of draw solutes can be utilised, thus, seawater can be applied as a draw solution as a potential additional source of calcium for calcium phosphate precipitation. These key attributes make FO possibly the most superior process to pre-concentrate digested sludge centrate for subsequent phosphorus recovery.

Recent demonstrations of FO to pre-concentrate nutrients prior to phosphate mineral precipitation have shown excellent potential to lower chemical requirements, increase precipitation kinetics, and improve the efficiency of phosphorus recovery from wastewater [4, 10, 13, 19-21]. Xie et al. [10] demonstrated struvite recovery from digested sludge centrate using a hybrid forward osmosis – membrane distillation system with $MgCl_2$ as the draw solution. In addition to providing favourable conditions for struvite precipitation (i.e. elevated ammonium and orthophosphate concentrations, and an elevated pH), the FO system supplied additional magnesium required for struvite precipitation by reverse draw magnesium flux. However, as noted above, a major drawback with the current approach for phosphorus recovery from digested sludge centrate via struvite precipitation is the need for costly magnesium addition. Furthermore, FO usually requires draw solution regeneration, thus, adding another significant cost component to the overall process.

Here, we demonstrate a novel seawater-driven FO technique to recover phosphorus from digested sludge centrate without any chemical addition and draw solute recovery. In this process, phosphate is retained in the digested sludge centrate by the FO membrane, and water is transferred to the seawater draw solution. The enrichment of phosphate, calcium, and magnesium ions, as well as a slightly alkaline condition in the digested sludge centrate allow phosphate minerals to spontaneously precipitate in the feed solution during the filtration process. This avoids the costs associated with calcium or magnesium addition, as well as pH adjustment – a critical requirement of conventional precipitation processes. In addition, the use of seawater as the draw solution eliminates the need for draw solute regeneration, thus providing an energetically favourable system. The process was evaluated in terms of nutrient pre-concentration efficiency, facilitation of phosphate mineral recovery, water flux dynamics, and membrane fouling.

2. Materials and methods

2.1. Forward osmosis system

A lab-scale, cross-flow FO membrane system with an effective membrane area of 123.5 cm² was used for all filtration experiments [22]. The FO membrane cell consisted of two symmetric flow channels each with a length, width, and height of 130, 95, and 2 mm, respectively. The feed and draw solutions were circulated through each flow channel by two variable speed gear pumps (Micropump, Vancouver, Washington, USA). Two rotameters regulated the circulation flow rate at 1 L/min, which corresponds to a cross-flow velocity of 9 cm/s. The feed solution reservoir was positioned on a digital balance (Mettler-Toledo Inc., Hightstown, New Jersey, USA) and weight changes were recorded to determine the permeate water flux during experiments.

A cellulose triacetate (CTA) membrane with embedded polyester screen support was used in this study, and was acquired from Hydration Technologies Innovation (HTI) (Albany, Oregon, USA). The membrane was operated in FO mode (i.e. active layer facing the feed solution).

2.2. Experimental protocol

The FO system was used to process digested sludge centrate until 80% water recovery had been achieved (approximately 3 days). The feed and draw (seawater) solutions had initial volumes of 3 and 10 L, respectively, and the system was operated in a closed loop arrangement. A large draw solution to feed solution volume ratio (i.e. V_{DS}/V_{FS}) was selected to minimise the effects of draw solution dilution, and feed solution concentration (i.e. approach of osmotic equilibrium) on water flux decline during experiments.

Water recovery (Rec) was used to represent the water extraction rate of the FO process for each filtration cycle and is defined by Equation 1. This was calculated based on the ratio of the cumulative permeate volume and the initial feed solution volume ($V_{f,0}$). Where A_m is the effective membrane area and J_w is the observed water flux at time t .

$$\text{Rec} = \frac{A_m \int_0^T J_w dt}{V_{f,0}} \quad (1)$$

Solution temperature, pH, and electrical conductivity were monitored throughout the duration of experiments. Samples of 20 mL were withdrawn from the feed and draw solutions at specific intervals for analysis. The rejection of nutrients by the FO membrane was calculated according to Equation 2 [23]. Where J_n is the solute flux (from feed to draw solution) and $c_{n,f}$ is the average concentration of nutrient in the feed solution.

$$R = 1 - \frac{J_n}{J_w c_{n,f}} \quad (2)$$

At the conclusion of the filtration cycle, the accumulated solids in the feed solution were collected by centrifuging the concentrated digested sludge centrate at $5,250 \times g$ at 20°C for 5 minutes. The solids were then dried in a desiccator at room temperature.

Water flux dynamics were investigated by determining the FO membrane water flux recoverability due to changes in solution osmotic pressure as well as due to membrane fouling. Firstly, at the end of the filtration cycle, the membrane was removed from the cell and was flushed with deionised water (DI) to remove the fouling layer. With the same feed and draw solutions, the membrane was returned to the cell and the flux recoverability due to membrane fouling was quantified. Next, to confirm the flux decline due to dilution of the draw solution, the feed solution was replaced with DI water, therefore excluding the feed solution osmotic pressure component. Lastly, the feed and draw solutions were replenished with fresh digested sludge centrate and seawater, and subsequent filtration cycles began. All experiments were conducted in duplicate.

2.3. Analytical methods

Key water quality parameters for the digested sludge centrate feed solution and seawater draw solution were measured according to standard methods. Phosphate and ammonia were analysed using Flow Injection Analysis (QuickChem 8500, Lachat, Loveland, CO). An inductively coupled plasma – optical emission spectroscopy (ICP-OES) system (ICP-OES 710, Agilent, Australia) was used to determine cation concentrations in the aqueous phase. Amounts of

phosphorus, calcium, magnesium, and potassium in the precipitate were determined by dissolving a known amount of precipitate in HNO₃ (5%) followed by ICP-OES analysis. Total organic carbon (TOC) and total nitrogen (TN) were measured using a TOC/TN analyser (TOC-V_{CSH}, Shimadzu, Kyoto, Japan). Temperature, pH, and electrical conductivity of solutions were monitored by an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Waltham, MA).

The obtained solids were characterised using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) (JOEL JSM-6490LV, Japan).

2.4. Digested sludge centrate and seawater

Digested sludge centrate was collected from a dewatering centrifuge at the Wollongong Water Recycling Plant (New South Wales, Australia). Seawater was collected from Wollongong (New South Wales, Australia), and was filtered by 0.5 µm paper filters prior to experiments. Key water quality parameters of the digested sludge centrate and seawater are provided in Table 1.

Table 1: Key physicochemical properties of seawater and digested sludge centrate (average ± standard deviation from triplicate measurements).

Parameters	Digested sludge centrate (FS)	Seawater (DS)
Total solids (g/L)	1.13 ± 0.01	36.80 ± 0.23
Electrical conductivity (mS/cm)	5.53 ± 0.05	53.65 ± 0.30
Osmotic pressure (as NaCl) (bar)	2.00 ± 0.02	26.80 ± 0.20
pH	8.03 ± 0.28	8.00 ± 0.01
Total organic carbon (mg/L)	589 ± 11	-
Total nitrogen (mg/L)	741 ± 21	-
Phosphate (mg/L)	88 ± 5	< 0.1
Calcium (mg/L)	63 ± 5	377 ± 13
Magnesium (mg/L)	14 ± 5	1,359 ± 10
Sodium (mg/L)	92 ± 4	10,366 ± 26
Potassium (mg/L)	106 ± 3	503 ± 6

2.5. Forward osmosis water flux model

Water flux dynamics were predicted using the established water flux model for FO membranes [24]. Specifically, as the FO system was operated in a closed loop, the effects of feed and draw solution osmotic pressure changes were scrutinised. The water flux in FO can be predicted using Equation 3, and considers the influence of internal concentration polarisation (ICP) in FO mode

operation (i.e. active layer facing the feed solution) [24]. Here, A is the membrane water permeability coefficient, B is the membrane draw solute permeability, and K_m is the mass transfer coefficient (i.e ratio of draw solute diffusion coefficient, D and membrane structural parameter, S (Equation 4)). The osmotic pressure of the feed and draw solutions are represented as π_{FS} and π_{DS} , respectively [25].

$$J_w = K_m \ln \left(\frac{A\pi_{DS} + B}{A\pi_{FS} + J_w + B} \right) \quad (3)$$

$$K_m = \frac{D}{S} \quad (4)$$

The key membrane transport parameters A , B , and S were determined using the protocol previously described by Cath et al. [25]. Details of the reverse osmosis system and procedure to determine A , B , and S are available elsewhere [26]. The experimentally determined values for A and B were 1.81×10^{-12} m/sPa and 6.94×10^{-8} m/sPa, respectively. The membrane S was 670 μ m.

Although the ionic composition of seawater is rather complex, it is dominated mostly by NaCl. Thus, for simplicity, the K_m of NaCl was adopted for calculations as opposed to seawater. OLI Stream Analyzer (OLI Systems, Inc., Morris Plains, New Jersey, USA) was used to determine the relationship between the concentration, conductivity, diffusivity, and osmotic pressure of NaCl. The dissolved salts in the digested sludge feed solution were also assumed to be made up of only NaCl. The filtration process was simulated by considering the effects of the loss or gain of permeate water on feed and draw solution osmotic pressure, thus water flux. In FO, water transport is driven by the osmotic pressure difference between the draw and feed solution. The influence of the bi-directional transport of ions on water flux is negligible. Thus, a simple mass balance of salt (NaCl) can be readily obtained to simulate the water flux and concentration of specific ions as a function of water recovery using equations 1-4.

2.6. Mineral species estimation

Visual MINTEQ (v. 3.0) was used as the chemical equilibrium model to estimate the mineral speciation of precipitates. Input data was based on experimentally determined values.

3. Results and discussions

3.1. Forward osmosis membrane nutrient rejection

Phosphate rejection was high under all experimental conditions (Figure 1A). It is noted that phosphate in the draw solution was below the detection limit, excluding the last measurement at

80% water recovery, which was less than 1 mg/L. The small decrease in phosphate rejection at 80% water recovery was probably due to analytical limitation. The high performance of the CTA-FO membrane can be attributed to the electrostatic repulsion between the negatively charged phosphate ions and the strong negative charge of the membrane at the working solution pH (i.e. between pH of 8.0 – 8.7) [20]. Steric hindrance (size exclusion) was also an important rejection mechanism, since phosphate has a large hydrated radius.

The FO membrane could also effectively retain calcium, magnesium, and potassium (Figure 1B – 2D). Since the seawater draw solution was allowed to dilute, the ion concentration gradually declined proportionally to the increase in volume. When there is no transfer of calcium and magnesium between the feed (sludge centrate) solution and draw (seawater) solution, as the draw solution becomes more diluted, their concentrations (i.e. $C_{Ca,DS}$ and $C_{Mg,DS}$) can be calculated by a mass balance. As can be seen in Figure 1B and 1C, the measured concentration of both calcium and magnesium in the draw solution are identical to their calculated values. In other words, calcium and magnesium in the sludge centrate feed were enriched as water was transferred into the draw solution. Results presented in Figure 1B and 1C also infer that reverse permeation of calcium and magnesium in seawater has minimal contribution towards supplementing feed solution concentrations. On the other hand, the experimental concentration of potassium in the draw solution declined at a discernibly faster rate than the calculated value (Figure 1D). Results in Figure 1D are consistent with the fact that FO membranes are more permeable to monovalent ions (e.g. potassium) than divalent ions (e.g. calcium and magnesium). The reverse permeation of sodium from seawater was also significant. While calcium, magnesium, and potassium can possibly interact with phosphate to form several kinds of phosphorus precipitates, there is no known sodium phosphorus precipitate. Thus, we do not show data related to sodium transport here. Overall, the rejection performance shown in Figure 1 suggests that the FO process can effectively pre-concentrate phosphate and other ions in digested sludge centrate.

The high rejection of the FO membrane and the closed loop operation led to the enrichment of phosphate, calcium, magnesium, and potassium in the feed solution. However, an increase in the feed solution concentration could only be observed for magnesium and potassium (Figure 1C and 1D). It appears that under the experimental conditions of this study, magnesium and potassium are not significantly involved in the precipitation of phosphate. Thus, magnesium and potassium concentrations steadily increased due to volume reduction of the feed solution. Magnesium was concentrated approximately by fivefold, in agreement with the rate of volume reduction and confirming the near complete rejection by the FO membrane. As discussed above, potassium enrichment in the feed solution was further augmented by the back diffusion of potassium from the seawater draw solution. It is noteworthy that phosphate and calcium concentrations in the feed sludge centrate did not increase as it was pre-concentrated (Figure 1A and 1B), despite their

high rejection by the FO membrane. Phosphate and calcium concentrations in the feed solution decreased overall, suggesting the spontaneous precipitation of calcium phosphate minerals during the filtration process.

Figure 1: Variation of feed solution and draw solution concentration, and FO membrane rejection of (A) PO_4^{3-} , (B) Ca^{2+} , (C) Mg^{2+} , and (D) K^+ during FO treatment of digested sludge centrate. The red solid lines ($C_{\text{Ca, DS}}$, $C_{\text{Mg, DS}}$, and $C_{\text{K, DS}}$) are the calculated Ca^{2+} , Mg^{2+} , and K^+ concentration in the draw solution, respectively. All calculations assume that the FO membrane retains 100% of Ca^{2+} , Mg^{2+} , and K^+ .

3.2. Phosphorus removal and recovery

3.2.1. Spontaneous precipitation of phosphate minerals

The enrichment of phosphate and calcium in digested sludge centrate by the FO process provides favourable conditions for spontaneous phosphate mineral formation. Throughout the experiment, the mass of phosphate and calcium in the feed solution drastically decreased from their initial values (Figure 2). This decline indicates their spontaneous precipitation out of solution, with flaky white solids clearly accumulating at the bottom of the feed solution tank. The mass of phosphate declined at a steady rate from 253 to 10 mg over the course of the experiment. The decline in phosphate coincided with a similar variation in calcium. Initially (i.e. between 0 – 25% water recovery), the mass of calcium in the feed decreased slightly. From 25% onwards, the

amount of calcium in the feed decreased gradually and eventually dissipated to below 10 mg. This suggests that the calcium presence actively induced the removal of phosphate through precipitation. The mass of magnesium in the feed solution slightly reduced during the initial stages of the experiment. This could indicate the incorporation of some magnesium into the precipitated solids. However, since the initial and final mass of magnesium in the feed solution are comparable, the uptake of magnesium is likely to be insignificant.

In addition to the sustained concentrative action of the FO process, the spontaneous precipitation of phosphate minerals was encouraged by the gradual increase in feed solution pH (Figure 2). The feed solution pH steadily increased from 8.0 – 8.7 during the experiment due to the diffusion of protons from the feed to the draw solution. This is an inherent phenomenon in FO [18, 27]. Here, the elevated pH further enhances the spontaneous precipitation of phosphate minerals, since calcium phosphate can readily precipitate at a slightly alkaline pH value. Overall, phosphorus removal occurred due to both the concentrative effects from FO membrane water extraction and the increase in the feed solution pH.

Figure 2: Variation of sludge centrate pH and the mass of PO₄³⁻, Ca²⁺, and Mg²⁺ in the feed solution during FO treatment of digested sludge centrate.

The seawater-driven FO process showed an excellent capacity to remove phosphate from digested sludge centrate. The total phosphate removal due to precipitation at the conclusion of the experiment was 92% (Figure 3), with only 4% of the initial phosphate content being lost to the draw solution, and 4% remaining in the feed solution. Phosphate removal increased as water recovery increased up to 65% (i.e. concentrated by three-fold). However, when the water recovery increased beyond 65%, phosphate removal reached a plateau value. This can be

explained by the deficiency of phosphate and calcium (i.e. both were less than 20 mg/L) in the sludge centrate, thus, lowering the precipitation efficiency from this point onwards. Furthermore, at a water recovery above 65%, phosphate removal by precipitation slightly declined, due to the breakthrough of phosphate through the FO membrane into the draw solution.

Figure 3: Indicative PO_4^{3-} removal by precipitation from digested sludge centrate during seawater-driven FO.

3.2.2. Recovered solids

SEM imaging shows a loose arrangement of mineral clusters and EDS analysis confirms that the recovered solids contain phosphorus and calcium (Figure 4A and 4B). Calculation of the saturation index (SI) of the initial digested sludge centrate solution using Visual MINTEQ showed the oversaturation of a number of possible calcium phosphate minerals, with hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) displaying the highest potential for precipitation (i.e. SI = 13.09). The increase of the solution pH to 8.7, alongside the five-fold concentration of nutrients in the feed solution, further increased the SI value for hydroxyapatite. Yet, the obtained solids were more likely to consist of amorphous calcium phosphate. This is due to the identification of carbon, oxygen, and magnesium in the solids, and indicates the incorporation of organic matter, as well as the co-precipitation of carbonate and magnesium in the solids [5]. The presence of magnesium [28], carbonate [29], and organic matter [30] was likely to inhibit the formation of hydroxyapatite in the digested sludge centrate. Nonetheless, despite the impact on hydroxyapatite formation, there was no discernible effect on phosphate removal. As can be seen in Figure 3, 92% of phosphate in the digested sludge centrate was removed via precipitation.

Despite the high phosphorus removal efficiency, elementary analysis (ICP-OES measurement of the precipitate dissolved in acid) of the obtained precipitate revealed that it only contained 3%

phosphorus (Figure 4C). This gives further evidence that the formation of calcium carbonate was prominent, and is likely to make up a significant portion of the solids. In other words, the mass percentage of phosphorus in the precipitate is rather small. **Given the high carbonate content of digested sludge centrate, additional processing may be required for the production of phosphorus fertilizer from the obtained precipitate.** However, the formation of calcium carbonate may have helped to improve the coagulation of phosphate precipitates [31].

Figure 4: (A) Scanning electron microscopic image, (B) energy dispersive X-ray spectrometry spectra, and (C) elementary composition of the recovered solids **(ICP-OES measurement of the precipitate dissolved in acid).**

3.3. Membrane fouling and water flux dynamics

The observed water flux decline in Figure 5 was mostly due to the decrease in osmotic pressure, as opposed to membrane fouling. The concentrative action of the feed solution caused an increase in osmotic pressure, whilst the dilution of the draw solution resulted in a decreased osmotic pressure (Figure 5A). These opposing effects together result in a gradual reduction of the effective osmotic pressure gradient (i.e. driving force) across the FO membrane, and therefore a negative effect on water flux. The feed solution salinity drives the loss of the osmotic driving force, particularly at high water recoveries (>70%) and is attributed to the high initial salinity of digested sludge centrate. As can be seen in Figure 5B, the simulated water flux (section 2.5) closely resembles the actual flux decline.

Membrane fouling was relatively small and was evidenced in the small difference between the simulated and actual water flux, particularly at high water recovery (Figure 5B). Nevertheless, membrane fouling was readily reversible. At 80% water recovery, after simply flushing the membranes surface, the component of flux decline due to membrane fouling was completely recovered. The actual water flux was the same as the simulated value (Figure 5B). Furthermore, after replacing the feed and draw solutions with fresh digested sludge centrate and seawater,

respectively, the initial water flux of subsequent cycles was also completely restored, thus, demonstrating the inherently low fouling propensity of FO. Results reported here is consistent with the literature. Due to absence of any hydraulic pressure and the low applied permeate water flux, which allows the fouling layer to be loose and fluid-like, fouling in FO is highly reversible [17]. The reversibility of membrane fouling in our experiment (Figure 5B) also confirms that the precipitate occurred in the bulk solution and did not induce scaling on the membranes surface.

Figure 5: (A) Simulated variation of feed and draw solution osmotic pressure resulting in the reduction of the osmotic driving force during closed-loop FO filtration (FS:DS volume = 3:10 L). (B) Simulated and experimental relative flux decline, with flux recoverability after membrane flushing and after replacing the feed and draw solutions. The experimental water flux was initially 6.4 L/m²h.

3.4. Implications

The reported data demonstrates that seawater-driven FO can recover phosphorus from digested sludge centrate without any additional chemical requirements and the need for draw solution regeneration. Phosphorus minerals spontaneously precipitate, as the FO membrane pre-concentrates the constituents already present in centrate, as well as elevating the solution pH. The use of seawater as the draw solution may negate the need to apply subsequent desalination processes, and therefore presents an energetically favourable system. The removal of phosphorus from digested sludge centrate also avoids the recycling of nutrients to the head of the treatment plant, thus preventing phosphorus build-up in plants and the associated blockages and equipment scaling. Importantly, the recovered solids containing phosphorus may be utilised as a raw material for phosphate fertiliser production.

During the FO process, a higher water recovery showed to improve phosphate removal from digested sludge centrate, however there is a limitation on the achievable phosphate removal efficiency. In this study, the highest phosphate recovery was achieved when the sludge centrate was pre-concentrated by three folds. At this point, the effects of osmotic pressure changes on water flux result in only a 30% reduction in the initial water flux. Adopting draw solutions with larger initial osmotic pressures, (i.e. seawater RO brine) is one option to improve system performance in terms of water flux enhancement. Similarly, a draw solution replenishment scheme can be investigated to optimise the trade-offs between the reduction in osmotic pressure due to seawater dilution, accumulation of contaminants in the draw solution, and pumping energy. Nevertheless, the overall restoration of water flux demonstrates the reversibility of membrane fouling and suitability of FO to pre-concentrate nutrients in digested sludge centrate.

4. Conclusion

In this study, we demonstrate a novel seawater-driven FO process to recover calcium phosphate from digested sludge centrate without any chemical addition and draw solute regeneration. The process was evaluated in terms of nutrient pre-concentration efficiency, facilitation of phosphate mineral recovery, water flux dynamics, and membrane fouling. The FO membrane effectively rejected phosphate and calcium, and led to their enrichment in the digested sludge centrate. The elevated nutrient concentrations and the gradual increase in pH due to the bi-directional transport of protons away from the sludge centrate, improved precipitation kinetics and promoted the spontaneous precipitation of calcium phosphate minerals in the digested sludge centrate. Up to 92% of the initial phosphate could be recovered from the digested sludge centrate as amorphous calcium phosphate solids. Membrane fouling did not significantly contribute to water flux decline, and was fully reversible after flushing the membrane with DI water. Overall, seawater driven FO presents a highly energetically favourable option for the sustainable management of digested sludge centrate. Nevertheless, further research is necessary to develop technique to enrich the phosphorus content in the obtained precipitate and to evaluate the economic viability of the proposed process.

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References

- [1] Withers, P.J.A., J.J. Elser, J. Hilton, H. Ohtake, W.J. Schipper, and K.C. van Dijk, Greening the global phosphorus cycle: how green chemistry can help achieve planetary P sustainability. *Green Chem.*, 2015. **17**(4): p. 2087-2099.
- [2] Desmidt, E., K. Ghyselbrecht, Y. Zhang, L. Pinoy, B. Van der Bruggen, W. Verstraete, K. Rabaey, and B. Meesschaert, Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques: A Review. *Crit. Rev. Env. Sci. Technol.*, 2014. **45**(4): p. 336-384.
- [3] Yuan, Z., S. Pratt, and D.J. Batstone, Phosphorus recovery from wastewater through microbial processes. *Curr. Opin. Biotechnol.*, 2012. **23**(6): p. 878-883.
- [4] Schütte, T., C. Niewersch, T. Wintgens, and S. Yüce, Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode. *J. Membr. Sci.*, 2015. **480**: p. 74-82.
- [5] de-Bashan, L.E. and Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Water Res.*, 2004. **38**(19): p. 4222-4246.
- [6] Le Corre, K.S., E. Valsami-Jones, P. Hobbs, and S.A. Parsons, Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Crit. Rev. Env. Sci. Technol.*, 2009. **39**(6): p. 433-477.
- [7] Bradford-Hartke, Z., J. Lane, P. Lant, and G. Leslie, Environmental Benefits and Burdens of Phosphorus Recovery from Municipal Wastewater. *Environ. Sci. Technol.*, 2015. **49**(14): p. 8611-8622.
- [8] Hermassi, M., C. Valderrama, J. Dosta, J.L. Cortina, and N.H. Batis, Evaluation of hydroxyapatite crystallization in a batch reactor for the valorization of alkaline phosphate concentrates from wastewater treatment plants using calcium chloride. *Chem. Eng. J.*, 2015. **267**: p. 142-152.
- [9] Tran, A.T.K., Y. Zhang, D. De Corte, J.B. Hannes, W. Ye, P. Mondal, N. Jullok, B. Meesschaert, L. Pinoy, and B. Van der Bruggen, P-recovery as calcium phosphate from wastewater using an integrated selectrodialysis/crystallization process. *J. Clean. Prod.*, 2014.
- [10] Xie, M., L.D. Nghiem, W.E. Price, and M. Elimelech, Toward Resource Recovery from Wastewater: Extraction of Phosphorus from Digested Sludge Using a Hybrid Forward Osmosis–Membrane Distillation Process. *Environ. Sci. Technol. Lett.*, 2014. **1**(2): p. 191-195.

- [11] Ali, A., C.A. Quist-Jensen, F. Macedonio, and E. Drioli, Application of membrane crystallization for minerals' recovery from produced water. *Membranes*, 2015. **5**(4): p. 772-792.
- [12] Quist-Jensen, C.A., F. Macedonio, and E. Drioli, Membrane crystallization for salts recovery from brine—an experimental and theoretical analysis. *Desalination Water Treat.*, (In Press).
- [13] Holloway, R.W., A.E. Childress, K.E. Dennett, and T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate. *Water Res.*, 2007. **41**(17): p. 4005-4014.
- [14] Coday, B.D., P. Xu, E.G. Beaudry, J. Herron, K. Lampi, N.T. Hancock, and T.Y. Cath, The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. *Desalination*, 2014. **333**(1): p. 23-35.
- [15] Xue-Mei, L., Z. Baolong, W. Zhouwei, X. Ming, S. Jianfeng, L.D. Nghiem, H. Tao, Y. Chi, L. Chunxia, and C. Gang, Water reclamation from shale gas drilling flow-back fluid using a novel forward osmosis–vacuum membrane distillation hybrid system. *Water Sci. Technol.*, 2014. **69**(5): p. 1036-1044.
- [16] Kazner, C., S. Jamil, S. Phuntsho, H.K. Shon, T. Wintgens, and S. Vigneswaran, Forward osmosis for the treatment of reverse osmosis concentrate from water reclamation: process performance and fouling control. *Water Sci. Technol.*, 2014. **69**(12): p. 2431-2437.
- [17] Shaffer, D.L., J.R. Werber, H. Jaramillo, S. Lin, and M. Elimelech, Forward osmosis: Where are we now? *Desalination*, 2015. **356**(0): p. 271-284.
- [18] Hancock, N.T. and T.Y. Cath, Solute Coupled Diffusion in Osmotically Driven Membrane Processes. *Environ. Sci. Technol.*, 2009. **43**(17): p. 6769-6775.
- [19] Qiu, G., Y.-M. Law, S. Das, and Y.-P. Ting, Direct and Complete Phosphorus Recovery from Municipal Wastewater Using a Hybrid Microfiltration-Forward Osmosis Membrane Bioreactor Process with Seawater Brine as Draw Solution. *Environ. Sci. Technol.*, 2015.
- [20] Xue, W., T. Tobino, F. Nakajima, and K. Yamamoto, Seawater-driven forward osmosis for enriching nitrogen and phosphorous in treated municipal wastewater: Effect of membrane properties and feed solution chemistry. *Water Res.*, 2015. **69**(0): p. 120-130.
- [21] Qiu, G. and Y.-P. Ting, Direct phosphorus recovery from municipal wastewater via osmotic membrane bioreactor (OMBR) for wastewater treatment. *Bioresour. Technol.*, 2014. **170**(0): p. 221-229.

- 472 [22] Ansari, A.J., F.I. Hai, W. Guo, H.H. Ngo, W.E. Price, and L.D. Nghiem, Selection of
473 forward osmosis draw solutes for subsequent integration with anaerobic treatment to
474 facilitate resource recovery from wastewater. *Bioresour. Technol.*, 2015. **191**: p. 30-36.
- 475 [23] Jin, X., C.Y. Tang, Y. Gu, Q. She, and S. Qi, Boric Acid Permeation in Forward Osmosis
476 Membrane Processes: Modeling, Experiments, and Implications. *Environ. Sci. Technol.*,
477 2011. **45**(6): p. 2323-2330.
- 478 [24] McCutcheon, J.R. and M. Elimelech, Influence of concentrative and dilutive internal
479 concentration polarization on flux behavior in forward osmosis. *J. Membr. Sci.*, 2006.
480 **284**(1-2): p. 237-247.
- 481 [25] Cath, T.Y., M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio,
482 A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, J. Lampi, L.D. Nghiem, M. Xie, and
483 N.Y. Yip, Standard Methodology for Evaluating Membrane Performance in Osmotically
484 Driven Membrane Processes. *Desalination*, 2013. **312**: p. 31-38.
- 485 [26] Xie, M., L.D. Nghiem, W.E. Price, and M. Elimelech, Relating rejection of trace organic
486 contaminants to membrane properties in forward osmosis: Measurements, modelling and
487 implications. *Water Res.*, 2014. **49**: p. 265-274.
- 488 [27] Xie, M., W.E. Price, and L.D. Nghiem, Rejection of pharmaceutically active compounds
489 by forward osmosis: Role of solution pH and membrane orientation. *Sep. Purif. Technol.*,
490 2012. **93**: p. 107-114.
- 491 [28] Ding, H., H. Pan, X. Xu, and R. Tang, Toward a Detailed Understanding of Magnesium
492 Ions on Hydroxyapatite Crystallization Inhibition. *Cryst. Growth Des.*, 2014. **14**(2): p.
493 763-769.
- 494 [29] Cao, X. and W. Harris, Carbonate and Magnesium Interactive Effect on Calcium
495 Phosphate Precipitation. *Environ. Sci. Technol.*, 2008. **42**(2): p. 436-442.
- 496 [30] Song, Y.-h., H.H. Hahn, E. Hoffmann, and P.G. Weidler, Effect of humic substances on
497 the precipitation of calcium phosphate. *J. Environ. Sci.*, 2006. **18**: p. 852-857.
- 498 [31] Ren, W., Z. Zhou, L.-M. Jiang, D. Hu, Z. Qiu, H. Wei, and L. Wang, A cost-effective
499 method for the treatment of reject water from sludge dewatering process using
500 supernatant from sludge lime stabilization. *Sep. Purif. Technol.*, 2015. **142**: p. 123-128.