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

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.

Disciplines

Engineering | Science and Technology Studies

Publication Details

Ansari, A. J., Hai, F. I., Price, W. E. & Nghiem, L. D. (2016). Phosphorus recovery from digested sludge centrate using seawater-driven forward osmosis. *Separation and Purification Technology*, 163 1-7.

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

3 Revised Manuscript Submitted to
4 *Separation Purification Technology*

5 Ashley J. Ansari¹, Faisal I. Hai¹, William E. Price², and Long D. Nghiem^{1,*}

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

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

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

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

40
41 **Keywords:** forward osmosis (FO); phosphorus recovery; digested sludge centrate; seawater;
42 calcium phosphates.

43 **1. Introduction**

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

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

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

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

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

103 Recent demonstrations of FO to pre-concentrate nutrients prior to phosphate mineral precipitation
104 have shown excellent potential to lower chemical requirements, increase precipitation kinetics,
105 and improve the efficiency of phosphorus recovery from wastewater [4, 10, 13, 19-21]. Xie et al.
106 [10] demonstrated struvite recovery from digested sludge centrate using a hybrid forward
107 osmosis – membrane distillation system with $MgCl_2$ as the draw solution. In addition to
108 providing favourable conditions for struvite precipitation (i.e. elevated ammonium and
109 orthophosphate concentrations, and an elevated pH), the FO system supplied additional
110 magnesium required for struvite precipitation by reverse draw magnesium flux. However, as
111 noted above, a major drawback with the current approach for phosphorus recovery from digested
112 sludge centrate via struvite precipitation is the need for costly magnesium addition. Furthermore,
113 FO usually requires draw solution regeneration, thus, adding another significant cost component
114 to the overall process.

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

127 **2. Materials and methods**

128 **2.1. Forward osmosis system**

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

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

140 **2.2. Experimental protocol**

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

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

$$151 \quad \text{Rec} = \frac{A_m \int_0^T J_w dt}{V_{f,0}} \quad (1)$$

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

$$157 \quad R = 1 - \frac{J_n}{J_w c_{n,f}} \quad (2)$$

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

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

171 **2.3. Analytical methods**

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

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

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

184 **2.4. Digested sludge centrate and seawater**

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

189 **Table 1:** Key physicochemical properties of seawater and digested sludge centrate (average ±
 190 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

191

192 **2.5. Forward osmosis water flux model**

193 Water flux dynamics were predicted using the established water flux model for FO membranes
 194 [24]. Specifically, as the FO system was operated in a closed loop, the effects of feed and draw
 195 solution osmotic pressure changes were scrutinised. The water flux in FO can be predicted using
 196 Equation 3, and considers the influence of internal concentration polarisation (ICP) in FO mode

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

$$202 \quad J_w = K_m \ln \left(\frac{A\pi_{DS} + B}{A\pi_{FS} + J_w + B} \right) \quad (3)$$

$$203 \quad K_m = \frac{D}{S} \quad (4)$$

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

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

219 **2.6. Mineral species estimation**

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

222 **3. Results and discussions**

223 **3.1. Forward osmosis membrane nutrient rejection**

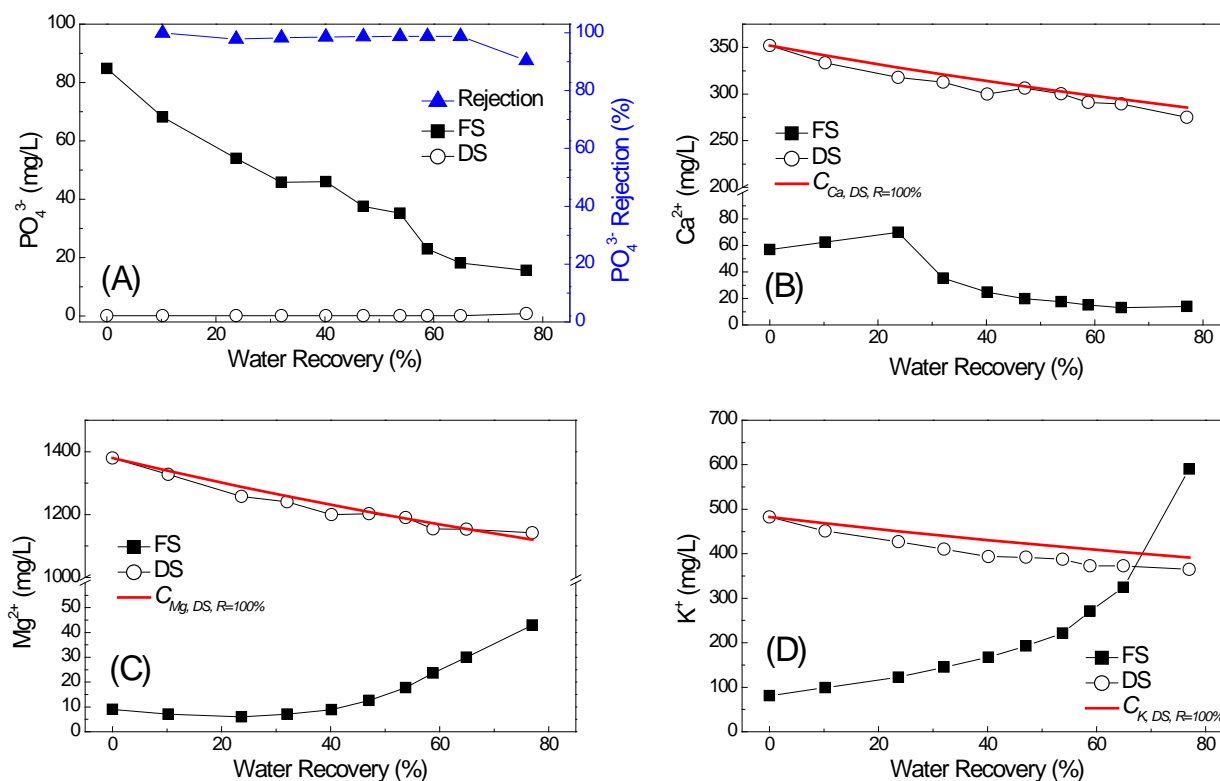
224 Phosphate rejection was **high** under all experimental conditions (Figure 1A). It is noted that
225 phosphate in the draw solution was below the detection limit, excluding the last measurement at

226 80% water recovery, which was less than 1 mg/L. **The small decrease in phosphate rejection at**
227 **80% water recovery was probably due to analytical limitation.** The high performance of the CTA-
228 FO membrane can be attributed to the electrostatic repulsion between the negatively charged
229 phosphate ions and the strong negative charge of the membrane at the working solution pH (i.e.
230 between pH of 8.0 – 8.7) [20]. Steric hindrance (size exclusion) was also an important rejection
231 mechanism, since phosphate has a large hydrated radius.

232 The FO membrane could also effectively retain calcium, magnesium, and potassium (Figure 1B –
233 2D). Since the seawater draw solution was allowed to dilute, the ion concentration gradually
234 declined proportionally to the increase in volume. When there is no transfer of calcium and
235 magnesium between the feed (sludge centrate) solution and draw (seawater) solution, as the draw
236 solution becomes more diluted, their concentrations (i.e. $C_{Ca,DS}$ and $C_{Mg,DS}$) can be calculated by a
237 mass balance. As can be seen in Figure 1B and 1C, the measured concentration of both calcium
238 and magnesium in the draw solution are identical to their calculated values. In other words,
239 calcium and magnesium in the sludge centrate feed were enriched as water was transferred into
240 the draw solution. Results presented in Figure 1B and 1C also infer that reverse permeation of
241 calcium and magnesium in seawater has minimal contribution towards supplementing feed
242 solution concentrations. On the other hand, the experimental concentration of potassium in the
243 draw solution declined at a discernibly faster rate than the calculated value (Figure 1D). Results
244 in Figure 1D are consistent with the fact that FO membranes are more permeable to monovalent
245 ions (e.g. potassium) than divalent ions (e.g. calcium and magnesium). The reverse permeation of
246 sodium from seawater was also significant. While calcium, magnesium, and potassium can
247 possibly interact with phosphate to form several kinds of phosphorus precipitates, there is no
248 known sodium phosphorus precipitate. Thus, we do not show data related to sodium transport
249 here. Overall, the rejection performance shown in Figure 1 suggests that the FO process can
250 effectively pre-concentrate phosphate and other ions in digested sludge centrate.

251 The high rejection of the FO membrane and the closed loop operation led to the enrichment of
252 phosphate, calcium, magnesium, and potassium in the feed solution. However, an increase in the
253 feed solution concentration could only be observed for magnesium and potassium (Figure 1C and
254 1D). It appears that under the experimental conditions of this study, magnesium and potassium
255 are not significantly involved in the precipitation of phosphate. Thus, magnesium and potassium
256 concentrations steadily increased due to volume reduction of the feed solution. Magnesium was
257 concentrated approximately by fivefold, in agreement with the rate of volume reduction and
258 confirming the near complete rejection by the FO membrane. As discussed above, potassium
259 enrichment in the feed solution was further augmented by the back diffusion of potassium from
260 the seawater draw solution. It is noteworthy that phosphate and calcium concentrations in the
261 feed sludge centrate did not increase as it was pre-concentrated (Figure 1A and 1B), despite their

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



265
 266 **Figure 1:** Variation of feed solution and draw solution concentration, and FO membrane
 267 rejection of (A) PO₄³⁻, (B) Ca²⁺, (C) Mg²⁺, and (D) K⁺ during FO treatment of digested sludge
 268 centrate. The red solid lines ($C_{Ca,DS}$, $C_{Mg,DS}$, and $C_{K,DS}$) are the calculated Ca²⁺, Mg²⁺, and K⁺
 269 concentration in the draw solution, respectively. All calculations assume that the FO membrane
 270 retains 100% of Ca²⁺, Mg²⁺, and K⁺.

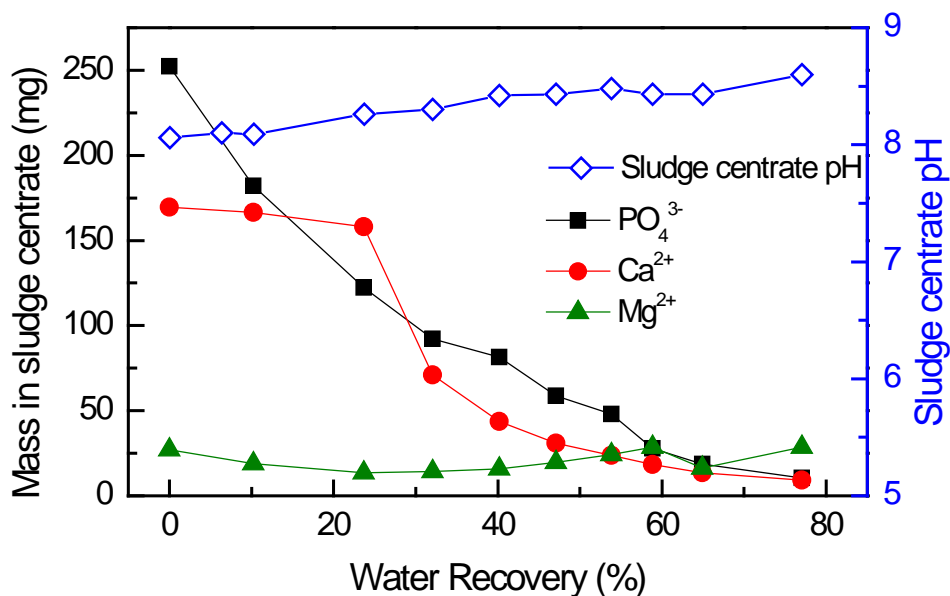
271 3.2. Phosphorus removal and recovery

272 3.2.1. Spontaneous precipitation of phosphate minerals

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

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

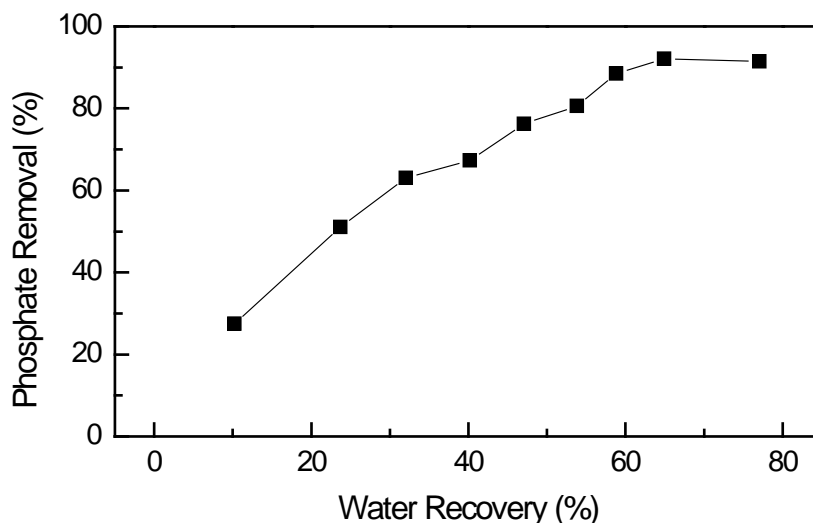
287 In addition to the sustained concentrative action of the FO process, the spontaneous precipitation
 288 of phosphate minerals was encouraged by the gradual increase in feed solution pH (Figure 2).
 289 The feed solution pH steadily increased from 8.0 – 8.7 during the experiment due to the diffusion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



295
 296 **Figure 2:** Variation of sludge centrate pH and the mass of PO₄³⁻, Ca²⁺, and Mg²⁺ in the feed
 297 solution during FO treatment of digested sludge centrate.

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

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



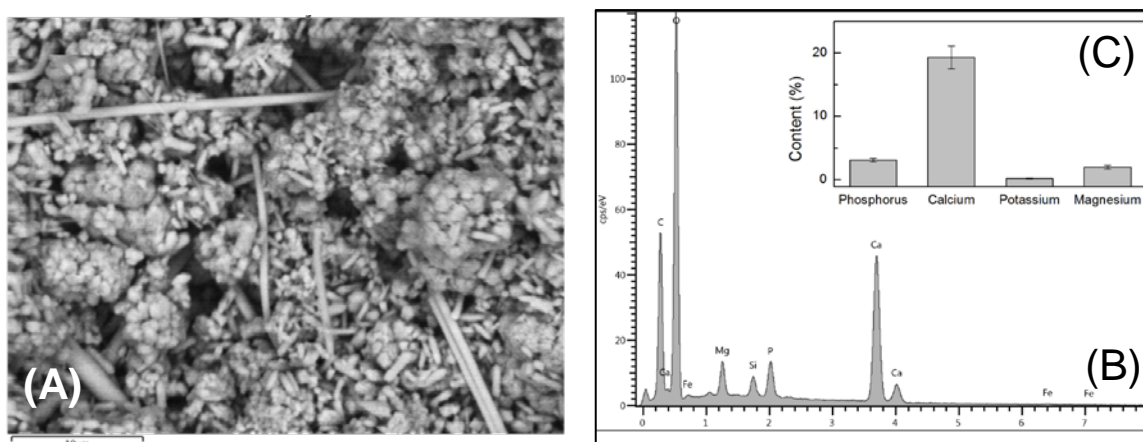
308
309 **Figure 3:** Indicative PO_4^{3-} removal by precipitation from digested sludge centrate during
310 seawater-driven FO.

311 3.2.2. Recovered solids

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

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

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



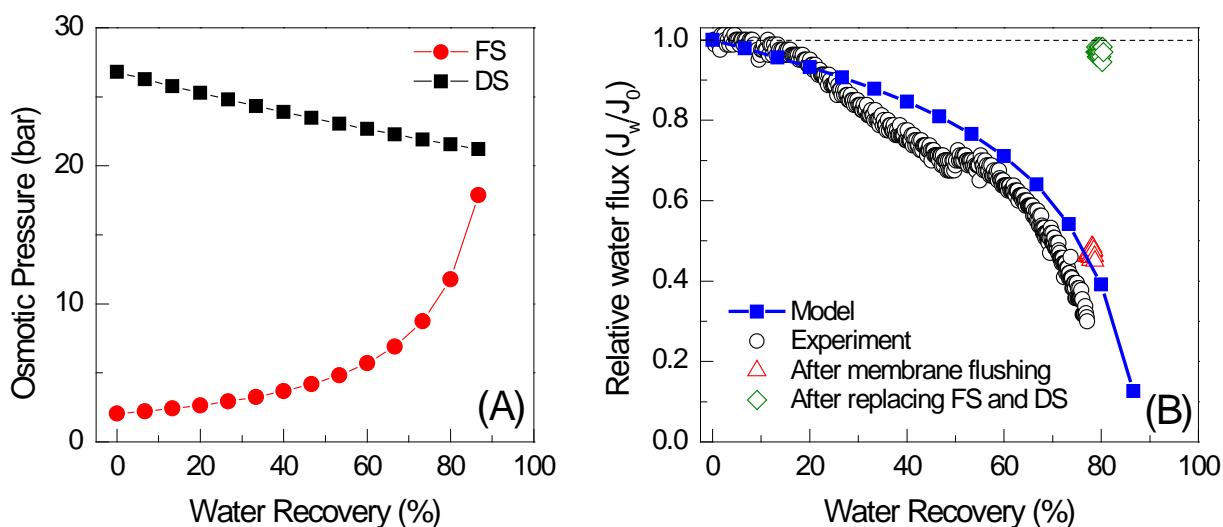
334
335 **Figure 4:** (A) Scanning electron microscopic image, (B) energy dispersive X-ray spectrometry
336 spectra, and (C) elementary composition of the recovered solids (ICP-OES measurement of the
337 precipitate dissolved in acid).

338 3.3. Membrane fouling and water flux dynamics

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

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

354 respectively, the initial water flux of subsequent cycles was also completely restored, thus,
 355 demonstrating the inherently low fouling propensity of FO. Results reported here is consistent
 356 with the literature. Due to absence of any hydraulic pressure and the low applied permeate water
 357 flux, which allows the fouling layer to be loose and fluid-like, fouling in FO is highly reversible
 358 [17]. The reversibility of membrane fouling in our experiment (Figure 5B) also confirms that the
 359 precipitate occurred in the bulk solution and did not induce scaling on the membranes surface.



360
 361 **Figure 5:** (A) Simulated variation of feed and draw solution osmotic pressure resulting in the
 362 reduction of the osmotic driving force during closed-loop FO filtration (FS:DS volume = 3:10 L).
 363 (B) Simulated and experimental relative flux decline, with flux recoverability after membrane
 364 flushing and after replacing the feed and draw solutions. The experimental water flux was
 365 initially 6.4 L/m²h.

366 3.4. Implications

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

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

388 **4. Conclusion**

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

404 **Acknowledgments**

405 This research was supported under Australian Research Council's Discovery Project funding
406 scheme (project DP140103864). Scholarship support to Ashley Ansari by the University of
407 Wollongong is gratefully acknowledged. The authors wish to thank Stewart Ramsay and his team
408 at the Wollongong Water Recycling Plant for their logistic support.

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