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## Microbial electrolysis followed by chemical precipitation for effective nutrients recovery from digested sludge centrate in WWTPs

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**Microbial Electrolysis Followed by Chemical Precipitation for Effective Nutrients  
Recovery from Digested Sludge Centrate in WWTPs**

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27 **Abstract**

28 A two-step sidestream process was investigated for nitrogen (N) and phosphorous (P) recovery  
29 from digested sludge centrate. In the first step, a dual-chamber microbial electrolysis cell (MEC)  
30 was used for N recovery on the cathode. In the second step, P was recovered as solid precipitates  
31 by the addition of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  salts in the anodic effluent. The operation of MEC with centrate  
32 indicate that N transport from the anode to the cathode chamber is primarily driven by anodic  
33 electron transport rather than diffusional transport. Low concentration of readily biodegradable  
34 organics in centrate significantly hindered current density ( $<0.15 \text{ A/m}^2$ ) and led to trivial N  
35 recovery on the cathode chamber. The addition of primary sludge fermentation liquor (25 vol%)  
36 with centrate as an exogenous source of readily biodegradable organics substantially increased  
37 current density up to  $6.4 \text{ A/m}^2$ , along with high TAN removal efficiency of  $53\pm 5\%$ . The energy  
38 requirement was calculated at  $5.8\pm 0.1 \text{ kWh/kg-TAN}$ ; however, the recovered  $\text{H}_2$  gas from the  
39 cathode was adequate to offset this energy input completely. The addition of  $\text{Ca}^{2+}$  salt at a Ca: P  
40 molar ratio of 3:1 was optimum for P recovery from the anodic effluent; Mg: P molar ratio of 2:1  
41 was found to be optimum for  $\text{Mg}^{2+}$  salt addition. However, optimum doses of both salts resulted  
42 in maximum P recovery efficiency of  $\sim 85\%$ , while  $\text{Mg}^{2+}$  addition provided an additional 38%  
43 TAN removal. These results demonstrate that microbial electrolysis followed by chemical  
44 precipitation can promote sustainable nutrients recovery from centrate at municipal wastewater  
45 treatment plants where sludge fermentation has already been adopted to provide readily  
46 biodegradable carbon source in the biological nutrient removal process.

47

48 **Keywords:** Digested sludge centrate; Chemical precipitation; Microbial electrolysis cell;  
49 Nitrogen and Phosphorous recovery; Sidestream process; Sludge fermentation liquor

## 50 **1. Introduction**

51 Anaerobic digestion for bio-methane production is one of the most popular approaches for  
52 sewage sludge management in centralized wastewater treatment facilities. During the anaerobic  
53 digestion process, a substantial amount of inorganic nutrients (primarily nitrogen and  
54 phosphorous) is released due to the hydrolysis of particulate organics [1–4]. Anaerobic  
55 methanogenic microbiome usually lacks adequate autotrophic metabolism of inorganic nutrients;  
56 hence, the liquid effluents from digesters contain a high concentration of these nutrients [1–4]. In  
57 many municipal wastewater treatment plants (WWTPs), digested sludge centrate is  
58 recycled back to the aerobic biological treatment process (i.e., activated sludge process), which  
59 leads to a significant increase in aeration cost due to 15-20% additional nitrogen (N) load  
60 depending on the influent wastewater characteristics [4,5]. Moreover, the extra load imposed by  
61 centrate may cause the effluent quality to exceed effluent regulatory limits of nutrient  
62 constituents [4].

63 The energy required for N removal in conventional two-stage nitrification-denitrification  
64 process is estimated to be 12.5 kWh/kg-N, while emerging anaerobic ammonia oxidation process  
65 (Anammox<sup>®</sup>) requires about 4.2 kWh/kg-N [6,7]. These biological treatment processes primarily  
66 remove N, while it would be more sustainable to recover N from concentrated wastewater stream  
67 like digested sludge centrate. There is a recognized market-value of nutrients available in  
68 digested sludge centrate. Currently, the Haber-Bosch process is widely used for  
69 ammonia synthesis for various industrial applications [8–10], which require high energy input of  
70 10-12.5 kWh/kg-N. Additionally, a significant portion of the phosphorus (P) used for agriculture  
71 and other industrial application is obtained by mining, while the global reserve of minable  
72 phosphate is expected to be depleted by the end of the twenty-first century [8]. Hence, there has

73 been a growing interest in developing effective processes for N and P recovery from centrate,  
74 which can eventually reduce the combined load of nutrients to the mainstream treatment process  
75 [4,5]. Different sidestream processes studied for N and P recovery from digested sludge centrate  
76 includes direct stripping, ion exchange, electrodialysis, chemical precipitation and microbial  
77 electrochemical technologies [1,3–5,10–15]. Most of these processes focus on recovery of one  
78 constituent (either N or P). Ammonia stripping with acid absorption for ammonium sulfate  
79 production has been proven to be an efficient method for N recovery, while high energy demand  
80 (~28 kWh/kg-N) is one of the major barriers to its widescale adoption [10]. Recovery of  
81 ammonia nitrogen using ion exchange resins has often been ruled out due to high regeneration  
82 cost as well as deterioration of their ion exchange capacities after multiple regeneration cycles  
83 [11]. Electrodialysis (ED), an emerging process which deploys a series of ion exchange  
84 membranes with applied electric potential, can efficiently recover N from various wastewater  
85 streams [4,10]. A recent study by Ward et al.[10] reported that the electrodialysis system could  
86 attain concentrated ammonium-N solution from digester sludge centrate with a relatively lower  
87 energy input of  $4.9 \pm 1.5$  kWh/kg-N. However, frequent cleaning of multiple membrane modules  
88 remained a concern, as membrane fouling can lead to higher energy inputs.

89         Chemical precipitation of nutrients as struvite (magnesium ammonium phosphate) from  
90 various wastewater stream has been predominantly investigated for P recovery. Recovered  
91 struvite can be directly utilized as a slow-release fertilizer [4,14,16,17]. Along with the addition  
92 of magnesium ( $Mg^{2+}$ ) salt, struvite process may consume a significant amount of base chemicals  
93 due to the requirement of high pH conditions for struvite precipitation [13]. Struvite process can  
94 provide up to 90% P recovery from wastewater with minimal N removal: theoretically, per gram  
95 of P removal as struvite removes 0.45 gram of N [4]. In comparison with struvite, only a few

96 studies reported efficient P recovery as calcium phosphate (CaP) from digested sludge centrate  
97 [15,18]. To the best of our knowledge, to date, no studies have compared P recovery efficiencies  
98 as struvite and calcium phosphate.

99         Microbial electrochemical systems, such as microbial electrolysis cells (MECs) and  
100 microbial fuel cells (MFCs), have recently received much attention for energy neutral wastewater  
101 treatment and value-added resources recovery [19,20]. Studies have also demonstrated that  
102 microbial electrochemical systems can simultaneously recover nutrients from wastewater, which  
103 makes them more attractive over other nutrients recovery technologies [21–26]. In dual-chamber  
104 microbial electrochemical systems having cation exchange membrane (CEM), efficient cathodic  
105 nitrogen recovery could be attained due to ammonium transport from the anode to the cathode  
106 chamber for meeting charge neutrality [23,24]. Thus, a concentrated ammonia nitrogen solution  
107 can be recovered from the cathode. Additionally, a few studies demonstrated that cathodic proton  
108 consumption for H<sub>2</sub> production in MEC might lead to highly alkaline local pH near the cathode  
109 which facilitates struvite precipitation on the cathode surface [22,27]. Interestingly, most of these  
110 studies primarily focused on nutrients recovery from source-separated urine [22–24,27–31]. In  
111 contrast, microbial electrochemical systems for nutrients recovery from digested sludge centrate  
112 has been rarely investigated. A recent study by Yuan and Kim [13] reported that a small  
113 concentration of readily biodegradable organics in digested sludge centrate resulted in low current  
114 density and inferior cathodic nutrients recovery in a MEC. Thus, inadequate readily biodegradable  
115 organics could be a possible reason that made digested sludge centrate a relatively unattractive  
116 stream for nutrients recovery with microbial electrochemical systems. Therefore, the development  
117 of an efficient engineering strategy to improve current density and nutrients recovery from centrate

118 would be essential to promote the microbial electrochemical system as a sidestream process for  
119 centrate, and thereby reduce nutrients load to mainstream biological process.

120 It is apparent that none of the abovementioned technologies can be used as a standalone  
121 process for simultaneous N and P recovery from digested sludge centrate. More efforts in  
122 developing integrated processes are required to promote sustainable nutrients recovery from  
123 centrate. Herein, a dual-chamber MEC having CEM followed by chemical precipitation was  
124 investigated as an integrated process for N and P recovery from digested sludge centrate  
125 collected from a full-scale municipal WWTP. First, primary sludge fermentation liquor was  
126 assessed as a supplementary source of readily biodegradable organics for enhancing  
127 electrochemical performance of MEC and ensuring efficient recovery of ammonium nitrogen on  
128 the cathode chamber. Second, the effluent from MEC was further assessed for P recovery  
129 through chemical precipitation with the addition of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salts. The overall goal of this  
130 current study was to determine if this integrated process of microbial electrolysis followed by  
131 chemical precipitation with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  could lead to a technically viable option for nutrients  
132 recovery from digested sludge centrate in municipal WWTPs.

## 133 **2. Materials and methods**

### 134 **2.1 MEC operation for nitrogen removal and recovery**

135 A bench-scale dual-chamber MEC constructed from plexiglass was used in this study. The  
136 design of MEC is similar to the one previously described by Zakaria et al. [32]. Briefly  
137 describing the design, the working volumes of anode and cathode chambers were 400 mL and  
138 140 mL, respectively (see Fig. 1a). A photograph of the MEC is provided in the Supplementary  
139 Information. Bundles of carbon fibers (2293-A, 24A Carbon Fiber, Fibre Glast Development  
140 Corp., Ohio, USA) integrated with a stainless-steel frame was used as the anode electrode.



141 Carbon fibers were pretreated according to a method previously described by Dhar et al. [33]. A  
142 stainless-steel mesh (Type 304, McMaster Carr, OH, USA) was used as the cathode electrode.  
143 In this study, the anode and cathode chambers were separated by a CEM (CMI-7000,  
144 Membranes International Inc, USA). Ag/AgCl reference electrode (MF-2052, Bioanalytical  
145 System Inc., WestLafayette, IN, USA) was placed within ~1 cm of the anode electrode. The  
146 anode potential was set at -0.4 V vs. Ag/AgCl using a multi-channel potentiostat system  
147 (Squidstat Prime, Admiral Instruments, Phoenix, AZ, USA) throughout the experiment. Effluent  
148 from a mother MEC was used as the inoculum for the enrichment of anode biofilms as  
149 previously reported by Zakaria et al. [32] and 25 mM of sodium acetate medium supplemented  
150 mineral nutrients, and 50 mM phosphate buffer served as the substrate for the enrichment of  
151 anode biofilms. The detailed composition of the mineral nutrients can be found in the literature  
152 [33]. The MEC was operated at room temperature ( $22\pm 1^\circ\text{C}$ ), and both the anolyte and catholyte  
153 were continuously mixed at  $130\pm 10$  rpm with magnetic stirrers.

154 During the enrichment process of anodic biofilms, MEC was operated in semi-continuous  
155 mode (i.e., 180 mL of fresh substrate medium was fed to the anode chamber using a syringe on a  
156 daily basis) until a repeatable peak current of  $10.4\pm 0.9$  A/m<sup>2</sup> was observed. Then, nitrogen  
157 recovery experiments were conducted with digested sludge centrate, centrate supplemented with  
158 exogenous readily biodegradable organics (acetate and ethanol), and centrate mixed with primary  
159 sludge fermentation liquor (see Fig. 1b). During Cycle-1 and 2, MEC was operated with real  
160 digested centrate. Anaerobic digester sludge was collected from a full-scale mesophilic  
161 anaerobic digester at the Gold Bar Wastewater Treatment Plant, Edmonton, Alberta, Canada.  
162 Anaerobic digester sludge was centrifuged at 18,670xg for 30 min, and the centrate was collected  
163 for experiments. During Cycle-3, 4, and 5, MEC was operated with centrate supplemented with

164 three different concentrations of exogenous readily biodegradable organics (435, 860, and 1355  
165 mg COD/L, respectively). A mixture of acetate and ethanol (COD ratio of 1:1) was used as  
166 exogenous readily biodegradable organics. During Cycle-6 and 7, MEC was operated with a  
167 mixture of digested sludge centrate (75 vol%) and liquor from primary sludge fermentation (25  
168 vol%). For sludge fermentation experiment, primary sludge was collected from Gold Bar  
169 Wastewater Treatment Plant, Edmonton, Alberta, Canada. The fermentation experiment was  
170 performed in a bench-scale glass anaerobic bioreactor (working volume of 2 L) equipped with a  
171 stirring shaft. The sludge was sparged with ultra-pure nitrogen gas (99.999%) for three minutes.  
172 The fermentation process was operated for 7 days at room temperature ( $22\pm 1^\circ\text{C}$ ), and the reactor  
173 media was stirred with a mixer at 300 rpm. After 7 days of operation, fermented sludge was  
174 centrifuged at  $18,670\times g$  for 30 min, and the supernatant (i.e., fermentation liquor) was collected  
175 and used for experiments (Cycle-6 and 7). Table 1 shows the average characteristics of centrate,  
176 primary sludge, and fermentation liquor. All experiments were conducted in fed-batch mode.  
177 Before each cycle, the cathode chamber was evacuated completely and cleaned multiple times  
178 with tap water to remove any residual ammonium that can influence the results of the following  
179 cycle.

## 180 **2.2 Chemical precipitation experiments for P recovery**

181 We performed nutrients precipitation experiments with anodic effluent collected during Cycle-5.  
182 The average soluble reactive phosphorous (SRP) and total ammonia-nitrogen (TAN)  
183 concentrations in the effluent were  $1387\pm 51$  mg/L and  $451\pm 15$  mg/L, respectively. For  
184 precipitation experiments, specific amounts of  $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$  or  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  salts are added into  
185 centrifuge vials having 50 mL of anodic effluent samples. The corresponding molar ratios of Ca  
186 to P and Mg to P are summarized in Table 2. These ratios were selected based on the possible

187 precipitation of  $\text{Ca}_3(\text{PO}_4)_2$  or  $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$  and struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), respectively, as  
188 previously suggested in the literature [34,35]. Phosphorous precipitation tests with  $\text{Ca}^{2+}$  salt was  
189 performed without any pH adjustment; pH of the anode effluent was 6.8. In contrast,  
190 precipitation tests with  $\text{Mg}^{2+}$  salt were carried out at two different pH (6.8 and 8.6); pH was  
191 adjusted to 8.6 using 3M NaOH. After addition of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  salts, vials were tightly capped,  
192 and liquids were mixed with a vortex mixer for 2 minutes. After 4 hours of settling period, vials  
193 were centrifuged at 18,670xg for 30 min, and solid precipitates were collected. The solid  
194 precipitates were examined for elemental composition, and supernatant samples were analyzed  
195 for COD, TAN, and SRP concentrations. All experiments were conducted at room temperature  
196 ( $22 \pm 1^\circ\text{C}$ ).

### 197 **2.3 Analytical methods**

198 Applied voltage and current were recorded every five minutes in a computer using Squidstat  
199 User Interface software (Squidstat Prime, Admiral Instruments, USA). COD, TAN, and SRP  
200 concentrations were measured using HACH reagent kits (HACH, Loveland, Colorado, USA).  
201 For analysis of soluble parameters, samples were filtered with 0.45  $\mu\text{m}$  nylon syringe filter. pH  
202 was measured using a bench-top pH meter (Accumet AR15, Fisher Scientific, Pittsburgh, PA,  
203 USA), and solution conductivities were measured using a portable conductivity meter (Extech  
204 EC100, EXTECH Instruments, USA). The concentrations of VFAs (acetate, propionate, and  
205 butyrate) were measured using an ion chromatograph (Dionex ICS-2100, Dionex, Sunnyvale,  
206 CA) equipped with an electrochemical detector (ECD) and microbore AS19 column. The  
207 elemental composition of the solid precipitates was examined with scanning electron microscopy  
208 (SEM) with energy dispersive X-ray spectroscopy (EDX). For analysis of the elemental  
209 composition, solid precipitates were air dried and mounted on SEM stubs. Then, the samples

210 were sputter coated with gold and examined using SEM (Zeiss Sigma 300 VP-FESEM, Carl  
211 Zeiss, Cambridge, UK).

## 212 **2.4 Calculations and economic assessment**

213 Current density was calculated based on the projected area of membrane ( $0.0038 \text{ m}^2$ ), as  
214 previously described in the literature [9,33,36]. The anodic TAN removal efficiency was  
215 calculated from the difference in initial and final TAN concentration of the anodic liquid during  
216 a fed-batch cycle. The cathodic TAN recovery efficiency was calculated from the amount of  
217 TAN accumulated in the cathode chamber and the amount of TAN removed from the anode  
218 chamber during a fed-batch cycle. A preliminary economic assessment for MEC was performed  
219 based on per kg TAN removal from centrate. Average experimental results from Cycle-6 and 7  
220 was used for these calculations. Electrical energy input (kWh) to MEC for an entire fed-batch  
221 cycle was computed from the current and applied voltage data recorded with time, as previously  
222 described in the literature [37]. The cost of electrical energy input and monetary value of  $\text{H}_2$   
223 produced from MEC were estimated at  $\$0.07/\text{kWh}$  and  $\$8/\text{kg-H}_2$ , respectively [38,39].

## 224 **3. Results and discussion**

### 225 **3.1 N recovery from centrate**

#### 226 **3.1.1 N recovery and current density from centrate**

227 Fig. 2a shows current density with time during MEC operated with digested sludge  
228 centrate (Cycle-1 and 2). The peak current densities from MEC in both cycles (Cycle-1:  $0.11$   
229  $\text{A}/\text{m}^2$ ; Cycle 2:  $0.13 \text{ A}/\text{m}^2$ ) were substantially lower than the peak current density of  $10.4 \pm 0.9$   
230  $\text{A}/\text{m}^2$  observed with  $25 \text{ mM}$  sodium acetate medium during enrichment of anode biofilms,  
231 indicating that current density was limited due to the lack of readily biodegradable organics

232 in centrate. As expected, a major portion of SCOD in centrate was unutilized by anodic  
233 microbial communities (Fig. 2b); SCOD removal efficiencies were ranged from 14% (Cycle-1)  
234 to 26% (Cycle-2). After the operation of both cycles, TAN concentrations in the anode chamber  
235 remained almost unchanged (Fig. 2c), while TAN concentration slightly increased in the cathode  
236 chamber (Fig. 2d). Thus, it is possible that additional ammonia nitrogen has been released  
237 through hydrolysis of particulate organics in the anode chamber. In MECs, ammonium transport  
238 through CEM comprises of migration (driven by electric field) and diffusion (driven by  
239 concentration gradient) mechanisms [23,24]. A few studies previously suggested that alkaline  
240 pH (~8.8) and high TAN levels in source-separated urine (>3 g/L) might trigger diffusional  
241 ammonium transport from the anode to the cathode chamber [23,24]. In contrast, the results of  
242 this current study demonstrated that migration would be the primary mechanism for ammonium  
243 transport from centrate possibly due to relatively lower pH (~7.9) and TAN level (~1 g/L).  
244 Therefore, increasing current density in MEC would be crucial to enhance ammonium migration  
245 to the cathode chamber.

### 246 **3.1.2 Enhanced N recovery from centrate supplemented with exogenous electron donors**

247 In response to the addition of exogenous readily biodegradable organics at different  
248 concentrations, current densities in MEC noticeably increased as compared to centrate alone  
249 (Fig. 3a). The peak current densities in Cycle-3, 4, and 5 were 2.4, 8.4, and 9.4 A/m<sup>2</sup>,  
250 respectively. Anodic TAN concentrations were observed to decrease as current densities  
251 increased (Fig. 3b). The addition of readily biodegradable organics at high concentrations  
252 (Cycle-4: 860 mg SCOD/L; Cycle-5: 1355 mg SCOD/L) showed a considerable decrease in  
253 anodic TAN concentrations. During Cycle 4 and Cycle-5, TAN concentrations in the anode  
254 chamber decreased from 1165 and 1178 mg/L to 594 and 456 mg/L, respectively; and TAN

255 concentrations in the cathode chamber increased up to 1152 mg/L (Cycle-4) and 1537 mg/L  
256 (Cycle-5), respectively (Fig. 3c). Thus, anodic TAN removal efficiencies were 49% (Cycle-4)  
257 and 61% (Cycle-5). Correspondingly, TAN fluxes through the membrane during these cycles  
258 were 13 g-TAN/m<sup>2</sup>-d (Cycle-4) and 18 g-TAN/m<sup>2</sup>-d (Cycle-5). However, transported ammonium  
259 recovery efficiencies on the cathode were 70% (Cycle-4) and 73% (Cycle-5). A portion of the  
260 transported ammonium (27-30%) were possibly lost through stripping as ammonia gas due to the  
261 highly alkaline cathodic pH (~12) as a result of proton reduction to H<sub>2</sub> gas on the cathode  
262 ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ). The detailed pH profiles are provided in the Supplementary Information. In  
263 comparison, low concentration of exogenous readily biodegradable organics (Cycle-3: 435 mg  
264 SCOD/L) exhibited relatively lower N recovery efficiency. As shown in Fig. 3d, a substantial  
265 decrease in SCOD concentrations were observed in comparison with MEC operation with  
266 digested sludge centrate alone, indicating the lower biodegradability of residual organics in  
267 digested centrate. As expected, there was no change in SRP concentrations due to the use of  
268 CEM (Fig. 3e). Overall, these results support that the addition of exogenous readily  
269 biodegradable organics favored current density and nitrogen recovery from digested centrate.

### 270 **3.1.3 Efficient N recovery from centrate supplemented with sludge fermentation liquor**

271 Because the addition of exogenous readily biodegradable organics improved current density and  
272 N recovery, primary sludge fermentation liquor was assessed as a potential source of readily  
273 biodegradable organics (Cycle-6 and 7) (Fig. 4). The TAN and SRP concentrations in digested  
274 sludge centrate were not substantially diluted by the addition of fermentation liquor (25% by  
275 volume). The operation of MEC with a mixture of centrate and fermentation liquor exhibited  
276 peak current density of 6.4 A/m<sup>2</sup> (Cycle-6) and 6.2 A/m<sup>2</sup> (Cycle-7) (Fig. 4a). Fig. 4b and 4c  
277 show the changes in TAN concentrations in anode and cathode chambers over the course of

278 these two cycles. On average, TAN concentrations in the anode chamber decreased from  $957\pm35$   
279 mg/L to  $455\pm45$  mg/L, and TAN concentrations in the cathode chamber increased to  $1194\pm117$   
280 mg/L. Average anodic TAN removal efficiency and corresponding flux through the membrane  
281 were  $53\pm5\%$  and  $26\pm4$  g-TAN/m<sup>2</sup>-d. On average,  $85\pm14\%$  of the transported TAN was  
282 recovered on the cathode. This performance was comparable with the operation of MEC with  
283 centrate supplemented with a high concentration of ethanol and acetate (i.e., Cycle-5). Average  
284 SCOD removal efficiency was  $21\pm2\%$  (Fig. 4d). SRP concentrations in the anode chambers  
285 were almost unchanged in both cycles, which is also consistent with previous cycles (Fig. 4e).  
286 To the best of our knowledge, the results of this study first evidently demonstrated that the  
287 addition of fermentation liquor could provide an adequate quantity of readily biodegradable  
288 organics in centrate to promote nitrogen recovery with microbial electrochemical  
289 systems. Several studies previously demonstrated that primary sludge fermentation liquor could  
290 serve as a promising exogenous carbon source for biological nutrients removal (BNR) process in  
291 WWTPs [40,41]. In fact, many WWTPs across North America already adopted sludge  
292 fermentation to produce short-chain volatile fatty acids for providing exogenous electron donors  
293 to the BNR process. We envision that a portion of sludge fermentation liquor can be diverted to  
294 MEC for enhancing N recovery from centrate.

295         Based on the results obtained from Cycle-6 and 7, the average electrical energy  
296 consumption per kg of TAN transport from the anode chamber to the cathode  
297 chamber was estimated at  $5.8\pm0.1$  kWh. Thus, electricity cost was calculated at  $\$0.40\pm0.01$ /kg-  
298 TAN. Simultaneously with N recovery, H<sub>2</sub> gas can be recovered on the cathode. An average  
299 H<sub>2</sub> production per cycle was  $189\pm33$  mL, which corresponds to H<sub>2</sub> productivity of  $0.08\pm0$  kg-  
300 H<sub>2</sub> per kg of TAN removal. The monetary value of H<sub>2</sub> that can be simultaneously

301 produced during MEC operation was estimated at  $\$0.64 \pm 0.1/\text{kg-TAN}$ , resulting in a net financial  
302 gain of  $\$0.23 \pm 0.01/\text{kg-TAN}$ , which does not include the economic value of concentrated  
303 ammonium solution. This preliminary economic evaluation based on the bench-scale  
304 experimental results indicates the potential of energy positive or energy neutral operation of  
305 MEC for N recovery from digested sludge centrate. It must be noted that further comprehensive  
306 economic assessment should be done at pilot-scale. Furthermore, to become a competitive  
307 technology for N recovery, anodic TAN removal efficiency ( $53 \pm 5\%$ ) and rate ( $26 \pm 4 \text{ g TAN/m}^2\text{-}$   
308  $\text{d}$ ) should be significantly increased. However, these values are within the range previously  
309 reported for MECs operated with real or synthetic urine. Haddadi et al. [23] reported N removal  
310 rate of  $8.5 \text{ g-N/m}^2\text{-d}$  in a MEC operated with synthetic urine. In contrast, Kuntke et al. [31]  
311 reported high ammonium removal rate of  $173.4 \text{ g-N/m}^2\text{-d}$  in a MEC operated with urine;  
312 however, ammonium removal efficiency was only  $\sim 30\%$ . As nitrogen recovery from digested  
313 centrate is primarily driven by migration or charge neutrality, improving current density would  
314 be critical to enhance N recovery. Notably, the current density can be significantly enhanced  
315 with multiple anode modules [42,43]. Additionally, more concentrated ammonium solution can  
316 be achieved by increasing the ratio between dilute to concentrate volumes ( $V_{D/C}$ ) until a certain  
317 limit [28]. In this study, a concentration factor of  $\sim 1.25$  with  $53 \pm 5\%$  TAN removal was attained  
318 at  $V_{D/C}$  of 2.86. This result is comparable with a concentration factor of  $\sim 1.75$  (63% ammonium  
319 removal from synthetic urine) at  $V_{D/C}$  of 2 reported by a previous study [28].

### 320 **3.2 P recovery from MEC effluent**

321 Fig. 5 shows the changes in SRP and TAN concentrations in the anodic effluent after chemical  
322 precipitation experiments at different conditions. The addition of  $\text{Ca}^{2+}$  salt induced a significant  
323 reduction in SRP concentrations, while TAN concentration remained unchanged. At Ca:P molar



324 ratio of 1.5:1 ( $\text{Ca}^{2+}_{\text{pH}=6.8}$  (1)), SRP concentration decreased by  $75\pm 1\%$ . In contrast, comparable  
325 SRP removals ( $\text{Ca}^{2+}_{\text{pH}=6.8}$  (2):  $85\pm 1\%$ ;  $\text{Ca}^{2+}_{\text{pH}=6.8}$  (3):  $87\pm 3\%$ ) were observed with higher doses of  
326  $\text{Ca}^{2+}$  salt. The SEM-EDX analysis suggested that the solid precipitate collected from  $\text{Ca}^{2+}_{\text{pH}=6.8}$   
327 (2) test was primarily composed of two major elements, namely, P and Ca (Fig. 6a). Thus,  
328 P was efficiently recovered without any pH adjustment of MEC effluent. In contrast, SRP and  
329 TAN concentrations did not change after addition of various doses of  $\text{Mg}^{2+}$  salt at pH 6.8 (i.e., no  
330 pH adjustment). While pH of the MEC effluent increased to 8.6, both SRP and TAN  
331 concentrations remarkably decreased with the addition of  $\text{Mg}^{2+}$  salt, which is consistent with  
332 previous studies reported that alkaline pH would be essential for struvite precipitation [4,12,16].  
333 In  $\text{Mg}^{2+}_{\text{pH}=8.6}$  (1) test, the average removals of SRP and TAN were  $77\pm 1\%$  and  $38\pm 3\%$ ,  
334 respectively. The addition of higher doses of  $\text{Mg}^{2+}$  salt did not result in further improvement in  
335 TAN removal efficiencies, while SRP removal efficiencies slightly improved ( $\text{Mg}^{2+}_{\text{pH}=8.6}$  (2):  
336  $84\pm 2\%$ ;  $\text{Mg}^{2+}_{\text{pH}=8.6}$  (3):  $84\pm 1\%$ ). As shown in Fig. 6b, the EDX spectrum confirmed the major  
337 components of the solid precipitates to be Mg (17.7%) and P (13.7%), which is comparable to  
338 that of the elemental composition of standard struvite (Mg: 9.79%; P: 13.49%) previously  
339 reported in the literature [44]. The absence of N peak was also consistent with the previous  
340 literature, which could be due to its light weight [44]. In this study, optimum doses of  $\text{Ca}^{2+}$  (C:P  
341 of 3:1 at pH=6.8; 4.8 g  $\text{Ca}^{2+}$  salt/g SRP) or  $\text{Mg}^{2+}$  (Mg:P of 2:1 at pH=8.6; 4.5 g  $\text{Mg}^{2+}$  salt/g SRP)  
342 salts exhibited comparable maximum P recovery efficiencies from MEC effluent. A comparison  
343 of the results indicated that  $\text{Mg}^{2+}$  addition at pH 8.6 could provide some additional benefit due to  
344 further removal of TAN, while the pH adjustment would induce some additional chemical costs  
345 [45,46].

346 To satisfy effluent discharge standard, the effluent (supernatant) from chemical  
347 precipitation process can be recycled to a mainstream treatment process for removal of  
348 unrecovered nutrients. The low pH of this stream can influence the performance of mainstream  
349 biological treatment process. It is evident that  $Mg^{2+}$ -based process can provide an advantage  
350 over  $Ca^{2+}$  addition due to relatively higher pH ( $\geq 7$ ) in the final effluent (See Supplementary  
351 Information). For  $Ca^{2+}$ -based process, post-adjustment of pH may be required before recycling  
352 supernatant liquid stream. This would be particularly important for activated sludge systems  
353 already having alkalinity limitations due to complete nitrification. However, a comprehensive  
354 techno-economic assessment would be required for the selection of an optimum process.  
355 Additionally, the recovered precipitates from both processes should be assessed for potential  
356 environmental risks, including pathogens, antibiotic resistance genes, heavy metals, and  
357 micropollutants, as suggested by recent studies [14,47,48]. To the best of our knowledge, this  
358 study first provides a systematic comparison between the phosphorous recovery efficiencies with  
359  $Ca^{2+}$  and  $Mg^{2+}$  salts. It must be asserted that P precipitation with  $Mg^{2+}$  salt has been extensively  
360 explored, while limited information is available in the literature on the P recovery with  $Ca^{2+}$  salt  
361 [15,18]. Therefore, our results substantiate the importance of further comprehensive assessment  
362 of various options for P precipitation from centrate.

#### 363 **4. Conclusions**

364 The use of primary sludge fermentation liquor as a supplementary source of readily  
365 biodegradable organics to digested sludge centrate appears to be a promising solution to boost  
366 current density and subsequent N recovery in a dual-chamber MEC. The addition of  
367 fermentation liquor (25% by volume) with centrate exhibited average anodic TAN removal  
368 efficiency and rate of  $53 \pm 5\%$  and  $26 \pm 4$  g-TAN/ $m^2$ -d, respectively. This performance was almost

369 comparable with the addition of acetate and ethanol as exogenous electron donors for anodic  
370 microbial communities. Additionally, recovered H<sub>2</sub> gas from the cathode was adequate to offset  
371 the cost of electrical energy input to the process. Under optimum precipitation conditions,  
372 maximum P recovery efficiencies from MEC effluents that could be achieved by either Ca<sup>2+</sup> or  
373 Mg<sup>2+</sup> salts were about 85%. Thus, the results of this study demonstrated that MEC followed by  
374 chemical precipitation can act as an efficient sidestream process for N and P recovery from  
375 centrate. The process should be investigated in pilot-scale for further optimization and  
376 application at municipal wastewater treatment plants.

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543 **List of Figures**

544 **Fig. 1.** (a) Schematic diagram of MEC, and (b) various experimental schemes with MEC.

545 **Fig. 2.** (a) Current density profiles, (b) SCOD concentrations, (c) changes in anodic TAN  
546 concentrations, and (d) changes in cathodic TAN concentrations during MEC operation with  
547 centrate in Cycle-1 and Cycle-2.

548 **Fig. 3.** (a) Current density profiles, (b) changes in anodic TAN concentrations, (c) changes in  
549 cathodic TAN concentrations, (d) SCOD concentrations, and (e) SRP concentrations during  
550 MEC operation with centrate supplemented with various concentrations of exogenous readily  
551 biodegradable organics (Cycle-3, 4, and 5).

552 **Fig. 4.** (a) Current density profiles, (b) changes in anodic TAN concentrations, (c) changes in  
553 cathodic TAN concentrations, (d) SCOD concentrations, and (e) SRP concentrations during  
554 MEC operation with centrate supplemented primary sludge fermentation liquor (Cycle-6 and 7).

555 **Fig. 5.** The changes in SRP and TAN concentrations in the anodic effluents at different doses of  
556  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salts.

557 **Fig. 6.** SEM-EDX spectrum of solid precipitates recovered from (a)  $\text{Ca}^{2+}_{\text{pH}=6.8}$  (2), and (b)  
558  $\text{Mg}^{2+}_{\text{pH}=8.6}$  (2) tests.

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560 **List of Tables**

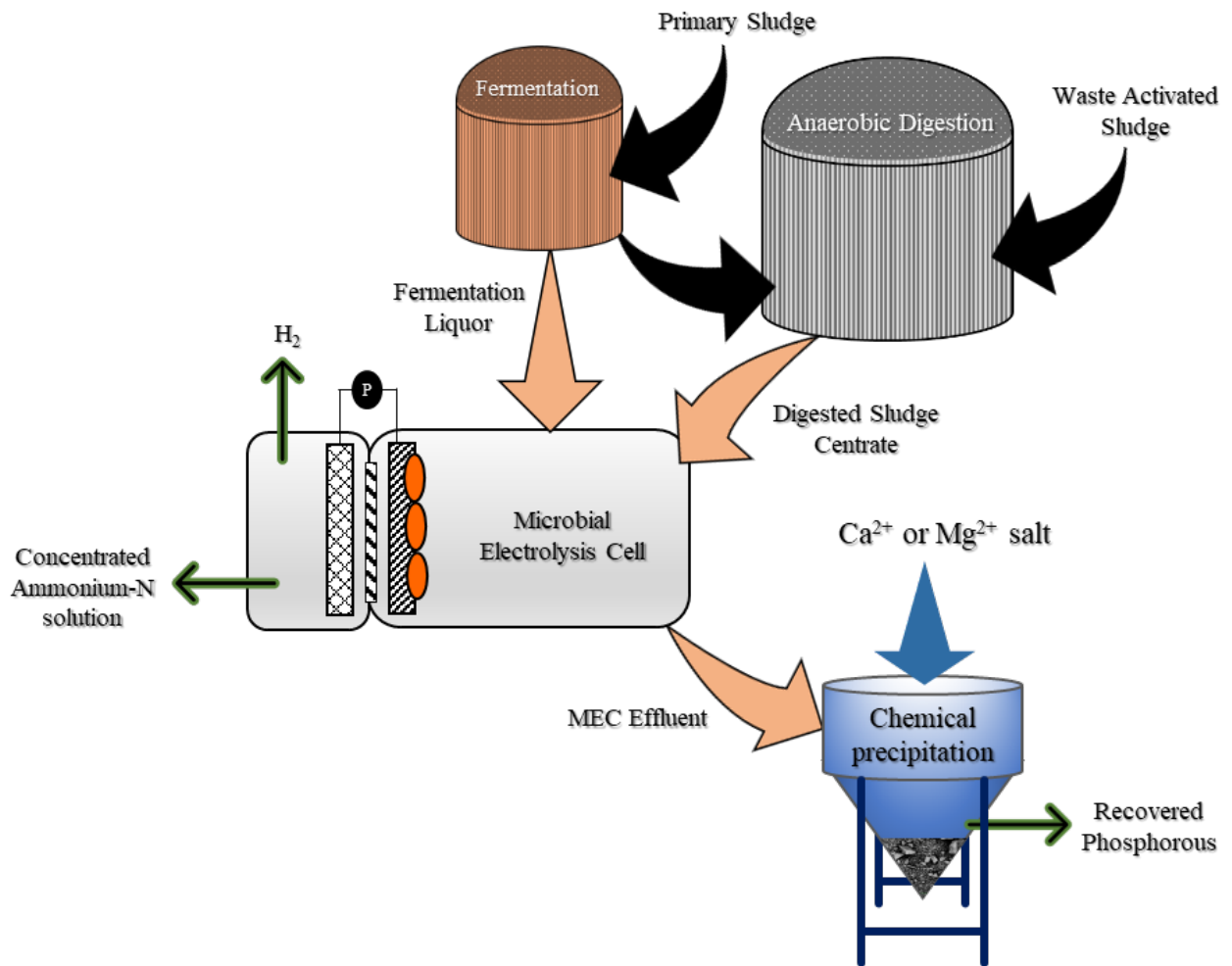
561 **Table 1.** Characteristics of centrate, primary sludge, and fermentation liquor.

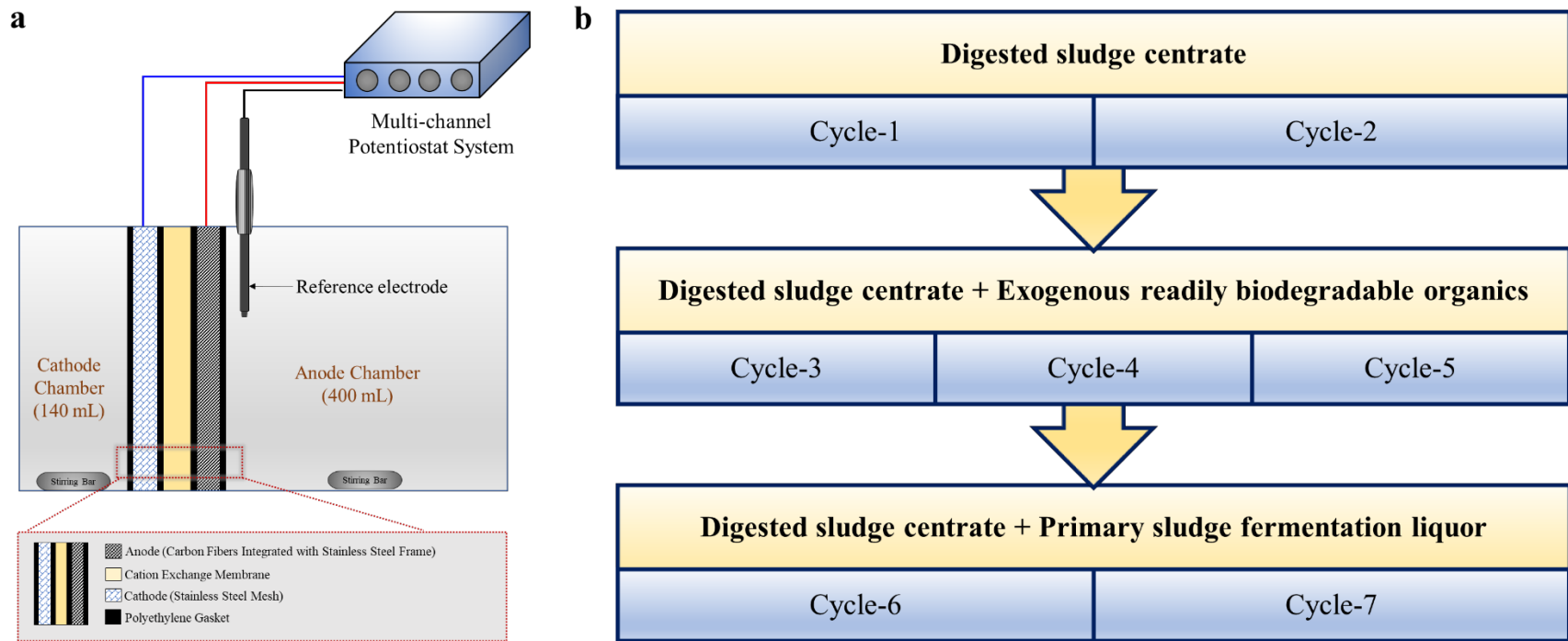
562 **Table 2.** Summary of chemical precipitation experiments with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salts for  
563 phosphorous recovery from anodic effluents.

## Highlights

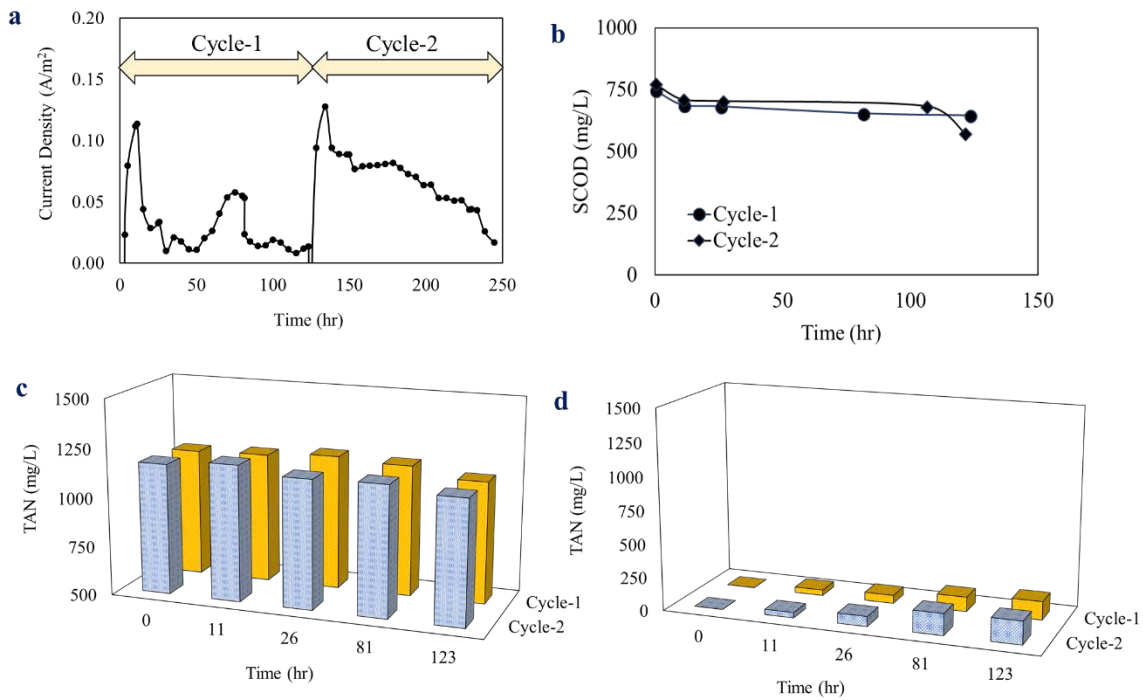
- MEC followed by chemical precipitation was studied for N&P recovery from centrate.
- Inadequate biodegradable COD in centrate led to ineffective N recovery in MEC.
- Centrate was mixed with sludge fermentation liquor to enhance N recovery in MEC.
- Recovered H<sub>2</sub> gas was adequate to offset the electricity cost of MEC operation.
- P was efficiently recovered from MEC anodic effluent using Ca<sup>2+</sup> or Mg<sup>2+</sup> salts.

# Graphical Abstract

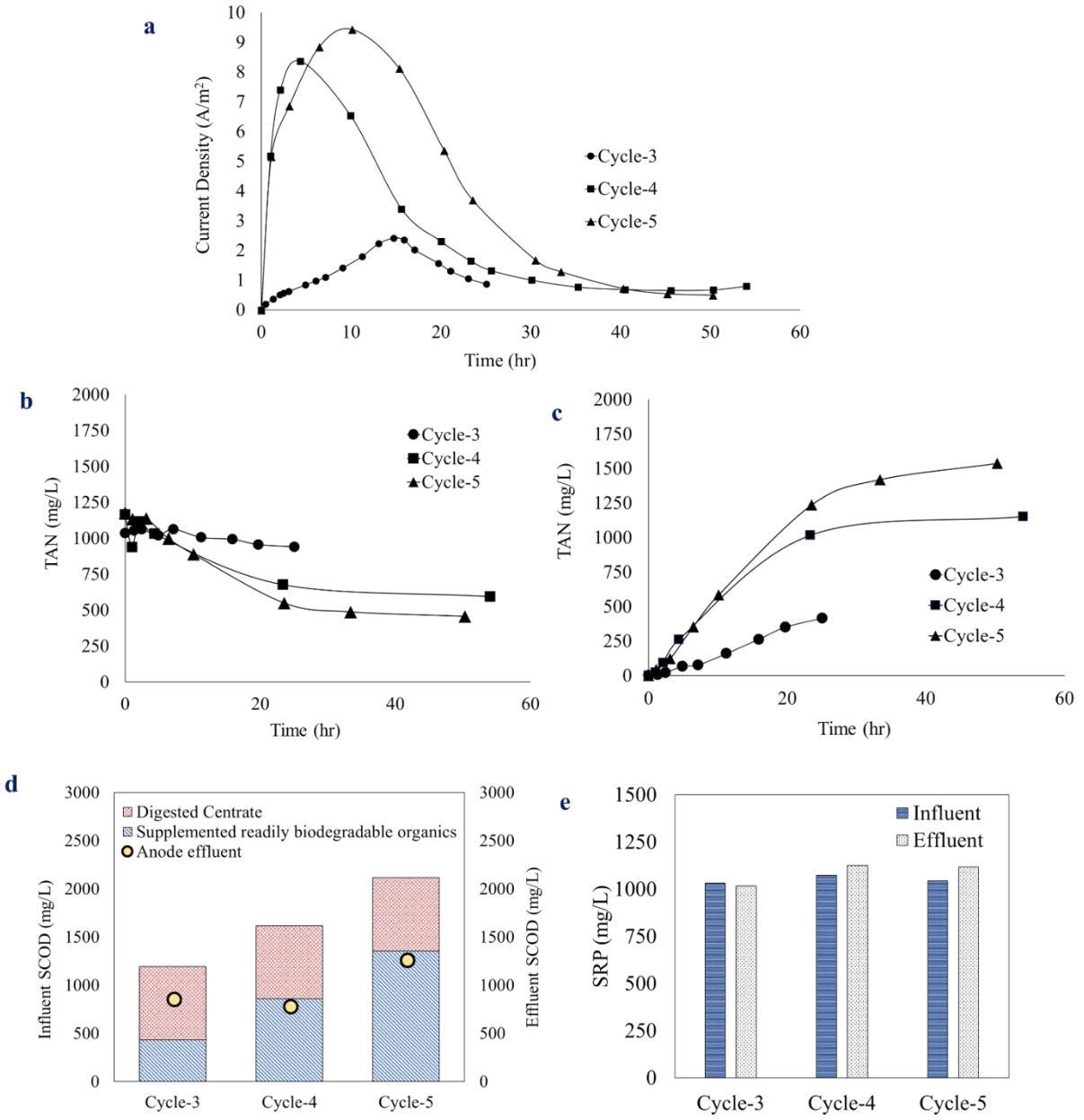




**Fig. 1.** (a) Schematic diagram of MEC, and (b) various experimental schemes with MEC.

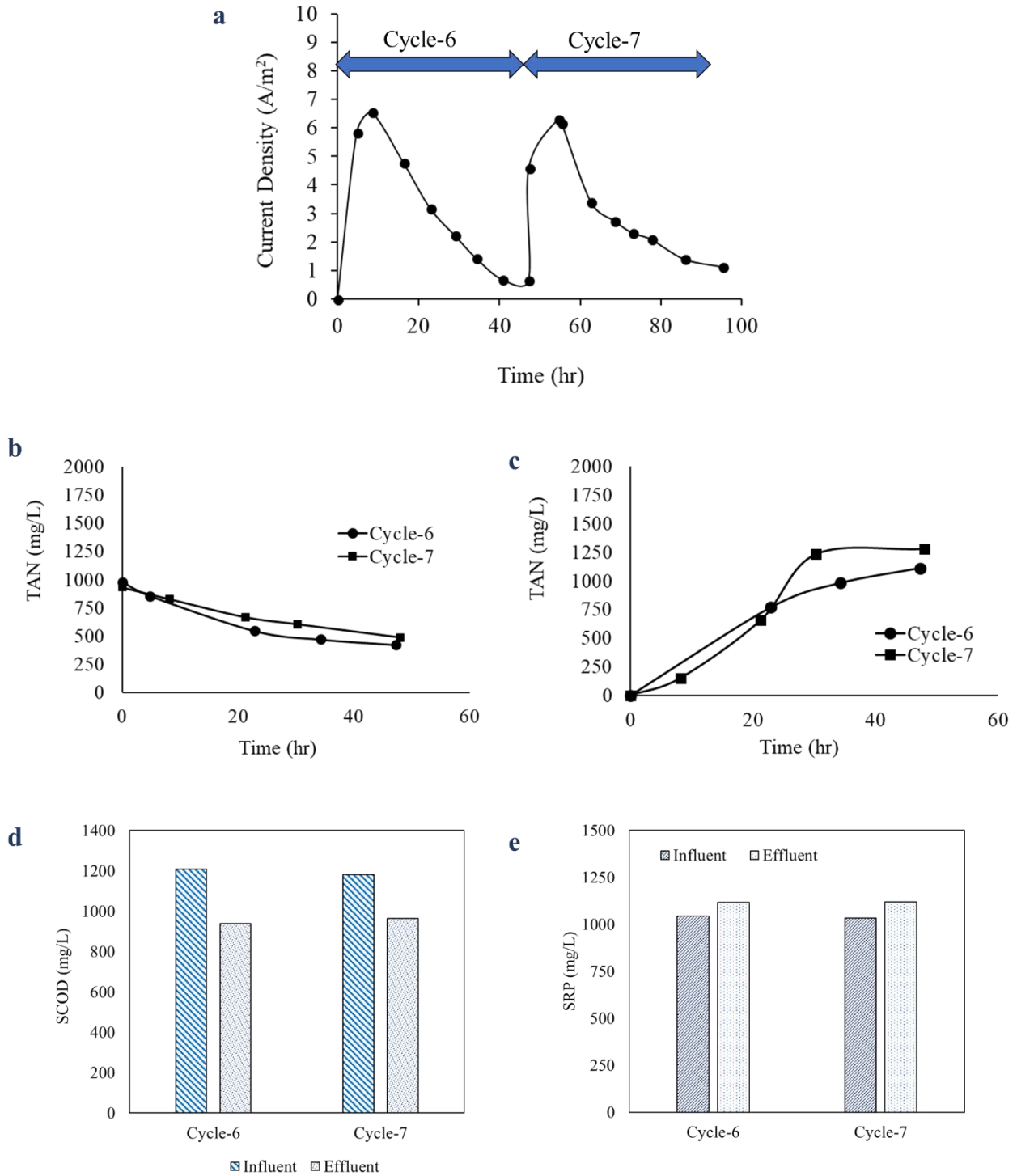


**Fig. 2.** (a) Current density profiles, (b) SCOD concentrations, (c) changes in anodic TAN concentrations, and (d) changes in cathodic TAN concentrations during MEC operation with centrate in Cycle-1 and Cycle-2.

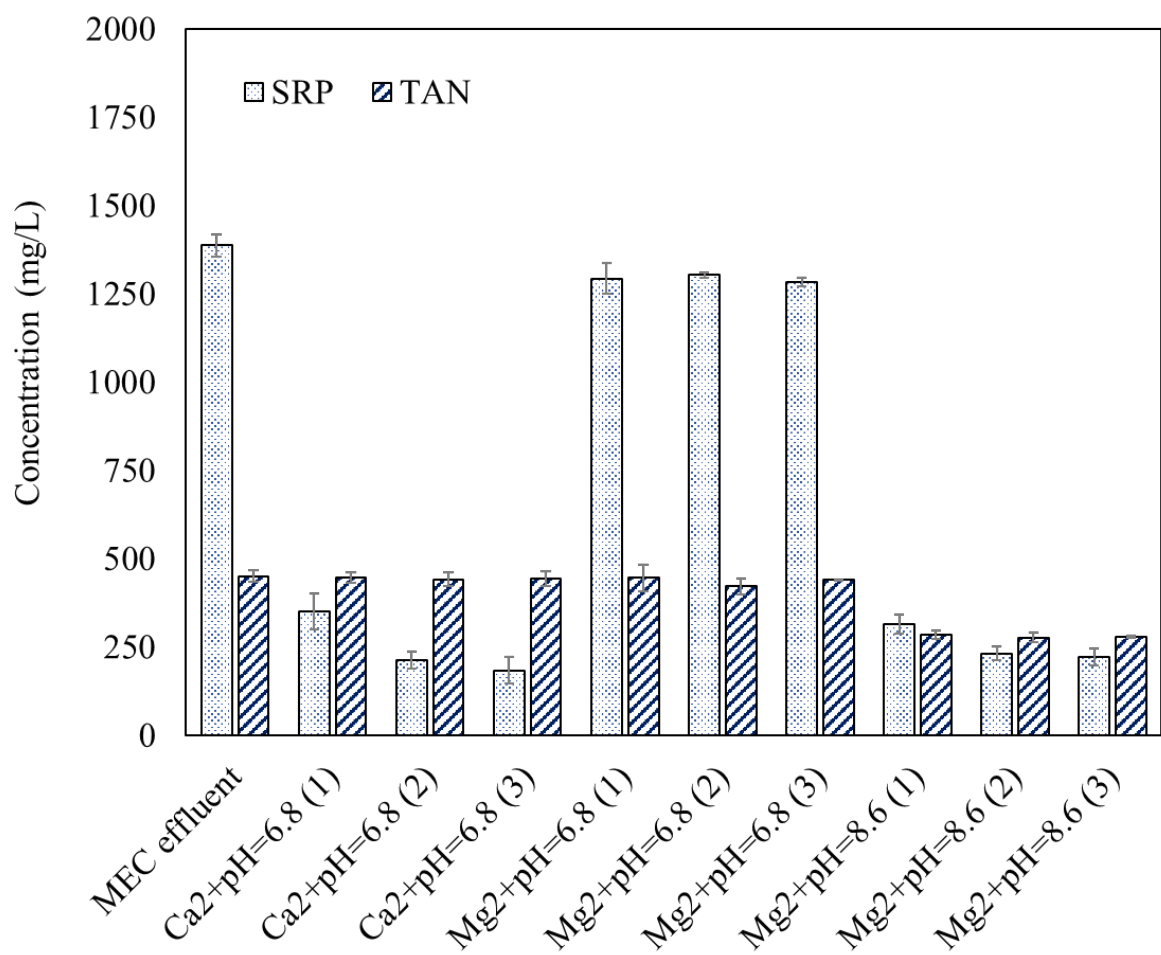


**Fig. 3.** (a) Current density profiles, (b) changes in anodic TAN concentrations, (c) changes in cathodic TAN concentrations, (d) SCOD concentrations, and (e) SRP concentrations during MEC operation with centrate supplemented with various concentrations of exogenous readily biodegradable organics (Cycle-3, 4, and 5).

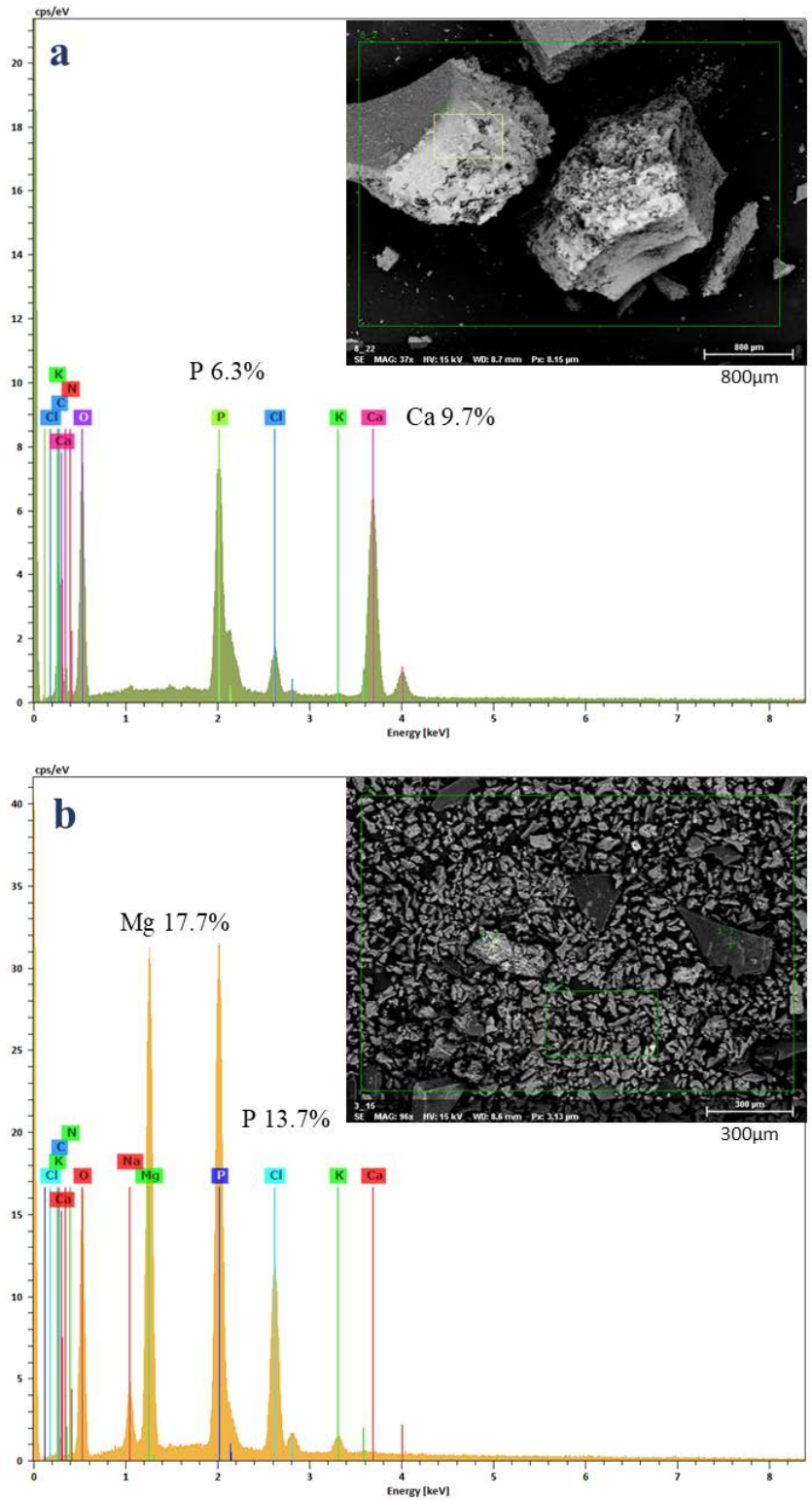




**Fig. 4.** (a) Current density profiles, (b) changes in anodic TAN concentrations, (c) changes in cathodic TAN concentrations, (d) SCOD concentrations, and (e) SRP concentrations during MEC operation with centrate supplemented primary sludge fermentation liquor (Cycle-6 and 7).



**Fig. 5.** The changes in SRP and TAN concentrations in the anodic effluents at different doses of Ca<sup>2+</sup> and Mg<sup>2+</sup> salts.



**Fig. 6.** SEM-EDX spectrum of solid precipitates recovered from (a)  $\text{Ca}^{2+}_{\text{pH}=6.8}$  (2), and (b)  $\text{Mg}^{2+}_{\text{pH}=8.6}$  (2) tests.

**Table 1.** Characteristics of centrate, primary sludge, and fermentation liquor.

Parameter	Digested sludge centrate	Primary sludge	Fermentation liquor
Total chemical oxygen demand, TCOD (mg/L)	2705±130	59130±580	10320±208
Soluble chemical oxygen demand, SCOD (mg/L)	740±6	9770±160	9292±4
Suspended solids, SS (mg/L)	1098±333	41950±1626	1038±265
Total ammonia-nitrogen, TAN (mg/L)	1177±23	530±13	547±5
Total volatile fatty acids, TVFA (mg COD/L)	31±3	3015±465	4605±785
Soluble reactive phosphorus, SRP (mg/L)	1387±51	668±6	447±3
pH	7.9	6.4	5.5

**Table 2.** Summary of chemical precipitation experiments with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salts for phosphorous recovery from anodic effluents.

Set	C: P <sup>c</sup>	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (g/L)	Mg: P <sup>c</sup>	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (g/L)
$\text{Ca}^{2+}_{\text{pH}=6.8}$ (1) <sup>a</sup>	1.5:1	3.3	-	-
$\text{Ca}^{2+}_{\text{pH}=6.8}$ (2) <sup>a</sup>	3:1	6.6	-	-
$\text{Ca}^{2+}_{\text{pH}=6.8}$ (3) <sup>a</sup>	4.5:1	9.9	-	-
$\text{Mg}^{2+}_{\text{pH}=6.8}$ (1) <sup>a</sup>	-	-	1:1	3.1
$\text{Mg}^{2+}_{\text{pH}=6.8}$ (2) <sup>a</sup>	-	-	2:1	6.2
$\text{Mg}^{2+}_{\text{pH}=6.8}$ (3) <sup>a</sup>	-	-	3:1	9.3
$\text{Mg}^{2+}_{\text{pH}=8.6}$ (1) <sup>b</sup>	-	-	1:1	3.1
$\text{Mg}^{2+}_{\text{pH}=8.6}$ (2) <sup>b</sup>	-	-	2:1	6.2
$\text{Mg}^{2+}_{\text{pH}=8.6}$ (3) <sup>b</sup>	-	-	3:1	9.3

<sup>a</sup>Without pH adjustment; <sup>b</sup>pH adjusted to 8.6; <sup>c</sup>molar ratio

## **Supplementary Information**

### **Microbial Electrolysis Followed by Chemical Precipitation for Effective Nutrients Recovery from Digested Sludge Centrate in WWTPs**

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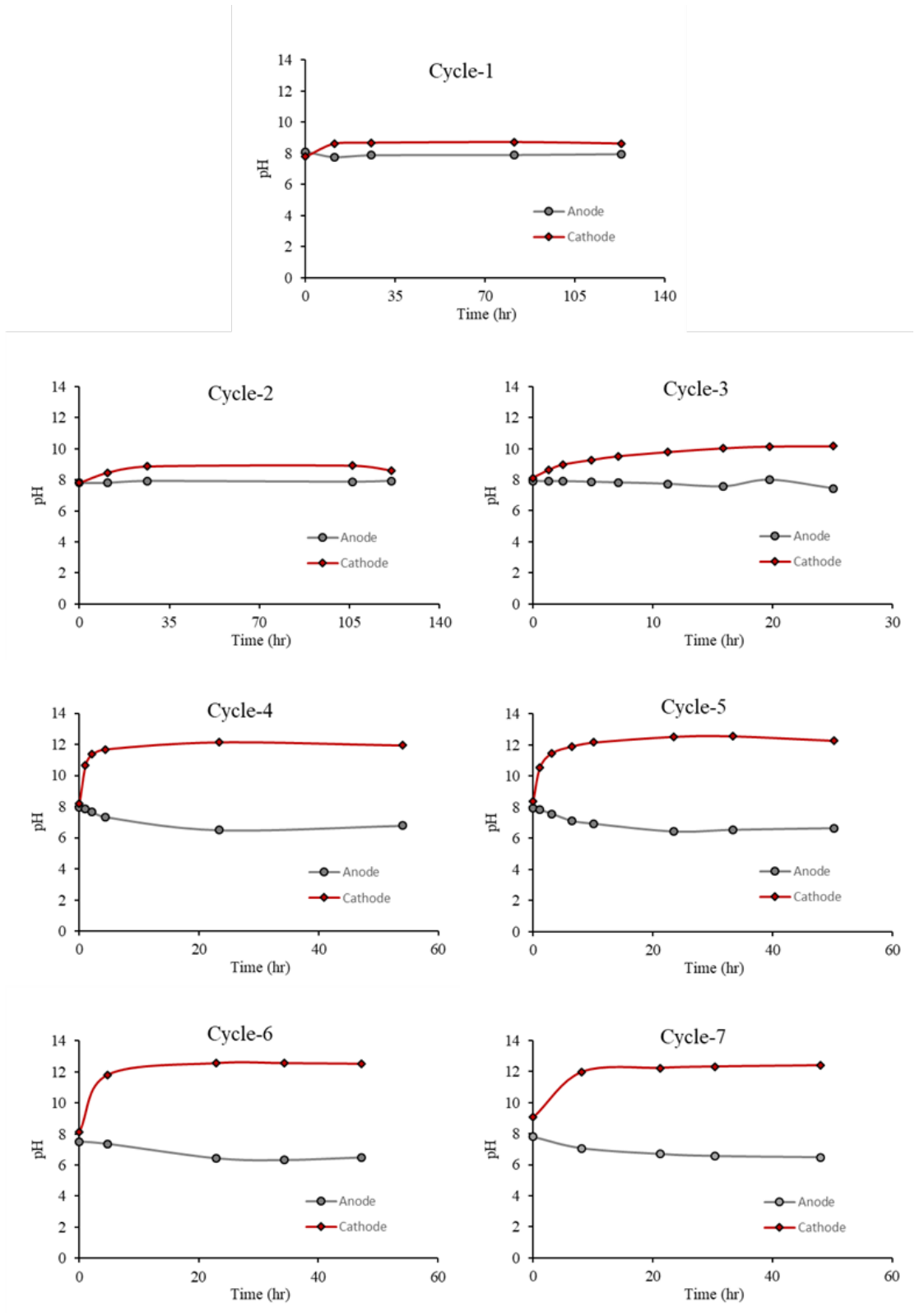
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**Fig. S1.** Photograph of microbial electrolysis cell (MEC) used in this study.



**Fig. S2:** pH profiles of anode and cathode chamber during different operating cycles.



**Table S1.** Summary of pH and conductivity at the end of chemical precipitation experiments with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  salts for phosphorous recovery from MEC effluents.

Set	pH	Conductivity
$\text{Ca}^{2+}_{\text{pH}=6.8}$ (1)	6.1±0.1	6.89±0.43
$\text{Ca}^{2+}_{\text{pH}=6.8}$ (2)	5.8±0.1	11.17±0.03
$\text{Ca}^{2+}_{\text{pH}=6.8}$ (3)	5.7±0.1	15.35±0.04
$\text{Mg}^{2+}_{\text{pH}=6.8}$ (1)	6.8±0	6.74±0.04
$\text{Mg}^{2+}_{\text{pH}=6.8}$ (2)	6.7±0	9.23±0.01
$\text{Mg}^{2+}_{\text{pH}=6.8}$ (3)	6.6±0	11.82±0.15
$\text{Mg}^{2+}_{\text{pH}=8.6}$ (1)	7.3±0.1	6.15±0.02
$\text{Mg}^{2+}_{\text{pH}=8.6}$ (2)	7.1±0	8.64±0.01
$\text{Mg}^{2+}_{\text{pH}=8.6}$ (3)	7±0	11.3±0.01