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

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Abstract

A two-step sidestream process was investigated for nitrogen (N) and phosphorous (P) recovery from digested sludge centrate. In the first step, a dual-chamber microbial electrolysis cell (MEC) was used for N recovery on the cathode. In the second step, P was recovered as solid precipitates by the addition of Ca^{2+} or Mg^{2+} salts in the anodic effluent. The operation of MEC with centrate indicate that N transport from the anode to the cathode chamber is primarily driven by anodic electron transport rather than diffusional transport. Low concentration of readily biodegradable organics in centrate significantly hindered current density ($<0.15 \text{ A/m}^2$) and led to trivial N recovery on the cathode chamber. The addition of primary sludge fermentation liquor (25 vol%) with centrate as an exogenous source of readily biodegradable organics substantially increased current density up to 6.4 A/m^2 , along with high TAN removal efficiency of $53 \pm 5\%$. The energy requirement was calculated at $5.8 \pm 0.1 \text{ kWh/kg-TAN}$; however, the recovered H_2 gas from the cathode was adequate to offset this energy input completely. The addition of Ca^{2+} salt at a Ca: P molar ratio of 3:1 was optimum for P recovery from the anodic effluent; Mg: P molar ratio of 2:1 was found to be optimum for Mg^{2+} salt addition. However, optimum doses of both salts resulted in maximum P recovery efficiency of $\sim 85\%$, while Mg^{2+} addition provided an additional 38% TAN removal. These results demonstrate that microbial electrolysis followed by chemical precipitation can promote sustainable nutrients recovery from centrate at municipal wastewater treatment plants where sludge fermentation has already been adopted to provide readily biodegradable carbon source in the biological nutrient removal process.

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

1. Introduction

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

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

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

Microbial electrochemical systems, such as microbial electrolysis cells (MECs) and microbial fuel cells (MFCs), have recently received much attention for energy neutral wastewater treatment and value-added resources recovery [19,20]. Studies have also demonstrated that microbial electrochemical systems can simultaneously recover nutrients from wastewater, which makes them more attractive over other nutrients recovery technologies [21–26]. In dual-chamber microbial electrochemical systems having cation exchange membrane (CEM), efficient cathodic nitrogen recovery could be attained due to ammonium transport from the anode to the cathode chamber for meeting charge neutrality [23,24]. Thus, a concentrated ammonia nitrogen solution can be recovered from the cathode. Additionally, a few studies demonstrated that cathodic proton consumption for H₂ production in MEC might lead to highly alkaline local pH near the cathode which facilitates struvite precipitation on the cathode surface [22,27]. Interestingly, most of these studies primarily focused on nutrients recovery from source-separated urine [22–24,27–31]. In contrast, microbial electrochemical systems for nutrients recovery from digested sludge centrate has been rarely investigated. A recent study by Yuan and Kim [13] reported that a small concentration of readily biodegradable organics in digested sludge centrate resulted in low current density and inferior cathodic nutrients recovery in a MEC. Thus, inadequate readily biodegradable organics could be a possible reason that made digested sludge centrate a relatively unattractive stream for nutrients recovery with microbial electrochemical systems. Therefore, the development of an efficient engineering strategy to improve current density and nutrients recovery from centrate

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

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

2. Materials and methods

2.1 MEC operation for nitrogen removal and recovery

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

Carbon fibers were pretreated according to a method previously described by Dhar et al. [33]. A stainless-steel mesh (Type 304, McMaster Carr, OH, USA) was used as the cathode electrode. In this study, the anode and cathode chambers were separated by a CEM (CMI-7000, Membranes International Inc, USA). Ag/AgCl reference electrode (MF-2052, Bioanalytical System Inc., WestLafayette, IN, USA) was placed within ~1 cm of the anode electrode. The anode potential was set at -0.4 V vs. Ag/AgCl using a multi-channel potentiostat system (Squidstat Prime, Admiral Instruments, Phoenix, AZ, USA) throughout the experiment. Effluent from a mother MEC was used as the inoculum for the enrichment of anode biofilms as previously reported by Zakaria et al. [32] and 25 mM of sodium acetate medium supplemented mineral nutrients, and 50 mM phosphate buffer served as the substrate for the enrichment of anode biofilms. The detailed composition of the mineral nutrients can be found in the literature [33]. The MEC was operated at room temperature ($22\pm1^{\circ}\text{C}$), and both the anolyte and catholyte were continuously mixed at 130 ± 10 rpm with magnetic stirrers.

During the enrichment process of anodic biofilms, MEC was operated in semi-continuous mode (i.e., 180 mL of fresh substrate medium was fed to the anode chamber using a syringe on a daily basis) until a repeatable peak current of 10.4 ± 0.9 A/m² was observed. Then, nitrogen recovery experiments were conducted with digested sludge centrate, centrate supplemented with exogenous readily biodegradable organics (acetate and ethanol), and centrate mixed with primary sludge fermentation liquor (see Fig. 1b). During Cycle-1 and 2, MEC was operated with real digested centrate. Anaerobic digester sludge was collected from a full-scale mesophilic anaerobic digester at the Gold Bar Wastewater Treatment Plant, Edmonton, Alberta, Canada. Anaerobic digester sludge was centrifuged at 18,670xg for 30 min, and the centrate was collected for experiments. During Cycle-3, 4, and 5, MEC was operated with centrate supplemented with

three different concentrations of exogenous readily biodegradable organics (435, 860, and 1355 mg COD/L, respectively). A mixture of acetate and ethanol (COD ratio of 1:1) was used as exogenous readily biodegradable organics. During Cycle-6 and 7, MEC was operated with a mixture of digested sludge centrate (75 vol%) and liquor from primary sludge fermentation (25 vol%). For sludge fermentation experiment, primary sludge was collected from Gold Bar Wastewater Treatment Plant, Edmonton, Alberta, Canada. The fermentation experiment was performed in a bench-scale glass anaerobic bioreactor (working volume of 2 L) equipped with a stirring shaft. The sludge was sparged with ultra-pure nitrogen gas (99.999%) for three minutes. The fermentation process was operated for 7 days at room temperature ($22\pm1^{\circ}\text{C}$), and the reactor media was stirred with a mixer at 300 rpm. After 7 days of operation, fermented sludge was centrifuged at $18,670\times g$ for 30 min, and the supernatant (i.e., fermentation liquor) was collected and used for experiments (Cycle-6 and 7). Table 1 shows the average characteristics of centrate, primary sludge, and fermentation liquor. All experiments were conducted in fed-batch mode. Before each cycle, the cathode chamber was evacuated completely and cleaned multiple times with tap water to remove any residual ammonium that can influence the results of the following cycle.

2.2 Chemical precipitation experiments for P recovery

We performed nutrients precipitation experiments with anodic effluent collected during Cycle-5. The average soluble reactive phosphorous (SRP) and total ammonia-nitrogen (TAN) concentrations in the effluent were 1387 ± 51 mg/L and 451 ± 15 mg/L, respectively. For 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 centrifuge vials having 50 mL of anodic effluent samples. The corresponding molar ratios of Ca to P and Mg to P are summarized in Table 2. These ratios were selected based on the possible

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

2.3 Analytical methods

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

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

2.4 Calculations and economic assessment

Current density was calculated based on the projected area of membrane (0.0038 m^2), as previously described in the literature [9,33,36]. The anodic TAN removal efficiency was calculated from the difference in initial and final TAN concentration of the anodic liquid during a fed-batch cycle. The cathodic TAN recovery efficiency was calculated from the amount of TAN accumulated in the cathode chamber and the amount of TAN removed from the anode chamber during a fed-batch cycle. A preliminary economic assessment for MEC was performed based on per kg TAN removal from centrate. Average experimental results from Cycle-6 and 7 was used for these calculations. Electrical energy input (kWh) to MEC for an entire fed-batch cycle was computed from the current and applied voltage data recorded with time, as previously described in the literature [37]. The cost of electrical energy input and monetary value of H_2 produced from MEC were estimated at \$0.07/kWh and \$8/kg- H_2 , respectively [38,39].

3. Results and discussion

3.1 N recovery from centrate

3.1.1 N recovery and current density from centrate

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

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

3.1.2 Enhanced N recovery from centrate supplemented with exogenous electron donors

In response to the addition of exogenous readily biodegradable organics at different concentrations, current densities in MEC noticeably increased as compared to centrate alone (Fig. 3a). The peak current densities in Cycle-3, 4, and 5 were 2.4, 8.4, and 9.4 A/m², respectively. Anodic TAN concentrations were observed to decrease as current densities increased (Fig. 3b). The addition of readily biodegradable organics at high concentrations (Cycle-4: 860 mg SCOD/L; Cycle-5: 1355 mg SCOD/L) showed a considerable decrease in anodic TAN concentrations. During Cycle 4 and Cycle-5, TAN concentrations in the anode chamber decreased from 1165 and 1178 mg/L to 594 and 456 mg/L, respectively; and TAN

concentrations in the cathode chamber increased up to 1152 mg/L (Cycle-4) and 1537 mg/L (Cycle-5), respectively (Fig. 3c). Thus, anodic TAN removal efficiencies were 49% (Cycle-4) and 61% (Cycle-5). Correspondingly, TAN fluxes through the membrane during these cycles were 13 g-TAN/m²-d (Cycle-4) and 18 g-TAN/m²-d (Cycle-5). However, transported ammonium recovery efficiencies on the cathode were 70% (Cycle-4) and 73% (Cycle-5). A portion of the transported ammonium (27-30%) were possibly lost through stripping as ammonia gas due to the highly alkaline cathodic pH (~12) as a result of proton reduction to H₂ gas on the cathode ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). The detailed pH profiles are provided in the Supplementary Information. In comparison, low concentration of exogenous readily biodegradable organics (Cycle-3: 435 mg SCOD/L) exhibited relatively lower N recovery efficiency. As shown in Fig. 3d, a substantial decrease in SCOD concentrations were observed in comparison with MEC operation with digested sludge centrate alone, indicating the lower biodegradability of residual organics in digested centrate. As expected, there was no change in SRP concentrations due to the use of CEM (Fig. 3e). Overall, these results support that the addition of exogenous readily biodegradable organics favored current density and nitrogen recovery from digested centrate.

3.1.3 Efficient N recovery from centrate supplemented with sludge fermentation liquor

Because the addition of exogenous readily biodegradable organics improved current density and N recovery, primary sludge fermentation liquor was assessed as a potential source of readily biodegradable organics (Cycle-6 and 7) (Fig. 4). The TAN and SRP concentrations in digested sludge centrate were not substantially diluted by the addition of fermentation liquor (25% by volume). The operation of MEC with a mixture of centrate and fermentation liquor exhibited peak current density of 6.4 A/m² (Cycle-6) and 6.2 A/m² (Cycle-7) (Fig. 4a). Fig. 4b and 4c show the changes in TAN concentrations in anode and cathode chambers over the course of

these two cycles. On average, TAN concentrations in the anode chamber decreased from 957 ± 35 mg/L to 455 ± 45 mg/L, and TAN concentrations in the cathode chamber increased to 1194 ± 117 mg/L. Average anodic TAN removal efficiency and corresponding flux through the membrane were $53 \pm 5\%$ and 26 ± 4 g-TAN/m²-d. On average, $85 \pm 14\%$ of the transported TAN was recovered on the cathode. This performance was comparable with the operation of MEC with centrate supplemented with a high concentration of ethanol and acetate (i.e., Cycle-5). Average SCOD removal efficiency was $21 \pm 2\%$ (Fig. 4d). SRP concentrations in the anode chambers were almost unchanged in both cycles, which is also consistent with previous cycles (Fig. 4e). To the best of our knowledge, the results of this study first evidently demonstrated that the addition of fermentation liquor could provide an adequate quantity of readily biodegradable organics in centrate to promote nitrogen recovery with microbial electrochemical systems. Several studies previously demonstrated that primary sludge fermentation liquor could serve as a promising exogenous carbon source for biological nutrients removal (BNR) process in WWTPs [40,41]. In fact, many WWTPs across North America already adopted sludge fermentation to produce short-chain volatile fatty acids for providing exogenous electron donors to the BNR process. We envision that a portion of sludge fermentation liquor can be diverted to MEC for enhancing N recovery from centrate.

Based on the results obtained from Cycle-6 and 7, the average electrical energy consumption per kg of TAN transport from the anode chamber to the cathode chamber was estimated at 5.8 ± 0.1 kWh. Thus, electricity cost was calculated at $\$0.40 \pm 0.01$ /kg-TAN. Simultaneously with N recovery, H₂ gas can be recovered on the cathode. An average H₂ production per cycle was 189 ± 33 mL, which corresponds to H₂ productivity of 0.08 ± 0 kg-H₂ per kg of TAN removal. The monetary value of H₂ that can be simultaneously

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

3.2 P recovery from MEC effluent

Fig. 5 shows the changes in SRP and TAN concentrations in the anodic effluent after chemical precipitation experiments at different conditions. The addition of Ca^{2+} salt induced a significant 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 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 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 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 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 Ca^{2+} (C:P
 341 of 3:1 at pH=6.8; 4.8 g Ca^{2+} salt/g SRP) or Mg^{2+} (Mg:P of 2:1 at pH=8.6; 4.5 g Mg^{2+} salt/g SRP)
 342 salts exhibited comparable maximum P recovery efficiencies from MEC effluent. A comparison
 343 of the results indicated that 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].

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

4. Conclusions

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

comparable with the addition of acetate and ethanol as exogenous electron donors for anodic microbial communities. Additionally, recovered H₂ gas from the cathode was adequate to offset the cost of electrical energy input to the process. Under optimum precipitation conditions, maximum P recovery efficiencies from MEC effluents that could be achieved by either Ca²⁺ or Mg²⁺ salts were about 85%. Thus, the results of this study demonstrated that MEC followed by chemical precipitation can act as an efficient sidestream process for N and P recovery from centrate. The process should be investigated in pilot-scale for further optimization and application at municipal wastewater treatment plants.

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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).

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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 H₂ gas was adequate to offset the electricity cost of MEC operation.
- P was efficiently recovered from MEC anodic effluent using Ca²⁺ or Mg²⁺ salts.

Graphical Abstract

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

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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 Ca^{2+} and Mg^{2+} salts for phosphorous recovery from anodic effluents.

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

^aWithout pH adjustment; ^bpH adjusted to 8.6; ^cmolar ratio

Supplementary Information

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

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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 Ca^{2+} and 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