Electrochemical struvite precipitation from digestate with a fluidized bed cathode microbial electrolysis cell

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A B S T R A C T

Microbial electrolysis cells (MECs) can be used to simultaneously convert wastewater organics to hydrogen and precipitate struvite, but scale formation at the cathode surface can block catalytic active sites and limit extended operation. To promote bulk phase struvite precipitation and minimize cathode scaling, a two-chamber MEC was designed with a fluidized bed to produce suspended particles and inhibit scale formation on the cathode surface. MEC operation elevated the cathode pH to between 8.3 and 8.7 under continuous flow conditions. Soluble phosphorus removal using digester effluent ranged from 70 to 85% with current generation, compared to 10–20% for the control (open circuit conditions). At low current densities (<2 mA/m²), scouring of the cathode by fluidized particles prevented scale accumulation over a period of 8 days. There was nearly identical removal of soluble phosphorus and magnesium from solution, and an equimolar composition in the collected solids, supporting phosphorus removal by struvite formation. At an applied voltage of 1.0 V, energy consumption from the power supply and pumping (0.2 Wh/L, 7.5 Wh/g-P) was significantly less than that needed by other struvite formation methods based on pH adjustment such as aeration and NaOH addition. In the anode chamber, current generation led to COD oxidation (1.1–2.1 g-COD/L-d) and ammonium removal (7–12 mM) from digestate amended with 1 g/L of sodium acetate. These results indicate that a fluidized bed cathode MEC is a promising method of sustainable electrochemical nutrient and energy recovery method for nutrient rich wastewaters.

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1. Introduction

Wastewater treatment plants use enhanced biological phosphorus removal (EBPR) to minimize nutrient discharge into waterways. Stabilization of excess activated and EBPR sludge in an anaerobic digester results in significant releases of nutrients, minerals, and alkalinity (Ca²⁺, Mg²⁺, K⁺, PO₄³⁻, NH₄⁺, and HCO₃⁻) (Pérez-Elvira et al., 2006). During digestion, 40–80% of the phosphorus contained in EBPR sludge is solubilized,

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leading to nutrient recycling within the plant, as well as calcium and magnesium phosphate salt precipitation within the digester and on equipment surfaces (Jardin and Popel, 1994; Liao et al., 2003).

In nutrient rich digester effluent, a number of sparingly soluble salts can form (Table 1). The most prevalent are magnesium ammonium phosphate hexahydrate (struvite), calcium carbonate (calcite) and amorphous calcium phosphate (ACP) (Battistoni et al., 2002). Precipitation occurs when the ionic product of a salt exceeds the solubility limit (aka super saturation) (Snoeyink and Jenkins, 1980). Since the ionic product of phosphate salts are pH dependent, precipitation takes place where carbonate desorption caused by turbulence raises solution pH. Scale formation within conduit and on pumps can lead to reduced pipe capacity and costly equipment failure (Ohlinger et al., 1999, 2000; Doyle and Parsons, 2002). The annual operational cost of dealing with scale formation at wastewater treatment plants has been estimated at roughly $40,000 per million cubic meters per day of dry weather capacity (Neethling and Benisch, 2004). The potential economic benefit of preventing scale formation while recovering renewable sources of nitrogen and phosphorus has led to the development of side-stream phosphate salt crystallization systems (Ohlinger et al., 2000; Bhuiyan et al., 2008a; Ohlinger et al., 1999). The majority of systems have focused on struvite crystallization because both nitrogen and phosphorus are removed.

Fluidized bed reactors (FBRs) are most commonly used for crystallized phosphate recovery because the design creates an abundance of reactive surface area and solution turbulence (Seckler et al., 1996a). These conditions promote rapid molecular growth at the crystal surface interface which eliminates the induction time associated with nucleating crystals directly from solution (Bhuiyan et al., 2008b). Struvite precipitation within crystallization reactors is affected by pH and molar concentration ratios. The minimum solubility of struvite has been reported at a pH of 10.7, but effective secondary crystal growth has been observed at pH values greater than 8.0 (Doyle and Parsons, 2002). When solution pH within an FBR is increased to 8.5 or greater, soluble phosphate removal often reaches 70–90% at short hydraulic retention times (1–4 h) (Bhuiyan et al., 2008a; Seckler et al., 1996a; b; Forrest et al., 2008). Struvite precipitation is adversely affected by the presence of calcium and carbonate. When solution Ca:P ratios are equal to or greater than Mg:P ratios, struvite crystal purity, size and phosphorus removal can be compromised by amorphous calcium phosphate co-precipitation (Le Corre et al., 2005; Moerman et al., 2009; Hao et al., 2009). In digester effluent, high alkalinity can lead to magnesium carbonate complexation, which reduces the amount of magnesium available for struvite precipitation (Cao and Harris, 2007; Mañas et al., 2012).

Despite high nutrient removal efficiencies, proliferation of phosphate salt crystallization systems has been limited by the monetary cost of increasing solution pH. Sodium hydroxide (NaOH) is often used because it is highly soluble and can rapidly increase the solution pH (Ohlinger et al., 1999; Bhuiyan et al., 2008a; Le Corre et al., 2005; Le Corre et al., 2007). Chemical addition can drive phosphorus recovery costs (as high as $3500/ton-P) to be significantly higher than the value of nutrients contained in struvite (~$765/ton-P) (Doyle and Parsons, 2002; Dockhorn, 2009). Stripping carbonate alkalinity by aeration has also been shown to effectively raise pH and reduce cationic complexation with carbonate (Moerman et al., 2009; Battistoni et al., 2001), but blowers are energy intensive and aeration releases ammonia into the atmosphere.

Recently, microbial electrochemical technologies (METs), such as microbial fuel cells (MFCs) and electrolysis cells (MECs) have been explored as a chemical-free and energy efficient method of struvite precipitation (Cusick and Logan, 2012; Hirooka and Ichihashi, 2013; Ichihashi and Hirooka, 2012). METs consist of an anode, where anaerobic microbes oxidize organic matter and transfer electrons to an external circuit, and a cathode where the electrons and protons catalytically combine by reducing oxygen to water (MFC) or producing hydrogen gas (MEC). Proton consumption increases pH at the cathode surface and induces struvite precipitation (Moussa et al., 2006). Simultaneously removing organic matter and nutrients from wastewater while generating renewable energy and fertilizer is, in concept, a sustainable approach for struvite production, but initial results with batch-fed, single-chamber reactors have shown low phosphorus removal efficiencies (20–50%) and cathode failure due to scale accumulation.

In this study, a two-chamber MEC reactor with a fluidized bed cathode chamber was developed to enhance phosphorus removal and minimize cathode scaling. To induce a bulk phase pH increase in the cathode chamber, a cation exchange membrane separated the electrodes. The cathode chamber was operated as a fluidized bed to increase struvite precipitation through production of high surface area particles. In addition, particles scoured the cathode and helped to minimize scale accumulation (Fig. 1). To investigate the effect of current density on struvite precipitation rate and cathode scaling, the FBR-MEC was operated under continuous flow at three applied cell voltages (0.8, 1.0, and 1.4 V). At each applied

<table>
<thead>
<tr>
<th>Common name</th>
<th>Formula</th>
<th>$pK_{so}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Struvite</td>
<td>MgNH₄PO₄·6H₂O(s)</td>
<td>13.2</td>
<td>(Ohlinger et al., 1998)</td>
</tr>
<tr>
<td>Newberyite</td>
<td>MgHPO₄·H₂O(s)</td>
<td>18.2</td>
<td>(Dempsey, 1998)</td>
</tr>
<tr>
<td>Bobierrite</td>
<td>Mg₃(PO₄)₂·22H₂O(s)</td>
<td>25.2</td>
<td>(Dempsey, 1998)</td>
</tr>
<tr>
<td>Calcium Hydrogen Phosphate</td>
<td>CaHPO₄(s)</td>
<td>6.7</td>
<td>(Snoeyink and Jenkins, 1980)</td>
</tr>
<tr>
<td>β-Amorphous Calcium Phosphate (ACP)</td>
<td>β-Ca₅(PO₄)₂·2H2O(s)</td>
<td>24.0</td>
<td>(Snoeyink and Jenkins, 1980)</td>
</tr>
<tr>
<td>Hydroxyapatite (HAP)</td>
<td>Ca₅(PO₄)₂OH₂(s)</td>
<td>55.9</td>
<td>(Snoeyink and Jenkins, 1980)</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃(s)</td>
<td>8.3</td>
<td>(Snoeyink and Jenkins, 1980)</td>
</tr>
</tbody>
</table>
2. Materials and methods

2.1. Reactor construction

The MEC was composed of two concentric cylindrical chambers. A tubular cation exchange membrane (CEM) separated the inner cathode chamber from the outer anode chamber (Fig. 1). The inner cathode chamber was designed to replicate the dimensions of fluidized bed columns previously used for struvite precipitation with chemical addition. The fluidization section of the cathode had a diameter to cross-sectional area ratio of 25 (inner diameter of \( d = 1.1 \) cm, height of \( h = 28 \) cm) (Seckler et al., 1996a, 1996c). The fluidization chamber consisted of a cylindrical CEM (\( d = 1.1 \) cm, \( h = 15 \) cm) and sections of clear PVC tubing at each end of the membrane tube (\( d = 1.1, h = 15 \) cm). The CEM tube was constructed by applying a monomer solution to the surface of a high-density polyethylene filtration membrane with 30 \( \mu \)m diameter pores (Porex, USA). The CEM layer created an ionic connection between chambers but prevented convective liquid flow. Above the fluidization section, an expansion vessel (\( d = 3.8 \) cm, \( h = 7.9 \) cm) was constructed to reduce liquid velocity and promote solids retention (Battistoni et al., 2001). The total cathode volume was 160 mL. The cathode electrode was a 3 cm \( \times \) 15 cm piece of stainless steel 304 mesh (30 \( \times \) 30, McMaster Carr, US) rolled into a 1 cm diameter cylinder and placed within the fluidization column. The outer chamber contained a carbon mesh anode (Wang et al., 2009) and had an empty bed volume of 180 mL.

2.2. Solutions

Anaerobic digester effluent samples were collected from the top section of the secondary digester at a local domestic wastewater treatment plant (University Park, PA) at least once per week, and stored at 4 °C. The treatment plant is comprised of two secondary treatment trains (activated sludge and trickling filters) followed by biological nutrient removal. The cathode chamber was fed raw digestate. The organic matter in the digestate at the point of collection was not adequate for MEC anode current generation. To provide sufficient electron donor to the anode microbial community, 1 g/L of sodium acetate was added to the digestate fed into the anode chamber, which increased the COD from 0.6 g/L to 1.3 g/L (Table 2).

2.3. Reactor operation

Solutions were pumped from reservoirs to the MEC reactor through Viton tubing (Masterflex L/S size 16, USA) using variable speed peristaltic pumps (Cole Parmer, USA). Solutions were recycled in both the anode and cathode chambers at a flow rate of 20 mL/min. Recirculation in the cathode chamber created an up-flow velocity of 0.3 cm/s, which was sufficient to fluidize a bed of glass beads (30–50 \( \mu \)m diameter, Polyscience, Inc, USA). Before each run, 20 g of glass beads were added to the cathode chamber.

The MEC was operated at applied cell voltages (\( E_{ap} \)) of 0.8, 1.0 and 1.4 V using an external power supply (BK Precision, USA). The reactor was also operated with an open circuit (control) to establish a baseline for ion removal in the absence of electrolytic pH changes. The digestate influent flow rate for each applied voltage was adjusted to maintain a cathode pH near 8.5. The influent flow rates for both the anode and cathode chambers were: 0.4 mL/min (0.8 V), 0.7 mL/min (1.0 V), and 1.0 mL/min (1.4 V). At each applied cell voltage condition, the MEC was continuously operated for 8 days.

2.4. Solution and electrochemical measurements

To monitor current generation, the voltage drop across a 10 \( \Omega \) resistor placed within the MEC circuit was measured every 2 h.

![Fig. 1 – Process flow of fluidized bed cathode microbial electrolysis cell with close up of electrode interface.](image)

### Table 2 – Solution characteristics of digestate fed to cathode and anode chambers. Molar ratios are based on soluble phosphorus concentrations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cathode</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.2 ± 0.1</td>
<td>7.2 ± 0.1</td>
</tr>
<tr>
<td>Cond. (mS/cm)</td>
<td>5.5 ± 0.2</td>
<td>6.0 ± 0.1</td>
</tr>
<tr>
<td>COD (g/L)</td>
<td>0.61 ± 0.1</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>tc (mg CaCO₃/L)</td>
<td>2100 ± 120</td>
<td>2300 ± 130</td>
</tr>
<tr>
<td>NH₄−N (mg/L)</td>
<td>490 ± 45</td>
<td>510 ± 52</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>46 ± 3</td>
<td>46 ± 3</td>
</tr>
<tr>
<td>sP (mg/L)</td>
<td>45 ± 3</td>
<td>45 ± 3</td>
</tr>
<tr>
<td>sMg (mg/L)</td>
<td>51 ± 3</td>
<td>52 ± 4</td>
</tr>
<tr>
<td>sCa (mg/L)</td>
<td>76 ± 4</td>
<td>76 ± 3</td>
</tr>
<tr>
<td>sk (mg/L)</td>
<td>57 ± 4</td>
<td>60 ± 5</td>
</tr>
<tr>
<td>sNa (mg/L)</td>
<td>230 ± 15</td>
<td>476 ± 30</td>
</tr>
<tr>
<td>Mg:P</td>
<td>1.4 ± 0.1</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>Ca:P</td>
<td>1.3 ± 0.1</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>Mg:Ca</td>
<td>1.1 ± 0.03</td>
<td>1.1 ± 0.1</td>
</tr>
</tbody>
</table>
15 min using a multimeter (Keithley Instruments, USA) connected to a computer. Catholyte pH was measured every 15 min by multi-parameter probe placed in a flow cell within the recirculation flow path. The pH probe was calibrated before each run. Liquid samples (50 mL) were collected from the influent reservoir as well as the anode and cathode effluent ports each day. Phosphorus, magnesium, calcium, potassium, and sodium concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin Elmer Optima 5300 DV, USA). To determine total ion concentrations, samples (10 mL) were acidified to dissolve any fine particles prior to filtration (0.45 µm pore diameter). Soluble ion concentrations were filtered, and then acidified to prevent precipitation during sample storage. Ammonium concentrations were determined with an ammonia probe (Thermo Scientific Orion, USA). Carbonate alkalinity was determined by titration to pH 4.5 with 20 mM H2SO4 according to standard methods (APHA, 1998). Chemical oxygen demand was determined with a chromic acid colorimetric method (Hach, CO).

2.5. Analysis

Phosphorus conversion efficiency (X) accounts for both fine phosphate salt particles leaving the reactor as well as solids retained and was calculated as the difference between reactor influent total P and effluent soluble P as:

\[ X = \frac{100 \times (\text{TP}_{\text{in}} - \text{sP}_{\text{out}})}{\text{TP}_{\text{in}}} \]  

where TP_{\text{in}} is total influent phosphorus (M), and sP_{\text{out}} is the effluent soluble phosphorus concentration (M). Precipitation efficiency (L), which measures the extent of precipitate retained within the fluidized bed, was calculated as the difference between influent and effluent total P concentrations as:

\[ L = \frac{100 \times (\text{TP}_{\text{in}} - \text{TP}_{\text{out}})}{\text{TP}_{\text{in}}} \]  

The rate of conversion and precipitation were calculated for each sample interval using:

\[ m_X = \frac{(\text{TP}_{\text{in}} - \text{sP}_{\text{out}}) V_{\text{dig}}}{V_{\text{cat}} \Delta t} \]  

\[ m_L = \frac{(\text{TP}_{\text{in}} - \text{TP}_{\text{out}}) V_{\text{dig}}}{V_{\text{cat}} \Delta t} \]  

where \( m_X \) is the phosphorus mass conversion rate (g-P/m³.cat⁻¹.d), \( m_L \) is the phosphorus precipitation rate (g-P/m³.cat⁻¹.d), \( V_{\text{dig}} \) is the volume of digestate treated by the cathode chamber during the sample interval (m³), \( V_{\text{cat}} \) is the cathode volume (m³), and \( \Delta t \) is the sample interval (d). The collection efficiency (η), which is used to determine the retention of converted particles within the fluidized bed, is the ratio of conversion to precipitation (\( m_X/m_L \)) (Moerman et al., 2009; Battistoni et al., 2001).

Energy input (E_{\text{in}}) to the MEC from pumping and applied potential was calculated for each sample interval (\( W_{\text{in}} = W_{\text{cell}} + W_{\text{pump}} \)). Energy input based on current generation and applied cell potential (\( W_{\text{cell}} \)) was calculated as previously described (Call and Logan, 2008). Energy input for the recirculation and influent feed lines were calculated as previously described based on hydraulic head and flow rates (Zhang et al., 2013). At the end of each run, solids were collected from the FBR cathode. A portion of the collected solids from each run was dissolved in an acidic solution (0.2 M HCl) to determine elemental composition. Solid dissolution supernatant was filtered and analyzed using ICP-AES. The saturation index of sparingly soluble salts and ionic complexation within the digestate were predicted at pH values ranging from 7 to 11 using an electrolyte modeling software package (Visual MINTEQ 3.0). The same software package was also used to estimate the NaOH dose required to raise the raw digestate to a pH of 8.5.

3. Results and discussion

3.1. Phosphorus removal in the fluidized bed cathode

Enhanced phosphorus removal and elevated pH were maintained in the fluidized bed cathode MEC. By generating current from soluble organic matter, solution pH within the cathode chamber was maintained between 8.3 and 8.7 under continuous flow conditions (Fig. 3a). Under these elevated pH conditions, phosphorus conversion (X: 70–85%) and precipitation efficiency (L: 66–71%) within the FBR cathode chamber were significantly higher than open circuit conditions (Fig. 2b). Without current generation, cathode solution pH (7.3 ± 0.1) did not increase as the solution passed through the fluidized bed, and phosphorus conversion (8.3 ± 6.1%) and precipitation within the reactor (7.3 ± 5.9%) were an order of magnitude lower than open circuit conditions.
lower (Fig. 2b). Increased removal with current generation led to FBR-cathode effluent soluble phosphorus concentrations that were significantly lower (13 ± 3 mg-P/L) than values obtained with an open circuit (46 ± 3 mg-P/L, Table 3). The level of phosphorus removal achieved by the FBR-MEC was comparable to previous crystallization reactor investigations in which solution pH was increased by aeration or chemical base addition (Ohlinger et al., 2000; Bhuiyan et al., 2008a; Battistoni et al., 2001). Because a bulk phase pH increase was generated in the two chamber FBR-MEC, overall phosphorous removal was higher, and soluble P effluent concentrations were significantly lower, than those previously reported using single chamber MET-based struvite recovery systems. These previous reactors relied on pH increases localized at the cathode surface (Cusick and Logan, 2012; Hirooka and Ichihashi, 2013; Ichihashi and Hirooka, 2012). Phosphorus removal in the FBR cathode was also achieved at much shorter hydraulic retention times than previous single chamber MET investigations.

3.2. Phosphorus precipitation in the fluidized bed cathode

The rate of solids precipitation within the FBR was dependent on influent flow rate and current density. Current density increased with applied voltage (Fig. 3a), which allowed the cathode influent flow rate to be raised while maintaining the solution pH between 8.3 and 8.7, leading to increased phosphorus removal within the FBR. To maintain elevated pH at the lowest applied potential and current density (0.8 V: 0.8 ± 0.03 A/m²-membrane), the solution flow rate was set to 0.4 mL/min (θh = 11.1 h), resulting in a precipitation rate of 67 ± 3 g of phosphorus per cubic meter of cathode volume per day (Fig. 4a). At 1.0 V, the current density (1.7 ± 0.2 A/m²) and flow rate (Qf,c = 0.7 mL/min, θh = 4.8 h) were approximately twice that produced at the lower applied voltage, and the phosphorus precipitation rate increased to 146 ± 15 g-P/m³-cat-day. At the highest applied voltage (1.4 V, 2.4 ± 0.4 A/m²-membrane) the flow rate was 1.0 mL/min (θh = 2.8 h), producing an average phosphorus precipitation rate of 210 ± 14 g-P/m³-cat-day. The highest rate is within the range previously reported for fluidized bed crystallization reactors with chemical base addition to increase pH (Ohlinger et al., 2000). Under open circuit conditions, the phosphate precipitation rate was 16 ± 15 g-P/m³-cat-day at an influent flow rate of 0.7 mL/min (θh = 4.8 h).

Acidic dissolution of solids recovered from the FBR cathode indicated that phosphorus to magnesium ratios were equal to or slightly greater than 1, for all of the elevated pH conditions (Table 4). Since newberyite is unstable at elevated pH values (Dempsey, 1998), these results indicate that struvite was likely the dominant precipitate in the MEC cathode. Previous MET phosphate salt precipitation studies have also shown predominance of struvite, and absence of newberyite in XRD patterns (Hirooka and Ichihashi, 2013). Molar Mg:P ratios greater than one at applied voltages of 1.0 and 1.4 V suggest that bobierrite or cattiite, magnesium phosphate salts with Mg:P ratios of 3:2, may have co-precipitated with struvite. It is also possible that magnesium carbonate (MgCO₃) was present in the precipitate. Under open circuit conditions, the Mg:P ratio of recovered solids was 0.8 suggesting that solids that accumulated in tests at near neutral pH were primarily magnesium phosphate salts. Calcium, potassium and sodium were present in all acid dissolution samples, but at very low concentrations.

| Table 3 – Cathode effluent ionic concentrations and ionic removal ratios. Ionic removal ratios were determined using net ionic removals from anode and cathode to account for cationic diffusion between chambers. |
|---|---|---|---|---|---|
| FBR cathode effluent | tP (mg/L) | sP (mg/L) | sMg (mg/L) | sCa (mg/L) | Ionic removal ratios |
| Applied voltage | | | | | Mg:P | Ca:P |
| OCV | 46 ± 3 | 46 ± 2 | 49 ± 2 | 76 ± 2 | 1.2 | 0.6 |
| 0.8 V | 14 ± 1 | 13 ± 1 | 34 ± 1 | 87 ± 2 | 1.0 | 0.0 |
| 1.0 V | 13 ± 3 | 7.9 ± 2 | 23 ± 2 | 71 ± 3 | 0.99 | 0.0 |
| 1.4 V | 15 ± 1 | 13 ± 3 | 31 ± 2 | 76 ± 3 | 0.98 | 0.0 |

Fig. 3 – a) MEC current density b) cathode pH and c) effluent soluble P concentrations during eight day continuous flow experiments.
Struvite precipitation may have been promoted by favorable influent ionic concentration ratios. The Mg:P ratio in digestate fed to the reactor varied slightly (1.3–1.5) and was above a common target ratio (1.2) that has led to efficient struvite precipitation in previous investigations (Nelson et al., 2003). Ratios of Mg:Ca and Ca:P greater than 2 have previously been shown to promote small diameter (<10 um) amorphous calcium phosphate precipitates (Moerman et al., 2009; Le Corre et al., 2005), which easily leave fluidized bed reactors and decrease recovery efficiencies. Relatively low influent magnesium to calcium (1.1–1.2) and calcium to phosphorus ratios (1.2–1.4) also likely contributed to high collection efficiency.

### 3.3. Cathode scaling

Cathode performance was maintained by particle scouring at current densities less than 2 A/m²-membrane (Fig. 3). At 0.8 and 1.0 V, current density and cathode pH were held stable through the continuous flow runs. As seen in SEM images (Fig. 5b and c), the majority of SS mesh cathode surface area in tests at 0.8 and 1.0 V remained clear, indicating that activity was maintained after 8 days of operation. Minor scale accumulation that occurred was localized to the wire junctions. At 1.4 V, the initial current density of 2.8 ± 0.2 A/m² began to decrease after 3 days of operation, and was reduced to 2 A/m² by the end of the 8-day run. By the end of the 1.4 V run, the cathode surface was completely covered with scale indicating that the drop in current was caused by scale accumulation on the surface of the cathode (Fig. 5d). It is unclear whether scale accumulation was caused by localized pH increase at higher current density or by higher precipitation rates. It is possible that larger particles and higher up-flow velocities could prevent scaling and enable higher precipitation rates.

### 3.4. Molar ionic removal in the fluidized bed cathode

Soluble magnesium and phosphorus removal from digestion effluent fed to the cathode were nearly equimolar, providing further evidence that struvite precipitation was the dominant P removal pathway within the fluidized bed. The similarity in molar phosphorus (0.9–1.1 mM) and magnesium (0.9–1.0 mM) removal for each applied potential interval also implied that hydraulic retention time, which decreased from 11 h at 0.8 V to 2.8 h at 1.4 V, did not influence the extent of struvite precipitation within the cathode chamber. When cationic flux from the anode chamber is considered, the molar Mg:P removal ratios for all of the elevated pH conditions are near 1.0 (Table 3). Co-precipitation of calcium phosphates was minimal in the MEC cathode and soluble calcium concentrations in the cathode solution actually increased due to transport across the CEM during MEC current generation (Fig. 2a). Soluble phosphorus concentration in the anode chamber solution did not increase, indicating that P removal in the cathode was caused by precipitation and that the CEM maintained high selectivity throughout the study (Fig. 6a).

Sodium acetate amendment to the anode digestate produced a concentration gradient between the anode and cathode, which led to increasing sodium flux across the CEM with HRT (Fig. 2a). Ammonium flux calculated from the cathode solution concentrations was highly variable due to ammonia volatilization caused by elevated pH and turbulence. Measurement of ammonium transport from anode to cathode was more consistent based on changes in anode concentration. Ammonia removal from the anode increased with current density and flow rate, ranging from 7.0 ± 1.3 mM at 0.8 V to 12 ± 2.3 mM at 1.4 V (Fig. 6b).

### 3.5. Electrolyte modeling

The influent digestate was modeled to gain a better understanding of why magnesium phosphate, rather than calcium phosphates, formed in the fluidized bed. Modeling results indicated that at pH ≥ 8, both magnesium and calcium phosphates became supersaturated. At the operating pH of the FBR cathode, several salts were supersaturated including calcite, hydroxyapatite (HAP), struvite, and amorphous calcium phosphate (ACP). Although hydroxyapatite was the most
supersaturated of the sparingly soluble phosphate salts (Fig. 7a), crystalline HAP does not form directly. The precursor, ACP, transforms into a homogeneous crystalline structure over a period of days, making it unlikely to occur within the hydraulic retention time of the FBR (Cao and Harris, 2007; Abbona and Baronnet, 1996). Despite high supersaturation of HAP, the competition for soluble phosphorus results primarily in the formation of ACP and struvite. Modeling results of the cathode influent show that struvite was much more supersaturated than ACP within the operating pH range of the FBR.

Modeling of the cathode effluent from the 1.0 V condition, which more closely reflects soluble concentrations within the FBR under continuous flow conditions, showed that only struvite and calcite were supersaturated within the operating pH range of the cathode (Fig. 7b). It is possible that the presence of Mg$^{2+}$, soluble organic ligands and organic particles may have inhibited ACP and calcite precipitation (Cao and Harris, 2007; Ferguson et al., 1973; Ferguson and McCarty, 1971; Van der Houwen et al., 2003; Reddy, 1977; Reddy and Wang, 1980).

Modeled ionization fractions for struvite constituents also reveal limitations of phosphorus removal from digestate with high levels of calcium and carbonate. At elevated pH, struvite precipitation was adversely affected by calcium phosphate and magnesium carbonate complexation (Figure S1). At pH ≥ 8.0, the amount of soluble phosphorus available for struvite precipitation was limited by calcium hydrogen...
phosphate (CaHPO₄) complexation. More significantly, 25–40% of soluble magnesium was unavailable for struvite precipitation due to complex formation with carbonate (MgCO₃), bicarbonate (MgHCO₃⁻), and hydrogen phosphate (MgHPO₄) (Figure S1a).

3.6. COD removal in the anode chamber

MEC current was generated by microbial oxidation of organic matter at the anode. COD removal rate in the anode chamber increased with current density, ranging from 1.1 ± 0.01 g-COD/L-d at 0.8 V to 2.1 ± 0.2 g-COD/L-d at 1.4 V (Figure S2). Coulombic efficiency ranged from 20 to 30%, suggesting that acetoclastic methanogenesis contributed to COD removal.

3.7. Energy consumption

Energy consumption during MEC operation resulted almost entirely from the power used to set the applied cell potential. At 0.8 V, the energy consumption normalized to the amount of phosphorus precipitated was 6.5 ± 0.5 Wh/g-P (0.20 ± 0.4 Wh/L). When the applied potential was increased to 1.0 V, a substantial increase in both current and precipitation rate offset the increased energy consumed at the higher applied voltage, resulting in a similar normalized energy input (6.6 ± 0.4 Wh/g-P, 0.22 ± 0.01 Wh/L) to that obtained at 0.8 V. At 1.4 V, the increase in current density and precipitation rate were insufficient to compensate for the increased energy, resulting in a much higher energy consumption of 10 ± 1.0 Wh/g-P (0.3 ± 0.07 Wh/L).

If high hydrogen recovery rates could be attained, energy production in the MEC could offset electrical energy demand. There was a lack of biogas recovery in the MEC cathode during continuous flow experiments. Possible sources of hydrogen loss include cathodic or hydrogenotrophic acetogenesis (Nevin et al., 2011), dissolved hydrogen in the effluent, as well as diffusion through the PVC reactor body and fittings. It is also possible that competing cathodic reactions, such as metal reduction at the cathode surface, played a role in low hydrogen recovery (Heijne et al., 2010). If 80% of the current produced at the 1.0 V condition were to be recovered as hydrogen, energy recovery from the FBR-MEC (based on the lower heating value) would exceed energy consumption.

Even without hydrogen gas recovery, energy consumption by the FBR-MEC remains below that needed for struvite recovery using other pH adjustment methods. Energy consumption rates observed here were 85–90% lower than a system in which aeration was used to increase digestate pH to 8.4 (~65 Wh/g-P, 1 Wh/L) (Battistoni et al., 2002). It is estimated, based on electrolyte modeling of the cathode influent digestate, that 5 mM (200 mg/L) of NaOH would be required to achieve an equivalent pH increase to 8.5 (Figure S3). Considering the embodied electrical energy of caustic soda produced by the Chlor-Alkali industry (114 Wh/mol-NaOH, (Pellegrino, 2000)), equivalent pH and phosphorus removal (1.0 V case) by caustic addition would represent 0.57 Wh/L and 17.5 Wh/g-P of energy consumption.

The energy required for operation of the FBR-MEC could be further improved in several ways (Figure S4). For example, constructing the cathode chamber with a thinner CEM would significantly reduce ionic transport resistance, which has limited MEC hydrogen production in previous investigations (Rozendal et al., 2008). Selecting a cathode catalyst with less activation over-potential for hydrogen evolution, such as nickel foam (Jeremiasse et al., 2010) or molybdenum disulfide (Tokash and Logan, 2011), would also reduce applied potential and energy consumption. With the system used in this study, treating waste with higher influent P concentrations would significantly reduce energy consumption normalized to grams of phosphorus removed (Figure S4).

4. Conclusions

The results of this study indicate that continuous microbial electrochemical struvite precipitation from digester supernatant is possible if the cathode is operated as a fluidized bed, with a scouring rate that is sufficient to prevent cathode scaling. The magnesium to phosphorus molar ratios of ions removed from solution and recovered as solids indicated that struvite formation was the primary method of phosphorus removal within the FBR cathode. MEC energy consumption (0.2–0.3 Wh/L) was lower than conventional pH adjustment systems used to recover struvite, such as aeration and chemical base addition.
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.01.051.

References


