



# Struvite precipitation and phosphorus removal using magnesium sacrificial anode



Damian J. Kruk<sup>a,\*</sup>, Maria Elektorowicz<sup>b</sup>, Jan A. Oleszkiewicz<sup>a</sup>

<sup>a</sup> Department of Civil Engineering, University of Manitoba, 15 Gillson St, Winnipeg, MB, Canada

<sup>b</sup> Department of Building Civil and Environmental Engineering, Concordia University, 1455 Blvd de Maisonneuve W, Montreal, QC, Canada

## HIGHLIGHTS

- Magnesium dosing by electro-dissolution was used for struvite precipitation.
- Study was conducted using synthetic solutions and fermented WAS supernatant.
- Impact of substrates concentration, pH and electric current on the process was assessed.
- High P removal rates of 4.0 mg PO<sub>4</sub>-P cm<sup>-2</sup> h<sup>-1</sup> at electric current density of 45 A m<sup>-2</sup>.
- Up to 98% of soluble P was removed from fermented WAS supernatant.

## ARTICLE INFO

### Article history:

Received 7 July 2013

Received in revised form 12 December 2013

Accepted 12 December 2013

Available online 31 December 2013

### Keywords:

Struvite  
Electro-dissolution  
Precipitation  
Electrocoagulation  
Magnesium anode  
Nutrient recovery

## ABSTRACT

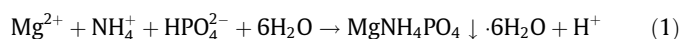
Struvite precipitation using magnesium sacrificial anode as the only source of magnesium is presented. High-purity magnesium alloy cast anode was found to be very effective in recovery of high-quality struvite from water solutions and from supernatant of fermented waste activated sludge from a wastewater treatment plant that does not practice enhanced biological phosphorus removal. Struvite purity was strongly dependent on the pH and the electric current density. Optimum pH of the 24 mM phosphorus and 46 mM ammonia solution (1:1.9 P:N ratio) was in the broad range between 7.5 and 9.3, with struvite purity exceeding 90%. Increasing the current density resulted in elevated struvite purity. No upper limits were observed in the studied current range of 0.05–0.2 A. Phosphorus removal rate was proportional to the current density and comparable for tests with water solutions and with the supernatant from fermented sludge. The highest P-removal rate achieved was 4.0 mg PO<sub>4</sub>-P cm<sup>-2</sup> h<sup>-1</sup> at electric current density of 45 A m<sup>-2</sup>. Initial substrate concentrations affected the rate of phosphorus removal. The precipitated struvite accumulated in bulk liquid with significant portions attached to the anode surface from which regular detachment occurred.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O) deposition in pipes, on reactor walls and on submerged surfaces of devices (Le Corre et al., 2005; Ben Moussa et al., 2006; Suzuki et al., 2007), significantly increases maintenance costs in conventional and biological nutrient removal (BNR) plants (Doyle et al., 2002). Controlled struvite precipitation, on the other hand, may not only reduce the load of phosphorus and ammonia returned to the mainstream treatment process but also produce a valuable and marketable fertilizer. Numerous researchers have shown feasibility of struvite production from anaerobically digested sludge dewatering liquors and from livestock manure (Schuiling and Andrade, 1999; Doyle et al., 2002; Suzuki et al., 2005; Zeng and Li, 2006; Suzuki et al., 2007) since they are

rich in phosphorus and ammonia. Struvite precipitates in form of stable white orthorhombic crystals (Le Corre et al., 2005) – the precipitation reaction can be expressed as (Zeng and Li, 2006):



Published research indicated the most important factors affecting struvite precipitation were found to be (Stratful et al., 2001; Doyle et al., 2002; Le Corre et al., 2005; Ben Moussa et al., 2006; Zeng and Li, 2006): the substrates saturation depending on the concentration, the molar ratio Mg<sup>2+</sup>:NH<sub>4</sub><sup>+</sup>:PO<sub>4</sub><sup>3-</sup> and pH, as well as the inhibition due to presence of other ions (e.g. Ca<sup>2+</sup>, K<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>). According to Hao et al. (2008) optimal molar ratio of Mg:N:P was 1.2:3:1 at 6 mM, 15 mM and 5 mM of magnesium, nitrogen and phosphorus, respectively. The pH affects saturation index by changing the speciation of struvite substrates and other competing precipitates, such as magnesium phosphate or magnesium carbonate. It is generally agreed that struvite precipitation in municipal

\* Corresponding author. Tel.: +1 2044749320.

E-mail address: [d\\_kruk@umanitoba.ca](mailto:d_kruk@umanitoba.ca) (D.J. Kruk).

wastewater and sludge dewatering liquor occurs when pH is higher than 7.5 and it rapidly increases until pH 10.5 (Doyle et al., 2002; Zeng and Li, 2006). Hao et al. (2008) showed that optimal pH for precipitation of high purity struvite (>90%) was between 7.5 and 9 and dropped to 7.0–7.5 when  $\text{Ca}^{2+}$  ions were present. Above pH of 9, or above pH of 7.5 in the presence of calcium, the precipitation of phosphorus took place in the form of magnesium or calcium phosphates (Hao et al., 2008).

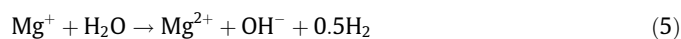
The most popular method of struvite production from wastewater is chemical precipitation by dosing magnesium salts and adjusting pH with a base (Schuiling and Andrade, 1999; Zeng and Li, 2006; Suzuki et al., 2007) or by stripping  $\text{CO}_2$  using aeration (Suzuki et al., 2005, 2007). Among magnesium sources most frequently used are  $\text{MgCl}_2$ ,  $\text{MgO}$  and  $\text{MgSO}_4$  (Hug and Udert, 2013). Other magnesium compounds like  $\text{Mg}(\text{OH})_2$  and  $\text{MgCO}_3$  are much less suitable due to their low solubility in water (Schuiling and Andrade, 1999; Zeng and Li, 2006).

Ben Moussa et al. (2006) and Wang et al. (2010) proposed to eliminate the need for alkalinity dosing using electrolytic cell with inert anodes. In accordance with the overall reaction of oxygen reduction and hydrogen evolution (Eqs. (2) and (3)), hydroxide anions are produced on the cathode surface. The process was shown to increase the interfacial pH of cathode by as high as 1.5 units in comparison to the bulk solution (Ben Moussa et al., 2006). Thus, struvite deposition can be done in neutral pH of bulk solution (Ben Moussa et al., 2006; Wang et al., 2010). Ben Moussa et al. (2006) reported that electrochemical methods allowed production of pure struvite. In both cases external magnesium source was dosed.



The phosphorus removal electrodes can also be used as the source of the coagulating ions (Holt et al., 2005; Wei et al., 2009; Tran et al., 2012; Hug and Udert, 2013). In that case besides elevating the pH, the electrodes are also used to provide iron, aluminium or magnesium cations by corrosion and/or electrolytic dissolution. Wei et al. (2009) reported instantaneous ortho-phosphorus removal improvement from 19% to 86% after electric current was applied to the aluminium electrodes in their electrically enhanced membrane bioreactor. The reactor was fed with synthetic municipal wastewater. The phosphorus removal mechanism was precipitation in form of  $(\text{AlOH})_3(\text{PO}_4)_2$  or  $\text{AlPO}_4$ , and adsorption on  $\text{Al}(\text{OH})_3$ .

Song et al. (1997) studied anodic dissolution of magnesium in chloride and sulphate solutions. They found that the magnesium dissolution process involves intermediate  $\text{Mg}^+$  species and suggested the following reaction sequence:



The reaction in Eq. (4) was assumed to be the rate determining step. Song et al. (1997) found also that the presence of  $\text{Cl}^-$  ions reduced passive film area, and accelerated the  $\text{Mg}^+$  ions release from the metal magnesium.

Hug and Udert (2013) employed electrolytical magnesium dissolution to precipitate struvite from source-separated urine. Phosphorus removal rate of  $3.7 \text{ mg P cm}^{-2} \text{ h}^{-1}$  at an impressed current density of  $55 \text{ A m}^{-2}$  was achieved in a sequencing batch reactor process with a 2 h cycle. Struvite production cost with electrochemical magnesium dosing at  $4.45 \text{ € kg}^{-1}$  was shown to be competitive with dosing of  $\text{MgCl}_2$  and  $\text{MgSO}_4$ .

The objective of this study was to assess the suitability of nutrient recovery at non-BNR plant by struvite precipitation from the supernatant of fermented waste activated sludge using a sacrificial magnesium anode as the sole source of magnesium. Specific objectives were to determine the impact of solution pH and electric current on purity of the produced struvite and the phosphorus removal ratio.

## 2. Material and methods

Both the synthetic pure water solution and the WAS supernatant tests were conducted in a 1 L reactor equipped with a set of two magnesium electrodes, pH probe (Accumet 13-620-108A by Fisher Scientific) and a magnetic stirrer. The electrodes were shaped as 2 mm thick rectangular plates with an active surface area of  $44 \text{ cm}^2$  (both sides of the electrodes were used) and were made of high purity alloy AZ91HP. Direct current was supplied to electrodes by BOP 100-2D (KEPCO, USA). Water deionized in Elix<sup>®</sup> Water Purification system (Millipore, USA) with electro conductivity  $0.08 \pm 0.01 \text{ μS cm}^{-1}$  was used for preparation of synthetic solutions. Conductivity measurements during tests were done with Accumet 13-620-165 conductivity electrode (Fisher Scientific) and Accumet 13-620-10 temperature electrode connected to Accumet XL50 meter (Fisher Scientific). Conductivity was compensated to the actual solution temperature.

### 2.1. Impact of pH and electric current on struvite purity and phosphorus removal rate

A series of 3 h batch tests were conducted. The value of pH was continuously adjusted with 0.02 N HCl solution dosed by Mini Variable-Flow Peristaltic Pump (Fisher Scientific) controlled by alpha pH200 controller (Eutech Instruments). Solution for all tests contained  $24 \text{ mM Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  ( $743 \text{ mg PL}^{-1}$ ) and  $46 \text{ mM NH}_4\text{Cl}$  ( $645 \text{ mg N L}^{-1}$ ), which accounts for 1:1.9 molar ratio of P:N. Conductivity of electrolyte was adjusted to  $10 \text{ mS cm}^{-1}$  by dosing NaCl.

Four tests (T1 through T4) were run with electric current of 0.05 A and pH set points of 6.5, 7.5, 8.5 and 9.5. Three tests (T5 through T7) were run with pH set point of 7.5 and with the electric current of 0.1, 0.15 and 0.2 A.

During the tests 6 mL solution samples were grabbed every 30 min. To assess the nutrient removal rate phosphorus and ammonia in the samples were determined by flow injection analysis FIA, QuikChem Method 10-115-01-1-O and 10-107-06-1-I (QuikChem8500 by Lachat Instruments, USA).

### 2.2. Impact of initial substrate concentration on phosphorus removal rate

Five 3 h tests (T8-T12) were conducted at different initial ammonia and phosphorus concentrations (Table 1). Applied electric current and pH set point (power source and pH control as in previous tests) were the same for all five tests, 0.1 A and 7.5 respectively. As in all other tests, 6 mL grab samples were collected every 30 min, filtered and analysed for ammonia nitrogen and ortho-phosphates using FIA.

An additional 7 h test T13 was conducted to assess phosphorus removal rate at the elevated N:P concentration ratio. Initial concentrations of ammonia nitrogen and phosphorus were  $482 \text{ mg N L}^{-1}$  and  $554 \text{ mg P L}^{-1}$  (N:P molar ratio 1.92), respectively. In order to keep ammonia concentration at a high level throughout the test, 10 mL of  $30.6 \text{ g NH}_4\text{Cl L}^{-1}$  (which accounts for  $80 \text{ mg N}$ ) solution was dosed manually to the reaction beaker every 2 h.

Download English Version:

<https://daneshyari.com/en/article/4408903>

Download Persian Version:

<https://daneshyari.com/article/4408903>

[Daneshyari.com](https://daneshyari.com)