


## RESEARCH ARTICLE

# Usage of phosphoric acid plant's circulate pond waters in struvite precipitation—Effect of conditions

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## Abstract

Struvite is a suitable fertilizer, and electrochemical precipitation of nutrients from industrial waters provides one answer to the circular economy. Molar ratio between ammonium and phosphate is crucial: Water suitable for the precipitation includes more or at least the same amount ammonium than phosphate. That kind of water typically does not exist in industry. Therefore, ammonium-rich industrial water was mixed with phosphorus-rich water to obtain a suitable molar ratio for struvite precipitation. Parameters were studied to determine their effect on removal-% and struvite yield. 100% struvite yield was obtained under several conditions even without pH control with pH 7–9. The highest phosphate removal (99.7%) was occurred with the molar ratio 1.7:2:1 for Mg:NH<sub>4</sub>:PO<sub>4</sub> (pH 9.0). Waters dilution prevents magnesium anode corrosion. Formed struvite has potential as recycled fertilizer due to low bio-availability of metals and high leachability of nutrients studied by four-stage sequential leaching.

## KEYWORDS

ammonium, electrochemical precipitation, phosphate, pond water, struvite

## 1 | INTRODUCTION

Phosphorus is vital element for life on the Earth, but in excess amount as a soluble form, it causes challenges in nature systems. Several human activities, such as agriculture and sewage discharge, and industrial activities, such as mining industry discharges, release high amounts of phosphorus, causing eutrophication (Bacelo et al., 2020). Phosphorus can be recovered from water by using several techniques, such as chemical precipitation, biological treatment, reverse osmosis, electrodialysis, electrocoagulation, ion exchange, and adsorption (Berninger et al., 2017; Kilpimaa et al., 2015). All technologies have advantages and disadvantages. In the case of chemical or

electrochemical precipitation, formation of precipitation products with utilization applications, such as struvite, exists.

The circular economy is an important viewpoint for the industrial sector today, and means of legislation have also been used to guide the circulation of valuables such as nutrients. Recently, legislation related to the circular economy in fertilizer markets has been updated. The EU Fertilizing Product Regulation (FPR) 2019/1009 covers secondary-raw-material-based fertilizer products. Additionally new recycled fertilizers could become valid to use under this regulation (The European Parliament and Council Regulation [EU] 2019/1009). The STRUBIAS report published the criteria for quality management systems in 2019. Precipitated phosphate salts, such as struvite or dicalcium phosphates,

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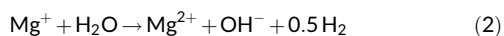
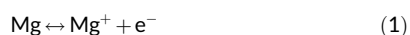
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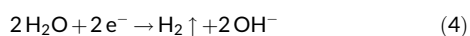
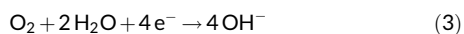
and their derivatives are included in these reviewed materials (Huygens et al., 2019). Therefore, precipitation would be a suitable technology for nutrient uptake and circulating as a recycled fertilizer.

Electrochemical precipitation of struvite can be carried out using a sacrificial magnesium anode. Magnesium corrosion is quite unique compared with other metals. Cathodic hydrogen evolution can occur on a magnesium anode's surface during anodic polarization. This is due to a phenomenon called the negative difference effect (NDE), which always accompanies electrochemical dissolution of magnesium. Because magnesium's potential is negative ( $\ll -1V_{SHE}$ ), the hydrogen evolution reaction (HER) on Mg occurs at high rates (Song, 2005; Thomas et al., 2015). Compared with chemical dosage, electrochemical dosage gives a continuous dose of magnesium as magnesium dissolves throughout the precipitation time as current is supplied. This leads to lower supersaturation, which promotes crystal growth (Hug & Udert, 2013).

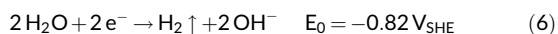
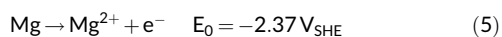
Magnesium dissolution has been found to involve an intermediate  $Mg^+$  species. Its formation has been identified as the rate-determining step. The reactions at the anode are as follows (Kruk et al., 2014):



At the cathode, water is reduced releasing hydroxide ions and hydrogen gas, which is presented in the following reaction equations (Kruk et al., 2014):



Mg dissolves rapidly in aqueous environments. The high rate of corrosion is due to the half reactions presented in Equations (5) and (6). The magnesium anode can also corrode non-galvanically, which reduces the energy demand for magnesium dissolution (Hug & Udert, 2013; Thomas et al., 2015).



The release of  $Mg^{2+}$  and  $OH^-$  in the electrochemical reaction can lead to a chemical reaction between these ions, especially if their local supersaturation is high.

Struvite precipitation occurs naturally, for example, in water storage tanks and pipes with molar ratios 1:1:1 for magnesium, phosphate, and ammonium (Hug & Udert, 2013; Le Corre et al., 2009). The main challenge in nutrients circulation as struvite is the needed molar ratio between ammonium and phosphate: water suitable for the precipitation include at least the same amount of ammonium than phosphate. That kind of water typically do not exist in industry. Hug and Udert

(2013) precipitated struvite from urine that contained 197 mg/L phosphate and 2540 mg/L ammonium. They found higher phosphate removal with increasing molar ratio between magnesium and phosphate. Typically ammonium concentration is low due to the volatilization (Hug & Udert, 2013). Kruk et al. (2014) used molar ratio 1:1.9 (P: N ratio, i.e., 24 mM phosphorus and 46 mM ammonia), and they found 90% purity for struvite (Kruk et al., 2014).

In this study, electrochemical precipitation as struvite was used for simultaneous removal of phosphate and ammonium. The waters used in this study were process waters from a phosphoric acid plant. They were mixed to obtain a suitable molar ratio between ammonium and phosphate to enable struvite precipitation because struvite formation requires a specific molar ratio between ammonium and phosphate. However, in this study, two kinds of water were mixed within the same industrial plant to obtain the optimum molar ratio for struvite precipitation. Magnesium was dissolved electrochemically, and some magnesium was also found already in the waters decreasing the amount of dissolved magnesium needed. Precipitation conditions were optimized to improve struvite yield and removal of phosphate and magnesium. In addition, magnesium plate detachment was prevented by optimizing the precipitation conditions. This study showed that precipitation conditions can be optimized through traditional methods by setting precipitation conditions as well as adjusting the needed nutrient concentrations by mixing two kinds of industrial process waters.

## 2 | MATERIAL AND METHODS

### 2.1 | Water solutions

The authentic waters used in electrochemical precipitation were process waters of company Yara in Finland, namely, KVA10 and LAT. Both waters are phosphoric acid plants' circulate pond waters. The pH of KVA10 water was 2.7, and the pH of LAT water was 3.9. The composition of KVA10 and LAT waters is expressed in Table 1. KVA10 waters contain high amounts of phosphate, and LAT waters contain high amounts of ammonium and nitrate. The ammonium and nitrate

**TABLE 1** Composition of KVA10 and LAT waters.

Parameter	Unit	Waters	
		KVA10	LAT
pH		2.7	3.9
PO <sub>4</sub> -P	g/L	10.4	0.16
NH <sub>4</sub> -N	g/L	–	2.08
NO <sub>3</sub> -N	g/L	–	2.15
K	g/L	0.36	0.087
Na	g/L	1.3	–
Ca	g/L	0.64	–
Mg	g/L	0.84	–
Al	g/L	0.04	–
Fe	g/L	0.03	–

concentrations are expressed as nitrogen. In this study, phosphorus-rich KVA10 waters and ammonium-rich LAT waters were mixed to obtain nutrient-rich water suitable for struvite precipitation. Therefore, commercial reagents to adjust nutrient concentrations were not needed.

## 2.2 | Experimental set-up

Electrochemical precipitations were carried out in a 2 L beaker with 1.6 L sample volume. The solution was stirred with a magnetic stirrer. A magnesium (Standard AZ3IB: ~95% Mg, 2.5–3.5% Al and 0.6–1.4% Zn) metal plate was used as an anode and a steel plate as a cathode. The sizes of the plates were 5.0 cm × 4.75 cm × 0.4 cm. Therefore, the reactive electrode area was 53.4 cm<sup>2</sup>. Molar ratios for ammonium and phosphate were adjusted by mixing suitable amounts of KVA10 and LAT waters. Experiments were implemented with NH<sub>4</sub>:PO<sub>4</sub> molar ratios of 2:1 (experiments EC1–EC10) and 1:1 (experiments EC11–EC13) based on the preliminary experiments in which those molar ratios led to pure struvite formation. The electrochemical dissolution of magnesium was carried out with such time periods and current densities that the calculated amount of magnesium that would dissolve would be suitable for the desired molar ratio when the magnesium already existing in the KVA10 was also considered. The amount of magnesium released from the anode was calculated with Faraday's law (7):

$$m = \frac{ItM}{zF} \quad (7)$$

In the equation, *m* is the mass (g) of magnesium released in the solution, *I* is the operating current (A), and *t* is the run time (s). *M* is the

atomic weight (g/mol) of magnesium, and *z* is the magnesium valence (2). *F* is Faraday's constant (96 484 C/mol). It can be seen from Faraday's law that high operating current and high treatment time result in a greater amount of magnesium generated (Holt et al., 2005).

Experiments, namely, EC1–EC13, were done with different conditions, which are described in detail in Table 2. All experiments were done in duplicate. The aim of different reaction conditions was to prevent magnesium anode corrosion, obtain as high as possible reduction for phosphate and magnesium, and obtain high struvite yield. The effects of time, dilution of the initial solution, different molar ratios, and different ways to control pH were studied. In experiments EC1–EC3, conditions remained the same, but the effect of current was studied by adjusting the time. The optimum time of 4 h was selected for the further experiments, and to prevent destroying the magnesium electrode plate, the effects of dilution of the solution and pH were studied (EC4–EC5). In experiments EC6–EC10, the amount of magnesium was decreased to the molar ratio of 1:1, and the effect of pH adjustment was studied. These experiments were done to prevent destroying the magnesium electrode. In experiments EC11–EC13, the effects of the adjusted molar ratio of nutrients and current were studied. A 10 M NaOH solution and 5 M HCl solution were used for pH adjustment. The EA-PS 3065-05 B laboratory power supply was used; it had a voltage range of 0–65 V and a current range of 0–5 A. With this power supply, the current could be set with a two-decimal accuracy.

All the experiments involved mixing the solution in the direction from cathode to anode with 250 rpm. The rotating direction of the magnetic stirrer was always counterclockwise. In all the experiments, the anode was on the left side of the beaker and cathode on the right side. Redox and pH were measured near the anode and another pH measurement point was placed as far as possible from the electrodes. The distance between electrodes (*l*) was 7 mm.

**TABLE 2** Conditions in different electrochemical precipitation experiments.

Experiment	Theoretical molar ratio (Mg:NH <sub>4</sub> :PO <sub>4</sub> )	Time (h)	Current <i>I</i> (A)	pH	Additional information
EC1	1.7:2:1	2	1.89	9.0	-
EC2	1.7:2:1	4	0.94	9.0	-
EC3	1.7:2:1	6	0.63	9.0	-
EC4	1.7:2:1	4	0.47	9.0	½ dilution
EC5	1.7:2:1	4	0.47	7.6	½ dilution
EC6	1.1:2:1	4	0.47	9.0	-
EC7	1.1:2:1	4	0.47	9.0	Raising pH to 7 before positioning the electrodes in water, then raising to 9
EC8	1.1:2:1	4	0.47		Raising pH to 7 before positioning the electrodes in water and not controlling pH after that (final pH 9.1)
EC9	1.1:2:1	4	0.47		Raising pH to 7 after turning the current on and not controlling pH after that (final pH 9.2)
EC10	1.1:2:1	4	0.47	8.0	
EC11	1.3:1:1	4	0.19	9.0	1/5 dilution
EC12	1.3:1:1	1.5	0.5	9.0	1/5 dilution
EC13	2.9:1:1	4	0.5	9.0	1/5 dilution

Note: Molar ratios were calculated based on Equation (7) and nutrient concentrations as presented in Table 1.

## 2.3 | Analytical methods

The IntelliCAL ORP-REDOX MTC101 probe was used for redox potential measurement. It was calibrated with ORP standard solution (ZoBell's solution) 221 eV  $\pm$  10 eV. Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> were analysed with an iCAP 6500 PLASMA spectrometer (ICP-OES). NH<sub>4</sub><sup>+</sup> was analysed with an HACH ISENH4181 ammonium probe. Phosphate as P<sub>2</sub>O<sub>5</sub> was analysed with the QuAAtro39 Continuous Segmented Flow Analyzer. Precipitates from the experiments were dried at room temperature (22  $\pm$  2°C) and analysed using an X-ray diffractometer (XRD; Rigaku SmartLab 9 kW; Japan).

## 2.4 | Sequential leaching

Chemical speciation of several impurities of sludge formed during electrochemical precipitation has been studied by using four-stage sequential leaching. In the first stage, water-soluble fraction and labile forms of metals are leached. In the second stage (i.e., in the exchangeable fraction), the precipitate is extracted in acetic acid, whereby metals bound to the surface by relatively weak bonds are leached. In the third step, the easily reducing fraction is extracted, and in the fourth step, the oxidizing fraction (Kuokkanen et al., 2006). Sequential leaching was done for the precipitate formed in experiment EC2 based on Table 3. All used glassware was washed overnight with 2 M HNO<sub>3</sub>.

In the first step, acid rain was modelled by extracting the precipitates in distilled water (pH adjusted to 4 by nitric acid). One gram of sample mass was used, and duplicate experiments were done. Samples were shaken in the laboratory shaker (300 rpm) for 16 h at room temperature. Eluate was separated using a centrifuge. The sample was washed using 20 mL of distilled water (15 min in the laboratory shaker). After washing, the sample was separated by centrifugation. Water was pipetted, and samples were transferred to the next stage.

In the next step, 40 mL of 0.11 M acetic acid was added to each centrifuge tube and left on a shaker (300 rpm) for 16 h. Eluate separating and sampling were done as in the first step, as well as sample washing. The third step was done in the same way as in the previous steps, except the leaching solution was 0.5 M NH<sub>2</sub>OH·HCl. The extraction in the fourth stage was started by adding 10 mL of H<sub>2</sub>O<sub>2</sub> to each tube. The mixture was shaken manually occasionally for one hour, after

which the solutions were poured into 50 mL beakers. Beakers were heated in a water bath (85°C) for 1 h, and then solvent was allowed to evaporate to less than 3 mL of hydrogen peroxide. In the next step, 10 mL of hydrogen peroxide was added, and the previous step was repeated, except the final volume of the solvent was evaporated to <1 mL. In the final stage, extraction with 1 mol/L CH<sub>3</sub>COONH<sub>4</sub> for 16 h in laboratory shaker was done. Eluates were analysed by ICP-OES (Agilent 5110 VDV ICP-OES, Santa Clara, CA, USA).

## 3 | RESULTS AND DISCUSSION

In this study, different reaction conditions in electrochemical precipitation were studied with the aims of preventing magnesium anode corrosion, removing the phosphate from authentic water as struvite, and obtaining high struvite yield. Residual magnesium concentration was also aimed to be as low as possible (i.e., magnesium removal was aimed to be as high as possible). However, the magnesium released in the solution goes through numerous different equilibrium reactions that correspond to redox, acid/base, complexation, and precipitation reactions in water. The occurring reactions and their role as a removal mechanism depends on the species that exist in the solution. With phosphate ions, precipitation, complexation, and adsorption are the most remarkable mechanisms. Industrial waters typically include several kinds of compounds, making precipitation more complex. Calcium cations, for example, co-precipitate, and fluoride anions form complexes and precipitate (Hakizimana et al., 2017).

### 3.1 | Reductions of different ions

The reductions of different ions during the experiments are presented in Table 4. In EC12, phosphate reduction was significantly lower compared with other experiments, indicating that the precipitation time of 1.5 h was not long enough. The most common trend was that PO<sub>4</sub> reduction was nearly 100% in all experiments. Magnesium reduction was calculated by considering the theoretical amount of Mg<sup>2+</sup> dissolved, as well as the magnesium that already existed in the authentic water sample. Calcium removal was calculated based on the initial concentration of this element that already existed in the sample.

**TABLE 3** Four-stage sequential leaching procedure.

Step	Fraction	Solvent	Experimental circumstances
F1	Water soluble	40 cm <sup>3</sup> H <sub>2</sub> O, pH 4 (adjusted by HNO <sub>3</sub> )	16 h, 22 $\pm$ 2°C, continuous shaking
F2	Exchangeable	40 cm <sup>3</sup> Acetic acid 0.11 mol/L	16 h, 22 $\pm$ 2°C, continuous shaking
F3	Reducing	40 cm <sup>3</sup> NH <sub>2</sub> OH·HCl 0.5 mol/L, pH 1.5 (adjusted by HNO <sub>3</sub> )	16 h, 22 $\pm$ 2°C, continuous shaking
F4	Oxidizable	10 cm <sup>3</sup> H <sub>2</sub> O <sub>2</sub> 300 g/L	1 h, 22 $\pm$ 2°C, random manual shaking, after that 1 h 85 $\pm$ 2°C. Volume after evaporation < 3 cm <sup>3</sup>
		10 cm <sup>3</sup> H <sub>2</sub> O <sub>2</sub> 300 g/L	1 h, 85 $\pm$ 2°C. Volume after evaporation < 1 cm <sup>3</sup>
		50 cm <sup>3</sup> CH <sub>3</sub> COONH <sub>4</sub> 1 mol/L, pH 2 (adjusted by HNO <sub>3</sub> )	16 h, 22 $\pm$ 2°C, continuous shaking

**TABLE 4**  $\text{NH}_4^+$ -,  $\text{PO}_4^{3-}$ -,  $\text{Mg}^{2+}$ -, and  $\text{Ca}^{2+}$ -reductions in different electrochemical precipitation experiments after the treatment time.

Experiment	Theoretical molar ratio (Mg:NH <sub>4</sub> :PO <sub>4</sub> )	PO <sub>4</sub> <sup>3-</sup> -reduction (%)	Mg <sup>2+</sup> -reduction (%)	Ca <sup>2+</sup> -reduction (%)
EC1	1.7:2:1	99.7 (±0.25)	80.9 (±0.89)	51.3
EC2	1.7:2:1	99.4 (±0.47)	85.2 (±3.2)	76.9
EC3	1.7:2:1	99.3 (±0.62)	82.1 (±0.96)	66.7
EC4	1.7:2:1	99.5 (±0.087)	81.9 (±1.2)	63.2
EC5	1.7:2:1	87.9 (±9.1)	77.1 (±4.1)	33.3
EC6	1.1:2:1	95.5 (±1.8)	99.5 (±0.013)	87.2
EC7	1.1:2:1	95.7 (±0.37)	98.7 (±0.23)	79.4
EC8	1.1:2:1	96.6 (±2.2)	99.2 (±0.018)	92.3
EC9	1.1:2:1	94.7 (±0.35)	99.5 (±0.050)	89.7
EC10	1.1:2:1	94.3 (±2.6)	97.5 (±1.5)	84.6
EC11	1.3:1:1	91.6 (±3.0)	83.8 (±1.6)	39.7
EC12	1.3:1:1	75.6 (±7.4)	81.7 (±5.3)	29.0
EC13	2.9:1:1	95.8 (±0.28)	66.4 (0.75)	62.1

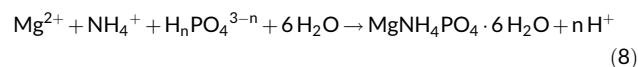
Struvite has low solubility, 0.018 g/100 mL at room temperature in water (Le Corre et al., 2009). However, in the experiments done with diluted solutions, minor amount of formed struvite could dissolve and decrease the rates of phosphate and magnesium removal.

In this study, an electrode distance of 7 mm was used. During pretests, a 12 mm distance between electrodes was used, and the shorter distance was found to be better according to evaluation the reduction of ions and struvite yield during the experiment. The distance between electrodes determines the cell's ohmic resistance, which regulates the production of coagulants and energy consumption. Hashim et al. (2019), for example, studied three different distances (5, 10, and 15 mm) for aluminium electrodes. Five millimeters was found to be the best out of these three distances because increasing the interelectrode distance increased the ohmic resistance, which led to an increase in energy consumption. Additionally, phosphate removal efficiency decreased due to decreased coagulant production (Hashim et al., 2019). The findings of other researchers also support the shorter electrode distance (Park et al., 2017).

The highest removal of both phosphate and magnesium was obtained in experiments EC6, EC7, EC8, EC9, and EC10. The theoretical molar ratio (Mg:NH<sub>4</sub>:PO<sub>4</sub>) was 1.1:2:1 in all these experiments. The duration of the precipitation was 4 h in all these experiments. This could indicate that the used molar ratio would be suitable, 4 h of precipitation time is enough, and the pH adjustment moment is not the most important case in this precipitation. Finally, the target pH value of 9 was achieved, except in experiment EC10. The results also show also that reduction of phosphate and magnesium was slightly lower in EC10 compared with the others, indicating that a pH value of 8 might not be enough.

### 3.2 | pH during precipitation experiments

The chemical reaction of struvite formation is presented in the following reaction equation (Li et al., 2019):



where  $n = 0, 1, \text{ or } 2$ , depending on the pH of the solution. Struvite can precipitate in a wide pH range from 7 to 11. An increase in pH generally decreases struvite solubility, but when pH increases to over 9, struvite solubility starts to increase. Optimum pH depends on other variables, such as the composition of the water treated. Increasing pH, as well as increasing temperature has been reported to reduce induction time. Even though struvite already precipitates at pH 7, at pH < 8, struvite precipitation is usually very slow (Doyle & Parsons, 2002). Kruk et al. (2014) reported optimum pH value for struvite precipitation 7.5–9.3 when struvite was electrochemically precipitated from water solutions and from supernatant of fermented waste activated sludge (Kruk et al., 2014). Presence of constituent ions other than struvite can limit struvite crystal growth rate by blocking the active crystal growth sites, or they can form some other precipitants as impurities. Calcium, for example, can compete with magnesium and produce precipitates such as  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{CaHPO}_4$ , and  $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$ . When the Ca:Mg molar ratio is 0.5–1.0, struvite formation is hindered, and a 0.75–1.0 or higher molar ratio restricts struvite precipitation (Muhmood et al., 2019). Therefore, the calcium reduction rate was also measured in the first series of experiments.

### 3.3 | Magnesium anode corrosion

During electrochemical precipitation experiments, magnesium corrosion destroying the anode occurred. Therefore, different conditions to prevent corrosion were studied. The theoretical amount of magnesium that should corrode from the anode is based on Faraday's law (Equation 7). The theoretical and real amounts of anode weight loss after brushing are expressed in Table 5. The anode weight losses before brushing the electrode surface show that almost every time

**TABLE 5** Wearing of the Mg-anode.

Experiment	Theoretical amount of Mg corrosion (g)	Weight loss after brushing the electrode (g)
EC1	1.71	2.06 ( $\pm 0.04$ )
EC2	1.71	1.76 ( $\pm 0.16$ )
EC3	1.71	1.88 ( $\pm 0.15$ )
EC4	0.85	0.89 ( $\pm 0.08$ )
EC5	0.85	0.89 ( $\pm 0.04$ )
EC6	0.85	0.91 ( $\pm 0.07$ )
EC7	0.91	1.01 ( $\pm 0.03$ )
EC8	0.91	0.89 ( $\pm 0.08$ )
EC9	0.85	0.83 ( $\pm 0.15$ )
EC10	0.85	0.93 ( $\pm 0.05$ )
EC11	0.34	0.22 ( $\pm 0.13$ )
EC12	0.34	0.32 ( $\pm 0.01$ )
EC13	0.91	0.88 ( $\pm 0.06$ )

prior to removing precipitate or uncorroded Mg from the surface, the weight loss was significantly smaller compared with the theoretical weight loss. Sometimes the mass of the anode even increased, and a white precipitate on the surface of the anode was found. In some cases, partly loosened magnesium pieces were still attached to the anode surface. Most of the time, the weight loss difference was due to a combination of both mentioned factors. After brushing the precipitate from the surface, the weight losses were more reliable and closer to the theoretical value, except in EC11. In experiment EC11, the current was smaller compared with in all the other experiments, which might have affected to the dissolution. If all the precipitate products are removed such as by brushing the anode surface, usually some of the uncorroded magnesium also gets removed. Therefore, the resulting weight loss is higher than the actual amount of magnesium separated or corroded from the anode. On the other hand, if the removal is too gentle, some of the precipitate stays on the anode and the resulting weight loss is less than the real amount of magnesium corroded. Destroying of the anode is typical phenomena in electrochemical precipitation but by optimizing the conditions, electrode will last more runs. The changes on the morphology of other sacrificial anodes like aluminium can also be found like reported by Hashim et al. (2019).

The potential where magnesium electrode activates is typically called the pitting potential, because the activation is accompanied by the initiation of irregular corrosion pits. Release of monovalent  $Mg^+$  ions and microgalvanic corrosion, which is corrosion of magnesium when impurity sites act as cathodes, improve struvite precipitation. Loss of chunks can have an opposite effect if the chunks do not dissolve. The chunk effect is mechanical loss of metal pieces from the anode surface. The chunk effect typically occurs after the electrode has been strongly corroded (Hug & Udert, 2013).

Measuring the anode weight loss is one way of determining the anode corrosion rate. However, precipitate also exists on the anode surface and was removed by brushing, which also enables the

uncorroded magnesium to be removed. The effects of pH adjustment, water sample dilution, and current were studied to prevent magnesium anode corrosion as chunks. It was hypothesized that aggressive ions such as chloride in KVA10 water could possibly corrode the magnesium anode aggressively and cause the chunk effect (Esmaily et al., 2017). Therefore, authentic water samples were diluted. Increasing the pH in EC7 and EC8 before placing the electrodes in water was studied because it was hypothesized that the highly acidic nature of the KVA10 + LAT mixture would corrode the electrodes so aggressively that it would cause the chunk effect of magnesium where magnesium would eventually corrode as big pieces. The cathode facing side of the anode clearly corrodes more than the other side of the anode. However, the timing of pH adjustment did not have an effect, and magnesium corrosion existed in both experiments. In addition, in some cases (EC13), a white film existed on the surface of the magnesium plate. This phenomenon can be explained due to  $Mg(OH)_2$  film formation and negative difference effect (NDE). In NDE, cathodic hydrogen evolution can occur on the surface of the magnesium anode during anodic polarization. The hydrogen evolution reaction (HER) on magnesium anode occurs at high rates due to the negative potential of magnesium ( $<< -1V_{SHE}$ ) (Song, 2005; Thomas et al., 2015). In addition, redox potential decreased throughout the experiments suggesting oxidizing conditions. Before, the effect of pH adjustment and current on the redox potential was positive, indicating reducing conditions.

In experiment EC11, the effect of lower current (0.19 A) and lower initial concentration with 1/5 dilution was studied, and magnesium corrosion as chunks was not detected. Dilution of 1/5 with a higher current (0.5 A) was also studied in EC12 and EC13, and it was found that the magnesium anode could also handle higher currents.

When initial concentration of the ions is high, more precipitate forms on top of the anode and more loose magnesium pieces are still attached to the anode. One possible explanation is that the precipitate forms a protecting layer on top of the anode which inhibits or slows down the detachment of the magnesium pieces at some point. Magnesium might first dissolve more smoothly, but when enough precipitate has formed, the detachment of magnesium slows down, and when the force is great enough, they finally detach, and then the big magnesium flakes can be detected in the reaction solution. The results showed that dilution of the authentic water sample improved the durability of the magnesium electrode.

Negative and decreasing redox potential indicates that the conditions at the redox probe are oxidizing. Before alkali addition, the redox potential was positive, indicating reducing conditions. After pH control, the conditions turned oxidizing.

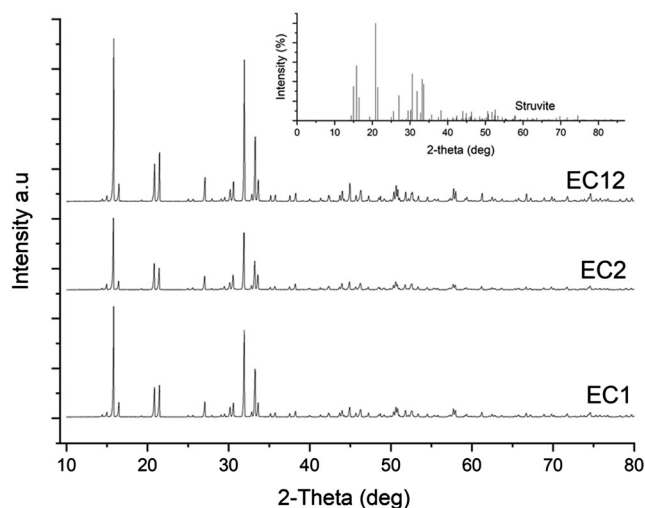
### 3.4 | Struvite yields and purity

Yields were calculated based on the limited ion, phosphate in experiments EC1–5, and EC11–13, and magnesium in experiments EC6–10. Yields are presented in Table 6.

Yields were calculated based on the theoretical amount of magnesium and magnesium that existed in the authentic water sample was also considered. Therefore, based on the yields, precipitation can occur in several conditions. Typically, the highest yields are obtained when pH values are 7.5–9.5, as used also in this study (Hao et al., 2008). The purity of selected samples was studied using XRD (Figure 1) Based on the analysis, only struvite peaks were identified in each case. Even though the yield and removal of phosphate were low in EC12 (Tables 4 and 6), the precipitate was still pure struvite.

**TABLE 6** Struvite yields in experiments EC1–EC13.

Sample	Yield (%)
EC1	100
EC2	100
EC3	100
EC4	100
EC5	69.9
EC6	100
EC7	100
EC8	100
EC9	100
EC10	100
EC11	84.0
EC12	72.9
EC13	82.3



**FIGURE 1** XRD analysis of the precipitate from EC1, EC2, and EC12.

**TABLE 7** Sequential leaching results of the formed struvite.

	Mg (mg/kg)	P (mg/kg)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
F1	149	17	0.09	0.001	0.001	0.003	0.012	0.0001	0.1
F2	4730	4821	3.39	0.006	0.001	0.041	0.608	0.0001	0.8
F3	3762	5394	1.75	0.085	0.000	1.3	2.2	0.0014	30
F4	67	540	0.04	0.015	0.071	0.396	0.153	0.0453	63

### 3.5 | Sequential leaching

Results of the sequential leaching are presented in Table 7. The first two fractions (F1 and F2) can be regarded as easily bioavailable. The sum of all fractions is the total bioavailability (i.e., the concentration that is available during a long period) (Pesonen et al., 2017).

The water-soluble fraction (F1) of all harmful elements is extremely small. The total bioavailability of all harmful elements is also generally quite low, especially the concentrations of Cd, Cr, Cu, and Pb. Only As seems to be somewhat bioavailable (F2), but the total the sum of fractions F1–F4 is still low, around 5 mg/kg. The limit value for As in EU fertilizer legislation is 40 mg/kg. Some Zn is leached in the final two steps, but this is not alarming because Zn is also considered as an important nutrient, and the limit value in fertilizer legislation is 800 mg/kg (“The European Parliament and Council Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 Laying down Rules on the Making Available on the Market of EU Fertilising Products and Amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and Repealing Regulation (EC) No 2003/2003;” 2019). Several studies have also indicated that heavy metals do not enrich on struvite and their concentrations do not affect the fertilizer use of struvite (Antonini et al., 2012; Ryu et al., 2012; Uysal et al., 2010).

Struvite is considered to be a slow-release fertilizers because its solubility to water is only around 0.2 mg/L (Li & Zhao, 2002; Negrea et al., 2010). Also here the solubility of the main components of struvite Mg and P in the first fraction F1 is low. Instead, they are mostly leachable in fractions F2 and F3, confirming the gradual decomposition of struvite fertilizers. Others have reported high solubility of struvite to mild organic acids such as citric acid and acetic acid. Around 50% of phosphate was released using 2% citric acid in a study by Cabeza et al. (2011), whereas Kern et al. (2008) reported a complete dissolution of phosphate in citric acid and ammonium citrate (Cabeza et al., 2011; Kern et al., 2008; Talboys et al., 2016).

## 4 | CONCLUSIONS

The aim of this study was to determine whether electrochemical precipitation would be a suitable treatment for phosphorus removal from nutritious circulate waters (KVA10 and LAT) from the Yara Siilinjärvi phosphoric acid plant to precipitate nutrients as struvite. The challenging and highly reactive nature of magnesium metal in an aqueous environment was considered during optimization of the precipitation conditions to prevent magnesium from detaching as big chunks.

Struvite could be formed in electrochemical precipitations in a wide pH range. Struvite formed even without any pH control, with the pH between 7 and 9, and 100% struvite yield was obtained in several conditions. For the best yields and reductions, pH must be raised with an alkali addition because the initial pH is low, and electrochemical formation of OH<sup>-</sup> alone does not raise the pH enough at the beginning. The highest phosphate removal rate obtained was 99.7%, and the highest magnesium removal was 99.5% indicating low residual magnesium concentrations.

It can be concluded that phosphate removal is very efficient, and struvite can be obtained as a precipitation product from the KVA + LAT mixture when using a magnesium plate (AZ31 type) as a source of magnesium. The results indicate that precipitation conditions can be optimized through by traditional methods by setting precipitation conditions and adjusting nutrient concentrations by mixing two kinds of industrial water.

As a future research with this topic should be considered continuous flow electrochemical precipitation. Economic feasibility should also be taken into account before industrial scale applications. It is also important to remember that case-specific evaluation is needed when considering real process waters.

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## CONFLICT OF INTEREST

Authors have no conflict of interests.

## DATA AVAILABILITY STATEMENT

Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.

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