Struvite precipitation in raw and co-digested swine slurries for nutrients recovery in batch reactors
Raffaele Taddeo and Raghida Lepistö

ABSTRACT

The release of nitrogen (N) and phosphorus (P) from agro-industrial sources is a major environmental concern. Furthermore, the scarcity of mineable P and the growing demand for food worldwide necessitate that we find an alternative P source. This study applied struvite precipitation for N-P recovery to slurries with high levels of organics and ammonia to achieve environmental protection from excessive nutrients diffusion and to generate a sustainable P source. Batch tests were carried out on raw and co-digested swine slurries to study the feasibility of struvite precipitation and the effect of several parameters, including pH, reaction time, competing ions (Ca²⁺, K⁺), total solids (TS), and alkalinity. The batch assays with raw swine slurries showed high N-P removals (up to 80%), while the anaerobic liquor returned lower recovery efficiency due to the high solids and alkali content. Struvite crystallization was detected at pH values as low as 6, and the characteristics of the recovered struvite matched those of the theoretical. Slight co-precipitation of calcium–phosphates occurred and was dependent on the Ca²⁺/Mg²⁺ ratio rather than on varying pH values. Struvite precipitation was shown to be feasible in complex matrices as agro-industrial effluents, characterized by high NH₄⁺, alkalinity, solids and organic content, and interfering ions such as Ca²⁺ and K⁺.

Key words | eutrophication, manure treatment, nutrients removal and recovery, struvite

INTRODUCTION

Nitrogen (N) and phosphorus (P) are vital nutrients for plants and crops, and are thus important for the world food supply, but they are also a recognized cause of environmental pollution. During recent decades, large amounts of nutrients have diffused into the environment leading to the over-enrichment of soils and water bodies, causing eutrophication, and deteriorating water quality and biodiversity (Diaz & Rosenberg 2008). Agro-industrial sources produce the most significant impact on the environment, as the amount of N and P released from agricultural settlements is higher than from any other point and non-point source (Cordell et al. 2009).

Livestock are commonly fed with over-enriched protein feeds: the N-surplus that is not metabolized is excreted and converted to ammonia (NH₃) by microbial action. Besides being toxic to aquatic animals, NH₃ is a preferential N source for algal growth and with P can trigger eutrophication; therefore, it is essential to reduce both N and P inputs for controlling long-term eutrophication and cyanobacterial bloom (Li et al. 2014). Furthermore, 7 MtonP/year are released from animal waste and 8 MtonP/year from agricultural runoff and soil erosion, while fertilizer production accounts for 85% of total mined P (Cordell et al. 2009). Moreover, the global consumption of P-N-K fertilizers increased by 600% between 1950 and 2000 (IFA 2006), corresponding to an accumulation of P in agricultural soils of more than 300 Mton³ over the same period (Bennett et al. 2001).

Phosphorus is a finite commodity and mineable P-rocks are the only available P source. Several researchers have predicted that the critical P production point will occur during the 21st century (Cordell et al. 2009; Udo de Haes et al. 2009). Since fertilizer production is expected to increase due to the steep rise in world food demand, P reserves could deplete sooner than estimated (Heffer & Prud’homme 2010). Therefore, nutrient removal and recovery from agro-industrial wastewaters is necessary for healthy soil and water environments, and for maintaining a sustainable P source.

A sustainable and interesting approach for nutrient recovery is the controlled precipitation of struvite,
MgNH₄PO₄·6H₂O. Struvite occurs spontaneously in wastewater treatment plants (WWTPs) and other purification systems where pressure drops or turbulence areas promote its precipitation. Struvite-controlled precipitation in well-defined sectors of WWTPs has already been described as favourable (von Münch & Barr 2001). Several studies have shown the feasibility of struvite crystallization on different liquors such as municipal wastewater (Battistoni et al. 1997, 2005), human urine (Tilley et al. 2008), potato processing effluents (Moerman et al. 2009), and digested dairy manures (Uludag-Demirer et al. 2005).

However, the above studies targeted either P (Battistoni et al. 1997; Moerman et al. 2009) or N recovery (Uludag-Demirer et al. 2005), or struvite precipitation was applied to nutrients-poor effluents (Battistoni et al. 2005; Tilley et al. 2008). Thus, there is a lack of knowledge about applying the technology to simultaneous N-P recovery from agro-industrial slurries characterized by high nutrients load as well as high organics and solids. This study aims to evaluate the feasibility of struvite precipitation in raw and co-digested swine slurries for simultaneous N and P removal and recovery, thus providing a sustainable technology to safeguard water and environmental quality.

Struvite crystallization is affected by several parameters, including element molar ratio, pH, organic load, and solids content. Struvite precipitation occurs at alkaline pH and a molar ratio of 1:1:1 between Mg²⁺, NH₄⁺, and PO₄³⁻. Struvite precipitation potential decreases in the presence of high-organic load due to increased struvite solubility (Schulze-Rettmer 1994). Moreover, the usual high concentration of Ca²⁺ and K⁺ in manures could also favour the formation of other compounds such as K-struvite, KMgPO₄·6H₂O and amorphous calcium phosphates (ACPs), including hydroxyapatite, Ca₅(PO₄)₃(OH).

### MATERIALS AND METHODS

#### Raw materials

Table 1 shows the characteristics of the samples used in the experiments. Raw swine slurry was collected from a farm in south-western Finland, where the pigs are separated into three categories: breeding sows with pre-weaners, growers, and finishers. Slurries are stored in open storage tanks and sent on a regular basis to a nearby biogas plant. We sampled twice (A, B), 3 months apart, but B was mostly used for the batch experiments since A and B showed similar characteristics. Furthermore, we sampled the reject water (C) from the above biogas plant, where pig slurries are co-digested with industrial and municipal...
biodegradable wastes under mesophilic conditions (38 °C, sludge retention time of 18–23 d, TS 10%).

**Analytical methods**

The raw samples, effluents, and precipitates from the batch experiments were characterized by various analytical methods. Ammonium was determined by the distillation-titration method (ISO 5664:1984) and the results were verified with an ammonia-selective electrode (Orion 95-12). The N content in the recovered precipitate was quantified by Kjeldahl digestion (APHA 2009, 4500-N(OH)). Total and soluble metallics (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$) in the influent, effluent, and in the precipitate (after HNO$_3$ digestion) were determined by Atomic Absorption Spectrometry using an A-Analyst 400 (Perkin–Elmer, Waltham, MA, USA). Soluble anions (Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$) were analysed by ion chromatography, using a DX-120 (Dionex, Sunnyvale, CA, USA) equipped with an analytical column RFIC IonPac AS23 (4×250 mm; Dionex), and helium as carrier gas. In addition, PO$_4^{3-}$ and the P contained in the precipitate (after acid extraction) were photo-chemically analysed by the ammonium-molybdate spectrometric method (ISO 6878:2004) using a UV-1601 spectrophotometer (Shimadzu, Kyoto, Japan). Then, TS, total volatile solids (TVS), and alkalinity were determined according to *Standard Methods* (APHA 2009; 2540 B & E, 2320). Moisture content of the precipitate was determined by thermogravimetric analysis. Total and soluble chemical oxygen demand (COD) were analysed using an LCK-114 (HACH LANGE, Düsseldorf, Germany). All solvents and reagents were AnalaR grade or equivalent.

**Batch experiments**

A series of batch assays was carried out on raw (B, C) and centrifuged (B’, C’) samples to study the effects of various parameters on the crystallization process, including pH, induction time, interfering ions such as Ca$^{2+}$ and K$^+$, and solids content. In particular, we tested various pH values (6–10), two different TS for each sample, and an extended reaction time (4 h) to determine the best conditions for struvite precipitation. All batch experiments were conducted in 350 mL stirred reactors and run in duplicates at room temperature and controlled pH. Two-hundred millilitres of slurry were transferred into each reactor, MgO and H$_3$PO$_4$ were added to achieve a stoichiometric ratio of 1:1:1, and the pH was adjusted to the desired value by adding NaOH.

Apart from the time effect test (4 h, pH 8), the reaction time was set to 30 min. After crystallization and settling, the precipitate was recovered by filtration through 11-μm cellulose filters. Final effluents were analysed for residual metals, NH$_4^+$, and PO$_4^{3-}$. The recovered precipitate was air-dried at ambient temperature and then analysed.

**RESULTS AND DISCUSSION**

The raw swine slurries (A, B) contained a significant amount of NH$_4^+$ (Table 1), along with high TS, organic content (COD), and high buffer capacity that could interfere with struvite crystallization and pH control. The effect of the reaction time was tested on B: precipitation quickly occurred when supersaturation was achieved, and within the initial 30 min of reaction both N and P were reduced from 160 mmol to around 60, whereas no tangible increase of N-P removal was detected for the rest of the experiment. Subsequently, the effect of pH (6.5, 7, 7.5, 8, 9, 10) was evaluated on B (Figure 1). Removal efficiency (%N-P) increased with increasing pH: minimum removal (50%) was achieved at pH 6.5, whereas the highest efficiency (80%) occurred at pH 10 where the solubility product of struvite is minimal, thus making the precipitation yield maximum (Ohlinger *et al.* 1999). On the other hand, the precipitation process at such a high pH value is difficult to control and requires significant alkali addition; therefore, a compromise between nutrient removal, process control, and cost-effectiveness is necessary to ensure process viability and sustainability.

Furthermore, PO$_4^{3-}$ removal efficiency was usually higher than NH$_4^+$, highlighting the competition between Ca$^{2+}$ and Mg$^{2+}$ to precipitate ACP along with struvite. Calcium was constantly reduced in every test (Table 2) and Ca was found in the solid precipitate along with higher P than

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**Figure 1** | Removal efficiency of N and P in sample B as a function of pH. Error bars refer to standard deviation of duplicates or triplicates.
expected. The original Ca²⁺/Mg²⁺ ratio, ~6 for A-B-B', and ~1.5 for C-C' was favourable for the co-precipitation of hydroxyapatite and struvite (LeCorre et al. 2005). However, after the external addition of MgO, Ca²⁺/Mg²⁺ was nearly 0.05, thus providing a favourable environment only for struvite formation. Nevertheless, during the tests, Ca²⁺/Mg²⁺ varied due to the sharp reduction of soluble Mg²⁺ to form struvite, presumably providing suitable conditions for co-precipitation. Our data showed clearly that Ca²⁺ reduction in solution was independent of pH values, but probably dependent on the Ca²⁺/Mg²⁺ ratio only. Furthermore, the presence of residual NH₄⁺ prevented K-struvite formation (Schuiling & Andrade 1999). No competition was, therefore, observed between K⁺ and NH₄⁺ in forming K-struvite in place of struvite, as the K⁺ concentration remained stable during the tests (Table 2), and no K was detected in the solid precipitate.

Batch tests were also run with B' (0.75% TS) at varying pH values (6.5, 7, 7.5, 8, 9) and the achieved N removal was then compared to the E%N achieved with B (1.1% TS) at the same pH values (Figure 2). Although NH₄⁺ removal was slightly higher at lower TS, no significant differences were detected: at pH 6.5, E%N increased from 49 to 55%, and at pH 8 from 58 to 63%, whereas the two samples displayed similar removals at pH 9 (65 vs. 66%).

The centrifuged slurry, B', showed a variation in the alkalinity type. Although at pH 4.3 the total alkalinity remained constant, at pH 5.8, B' showed lower alkalinity content than the original sample B (Table 3). The lower alkalinity had no significant effect on the removal efficiency, but affected the whole process efficiency by decreasing the amount of NaOH needed to reach the desired pH value.

The reject water (C), a more complex matrix than A and B, with higher TS (5.5%), COD (44 g/L), and alkalinity (22 g/L), showed increased interference to struvite crystallization as only 10% N-P removal was achieved at pH 8 (Figure 3(b)). Consequently, samples were centrifuged and the precipitation process was investigated with varying pH values (6, 7, 7.5, 8, 9, 10). As shown in Figure 3(b), E%N-P at pH 8 rose fourfold at the lower TS (1.85%), as the removal efficiency of NH₄⁺ and PO₄³⁻ was 40% and 49%, respectively. As for the raw swine slurry, the E%N-P in C' increased with increasing pH: at pH 6, the removal efficiency was around 30%; at pH 8; it was 40%; and at pH 10, E%N-P was higher than 60% (Figure 3(a)).

These results showed the effect of solids on the precipitation process as C exhibited no appreciable precipitation at 5.5% TS, whereas moderate crystallization occurred at 1.85% TS. On the other hand, the removal efficiency in B only slightly increased after TS reduction from 1.1 to 0.75%. So far, few studies have focused on the role of solids and organics in the crystallization process. Schuiling & Andrade (1999) reported that TSS >1,000 mg/L interferes with crystallization. However, the relationship between the amount and composition of solids and crystallization in agro-industrial media is still to be ascertained, and further studies must be carried out to clarify it.

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**Table 2 | Slurry B residual concentrations of alkali metals after struvite precipitation**

<table>
<thead>
<tr>
<th>pH</th>
<th>Ca²⁺ mg L⁻¹</th>
<th>K⁺ mg L⁻¹</th>
<th>Mg²⁺ mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.7*</td>
<td>196</td>
<td>1,406</td>
<td>35</td>
</tr>
<tr>
<td>6.5</td>
<td>31</td>
<td>1,389</td>
<td>138</td>
</tr>
<tr>
<td>7</td>
<td>24</td>
<td>1,402</td>
<td>121</td>
</tr>
<tr>
<td>7.5</td>
<td>13</td>
<td>1,399</td>
<td>56</td>
</tr>
<tr>
<td>8</td>
<td>34</td>
<td>1,392</td>
<td>87</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>1,402</td>
<td>33</td>
</tr>
<tr>
<td>10</td>
<td>31</td>
<td>1,406</td>
<td>98</td>
</tr>
</tbody>
</table>

*Original sample.

**Table 3 | Comparison of the alkalinity content of B and B' and NaOH dosage**

<table>
<thead>
<tr>
<th>pH</th>
<th>NaOH (mmol)</th>
<th>E% NH₄-N</th>
<th>NaOH (mmol)</th>
<th>E% NH₄-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>/</td>
<td>49 ± 1.0</td>
<td>/</td>
<td>51 ± 3.6</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>52 ± 1.6</td>
<td>3.5</td>
<td>55 ± 0.7</td>
</tr>
<tr>
<td>7.5</td>
<td>8</td>
<td>54 ± 2.0</td>
<td>7</td>
<td>57 ± 0.4</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>57 ± 1.8</td>
<td>7.5</td>
<td>64 ± 1.1</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>65 ± 0.7</td>
<td>10</td>
<td>66 ± 1.4</td>
</tr>
</tbody>
</table>

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![Figure 2 | NH₄-N removal efficiency in samples B (TS 1.1%) and B' (TS 0.75%). Error bars refer to standard deviation of duplicates and triplicates.](image-url)
The recovered precipitate (from all the experiments) was analysed afterwards to assess its characteristics. Small differences were found between the precipitate and the theoretical struvite, as PO$_4^{3-}$ (12.81 $\pm$ 0.6%) and Mg (10.18 $\pm$ 0.22%) contents were slightly higher than the theoretical 12.64% and 9.91%, respectively. The higher P content is due to the co-precipitation of ACPs, whereas the higher Mg content is due to incomplete Mg solubilization. Furthermore, NH$_4^+$ (5.15 $\pm$ 0.14%) was slightly lower than the theoretical value, 5.71%, and Ca accounted for an average of 0.36 $\pm$ 0.13% of the total precipitate, whereas K was not found. The water of crystallization was 41 $\pm$ 0.47% (in struvite 44.03%).

Clear evidence of struvite was detected at pH < 7, whereas most previous research describes such pH values as unfavourable for its crystallization. However, Frazier & Waerstad (1992) found that struvite can form at pH < 7, i.e., down to pH 5, but only with a low Mg concentration. Our experiments were run in an Mg-enriched environment and showed struvite formation at pH 6 (E%N-P around 30%), whereas precipitation was not observed at lower pH values (data not shown).

Previous research (Boistelle et al. 1983; Schuiling & Andrade 1999) observed a pH decrease after the completion of the crystallization process, suggesting HPO$_4^{2-}$ ion activity rather than PO$_4^{3-}$ in struvite formation. Furthermore, Abbona & Boistelle (1979) proposed that struvite could form via a reaction between MgHPO$_4$ and NH$_4$. In our experiments, the pH remained stable and never varied during or after the crystallization process, thus suggesting the involvement of PO$_4^{3-}$ in struvite formation.

The batch tests also emphasized Mg$^{2+}$ as the limiting factor of the crystallization process (Stratful et al. 2001). Part of the externally added MgO was not available for the reaction, and the amount of Mg in the precipitate was higher than expected, while residual NH$_4^+$ and PO$_4^{3-}$ were still available in the solution. Thus, for higher struvite precipitation, more Mg should be made available by dosing it in excess (Song et al. 2007), or by examining different techniques for MgO addition and dissolution.

**CONCLUSIONS**

This study applied P and N recovery as struvite under controlled precipitation to agro-industrial effluents with a high NH$_4^+$ load, specifically raw and co-digested swine slurries. To the best of our knowledge, few studies have applied struvite precipitation to swine slurries pursuing simultaneous N-P removal and recovery as struvite. Our experiments showed that struvite crystallization is feasible in complex matrices with high solids, organics, and alkalinity, which have the potential for significantly interfering with the crystallization process. Struvite precipitation was achieved at pH values as low as 6, and the maximum N-P recovery was found at pH 10 (80%) at TS 1.1%, although at pH 8 and 9, E%N-P was already significant (around 60% and 70%, respectively). Soluble magnesium was the process limiting factor: for a 100% removal target, different approaches must be considered to increase Mg$^{2+}$ availability.

**ACKNOWLEDGEMENTS**

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REFERENCES


Stratful, I., Scrimshaw, M. D. & Lester, J. N. 2001 Conditions influencing the precipitation of magnesium ammonium phosphate. Water Res. 35 (17), 4191–4199.


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