Potassium recovery from centrate: taking advantage of autotrophic nitrogen removal for multi-nutrient recovery

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Abstract

BACKGROUND: Potassium is a key macronutrient, but little attention has been paid to its recovery from waste streams. This study investigates simultaneous recovery of phosphorus and potassium in the form of potassium struvite (MgKPO₄·6H₂O) from centrate after nitrogen removal by partial nitritation–anammox (PNA). Lab-scale batch experiments to assess the influence of pH, Mg:P ratio and temperature on nutrient removal were conducted on effluent from two PNA reactors fed with centrate from municipal wastewater treatment plants.

RESULTS: pH had a strong impact on potassium removal, which increased up to pH 11. At this pH, a product containing 11.4% P, 3.51% N and 4.34% K was obtained. X-ray diffraction confirmed the presence of potassium struvite together with ammonium struvite (MgNH₄PO₄·6H₂O). PNA reduced the alkalinity by 90%, which surpasses the performance of conventional CO₂ stripping by aeration.

CONCLUSION: Coupling PNA with struvite precipitation allows for the recovery of N, P and K in a multi-nutrient product and may drastically reduce the need for alkali dosing for pH control.

Keywords: nutrient recovery; partial nitritation–anammox; struvite; potassium; phosphorus

NOMENCLATURE

Bio-P Biological phosphorus removal
Bio-P PNA PNA fed with centrate from a Bio-P plant
Chem-P Chemical phosphorus removal
Chem-P PNA PNA fed with centrate from a Chem-P plant
IAP Ion activity product
Ksp Solubility product
MAP Magnesium ammonium phosphate
MgNH₄PO₄·6H₂O (ammonium struvite)
MPP Magnesium potassium phosphate
MgKPO₄·6H₂O (potassium struvite)
Ω Degree of saturation
p.e. Population equivalent
PNA Partial nitritation–anammox
poly-P Polyphosphate
WWTP Wastewater treatment plant
XRD X-ray diffraction

INTRODUCTION

Recycling of nutrients from waste streams has been recognized by the European Union as an important step towards a sustainable and resource-efficient economy.¹ However, recovery strategies have been overwhelmingly focused on phosphorus. Recovery and reuse of potassium have received much less attention, although potassium too is a key macronutrient and, just like phosphorus, derived from limited geological sources. In fact, at current consumption rates potash reserves are estimated to run out in 93 years, while phosphate rock reserves are estimated to last for 266 years.²,³ The need for local, sustainable and reliable sources of potassium is substantial; the European Union, as well as many large agricultural countries, are depending on imports of potash for fertilizer production.⁴,⁵ At the same time, the geographical distribution of potash mines is narrowly limited, with five countries accounting for 80% of the world’s potash production.⁶

On a global basis, more potassium than phosphorus is applied to soils (21 Mton P and 32 Mton K annually).⁷ This ratio is reflected in the load from households, which has been estimated to be 2.1 g P, 13.5 g N and 4.0 g K per person per day based on Swedish conditions,⁸ which provide an order of magnitude of the recovery potential of potassium from municipal wastewater.

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Within municipal wastewater treatment plants (WWTPs), centrate is a small but concentrated stream, typically accounting for <1% of the incoming flow, while it can represent up to 20% of nitrogen and phosphorus loads. A separate treatment of this stream is therefore an efficient way to decrease the nutrient load to the main water line. Phosphorus recovery in the form of struvite (MgNH₄PO₄·6H₂O, MAP) has been successfully implemented in the full-scale treatment of centrate centrate by Ueno and Fujii and Abma et al., among others. Potassium can replace ammonium in the struvite crystal lattice and form potassium struvite (MgKPO₄·6H₂O, MPP). Similar to MAP, MPP exhibits slow release of nutrients, which makes it suitable as a fertilizer.

Ammonium has a negative effect on the formation of MPP. Thus the recovery of MPP should be applied to high nutrient streams after nitrogen removal. Previous approaches to recover MPP from waste streams include a full-scale plant treating denitrified calf manure, and lab-scale experiments on digested manure, synthetic urine or hydrolysed urine subjected to ammonia stripping.

Ammonia stripping efficiency relies on a high operational pH, which is typically adjusted by addition of NaOH. Presence of Na can lead to formation of sodium struvite (MSP, MgNaPO₄·7H₂O), which is competing with MPP formation. Therefore, other ammonium removal processes such as PNA are preferred.

The recovery of MPP from centrate has not been explored so far. Neither have novel processes, such as partial nitritation–anammox (PNA) been assessed as a nitrogen removal step for subsequent MPP recovery. PNA is being increasingly applied to treat centrate in municipal WWTPs because of the drastically lower energy consumption compared to conventional nitrification–denitrification.

Centrate is characterized by high alkalinity with a correspondingly high buffer capacity, and dosing of chemicals to adjust pH is a major cost in struvite production. CO₂ stripping through aeration has been applied to decrease the alkalinity. However, this is an energy-demanding process. PNA biomass is autotrophic and relies on bicarbonate as sole carbon source. Thus PNA could be an energy-efficient way to reduce alkalinity before struvite precipitation.

This work aims to demonstrate the feasibility of combining PNA and struvite precipitation for the simultaneous recovery of potassium and phosphorus in the form of MPP from municipal wastewater, and to assess PNA as an alternative to conventional CO₂ stripping. The influence of Mg:P ratio, pH and temperature on nutrient removal was investigated in lab-scale batch experiments conducted on effluent from two different PNA reactors: (i) a lab-scale reactor fed with centrate from a WWTP operated with chemical P-removal (Chem-P) and (ii) a pilot-scale reactor fed with centrate from a WWTP operated with biological P-removal (Bio-P).

A sampling campaign was conducted over the sludge line of a municipal wastewater treatment plant that applies biological phosphorus removal. PNA effluent was collected from a pilot-scale installation operated by Aquafin at WWTP Antwerp Terri (Cornellà de Terri, Catalonia, Spain). WWTP Terri treats 10 000 m³ day⁻¹ of municipal and industrial wastewater and applies chemical P-removal. During the experimental period, the Chem-P PNA reactor was operated at 25 °C, with a hydraulic retention time of 3.6 days and nitrogen loading rate 266 ± 22 mg N-NH₄⁺ L⁻¹ day⁻¹. The nitrogen removal efficiency was 79% ± 3% and the volatile suspended solids concentration in the reactor was 2.0 g L⁻¹.

Once the possibility of precipitating MPP from PNA effluent had been confirmed, the concept was validated using effluent from a pilot-scale PNA reactor (Bio-P PNA) fed with centrate from a plant that applies biological phosphorus removal. PNA effluent was collected from a pilot-scale installation operated by Aquafin at WWTP Antwerp South (Antwerp, Belgium) that treats 77 570 m³ of municipal wastewater per day. Effluent from the Bio-P PNA reactor was collected and brought to the lab in plastic containers, where it was stored at room temperature for a maximum of 2 days until the date of the experiment.

Table 1 shows the composition of the centrate fed to each reactor and the PNA effluents used for each set of experiments.

### MATERIAL AND METHODS

#### PNA reactors and effluent collection

A lab-scale PNA sequencing batch reactor (Chem-P PNA) with a minimum volume of 10 L was operated as previously described by Johansson et al.. The reactor was fed with centrate collected from WWTP Terri (Cornellà de Terri, Catalonia, Spain). WWTP Terri treats 10 000 m³ day⁻¹ of municipal and industrial wastewater and applies chemical P-removal. During the experimental period, the Chem-P PNA reactor was operated at 25 °C, with a hydraulic detention time of 3.6 days and nitrogen loading rate 266 ± 22 mg N-NH₄⁺ L⁻¹ day⁻¹. The nitrogen removal efficiency was 79% ± 3% and the volatile suspended solids concentration in the reactor was 2.0 g L⁻¹.

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#### Experimental procedure

Three factors that affect precipitation were evaluated in batch experiments: Mg:P molar ratio, pH and temperature. Table 2 presents the experimental outline. The experiments were carried out in duplicate in glass reactors fitted with water jackets for temperature control. The pH and Mg:P ratio were adjusted before the

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### Table 1. Composition of centrate and PNA effluent used for the different experiments

| Centrate | Chem-P PNA | Bio-P PNA |
|----------|------------|-----------|
| pH       | 8.0 ± 0.02 | 8.0 ± 0.02 |
| Alkalinity | 3276 ± 174 | 3276 ± 174 |
| P-P(O₄)³⁻ | 59 ± 6.0 | 59 ± 6.0 |
| N-NH₄⁺ | 949 ± 80 | 949 ± 80 |
| K⁺ | 251 ± 2.1 | 251 ± 2.1 |
| Mg²⁺ | 12 ± 0.3 | 12 ± 0.3 |
| Ca²⁺ | 54 ± 0.55 | 54 ± 0.55 |
| Na⁺ | – | – |
| Cl⁻ | – | – |
| pH essay | 7.7 | 7.7 |
| Temp. essay | 7.7 | 7.7 |

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* Converted from meq L⁻¹.
solutions were mixed for 1 h using magnetic stirrers. Background Mg²⁺ concentration was taken into account when the magnesium dosing was calculated. After the experimental time, liquid samples were pipetted from the supernatant. The solids were allowed to settle for 30 min before the supernatant was discarded, and the solids were captured using 0.60 μm filters and dried at 46 °C for 48 h for analysis by X-ray diffraction (XRD).

To assess the effect of pH and temperature on the removal of ammonium through stripping, separate tests were made using Chem-P PNA effluent where no magnesium source was added. The experimental outline is presented in Table 3. The ammonium concentration was measured before and after stirring for 1 h.

The second set of precipitation experiments, with Bio-P PNA effluent, was carried out in 4 L glass reactors, with 3000 mL working volume. 32% magnesium chloride solution in powder form (MgCl₂·6H₂O) was used to adjust pH and Mg:P ratio. The solids were captured using 0.2 μm filters and dried at room temperature for 36 h for analysis by XRD and of chemical composition.

### Table 2. Experimental conditions for batch experiments assessing the influence of pH, temperature, and Mg:P ratio on nutrient removal

| Serial | pH | Temp. (°C) | Molar Mg:P ratio |
|--------|----|------------|------------------|
| 1      | 10 | 25        | 0.75:1           |
| 2      | 10 | 25        | 1.0:1            |
| 3      | 10 | 25        | 1.25:1           |
| 4      | 10 | 25        | 1.5:1            |
| 5      | 10 | 25        | 1.75:1           |
| 6      | 8  | 25        | 1.25:1           |
| 7      | 9  | 25        | 1.25:1           |
| 8      | 10 | 25        | 1.25:1           |
| 9      | 11 | 25        | 1.25:1           |
| 10     | 12 | 25        | 1.25:1           |
| 11     | 10 | 20        | 1.25:1           |
| 12     | 10 | 25        | 1.25:1           |
| 13     | 10 | 30        | 1.25:1           |
| 14     | 10 | 35        | 1.25:1           |
| 15     | 10 | 40        | 1.25:1           |

### Table 3. Experimental conditions for batch experiments assessing the influence of pH, temperature on ammonia stripping conducted on Chem-P PNA effluent

| Serial | pH | Temp. (°C) |
|--------|----|------------|
| 1      | 10 | 20        |
| 2      | 10 | 25        |
| 3      | 10 | 30        |
| 4      | 10 | 35        |
| 5      | 10 | 40        |
| 6      | 8  | 25        |
| 7      | 9  | 25        |
| 8      | 10 | 25        |
| 9      | 11 | 25        |
| 10     | 12 | 25        |

Wet samples of the precipitates were taken for microscopic imaging. The solids were captured using 0.60 μm filters and dried at room temperature for 36 h for analysis by XRD and of chemical composition.

### Analytical characterization of the liquid and solid phases

In the experiments on Chem-P PNA effluent, analysis of N-NH₄⁺, suspended solids and alkalinity were performed according to Standard Methods.²⁷ P-PO₄³⁻ was analysed using ion chromatography (Dionex IC5000). Mg²⁺ and Ca²⁺ were analysed using cuvette tests (Hach LCK327) read with a spectrophotometer (Hach DR3900). All samples for ion analysis were filtered using 0.2 μm filters prior to analysis. XRD analysis was performed on a Bruker D8 Advance.

In the experiments on Bio-P PNA effluent, samples for P-PO₄³⁻ and N-NH₄⁺ were filtered using 0.45 μm filters and immediately analysed using cuvette tests (Test 0-79 and Test 0-60, Macherey-Nagel) read with a spectrophotometer (PF-12, Macherey-Nagel). Remaining filtered samples were acidified to pH <4.5 with HCl in order to prevent further crystallization and analysed for all other ions using inductively coupled plasma–optical emission spectrometry (Optima 8300, PerkinElmer), which was also used to analyse the composition of the recovered precipitates.

### Saturation index

The saturation index (SI) was calculated using the software Visual MINTEQ (version 3.0). MPP is not included in the standard database and was therefore added with log $K_{sp} = -11.68$ according to Luff and Reed.²⁸ The degree of saturation, Ω, and the saturation index, with respect to the mineral phases were defined as follows:

\[
Ω = \frac{\text{IAP}}{K_{sp}},
\]

\[
SI = \log Ω = \log \text{IAP} - \log K_{sp},
\]

where IAP is the ion activity product and $K_{sp}$ is the solubility product of the precipitated mineral. The solution is considered to be oversaturated when the SI is above zero, at saturation when zero, and undersaturated when less than zero.

### Sampling campaign

A sampling campaign was conducted over the sludge line of WWTP Antwerp South in order to assess the scope of potassium recovery in the side-stream. The WWTP receives external sludge from other WWTPs, which is fed to the digester together with the thickened sludge from the plant. The external sludge accounts for 14% and the thickened sludge for 86% of the flow to the digester on a volumetric basis. Samples were taken twice per week over 6 weeks. Data on flows of thickened sludge, external sludge and digestate were obtained from Aquafin. The flow of centrate was calculated using a solids mass balance over the centrifuges.

### RESULTS AND DISCUSSION

#### PNA reactor: ammonium and alkalinity removal prior to struvite precipitation

**Ammonium removal**

The lab-scale Chem-P PNA reactor decreased the ammonium concentration by more than 85% (Table 1). This is comparable to the performance of full-scale PNA reactors. Ammonium has been shown to negatively impact the formation of MPP due to the formation of MAP. The reason for this is that the solubility product...
for MAP is slightly smaller than the one for MPP. Reported values of the negative logarithm of the solubility product ($pK_{sp}$) for MPP range between 10.6 and 12.2,\textsuperscript{20,28,29} while the most commonly used value for MAP is 13.26.\textsuperscript{30} Consequently, when struvite precipitation is applied to streams with high ammonium concentrations, such as centrate, only traces of K are detected in the recovered product.\textsuperscript{31}

Potassium and phosphate are not consumed in any significant amounts by PNA biomass, and the concentrations of these ions remained virtually unchanged after the PNA step (Table 1). The Chem-P PNA effluent had an N:P:K molar ratio of 5.2:1.0:3.9, with both potassium and ammonium in excess over phosphorus for MPP or MAP formation, leaving magnesium as the limiting ion.

**Alkalinity removal**

Alkalinity represents the acid-neutralizing capacity of a system, and is mainly composed of carbonate species, while phosphate and ammonium can contribute in concentrated waters such as centrate. Stripping of CO$_2$ by aeration has been applied as a strategy to raise the pH for struvite crystallization. It also reduces the risk for calcium carbonate formation. PNA biomass is autotrophic and uses bicarbonate as the only carbon source and virtually functions as a biological CO$_2$ stripper.
Figure 2. Saturation indices for MAP and MPP as a function of pH and temperature for Chem-P PNA (A, C) effluent and Bio-P PNA effluent (B, D), simulated with Visual Minteq.

The Chem-P PNA reactor reduced the alkalinity by 2910 mg CaCO₃ L⁻¹, which accounts for 90% removal (Table 1). This is more efficient compared to results from previous studies on CO₂ removal using air stripping. A pilot-scale CO₂ stripper removed up to 20 mg CaCO₃ L⁻¹ from centrate,32 while a pilot-scale cascade stripper, also operating on centrate, was reported to reach a CO₂ reduction of 20% (measured as dissolved CO₂), which resulted in caustic use savings of 32%.25 In a study on a mix of centrate and urine, the implementation of a CO₂ stripper decreased the NaOH consumption by 57% as compared to operation without the stripper in place (the CO₂ removal efficiency was not reported).33 Thus even a small reduction in the alkalinity results
in important savings in terms of alkali dosing. This implies that the high alkalinity removal by PNA would strongly reduce the need for chemical and energy input to control the pH in struvite precipitation.

Establishing optimal parameters for maximum potassium recovery from Chem-P PNA effluent

Assessment of optimal Mg:P ratio

Precipitation experiments were conducted at pH 10 to determine the effect of molar Mg:P ratio on the removal of P, K and N. Phosphate and ammonium removal increased with Mg:P ratio, whereas potassium removal remained rather constant at 4.9 ± 0.7% (Fig. 1(A)). Phosphate removal increased to a maximum of 96% at Mg:P ratio 1.75, but a ratio of 1.25 was sufficient to attain a phosphate removal above 90%, with residual P-PO$_4^{3-}$ concentration of 4.0 ± 0.14 mg L$^{-1}$. Remaining experiments were conducted at an Mg:P ratio of 1.25 in order to minimize magnesium chloride dosing.

As the PNA effluent had an excess of potassium and ammonium over phosphate, only a fraction of these ions were removed through struvite precipitation, even when a good phosphate removal was achieved. The ammonium removal was slightly higher than the phosphate removal on a molar basis, indicating that some ammonium was stripped as ammonia.

Influence of pH

The pH affects solubility as well as supersaturation and therefore strongly influences precipitation and nutrient recovery. Phosphate removal showed a peak between pH 10 and 11, while potassium and ammonium removal increased up to pH 11 (Fig. 1(B)). A sharp drop in nutrient removal was observed at pH 12. Simulation results showed that alkaline conditions favour the formation of magnesium hydroxides such as brucite (Mg(OH)$_2$) and magnesium phosphate (Mg$_3$(PO$_4$)$_2$), which both compete with struvite for magnesium ions.

A maximum nutrient removal of 94%, 7.1% and 44% of phosphate, potassium and ammonium respectively was observed at pH 11. The experimental results were confirmed with simulations that showed that the SI for MAP peaks at pH 10, while for MPP the SI peaks at pH 11 (Fig. 2(A)). The results are in line with Xu et al., who found that the optimum pH for P and K removal from urine was at 11. A mix of MPP together with MAP was detected by XRD at pH 11 (Fig. 3), confirming the presence of a multi-nutrient product containing all three macro-nutrients N, P and K.

There was no difference in phosphate removal at pH 10 and 11, and remaining experiments were conducted at pH 10 in order to minimize sodium hydroxide dosing.

The molar removal of ammonium was higher than that of phosphate throughout the range of pH tested, indicating that removal of ammonia through stripping plays a role. Separate ammonia stripping experiments showed that the ammonium removal due to stripping becomes important at pH > 9 and can amount to 25% at pH 10 and 25°C (Fig. 4(A)).

Effect of temperature

Temperature affects the solubility and thus the supersaturation, as decreasing solubility leads to a higher supersaturation. Phosphate and potassium removal decreased with temperature whereas ammonium removal increased (Fig. 1(C)). Phosphate removal decreased steadily from 94% down to 81% as the temperature was increased from 20 to 40 °C. Potassium removal also decreased with temperature, from 3.8% down to 0.4%. Already at
35 °C there was virtually no removal of potassium. Ammonium removal, on the other hand, increased from 15% up to 28% in the temperature range of 20–40 °C.

The removal of ammonium is caused both by precipitation and ammonia stripping. The amount of free ammonia increases with temperature, which allows for more ammonium to be removed through stripping. The molar removal of ammonium surpassed that of phosphate at 25 °C, meaning that above this temperature ammonium is also removed by stripping. Results from stripping experiments (with no magnesium addition) showed that ammonium removal increased from 12% to 44% along the temperature range of 20–40 °C (Fig. 4B).

It has been reported that the solubility of MAP reaches its minimum at around 20 °C.34 However, a more recent study reports that the solubility decreases with lower temperature (in the range 5–30 °C).35 In this study no temperatures below 20 °C were investigated as PNA applied in the side-stream typically operates above 20 °C. Chemical equilibrium simulations confirmed that the SI for MAP decreases with increasing temperature, whereas the SI for MPP showed just a slight decrease (Fig. 2(C)).

Validation of results using Bio-P PNA effluent

The experiments to assess the influence of pH and temperature on nutrient removal were repeated using effluent from a pilot-scale Bio-P PNA unit. Potassium and magnesium play important roles in biological-P removal and are co-transported together with phosphorus into bacterial cells, where they are incorporated into the poly-P structure (general formula (K, Mg, PO4)n).36 During
anaerobic digestion the poly-P is hydrolysed, with subsequent nutrient release. Thus centrate from Bio-P WWTPs is characterized by higher concentrations of phosphate and potassium compared to centrate from conventional activated sludge WWTPs.

Consequently, the phosphate concentration of the Bio-P PNA effluent was considerably higher (around 230 mg P-P04− L−1) compared to the Chem-P PNA effluent (50–60 mg P-P04− L−1) (Table 1). However, the pilot-scale PNA reactor did not reach the same nitrogen removal efficiency as the lab-scale reactor, resulting in higher ammonium concentrations (close to 230 mg N-NH4+ L−1 as compared to 130 mg N-NH4+ L−1) (Table 1). The resulting molar N:P:K ratio in the Bio-P PNA effluent was 2.1:1.0:1.2.

The higher nutrient concentration in the Bio-P PNA effluent led to generally higher removal compared to the Chem-P PNA effluent, the endpoint of precipitation being defined by equilibrium concentrations. This is also reflected in the SI, which is higher for MAP and MPP in the Bio-P PNA effluent (Fig. 2(B)) as compared to the Chem-P PNA effluent (Fig. 2(A)). These results are in line with previous work from Nakao et al., who conducted experiments on a synthetic solution simulating digested sludge liquors subjected to ammonia stripping and concluded that P and K concentrations that are too low can impede MPP formation.

Removal of phosphate and ammonium showed peaks at pH 11 and 10, respectively, while the removal of potassium increased up to pH 11 (Fig. 1D). Above pH 11 there was a sharp drop in the removal of all three nutrients. This confirms the results obtained with Chem-P PNA effluent that increasing pH up to 11 favours the formation of MPP. The same trend is observed in the results from SI calculation where the curves of MPP lie above that for MAP at pH 11 and higher (Fig. 2(A), (B)).

Maximum potassium removal was observed at pH 11, with removal of phosphate, potassium and ammonium being 98%, 30% and 38%, respectively.

Temperature had less of an influence on nutrient removal from the Bio-P PNA as compared to the Chem-P PNA effluent (Fig. 1(E)). Phosphate and potassium removal remained virtually unaffected, while an increase in the ammonium removal from 39% to 46% was noted when the temperature was increased from 30 to 40 °C. Again, pH has a stronger influence than temperature on struvite formation and, because the experiment was conducted at constant pH, the nutrient removal due to precipitation remained close to constant. Ammonium removal, on the other hand, increased with temperature due to ammonia stripping.

Quality of the product: multi-nutrient recovery through co-precipitation of MPP and MAP

Table 4 shows the composition of precipitates recovered from experiments using Bio-P PNA effluent at pH 8–12. The experimental results are listed together with the theoretical composition of MAP and MPP for comparison. The experimental results reflect the recorded values on nutrient removal from the liquid phase (Fig. 1D); the nitrogen content of the precipitates decreases with increasing pH, whereas the potassium concentration increases up to pH 11. At pH 8 the molar ratio of Mg::K:N:P was 1.0:0.03:0.94:0.96, which is close to the theoretical ratio of MAP. At pH 11 the Mg::K:N:P ratio was 1.0:0.29:0.66:0.97, indicating that it was composed of one third MPP and two thirds MAP.

Not only the chemical composition but also the morphology of the crystals changed with pH (Fig. 5). When the pH was increased from 8 to 12, the crystals became thinner and more elongated. Whether this was due to a higher fraction of MPP or was merely an effect of pH needs to be further examined. In a study by Wilsenach et al., it could not be concluded that MPP has a different particle shape and size from MAP.

Augmenting MPP recovery

The experimental results show that pH strongly influences the ratio between MAP and MPP formed (Fig. 1(B), (D)). The highest potassium removal was recorded at pH 11, which represents the highest supersaturation but not necessarily the optimal operational pH. High supersaturation promotes nucleation and the formation of small crystals that are easily washed out. Although the higher phosphate removal was recorded between pH 10 and 11, full-scale MAP crystallizers operate at a pH that represents a lower degree of supersaturation, typically in the range of 8.0–8.5, in order to promote growth over nucleation. The optimal operational pH for MPP recovery needs to be assessed further in continuous experiments, but the results from this study suggest that a slightly higher pH than for MAP recovery from centrate would be beneficial. The drastically lower alkalinity of PNA effluent compared to centrate could counteract the need for additional alkali dosing to reach this higher pH.

The second factor influencing the MAP:MPP ratio is the residual ammonium in the PNA effluent, which has a negative impact on MPP formation. Traces of ammonium will always be present after autotrophic N removal, but the amount depends on the ammonium concentration of the centrate and the performance of the PNA reactor. Simulations based on the composition of the Bio-P PNA effluent showed that, at pH 11, the SI for MPP is above that for MAP up to ammonium concentration 175 mg N-NH4+ L−1 (Fig. 6). This represents an N:P:K molar ratio of 1.7:1.0:1.2. At the time of the experiments the Bio-P PNA reactor reached an ammonium removal of only 76%, which resulted in an effluent ammonium concentration of 227 ± 1.5 mg N-NH4+ L−1 and corresponding N:P:K ratio 2.2:1.0:1.2. However, full-scale PNA reactors fed with centrate of a similar ammonium concentration can reach effluent ammonium concentrations of as low as 100 mg N-NH4+ L−1 or less. This residual ammonium concentration would represent an N:P:K ratio of 0.9:1.0:1.2. In this case, the molar ammonium nitrogen concentration is less than half compared to the PNA effluent used for the
experiments, and also less than the molar concentration of potassium. Consequently, at this ammonium concentration the SI for MPP is above that for MAP (Fig. 6), and a higher fraction of MPP in the precipitate would be expected. Correct operation of the PNA reactor to reach a low effluent ammonium concentration is therefore crucial if MPP recovery is targeted.

A third factor influencing MPP recovery is the phosphate concentration. A higher phosphate concentration can polish residual ammonium and still allow for MPP formation. Augmented phosphate concentrations can be achieved by fermentation of waste activated sludge prior to anaerobic digestion.39 The anaerobic conditions hydrolyse the poly-P and release phosphate and magnesium in a stream that is fed to the crystallizer.40 Potassium is a counter-ion in the poly-P structure and is released together with phosphate and magnesium under anaerobic conditions. Thus the fermented stream to the crystallizer would have higher phosphorus, magnesium and potassium concentrations, all of which promote MPP formation.

### Potential for multi-nutrient recovery from PNA effluent

The number of PNA installations is growing, with more than 100 already in place, most of them treating centrate at municipal WWTPs.22 This implies a large and expanding market for the implementation of struvite recovery from PNA effluent. The amount of potassium, phosphate and ammonium available for recovery in the side-stream was assessed by a sampling campaign over the sludge line at Antwerp South WWTP (Table 5). In the stream fed to the digester the concentrations of phosphate, potassium and ammonium were less than 30 mg L⁻¹, corresponding to a flow of 49, 241 and 85 kg day⁻¹, respectively. There was a slight decrease in nutrient concentration from the digestate to the centrate, which could be attributed to a buffer tank between the anaerobic digester and the centrifuge, where some precipitation could have occurred. The flow of centrate was calculated as 198 m³ day⁻¹, corresponding to a flow of 49, 241 and 85 kg day⁻¹ of P-PO₄³⁻, N-NH₄⁺ and K⁺, respectively. Expressed on a population equivalent basis this represents 0.28 g P-PO₄³⁻ p.e.⁻¹ day⁻¹, 1.41 g N-NH₄⁺ p.e.⁻¹ day⁻¹ and 0.50 g K⁺ p.e.⁻¹ day⁻¹, and an interesting nutrient mining opportunity in accordance with the circular economy framework.

### CONCLUSIONS

Coupling of PNA with struvite precipitation allows for the recovery of a multi-nutrient product containing all three macronutrients (N-P-K) from centrate. Formation of MPP was favoured by increasing pH up to 11, where a product containing 11.4% P, 3.51% N and 4.34% K was recovered.

PNA biomass reduced the alkalinity of centrate by 90%, which surpasses the performance of CO₂ strippers using aeration. PNA could substitute conventional CO₂ stripping as a pretreatment of centrate before struvite precipitation with subsequent savings of energy and NaOH dosing for pH control.

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**Table 5.** Nutrient concentrations in digestate and centrate at WWTP Antwerp South

| Ion  | Before digester | After digester | Centrate |
|------|-----------------|----------------|----------|
| Unit | P-PO₄³⁻ mg L⁻¹ | N-NH₄⁺ mg L⁻¹ | K⁺ mg L⁻¹ |
| Concentration | 15.5 ± 17 | 22.2 ± 57 | 29.9 ± 14 |
| | 318 ± 46 | 1525 ± 205 | 485 ± 18 |
| | 246 ± 16 | 1218 ± 115 | 429 ± 16 |
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