The inhibitory effect of inorganic carbon on phosphate recovery from upflow anaerobic sludge blanket reactor (UASB) effluent as calcium phosphate

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ABSTRACT

After treatment of the wastewater from the potato processing industry in an upflow anaerobic sludge blanket reactor (UASB) the effluent is rich in phosphate and dissolved inorganic carbon (IC). Increasing the pH of the UASB effluent with NaOH to precipitate phosphate as calcium phosphate leads to contamination with magnesium phosphate. Increasing the pH with Ca(OH)2 had a positive effect on phosphate precipitation, but after increasing the pH with Na2CO3 no precipitate was formed. After prior nitrification of the UASB effluent to remove IC, less NaOH was needed to increase the pH and the ions precipitated in a ratio that agreed with calcium phosphate formation. When the pH of the nitrified effluent was increased with Na2CO3 neither calcium nor phosphate precipitated. This inhibitory effect of IC on phosphate precipitation as calcium phosphate could not be derived from the saturation indexes calculated by the geochemical modelling program PHREEQC.

Key words | hydroxyapatite, inorganic carbon, nitrification, nutrient recovery, phosphate removal, struvite

INTRODUCTION

The ever-growing world population that also wants to continuously enhance its living standards puts stress on agriculture and on the use of fertilizers. The use of phosphorus in particular has increased, all the more so because of the growing importance of biofuels. As the world phosphorus reserves are limited we must use them wisely (Xu et al. 2018). This is somewhat different to what is the case for nitrogen, where the Haber–Bosch process can supply all the ammoniacal nitrogen that might be needed. In this context the recovery of phosphorus from wastewater has become a hot topic in recent years (Desmidt et al. 2015), and recovery is carried out in two main ways: (1) the phosphorus is recovered from wastewater or (2) after wastewater treatment, from the ashes of the sludge.

Where it is recovered from wastewater this is mostly done after an anaerobic pre-treatment in which full mineralization occurs. In vegetable and potato processing plants an upflow anaerobic sludge blanket reactor (UASB) is mostly used. In this step, organically bound phosphorus and polyphosphates solubilize to phosphate and enrich the phosphate that is already present in the wastewater. The phosphate in the anaerobic effluent of potato processing plants, for example originate from the potatoes and from the pyrophosphate that is added to the blanching water during potato processing to prevent both enzymatic and non-enzymatic discoloration. The phosphate-P concentration in the effluent easily reaches values of 75 mg L⁻¹ and sometimes 130 mg L⁻¹. When not treated for phosphate removal, this type of effluent is a serious environmental threat when discharged into surface waters, even if they are subsequently treated in an active sludge system. In most cases the phosphate is precipitated by the addition of an excess of FeCl₃ during the aerobic treatment.

Some companies, however, try to recover the phosphate together with part of the ammonium as struvite between the anaerobic and aerobic treatments. The recovery of phosphate as struvite from neutral solutions is a two-step process. First a pH increase is obtained by air blowing and removing part of the dissolved inorganic carbon (IC) as shown in reaction (1). In the second step the pH is further increased to 8.5–9.5 by adding a solution of NaOH, while simultaneously, relative to the amount of phosphate, a slight excess of Mg²⁺ ions is
added as, for example, MgCl\(_2\) (Egle et al. 2013).

\[
\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 \uparrow + \text{OH}^- \\
\text{sum HCO}_3^- \rightarrow \text{CO}_2 \uparrow + \text{OH}^- 
\]

(1)

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{HPO}_4^{2-} + \text{OH}^- + 5\text{H}_2\text{O} \rightarrow \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} 
\]

(2)

Based on the nature and the occurrence of struvite-containing kidney stones, an alternative for the second step of the struvite process has been developed. Infection of the urogenital tract by urease-positive microorganisms such as Proteus mirabilis results in the cleavage of the urea present in the urine (reaction (3)) (Jones & Mobley 1988). Because of this enzymatic activity of the infectious microorganisms, both the pH and ammonium concentration increase in the urine. Under these conditions, and since the urine also contains Mg\(^{2+}\) ions (0.05–0.15 g in 1.0–1.5 L in 24 hours) and phosphate (0.36–1.04 g in 1.0–1.5 L in 24 hours) (Taylor & Curhan 2007), following reaction (2), struvite-based kidney stones are formed.

\[
(\text{NH}_2\text{H})_2\text{CO} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{HCO}_3^- + \text{OH}^- 
\]

(3)

Our research group implemented this type of biomineralization for the recovery of phosphate as struvite by using an activated sludge that underwent an adaptation to urea. This idea was carried out both at the laboratory scale and the pilot scale (Desmidt et al. 2009, 2012).

The formation of other insoluble phosphate-containing structures can inspire the development of new techniques for phosphate recovery: for example, the formation of dental tartar starts with secretion of bicarbonate by the salivary glands, especially by the sublingual and the submandibular glands. With the loss of a hydroxyl ion, the bicarbonate is converted into carboxylic acid, which is split into carbon dioxide and water by the enzyme carboxylic acid anhydrase also present in the saliva; overall this reaction is identical to reaction (1) (Kivelä et al. 1999; Lomelino et al. 2016). The net effect is the removal of IC and a pH increase, creating the optimal conditions for the precipitation of Ca\(^{2+}\) ions as calcium phosphate as they are no longer retained by the (bi)carbonate. The role of IC in dental tartar formation is thus crucial: although it initiates the process, the precipitation of calcium phosphate only occurs after its removal.

During mineralization in a UASB, organic carbon is converted into biogas, a mixture of carbon dioxide and methane. Part of the carbon dioxide is retained in the anaerobic effluent by the inverse of reaction (1). The effluent from a UASB in the potato processing industry often contains up to 800 mg L\(^{-1}\) of IC (Desmidt et al. 2012).

The recovery of phosphate as struvite is not always appropriate. The phosphorus industry cannot use struvite and its sole use is as fertilizer (Lei et al. 2017). Although the recovery of phosphate as struvite is a good option in many parts of the world, it is not advisable where the soils are already supersaturated with phosphorus, eutrophication of surface waters is a problem and consequently the use of fertilizers is restricted. In this context the recovery of phosphorus/phosphate as calcium phosphate can be an option – it is the main component of phosphorus ores (Cunha et al. 2018). Recovered calcium phosphate or its crystalline equivalent, hydroxyapatite, could simply be mixed with phosphorus ore if it meets the required standards.

The role of IC was investigated in the context of the development of a method for phosphate recovery as calcium phosphate from IC-containing UASB effluent, which mimics dental calculus formation, in particular, whether the addition or removal of IC influences calcium phosphate precipitation from UASB effluent. For the precipitation of phosphate as calcium phosphate, the pH needs to be increased. To study the effect of supplementary IC, the effect on phosphate precipitation of alkalization with different bases, including Na\(_2\)CO\(_3\), was compared. Also, the effect of IC removal by prior nitrification on the calcium phosphate precipitation was studied. Indeed, during nitrification, relative to the molecular amount of ammonium, double the equimolecular amount of IC is removed (reaction (7)).

\[
\text{NH}_4^+ + 1.5\text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2\text{H}^+ 
\]

(4)

\[
\text{NO}_2^- + 0.5\text{O}_2 \rightarrow \text{NO}_3^- 
\]

(5)

\[
2\text{H}^+ + 2\text{HCO}_3^- \rightarrow 2\text{H}_2\text{CO}_3 \rightarrow 2\text{CO}_2 \uparrow + 2\text{H}_2\text{O} 
\]

(6)

\[
\text{NH}_4^+ + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{NO}_3^- + 2\text{CO}_2 \uparrow + 3\text{H}_2\text{O} 
\]

(7)

Applying the same principle of nitrification to reduce the buffering capacity, Vanotti & Szogi (2009) and Vanotti et al. (2005) developed an economical method for phosphate recovery from livestock manure using calcium hydroxide. For this paper, however, a completely different waste stream was investigated for phosphate recovery, i.e. the effluent of a UASB. Simple batch tests were performed to
investigate how IC interferes with phosphate recovery as calcium phosphate.

**MATERIAL AND METHODS**

**Experiments in batch mode**

All chemicals used during this experiment were of analytical grade and were obtained from Sigma Aldrich (Bornem, Belgium). Phosphate-containing UASB effluent was collected at a Belgian potato processing plant. The experimental setup consisted of three beakers that contained 1.5 L wastewater each, and these were mechanically stirred. The pH of the wastewater was increased to 8.5 and 9.0 by means of three different bases, being NaOH (1 mol L⁻¹), Na₂CO₃ (1 mol L⁻¹) and Ca(OH)₂ (as solid product); samples were taken after 1 hour of reaction time. During the study, special attention was given to the alkalinity of the wastewater. For that reason, this batch experiment was repeated on nitrified UASB effluent. The nitrification was carried out in a laboratory-scale membrane bioreactor (MBR) which was fed with UASB effluent that had previously undergone a urease-induced partial phosphate removal. This sample was in fact derived from an experiment in which ammoniacal nitrogen was recovered as nitrate. In this way, both the endogenous ammoniacal nitrogen, which was thus already originally present in the UASB effluent, and the exogenous ammoniacal nitrogen, which was derived from the urea that was used during ureolytic phosphate recovery, were recovered (Desmidt et al. 2015). The reactor configuration is presented in Figure 1.

**Calculation of the precipitation behavior of different salts**

To predict the precipitation behaviour of struvite, calcium phosphate and possible contaminants, the saturation index (SI) of the different ionic combinations in the UASB effluent was calculated with the geochemical computer program PHREEQC. Precipitation of relevant compounds may occur if their SIs are above zero; if the solution is undersaturated, the SI is lower than zero and therefore precipitation may not occur (Parkhurst & Appelo 2013).

**Analytical methods**

The pH of the samples was determined with a pH meter from Mettler Toledo (Zaventem, Belgium). IC was measured on the undiluted and unfiltered samples with a total carbon analyzer (Shimadzu, Japan). Ion concentrations were measured with a Metrohm ion chromatograph equipped with a conductivity detector (Antwerp, Belgium). Samples were filtered through a 0.45 μm syringe filter prior to dilution. For the detection of the cations (NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) the ion chromatograph was supplemented with the combination of a Metrosep C-4 40/5.0 column and Metrosep C-4 Guard/4.0 precolumn with 0.7 mmol L⁻¹ dipicolinic acid and 1.7 mmol L⁻¹ HNO₃ as the eluent at a constant flow rate of 0.9 mL min⁻¹. The anions (NO₂⁻, NO₃⁻ and PO₄³⁻) were separated on a Metrosep A Supp 5 150/4.0 column and Metrosep A Supp 4/5 Guard precolumn with 0.7 mL min⁻¹ 3.2 mmol L⁻¹ Na₂CO₃ and 1.0 mmol L⁻¹ NaHCO₃ as the eluent.

**RESULTS AND DISCUSSION**

**Characteristics of the anaerobically treated wastewater**

Table 1 shows the analytical results for the characterization of the UASB effluent and its nitrified part. The UASB effluent has a phosphate concentration of 36 mg L⁻¹ P and the Ca²⁺ concentration is 121 mg L⁻¹. The [Ca²⁺]/[P] ratio is 2.6. With a [Ca²⁺]/[P] ratio higher than 1 this effluent is not well suited for the recovery of phosphate as struvite (Moerman et al. 2009), but appears to be more suited for phosphate recovery as calcium phosphate. Because of the preceding ureolytic phosphate removal, the effluent of the MBR nitrification reactor had a pH value of about 8.5,
and 66% of the initial phosphate had already been removed. After nitrification the concentration of ammonium dropped to zero and an equivalent amount of nitrate formed.

The effect on IC is also clear: the double pretreatment resulted in a decrease of IC from 455 to 32 mgC L\(^{-1}\). The nitrified UASB effluent had a phosphate concentration of only 12 mg L\(^{-1}\) P and the Ca\(^{2+}\) concentration dropped to 74 mg L\(^{-1}\). By contrast, the [Ca\(^{2+}\)]/[P] ratio increased to 4.8. The addition of Mg\(^{2+}\) ions during the ureolytic phosphate removal resulted in an increase of the Mg\(^{2+}\) ion concentration to 115 mg L\(^{-1}\); the molar [Ca\(^{2+}\)]/[Mg\(^{2+}\)] ratio decreased from 1.7 to 0.4. It is not ideal to try to further reduce the phosphate concentration in this nitrified effluent by calcium phosphate precipitation: not only is the P concentration already 66% lower but also the increased Mg\(^{2+}\) ion concentration can result in magnesium phosphate precipitation instead of calcium phosphate precipitation.

**Calculation of the saturation indexes of the different salts**

An estimate of the precipitation behavior of phosphate salts in the effluents can be obtained by calculating the SI of the different ionic combinations that can form. In Figure 2(a) it can be seen that the UASB effluent at its native composition is indeed not suited for phosphate recovery as struvite: only in a narrow pH range (between pH 8.4 and pH 9.8) is there a very small positive SI for struvite. Furthermore, the SI of calcium phosphate is maximal at pH 9.5 and this is within the range for struvite precipitation.

However, based on the SI values of calcium phosphate and struvite, it must be possible to precipitate phosphate as calcium phosphate that is not contaminated with struvite from the native effluent between pH 7.3 and 8.4. However, in this neutral pH range, the SI of calcium carbonate, magnesium carbonate and magnesium phosphate are also positive. Recovery of phosphate as pure calcium phosphate can thus only succeed if the coprecipitation of carbonates is avoided by removing the carbonates from the water and if one can work in the pH range where the SI of calcium phosphate is positive and the SI of magnesium phosphate still is negative.

For the nitrified effluent, Figure 2(b) shows that struvite contamination can never be a problem: as no ammonium is present, it cannot be formed. The SI values are strongly negative and do not appear in the figure. The effect of the lowered phosphate concentration on the SI of calcium phosphate is partially compensated by the enhanced [Ca\(^{2+}\)]/[P] ratio, but the calculated SI is smaller than for the native

**Table 1 | Concentration of the relevant ions in the UASB effluent used**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>UASB effluent</th>
<th>Nitrified effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (°C)</td>
<td>7.5</td>
<td>8.5</td>
</tr>
<tr>
<td>NH(_4)(^{-})-N (mgN L(^{-1}))</td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>K(^{+}) (mg L(^{-1}))</td>
<td>997</td>
<td>997</td>
</tr>
<tr>
<td>Ca(^{2+}) (mg L(^{-1}))</td>
<td>121</td>
<td>74</td>
</tr>
<tr>
<td>Mg(^{2+}) (mg L(^{-1}))</td>
<td>43</td>
<td>115</td>
</tr>
<tr>
<td>NO(_3)(^{-})-N (mgN L(^{-1}))</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>NO(_2)(^{-})-N (mgN L(^{-1}))</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>PO(_4)(^{3-})P (mgP L(^{-1}))</td>
<td>36</td>
<td>12</td>
</tr>
<tr>
<td>Inorganic carbon (mgC L(^{-1}))</td>
<td>455</td>
<td>32</td>
</tr>
<tr>
<td>[Mg]:[NH(_4)]:[P] (molar ratio)</td>
<td>1.5:11.1:1.0</td>
<td>12.2:0.0:1.0</td>
</tr>
<tr>
<td>[Ca(^{2+})]:[P] (molar ratio)</td>
<td>2.6:1.0</td>
<td>4.8:1.0</td>
</tr>
<tr>
<td>[Ca(^{2+})]:[Mg(^{2+})] (molar ratio)</td>
<td>1.0:0.6 = 1.7:1.0</td>
<td>1.0:2.6 = 0.4:1.0</td>
</tr>
</tbody>
</table>

**Figure 2 | Saturation indexes of the different salts that can form from ions present in the UASB effluent (a) and the nitrified effluent (b) as a function of pH. The calculations are based on the concentrations given in Table 1.**
increasing the pH with NaOH or Na$_2$CO$_3$ 1 mol L$^{-1}$ ionic combinations at the initial pH and after further the ureolytic phosphate removal. The SI of some relevant removed. The pH of the MBR ef
during this process two-thirds of the phosphate was fed with the UASB ef
of a ureolytic phosphate removal reactor which in turn was fed with the UASB ef
was performed in an MBR that was fed with the ef
and 9.0 with three different bases (NaOH 1 mol L$^{-1}$ with that of alkalinization with sodium hydroxide or calcium hydroxide. We also investigated the possible effect of prior nitrification.
The pH of the UASB effluent was increased to 8.5 and 9.0 with three different bases (NaOH 1 mol L$^{-1}$, Na$_2$CO$_3$ 1 mol L$^{-1}$ and Ca(OH)$_2$ as solid product). The experiment was performed on the effluent as such and on a nitrified amount of the same effluent. This nitrification was performed in an MBR that was fed with the effluent of a ureolytic phosphate removal reactor which in turn was fed with the UASB effluent (Desmidt et al. 2012). During this process two-thirds of the phosphate was removed. The pH of the MBR effluent was 8.5 because of the ureolytic phosphate removal. The SI of some relevant ionic combinations at the initial pH and after further increasing the pH with NaOH or Na$_2$CO$_3$ 1 mol L$^{-1}$ are compared in Table 2 for the native effluent and for the nitrified effluent; the values for the alkalinization with NaOH can also be derived from Figure 2. The SIs for the addition of solid Ca(OH)$_2$ could not be calculated as the exact amount of added Ca$^{2+}$ was not known.

The results of this batch experiment are given in Figure 3. Increasing the pH of the untreated effluent with NaOH resulted in a decrease in the concentration of both phosphate and Ca$^{2+}$ ions, which is an indication for calcium phosphate precipitation. As the initial [Ca$^{2+}$]/[P] ratio in the wastewater was 2.6, more than enough Ca$^{2+}$ ions were present to precipitate all the phosphate as calcium phosphate. Between pH 7.5 and 8.5 the phosphate concentration dropped from 1.17 mmol L$^{-1}$ to 0.70 mmol L$^{-1}$, a decrease of 0.47 mmol L$^{-1}$; simultaneously the concentration of Ca$^{2+}$ ions dropped from 3.0 to 2.4 mmol L$^{-1}$, a decrease of 0.6 mmol L$^{-1}$. The (Δ[Ca$^{2+}$]/Δ[P]) ratio was 1.3 which is a bit too low for pure calcium phosphate and may have been due to the coprecipitation of some magnesium phosphate as the UASB effluent also contained Mg$^{2+}$ ions (2 mmol L$^{-1}$; Table 1); this coprecipitation of magnesium phosphate was expected, based on its positive SI values above pH 7.8. Between pH 8.5 and 9.0 the phosphate concentration decreased only 0.09 mmol L$^{-1}$ while the concentration of Ca$^{2+}$ ions decreased 0.60 mmol L$^{-1}$. The (Δ[Ca$^{2+}$]/Δ[P]) ratio in this case was about 7. Thus the Ca$^{2+}$ ions disappeared from the solution without a simultaneous decrease in the phosphate concentration. This disproportionate decrease of the Ca$^{2+}$ ions was probably due to the precipitation of calcium carbonate, as the SI was positive (Figure 2(a)).

Due to the poor solubility of Ca(OH)$_2$ the pH of the anaerobic effluent could only be increased to 8.5. This observation may suggest that the observed precipitation of Ca$^{2+}$ ions when the pH was increased above pH 8.5 was due to calcium hydroxide precipitation. However, the SI of calcium hydroxide was always strongly negative, which excluded its

| Table 2 | SI of some relevant ionic combinations when the pH of untreated UASB effluent and of nitrified UASB effluent are increased with NaOH 1 mol L$^{-1}$ and Na$_2$CO$_3$ 1 mol L$^{-1}$ to the pH values indicated |
|---------|-------------------------------|----------------|----------------|
| **Untreated effluent** | **NaOH** | **Na$_2$CO$_3$** | **Nitrified effluent** | **NaOH** | **Na$_2$CO$_3$** |
| Initial values | | | | |
| SI (--)/pH (--) | 7.50 | 8.50 | 9.00 | 8.50 | 9.00 |
| Ca$_3$(PO$_4$)$_2$ | 0.43 | 2.19 | 2.63 | 2.17 | 2.56 |
| Mg$_3$(PO$_4$)$_2$.8H$_2$O | -0.70 | 1.09 | 1.60 | 1.08 | 1.57 |
| MgNH$_4$PO$_4$.6H$_2$O | -0.77 | 0.09 | 0.26 | 0.08 | 0.25 |
| CaCO$_3$ | 0.56 | 1.54 | 1.93 | 1.59 | 2.03 |
| MgCO$_3$ | 0.01 | 0.99 | 1.41 | 1.04 | 1.52 |

The effect of the increased Mg$^{2+}$ ion concentration is seen on the increased SI of magnesium phosphate. The effect of removing IC is reflected in lower SIs for both calcium carbonate and phosphate. The pH must increase to 8.2 before carbonate precipitation is a problem.

Effect of the concentration of IC in batch precipitation experiments

We investigated the way that the addition of extra IC influences the precipitation of phosphate as calcium phosphate by comparing the effect of alkalinization with sodium carbonate with that of alkalinization with sodium hydroxide or calcium hydroxide. We also investigated the possible effect of prior nitrification.

Increasing the pH causes the SI of all mentioned ionic combinations to increase, irrespective of the type of base used. When Na$_2$CO$_3$ is used to increase the pH, the SI of CaCO$_3$ and MgCO$_3$ become more positive. After nitrification and at pH 9, the SI after alkalinization with NaOH 1 mol L$^{-1}$ or with Na$_2$CO$_3$ 1 mol L$^{-1}$ are very similar. It appears that IC has no influence on the precipitation behavior of either calcium phosphate or magnesium phosphate.

The concentration of IC in batch precipitation experiments
precipitation. When the pH was increased to 8.5 with Ca(OH)$_2$, the dosage of extra Ca$^{2+}$ ions resulted in better phosphate removal (0.59 mmol L$^{-1}$/C$_0$) in comparison with the experiment in which NaOH was used (0.45 mmol L$^{-1}$/C$_0$). The addition of Na$_2$CO$_3$ to increase the pH almost completely excluded phosphate precipitation. This experimental result was unexpected, based on the SI values of the different phosphate salts (Table 2). In the pH region under study (7.5–9.0) the added carbonate mostly became bicarbonate (pK$_b$ carbonate = 10.3). This observation is thus in agreement with the hypothesis that bicarbonate somehow inhibits phosphate precipitation as calcium phosphate. Contrary to what was expected based on the SI value of calcium carbonate (Table 2), there was no obvious sign of calcium carbonate precipitation as no Ca$^{2+}$ ions disappeared from the wastewater.

For the nitrified sample of the UASB effluent, the addition of NaOH 1 mol L$^{-1}$ to increase the pH from 8.5 to 9.0 resulted in a decrease of the Ca$^{2+}$ and PO$_4^{3-}$ concentration in a ratio of 0.50 mmol L$^{-1}$ to 0.29 mmol L$^{-1}$ or 1.72 which is consistent with Ca$_3$(PO$_4$)$_2$ precipitation. It is striking that this already low phosphate concentration of 0.39 mmol L$^{-1}$ could be decreased to 0.1 mmol L$^{-1}$. Indeed, for the nitrified sample the SI value of calcium phosphate was, although still positive (0.94 at pH 9.0), much lower than in the native sample (2.63 at pH 9.0). As the phosphate had already been partly removed from the UASB effluent, the [Ca$^{2+}$]/[P] ratio increased to 4.8 and this high value may explain the increased removal of phosphate, without a coprecipitation of magnesium phosphate.

However, the relatively high concentration of Ca$^{2+}$ ions did not result in an increased precipitation of calcium carbonate as the [Ca$^{2+}$]/[P] ratio of the removed ions was fully consistent with calcium phosphate precipitation. In the equivalent sample that was not nitrified, for a lower [Ca$^{2+}$]/[P] ratio of 2.6 the ($\Delta$[Ca$^{2+}$]/$\Delta$[P]) ratio was 7, indicating the coprecipitation of calcium salts such as calcium carbonate.

Thus, nitrifying the wastewater improved the conditions for phosphate removal as calcium phosphate: as ammonium was no longer available, struvite precipitation was avoided. As per reaction (7), the nitrification also reduced the IC concentration. As the original concentration of total ammonial nitrogen (TAN) was 180 mg L$^{-1}$ (13 mmol L$^{-1}$) the nitrification should have consumed about 26 mmol L$^{-1}$ IC or 312 mgC L$^{-1}$. The IC concentration in the native UASB effluent was 455 mg L$^{-1}$ and after ureolytic phosphate removal and nitrification it was reduced to 32 mg L$^{-1}$, somewhat more than expected. This large removal of IC (nearly
93%) avoided the calcium carbonate precipitation that was observed in the experiment with the native UASB effluent.

To increase the pH of the nitrified sample from 8.5 to 9 only 35% of the amount of NaOH 1 mol L\(^{-1}\) was needed when compared to the amount needed for the alkalinization of the equivalent sample that was not nitrified. This indicates that 65% of the buffering capacity was removed from the wastewater in the pH region of 8.5–9, which can be explained by the combined removal of ammonium and bicarbonate ions by the nitrification process.

In Figure 3 it can be seen that alkalinization with Na\(_2\)CO\(_3\) 1 mol L\(^{-1}\) of the nitrified wastewater completely hampered the precipitation of both calcium and phosphate, the same result obtained for the UASB effluent that was not subjected to nitrification, and a result that was also not predicted by the SI values calculated for calcium phosphate, for example. The SI calculated for calcium phosphate after increasing the pH with Na\(_2\)CO\(_3\) to pH 9.0 was 0.90 and was about the same (0.94) as that calculated for a pH increase with NaOH. Under these circumstances, carbonate and most likely its protonated form, bicarbonate, which spontaneously arises from carbonate at the pH under study (pH 8.5–9.0; pK\(_b\) carbonate = 10.3), is thus completely inhibiting phosphate precipitation as calcium phosphate.

As already mentioned for the above case in which the sample was not subjected to nitrification, the alkalinization of the nitrified sample with Na\(_2\)CO\(_3\) to pH 9 did not result in a decrease of the Ca\(^{2+}\) ions either. Alkalinization with carbonate ions thus did not result in the precipitation of either calcium carbonate or calcium hydroxide. It appears that in these circumstances the Ca\(^{2+}\) ions from the solution immediately form soluble complexes with the exogenous carbonate ions and are retained in solution, a phenomenon observed as early as in 1945 by Greenwald. This behavior of exogenous carbonate appears to be different from that of the endogenous carbonate that arises in solution by deprotonation of bicarbonate. Several indications were found that carbonate in this situation precipitates as calcium carbonate.

Among the inhibiting compounds reported for phosphate precipitation, bicarbonate is frequently mentioned (Hermassi et al. 2016; Cunha et al. 2018). The present results seem to confirm this hypothesis, although it is difficult to distinguish the effect of bicarbonate from that of carbonate in all cases. As nitrification consumes bicarbonate (reaction (7)) and carbonate – via its conversion to bicarbonate – it not only circumvents the observed inhibitory effect of bicarbonate on the precipitation of phosphate as calcium phosphate, but also the competing calcium carbonate precipitation. These effects, in combination with the fact that no more struvite can be formed, explain why nitrification circumvents most of the problems that occurred in precipitating phosphate as calcium phosphate in the native UASB effluent.

As Vanotti & Szogi (2003) and Vanotti et al. (2005) concluded for livestock manure, it is concluded that prior nitrification thus facilitates phosphate recovery from the effluent of a UASB. The method is bioinspired and mimics dental calculus formation in the sense that before phosphate precipitation, enzymatic decarbonation occurs. In calculus formation, this decarbonation is the result of the activity of carbonic acid anhydrase; in the case of phosphate recovery from livestock manure and UASB effluent, the decarbonation is a side effect of prior nitrification. The positive effect of prior nitrification on the recovery of phosphate as calcium phosphate from the effluent of a UASB has also been investigated in batch experiments (Monballiu et al. 2018b) and in a long-term experiment with a continuous reactor (Monballiu et al. 2018a).

This experiment indicates that prior nitrification of UASB effluent ensures better conditions for calcium phosphate precipitation. The combination of both processes guarantees that the calcium phosphate product is, in case of successful nitrification, free from struvite. The co-precipitation of calcium carbonate is minimalized, but this is dependent on the initial ratio of IC and TAN in the wastewater. If the IC/TAN ratio is equal to 2, then all the IC will be consumed during the biological oxidation of ammonium; see reactions (4)–(7). The precipitation of magnesium phosphate is still possible as is indicated by its positive SI value, but of course this is strongly dependent on the magnesium concentration (Monballiu et al. 2018b). It was also demonstrated that the reaction time for calcium phosphate recovery could be kept quite short, as the precipitation was accomplished in 1 hour (Monballiu et al. 2018b).

**CONCLUSIONS**

This research demonstrated that the addition of extra IC to a UASB effluent hampers phosphate removal as calcium phosphate. Removing part of the IC by prior nitrification facilitates the recovery of phosphate as calcium phosphate as it avoids competing struvite precipitation and removes IC. Adding extra IC to a nitrified UASB effluent, however, abolishes the positive effect of prior nitrification on phosphate precipitation as calcium phosphate. These results clearly demonstrate that IC influences phosphate precipitation and thus phosphate recovery as calcium phosphate.
The results also show that this influence of IC on phosphate precipitation is not predicted by PHREEQC modelling.

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REFERENCES


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