Simultaneous removal of N and P in a SBR with production of valuable compounds: application to concentrated wastewaters

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ABSTRACT

This article examines the optimisation of recovery of phosphorus and nitrogen (via struvite) in small treatment units for high strength wastewaters using biologically assisted precipitation. The particular focus was the synergetic effect between removal of orthophosphate and the biological reactions occurring during nitrogen removal. The most sensitive parameter influencing the phosphate solid forms (HAP, MAP) is pH. Sequencing batch mode helps maintain high gradients in ammonia concentration, which encourages struvite precipitation. Nitrification has a key effect on the precipitation, through its influence on pH and ammonia concentration, determining the remaining soluble phosphorus concentration. Denitrification and CO₂ stripping, by increasing pH also improve precipitation of phosphorus. Optimal operating conditions will therefore depend on the chosen strategy: thus nitrification may help to keep phosphorus in a soluble form (as needed in direct urine reuse), whereas if co-precipitation is desired in the biological reactor, nitrification should be controlled in relation with others processes responsible for pH increase.

Key words | concentrated wastewater, decentralised treatment systems, nitrogen removal, phosphorus recovery, sequencing batch reactor

INTRODUCTION

In the future wastewater treatment facilities need to be adapted to make wastewater management more affordable and sustainable. Management of nutrients is a key issue as some of them are scarce resources (Wilsenach et al. 2003). For example phosphorus presents a finite resource and should thus be recovered. In addition, during the production of N-based fertilizers a high amount of energy is consumed (35 to 50 MJ/kgN) and dangerous compounds may be released.

Especially in the case of nitrogen and phosphorus rich wastewaters, nutrients could be recovered in a mineral form to be used in agriculture. These concentrated effluents are provided by agrofood-industry sector, and even by domestic wastewater: anaerobic sludge digester supernatant or urine if treated separately.

Many innovative experiences have been obtained during the last decade in the field of nutrient removal from high-strength wastewaters (Bernet & Sperandio 2006). For optimising nutrient removal and recovering phosphorus from domestic wastewater, one key point consists in avoiding dilution of these substances. As nitrogen and phosphorus are mainly present in urine, urine separation should be applied. Urine represents a small volume (500 l·(peq·year)⁻¹, around 1% of the total effluent volume) and contains 80% of the nitrogen and 50% of the phosphorus of the produced pollution. These elements are one hundred times more concentrated in urine than in a normal wastewater (fed to a centralised treatment plant). High concentration definitively creates favourable conditions for nitrogen and phosphorus removal and recovery through physical transfer to gas phase or solid phase respectively (precipitation or stripping). Indeed, most promising options to recover phosphorus are the pro-

duction of phosphate solid as struvite (Doyle & Parsons 2002), and stripping of ammonia (Janus & Van der Roest 1997; Mulder 2003). Basically, phosphorus precipitation mainly depends on pH, concentrations of the ionic substances and temperature. Various compounds can be formed depending on the pH of operation. Calcium phosphate (Ca₃(PO₄)₂), hydroxylapatite (Ca₅(PO₄)₃OH), and struvite (MgNH₄PO₄·6H₂O) are the most commonly found products.

In this work, research focuses on the optimisation of recovery of phosphorus (and nitrogen via struvite) on small treatment units for high strength wastewaters using biologically assisted precipitation. In that way, production of valuable mineral P-species from pig manure to be reused as fertilizers have been investigated by Daumer et al. (2007). In the work of Pambrun et al. (2006), the combination of nitrification (or nitrogen removal) and phosphate precipitation in the same reactor was assessed. These recent works demonstrated the synergetic effect between the elimination of nitrogen and orthophosphate compounds.

Nitrification and denitrification play a major role as these reactions significantly affect the pH. Acidification induced by nitrification has been proposed as a mechanism to explain the dissolving of phosphorus during the aerobic stage (Boursier 2003; Choi et al. 2006) which was also demonstrated by Daumer et al. (2007). Nitrification of one molecule of ammonia leads to two protons released. In concentrated effluents, even if the buffering capacity of the slurry is high (Sommer & Husted 1995), nitrification can significantly affect pH (Daumer et al. 2007). Ammonia consumption can also have an impact on struvite saturation level. Moreover denitrification and CO₂ stripping are also significant phenomena which need to be taken into account. Thus, this study focused on: (1) characterization of interactions between precipitation of phosphorus compounds and nitrogen removal (nitrification and denitrification) in SBR process, (2) characterization of phosphorus mineral species obtained in this hybrid biological-chemical process, (3) optimization ways for the P removal strategy in relation with nitrogen removal.

**METHODS**

**Experimental conditions**

This work has been carried out in a 10L reactor, operated in a sequencing Batch Reactor (SBR). Process cycles were controlled as presented in the Figure 1. Temperature, pH and dissolved oxygen were continuously controlled. The Oxygen Uptake Rate (OUR) was continuously calculated based on the oxygen mass balance on the reactor. During all the experiments presented here, the effluent to be treated was a synthetic substrate which contains 500 mgNH₄−N/L, a COD/N of 14,700 mg HCO₃⁻/L (NaHCO₃), 45 mgMg/L (MgSO₄·7H₂O), 115 mgCa/L (CaCl₂·2H₂O), 100 mgP/L (KH₂PO₄). The applied loads varied from 0.5 to 1.5 KgNH₄⁺N·m⁻³·d⁻¹, the hydraulic retention time varied between 0.8 and 1.5 h, and the sludge retention time was fixed at 18 days.

**Analytical methods for characterizing the liquid phase**

Chemical analyses were conducted according to the procedures outlined in the standard methods (AFNOR 1994). Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) were determined with GF/C Whatman filters, by measuring the mass loss after passing at 105°C and 500°C. Ammonia concentration (NFT 90.015), nitrate and nitrite concentrations (NFT 90.012) and phosphate concentration (NFT 90.023) were determined by spectrophotometric methods, based respectively on Nessler, Griess reagents and ascorbic acid methods. To determine total phosphorus concentration, samples were mineralized with sodium persulphate in order to convert all phosphorus into phosphate forms that were quantified by the preceding method. Calcium and magnesium concentrations were determined by atomic absorption spectrometry with flame (air/acetylene).

**Solid phase analysis**

- Microscopic observations

  In order to identify the structure of biological flocs, some microscopic observations of sludge samples were
realised with a photonic microscope binocular Biomed-Leitz® (objectives × 4, × 10, × 25, × 100—objective with immersion; eyepieces × 12.5). For the observations (fresh state), the samples were placed between blade and plate and were observed under the photonic microscope without colouring. These microscopic observations also allowed to identify the presence of crystals in the sludge, in form crystalline or included in very dense flocs.

- X-ray diffraction analysis
  Sludge samples were also analyzed by diffraction of X-rays in order to have qualitative information on the composition of the mineral fraction of solid. The general method consists in bombarding the sample with X-rays, and looking at the intensity of X-rays which are diffracted. The intensity of rays depends on the angle of deviation $2\theta$ of the beam, the curve of intensity obtained is called a “diffractogram”. The composition of the solid is then estimated based on a comparison between the diffractogram obtained and the known spectra of reference compounds.

RESULTS AND DISCUSSION

The SBR was run during more than 200 days under aerobic conditions and an anoxic period was included during the last 40 days for performing denitrification. Mass balances for N and P species were performed in order to characterize the global removal performances during the working period and the removal kinetics during one cycle of the SBR. Based on the observations, strategies to optimize the biological processes to get the phosphorus either soluble or under a precipitate will be discussed.

**Phosphate and ammonia concentrations during aerobic batch cycle at different pH**

Phosphate and ammonia concentrations in the reactor during a typical cycle of SBR process are presented in Figure 2 at different pH (pH = 7; pH = 7.5; pH = 8.5). Results show an immediate removal of phosphates during the first 15th minutes due to rapid precipitation. It is followed by a stabilisation of the concentration at pH 7, whereas a slightly increase in phosphate concentration is observed at pH 7.5 and 8.5. This last increase could be explained by a solubilisation of the initially precipitated phosphorus.

Actually when the pH is higher than 7.5, due to possible co-precipitation of ammonia with phosphate (as struvite), the phosphate concentration is linked to the nitrification kinetic. Consuming ammonia, nitrification induces a decrease of ionic product which controls the struvite solid amount in the reactor. This phenomenon is not observed at pH 7 probably because the co-precipitation of ammonium phosphate does not occur (see below). At the end of the cycle the remaining phosphate is about 72 mg P·L$^{-1}$ at pH 7, whereas the final concentration is about 45 mg P·L$^{-1}$ at pH 8.5, which means that about 55% of phosphate have been removed from liquid phase in the last case. This confirms that higher is the pH the higher phosphates removed from liquid phase.

This is clearly explained by the fact that solubility of struvite and calcium phosphate decrease when pH increases (Doyle & Parsons 2002), in relation with the increase in the proportion of the PO$_4^{3-}$ form compared to other forms (HPO$_2^{2-}$ and H$_2$PO$_4^{-}$). Indeed, microscopic observations showed the presence of a large number of...
mineral crystals, growing with time, into the sludge matrix (Figure 3). X-ray analysis showed that phosphate precipitates into different forms depending on pH: mainly hydroxyl-apatite at pH above 7.5, and partly as struvite at pH above 8. Figure 4 presents X-ray spectra obtained at pH 8.2 after denitrification phase was implemented. It clearly demonstrates the presence of struvite as one the main crystallised mineral form into the sludge (associated to calcite). Collected data tends to shows that calcite appearance was regularly concomitant to struvite. This could be explained by the fact that calcium precipitation with carbonate and consequently the fraction of phosphate precipitating with magnesium instead of calcium increases.

Due to phosphate mineral enrichment, the VSS:TSS ratio of the sludge ranged from 0.6 down to 0.4 (around 0.8–0.9 in a conventional process). The total mineral fraction was therefore relatively high compared to conventional sludge. Total phosphorus analysis of the sludge showed that P content reached a value closed to 10% of TSS, and 20% of mineral content, when the system was working at pH 7.5. This tends to show that most of the mineral fraction of the sludge was composed of phosphorus mineral and then could provide high fertiliser capacity.

Overall performance of phosphorus removal with respect to nitrification

Figure 5 presents the ammonium and phosphate removal yields in the SBR reactor during the all working period at a pH of 7.5 (aerobic conditions only).

Phosphate removal efficiency varies from 40 to 90%. When ammonia is totally removed by biological reaction, phosphate removal yield is between 40 and 60%. Conversely, if nitrification is not completed, an increase of the phosphorus removal yield from 40% to 80% is observed as ammonia varies from 0 to 300 mgN/L. It can be explained by the fact that for a total nitrification at pH 7.5, phosphate is mainly precipitated as calcium phosphate. Then when ammonia accumulated struvite precipitation becomes more and more significant due to increase of saturation product. No more significant increase in P removal is observed for ammonia concentration higher than 300 mgN/L, probably because magnesium becomes the limiting compound in this case.

Optimization of the process for P recovery

Different strategies for nutrient reutilization can be considered: (i) reuse phosphorus in a soluble form together with the effluent; or (ii) reuse phosphorus in solid forms.
separated from nitrogen or (iii) combined with nitrogen (struvite). These objectives should be achieved while minimizing consumption of additives. Recalling that the main parameters that control precipitation of phosphorus are pH and ammonia concentration in the bulk liquid, the following paragraph intends to summarize the different possibilities to get a synergetic effect between removal of orthophosphate and the biological reactions occurring during nitrogen removal.

If the objective is to recover the phosphorus in a soluble form, precipitation must be avoided. It could be the case of urine for reuse as fertilizer. In that case, nitrification clearly is the process which improves the soluble fraction of phosphorus by reducing pH. Complete nitrification and a rather low (but not limiting) bicarbonate concentration accentuate this effect.

Conversely, focusing on the efficiency of phosphorus removal by precipitation, Table 1 presents different case studies that was tested in our laboratory and that may be representative of different concentrated effluents.

If phosphorus is needed in a solid form, precipitation must be achieved and resolubilisation must be avoided. In order to maximize precipitation, high concentration of ammonia must be maintained. Therefore, the SBR operating mode appears as a good way for improving phosphate precipitation because concentration gradients are high due to batch feeding mode. If magnesium is not limiting, high concentration of ammonia leads to higher struvite formation and phosphate removal. However, when advanced nitrification must be achieved, resolubilisation occurs due to both pH decrease and ammonia ion depletion. The pH drop depends mainly on the concentration of nitrogen to be nitrified and on alkalinity concentration. From our works and thus under our operating conditions, when alkalinity is low and nitrified nitrogen is high, thus nitrification occurs but is not complete. In this condition of low buffering capacity, pH decreases proportionally to the nitrified nitrogen reaching value below 7. Phosphorus resolubilisation occurs and the P removed as a precipitate is lower than 20% (Case 1 in Table 1). When bicarbonates are in excess with respect to the amount required for nitrification, the pH drop is much smaller. The removed phosphorus increases to 50% (Case 2 in Table 1). In our operating conditions, it can even reach more than 90% if nitrification is maintained unfinished (case 3 in Table 1). Finally, it was observed in our pilot that complete nitrification and phosphorus removal is achieved when increasing pH. In practice this can be achieved by performing denitrification or CO₂ stripping (case 4 in Table 1). Table 1 also indicates how the precipitates type depends on the main variables: pH, ammonia concentration or nitrification degree. At the lowest pH value, apatite will mainly dominate in the precipitates. Probability of struvite and calcite appearance increases as the pH increases (phenomenon is reinforced for struvite if nitrification is not completed).

Concomitantly, nitrification kinetics (both steps) are significantly influenced by these parameters changes (pH, initial ammonia concentration). The increase of the ammonia concentration at the beginning of the cycle may lead to an increase of the free ammonia concentration especially at

Table 1 | Different case studies obtained from bench-scale pilot plant. Nitrification and denitrification degree, P-removal efficiency, type of precipitate are given

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon supply</td>
<td>High bicarbonate limitation</td>
<td>Bicarbonate supply (stoichiometry or excess)</td>
<td>Bicarbonate supply (excess)</td>
<td>CO₂ stripping or denitrification or pH control</td>
</tr>
<tr>
<td>Nitrification</td>
<td>Unfinished</td>
<td>Complete</td>
<td>Unfinished</td>
<td>Complete</td>
</tr>
<tr>
<td>NH₄⁺ removal</td>
<td>50%</td>
<td>&gt;99%</td>
<td>50–90%</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Denitrification</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Advanced</td>
</tr>
<tr>
<td>pH</td>
<td>6.5–7</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5–8.5</td>
</tr>
<tr>
<td>PO₄³⁻ precipitation</td>
<td>&lt;20%</td>
<td>50%</td>
<td>70–90%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>Observed mineral forms (in order of importance)</td>
<td>undetermined</td>
<td>Apatite (HAP)</td>
<td>Struvite (MAP)</td>
<td>Struvite (MAP), Calcite, Apatite (HAP)</td>
</tr>
</tbody>
</table>
the highest pH values. As a consequence, inhibition of Nitrite Oxidizing Bacteria (NOB) by free ammonia occurs. If nitrite build up must be avoided, thus a compromise must be founded with respect to the pH and ammonia concentration.

CONCLUSIONS

The treatment of concentrated wastewaters such as effluent of agro-food industries, effluent of anaerobic digestion, or urine needs new specific approaches. The idea developed in the present study is to investigate the synergetic effect between removal of orthophosphate and the biological reactions occurring during nitrogen removal. Results were obtained for a given influent with fixed calcium, magnesium and phosphates concentration, and the main modified parameters were the pH, and SBR cycle operation parameters.

pH is certainly the most sensitive parameter which influences the phosphate solid forms (HAP, MAP). Sequencing batch mode allows maintaining high gradients in ammonia concentration which encourages struvite precipitation. Nitrification progress plays a key role on the precipitation, through its influence on pH and ammonia concentration, determining the remaining soluble phosphorus concentration. This effect obviously depends on the buffer capacity of the liquid. Denitrification and CO2 stripping, by increasing pH also improves precipitation of phosphorus. Therefore, optimal operating conditions will depend on the chosen strategy. On one hand, nitrification may help to keep phosphorus in a soluble form if necessary (for example in the case of direct urine reuse). On the other hand, if co-precipitation is desired in the biological reactor, nitrification should be controlled in relation with others processes responsible for pH increase.

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REFERENCES