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ABSTRACT

Phosphorus (P) recycling as mineral fertilizer from wastewater activated sludge (WAS) depends on the amount that can be dissolved and separated from the organic matter before the final crystallization step. The aim of the biological phosphorus dissolution potential (BPDP) test developed here was to assess the maximum amount of P that could be biologically released from WAS prior that the liquid phase enters the recovery process. It was first developed for sludge combining enhanced biological phosphorus removal and iron chloride. Because carbohydrates are known to induce acidification during the first stage of anaerobic digestion, sucrose was used as a co-substrate. Best results were obtained after 24–48 h, without inoculum, with a sugar/sludge ratio of 0.5 gCOD/gVS and under strict anaerobic conditions. Up to 75% of the total phosphorus in sludge from a wastewater treatment plant combining enhanced biological phosphorus removal and iron chloride phosphorus removal could be dissolved. Finally, the test was applied to assess BPDP from different sludge using alum compounds for P removal. No dissolution was observed when alum polychloride was used and less than 20% when alum sulphate was used. In all the cases, comparison to chemical acidification showed that the biological process was a major contributor to P dissolution. The possibility to crystallize struvite was discussed from the composition of the liquids obtained. The BPDP will be used not only to assess the potential for phosphorus recycling from sludge, but also to study the influence of the co-substrates available for anaerobic digestion of sludge.

Introduction

Phosphorus (P) is indispensable to human diet as it is a part of the energy carrier in cells (ADP/ATP), of DeoxyriboNucleic Acid (DNA), the main structures of genes, of bones and teeth and a lot of other tissues. It is not replaceable in plant cultivation and consequently for making food production sustainable, there is a need for sustainable access to the nutrient P.[1] As the P life cycle does not include an atmospheric part, phosphorus cannot be considered as a renewable resource on short time scales. Coupled to the fact that P extracted from mining activity represents the biggest part of fertilizer, there is a real need to set up P recovery and valorization processes, particularly regarding global food security. There is thus an increasing demand for nutrient recovery and P from wastewater can be considered as a valuable resource. In wastewater treatment plants (WWTPs), P is typically present in effluent in concentrations around 10 mg.L^{-1} [2] although this value can suffer large variations. It has to be removed before water discharge in rivers. The limits vary from 0. 2 to 2 mg.L^{-1}, depending on the local regulation. There are two ways developed to remove P from wastewater and concentrate it in sludge. The first one is by adding calcium, iron or alum to form solid minerals precipitated in sludge. The second one is known as enhanced biological P removal (EBPR). It is based on phosphate accumulating organisms (PAO) able to accumulate more P than strictly required for their metabolism. In anaerobic conditions the PAO are degrading the energy stored as polyphoshate and glycogen to stored short chain organic substrates like volatile fatty acids (VFA) as polyhydroxyalcanoates (PHA). Polyphosphate catabolism induces phosphate excretion in the media. In aerobic conditions or when electron receivers are available (anoxic stage), the PAO oxidize the PHA to regenerate the intracellular energy storage. P accumulated during this phase is higher than the amount of P released in the anaerobic one and so P is accumulated by the biomass.[3] Moreover, depending on the pH and on the calcium concentration in wastewater, a part of P released by the PAO can be precipitated with dissolved calcium or magnesium, contributing to P accumulation in sludge. Depending on the legal limits for P in the effluent, both EBPR and

chemico-physical removal can co-exist. So more often, there are two main forms of P in sludge. The first one is P accumulated in PAO that can be released by anaerobic digestion (AD) when VFA are produced by acidogenic microorganisms from readily available carbon sources. The second one is calcium or iron phosphate salts that required low pH to be chemically dissolved. P in wastewater is rather diluted to make recovery and reuse feasible. Thereby, phosphorus-rich side streams or process water with phosphorus concentrations >50 mg/L can be considered as economically rewarding.[4] So, usually, nutrient removal is performed after concentration in sludge, especially when WWTPs have anaerobic digestion, Indeed, the P released at this stage is often recirculated directly back to the liquid processing stream with rather high concentrations. It can constitute about 20–30% of the load on the activated sludge system.[5,6] Crystallization reactor for struvite or calcium phosphate recovery can be implemented on these streams to recover P. Recovery of dissolved P requires relatively basic technologies. This kind of system provides synergistic benefits to the plant as described in a recent paper that presents the first results from full-scale operation of a nutrient recovery facility in North America during three years.[7] The reduced nutrient loads in centrate (85% less P and 15% less ammonia) lowered the load to enhanced biological P removal (EBPR) and made it more stable. This resulted in reducing alum, which induced a reduction in dry tons of sludge production. This sludge had less P, which could promote its beneficial reuse on farmland where P concentration is limiting. The limiting step of P recovery from wastewater is the solubilization of the P concentrated in sludge. Cullen et al. [7] presented the first results obtained with a new process. The concept is to provide VFA to wastewater activated sludge (WAS) from EBPR in anaerobic conditions to increase P release by PAO prior to anaerobic digestion. A simultaneous release of Mg occurs and the liquid stream is provided to a crystallization reactor. From laboratory- and pilot-scale tests, phosphate release rates from the process were estimated to be between 25 and 40%.[8–10] This configuration may have several beneficial impacts: higher amounts of soluble P and Mg in struvite recovery facility and decrease of these values in AD reactors which enables to prevent the formation of struvite on it and avoid the maintenance operation because of scaling. However, the minimum pH reached by this process was close to 6.5, which is too high to dissolve a significant amount of mineral P salts and to avoid precipitation, of a part of the P biologically released by the PAO with calcium or iron. Another solution to solubilize P is chemical acidification.[11] P is first solubilized in a tank with

sulphuric acid dosage at pH 4. Then metal ions are precipitated with citric acid. Finally, crystallization is carried out on the P-rich supernatant after pH adjustment (8.5 with NaOH). In the first tests, a dissolution rate of 75% was obtained by these authors. In continuous operation at full scale during 5 months, the dissolution rate was 40 80%. Dissolution was the limiting process step and correlated directly to the phosphorus recovery rate since almost all of the dissolved phosphorus (approx. 98%) precipitates, mostly as struvite. Comparable results were obtained by chemical acidification performed to dissolve P from pig manure in order to recover it as struvite at a pilot scale. Chemical acidification was also the limiting step from an economic point of view.[12] Most of the WWTPs are combining EBPR and iron or alum salts to reach the P limit in the effluent.[13] The distribution of P between the intracellular forms (sensitive to biological release) and mineral forms (sensitive to chemical dissolution) depends on process configuration. Our midterm objective is to contribute to developing a process combining the biological and chemical mechanisms that enable maximal P solubilization during the hydrolysis stage. The aim is to provide selected substrate to PAOs in anaerobic conditions to enable the release of intracellular P and lower the pH, without the use of chemicals, to solubilize mineral forms of P and/or prevent crystallization of the released P with magnesium or calcium. The following steps of the recovery process would be the same as those usually used on liquid effluent from digested sludge dewatering. Struvite crystallization process parameters and quality of the product will depend on characteristics of the liquid phase after biological P dissolution.[14] After being mixed with effluent from struvite crystallization (pH about 8), sludge from the biological acidifying step could enter the anaerobic digestion process.

This paper presents the biological phosphorus dissolution potential (BPDP) test developed to compare, in standardized conditions, the maximum P that could be released and remained dissolved by providing readily available carbon wastewater sludge depending on the previous P removal process parameters. The potential for struvite crystallization was discussed from the composition of the liquid phase obtained. It could also be used to compare the efficiency of different co-substrates in dissolving the P immobilized in a sludge.

Materials and methods

Experiments

Twenty-six biological tests and four chemical tests were performed. The conditions of the biological tests performed in this study are described in Table 1.

Table 1. Biological dissolution tests. N2: inerted with N2.

N°	Objective	WAS	CoS/S gCOD/gVS	B/I gVS/gVS	Air conditions
B1	Optimal coS/S ratio	S1a	0	–	Closed,N₂
B2		S1a	0.1	–	
B3		S1a	0.5	–	
B4		S1a	2	–	
B5		S1a	5	–	
B6	Influence of O₂	S1b	0	–	Closed, N₂
B7		S1b	0.5	–	Closed, N₂
B8		S1b	0.5	–	N₂ after opening
B9		S1b	0.5	–	No N₂ after opening
B10		S1b	0.5	–	Open
B11	Influence of inoculum	S1c	0.5	–	Closed, N₂
B12		S1c	0.5	–	
B13		S1c	0.5	2	
B14		S1c	0.5	5	
B15		S1c	0.5	8	
B16		S1c	0.5	11	
B17	Application to other sludge	S2	0	–	Closed, N₂
B18		S2	0.5	–	
B19		S3	0	–	
B20		S3	0.5	–	
B21		0	0.5	–	
B22		S2	0.5	2	
B23		S2	0.5	11	
B24		S3	0.5	2	
B25		S3	0.5	11	
B26	Iron dissolution	S1d	0.5	–	Closed, N2

WAS samples

Activated sludge was sampled on three different WWTPs with different phosphorus treatments: Measurements were realized on the same day of WAS sampling, except chemical acidification test of S1 (C1) which was performed after 24 h storage at 4°C. Characteristics of the activated sludge are summed up in Table 2.

Biological acidification tests

Co-substrates (coS) with a high C/N ratio are known to improve acidification.[15] To favour a short-term test, readily available carbon was provided as sucrose (commercial white sugar). To develop the test, thickened WAS (S1) coming from WWTP1 (with coupled EBPR and P removal with FeCl₃) was sampled just after centrifugation, the day of the tests, in the municipal WWTP close to the laboratory. It was diluted to around 25 gVSS.kg⁻¹ to enable correct stirring. A volume of 640 mL of a mix of diluted WAS and sucrose (white sugar) was introduced in 1 280 mL Erlenmeyer flasks which were closed with a rubber septum. Depending on the test, the gaseous top of the reactors was flushed with N2 to set anaerobic conditions before starting the process. Tests were run at 35°C with continuous stirring at 250 rpm in batch mode. Overpressure was removed

daily with a needle through the rubber septum to avoid vial burst. Liquid was sampled by a tap at the bottom of the Erlenmeyers which prevented the introduction of oxygen. Repeatability was assessed prior to the operation of these experiments by triplicates with sugar at loads of 2 and 5 gCOD.gVS⁻¹ and provided more than 95% repeatability on pH and soluble P. Tests were consequently not duplicated.

Inoculum preparation

To study the influence of inoculum, an inoculum was prepared with sludge from WWTP1. In order to favour acidogenesis and to inhibit methanogenesis, the sludge was placed in a reactor under gentle mixing and fed with a solution of sucrose (ratio 0.5 gCOD.gVS⁻¹). Because oxygen is not a problem for acidogenesis, the reactor was closed but not inerted with N₂ at the beginning of the process. When the pH was stabilized at about 4, the inoculum was used for experiments.

Chemical acidification tests

Chemical acidification tests were run on S1 (C1 and C4), S2 (C2) and S3 (C3) to estimate the fraction of P released by chemical mechanism. Perchloric acid (0,5 N) was used as acid. pH was maintained for 15 min at each pH value under continuous stirring and then lowered from 1 unit till reaching 2. Acidified activated sludge was sampled at every pH unit, and cation and anion concentrations were measured in the supernatant.

Analysis

Total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN) and chemical oxygen demand (COD) were measured with standard methods.[16] After an acidic mineralization (110°C, 1bar, 60 min), Total phosphorus (TP) was analysed with ascorbic acid method using automated colorimetric methods on QuikChem® FIA + from Lachat Instruments with QuikChem method 10-115-01-1-P. Supernatants were recovered after 20 min of centrifugation (4°C, 20,000 g) and filtration on 0.45 µm polypropylene membrane. Ionic composition of the supernatant was measured with anion (Cl⁻, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) and cation (Na⁺, NH₄⁺, Mg²⁺, Ca²⁺, K⁺) chromatography with Metrohm 940 Professional Vario IC, respectively, with Metrosep A sup 5 and Metrosep C4 -250/4,0 columns. Total calcium and magnesium were measured in the same conditions on mineralized products. Dissolved total iron was measured using Merck Spectroquant 1.14896.0001 kit and alum using Merck Spectroquant 1.00594.0001 kit. The analyses were run in triplicate.

Results and discussion

Determination of the Co-substrate/Sludge ratio

The co-substrate/sludge (coS/S) ratio was tested at 4 levels as described in Table 1 (tests B1–B5). The pH and ionic composition were measured on each sample at time 4, 24, 48, 72, 144 and 216 h.

Low pH was reached at higher loads (2 and 5 gCOD. gVS^{-1}) (Table 3). The pH quickly stabilized (between 24 and 48 h) for the loads of 0.1, 2 and 5 gCOD.gVS^{-1}, respectively, at around 5.7, 3.4 and 3.3. When the ratio was 0.5, the pH quickly decreased to 4 (24 h) but increased up to 5.5 between 50 h and 150 h (Figure 1 (a)). For the higher loads, a first maximum of dissolved P was quickly reached (~400 mg.L^{-1} at 24 h), followed by a slight diminution which could be due to inhibition and a necessary re-adaptation on several days, and another maxima was observed around 540 mg.L^{-1} at 144 h. When the ratio was 0.5, only one maximum (520 mg.L^{-1}) was reached after 50 h only (Figure 1(b)). Dealing with the test B3, soluble P seems strongly related to pH variations. Chemical precipitation of the biologically released P with calcium and magnesium could explain the P decrease when pH increased (Figure 1(c) and 1(d)).

The effect of the co-substrate load on pH and kinetics was in compliance with the literature even if in most of the studies the ratio is expressed in relation to the

inoculum added.[17–19] Low pH is an inhibitor for methanogenesis that could explain why the VFA could accumulate, stabilizing the pH for the highest load. The inhibition of P released when pH is lower than 5 is also described by Wu et al. [20].

The following experiments were performed at 0.5 gCOD.gVS^{-1}.

Influence of oxygen

To verify if it was possible to open the vial to add co-substrate or adjust pH during the test, five different tests were performed (B6–B10). From previous results the loading rate in the tests was chosen at 0.5 gCOD/g. VS^{-1} and the duration was 48 h. A control test in which the vial was closed without sugar was performed. Dissolved O$_2$ was measured in all the reactors that have been opened at 6 h. No dissolved oxygen was measured even in the continuously open flask.

The evolution of pH was the same in all the tests except the control. The pH reached 4 in 24 h and remained stable for 48 h (Figure 2(a)). On the contrary, the evolution of dissolved P was strongly dependent on the presence of air in the headspace.

When the flasks were closed and re-inerted just after 1 min opening, the evolution of dissolved P was the same as in the permanently closed flask and reached the maximum (450 mg.L^{-1}) after 24 h. If the flask was
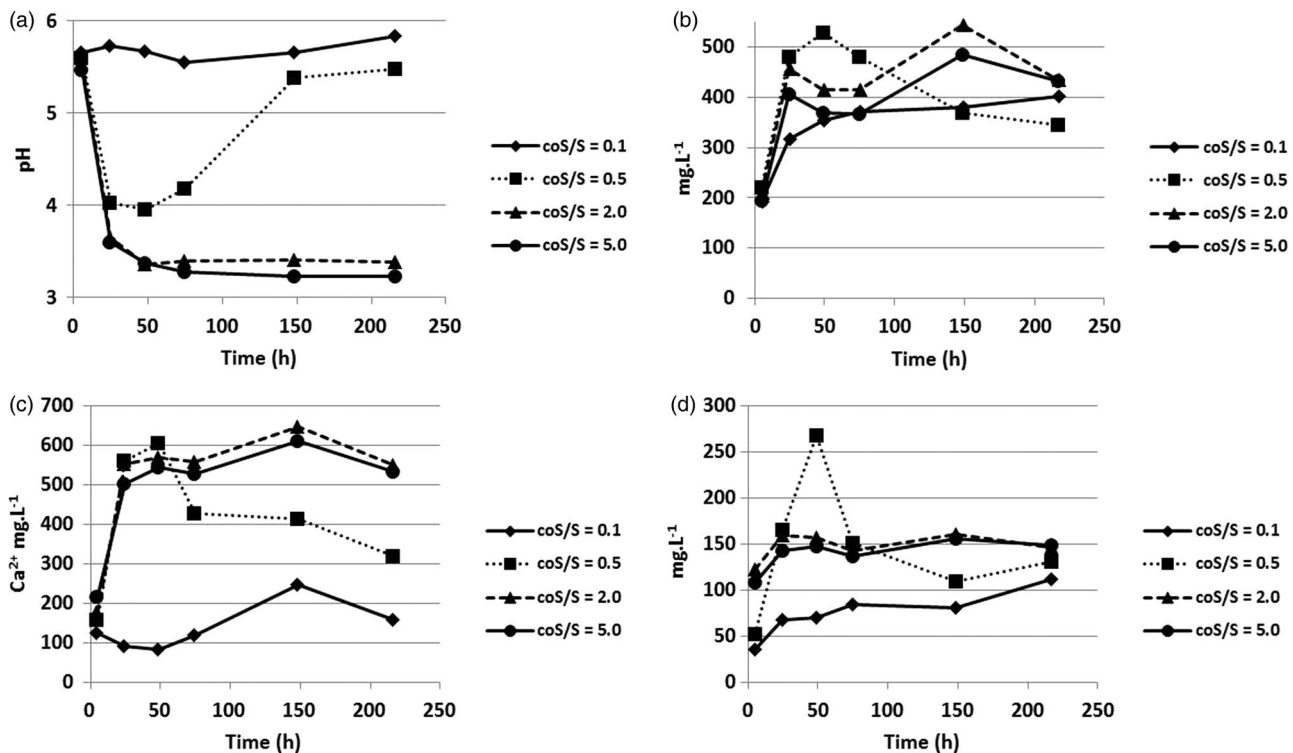

Figure 1. Evolution of pH(A), dissolved P(B), Ca^{2+}(C) and Mg^{2+}(D) depending on coS/S ratio.
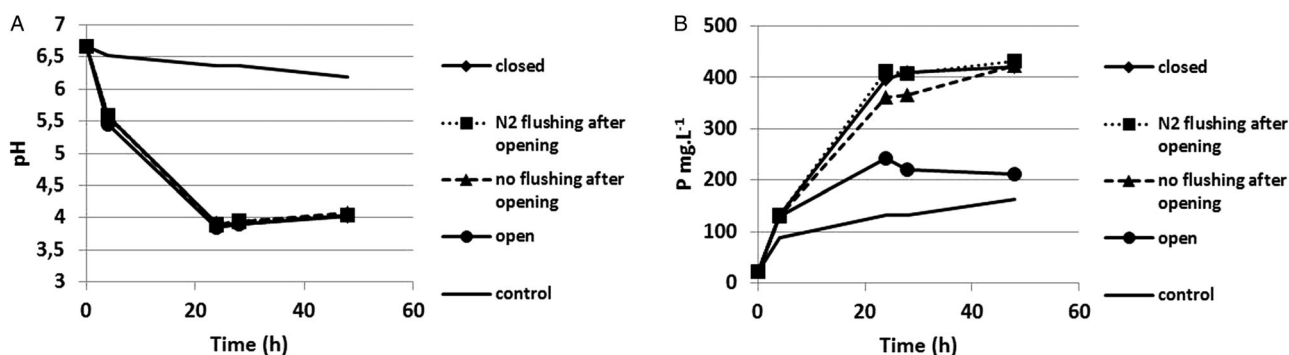
Figure 2. pH and dissolved P evolution depending on air in the headspace.

just closed without inerting, the maximum was obtained after 48 h. In the open flask, even if no dissolved oxygen was measured, the dissolved P was only 250 mg.L^{-1} at 24 h and remained stable for 48 h (Figure 2(b)). In this latter case, acidogenesis was not affected, but anoxic conditions were sufficient to inhibit P release by the PAO. These results are in compliance with the literature on EBPR which set up that when oxygen or another electron receiver is present, PAO oxidize the available carbon instead of storing it as PHA. So P is not released.[21,22]

The following experiments were performed under N$_2$ atmosphere and the flasks were re-inerted when they had to be opened during the test.

Influence of inoculum

To see if it was possible to shorten the test with inoculum addition, 6 trials were performed at S/I ratio from 2 to 11 corresponding to coS/I ratio of 1, 2.5, 4 and 5.5, and two controls were run without inoculum (Table 1 tests B11–B16).

Kinetics of both acidification and P dissolution were higher when an inoculum was added, but the ratio had no effect. The first inflexion of the dissolved P curve occurred after 6 h when an inoculum was added. At this time, the dissolved P was 380 mg.L^{-1} and 170 mg.L^{-1} with and without inoculum, respectively. However, after 6 h dissolved P increased quickly without inoculum when the dissolution was slowing down with inoculum. After 24 h dissolved P was maximal without inoculum (Figure 3). These results could be explained by the fast growth of acidogenic bacteria. After 24 h, the activity of these endogeneous microorganisms would be even higher than those of the inoculum added. A high coS/I ratio is known to be responsible for methanogenesis inhibition due to acidification as described by Raposo et al. [18], Zhou et al. [19] or Hashimoto et al. [23].

The maximum was only 10% more (550 mg.L^{-1}) and reached later (80 h) with inoculum. Moreover, variability

of the inoculum in time could contribute to variability in the test.

For sludge coming from the process including an EBPR stage, the BPDP test could be performed without inoculum.

Chemical acidification

To assess the role of the pH to the total P release during the biological test, acid was added to the sludge stored 24 h, decreasing the pH step by step up to 2. The curve could be described by a polynomial function described by Equation (1).

$$P_d = 7.1pH^3 - 92.7pH^2 + 311pH + 35.7 (R^2 = 0.9851) \qquad (1)$$

This function was used to estimate the contribution of chemical dissolution due to low pH when dissolved P was maximum during biological tests B1–B5 (data at 24 and 48 h).

The biological P release was calculated as the difference between total dissolved P and chemically dissolved P; non-dissolved P was the difference between total P and total dissolved P. The contribution of chemical dissolution during the biological test increased, while pH decreased to reach 40–45% when the pH was under 4. Conversely, biological P release decreased when pH was under 4 probably due to PAO inhibition from the beginning of the test. Dissolved P was maximum at pH4 (77%) with an equal contribution of chemical and biological processes (Figure 4). When pH was above 4, the contribution of the biological process was probably underestimated because of precipitation of P with cations.

Finally, in tests B1–B5, up to 77% of the total P from sludge resulting from combined EBPR and iron chloride P removal process dissolved in a biological way at 48 h. This high dissolution rate was the outcome of the combination of biological P release by PAO, due to easily
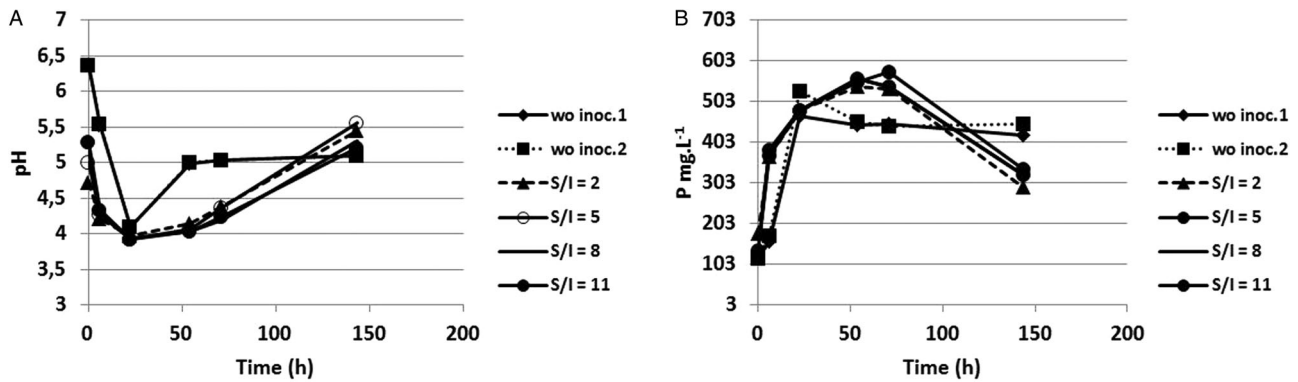
Figure 3. pH and dissolved P evolution depending on S/I ratio.

biodegradable carbon provided in anaerobic conditions, and acidification induced by the co-substrate (sucrose), which maintained P released in solution. The biological dissolution rate that we obtained was in compliance with Cullen et al. [7], who measured 25–40% of total P entering the crystallization process after that P release had been favoured by VFA produced from primary sludge hydrolysis but at a pH close to 7. Hydrolysis is usually studied as a way to increase methane production and very few references describe the influence of this stage on P dissolution. Depending on the pH, 250 mg. L^{-1} of dissolved P has been reached by Chen et al. [24] from WAS and 50 mg.L^{-1} by Wu et al. [20] from primary sludge. However, no information on the waste-water treatment performed to produce WAS is available in the first paper and results are not discussed in regard of the total P or cationic composition of sludge which are not presented in these studies.

The contribution of the chemical mechanism to biological dissolution that we observed (30–75% when pH was below 4 in tests B1–B5) was corresponding to the value obtained by Antyakali et al. [11] by chemical acidification performed on digested sludge (40–80%), but these authors were studying digested sludge where mineralization already occurred. The rate that we obtained by chemical acidification of S1a stored for 24 h (C1) (50%) was higher than the results obtained on WAS by Xu et al. [25] (37% at pH2), but the value that we obtained with non-stored S1d (C4) (15%) was lower. The amount of P released from the biomass either by PAO metabolism during short-term anaerobic storage or by mineralization before chemical acidification seems to be the main driver of the amount that can be chemically dissolved.

Evolution of iron during the BPDP test

In order to discover what interferences could be caused by foreign cations during further struvite crystallization,

the iron concentration was measured during a new BPDP test (B26) performed on sludge from WWTP1 (S1d). For this experiment both biological and chemical acidification were performed on the sampling day. More than 82% of the total P was dissolved during this test. The contribution of the biological P release to this result was 85%. The contribution of the biological P released by the PAO was high compared to that of the biological test performed on sludge sampled in the same WWTP previously (B1–B5), and the contribution of acidification was low. Due to probable P released by PAO and precipitation during the 24 h storage at 4°C, the effect of pH during the biological dissolution of sludge measured for B1–B5 could be overestimated.

Surprisingly, iron was dissolved as soon as the P was biologically released (Figure 5). To assess the contribution of pH to iron dissolution, Fe dissolution by chemical acidification was calculated from an acidification test performed on the same sludge as previously described for P (C6). Dissolved iron was related to the pH by a polynomial function described by Equation (2):

$$Fe_d = 1.9pH^2 - 38.6pH + 178 (R^2 = 0.999) \qquad (2)$$

The amount of iron chemically dissolved during the biological test was estimated from this equation. It remained low compared to the biological dissolution and even when the pH was close to 4, the contribution of chemical dissolution was less than 15%. The biologically induced mechanism involved in Fe dissolution was not identified in this study.

Iron chloride dosing in WWTP is usually done considering that iron phosphate is the main compound responsible for P removal. Iron dissolution at relatively high pH showed that it was not the case in the sludge S1. PAO metabolism could induce some modification in the local chemical and physical conditions (pH, redox, etc.) or break down the organic matter structure, disrupting the complexes formed with iron, explaining Fe
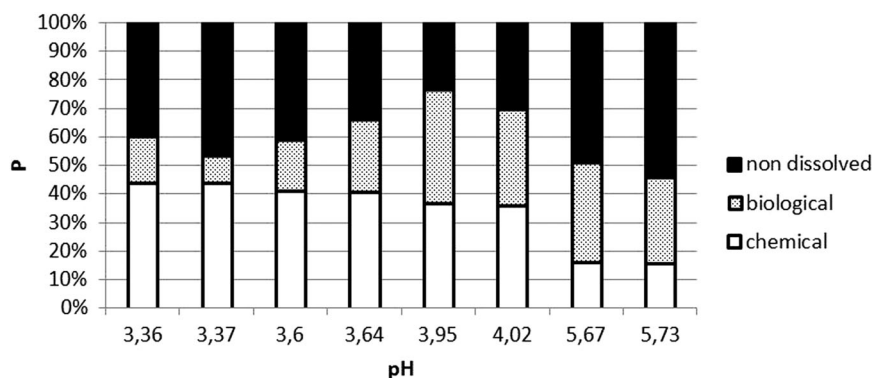
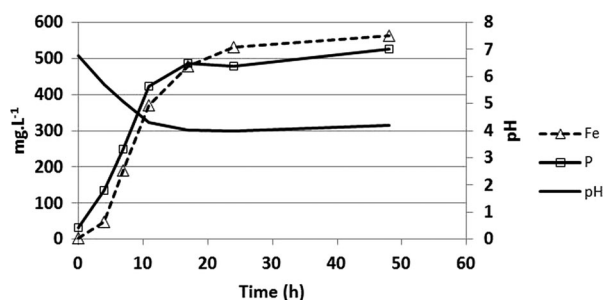**Figure 4.** Contribution of chemical and biological processes to P dissolution during the BPDP test.

Figure 5. Fe and P dissolution during the BPDP test.

dissolution. The complexity of P and iron chemistry and relation to organic matter in sludge are worth studying in order to increase P recycling potential as suggested by Wilfert et al. [13]. The influence of this high-dissolved iron concentration on struvite crystallization has to be taken into account too.

Application to other sludge

The BPDP test was applied to two different sludge coming from WWTP where P was removed in a physico-chemical way (tests B17–B21). The first sludge S2 was coming from a WWTP which was supposed to use $FeCl_3$ as the flocculent reagent. However, it was known afterwards that during the sampling period the sludge was mixed with sludge from drink water production using aluminium polychloride (sludge-PCAl) and no $FeCl_3$ was added. For S3, the P removal was done with aluminium sulphate (Sludge-Al).

S2 was slightly acidified during the test (from pH 7.4 to 6.6) and P dissolution was not observed. Acidification was more efficient with S3 (from 6.6 to 4.1). However, P dissolution was limited to 18% of the total P. The difference between the sludge could be explained by biomass activity (no biomass able to degrade sugar in S2) or by the buffer effect of the sludge (Figure 6(a) and 6(b)).

As for S1, chemical acidification tests were performed on S2 and S3 (C2, C3), to estimate the contribution of the biological process to the dissolution. No dissolution was observed for pH above 5 for S2 and dissolved P was only 30 mg.L^{-1} at pH 4 for S3. The biological P release was contributing to 63% of P dissolved by the BPDP test in S3.

To test the possibility to improve acidification and P dissolution by adding a biomass able to degrade sugar, an inoculum was prepared as described above and added at two levels (S/I = 2 or S/I = 11) (tests B22–B25). A control test was performed with the inoculum alone (B21). The pH was slightly lowered by inoculum and did not decrease under 5.5 whatever the ratio of S/I tested for S2. No significant difference was observed at 24 h for S3, only the kinetic was changed (Figure 6(c) and 6(d)).

P dissolution was not observed for S2. Moreover, the dissolved P brought by the inoculum was precipitated too. Two hypotheses could explain this. The biomass of the inoculum was inhibited by S2 and/or the P released from the inoculum was precipitated due to the high pH and the high Ca concentrations (Table 2). Contribution of the P released from the inoculum was calculated from the dilution rate of the inoculum in sludge. The contribution of the P from S3 was calculated from the difference between the measured value and the calculated contribution of the inoculum. No increase in the P released by the S3 itself was observed. The higher dissolved P was mainly due to the P of the inoculum added. When the B/I ratio was 2, the dissolved P was even less than the calculated contribution of P from the inoculum (Figure 7).

The potential for P recycling from physico-chemical sludge using aluminium compounds was dependent on the flocculant. It remains low (<20%) compared to the sludge from combined EBPR + $FeCl_3$ process (Table 3). As for Iron salts, alum and P chemistry in sludge has to be investigated and the contribution of the biological process to Al dissolving has to be studied in order to explore the possibility to improve it. Unfortunately, sludge from WWTP using $FeCl_3$ without EBPR could not be tested in this study.
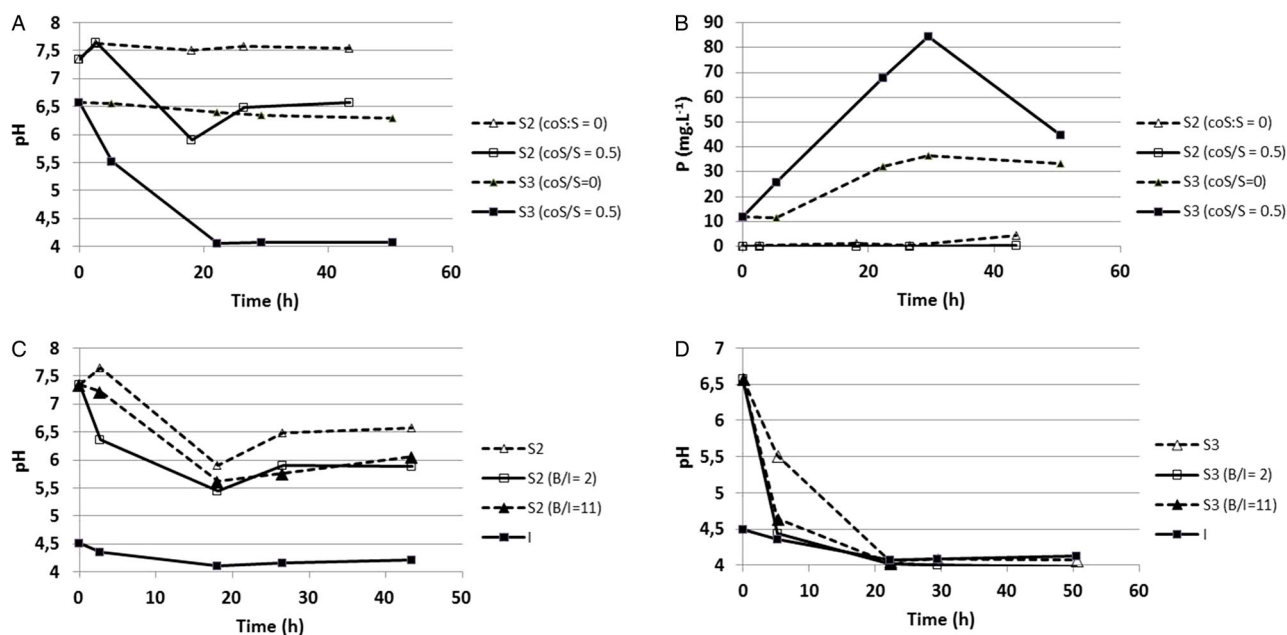
Figure 6. pH and dissolved P evolution during the BPDP test with and without inoculum. A and B: pH and dissolved P without inoculum. C and D: pH with inoculum.

Table 2. Characteristics of WWTP sludge.

	P treatment	TS	VS	Total COD	Soluble COD	TKN	Soluble NH_4^+	Total P	PO_4^{3-}	Total Ca	Ca^{2+} soluble	Total Mg	Mg^{2+} soluble
		(g/kg)						(mg/L)					
S1a	EBPR + FeCl$_3$	48	35	51690	170	3070	17	1250	105	728	72	174	41
S1b		48	32	nd	nd	nd	nd	1115	22	nd	nd	nd	nd
S1c		44	30	nd	nd	nd	nd	1298	42	nd	nd	nd	nd
S1d		49	33	nd	nd	nd	2	1156	31	nd	44	nd	13
S2	Sludge-PCAl	32	19	nd	nd	nd	69	846	1	nd	231	133	59
S3	Sludge-Al	25	18	22060	120	NA	22	602	41	652	35	149	21

Potential for P recycling as struvite

The ionic composition of the supernatant of biologically acidified sludge from WWTP1 (test B3) and WWTP3 (test B20) is presented in Table 4.

Struvite is an equimolar compound of Mg^{2+}, NH_4^+ and PO_4^{3-}. Ammonium is the main limiting factor in the sludge S1 especially if we consider that when calcium is the main cation, the ratio should be more than one. to favour struvite instead of calcium phosphate precipitation [14] However, in the test, the co-substrate was only white sugar. At full scale, even if the most adapted co-substrate should be mainly carbohydrate, waste from the food industry very often contains nitrogen that could be degraded into ammoniacal nitrogen during the hydrolysis stage. If not, supernatant from digestate dewatering could be used as the nitrogen source for crystallization. Depending on the co-substrate composition, magnesium concentration should be adjusted too. The influence of ferrous or ferric ions on struvite crystallization is poorly documented. However, Antyakali et al. [11] consider that iron can be trapped by sodium citrate addition. The conditions for

struvite crystallization are more favourable in the supernatant from WWTP3. N/P ratio is above 1 and the high Ca/Mg ratio could be counterbalanced by adding magnesium in the reactor as it is usually done. Unfortunately, the sample from WWTP3 was spoiled before alum measurement in the supernatant. Nevertheless, the P dissolution rate by biological acidification was low and has to be improved to recycle significant amount of P from this sludge.

The effect of dissolved organic matter as VFA on struvite crystallization is also poorly documented. A contradictory effect was demonstrated by Capdevielle [26] who showed that less struvite was formed but crystal size was increased by organic matter, aiming to better harvest the struvite crystals.

Conclusions

In the aim to replace chemical acidification by biological acidification before struvite crystallization in the P recycling process from WAS, a BPDP test was designed. The best results were obtained after 24–48 h, without

Table 3. Minimum pH, maximum dissolved P (% of total P) and relative contribution of the chemical and biological dissolution (% dissolved P) in biological and chemical tests.

| N°	Objective	pHmin	P_d max (h)	$P_d$bio	$P_d$chem
			%Ptotal	Approximate relative contribution (%)	
B1	Optimal coS/S ratio				
B2		5.6	58 (216)	70	30
B3		3.9	77 (48)	50	50
B4		3.3	79 (144)	40	60
B5		3.2	71 (144)	25	75
B6	Influence of O_2	6.2	27 (48)	nd	nd
B7		3.9	69(48)	nd	nd
B8		3.9	70(48)	nd	nd
B9		3.9	69(48)	nd	nd
B10		3.9	40(48)	nd	nd
B11	Influence of Inoculum	4.1	66(24)	nd	nd
B12		4.1	74(24)	nd	nd
B13		4.0	75(48)	nd	nd
B14		3.9	79(72)	nd	nd
B15		3.9	78(48)	nd	nd
B16		3.9	80(72)	nd	nd
B17	Application to other sludge	7.4	<1	nd	nd
B18		5.9	<1	nd	nd
B19		6.3	10	nd	nd
B20		4.1	14	65	35
B21		4.1	63	nd	nd
B22		5.4	<1	nd	nd
B23		5.6	<1	nd	nd
B24		4.0	28	nd	nd
B25		4.0	20	nd	nd
C1	Chemical dissolution by acid	2.0	51	–	100
C2	addition	2.0	nd	–	100
C3		2.0	30	–	100
B26	Iron dissolution	3.98	82(48)	85	15
C4		2	16	–	100
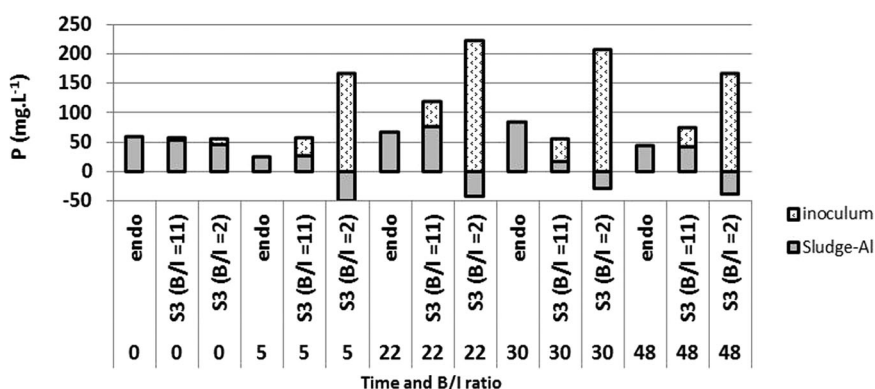
Figure 7. Contribution of the P from S3 and from the inoculum to the dissolved P measured during the BPDP test. Endo is sludge without inoculum.

inoculum, a sugar/sludge ratio of 0.5 gCOD/gVSS and under strict anaerobic conditions. Up to 82% of the initial total P was dissolved by combining P release and acidification at pH around 4 which maintained P in the sludge from WWTP by combining EBPR and iron chloride process for P removal. No dissolution and a poor acidification were observed with sludge from WWTP using aluminium polychloride and less than 20% of the initial total

P in sludge from WWTP using aluminium sulphate. The BPDP test will be used as a comparative tool to classify the sludge depending on their potential for biological P dissolution and to establish a relation between P dissolution potential and previous P removal process parameters in the WWTP. It will enable assessing the acidifying potential of co-substrates and the potential for struvite formation depending on the liquid ionic

Table 4. Ionic concentrations (mM.L^{-1}) in supernatant after the BPDP test (24 h).

	P treatment	NH_4^+	PO_4^{3-}	Ca^{2+}	Mg^{2+}	$Fe^{2+} + Fe^{3+}$
WWTP1 (S1a)	EBPR + FeCl$_3$	3	16	14	7	10
WWTP3 (S3)	Sludge-Al	4	3	8	4	–

composition. This study has also highlighted some mechanisms, poorly described in the literature because of the novelty of the concept of biological dissolution of P. These effects that have to be investigated with the aim of optimizing P recovery rate from WAS, such as the role of biological metabolism on iron or alum dissolution and the influence of VFA on struvite crystallization.

Disclosure statement

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