Phosphorus recovery by struvite crystallization in WWTPs: Influence of the sludge treatment line operation

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ABSTRACT

Phosphorus recovery by struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystallization is one of the most widely recommended technologies for treating sludge digester liquors especially in wastewater treatments plants (WWTP) with enhanced biological phosphorus removal (EBPR). In this paper, phosphorus recovery by struvite crystallization is assessed using the rejected liquors resulting from four different operational strategies of the sludge treatment line. Phosphorus precipitation and recovery efficiencies of between 80–90% and 70–85%, respectively, were achieved in the four experiments. The precipitates formed were mainly struvite, followed by amorphous calcium phosphate and, in some experiments, by calcite. The highest global phosphorus recovery taking into account both the sludge line and the crystallizer was achieved when mixed thickening and high elutriation were carried out (8.4 gP/kg treated sludge). However, low struvite content was obtained in the crystallizer with this operation scheme due to the high calcium content in the elutriation stream. Therefore, if the final purpose is to obtain struvite, the reduction of the elutriation flowrate is widely recommended in the case of high water hardness.

1. Introduction

Phosphorus recovery by struvite ($MgNH_4PO_4 \cdot 6H_2O$-MAP) crystallization is one of the most widely recommended technologies for treating sludge digester liquors (von Münch et al., 2001; Battistoni et al., 2002; Parsons and Doyle, 2004) especially in wastewater treatments plants (WWTP) with enhanced biological phosphorus removal (EBPR).

In the EBPR process, phosphates and other ions (i.e., Mg^{2+}, K^{2+}) are taken up and stored as polyphosphates (Poly-P) inside the bacterial cells. During the anaerobic digestion process, these polyphosphates are released to the liquid phase (Wild et al., 1997) increasing notably the phosphate, magnesium and potassium concentration. Moreover, ammonium concentration increases significantly as proteins are degraded, and dissolved magnesium, phosphorus, calcium and potassium concentrations increase due to the cell lysis. Therefore, the rejected liquors from digested sludge dewatering show high phosphorus, ammonium and magnesium concentrations which make these streams very appropriate for recovering phosphorus as struvite in a crystallization process. The thickener supernatant could also be used in the crystallizer since Poly-P hydrolysis can take place in the gravity thickener.

Other studies have shown that the product obtained by struvite crystallization can be used as an effective slow release fertilizer in agriculture (de-Bashan et al., 2004; Shu et al., 2006); hence, an economical benefit can be obtained. The use of struvite as fertilizer allows not only the recovery but also the

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Nomenclature

$\%P_{MAP}$	Percentage of phosphorus fixed as MAP
ACP	Amorphous calcium phosphate
ALK_P	Bicarbonate alkalinity
HAP	Hydroxyapatite
MAP	Struvite
NH_4-N	Ammonia nitrogen
PO_4-P	Orthophosphate
P_T	Total phosphorus
Q	Volumetric flowrate
$w_{P\ AV}$	Mass of available phosphorus per mass of treated sludge

$w_{P\ LOST}$	Mass of phosphorus lost per mass of treated sludge
$w_{P\ prec}$	Mass of phosphorus precipitated per mass of treated sludge
$w_{P\ rec}$	Mass of phosphorus recovered per mass of treated sludge
$w_{P\ rec\text{-}MAP}$	Mass of phosphorus recovered as struvite per mass of treated sludge
$w_{P\ TOT}$	Mass of total phosphorus (AV + LOST) per mass of treated sludge
w_P	Mass of phosphorus per mass of treated sludge
α	Thickener supernatant volume/Centrate volume

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reuse of nutrients, thereby increasing the sustainable management of the WWTP.

Accumulation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) on pipe walls and equipment surfaces of anaerobic digestion and post-digestion processes significantly increases operational problems and maintenance costs of WWTPs (Ohlinger et al., 1998; Parsons and Doyle, 2004). This uncontrolled precipitation reduces phosphorus concentration in the sludge liquors. Therefore, in order to guarantee phosphorus rich streams and thereby obtain high struvite production in the crystallization process, the uncontrolled phosphorus precipitation in the digester should be reduced.

In a previous work (Martí et al., 2008a), four operational strategies were tested in a pilot plant in order to minimise uncontrolled phosphorus precipitation in the digester and to increase the phosphorus to be recovered. In the present work, phosphorus recovery as struvite crystallization is assessed using the rejected liquors resulting from these four operational strategies. Finally, this study evaluates the global phosphorus recovery by struvite crystallization in the system taking into account both the sludge line and the crystallizer.

2. Materials and methods

2.1. Pilot plant description

The pilot system used in this work was composed of different elements: a primary sludge settler/fermenter, a biological nutrient removal system, an anaerobic digester for the stabilization of primary and secondary waste sludge, and a crystallization reactor. All of them are located in the Carraixet WWTP (Valencia), except the crystallizer (which is located in the Environmental Technologies Laboratory of the University of Valencia). A detailed description of these three pilot plants can be found at Bouzas et al. (2007), García-Usach et al. (2006) and Martí et al. (2008b), respectively.

The crystallization pilot plant (Fig. 1) is composed of the crystallization reactor, three stainless steel injection tubes for the influent and reactants, two peristaltic pumps, one membrane pump, and two balances. The reactor is a stirred tank reactor that is composed of two parts: a reaction zone and a settling zone that prevents fine particles from being driven out with the effluent. The reactor was equipped with
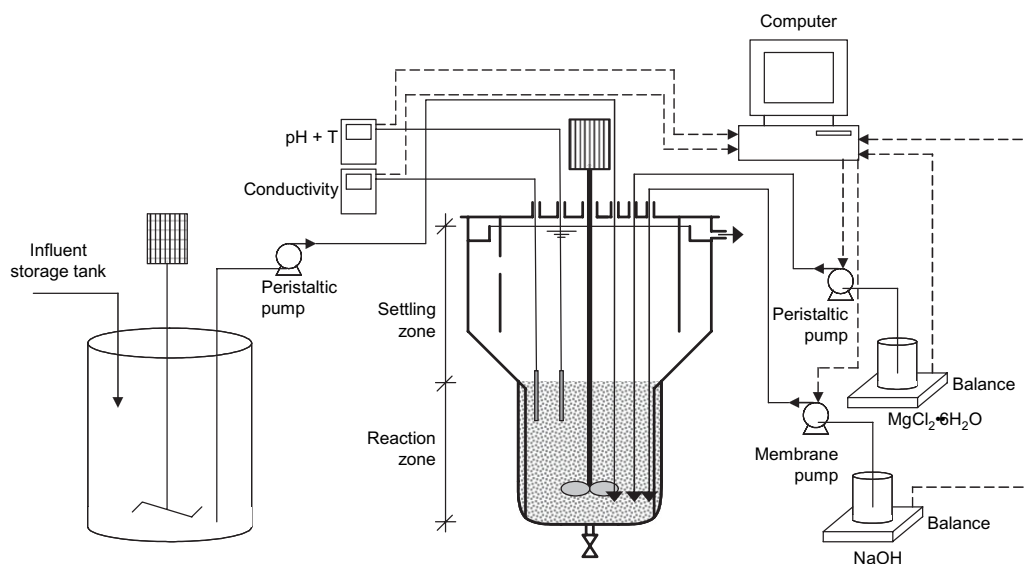

Fig. 1 – Layout of the crystallization pilot plant.

conductivity, temperature and pH electrodes as well as a data acquisition program to store these parameters. The crystallization pilot plant and the reactor are described in detail in Pastor et al. (2008a).

2.2. Experimental procedure

Four crystallization experiments were carried out using the rejected liquors resulting from different strategies of the sludge treatment line. The four configurations studied are based on separated or mixed sludge thickening, the use of a contact tank, the elutriation of the thickened sludge and the flowrate of the elutriation stream. Fig. 2 outlines the four operational configurations which are described in detail in Martí et al. (2008a). The primary sludge from the settler/fermenter and the waste activated sludge from the BNR system were both treated in the anaerobic digester. As can be observed in Fig. 2, configuration C1 differs from the others in the separate thickening of the two sludges. In configuration C2, mixed thickening and elutriation of the resulting thickened sludge were carried out. In configuration C3, a stirred contact tank was used previous to the mixed thickening step instead of the elutriation system. In configuration C4, the EBPR sludge from the aerobic reactor was used as a "washing-stream" that elutriates the thickened sludge to a greater extent than in configuration C2. The supernatants and centrates obtained in the different configurations were used in the phosphorus recovery process by struvite crystallization.

The crystallizer was operated in continuous mode for the liquid phase and in batchwise mode for the solid phase. The resulting hydraulic retention time in the reaction zone was 2.5 h. Since the struvite precipitation process leads to a decrease in the pH value, NaOH was added to maintain the pH at the desired value. Software that is based on fuzzy logic control was used to maintain the pH at the set value (Chanona et al., 2006).

2.3. Analytical methods

Total phosphorus (P_T) analysis was performed in accordance with Standard Methods (APHA, 2005). PO_4-P, NH_4-N and soluble calcium, magnesium and potassium were analysed by ion chromatography (Metrohm IC).

Precipitates obtained in the crystallizer were analysed by X-Ray diffraction (XRD) in order to check whether struvite crystals were formed. The XRD measurements were performed on a BRUKER AXS D5005 powder diffractometer.

2.4. Phosphorus precipitation assessment in the crystallization process

Phosphorus precipitation in the crystallizer was assessed taking into account two types of efficiencies: precipitation efficiency (Eq. (1)) and recovery efficiency (Eq. (2)) The precipitation efficiency represents the process efficiency from a thermodynamic point of view provided that the supersaturation can be almost completely consumed, which should be the case with sufficient residence time. The recovery efficiency takes into account both the precipitation and crystal growth efficiency.

$$\text{Precipitation Efficiency} = \frac{PO_4 - P_{in} - PO_4 - P_{ef}}{PO_4 - P_{in}} \cdot 100 \qquad (1)$$

$$\text{Recovery Effiency} = \frac{P_{Tin} - P_{Tef}}{P_{Tin}} \cdot 100 \qquad (2)$$

The percentage of precipitated phosphorus as struvite (%P_{MAP}) (Eq. (3)) was calculated assuming that, at the crystallizer conditions, all magnesium precipitates mainly as struvite (Musvoto et al., 2000).

$$\%P_{MAP} = \frac{Mg^{2+}_{prec}}{PO_4 - P_{prec}} \cdot 100 \qquad (3)$$

3. Results

3.1. Characteristics of the liquors fed to the crystallization pilot plant

The experimental characteristics of the main streams involved in the process (Fig. 2) are summarized in Table 1 for the four sludge line operational configurations.

As Fig. 2 shows, the thickener supernatant and the centrate obtained in the digested sludge dewatering are mixed and sent to the crystallization process, except for configuration C1 (where only the sludge dewatering centrate is fed to the crystallizer). The parameter α has been defined as the relation of volumes between the thickener supernatant and the centrate from the digested sludge centrifugation (calculated taking into account a reduction of 4/6 of the digester effluent volumetric flowrate). Table 2 reports the crystallizer influent characteristics for the 4 experiments, including the value of α, the need for an extra dose of magnesium and the 4 molar ratios Mg/P, N/P, Ca/P and Ca/Mg. As can be observed, α is 0 for configuration C1 and is 0.6, 0.7 and 7.5 for configurations C2, C3 and C4, respectively.

Phosphorus concentrations in the liquors fed to the crystallizer ranged from 43 to 151 mg/l for the different configurations (see Table 1). Configurations C1 and C2 showed that influent phosphorus concentrations in the crystallizer were three times higher than those observed in C3 and C4. In general, a decrease in PO_4-P concentrations was observed as the proportion of the thickener supernatant in the influent to the crystallizer increased, except for configuration C3 where a low PO_4-P concentration in the thickener supernatant was achieved. This low PO_4-P concentration was attributed to a low biological phosphorus removal efficiency in the wastewater treatment line, which decreased the polyphosphate concentration in the sludge line.

With regard to NH_4-N concentrations, configurations C1, C2 and C3, showed high values between 355 and 542 mg/l. These values are normally found in anaerobic digested sludges from activated sludge processes (Brooker et al., 1999). The low NH_4-N concentration in configuration C4 is due to the low proportion of centrate from the anaerobic digested sludge dewatering. In general, NH_4-N concentrations were higher than PO_4-P concentrations giving rise to a very high N/P molar ratio (see Table 2), which indicates that NH_4-N concentration will not limit the struvite formation when liquors from anaerobic digested sludge are employed.
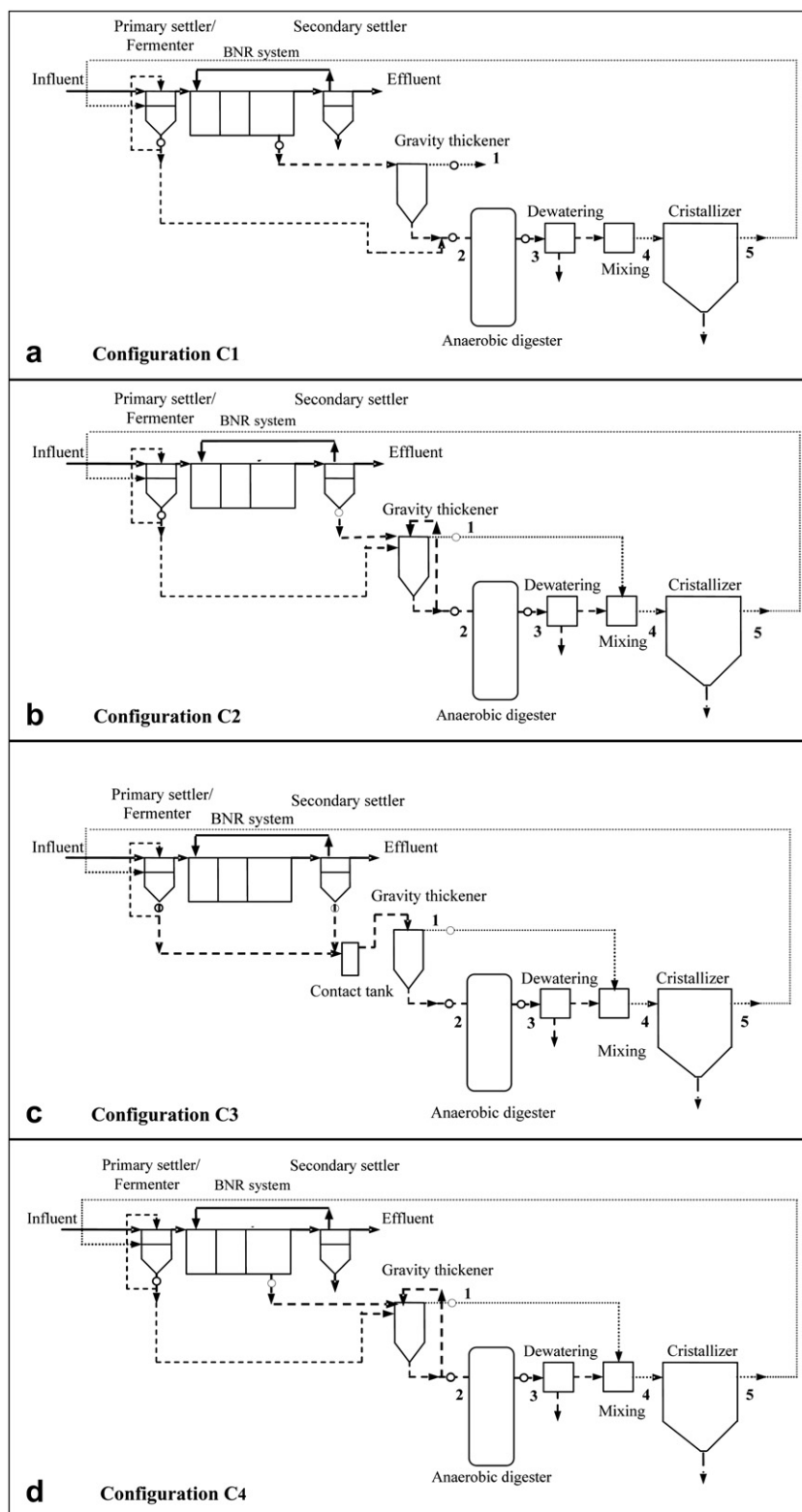
Fig. 2 – Layout of the four pilot plant configurations.

Magnesium was the struvite component with the lowest concentration in the liquors employed. Specifically, experiments C1 and C2 had very low Mg/P molar ratios (0.24 and 0.26, respectively). Therefore, in order to satisfy the stoichiometric requirement for struvite formation, an extra dose of magnesium ($MgCl_2 \cdot 6H_2O$) was added in these two experiments, achieving Mg/P molar ratios up to 0.77 and 0.90 for C1 and C2, respectively. In configurations C3 and C4, no magnesium addition was necessary since Mg/P molar ratios were higher than 1.

Table 1 – Experimental characteristics of the main streams involved in the process.

Stream		1		2		3		4		5	
		av.	sd.	av.	sd.	av.	sd.	av.	sd.	av.	sd.
Configuration n C1	Q (l/d)	41.3		6.8		6.8		4.5		4.5	
	PO$_4$-P (mg/l)	11.3	±1.8	70.7	±19.8	152.2	±25.8	150.6	±4.4	15.7	±2.6
	NH$_4$-N (mg/l)	10.9	±1.6	104.1	±51.8	617.4	±60.6	541.7	±18.4	466.0	±11.7
	Mg^{2+} (mg/l)	NA		60.2	±14.8	11.9	±5.8	93.2	±24.1	7.6	±2.1
	Ca^{2+} (mg/l)	NA		151.3	±20.9	49.8	±18.6	69.0	±1.8	51.7	±7.1
	K$^+$ (mg/l)	NA		71.8	±23.6	237.4	±13.2	213.1	±5.9	212.9	±3.7
	P$_T$ (mg/l)	NA		1020	±102	985	±22	154.7	±26.5	30.6	±14.5
	ALK$_P$ (mg/l)	NA		407	±106	2381	±371	1581	±126	NA	
	pH	NA		6.4	±0.1	7.0	±0.1	7.2	±0.1	8.70	±0.01
Configuration C2	Q (l/d)	5.3		6.8		6.8		9.8		9.8	
	PO$_4$-P (mg/l)	127.0	±22.6	253.7	±67.4	201.4	±109.1	145.8	±4.3	15.2	±7.2
	NH$_4$-N (mg/l)	175.0	±1.8	69.0	±35.0	580.0	±81.1	355.2	±9.2	289.5	±7.1
	Mg^{2+} (mg/l)	90.7	±9.8	113.5	±29.9	26.1	±9.2	104.5	±2.6	13.8	±1.4
	Ca^{2+} (mg/l)	71.5	±8.6	104.9	±19.9	40.8	±7.6	65.8	±0.3	55.1	±4.6
	K$^+$ (mg/l)	115.0	±16.2	160.2	±39.9	258.6	±30.3	185.7	±4.9	184.5	±2.8
	P$_T$ (mg/l)	NA		981	±126	902	±145	155.3	±18.6	23.1	±10.7
	ALK$_P$ (mg/l)	346	±94	414	±105	2308	±307	1227	±73	NA	
	pH	NA		6.1	±0.1	7.0	±0.2	7.0	±0.1	8.70	±0.01
Configuration C3	Q (l/d)	2.0		8.0		8.0		7.3		7.3	
	PO$_4$-P (mg/l)	79.8	±16.9	109.1	±25.1	69.1	±11.1	50.1	±3.4	7.6	±0.4
	NH$_4$-N (mg/l)	12.5	±2.1	126.3	±46.9	651.4	±26.2	400.4	±8.4	371.3	±12.5
	Mg^{2+} (mg/l)	65.5	±10.1	72.8	±6.1	62.8	±5.2	69.7	±1.8	36.8	±1.7
	Ca^{2+} (mg/l)	95.3	±12.1	123.1	±12.3	70.5	±10.8	91.9	±2.9	52.1	±4.7
	K$^+$ (mg/l)	19.6	±2.9	100.4	±19.1	179.8	±59.0	102.2	±2.0	98.9	±3.4
	P$_T$ (mg/l)	NA		730	±147	687	±100	61.3	±8.6	12.6	±0.3
	ALK$_P$ (mg/l)	506.0	±103	523	±127	2069	±482	1240	±96	NA	
	pH	NA		6.2	±0.1	6.9	±0.1	6.9	±0.1	8.70	±0.01
Configuration C4	Q (l/d)	43.8		4.3		4.3		46.6		46.6	
	PO$_4$-P (mg/l)	46.5	±10.1	98.6	±24.1	67.6	±14.3	43.0	±2.7	7.3	±0.5
	NH$_4$-N (mg/l)	84.2	±7.6	110.6	±18.9	796.0	±68.2	129.0	±2.3	123.7	±5.6
	Mg^{2+} (mg/l)	57.2	±6.9	72.3	±9.1	56.4	±9.5	49.8	±1.1	39.4	±1.3
	Ca^{2+} (mg/l)	157.5	±13.6	124.7	±23.6	57.0	±10.7	129.9	±3.5	71.6	±4.5
	K$^+$ (mg/l)	24.9	±3.1	65.9	±20.3	132.6	±6.2	35.3	±0.9	36.1	±0.6
	P$_T$ (mg/l)	NA		577	±20	433	±47	46.4	±6.4	14.0	±0.7
	ALK$_P$ (mg/l)	395.0	±62	397	±105	2245	±330	354	±33	NA	
	pH	NA		6.2	±0.1	7.2	±0.1	6.7	±0.1	8.70	±0.01

av.: Average; sd.: standard deviation; NA: not available; ALK$_P$ is expressed as mgCaCO$_3$/l.

Other cations such as Ca^{+2} and K$^+$ were present in significant concentrations in the liquors used in the crystallization process. In the different configurations, calcium and potassium concentrations ranged from 65 to 130 mg/l and from 35 to 213 mg/l, respectively.

3.2. Phosphorus recovery in the crystallization process

Using the crystallizer influent and effluent PO$_4$-P and P$_T$ concentrations (streams 4 and 5, Table 1), the precipitation and recovery efficiencies were calculated using Eqs. (1) and (2).

Table 2 – Crystallizer influent characteristics.

Configuration	α	Extra Mg dose	Influent molar ratios			
			Mg/P	N/P	Ca/P	Ca/Mg
C1	0.0	Yes	0.77 ± 0.05	7.96 ± 0.26	0.34 ± 0.01	0.45 ± 0.02
C2	0.7	Yes	0.90 ± 0.02	5.44 ± 0.29	0.36 ± 0.02	0.38 ± 0.01
C3	0.6	No	1.78 ± 0.08	17.77 ± 1.34	1.42 ± 0.01	0.80 ± 0.03
C4	7.5	No	1.48 ± 0.09	6.77 ± 0.41	2.34 ± 0.18	1.58 ± 0.05

α: Thickener supernatant volume/centrate volume from digested sludge dewatering.
Extra Mg dose: magnesium added as MgCl$_2$·6H$_2$O.

The results obtained for the four experiments carried out are shown in Table 3. As this table shows, high precipitation efficiencies of between 80% and 90% were obtained in the four experiments. These high precipitation efficiencies cannot only be attributed to struvite formation since soluble calcium decreased in the crystallizer, which indicates the possible formation of calcium phosphates.

The recovery efficiencies showed values of between 70% and 85%, which are slightly lower than the precipitation ones. Differences between the two parameters are attributed to the formation of fine crystals that are driven out with the effluent and, consequently, cannot be recovered.

3.3. Precipitates formed in the crystallization process

The moles per liter of PO_4-P, NH_4-N, Mg^{2+}, Ca^{2+}, and K^+ precipitated were calculated in order to evaluate the solids formed in the crystallization process. Table 4 shows the results obtained for the four experiments. As this table shows, equal or higher moles of PO_4-P than Mg^{2+} precipitated in all the experiments. It can also be observed that Ca^{2+} precipitation took place in the crystallizer and no K^+ precipitation occurred.

The percentage of precipitated phosphorus as struvite (%P_{MAP}) was calculated using Eq. (3). As Table 4 shows, high %P_{MAP} was obtained in experiments C1–C3. In experiments C1 and C2, the calcium removal observed indicates that calcium phosphates may also precipitate. Nevertheless, no calcium phosphates were formed in experiment C3 since all the PO_4-P precipitated as struvite (PO_4-P precipitated = Mg^{2+} precipitated = 1.4 mmol/l). Therefore, the calcium precipitation observed in this experiment could be attributed to the formation of calcite. The lowest %P_{MAP} was obtained in experiment C4 where high calcium precipitation was also observed. In this case, calcium could precipitate as both calcite and calcium phosphates.

Fig. 3 shows the X-ray diffractogram obtained in the analysis of the solids precipitated in experiment C1 together with the struvite pattern. The good correlation between the peaks of the diffractogram obtained for the solid collected in the reactor and the peak of the struvite pattern confirms that the solid formed was mainly struvite. Similar diffractograms were obtained in the rest of the experiments.

3.4. Evaluation of global phosphorus recovery

The global phosphorus recovery in the system was evaluated according to the results obtained in the crystallization process and taking into account the sludge treatment line results obtained in Martí et al. (2008a) for the four pilot plant configurations.

As stated above, two P-rich streams can be used for phosphorus recovery by struvite crystallization: the centrate from the digested sludge dewatering and the thickener supernatant. On the other hand, phosphorus is lost during the sludge treatment system in the anaerobic digester due to precipitation as different phosphate salts, and during the dewatering process where part of the soluble phosphorus remains in the dewatered sludge. In configuration C1, the phosphorus content in the thickener supernatant is also considered as a loss of phosphorus, since this stream was not used in the crystallizer. Moreover, phosphorus precipitation can also occur in the storage tank where both liquors are mixed before entering the crystallizer. Table 5 shows the results obtained for the four experiments in the system considering both the sludge treatment line and the crystallization process. The results have been calculated per kilogram of treated sludge in order to compare the different sludge line operations (0.251, 0.293, 0.283, and 0.166 kg sludge treated per day in configuration C1, C2, C3 and C4, respectively).

Among the different configurations, C4 allows the highest mass of phosphorus per kilogram of treated sludge (8.4 gP/kg sludge) to be recovered. This result is significantly higher than the ones obtained in the other experiments. However, the mass of phosphorus recovered as MAP per kilogram of treated sludge was notably reduced (3.1 gP recovered as MAP/kg sludge). This is due to the low percentage of phosphorus precipitated as struvite (%P_{MAP} = 37.0) in this configuration. In fact, if we focus on the phosphorus recovered as struvite, configuration C2 provides better results (3.7 gP recovered as MAP/kg sludge) than C4.

The global phosphorus recovery as struvite can be defined as the phosphorus mass recovered as MAP with regard to the total phosphorus in the sludge treatment system. This parameter indicates the capability of the total process (sludge line + crystallizer) to recover the available phosphorus as struvite. As Table 5 shows, configurations C1 and C3 present the lowest global phosphorus recovery (11% and 9%, respectively), whereas C2 shows the highest value (26%). Therefore, if the sludge treatment plant is operated according to

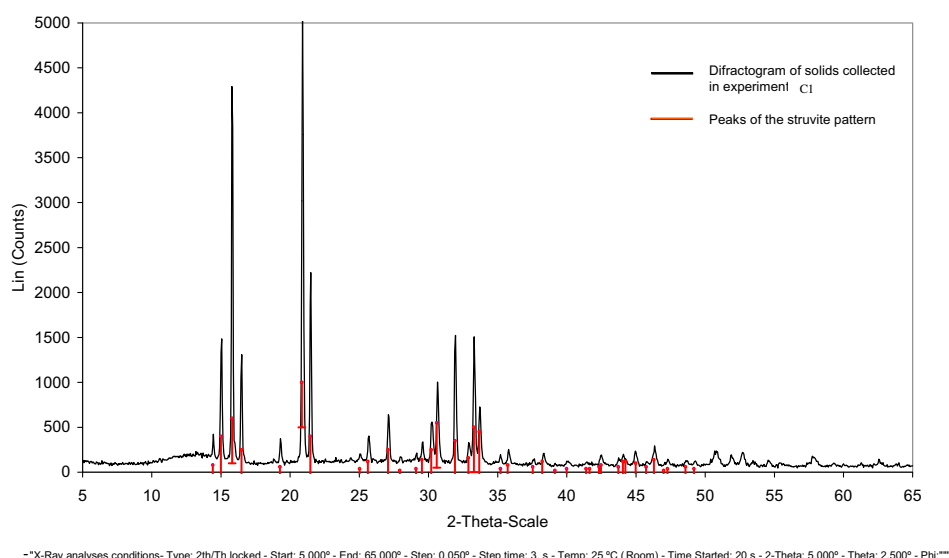| Table 4 – Precipitation in the crystallizer.						
Experiment	mmol/l Precipitated					%P_{MAP}
	PO_4-P (mmol/l)	NH_4-N (mmol/l)	Mg^{2+} (mmol/l)	Ca^{2+} (mmol/l)	K^+ (mmol/l)	
C1	4.4	5.4	3.5	0.4	0.0	80.9
C2	4.2	4.7	3.7	0.3	0.0	88.4
C3	1.4	2.1	1.4	1.0	0.1	98.7
C4	1.2	0.4	0.4	1.5	0.0	37.0

Fig. 3 – XRD analysis of the solids of experiment C1. Struvite pattern.

configuration C2, 3.9 g of phosphorus can be recovered as MAP per kilogram of treated sludge in the system.

4. Discussion

4.1. Liquors fed to the struvite crystallization pilot plant

The different characteristics observed among the four liquors used in the phosphorus recovery process by crystallization can be attributed to the different sludge line operations described in Martí et al. (2008a). The significantly high value of α in configuration C4 indicates that the stream fed to the crystallizer consists mainly of the thickener supernatant. This high thickener supernatant flowrate is due to the use of the EBPR sludge purge, which is directly taken from the aerobic

reactor (i.e., not settled) as a "washing-stream" that enhances the thickened sludge elutriation.

Magnesium was added in experiments C1 and C2 to increase the molar ratio Mg/P to around 1, in order to achieve the stoichiometric requirement for struvite formation. Moreover, the addition of magnesium in experiments C1 and C2 decreased the Ca/Mg molar ratio, which favours the precipitation of struvite rather than calcium phosphates. Previous studies using anaerobic supernatants (Pastor et al., 2008b) proved the detrimental influence of high calcium concentrations on struvite crystallization, showing a precipitation of calcium phosphates rather than struvite.

The presence of potassium, as well as magnesium and phosphorus, is related to Poly-P hydrolysis during the anaerobic digestion process. As shown in Martí et al. (2008a), Poly-P hydrolysis can be increased in the thickener. Therefore, both the dewatering centrate and the thickener supernatant account for magnesium, phosphorus and potassium in the crystallizer influent stream.

4.2. Phosphorus recovery in the crystallization process and precipitates formed

The precipitation and recovery efficiencies obtained in the four experiments show that the crystallizer characteristics are suitable for struvite precipitation.

The amount of phosphate precipitated as struvite ($\%P_{MAP}$) was calculated using Eq. (3). The struvite formation was confirmed by XRD analysis. More phosphorus precipitation than that required for struvite formation was obtained in all the experiments, except for C3. This indicates that other phosphate salts, as well as struvite, precipitated in the crystallizer. As mentioned above, precipitation of calcium phosphates was considered since soluble calcium showed a significant decrease in the crystallizer. Several calcium phosphates can be formed in an aqueous solution. The most common are amorphous calcium phosphate (ACP), dicalcium phosphate dehydrate (DCPD), octacalcium phosphate (OCP),

Table 5 – Global phosphorus recovery in the system.				
Loss of phosphorus $w_{P\ LOST}$ (gP/kg sludge)	C1	C2	C3	C4
Thickener supernatant	1.9	0	0	0
Precipitation in the digester	10.8	7.6	8.0	5.9
Dewatered sludge	1.4	1.5	0.7	0.6
Precipitation in the storage tank	0.0	0.5	0.6	1.3
Total	14.1	9.7	9.3	7.8
Available phosphorus to be recovered $w_{P\ AV}$ (gP/kg sludge)				
Thickener supernatant	0.0	2.3	0.6	12.3
Dewatered centrate	2.7	3.1	1.3	1.2
Total	2.7	5.4	1.9	13.4
$w_{P\ TOT} = w_{P\ LOST} + w_{P\ AV}$ (gP/kg sludge)	16.8	15.0	11.1	21.2
Phosphorus recovery in the crystallizer (gP/kg sludge)				
$w_{P\ prec}$ (gP/kg sludge)	2.4	4.3	1.1	10.0
$w_{P\ rec}$ (gP/kg sludge)	2.2	4.4	1.0	8.4
$P_{rec\text{-}MAP}$ (gP/kg sludge)	1.8	3.9	1.0	3.1
Global phosphorus recovery as struvite (%)	11	26	9	15

and hydroxyapatite (HAP). Since experiment C4 shows the highest calcium phosphate formation, XRD analyses were used to determine whether any crystalline calcium phosphate was present. The XRD analyses of the recovered solids showed that none of the crystalline calcium phosphates mentioned above were recovered (data not shown). These results suggest that the calcium phosphate precipitated was an amorphous calcium phosphate. It is also known that calcium phosphates formation takes place according to the Ostwald rule of stages, forming thermodynamically less stable forms before forming the most stable forms (i.e., HAP). A previous study by Pastor et al. (2008a) that used the reactor described above and solutions prepared in the laboratory showed that the transformation of ACP to HAP does not take place within the length of time that the experiments lasted.

The presence of calcite in experiments C3 and C4 was attributed to the high Mg/P and Ca/P molar ratios in the crystallizer influent. The existence of calcite was also observed by Battistoni et al. (2001) when using liquors from anaerobic digested sludge with higher calcium than phosphorus concentrations.

No potassium struvite (KMgPO$_4 \cdot$6H$_2$O) was formed in the crystallizer, which is in agreement with other authors (Schuiling and Andrade, 1999; Wilsenach et al., 2006) who state that potassium struvite (KMgPO$_4 \cdot$6H$_2$O) could precipitate instead of struvite only in the case of low ammonium concentrations.

The percentage of phosphorus forming struvite in configuration C4 was significantly lower (37.0%) than the others. This low struvite percentage was attributed to the high Ca/Mg molar ratio in the crystallizer inlet stream, which favoured the calcium phosphate formation as stated above.

4.3. Evaluation of global phosphorus recovery

The phosphorus recovery in the system by struvite crystallization was assessed, from a global point of view, taking into account both the crystallization process and the sludge treatment operational strategy.

As Table 5 shows, the main loss of phosphorus ($w_{P\ LOST}$) is due to precipitation in the anaerobic digester, which indicates the great importance of reducing this precipitation in order to increase the potential phosphorus available for the crystallization process. On the other hand, the dewatered centrate accounts for the principal availability of phosphorus ($w_{P\ AV}$), except for configuration C4 where the main contribution of phosphorus comes from the thickener supernatant stream.

The phosphorus available to be recovered in the crystallizer ($w_{P\ AV}$) is clearly higher in configuration C4, followed by configuration C2. As discussed in Martí et al. (2008a), the operational characteristics of each configuration determine the potential phosphorus that can be fed to the crystallizer. In the case of configuration C4, this high level of available phosphorus is primarily due to the high phosphorus content in the thickener supernatant and secondarily due to the low phosphorus precipitation in the digester. Consequently, configuration C4 showed the highest phosphorus precipitation and recovery in the crystallization process per kilogram of treated sludge (10.0 gP/kg sludge and 8.4 gP/kg sludge, respectively). However, regarding the phosphorus recovered

as struvite, the results obtained using liquor from configuration C4 showed a significant decrease. This low struvite recovery was attributed to the high Ca/Mg molar ratio in the crystallizer influent, which favoured the calcium phosphate formation. The high Ca/Mg molar ratio obtained in C4 is due to the high proportion of thickener supernatant in the crystallizer influent (i.e., a high α value). In the case of the city of Valencia the water hardness is very high, so most of the calcium content in the wastewater was transferred to the crystallizer inlet stream.

These results prove that if the sludge treatment system is operated according to configuration C4 (mixed thickening and a high flowrate ''washing-stream'' in the thickener) high phosphorus recovery can be achieved, but with a low percentage of struvite content. Therefore, if the production of struvite is not the main objective or calcium concentrations are not significant, configuration C4 leads to a higher phosphorus recovery. In this case, an economical study considering the higher construction costs of the crystallizer reactor should be carried out.

The use of a low elutriation flowrate stream (configuration C2) obtained higher amounts of struvite (3.9 gP/kg sludge) than configuration C4, even though the phosphorus recovery was lower (4.4 gP/kg sludge). Since the thickener supernatant was reduced, the molar ratio Ca/P decreased (see Table 2), and the liquor fed to the crystallizer was more suitable for the struvite precipitation. Therefore, if the main objective is to achieve an efficient recovery of phosphorus as struvite using liquors with high calcium concentrations, the sludge treatment line should be operated according to configuration C2. Finally, it must be pointed out that the problem is not the flowrate of the elutriation stream but its high calcium concentration. Therefore, the use of an external high flowrate elutriation stream with low calcium concentration would be a very interesting option.

5. Conclusions

In this paper, the influence of the sludge treatment line operation on the global phosphorus recovery by struvite crystallization has been evaluated. The main conclusions are shown below:

- The agitated crystallizer showed to obtain satisfactory results for the struvite precipitation (70–85% of precipitation efficiency and 70–85% of recovery efficiency)
- The presence of calcium in the crystallizer inlet stream diminished the percentage of phosphorus precipitated as struvite and gave rise to ACP formation.
- The operational scheme of the sludge line determines the suitability of the liquors for recovering phosphorus in WWTPs. Struvite production is favoured when mixed thickening and elutriation of sludges are carried out.
- The use of an external high flowrate elutriation stream increases phosphorus recovery. However, low percentage of struvite is obtained if high calcium concentrations are present in this external stream. Therefore, in the case of high water hardness, the reduction of the elutriation flowrate is widely recommended if the final purpose is to obtain struvite.

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