



A pilot-scale study of struvite precipitation in a stirred tank reactor: Conditions influencing the process

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Abstract

Currently, the two most developed techniques for recovering phosphorus from wastewater consist of the formation of calcium phosphates and struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). In this work the influence of the operational conditions on the struvite precipitation process (pH in the reactor, hydraulic retention time, and magnesium:phosphorus, nitrogen:phosphorus, and calcium:magnesium molar ratios) have been studied. Twenty-three experiments with artificial wastewater were performed in a stirred reactor. In order to obtain the pH value maintenance during the crystallization process, a fuzzy logic control has been developed. High phosphorus removal efficiencies were reliably achieved precipitating the struvite as easily dried crystals or as pellets made up of agglomerated crystals.

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1. Introduction

The high demographic and industrial development that has occurred in recent years has produced an increase in water pollution. Nutrient discharges to natural waters have contributed to an increase in eutrophication problems, producing grave consequences for aquatic life as well as for the water supply for industrial and domestic uses. A great number of legal initiatives to solve this problem have emerged, one of which is the 91/271 CEE Directive about urban wastewater treatments. One of the key issues of this directive is the elimination of nitrogen and phosphorus when the discharge is made to “sensitive areas” (Molinari et al., 2004). Furthermore, the known reserves of phosphate rocks are limited. Some studies suggest that within 60 to 70 years about half the world’s current economic phosphate resources will have been used up (Driver et al.,

1999). This fact justifies the development of new techniques to recover phosphorus. On the other hand, the work of Shu et al. (2006) shows that phosphorus recovery as struvite is technically feasible and economically beneficial.

Much of the phosphorus and part of the ammonium of the supernatant obtained after centrifuging the sludge that comes from a biological phosphorus removal treatment can be used for struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) production (Pastor et al., 2007). This solution can achieve high concentrations of ammonium and phosphorus due to the fact that phosphorus and ammonium are released in the solution when the sludge passes through an anaerobic digestion treatment (Booker et al., 1999). This permits the phosphorus and ammonium to be recovered as struvite through the crystallization process.

The formation of struvite in aqueous solutions takes place following the development of supersaturation, the driving force to all crystallization processes. Supersaturation is a measure of the deviation of a dissolved salt from its equilibrium value. The struvite formation occurs

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relatively quickly because of the presence of excess supersaturation in the liquid, as a result of the chemical reaction of magnesium with phosphate in the presence of ammonium. Supersaturation may be developed by increasing the aqueous medium content in ammonium, magnesium or orthophosphate and/or the pH. Although H^+ concentration does not directly enter the solubility product equation for struvite, struvite precipitation is highly pH dependent. The temperature and the presence of other ions in the solution such as calcium (Ca^{2+}) can also affect the struvite crystallization. The temperature influences the struvite solubility product and the presence of calcium may imply a competition between struvite and calcium phosphate precipitation.

The most promising application of struvite is as a fertilizer of slow activity, which is important for certain types of crops that need fertilizers with low solubility. The presence of magnesium makes struvite useful for crops that need this ion, such as sugar beets (de-Bashan and Bashan, 2004). Finally struvite recovered from wastewaters by Unitika Ltd., Japan, is already being sold to American fertilizer companies (Driver et al., 1999).

The main objective of this paper is to study the influence of the different operating parameters of the industrial process (pH, inlet concentrations and hydraulic retention time) in order to optimize the crystallization process. The process has been analyzed from the point of view of phosphorus removal and recovery including the product quality. The efficiencies obtained from the experimental results are also discussed with respect to the global parameter: supersaturation.

2. Methods

2.1. Pilot plant

The pilot plant is composed of the crystallization reactor, three stainless steel injection tubes for influent and reactants, two peristaltic pumps, one membrane pump, and two balances. The balances were used to continuously monitor the magnesium and sodium hydroxide flows. The reactor is a glass stirred reactor with a total volume of 21 l. The reactor is composed of two parts. The bottom part is the reaction zone, and the top part is a settling zone that prevents fine particles from being lost in the effluent. The reaction zone was designed according to the typical dimensions of a perfectly mixed reactor (Mangin and Klein, 2004). This zone is equipped with four baffles to prevent the formation of vortexes and to favour mixing. The space between the baffles and the tank wall prevents the accumulation of solid particles on the baffles. The settling zone is located above

the reaction zone and is cone-shaped with an angle of 45° between the two zones. This part is also equipped with a baffle to guide the flow. The effluent flows out at the top of the settling zone over a weir. The agitator employed in the reactor is a profiled propeller (TT type from Mixel® Company, France). It is an axial flow propeller. A second agitator was added at the end of the axis. This second agitator is a small turbine that is equipped with two flat blades that are perpendicular to the axis whose aim is to prevent deposition at the bottom flow gate.

2.2. Substrates

The solution fed into the reactor was a pure reagent solution of phosphate, ammonium, and tap water. This pure reagent solution permitted us to control the concentrations of the ions involved so that their influence on the process could be studied. Tap water was used to ensure enough ionic strength for the process. It was previously analyzed to ensure that the presence of Ca^{2+} and Mg^{2+} was negligible. Table 1 shows the average ion concentration of the tap water that was used to prepare the feed solution. This solution was prepared with ammonium dihydrogenophosphate and ammonium chloride. It had a concentration of phosphorus of approximately 87 mg/l. The ammonium ions were in excess, as occurs with the supernatant obtained by dewatering the biological digested sludge of a phosphorus removal process. A peristaltic pump injected this solution in the reactor through a stainless steel tube with an internal diameter of 4 millimetres (mm).

The magnesium chloride ($MgCl_2 \cdot 6H_2O$) solution (720 mgMg/l) provides the magnesium ions needed for struvite formation. This solution was added separately by means of another peristaltic pump. To study the influence of Ca^{2+} ions on the process, a solution containing both, Ca^{2+} and Mg^{2+} was prepared ($MgCl_2 \cdot 6H_2O + CaCl_2$) for some of the experiments.

The pH was adjusted with a sodium hydroxide (NaOH) solution (0.1 M) added through a membrane pump.

2.3. Experimental procedure

The experimental work was divided into twenty-three experiments. The parameters studied in these experiments were:

- Mg/P molar ratio. It was adjusted by varying the magnesium chloride solution flow rate.

Table 1
Average ion concentration of the tap water employed in the experiments

Na^+ (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	CO_3^{2-} (mg/l)	SO_4^{2-} (mg/l)
294.1	2.6	4.7	3.8	114.7	25.5	58.7	172.6

- N/P molar ratio. Ammonium dihydrogenophosphate and ammonium chloride solutions with different concentrations were employed.
- pH inside the reactor. It was controlled by increasing or decreasing the pump frequency in order to increase or decrease the NaOH dose rate, respectively.
- Hydraulic retention time (HRT). The desired HRT were fixed by varying the feed flow rate.
- Presence of Ca^{2+} in the influent. Solutions of different Ca^{2+} concentrations were employed.

Due to the relatively low phosphate concentration, the reactor was operated in continuous mode for the liquid phase and in batchwise mode for the solid phase. This way of operating provided enough solids for growth and for obtaining large crystals. From an economical point of view, it is important to achieve large crystals to facilitate the recovery, transport, and commercial operations of the final product. Samples of the effluent were taken every day to measure total phosphorus, orthophosphate, ammonium, total magnesium, and dissolved magnesium. Total calcium and dissolved calcium in the effluent were also analyzed when required. All the analyses were performed in accordance with Standard Methods (APHA, 2005). At the end of the experiments, the precipitated solids were recovered from the reaction zone and were air dried. The solids were observed under a light microscope. These solids were also analyzed by X-ray diffraction (XRD), and the crystal size distribution (CSD) was measured using a Malvern particle-sizer.

Table 2
Influent and effluent concentrations

Experiment	Influent				Effluent	
	$\text{PO}_4\text{-P}$ (mg/l)	$\text{NH}_4\text{-N}$ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	P_i (mg/l)	$\text{PO}_4\text{-P}$ (mg/l)
E1	80.1	60.7	57.5	4.1	29.3	27.2
E2	80.3	87.4	60.6	4.1	20.3	14.9
E3	79.7	64.9	53.5	2.1	36.3	31.3
E4	81.0	54.0	60.3	4.2	38.0	34.6
E5	77.2	63.5	68.8	4.1	24.9	23.0
E6	80.1	64.8	50.2	4.2	33.6	31.8
E7	77.6	60.8	66.1	9.6	24.3	23.9
E8	78.8	64.2	67.1	0.4	26.8	26.4
E9	79.7	74.8	54.6	53.8	26.7	19.3
E10	79.2	78.3	58.0	5.5	26.3	25.3
E11	79.4	64.6	58.9	10.5	30.0	28.9
E12	80.7	61.7	57.5	2.5	33.8	32.3
E13	79.7	66.3	54.8	10.2	30.4	26.4
E14	78.9	63.2	58.7	2.2	24.6	23.4
E15	78.9	60.3	52.9	0.8	33.5	32.1
E16	79.4	63.1	55.4	0.2	39.0	38.5
E17	79.7	63.9	61.9	4.7	50.0	48.6
E18	81.4	62.5	56.4	0.4	25.9	24.6
E19	75.0	58.4	53.8	88.6	17.5	10.7
E20	81.0	64.2	58.9	3.6	24.6	23.1
E21	80.6	63.3	57.8	172.2	6.7	5.3
E22	79.7	60.9	58.2	4.3	21.2	21.3
E23	80.7	61.2	57.6	3.7	19.3	18.5

Table 2 summarizes the influent solution concentrations assuming mixing of the three feed flows and the effluent total phosphorus and orthophosphate concentrations at the end of the experiments.

2.4. Data acquisition program and fuzzy logic control

A data acquisition program continuously monitors the operating parameters: pH, conductivity, temperature, and magnesium chloride and sodium hydroxide flows rates. The acquisition frequency was less than a measurement per minute.

In most of the experiments (E5–E23), the pH was controlled by employing a fuzzy logic algorithm control (Chañona et al., 2006). The control algorithm was implemented in the data acquisition program. The reasons for choosing fuzzy logic were the following:

- The highly non-linear and time variant response of the pH value to the addition of base in the struvite precipitation process makes pH control by conventional methods very difficult.
- Fuzzy logic control does not require any mathematical model.

3. Results and discussion

Process efficiency was calculated on the basis of phosphorus removal from the solution. Two types of efficiencies were calculated:

- Precipitation efficiency. It represents the process efficiency from a thermodynamic point of view assuming that the supersaturation can be almost completely consumed, which should be the case with sufficient residence time. It is calculated as the percentage of the soluble phosphorus entering the reactor that precipitates.
- Recovery efficiency. It takes into account both precipitation and crystal growth efficiency. It is obtained as the percentage of the total phosphorus entering the reactor that is not lost with the effluent (total phosphorus entering the reactor minus total phosphorus leaving the reactor).

The difference between precipitation efficiency and recovery efficiency corresponds to the fine crystals lost in the effluent of the reactor.

3.1. Effect of pH and Mg/P, N/P molar ratios

The phosphorus precipitation and recovery efficiencies can be calculated from the average values obtained from the analyses. Table 3 shows the results of the influence of pH, Mg/P ratio, and N/P ratio on the two efficiencies. As Table 3 shows, struvite precipitation and recovery is highly

Table 3
Recovery and precipitation efficiencies at different pH, HRT, and Mg/P and N/P molar ratios

Experiment	Operational conditions					Efficiency		SI _{MAP}
	Mg/P molar	N/P molar	Ca/P molar	pH	HRT (h)	Recovery (%)	Precipitation (%)	
<i>pH</i>								
E17	0.9	1.8	0.0	8.2	11.0	37.3	39.0	0.66
E16	0.9	1.8	0.0	8.3	10.7	50.9	51.5	0.71
E15	0.9	1.7	0.0	8.4	10.9	57.6	59.3	0.76
E3	0.9	1.8	0.0	8.5	10.6	54.4	60.8	0.89
E11	1.0	1.8	0.1	8.6	10.7	62.2	63.6	1.00
E12	0.9	1.7	0.0	8.8	11.0	58.2	60.0	1.14
E13	0.9	1.8	0.1	8.8	10.8	61.9	67.0	1.14
E14	1.0	1.8	0.0	8.9	11.1	68.8	70.4	1.23
E22	0.9	1.7	0.0	9.5	10.5	73.5	73.3	1.53
E23	0.9	1.6	0.0	9.5	10.3	76.1	77.0	1.53
<i>Mg/P</i>								
E6	0.8	1.8	0.0	8.7	11.0	58.1	60.3	1.04
E8	1.0	1.8	0.0	8.7	10.7	66.0	66.6	1.13
E7	1.1	1.8	0.1	8.7	10.7	68.6	69.2	1.08
E5	1.1	1.8	0.0	8.7	10.2	67.8	70.3	1.12
<i>N/P</i>								
E4	0.9	1.5	0.0	8.5	10.9	53.2	57.2	0.86
E1	1.0	1.7	0.0	8.7	10.8	63.5	66.0	1.06
E9	0.9	2.1	0.5	8.7	10.6	66.5	75.7	1.02
E10	0.9	2.2	0.1	8.7	10.7	66.8	68.1	1.16
E2	0.9	2.4	0.0	8.7	10.5	74.7	81.4	1.23
<i>HRT</i>								
E18	0.9	1.7	0.0	8.9	7.1	68.2	69.8	1.22
E20	0.9	1.8	0.3	8.9	2.1	69.7	71.4	1.24

Influent solution SI_{MAP}.

Hydraulic retention time on the basis of the whole reactor volume.

pH-dependent. The results demonstrate that as the pH increases (from 8.2 to 9.5), the precipitation and the recovery efficiency increase (from 40% to 80%). This high level of pH dependency is in accordance with the results obtained by Katsuura (1998). Furthermore, the two efficiencies improve at high Mg/P and N/P ratios. These evolutions are logical. Indeed, the precipitation efficiency corresponds to the thermodynamic efficiency since the equilibrium between the solid and the solution is reached in the reactor effluent (see Section 3.5).

In experiments E17, E12 and E22 (pH 8.2, 8.8 and 9.5, respectively) an important fouling on the stirrer was observed. This fouling produced a decrease in mixing efficiency and in the quantity of suspended solids in the reaction zone, resulting in a decrease in precipitation efficiency. This effect can be observed comparing the efficiencies obtained for experiments E12 and E13, and between the experiments E22 and E23, carried out at the same conditions. Fouling appears as an important problem when scaling to industrial crystallizers. Therefore, special attention must be paid to study the conditions at which no fouling occurs for each crystallization system. Fouling is caused by the creation of a zone of high supersaturation in the vicinity of a “receptive” metal surface, in regions of poor agitation or low flow rate and points at which different liquors streams meet and mix (Mullin, 2001).

In experiment E9 (Table 3) a higher phosphorus precipitation efficiency than expected was obtained due to the presence of calcium in the feed (Table 2) that precipitated as calcium phosphate.

The biggest differences between the two efficiencies, which indicates a loose of fine crystals with the effluent, correspond to experiments where calcium at high concentration was present in the influent (experiment E9) and experiments that were conducted with a manual control of pH (experiments E2, E3 and E4). The recovery efficiency is affected by the level of supersaturation obtained in the reactor, which could produce a large number of fine crystals. These fine run-offs decrease the value of recovery efficiency, thereby increasing the difference between the two efficiencies. However, in the intervals studied there has not been observed any relation between the increase in pH, and Mg/P and N/P molar ratio and the quantity of crystals lost with the effluent. This suggests that within the supersaturation degree at which the reactor has been operated it has been able to keep the majority of the solids inside.

3.2. Saturation index

The effect on the struvite precipitation of pH, N/P and Mg/P molar ratios can be observed with a single parameter that includes all these effects. The Saturation Index value for struvite (SI_{MAP}, Eq. 1) is used to establish the stability

order of precipitation or dissolution of solids. If the saturation index is negative, the system is undersaturated with respect to struvite. If the index is positive, the solution is supersaturated. The SI values were calculated for all the experiments (except those with high calcium concentration in the inlet) using the equilibrium speciation model MINT-EQA2 (Allison et al., 1991), assuming complete mixing of the three feed flows. The activity coefficients were obtained from the Davies equation with a Davies B parameter of 0.3. This equation is quite satisfactory for values of ionic strength up to about 0.2 mol/l (Mullin, 2001). The ionic strength of the feed solution used in all the experiments carried out was between 0.02 and 0.03 mol/l. The struvite pK_{SMAP} used was of 13.31 (see Section 3.5).

$$SI_{\text{MAP}} = \log \frac{[\text{Mg}^{2+}] \cdot [\text{NH}_4^+] \cdot [\text{PO}_4^{3-}]}{K_{\text{SMAP}} \gamma_{\text{Mg}} \gamma_{\text{NH}_4} \gamma_{\text{PO}_4}} \quad (1)$$

where $[\text{Mg}^{2+}]$, $[\text{NH}_4^+]$ and $[\text{PO}_4^{3-}]$ are magnesium, ammonium and phosphate concentrations (mol/l); γ_{Mg} , γ_{NH_4} and γ_{PO_4} are the activity coefficients of $[\text{Mg}^{2+}]$, $[\text{NH}_4^+]$ and $[\text{PO}_4^{3-}]$ species, respectively; K_{SMAP} is the struvite solubility product.

The representation of the two efficiencies obtained at different SI_{MAP} results in two straight lines with approximately the same slope (34.4 and 35.7 for the recovery and precipitation efficiency, respectively). This means that a higher SI_{MAP} does not imply a higher difference between both efficiencies, what would imply a higher formation of fine crystals.

Fig. 1 shows the percentage of the total phosphorus entering the reactor lost with the effluent ($\%P_{\text{prec lost}}$) in the form of crystals versus the SI_{MAP} of each experiment. As can be observed, except the anomalous value in experiment E2, this percentage is less than 3% being in most of the cases around 2%. Furthermore, no relation between the percentage of the total phosphorus lost with the effluent and the SI_{MAP} has been found.

3.3. Effect of Ca/Mg molar ratio

The increase of calcium concentration in the influent (keeping pH, magnesium concentration, and other ion con-

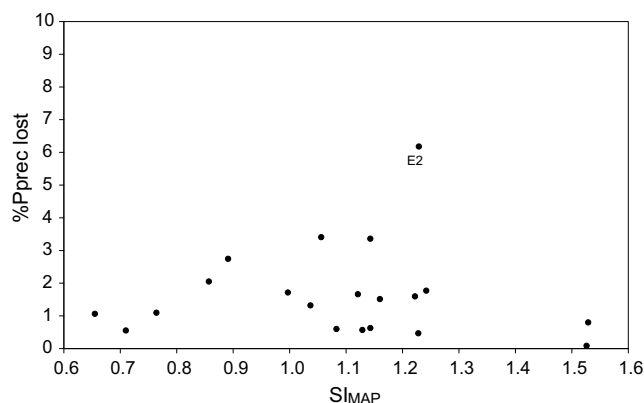


Fig. 1. Percentage of the total phosphorus entering the reactor lost with the effluent vs. SI_{MAP} .

centrations constant) in an interval of the Ca/Mg molar ratio of 0 to 1.8 resulted in an increase from 58 to 92%, and from 60 to 93% in the recovery and precipitation efficiency, respectively. This was due to a phosphorus coprecipitation as struvite and calcium phosphates.

The MINTEQA2 model indicates that struvite and magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2$) are the only two magnesium precipitates that can be formed in these solutions. Since there are large amounts of ammonium, it can be assumed that the decrease in magnesium concentration is only due to struvite precipitation. Taking the decrease in magnesium and phosphate concentration into account, the percentage of phosphorus precipitated which precipitated as struvite ($\%P_{\text{MAP}}$) can be estimated by:

$$\%P_{\text{MAP}} = \frac{[\text{Mg}^{2+}]_{\text{in}} - [\text{Mg}^{2+}]_{\text{ef}}}{[\text{PO}_4 - \text{P}]_{\text{in}} - [\text{PO}_4 - \text{P}]_{\text{ef}}} \cdot 100 \quad (2)$$

where the concentrations are in molar units and refer to dissolved species.

This calculation resulted in a lower percentage of phosphorus precipitated as struvite when the calcium concentration entering the reactor was increased. For Ca/Mg molar ratios of 0.1, 0.6, 1.0 and 1.8, $\%P_{\text{MAP}}$ values of 93, 62, 39 and 12% were obtained, respectively.

In order to observe the effect of Ca/Mg molar ratio on the crystal size, the crystal size distribution (CSD) of the solids obtained in experiments E6 (Ca/Mg = 0.1) and E19 (Ca/Mg = 1.0) were measured using the Malvern particle-sizer. These analyses showed that as the Ca/Mg molar ratio increased, the proportion of crystals with a size between 10 and 100 μm (small size) also increased.

3.4. Effect of HRT

Three experiments were carried out at different influent flow rates in order to study the effect of hydraulic retention time on process efficiencies. The HRT values employed were calculated on the basis of the whole reactor volume. These experiments showed no effect on the process efficiencies. The precipitation efficiencies obtained working at HRT values of 11.1, 7.1 and 2.1 h (Experiments E14, E18 and E20) were 70.4, 69.8 and 71.4, respectively. Recovery efficiencies of 68.8, 68.2 and 69.7 were obtained for values of the HRT of 11.1, 7.1 and 2.1 h, respectively (Table 3). However, the CSD was affected by a change in HRT. The proportion of particles between 10 and 100 μm increased at low HRT. The decrease in HRT changed the hydraulics of the reactor causing a decrease of the crystal size, while the extension of the phosphorus precipitation remained invariable.

3.5. Experimental struvite solubility product

Due to the high variability found in the literature for the struvite solubility product, it has been considered important to obtain a value for this constant from the experimen-

Table 4

Values introduced in MINTEQA to calculate the experimental pK_{SMAP}

Experiment	PO_4^{3-} (mg/l)	NH_4^+ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	Na^+ (mg/l)	CO_3^{2-} (mg/l)	pH
E1	245.6	78.1	57.5	4.1	338.8	25.5	172.6	254.8	95.2	8.7
E4	248.4	69.5	60.3	4.2	335.6	25.5	172.6	263.7	95.2	8.5
E6	245.7	83.5	50.2	4.2	314.3	25.5	172.6	266.0	95.2	8.7
E8	241.7	82.7	67.1	0.4	360.5	25.5	172.6	259.6	95.2	8.7
E14	241.8	81.4	58.7	2.2	341.4	25.5	172.6	259.3	95.2	8.9
E15	242.0	77.6	52.9	0.8	331.5	25.5	172.6	263.4	95.2	8.4
E16	243.5	81.2	55.4	0.2	337.2	25.5	172.6	265.1	95.2	8.3
E18	249.5	80.5	56.4	0.4	332.1	25.5	172.6	263.7	95.2	8.9
E20	248.3	82.7	58.9	3.6	340.8	25.5	172.6	267.3	95.2	8.9
E23	247.5	78.8	57.6	3.7	330.4	25.5	172.6	256.8	95.2	9.5

tal results of this work. The experimental pK_{SMAP} value for struvite was obtained by minimising the error between the results predicted by MINTEQA2 and the experimental results (Eq. 3).

$$\begin{aligned} \text{Objective function} = & \sum \left([\text{PO}_4^{3-}]_{\text{eq}}^{\text{cal}} - [\text{PO}_4^{3-}]_{\text{eq}}^{\text{exp}} \right)^2 \\ & + \left([\text{NH}_4^+]_{\text{eq}}^{\text{cal}} - [\text{NH}_4^+]_{\text{eq}}^{\text{exp}} \right)^2 \\ & + \left([\text{Mg}^{2+}]_{\text{eq}}^{\text{cal}} - [\text{Mg}^{2+}]_{\text{eq}}^{\text{exp}} \right)^2 \quad (3) \end{aligned}$$

where eq indicates equilibrium concentrations, calculated with MINTEQA2 (cal) or obtained experimentally (exp).

The equilibrium has been reached in all the experiments carried out. Once an experiment was finished the solution was kept inside the reactor for several hours. It was agitated but not fed. Samples from the reaction zone were analysed for soluble phosphorus every two hours and no variation in the concentration was observed, assuming the equilibrium was reached (Seco et al., 2004).

For this calculation, only the experiments without calcium in the influent and those where no operational problems such as fouling occurred, were employed. Table 4 shows the values introduced in MINTEQA2 to obtain the calculated equilibrium concentrations. The pK_{SMAP} values tested varied between 13.5 and 13.0.

A pK_{SMAP} of 13.31 has been obtained. This value is similar to the ones obtained in the most recent literature. The values of $13.26(\pm 0.04)$, $13.36(\pm 0.284)$ and $13.40(\pm 0.31)$ obtained by Ohlinger et al. (1998), Babic-Ivancic et al. (2002) and Ronteltap et al. (2003), respectively, are the closest ones.

3.6. Fuzzy logic control

The results obtained show that struvite precipitation is highly pH-dependent. The manual pH control proved to be insufficient for a correct pH control. In fact, it was very difficult to maintain the pH in a constant value with this control. Therefore, a fuzzy logic algorithm was developed to control the pH in the reactor for the next experiments. This control allowed a high stability in the pH, maintaining the pH at the set point through the entire experiment.

3.7. Solids

Solids from the experiments were analysed by X-ray diffraction. The analyses showed that the solid obtained in the experiments was struvite. The XRD analysis for experiments E19 and E21 resulted in the presence of struvite in experiment E19 and its absence in experiment E21. These results are in concordance with the percentage of struvite present in the precipitate mentioned in Section 3.3. The absence of peaks in the XRD spectrum for experiment E21 suggests that the solid precipitated was amorphous calcium phosphate (ACP).

4. Conclusions

The stirred reactor tested has proven to successfully crystallize struvite, achieving phosphorus precipitation and recovery efficiencies up to 80%. An increase in pH and Mg/P and N/P molar ratios increases these efficiencies. HRT in an interval of 2–11 h had no effect on the extension of precipitation, but higher levels of small crystal production were observed when HRT was decreased. At a Ca/Mg molar ratio of 2, almost all the phosphorus precipitated as ACP. This parameter also influenced the crystal size, increasing the proportion of small crystals as the parameter increased.

The application of fuzzy logic control enabled very stable pH conditions.

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