

Evaluation of a low-cost magnesium product for phosphorus recovery by struvite crystallization

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Abstract

BACKGROUND: The development of a cost-effective process of struvite crystallization requires the selection of appropriate sources of alkali and magnesium. In this study, the effectiveness of two industrial grade products, MgO and Mg(OH)₂, as magnesium and alkali sources to recover phosphorus as struvite were investigated and compared in a first set of experiments. Subsequently, the use of industrial Mg(OH)₂ was compared in two different struvite crystallization systems, an upflow fluidized bed reactor (FBR) and a continuous stirred tank reactor (CSTR) coupled to a settler tank.

RESULTS: At the same operational conditions, the consumption of MgO was higher than Mg(OH)₂ consumption. Moreover, industrial Mg(OH)₂ consumption for FBR and the CSTR operation was 1.6 and 1.1 1 mol Mg added mol⁻¹ P precipitated, respectively. This difference was caused by the high mixing intensity and the higher contact time between the Mg(OH)₂ slurry and the influent in the CSTR, favouring the conversion.

CONCLUSIONS: Both industrial grade magnesium products are promising options for struvite crystallization. However, Mg(OH)₂ was more effective than the starting material, MgO, to recover phosphorus. Struvite crystallization by adding an industrial grade Mg(OH)₂ could be economically viable with regard to alternative physico-chemical P removal processes using metal salts, increasing the attractiveness of this P recovery process.

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Supporting information may be found in the online version of this article.

Keywords: continuous stirred tank reactor; fluidized bed reactor; industrial magnesium hydroxide; phosphorus recovery; struvite

INTRODUCTION

The crystallization of struvite could be a sustainable alternative to recover the phosphorus from phosphate concentrated wastewater. Nevertheless, due to the low market volume compared with industrial fertilizers, struvite recovery in municipal wastewater treatment plants (WWTP) only would be feasible if there is an economic incentive to implement phosphorus recovery technologies. The cost-effectiveness of the struvite crystallization process is strongly dependent on the characteristics of the wastewater, as well as the selection of appropriate alkali and magnesium sources. The main cost factors affecting the economy of struvite crystallization are magnesium and alkali sources¹. Generally, wastewater contains less magnesium compared with phosphate and ammonium. Consequently, it is necessary to supply a source of magnesium to promote the crystallization of struvite. Besides, the reaction of struvite crystallization causes a release of protons ions as shown in Equation (1) and consequently, could cause a pH drop. Therefore, an alkali source must be added to the crystallization system in order to maintain the pH in a range suitable for struvite crystallization. The pH range in which struvite may crystallize is between 7.0 and 11.5,² but due to environmental

and efficiency reasons, the suitable pH range is limited to 8.0 to 9.0.



In recent years, several studies based on struvite crystallization have been carried out using different magnesium sources, such as direct dosage of high quality MgCl₂, MgSO₄, MgO, Mg(OH)₂, or by

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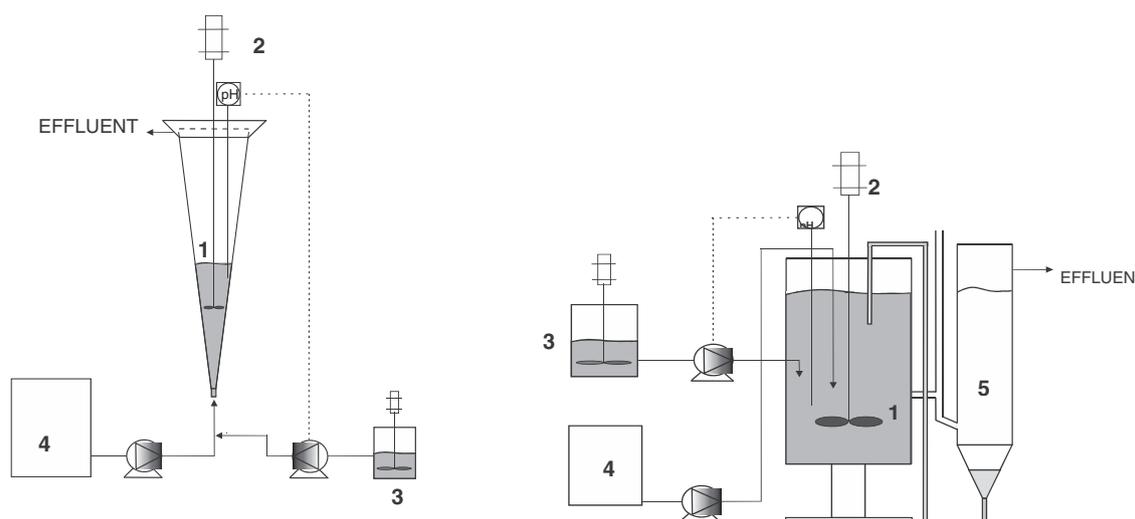


Figure 1. Experimental set-up of FBR (left) and CSTR (right). (1) reactor; (2) stirrer; (3) $\text{Mg}(\text{OH})_2$ slurry stirred tank; (4) influent tank; (5) external settler of CSTR.

a process based on magnesium dosing by electro-dissolution.^{3–8} However, the use of these expensive magnesium sources can lead to high operating costs. Other magnesium sources proposed are the addition of either seawater or bittern.^{9–11} Nevertheless, use is generally limited by the proximity to these diluted magnesium sources. The utilization of low cost magnesium sources, such as industrial grade MgO or $\text{Mg}(\text{OH})_2$, can significantly reduce the cost of struvite crystallization.¹² Hug and Udert¹³ stated that the use of MgO is a cheaper alternative than other magnesium sources such as MgCl_2 , MgSO_4 or electrochemical magnesium dosage. In addition, hydroxyl ions provided by magnesium hydroxide and magnesium oxide, may also be used to maintain pH in an optimal range to promote the crystallization of struvite.¹⁴ Both magnesium compounds, $\text{Mg}(\text{OH})_2$ and MgO , are powdered products. It should also be taken into account that the external surface of powdered MgO reacts with water in a first stage forming $\text{Mg}(\text{OH})_2$, which is the active compound in water. The solubility of $\text{Mg}(\text{OH})_2$ is low and depends on pH. Oppositely to NaOH or other alkali sources, overdosing of either MgO or $\text{Mg}(\text{OH})_2$ did not cause an excessive increase in pH, pH increased to 9–9.5.

To check the economic feasibility of struvite crystallization systems in WWTP, their costs need to be compared with those plants using other chemical phosphorus removal processes. The cost of mature processes, such as phosphorus precipitation with aluminium or iron salts, is around 2000–3000 $\text{€}\cdot\text{t}^{-1}\cdot\text{P}^{-1}$ at minimum, and this cost could increase to over 10 000 $\text{€}\cdot\text{t}^{-1}\cdot\text{P}^{-1}$ under specific conditions.¹ In addition, precipitates obtained in those processes are hardly reusable. For the case of struvite, Dockhorn¹ performed an economic analysis and stated that costs were in a wide range of 2000–11 000 $\text{€}\cdot\text{t}^{-1}\cdot\text{P}^{-1}$, depending on the conditions of the process. The production costs of struvite are reliant on phosphorus concentration and they decrease with increasing phosphorus concentration.¹ Furthermore, phosphorus concentrations should be above 50 $\text{mg P-PO}_4^{3-}\text{L}^{-1}$ in order to guarantee the economic viability of the process.^{15,16}

Struvite crystallization can be carried out in different reactor configurations, such as continuous stirred tank reactors (CSTR) and either two- or three-phase fluidized bed reactors (FBR).^{2,17} CSTRs provide a simple operation mode of struvite crystallization. This type of reactor allows increase of the precipitates size and can

increase the surface area of the precipitates. However, the CSTR could limit crystal growth as well as produce fine crystals due to the high shear stress caused by the mixers required to keep the crystals in suspension. On the other hand, FBRs have been commonly used for the production of large crystals, like pellets. This type of reactor allows the production of product crystals with controlled particle size distribution.¹⁸

The main objective of this work was to investigate the feasibility of the use of two different low cost industrial grade magnesium products: MgO and $\text{Mg}(\text{OH})_2$ as alkali and magnesium sources to promote struvite crystallization. The potential of two different reactor configurations, a fluidized bed reactor and a completely stirred tank reactor, for struvite crystallization was also studied.

MATERIALS AND METHODS

Experimental set-up and operating strategy

Reactors set-up

Two different reactors, an upflow fluidized bed reactor (FBR) and a completely stirred tank reactor (CSTR) were used during the experiments. The FBR was a glass cone-shaped reactor (Fig. 1) with a working volume of 1.8 L, a height of 48 cm and an internal reactor diameter of 12 cm at the top of the reactor. The reactor was divided into two different zones: a reaction zone and a separation zone. The reaction zone, composed by a mixture of particles of solids in suspension, was located at the bottom of the reactor. The upper zone acted as a two-phase solid–liquid separator designed for retaining most of the solid particles. For this reason, the flow velocity of the liquid in this zone was lower than the terminal particle velocity that guarantees the appropriate solids retention, mainly of small struvite crystals. In the first part of this work, the FBR was operated continuously and then the FBR was operated semi-continuously. Overall hydraulic retention time (HRT) of the FBR was fixed at 51 min, referred to the whole FBR volume. Due to the presence of a solid phase, reaction time (RT) was defined as the time that the influent remained in this zone, in which the heterogeneous reactions took place. RT was lower than HRT, and it was dependent on the apparent volume of solids. RT varied between 10.0 and 13.5 min. Moreover, in this system mechanical stirring was gently applied at 60 rpm to avoid preferential pathways in the FBR.

The CSTR was made in acrylic glass and had a working volume of 2.15 L and a height to diameter ratio of 2.0. The CSTR was coupled in series with an external settler (Fig. 1) to recover and recycle back the fine crystals washed out from the reactor, using mammoth pump. The volume of external settler was 1.15 L and a height to diameter of 6.0. The system was operated for 8 h per day, with a HRT of 61 minutes. A mechanical stirrer at 120 rpm was used in the CSTR in order to avoid the settling of solid particles in the reactor. In this system HRT and RT were the same, as the volume occupied by the solid particles suspension was the same as the volume of the reactor previously indicated.

Magnesium and alkali sources

Different industrial grade magnesium products to promote the crystallization of struvite were used and compared: MgO and Mg(OH)₂. MgO was supplied by Magnesitas de Rubián SA, one of the two Spanish industrial grade providers.¹⁹ The MgO product was a powdered product composed of fine particles with a size lower than 128 μm. 95% of the weight are particles with a size lower than 48 μm. This product contained 80.5% of MgO, and was produced by firing flue magnesite dust (MgCO₃) in a fluidized bed kiln.

Two different Mg(OH)₂ suspensions were obtained in the laboratory by hydration of the aforementioned industrial MgO. This chemical was hydrated using a procedure similar to that described by Matabola *et al.*²⁰ To prepare the two Mg(OH)₂ suspensions, MgO, and a water solution with two different hydrating agents were mixed at a ratio of 55:45 (w/w, %). Hydrating agents used were aqueous solutions of sodium chloride (NaCl, 4.7 g L⁻¹) and magnesium acetate (MgAc₂, 10 g L⁻¹), which were added to the water to speed up the hydration reaction. The mixture of MgO, water and hydrating agent was stirred at 200 rpm, while the temperature was maintained at 75 °C for 6 h. The product obtained was a suspension of powdered product in water, with a density of 1400 g L⁻¹. Due to the powdered nature of the product, MgO was not fully converted to Mg(OH)₂ as also stated by Matabola *et al.*²⁰ These powder particles were formed by an inner part comprised of unreacted MgO and an external layer of Mg(OH)₂. The conversion of MgO to Mg(OH)₂ was 64% and 74% for Mg(OH)₂ suspensions prepared with NaCl and MgAc₂, respectively.

Influent and operating strategy

The experiments were carried out over two different periods: period I, in which the industrial grade magnesium products, MgO and Mg(OH)₂, were assessed and compared, using the FBR; and period II, in which both FBR and CSTR were fed and operated under similar conditions in order to analyze the advantages and inconveniences of each reactor.

During the whole experimental period both reactors were fed using a prepared wastewater composed of dipotassium dihydrogen phosphate (KH₂PO₄) and ammonium chloride (NH₄Cl) as phosphate and ammonium sources, respectively (Tables 1 and 2). The composition was similar to those observed in the centrate of anaerobic sludge dewatering stage in the municipal WWTP of Vigo (NW Spain). All the experiments started with the addition of 5 g L⁻¹ of seed struvite crystals.

Period I lasted for 12 days that could be divided into four different stages: stage I, stage II, stage III and stage IV, in which the industrial grade MgO and two different Mg(OH)₂ were used (Table 1). The different stages were implemented in order to compare the MgO versus one of the Mg(OH)₂ products (stages I and II); to study

Table 1. Characteristics of the wastewater fed to the FBR during period I

Parameter	Stage I	Stage II	Stage III	Stage IV
pH	7.6	7.4	7.4	5.6
Conductivity (mS cm ⁻¹)	9.7	10.3	10.3	3.5
Mg product used	MgO	Mg(OH) ₂ ^a	Mg(OH) ₂ ^b	Mg(OH) ₂ ^b
PO ₄ ³⁻ (mmol L ⁻¹)	1.7	1.7	1.7	4.4
NH ₄ ⁺ (mmol L ⁻¹)	43.3	43.5	42.6	24.7
Mg ⁺² (mmol L ⁻¹)	4.2	4.6	3.7	-
Ca ⁺² (mmol L ⁻¹)	3.3	4.2	4.2	-
HCO ₃ ⁻ (mmol L ⁻¹)	29.7	28.6	29.5	-
K ⁺ (mmol L ⁻¹)	1.7	1.8	1.7	4.4

^aMg(OH)₂ slurry formed from hydration in NaCl.

^bMg(OH)₂ slurry formed from hydration in magnesium acetate.

Table 2. Characteristics of the wastewater fed during period II

Parameter	Stage V		Stage VI	
	FBR	CSTR	FBR	CSTR
pH	6.0 ± 0.3	5.8 ± 0.1	5.7 ± 0.1	5.9 ± 0.2
Conductivity (mS cm ⁻¹)	1.6 ± 0.1	1.7 ± 0.2	3.0 ± 0.1	1.9 ± 0.1
PO ₄ ³⁻ (mmol L ⁻¹)	2.0 ± 0.3	2.2 ± 0.1	2.1 ± 0.1	4.1 ± 0.1
NH ₄ ⁺ (mmol L ⁻¹)	8.4 ± 0.3	8.4 ± 0.4	20.0 ± 1.4	8.3 ± 0.8
K ⁺ (mmol L ⁻¹)	2.0 ± 0.3	2.2 ± 0.1	2.1 ± 0.1	4.0 ± 0.3

the performance of the Mg(OH)₂ prepared with the two different hydrating agents (stage II and III); and to assess the impact of the concentration of NH₄⁺ and HCO₃⁻ ions that are usually found at high concentrations in centrates of anaerobic sludge dewatering process (stage III and IV).

At the beginning of stage I, MgO was batch-added. The industrial MgO was a powdered product and it was not possible to add this product gradually, as was done with Mg(OH)₂. During this stage, the pH was not controlled. The influent was fed until the industrial MgO was exhausted. MgO depletion was detected by a decrease in the operating pH (below 7.8).

For stages II, III and IV, the pH was controlled by adding small amounts of the Mg(OH)₂ slurry with a peristaltic pump when the pH value approached 7.8. The addition of Mg(OH)₂ was stopped when the pH value reached 7.9. Mg(OH)₂ slurry was injected through the feeding point of the reactor to improve the contact between the influent fed and the slurry. The Mg(OH)₂ slurry used in stage II was prepared by using NaCl, meanwhile the Mg(OH)₂ slurry used in stages III and IV was prepared using magnesium acetate. Magnesium acetate and NaCl were used as hydrating agents during the hydration process of industrial MgO, as described in Materials and methods. Both Mg(OH)₂ were used in order to compare the reactivity of two industrial Mg(OH)₂ products with different MgO conversion, which were prepared using two different hydrating agents. Because the particles of Mg(OH)₂ settled rapidly, it was necessary to maintain Mg(OH)₂ particles in suspension in the slurry tank by using an agitator.

The composition of the influent was similar in the first three operating stages, and has a similar ion composition to the centrates analyzed in two urban WWTP in Galicia (NW Spain) (Table 1). Phosphorus concentration in the influent was 1.7 mmol PO₄³⁻ L⁻¹.

During this period, Mg^{2+} and NH_4^+ concentrations were higher than PO_4^{3-} concentration. The molar ratio of $\text{Mg}^{2+}:\text{PO}_4^{3-}:\text{NH}_4^+$ was 2.3:1.0:25.0 (Table 1). The influent also contained calcium and bicarbonate ions, with a $\text{Ca}^{2+}:\text{HCO}_3^-:\text{PO}_4^{3-}$ molar ratio of 2.2:18.0:1.0 (Table 1). For stage IV, the influent composition was modified to determine the effect of the influent composition on struvite crystallization process. In the influent of stage II, PO_4^{3-} concentration was increased to $4.4 \text{ mmol PO}_4^{3-} \text{ L}^{-1}$ and the concentration of NH_4^+ was halved ($24.7 \text{ mmol NH}_4^+ \text{ L}^{-1}$), with a $\text{NH}_4^+:\text{PO}_4^{3-}$ molar ratio of 6.0:1.0. Also, Mg^{2+} , Ca^{2+} and HCO_3^- ions were not added in the reactor influent.

The period II lasted for 51 days that could be divided into two different experimental stages: stage V and stage VI, in which the FBR and CSTR were operated and compared, using industrial $\text{Mg}(\text{OH})_2$ slurry as magnesium and alkali sources. This $\text{Mg}(\text{OH})_2$ was formed by hydration of the industrial MgO product in magnesium acetate. For stage V, the composition of the influents were similar in both reactors in order to compare the consumption of $\text{Mg}(\text{OH})_2$ and the quality of the solid phase obtained. For stage VI, the influents composition for CSTR and FBR were varied to determine the effect of PO_4^{3-} and NH_4^+ concentrations on the industrial $\text{Mg}(\text{OH})_2$ consumption and if the $\text{Mg}(\text{OH})_2$ efficiencies obtained during stage V could be improved in this stage. Both reactors were semi-continuously operated 8 h per day. Liquid samples were taken after 7 HRTs in order to ensure steady state.

In both crystallization reactors, the operating pH was maintained above 8.0 by adding $\text{Mg}(\text{OH})_2$ slurry, when the pH value approached 8.0. For operation of the FBR, the $\text{Mg}(\text{OH})_2$ was injected through the feeding point of the reactor to increase the contact time between influent ions, $\text{Mg}(\text{OH})_2$ and crystals in suspension. For CSTR operation, the $\text{Mg}(\text{OH})_2$ slurry was added in the centre of the reactor. In both reactors, the pH value was continuously monitored for the entire operation (Crison PH29 and HACH HQ40D multi for FBR and CSTR operations, respectively).

Throughout all stages of the experiment, both reactors were operated semi-continuously for time periods of 8 h per day. Table 2 shows the composition of the synthetic wastewater used for FBR and CSTR operations during stages V and VI.

For stage V, seed crystals of struvite were added to the reactors at the beginning of the stage in order to obtain a solids fluidized bed in which the struvite can be crystallized under controlled conditions. During this stage, the reactors were fed with an influent containing phosphorus ($2.0\text{--}2.2 \text{ mmol PO}_4^{3-} \cdot \text{L}^{-1}$) and ammonium ($8.4 \pm 0.4 \text{ mmol NH}_4^+ \text{ L}^{-1}$) (Table 2). For the final stage (stage VI), phosphorus concentration in the FBR influent was similar to that for stage V, while the ammonium concentration was increased to $20.0 \pm 1.4 \text{ mmol NH}_4^+ \text{ L}^{-1}$ (Table 2). For CSTR operation for stage VI, phosphorus concentration in the CSTR influent was two-fold higher than for stage V ($4.1 \pm 0.1 \text{ mmol PO}_4^{3-} \text{ L}^{-1}$), while ammonium concentration was similar to that in the CSTR influent for stage V.

Analytical methods

Ions concentrations, pH and conductivity were determined in the influent and effluent of both reactors. The concentrations of P-PO_4^{3-} and N-NH_4^+ were analyzed according to Standard Methods for the Examination of Water and Wastewater.²¹ Mg^{2+} , Ca^{2+} and K^+ concentrations were analyzed by ionic chromatography using a Metrohm 861 Advanced Compact IC equipped with a column Metrosep A Supp 5-250 and a 853 CO_2 Suppressor. pH measurements were conducted using an electrode Crison 5202 model,

connected to a pH meter (Crison PH 29). Conductivity was measured with a conductivity meter (Crison CM 35).

Solid samples were periodically taken from both reactors for observation and analysis. The mineral solids were observed regularly using a digital camera (Coolsnap, Roper Scientific Photometrics) combined with a stereomicroscope (Stemi 2000-C, Zeiss) in order to determined changes in appearance. The samples were washed with distilled water in order to eliminate impurities and soluble salts. Thereafter, they were settled for 30 min in a beaker in order to separate the precipitate from the bulk liquid. Precipitates were dried at 45°C for 24 h in order to avoid struvite thermal decomposition, which occurs above 55°C .⁶ Chemical composition and appearance of the precipitates were analyzed using a scanning electron microscope (SEM, ZEISS EVO[®]LS 15) coupled to an energy dispersive X-ray microanalysis detector (EDX, Oxford 300; LEICA Microsystems, Cambridge, UK). The crystalline nature of the precipitates was determined by X-ray diffraction (XRD; Siemens D505).

RESULTS AND DISCUSSION

Period I: phosphorus precipitation in the FBR

Stages I and II: Comparison of the use of industrial grade MgO and $\text{Mg}(\text{OH})_2$

For stage I, the operating pH in the reactor ranged between 9.6 and 7.8 (Fig. 2(A)). After batch addition of MgO powder the initial pH rose to 9.6 and decreased gradually to 7.8. It was considered that most of the MgO had been exhausted at this operating pH. As mentioned in Materials and methods the pH was not controlled during this stage. Attempts to control pH using a MgO slurry in water failed due to the tendency to agglomerate, leading to plugging of the tubing and lower part of the reactor (Fig. S1 in the Supporting information). Meanwhile, the pH in the reactor varied between 7.8 and 8.5 when adding the slurry of $\text{Mg}(\text{OH})_2$ (Fig. 2(B)). The maximum pH value observed for stage II was higher than the maximum set-point because solid particles of $\text{Mg}(\text{OH})_2$ slurry added continued to react with water, increasing the operational pH.

Regarding the phosphorus recovery efficiency, 84% phosphorus crystallization percentage was obtained using MgO as magnesium and alkali sources (stage I). In the first part of stage I, in which the pH was above 8.2, phosphorus concentration in the effluent was lower than $0.06 \text{ mmol PO}_4^{3-} \text{ L}^{-1}$ ($1.8 \text{ mg PO}_4^{3-} \cdot \text{mg P L}^{-1}$) while at lower pH values than 8.2, phosphorus concentration began to increase and reached values of $0.51 \pm 0.26 \text{ mmol PO}_4^{3-} \text{ L}^{-1}$ ($15 \text{ mg PO}_4^{3-} \cdot \text{P L}^{-1}$; Fig. 2(A)). Furthermore, the phosphorus recovery percentage was 95% in stage II (Fig. 2(B)). For stage II, phosphorus concentration in the effluent was $0.10 \pm 0.01 \text{ mmol PO}_4^{3-} \text{ L}^{-1}$. Thus, a phosphorus crystallization percentage higher than 84% was obtained using these industrial magnesium products, MgO and $\text{Mg}(\text{OH})_2$ slurry.

According to the magnesium products performance, the consumption of MgO was $5.5 \text{ mol Mg added mol}^{-1} \text{ P precipitated}$. This result indicated that the amount of MgO added was higher than the molar ratio of 1:1 to crystallize the phosphate as struvite. Moreover, the consumption of $\text{Mg}(\text{OH})_2$ slurry was lower than the consumption of MgO , which was around $3.2 \text{ mol Mg added mol}^{-1} \text{ P precipitated}$.

The slurry of $\text{Mg}(\text{OH})_2$ was more effective than the starting material, MgO , to recover the phosphorus by struvite crystallization. Moreover, the use of the industrial MgO was cumbersome. As mentioned previously, this powdered product, in contact with water

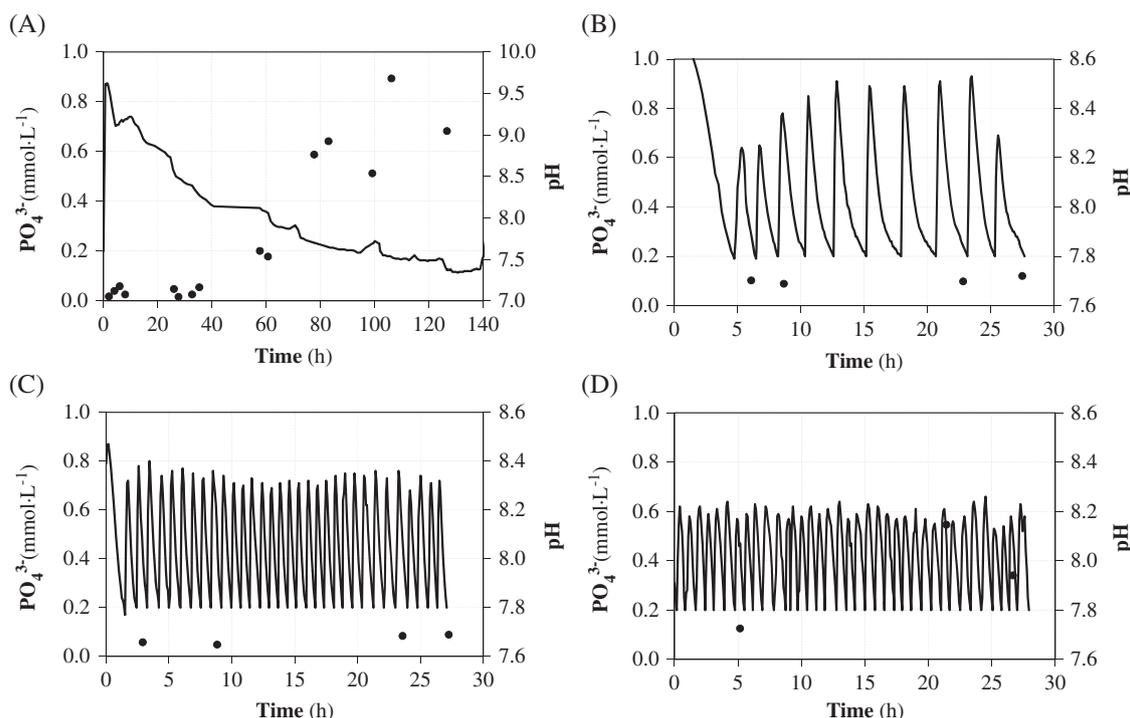


Figure 2. Phosphorus concentration (●) and pH (—) in the effluent for stage I (A); stage II (B); stage III (C); stage IV (D).

at room temperature, tends to agglomerate creating large stones, causing the plugging of tubing in the inlet of the reactor or accumulated at the bottom of the FBR. In contrast, agglomeration of $\text{Mg}(\text{OH})_2$ was not observed, which could be the reason for the lower product requirements. Thus MgO should be first converted to $\text{Mg}(\text{OH})_2$ by hydration in hot water in order to avoid the formation of agglomerates in the facility. Furthermore, the higher MgO consumption was attributed to the formation of these agglomerates.

The characteristics of MgO or $\text{Mg}(\text{OH})_2$ were usually ignored in previous work. For industrial grade products, percentage of MgO , specific surface area and the presence of unburned MgCO_3 were not taken into account. Probably for this kind of product, the specific surface and the presence of unburned MgCO_3 are two of the most important physical characteristics, together with the crystal size, determining the chemical reactivity of magnesium mineral.²² The specific surface area strongly influences chemical reactivity and depends on the production process conditions. Also the presence of unburned MgCO_3 could decrease the chemical reactivity of the magnesium product and, consequently, the efficiency of the hydration process. In the present case, the specific surface area of the industrial magnesium products used in this study was 18.4 and 20.5 $\text{m}^2 \text{g}^{-1}$ for MgO and $\text{Mg}(\text{OH})_2$, respectively.²³ Aforementioned results indicate that the hydration process increased the specific surface area. Reactivity of these products was measured using a batch test in which citric acid was used. The citric acid reactivity test of MgO and $\text{Mg}(\text{OH})_2$ slurry were previously performed in our laboratory by Silva.²³ The shorter the time of the test, the higher the reactivity of the Mg product. The chemical reactivity values were 5.1 min and 0.8 min, respectively.²³ These values correspond to the time needed for magnesium product to increase the pH of a citric acid solution from 4.0 to 8.2. Thus, the reactivity of $\text{Mg}(\text{OH})_2$ slurry is at least 6 times higher than the starting material, the industrial grade MgO product.

Stages II and III: comparison of the use of industrial grade $\text{Mg}(\text{OH})_2$ prepared from hydration in NaCl and MgAc_2

The pH in the reactor oscillated between 7.8 and 8.5 for stage II, and between 7.8 and 8.4 for stage III (Fig. 2(B) and(C)). However, in Fig. 2 it can be observed that the operating pH fluctuated more rapidly in stage III than in stage II. pH increased quickly once $\text{Mg}(\text{OH})_2$ slurry was added during stage III. This pH behaviour could be because the $\text{Mg}(\text{OH})_2$ slurry used for stage II was less reactive than $\text{Mg}(\text{OH})_2$ slurry added for stage III. $\text{Mg}(\text{OH})_2$ slurry used in stage III was prepared by using magnesium acetate, while $\text{Mg}(\text{OH})_2$ slurry added in stage II was prepared using NaCl . In order to confirm the influence of $\text{Mg}(\text{OH})_2$ on the behavior of reactor pH, the reactivity of both $\text{Mg}(\text{OH})_2$ slurries was determined. The citric acid reactivity test of these $\text{Mg}(\text{OH})_2$ slurries were 0.8 min and 2.8 min for the slurry of $\text{Mg}(\text{OH})_2$ formed from hydration in magnesium acetate and in NaCl , respectively. Thus, the $\text{Mg}(\text{OH})_2$ prepared with magnesium acetate was clearly more reactive than $\text{Mg}(\text{OH})_2$ prepared using NaCl .

Regarding phosphorus recovery, phosphorus crystallization efficiency was 94% when adding the $\text{Mg}(\text{OH})_2$ slurry prepared with NaCl (stage II). During this stage, phosphorus concentration in the effluent was $0.10 \pm 0.01 \text{ mmol PO}_4^{3-} \text{L}^{-1}$ (Fig. 2(B)). For stage III, the phosphorus crystallization efficiency was increased to 96%. In this stage, phosphorus concentration in the effluent was $0.07 \pm 0.02 \text{ mmol PO}_4^{3-} \text{L}^{-1}$ (Fig. 2(C)). Even considering that the reactivity of hydrated magnesium acetate product is higher than $\text{Mg}(\text{OH})_2$ formed from hydration in NaCl , the nature of the $\text{Mg}(\text{OH})_2$ hydration method affected slightly the concentration of phosphorus in the effluent. The reason for this behaviour is related to the high reactivity of both $\text{Mg}(\text{OH})_2$ slurries, the struvite kinetics and the high HRT. To determine the equilibrium concentration of phosphate, under these operational conditions, a chemical equilibrium software (Visual Minteq)²⁴ was used. This simulation software determined a phosphate concentration of 0.06 mmol PO_4^{3-}

L⁻¹, similar to that observed in the effluent of these stages. Therefore, the equilibrium was achieved due to the high HRT of the reactor and the high reaction rate of struvite crystallization. In this regard, the concentration of phosphorus in the effluent is influenced by the operating conditions, especially temperature and operating pH.

The consumption of both Mg(OH)₂ slurries was similar, 3.2 mol Mg added mol⁻¹ P precipitated and 3.1 mol Mg added mol⁻¹ P precipitated by adding Mg(OH)₂ slurry prepared with NaCl and MgAc₂, respectively. From the results obtained it can be determined that the hydration method used, Mg(OH)₂ slurry formed from hydration in MgAc₂ or in NaCl, did not affect the Mg(OH)₂ slurry consumptions for struvite crystallization. There was no difference in terms of phosphorus recovery efficiency between the use of both Mg(OH)₂ slurries.

Stages III and IV: effect of bicarbonate and ammonium ions on Mg(OH)₂ slurry consumptions

During period IV, bicarbonate ion was not present and ammonium concentration was halved (24.7 mmol NH₄⁺·L⁻¹) in the fed influent. In this stage, even when the phosphorus concentration in the influent was increased (4.4 mmol PO₄³⁻·L⁻¹), the phosphorus recovery percentage was 92% (Fig. 2(D)). Moreover, the Mg(OH)₂ consumption was significantly reduced from 3.1 (stage III) to 1.8 mol Mg added mol⁻¹ P precipitated (stage IV). These results indicated that the presence of bicarbonate ion and a high ammonium concentration affected the requirements of the alkali source added to recover the phosphorus as struvite, increasing the amount added of the Mg(OH)₂ slurry. A fraction of alkali added was consumed to counteract the protons released by the equilibrium reactions in which both ions are involved when pH value increased from the pH of the influent, around 7.5, to the operating pH of the reactor. An increase in pH caused an increase in free ammonia or the shifting of the carbonic acid equilibrium towards the two ionized forms of carbonic acid, bicarbonate and carbonate. In this way, the presence of ammonium is necessary to recover the phosphorus as struvite, but an excessive ammonium concentration produces an increase in the requirements for Mg(OH)₂ for struvite crystallization.

In this study, Visual Minteq was also used to corroborate the effect of bicarbonate and ammonium ions on the consumption of alkali (Fig. S2 in Supporting information). The theoretical Mg(OH)₂ slurry consumption was 2.8 mol Mg added per mol P recovered to increase the operating pH from 7.5 to 7.9. This value was slightly lower than the value obtained experimentally (3.2 and 3.1 mol Mg added mol⁻¹ P recovered for stages II and III, respectively). From the simulation results it was observed that the consumption of Mg(OH)₂ slurry is reduced by decreasing the concentrations of ammonium and bicarbonate in the influent. The presence of bicarbonate has a stronger effect on alkali requirements than the concentration of ammonium.

Analysis of precipitates obtained for period I

The appearance of the solid phases obtained in period I was observed using a stereomicroscope. The microscopical observations showed that most precipitates were transparent monocystals with the typical orthorhombic shape of struvite (Fig. 3). The nature of these solid phases was determined by XRD analysis (Fig. 3), which showed that phosphorus was crystallized entirely as struvite for all stages (Fig. 3). The amount of struvite in the solid phase was 76.0%, 60.9%, 65.6% and 98.0% for stages I, II, III and IV. The highest purity of struvite was detected for stage IV when a

bicarbonate-depleted medium was used (Table 1). So, solid phase purity was lower in the first three operating stages, when the bicarbonate and calcium ions were present in the influent, due to the formation of monohydrocalcite (CaCO₃·H₂O). The amount of this calcium carbonate was around 23% of the total dry mass of solid phase for the first three experimental stages.

Brucite, also known as magnesium hydroxide (Mg(OH)₂), was also detected in the solid phase of stages II and III (Fig. 3(B) and (C)). The amount of brucite was around 16% and 8% of the total dry mass for stages II and III, respectively. The presence of brucite was due to Mg(OH)₂ slurry added that either did not solubilise or react in the crystallization system. Also, quartz was detected in the solid phase of all experimental stages, which was less than 2% of the total dry mass. Quartz was present in the mineral composition of the industrial grade MgO used to prepare the slurry of Mg(OH)₂.

Period II: comparison of FBR and CSTR operations for struvite crystallization using an industrial grade Mg(OH)₂

Stages V and IV: Crystallization systems performance

During period II, the pH was maintained above 8.0 by adding Mg(OH)₂ slurry. During the whole experimental period, pH remained in the same range in both reactors (Fig. S3 in the Supporting information). The pH was between 8.0 and 8.6 for FBR operation, while pH varied between 8.0 and 8.9 for CSTR operation. For both reactor operations, instances were observed in which the pH was higher than 9.0. These pH values corresponded to the beginning of the daily operation. Once the daily operation was discontinued, the remaining Mg(OH)₂ continued to react, raising the reactor pH above 9.0.

Regarding phosphorus recovery efficiency during stage V, the phosphorus concentration in the effluent of the CSTR was lower than for the FBR. Figure 4 shows the evolution of reactor pH and phosphorus concentration in the effluent for both reactors. For the entire experimental operation of both reactors, it can be observed that these parameters were inversely related as the phosphorus concentration decreased as the operational pH increased. The average PO₄³⁻ concentration in the effluent of FBR and CSTR were 0.59 ± 0.33 and 0.43 ± 0.09 mmol PO₄³⁻·L⁻¹, respectively (Fig. 4). For this stage, the phosphorus recovery percentage was 71.3% and 80.3% for the operation of FBR and CSTR, respectively.

In the final stage of the operation of the FBR (stage VI), in which the ammonium concentration in the FBR influent was increased to 20.0 mmol NH₄⁺·L⁻¹, phosphorus concentration in the effluent was slightly reduced to 0.50 ± 0.21 mmol PO₄³⁻·L⁻¹ (Fig. 4(A)). This indicates that the increment of ammonium concentration increased the phosphorus recovery percentage from 71.3% to 74.7%. For the final stage of CSTR operation (stage VI), in which the phosphorus concentration in the influent was two-fold higher than for the previous stage, phosphorus concentration was 1.13 ± 0.62 mmol PO₄³⁻·L⁻¹ (Fig. 4(B)). Thus, the percentage of phosphorus recovery decreased to 70.5% for this stage. Probably, the main reason for the decrease of phosphorus recovery percentage was the variation of the operating temperature (Fig. 4(C)). The struvite dissolution process is an endothermic reaction, thus an increase in the temperature causes an increase in struvite solubility as stated in Crutchik and Garrido.²⁵ The operating temperature was not controlled during the operation of both reactors. It is important to note that the operation of both reactors was performed in different laboratories. As can be seen in Fig. 4(C), the operating temperature for CSTR varied from 14.5 °C to 29.0 °C over the operation time of stages V and VI. For CSTR, the phosphorus crystallization percentage decreased from 80.3% to 70.5% during stages V and VI, respectively. Thus,

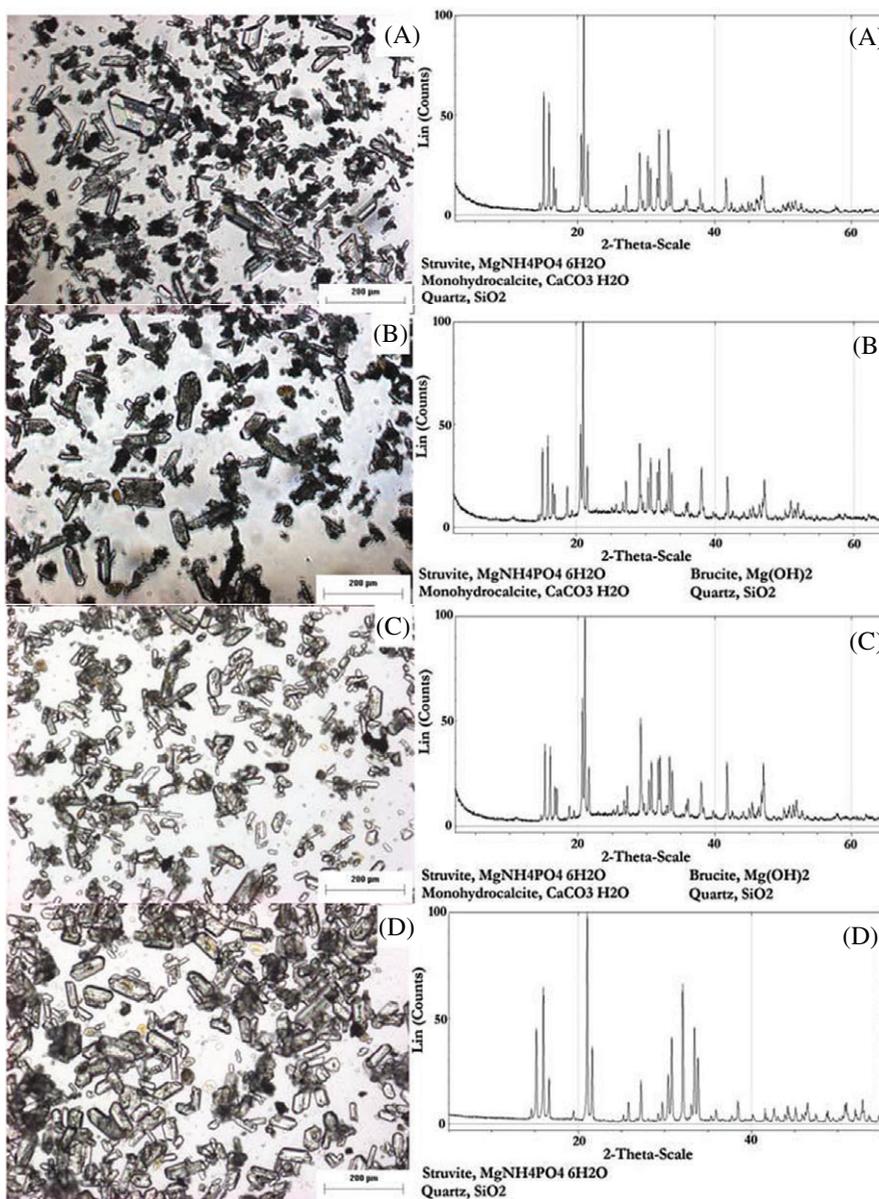


Figure 3. Stereomicroscope photographs (left) and XRD diffractograms (right) of precipitates formed for stage I (A); stage II (B); stage III (C); stage IV (D).

as expected, this increase of temperature led to an increase of the phosphorus concentration in the effluent. Wu *et al.* and Song *et al.*^{26,27} reported that high efficiencies of struvite crystallization can be obtained at low operating temperatures. With regard to FBR operation, the effect of temperature on the efficiency of struvite crystallization could not be observed. In this case, the temperature did not vary significantly throughout the experimental time. The room temperature was around 20 °C during the whole experimental time of FBR operation.

Analysis of precipitates of the FBR and CSTR operations

Both in FBR and CSTR operations, the appearance and nature of Mg(OH)₂ slurry and precipitates produced were analyzed. An XRD technique was used to identify the crystalline nature of these solid phases. Also, a semi-quantitative determination of solid phases was performed using XRD technique. Besides, microscopical observations of solid phases were made by SEM – EDX analysis.

For the slurry of Mg(OH)₂, XRD results detected that brucite was the most abundant mineral present at 66%. Periclase (MgO) was also detected (Fig. S4(A) in the Supporting information). The presence of periclase, 12%, was attributed to the fraction of magnesium oxide that was not hydrated during the hydration of this magnesium product. Other minerals such as gypsum (CaSO₄·2H₂O, 8%), quartz (SiO₂, 4%), muscovite (KAl₃Si₃O₁₀(OH,F)₂, 2%) and hornblende ((Ca,Na)₂(Mg,Fe,Al)₅(Al,Si)₈O₂₂(OH)₂, 8%) were also detected in the slurry of Mg(OH)₂ (Fig. S4(A) in the Supporting information). The presence of these elements can be attributed to impurities in the raw material, magnesium ore, used to produce the industrial Mg(OH)₂ used in this study.

Regarding the precipitates produced by the operation of FBR and CSTR, both precipitates had similar appearance (Fig. S4(B) and (C) in Supporting information). SEM microphotographs show that most of the precipitates were monocrystals. In both reactor

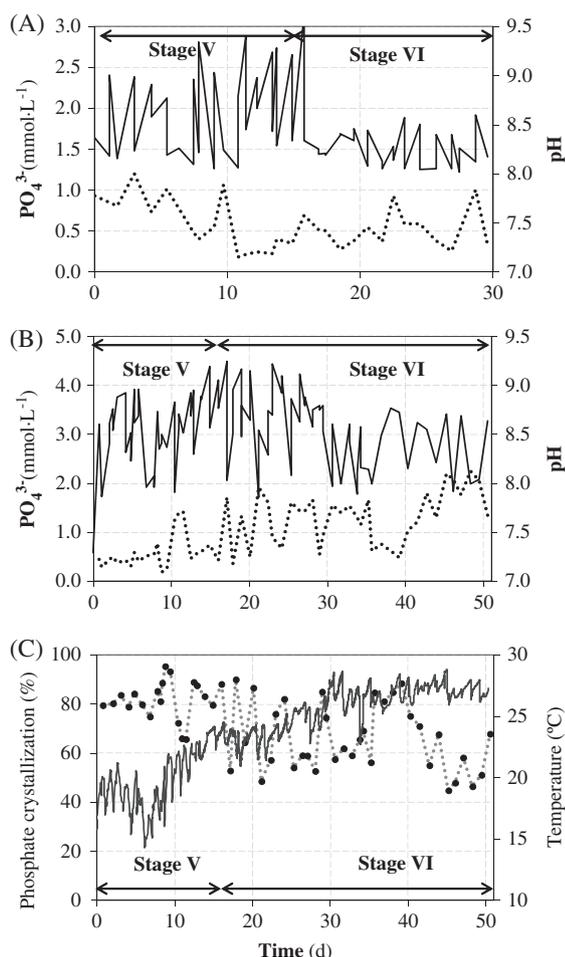


Figure 4. (A) pH (—) and phosphorus concentration (●●) in the effluent for FBR, and (B) CSTR; and (C) temperature (—) and phosphorus concentration (●●) in the effluent for CSTR operation.

operations, agglomeration of struvite crystals was not observed. Besides, the amount of fine crystals in the precipitates of FBR was higher than in the CSTR precipitates.

XRD results determined that phosphorus was crystallized totally as struvite. The content of struvite was 84% and 87% of the total mass for the FBR and CSTR precipitates, respectively. XRD analysis also determined the presence of a small fraction of brucite, 4% and 1% in the precipitates of FBR and CSTR, respectively (Fig. S4(B) and (C) in Supporting information). The presence of brucite was attributed to the added $Mg(OH)_2$ that did not dissolve in the crystallization systems. The lower content of $Mg(OH)_2$ in the solid phase of CSTR was because the CSTR promoted effective use of $Mg(OH)_2$. CSTR had a high mixing capacity and high contact time between influent ions, $Mg(OH)_2$ and crystals in suspension. Also, muscovite, quartz and albite were identified by XRD analysis (Fig. S4(B) and (C) in Supporting information). The amount of these minerals was less than 6% of the total dry mass. The presence of these minerals was due to the impurities present in the industrial $Mg(OH)_2$ slurry used.

Technical and economic evaluation of the use of the industrial $Mg(OH)_2$ slurry for struvite crystallization

For stages V and VI, the use of industrial $Mg(OH)_2$ slurry as magnesium and alkali sources was evaluated to determine the most

efficient reactor configuration. For stage V, the consumption of $Mg(OH)_2$ slurry was 1.6 and 1.1 mol Mg added mol^{-1} P precipitated (3.7 and 2.5 t-industrial Mg product added t^{-1} P precipitated) for FBR and CSTR, respectively. So, the amount of added $Mg(OH)_2$ slurry in CSTR was 10% higher than the stoichiometric amount required to crystallize the phosphorus as struvite. These results indicated that CSTR was more efficient than FBR to recover the phosphorus as struvite by adding $Mg(OH)_2$ slurry under similar operating conditions. The difference of the chemical requirements was caused by the high mixing intensity in the CSTR and the higher contact time between the slurry and the influent. As mentioned above, the TR corresponded to 21% of HRT for the FBR configuration; however, the HRT and RT were the same in the CSTR configuration. Thus, the good mixing ability of the CSTR facilitated contact between the solid phase and influent in the liquid phase.

For stage VI, the composition of the influents for FBR and CSTR were varied to determine the effect of ammonium and phosphate concentrations on the consumption of $Mg(OH)_2$ slurry. During the operation of FBR, when the ammonium concentration was increased, the consumption of $Mg(OH)_2$ increased from 1.6 to 3.6 mol $Mg(OH)_2$ added mol^{-1} P precipitated (8.5 t-industrial Mg product added t^{-1} P precipitated). This increase of the amount of $Mg(OH)_2$ slurry added was similar to the increase of the molar ratio of $NH_4^+ : PO_4^{3-}$ in the FBR. In light of the above, a high ammonium concentration increased the requirements of $Mg(OH)_2$ for recovering phosphorus as struvite, which is in agreement with results found during stage IV (period I).

For the final stage of CSTR operation (stage VI), when the phosphate concentration was twice than for stage V, the amount of $Mg(OH)_2$ added was less than for the previous stage. In this stage, the consumption of $Mg(OH)_2$ was reduced from 1.1 to 1.0 mol $Mg(OH)_2$ added mol^{-1} P precipitated (2.2 t-industrial Mg product added t^{-1} P precipitated). This indicated that the amount of $Mg(OH)_2$ slurry added was the stoichiometric amount required to crystallize the phosphorus as struvite. This improvement in the efficiency of the $Mg(OH)_2$ was related with the increased concentration of phosphorus in the influent, which improved the potential for phosphorus crystallization.

The costs associated with the use of the industrial $Mg(OH)_2$ for struvite crystallization were determined for period II. In this study, the operating costs due to $Mg(OH)_2$ requirements were estimated considering an estimated cost of the industrial grade $Mg(OH)_2$ of 350 € t^{-1} . In this sense, the estimated operating costs were 770 € t^{-1} P precipitated using the CSTR; while the operating cost was 1310 € t^{-1} P precipitated using the FBR. Thus, the CSTR was more efficient and cheaper than the FBR. In addition, these operating costs are much lower than those estimated using other processes to remove/recover phosphorus from wastewater. In this regard, the cost of phosphorus precipitation by conventional processes, adding aluminium or iron salts, is between 2000 and 3000 € t^{-1} P precipitated.¹ In struvite crystallization, the cost of the addition of an external magnesium source has been estimated between 700 and 4000 € t^{-1} P precipitated. Indeed, the struvite crystallization cost by adding $MgCl_2$ and NaOH is around of 4000 € t^{-1} P precipitated;²⁸ while the cost for struvite crystallization using $MgSO_4$ is estimated around 2000 € t^{-1} P precipitated.^{29,30} Similar struvite operating cost has been determined by using magnesium dosing by electro-dissolution.¹³ On the other hand, Señoráns *et al.*⁹ reported that the operating cost of struvite crystallization at industrial scale was around 2900 € t^{-1} P precipitated. These authors used seawater as magnesium source, in fact, the chemical cost was mainly due to the alkali requirements.

Thus the use of industrial $\text{Mg}(\text{OH})_2$ could be an economical alternative to other magnesium sources such as MgCl_2 , NaOH , MgSO_4 or magnesium dosing by electro-dissolution. The estimated costs of the use of $\text{Mg}(\text{OH})_2$ are in agreement with other studies.^{14,29,30} Wu et al.¹⁴ claimed that $\text{Mg}(\text{OH})_2$ could be a very promising alternative magnesium and alkali source for struvite crystallization. These authors mentioned that the use of $\text{Mg}(\text{OH})_2$ could reduce the operating costs of the struvite crystallization process. Furthermore, it is important to take into account that struvite could be commercialized as agricultural fertilizer. In the literature, the estimated market price of struvite is between 2000 and 4500 € t⁻¹ P.^{30–32} On the basis of our experimental results, struvite crystallization by adding an industrial $\text{Mg}(\text{OH})_2$ could be economically viable.

CONCLUSIONS

- MgO and specially $\text{Mg}(\text{OH})_2$ industrial grade products are two promising options for struvite crystallization. However, $\text{Mg}(\text{OH})_2$ slurry was more effective than the starting material, MgO, to recover phosphorus. At the same operational conditions, the observed consumption of MgO was 5.5, higher than that using $\text{Mg}(\text{OH})_2$ of 3.2 mol Mg added mol⁻¹ P precipitated. Moreover, MgO tends to agglomerate creating large stones, causing operating problems.
- Ammonium and bicarbonate ions affected the requirements of the alkali source added, $\text{Mg}(\text{OH})_2$ slurry, to recover phosphorus as struvite.
- The CSTR was more efficient than the FBR for struvite crystallization using industrial $\text{Mg}(\text{OH})_2$. However, if the aim of struvite crystallization is to recover phosphorus into granular product, the FBR can be a good option. CSTR could limit the growth of crystals due to the high shear stress caused by the mixers required to keep the crystals in suspension.
- Struvite crystallization by adding an industrial grade $\text{Mg}(\text{OH})_2$ could be economically viable with regard to alternative physico-chemical P removal processes using metal salts, increasing the attractiveness of this P recovery process.

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Supporting Information

Supporting information may be found in the online version of this article.

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