



Phosphate recovery through struvite precipitation by CO₂ removal: Effect of magnesium, phosphate and ammonium concentrations

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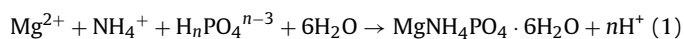
ABSTRACT

In the present study, the precipitation of struvite (MgNH₄PO₄·6H₂O) using the CO₂ degasification technique is investigated. The precipitation of struvite was done from supersaturated solutions in which precipitation was induced by the increase of the solution supersaturation concomitant with the removal of dissolved carbon dioxide. The effect of magnesium, phosphate and ammonium concentrations on the kinetics and the efficiency of struvite precipitation was measured monitoring the respective concentrations in solution. In all cases struvite precipitated exclusively and the solid was characterized by powder XRD and FTIR. The morphology of the precipitated crystals was examined by scanning electronic microscopy and it was found that it exhibited the typical prismatic pattern of the struvite crystals with sizes in the range between 100 and 300 μm. The increase of magnesium concentration in the supersaturated solutions, resulted for all phosphate concentration tested, in significantly higher phosphate removal efficiency. Moreover, it is interesting to note that in this case the adhesion of the suspended struvite crystals to the reactor walls was reduced suggesting changes in the particle characteristics. The increase of phosphate concentration in the supersaturated solutions, for the magnesium concentrations tested resulted to the reduction of struvite suppression which reached complete suppression of the precipitate formation. Excess of ammonium in solution was found favour struvite precipitation. Contrary to the results found with increasing the magnesium concentration in solution, higher ammonium concentrations resulted to higher adhesion of the precipitated crystallites to the reactor walls. The results of the present work showed that it is possible to recover phosphorus in the form of struvite from wastewater reducing water pollution and at the same time saving valuable resources.

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1. Introduction

The content of wastewater in pollutants responsible for eutrophication [1] like phosphate and ammonia is in general high and there is urgent need to regulate their concentration levels prior to disposal to aquatic reservoirs. Eutrophication may also occur in nature provided that there is abundance of nutrients stimulating plant growth in lakes, estuaries, or slow-moving streams. Phosphate and ammonia can be removed simultaneously in the presence of magnesium through by precipitation as the sparingly soluble magnesium ammonium phosphate salt, known as struvite (MgNH₄PO₄·6H₂O) [2,3]. Struvite crystals are white in color with orthorhombic habit and precipitate according to reaction (1) [4]:



with $n = 0, 1$ and 2 , depending on the solution pH, which regulates the distribution of the various phosphate species.

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Key parameters controlling the precipitation process of struvite from the respective supersaturated solutions, include solution pH [5,6], temperature [6], rate of stirring [7,8], supersaturation [9,10], nature of materials [11,12] and the presence of foreign ions including calcium [8,13] and sulphate [14]. Ali [15] investigated struvite precipitation using thermodynamic models and simulation processes in which all equilibria were taken into consideration. In aqueous solutions containing dissolved magnesium, ammonium and phosphate ions a number of complexes are formed which result in the reduction of the concentrations of the free ions (Mg²⁺, NH₄⁺ and PO₄³⁻) which are the constituents of the crystalline precipitate. Abbona et al. [6] studied the effect of pH and concentration and of the corresponding supersaturation ratios, β_S and β_N , of struvite and newberyite (MgHPO₄), respectively, on the crystallization of these two magnesium phosphate compounds. They showed that when $\beta_N/\beta_S < 2$, struvite always crystallizes first, whereas for $\beta_N/\beta_S > 4$ the precipitation of newberyite precedes.

The effect of magnesium concentration in the supersaturated solutions on the precipitation of struvite has been widely investigated [16,17]. However, the effect of phosphate concentration on struvite precipitation has not been adequately investigated so far,

especially in cases where magnesium concentration was kept constant in a series of experiments. Quintana et al. [17] showed that the yield of struvite, precipitated by magnetic stirring and aeration, increased upon increasing magnesium concentration in solution. Pastor et al. [18] showed that higher than 80% of phosphorus was removed through struvite precipitation in a stirred reactor. This efficiency could be improved by increasing the $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio. Lee et al. [19] showed that adding less than 0.05 M of both magnesium and phosphate salt or more than ~ 0.07 molar ratio of magnesium with respect to total nitrogen resulted in the continuous formation of struvite during the composting process of swine manure.

The recovered ammonium and phosphate through struvite crystallization can be used efficiently as a valuable mineral fertilizer for plants. On the other hand however severe scaling problems because of the formation of struvite deposits in pipes, pumps and screens in wastewater treatment plants (WWTP) have been reported [11,12]. The determination of the experimental conditions for maximum phosphate removal efficiency from wastewater effluents without at the same time forming undesirable scale on WWTP equipment, is of paramount importance.

Carbon dioxide stripping could be applied to struvite crystallization [20,21]. CO_2 removal from the aqueous solutions results to the increase of pH. Since the solution supersaturation with respect to struvite increases drastically upon increasing the solution pH, struvite precipitation is favoured, thus reducing the need to increase solution pH by the addition of alkali [22]. The removal efficiency of the CO_2 stripper depends on several parameters, i.e., the characteristics of the influent, including total alkalinity, temperature, initial concentration of dissolved CO_2 gas and influent flow rate, effluent recycle rate and aeration rate [23]. In an earlier report by our research group [24] the effects of the airflow rate and solution pH on struvite precipitation by the dissolved CO_2 degasification technique were presented. It was shown that the phosphate removal efficiency could be improved by increasing the airflow rate to 25 L min^{-1} , or by increasing the initial solution pH for higher air flow rates [24]. In the present work, in an attempt to ameliorate phosphorus removal through struvite precipitation avoiding scale formation, the effect of magnesium, phosphate and ammonium concentrations in the supersaturated solutions on struvite precipitation were investigated. Experiments were done in which magnesium concentrations were increased while phosphate concentration was kept constant. In a second series of experiments phosphate and ammonium concentrations in solutions were varied for given, constant magnesium concentration in the supersaturated solutions.

2. Materials and experimental methods

The experimental solutions were prepared by mixing accurately measured volumes of magnesium chloride, ammonium dihydrogen phosphate (or alternatively potassium dihydrogen phosphate and ammonium chloride) stock solutions in a 50 mg L^{-1} CaCO_3 solution. The solutions were prepared from the crystalline solids: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Fluka, >99%), $\text{NH}_4\text{H}_2\text{PO}_4$ (Fluka, >99%) KH_2PO_4 (Sigma–Aldrich, >99%) and NH_4Cl (Sigma–Aldrich, >99%) dissolved in distilled water. The 50 mg L^{-1} CaCO_3 solution was prepared by dissolving the appropriate amount of solid calcium carbonate (Merck, >99%) in distilled water by CO_2 bubbling at atmospheric pressure till saturation of the solution with CO_2 . Next, the dissolved carbonate was removed bubbling atmospheric air through the solution using a sparger for better dispersion of the gas into the aqueous phase.

Past pH adjustment to an initial value of 6.5 with 1 M NaOH solution, 600 mL of the experimental solution were introduced in a 1 L

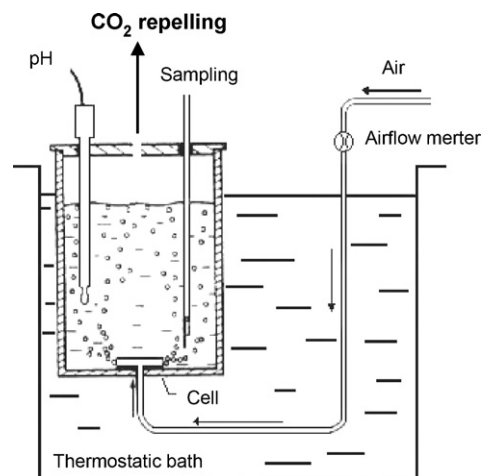


Fig. 1. Schematic experimental setup of the dissolved carbonate removal technique.

cylindrical polyvinyl chloride (PVC) reactor covered with a lid from the same material, bearing ports for sampling, air sparger, sensors, etc. The struvite precipitation was induced by the dissolved CO_2 degasification technique. Bubbling the air supply through the solution resulted in the increase of the solution pH to higher values. Depending on the concentration of the magnesium, phosphate and ammonium in solution, struvite precipitation was initiated spontaneously at the appropriate pH value corresponding to a critical value of supersaturation with respect to struvite. Airflow through the reactor was controlled and monitored by a precalibrated airflow meter. The solution temperature was controlled by a thermostat with circulating water. The solution pH in the reactor was monitored with a combination glass/Ag/AgCl electrode, calibrated with the appropriate standard buffer solutions. A schematic illustration of the experimental setup is given in Fig. 1.

All experiments were carried out at a fixed airflow rate of 40 L min^{-1} . It was shown that the yield of struvite decreased upon increasing solution temperature from 25 to 60°C [25]. All experiments were done at 25°C . A series of experiments was done for the investigation of the effect of magnesium concentration in the supersaturated solutions on the precipitation of struvite. In this series of experiments various increasing magnesium concentrations were used for the initial phosphorus concentration was 130.2 mg L^{-1} . The $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio varied from 1 to 5. In a second series of experiments, phosphate concentration in the solutions varied while the magnesium concentration was kept constant and equal to 92.3 mg L^{-1} . In this series of experiments, ammonium and phosphate ions were added as $\text{NH}_4\text{H}_2\text{PO}_4$ so that the molar ratio $\text{N}:\text{H}_n\text{PO}_4^{n-3}$ was equal to 1:1. The $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio varied from 1/5 to 5. Finally, a third series of experiments were carried out in which initial magnesium concentration was 130.2 mg L^{-1} while ammonium concentration in solution varied, in order to investigate the effect of this parameter as well. For these experiments, magnesium, ammonium and phosphate ions were added as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NH_4Cl and KH_2PO_4 , respectively. The molar ratio $\text{Mg}:\text{H}_n\text{PO}_4^{n-3}$ was kept equal to 1:1 and the $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$ molar ratio varied from 1/4 to 3 (corresponding to ammonium concentration in the range $18.93\text{--}227.27 \text{ mg L}^{-1}$). In all experiments, samples were withdrawn periodically, filtered through $0.45 \mu\text{m}$ membrane filters and the filtrates were analyzed for phosphate spectrophotometrically [26]. At the end of each experiment, the solution was filtered through $0.45 \mu\text{m}$ membrane filters and the solid precipitates were characterized by powder X-ray diffraction (XRD), Fourier transform infra-red (FTIR) and scanning electron microscopy (SEM). XRD was carried out at room temperature with a Philips X'PERT PRO diffractometer in step scanning mode using

Co K α radiation. The XRD patterns were recorded in the range $2\theta = 5\text{--}70^\circ$. A small angular step of $2\theta = 0.017^\circ$ and a fixed counting time of 4 s were used. The XRD reflection positions were determined using 'X-Pert HighScore Plus' software. The FTIR spectra were recorded on Shimadzu IRAffinity-1 in the $400\text{--}4000\text{ cm}^{-1}$ range using pressed powder samples in KBr medium.

Particle size measurements were done in a Mastersizer 2000 combined with a Hydro 2000MU (Malvern Instruments).

The mass fractions of the precipitates formed in the bulk solution, τ_{sol} (%), and on the cell walls, τ_{walls} (%), were calculated as follows:

$$\tau_{sol} = \frac{m_{sol}}{m_T} \times 100 \quad (2)$$

$$\tau_{wall} = 100 - \tau_{sol} \quad (3)$$

where m_T is the total mass of precipitates and m_{sol} is the precipitates mass in the bulk solution. m_T was determined directly by weighing the collected solids or from the phosphorus concentration (M)–time profiles using the following equation:

$$m_T = ([P]_0 - [P]_f) \times M_{struvite} \quad (4)$$

where $[P]_0$ is the initial phosphorus concentration, $[P]_f$ is the phosphorus concentration at the end of precipitation and $M_{struvite}$ is the molar weight of struvite.

For struvite, the activity-based supersaturation ratio Ω was calculated according to:

$$\Omega = \frac{a_{Mg^{2+}} a_{NH_4^+} a_{PO_4^{3-}}}{K_{sp}} \quad (5)$$

where K_{sp} is thermodynamic solubility product of struvite and $a_{Mg^{2+}}$, $a_{NH_4^+}$ and $a_{PO_4^{3-}}$ are the activities of Mg^{2+} , NH_4^+ and PO_4^{3-} ions, respectively. The relationship between the activity of an ion i , a_i , with the respective analytical concentration, C_i , is given by:

$$a_i = \gamma_i C_i \quad (6)$$

In Eq. (6), γ_i is the activity coefficient for the ion i and it was calculated according to the modification of the Debye–Huckel equation proposed by Davies [27]:

$$\log(\gamma_i) = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (7)$$

where A is the Debye–Hückel constant dependent on temperature ($A = 0.499$ at 25°C [28]), Z_i is the charge of an ion i , and I is the ionic strength defined by

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (8)$$

with C_i being the molar concentration of the ion i .

3. Results

3.1. Effect of magnesium concentration on struvite precipitation

The time profiles of pH and phosphate concentration for different $Mg/H_nPO_4^{n-3}$ molar ratios are shown in Fig. 2. In the series of the experiments shown, the initial phosphorus concentration was 130.2 mg L^{-1} . A rapid increase of the pH was observed during first few minutes because of the removal of carbonate from solution. Past the attainment of a maximum pH value (defined as the precipitation pH) the level of which depended on the $Mg/H_nPO_4^{n-3}$ molar ratio, the pH decreased due to struvite precipitation. At the end of precipitation and following a period of negligible pH change, it started drifting towards higher values due to the continuing carbonate removal the rate of which was apparently higher than the

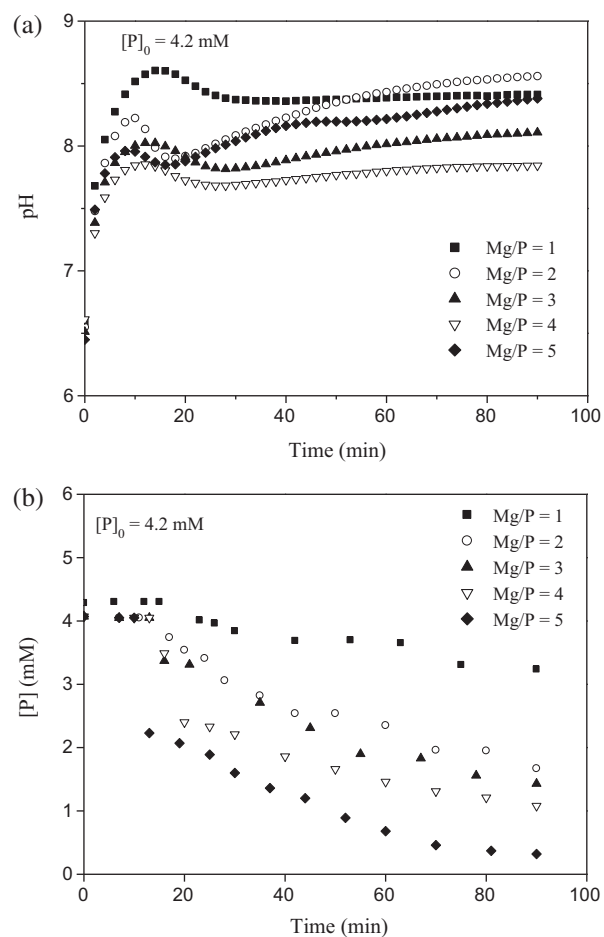


Fig. 2. Variation of (a) pH and (b) phosphate concentration as a function of time for different values of the molar ratio $Mg/H_nPO_4^{n-3}$ ($[P]_0 = 130.2\text{ mg L}^{-1}$).

rate of precipitation (Fig. 2a). The precipitation pH shifted to lower values for an increase of the $Mg/H_nPO_4^{n-3}$ molar ratio from 1 to 4. For example, the precipitation pH 8.6 corresponding to a molar ratio $Mg/H_nPO_4^{n-3} = 1$ was reduced to 7.8 for a value of the molar $Mg/H_nPO_4^{n-3}$ ratio equal to 4 (Table 1). For $Mg/H_nPO_4^{n-3}$ molar ratio of 5, a slight increase of the precipitation pH was observed and it was attributed to the precipitation of other solids originating from the different species present in the supersaturated solutions. The XRD patterns of the solids collected past the precipitation cycle are shown in Fig. 3. It should be noted that the intensities of the reflections correspond to normalized values with reference to the most intense reflection. The excellent agreement of the 2θ position of the reflections of the XRD patterns obtained for precipitates formed from supersaturated solutions in which the $Mg/H_nPO_4^{n-3}$ molar ratios were between 1 and 4, with the reflections of reference struvite [29] identified the precipitate as struvite. It is interesting to note that the relative intensities of the precipi-

Table 1

Induction time (t_n), precipitation pH, phosphate removal, precipitates mass fractions on the cell walls (τ_{wall}) and in the bulk solution (τ_{sol}) for different $Mg/H_nPO_4^{n-3}$ molar ratios ($[P]_0 = 130.2\text{ mg L}^{-1}$).

$Mg/H_nPO_4^{n-3}$	t_n (min)	Precipitation pH	Phosphate removal (%)	τ_{wall} (%)	τ_{sol} (%)
1	15	8.6	25	94	6
2	11	8.2	59	65	35
3	13	8	65	63	37
4	13	7.8	73	56	44
5	10	7.9	92	2	98

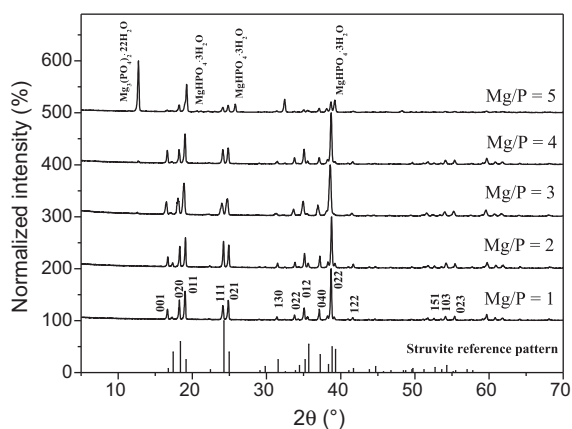


Fig. 3. XRD patterns of the precipitates obtained for different values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ ($[\text{P}]_0 = 130.2 \text{ mg L}^{-1}$) in comparison with the reference diffraction pattern for struvite [29].

tates showed differences in comparison with the reference struvite material and the changes were related with the excess of magnesium in the supersaturated solutions. For example, the relative intensities of the reflections 1 1 1 and 0 2 1 of struvite corresponding to $d_{hkl} = 4.284 \text{ \AA}$ ($2\theta = 24.117^\circ$) and 4.154 \AA ($2\theta = 24.896^\circ$), respectively, decreased with the increase of magnesium in the solution. Changes of the relative intensity of reflections in the crystalline XRD pattern suggested changes in the texture of the crystalline material and more specifically changes in the crystallite size. On the other hand, a reflection at $d_{hkl} = 8.067 \text{ \AA}$ ($2\theta = 12.740^\circ$) with a very low intensity, appeared in the XRD pattern of the precipitate formed for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio in the supersaturated solutions equal to 3 and 4. This reflection, was attributed to cattite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O}$), its intensity becoming the most intense for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$ (Fig. 3). Moreover, the XRD pattern of the precipitates obtained for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$ showed both the presence of struvite and newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$). The reflections and the relative intensities for struvite and cattite in the respective XRD patterns were low. As may be seen, the increase of magnesium concentration in the supersaturated solutions in a way that the molar $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ value may be 5, affected the purity of the struvite precipitates.

Concerning the solution composition in this first series of experiments, as may be seen in Fig. 2b, phosphate concentration remained constant during first few minutes, suggesting that during the respective time period the solution was stable. Following this stability time, phosphate concentration started decreasing with time, due struvite precipitation for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio values ≤ 4 and of newberyite and cattite for values of $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$. The slope of the variation of phosphate concentration in solution with time kept decreasing till it reached a value practically zero, suggesting that the precipitation was over (Fig. 2b).

The pH time profiles were used as traces indicative of the precipitation process. Changes of slope in the respective plots observed past time periods during which the slope was zero, were used for the calculation of the induction time, t_n , preceding the precipitation of struvite (Fig. 2a). The values obtained were in good agreement with the respective values obtained from the phosphate concentration–time profiles. In this latter case, the transition from $d[\text{phosphate}]/dt = 0$ to $d[\text{phosphate}]/dt > 0$ was taken as the criterion for the onset of precipitation. The values obtained for the induction times at various solutions supersaturations are summarized in Table 1. The increase of the magnesium concentration in the supersaturated solutions caused a decrease of t_n . In fact, t_n decreased from 15 min for values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$ to 10 min for values of $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$. Com-

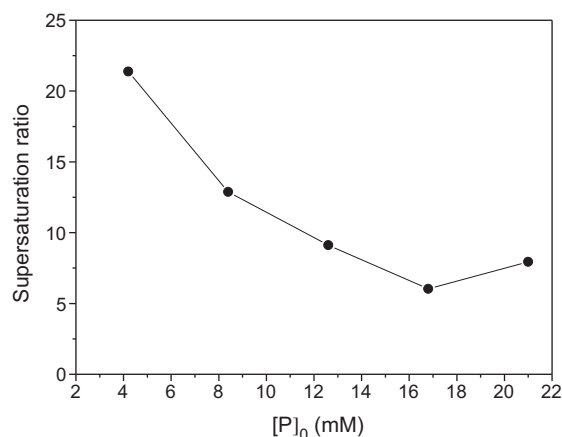


Fig. 4. Supersaturation ratio with respect to struvite as a function of the initial phosphate concentration in the supersaturated solutions ($[\text{P}]_0 = 130.2 \text{ mg L}^{-1}$).

parable results were found by Bhuiyan et al. [30], who showed that increase of magnesium concentration from 71 to 107 mg L^{-1} resulted in the decrease of the induction time for struvite precipitation, in a stirred fluidized bed reactor, from ~ 5 to ~ 1 min, respectively. Bouroupoulos and Koutsoukos [31] found that for a magnesium concentration of 66.82 mg L^{-1} , $\text{Mg}:\text{N}:\text{H}_n\text{PO}_4^{n-3}$ molar ratio equal to 1 and pH 8.5, the struvite induction time was 125 min, which is significantly higher than that obtained in the present work where higher magnesium concentrations (102 mg L^{-1}) were used. Increase of the magnesium concentration to 97.20 mg L^{-1} resulted in the decrease of the struvite induction time to 6 min [31]. This induction time is comparable to that obtained in the present work for a higher magnesium concentration of 510.4 mg L^{-1} ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$). It should be noted that t_n decreased increasing the airflow rate at constant magnesium concentration or at higher initial solution pH [24].

It is interesting to note that the phosphate concentration in solution at the end of precipitation was lower for the experiments in which the initial concentration of magnesium concentration in solution was higher. Thus for example, phosphate concentration in solution decreased from 3.24 mM for values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$ to 0.32 mM for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$, corresponding to an increase of the phosphate removal from 25 to 92%, respectively (Table 1). It should be noted that upon increasing the magnesium concentration in solution, a significant drop of the phosphate concentration was observed past the onset of precipitation. Past this initial drop, phosphate concentration decreased progressively. For values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$, a slight decrease of phosphate concentration was observed, i.e., the phosphate removal efficiency was equal to 6% after 23 min ($t_n = 15$ min). For higher values of the $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio, the phosphate removal efficiency reached 49% after 19 min ($t_n = 10$ min). This removal efficiency value is lower in comparison with the value reported by Nelson et al. [16]. In their investigation, the authors showed that the precipitation of struvite from anaerobic swine lagoons resulted in a decrease of $\text{PO}_4\text{-P}$ concentrations by 85% within 20 min for initial value of $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio of 1.2/1. This difference may be due to the different solution composition and the higher pH (=9) in comparison to the present work. In general, the experimental data suggest that higher magnesium concentrations in the supersaturated solutions, resulted in higher phosphate removal within a few minutes (10–15 min). The evolution of the supersaturation ratio (SSR) with respect to struvite in the effluent with the magnesium concentrations used in the different experiments is shown in Fig. 4. For $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ values ≤ 4 , SSR decreased with increasing magnesium concentra-

tion in the solutions, while slightly higher values were obtained in the effluent for values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$. More specifically, SSR decreased from ~ 21 to ~ 6 upon increasing magnesium concentration from 130.2 ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$) to 520.8 mg L^{-1} ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 4$), respectively. Decrease of the SSR in the effluent solution was identical with a significant improvement of the phosphate removal efficiency (Table 1). According to the findings of the present work, higher initial values for the SSR do not necessarily imply the formation of higher mass of struvite precipitates. Pastor et al. [18] suggested that the percentage of the total phosphate removed from artificial wastewater was not related with the SSR. It should be noted that a number of physico-chemical parameters may influence phosphorus removal, i.e., the final solution pH, the background solution composition, the supersaturation, the mixing energy (turbulence) and the nature of seed material used to initiate or promote precipitation. The increase of magnesium concentration in solution is accompanied with an increase of the chloride concentration (counter ion) resulting in higher ionic strength and lower SSR values (Eq. (7)). Moreover, ion pairing of the carbonate ions with the free magnesium ions in solution reduces further the SSR with respect to struvite in solution. For given magnesium concentration, the SSR of the background solution with respect to struvite increased ($\geq \sim 6$) as a result of carbonate scrubbing from the solution which shifted the solution pH to more alkaline values, thus providing conditions suitable for struvite nucleation and crystal growth. It should be however noted, that during the course of precipitation, the solution pH is not only affected by the carbonate removal but also by the rate of struvite precipitation, a process accompanied by proton release in solution (Eq. (1)). It should be noted that for values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$, the solution was also supersaturated with respect to cattite ($\Omega_{\text{cattite}} = \sim 28$) and newberyite ($\Omega_{\text{newberyite}} = \sim 3$).

The increase of the phosphate removal efficiency with increasing magnesium concentration was also found upon inducing struvite precipitation by magnetic stirring [17]. The higher phosphate removal efficiency with increasing the magnesium concentration in synthetic solutions, found in the present work, is in agreement with earlier reports concerning struvite precipitated from swine wastewater [32] or from artificial wastewater [18]. For example, Pastor et al. [18] showed that an increase of the $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio from 0.8 to 1.1 resulted in an increase of phosphorus removal efficiency, from artificial wastewater in a stirred tank reactor, from 60 to 70.3%, respectively. However, Jaffer et al. [33] have reported that phosphate removal efficiency from liquors obtained from slough sewage treatment works did not change upon increasing magnesium concentration in solution. In fact, phosphate removal efficiency of $\sim 95\%$ was reached for magnesium concentration of 62.69 mg L^{-1} while for concentrations in the range 62.69–255.63 mg L^{-1} , the phosphorus concentration in solution remained constant.

It is interesting to note that increase of the magnesium concentration in solution reduced the crystals adhesion on the walls of the reactor vessel. This process of precipitation–adhesion may be consists the primary cause of fouling. Bulk precipitation was favoured over solid deposition at the reactor walls as suggested by the fact that τ_{sol} increased and τ_{wall} decreased. More specifically, τ_{wall} decreased from 94% for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$ to 2% for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$ (Table 1). It may be suggested that fouling is due to the development of higher local supersaturation near a part of the surface area provided by the reactor walls or other reactor equipment parts because of poor agitation or because of inhomogeneities in the flow rate [28]. Higher bulk solution supersaturation with respect to struvite resulted in lower amounts of crystals adhering to the cell walls while bulk solution precipitation was higher. Struvite fouling is a serious problem in industrial processes like those involved with wastewater treatment [18]. The results of the present work sug-

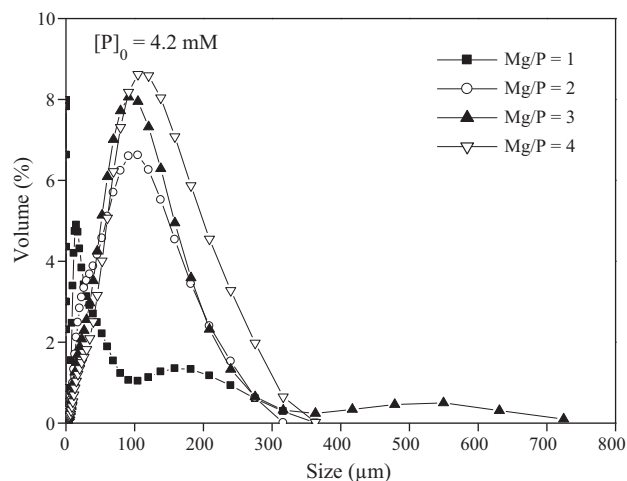


Fig. 5. Particle size distribution for different values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ obtained by varying magnesium concentration ($[\text{P}]_0 = 130.2 \text{ mg L}^{-1}$).

gested that the addition of magnesium in solution is a potential method for the amelioration of the performance of the processes. However, high concentrations of magnesium are not recommended for seeded struvite growth on a foreign substrate, for example when a stainless steel mesh system immersed in a pilot scale reactor is used as a substrate for struvite crystallization and recovery [34]. However, experiments on struvite crystallization at higher magnesium concentrations in the presence of stainless steel substrates need further exploration.

Increasing the magnesium concentration in solutions did not only affect the purity of struvite crystals but it also had a significant effect on the crystal size of the crystalline precipitates as may be seen in Fig. 5. For $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$, the variation of particles volume as a function of their size (Fig. 5) showed in principle a bimodal distribution of the particle size with two maxima in the size distribution curve: the first at $\sim 15 \mu\text{m}$ and the second one at $\sim 160 \mu\text{m}$. Increase of magnesium concentration in the supersaturated solutions from 8.4 ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 2$) to 16.8 mM ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 4$), the distribution of the particle size became monomodal covering a broad range of particle sizes up to 300 μm . The maximum of the particle size distribution curves shifted to larger mean diameter sizes upon increasing, and for values for the molar ratio in solution from $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 2$ –4. More specifically, the maximum particle size increased from ~ 100 to $\sim 120 \mu\text{m}$ and the corresponding particles volume varied from 6.6 to 8.6% when $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio increased from 2 to 4, respectively. For the precipitates formed when the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ in solution was 5, particle size measurements were not done because of the fact that mixed struvite, newberyite and cattite precipitates were obtained. It should be noted that changes in particle size distribution of the polycrystalline precipitates, induced by changes in magnesium concentrations in the supersaturated solutions may also affect the preferential orientation of the struvite crystallites suggested by the changes of the relative intensities of the diffraction peaks in the respective XRD patterns. Bouroupolos and Koutsoukos [31] in their study of the kinetics of spontaneous precipitation of struvite in aqueous supersaturated stirred solutions, reported the formation of prismatic struvite crystals grown in the (1 0 0) direction. Ben Moussa et al. [35] found that the struvite exhibited a growth texture with the (0 1 0) plane preferentially oriented in parallel with the substrate used for the electrochemical precipitation of struvite.

SEM micrographs of the precipitates obtained for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$, 4 and 5 are presented in Fig. 6. For $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$, more or less elongated crystals in the form of needles, typical of struvite precipitates, were observed (Fig. 6a).

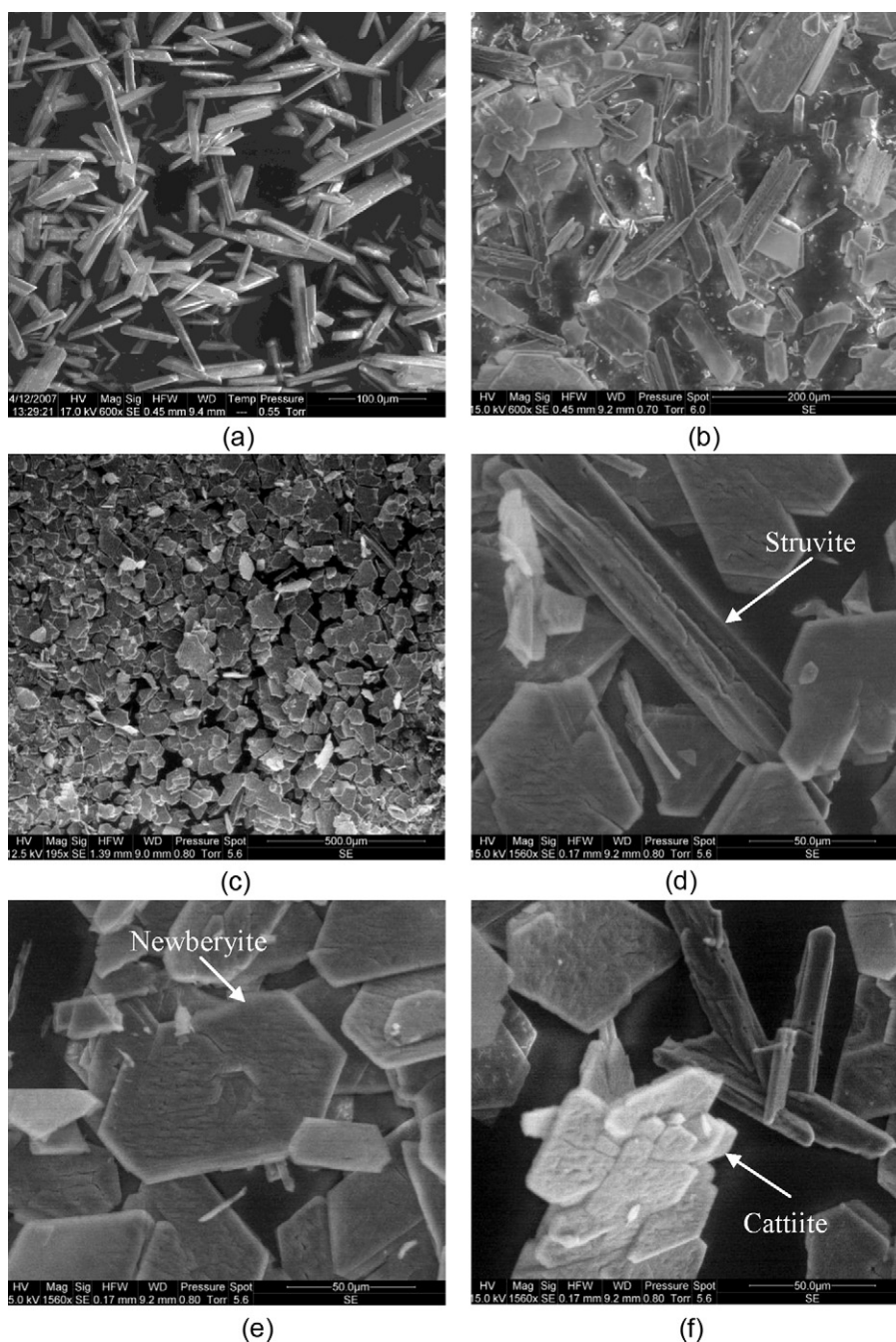


Fig. 6. SEM micrographs of the precipitates obtained for (a) $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$, (b) $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 2$ and (c–f) $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$ ($[\text{P}]_0 = 130.2 \text{ mg L}^{-1}$).

Increasing magnesium concentration in solution, the particles became more plate-like (Fig. 6b). For molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$ in solution, the majority of the precipitated crystallites were large and plate-like (Fig. 6c). SEM analysis showed the presence of struvite crystals (Fig. 6d) and crystals with triangular lead ends similar to those obtained by Babic-Ivancic et al. [36], typical of newberyite (Fig. 6e). In the same precipitates, cattite crystals were also identified (Fig. 6f). The results from the morphological examination of the precipitates were in agreement with the XRD mineralogical analysis which suggested that increasing magnesium concentrations in the supersaturated solutions, past a threshold value influenced the purity of the precipitated struvite.

3.2. Effect of phosphate and ammonium concentrations in the supersaturated solutions on struvite precipitation

3.2.1. Effect of phosphate concentration

The variation of pH and phosphate concentrations with time for different values of the $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio in the supersaturated solutions for a given initial magnesium concentration of 92.3 mg L^{-1} are shown in Fig. 7. For values of the molar ratio: $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1/3, 1/4, \text{ and } 1/5$, the pH increased rapidly reaching a maximum value of ~ 7.3 , past which it remained constant (Fig. 7a). It should be noted that in this series of experiments, there was no precipitation either of struvite or of any other phosphate salt. The

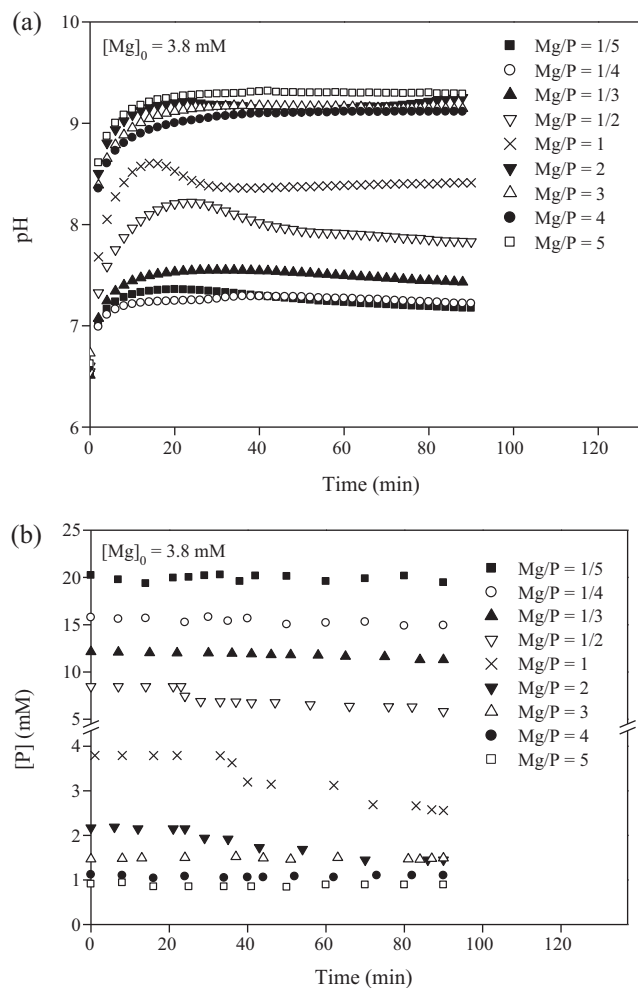


Fig. 7. Variation of (a) pH and of (b) phosphate concentration as a function of time for different values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ ($[\text{Mg}]_0 = 92.3 \text{ mg L}^{-1}$).

stability of the respective solutions with respect to precipitation was also confirmed from the invariability of the phosphate concentration in solution as a function of time over a time period of at least 2 h (Fig. 7b). For values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1/2, 1$ and 2 , the solution pH increased rapidly to reach $8.2, 8.6$, and 9.2 , respectively. As already explained, the increase in solution pH was attributed to the removal of the carbonate from the solutions through air bubbling. Following the attainment of the maximum pH value (precipitation pH) the solution pH decreased because of proton release in the solution concomitant with struvite precipitation. It should be noted that for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 2$, the quantity of the precipitate formed was low and so was the pH variation as a function of time. For values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1/2$ and 1 , both the pH drop and the amount of crystals obtained were significantly higher. Past the end of precipitation, the pH increased as in the previous series of experiments because apparently the rate of carbonate removal from the solutions was higher than the rate of precipitation from the respective supersaturated solutions (Fig. 7a). The change of phosphate concentration in solution, was in accordance with the pH changes, remaining constant for a time period corresponding to the induction time t_n , following the lapse of which it decreased reaching a plateau value (Fig. 7b). When the phosphate concentration increased/decreased yielding values of $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio of $1/2$ and 2 , respectively, the induction times, t_n preceding the onset of struvite precipitation were shorter in comparison with values of $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ equal to 1 . More

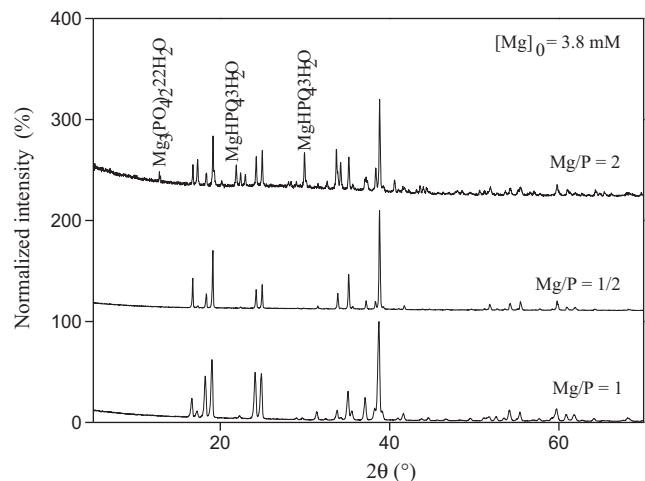


Fig. 8. XRD patterns of the precipitates obtained for different values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ ($[\text{Mg}]_0 = 92.3 \text{ mg L}^{-1}$).

specifically, t_n decreased from 33 min for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$ to 24 and 29 min for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1/2$ and 2 , respectively. Phosphate removal efficiency values were comparable for all the experiments. More specifically, the phosphate removal efficiency values were 31, 32 and 33% for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1/2, 1$ and 2 , respectively. These values were significantly lower in comparison with values obtained increasing magnesium concentration at a constant phosphorus concentration of 130.2 mg L^{-1} .

The XRD patterns of the precipitates obtained for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1/2, 1$ and 2 are shown in Fig. 8. For $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1/2$ and 1 , the solid formed was mainly struvite as shown from comparison with the reference material (Standard no. 15-0762 [29]). The 111 and 021 reflection intensities decreased with increasing phosphate concentration in the solution, suggesting presence of texture in the crystals obtained, a similar finding with the case in which magnesium concentration in solution was higher. The struvite crystals obtained were larger in size in comparison with struvite crystals formed with increasing magnesium concentrations in solution (Fig. 9a). Decrease of the phosphate concentration in solution however ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 2$), affected the purity of the struvite since co-precipitation of newberyite and cattite were also seen in the morphological examination of the precipitates (Fig. 8). The formation of mixed precipitates is comparable with the precipitates formed for values of $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio of 5 , obtained by increasing the magnesium concentration at a fixed phosphate concentration. The crystals shape and size were, however, different (Fig. 9). The results of this series of experiments suggested that the variation of the phosphate concentration in the solution at a fixed magnesium concentration affected the crystal shape, size and purity of struvite.

For higher values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ equal to $3, 4$ and 5 , the pH increased rapidly to reach maximum values of $9.2, 9.1$ and 9.3 , respectively. Past the attainment of the maximum value, pH remained constant (Fig. 7a). Despite the alkaline solution pH, struvite precipitation was not detected. Additional evidence for the lack of precipitation was provided by the invariability of phosphate concentration in solution with time (Fig. 7b).

For values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} < 1/2$ corresponding to a fixed magnesium concentration of 92.3 mg L^{-1} , the maximum pH value reached was ~ 7.3 and again struvite precipitation was not detected. Mijangos et al. [37] suggested that in alkaline media, in the presence of magnesium, a number of magnesium species including $\text{Mg}_3(\text{PO}_4)_2$ reduced the driving force for the precipitation of struvite. However, the neutral magnesium phosphate complex suggested as explanation of the absence of struvite crystallization

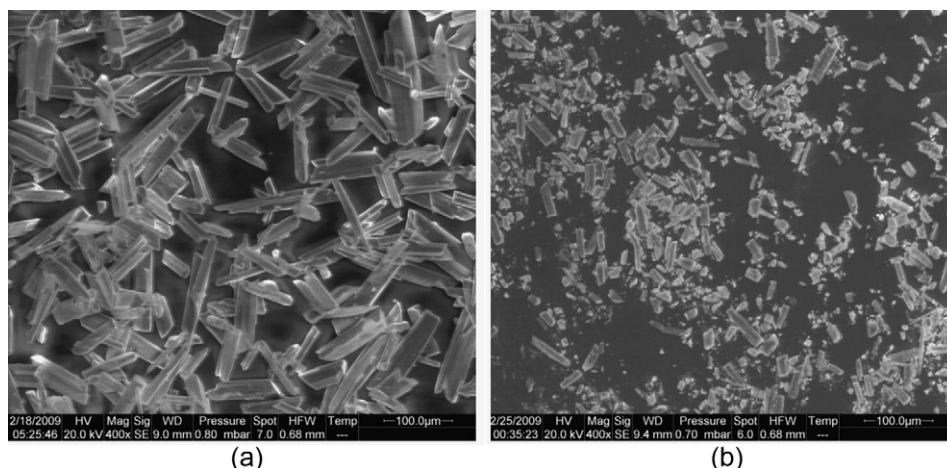


Fig. 9. SEM micrographs of the precipitates obtained for (a) $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$ and (b) $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 2$ ($[\text{Mg}]_0 = 92.3 \text{ mg L}^{-1}$).

at high phosphate concentration is very unlikely since Mijangos et al. [37] gave no literature reference to the stability constant of this complex. In an earlier publication [24] we have reported that, using the carbonate removal technique, struvite precipitation took place at alkaline $\text{pH} > 8.1$. For $\text{pH} < 8.1$, no precipitation was detected. Stratful et al. [38] reported, without further explanation, that at $\text{pH} 7$, struvite did not precipitate in any detectable quantity while at $\text{pH} 7.5$ the quantities of struvite obtained were very small.

For $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} > 2$ ($[\text{Mg}^{2+}] = 92.3 \text{ mg L}^{-1}$), despite the alkaline solution $\text{pH} (\sim 9.2)$, no precipitation was detected. Wang et al. [39] suggested that for $\text{Mg}:\text{N}:\text{H}_n\text{PO}_4^{n-3}$ molar ratio of 1:1:1, the optimal pH for the struvite crystallization is 9 slightly increasing with increasing values of the $\text{N}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio. At $\text{pH} 9$, 98.5% of the total phosphate in solution (0.76–1.26 mM), is present as HPO_4^{2-} (0.76–1.26 mM), the initial NH_4^+ ions concentration was low since ammonium and phosphate were added in the solution equimolar ratios. The low ammonium concentration decreased with increasing pH . Indeed, as pH increased from 7 to 9, the percent of total nitrogen present as NH_4^+ decreased from 99 to 64% [40]. For the experimental conditions of the present work, the ammonium concentrations were in the range 0.48–0.81 mM ($\text{N}/\text{H}_n\text{PO}_4^{n-3}$ in the range 0.63–0.64 mM). Struvite precipitation at low concentrations of $\text{H}_n\text{PO}_4^{n-3}$ and NH_4^+ could be affected by fluid dynamics. For airflow rate of 40 L min^{-1} , the mixing energy was high, resulting in turbulent flow [24] and high fluid shear stress. Fluid dynamics played an important role in the ionic diffusion in the fluid, retarded surface reactions in which these ions participate, thus reducing the rates of struvite crystal formation. It is suggested that it is for this reason that there is a threshold supersaturation between 6 and 8 for the precipitation of struvite [24]. Moreover, the results of the present work, concerning the effect of magnesium on struvite precipitation, suggested that a value of SSR with respect to struvite of ~ 6 should be reached for struvite crystallization by the carbonate removal technique using an airflow rate of 40 L min^{-1} (Fig. 4). A more plausible explanation, therefore, is that in the experiments with high phosphate concentration, the solution supersaturation was below the critical value needed for struvite nucleation. This occurs only in the intermediate range of $1/2 < \text{Mg}/\text{H}_n\text{PO}_4^{n-3} < 2$ for Mg concentration in solution equal to 92.3 mg L^{-1} (Fig. 10). The buffer capacity of the combined carbonate/phosphate system maintained solution pH below 7.5 and the supersaturation below the critical value for molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ values $< 1/2$. At the other end, for molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ values > 2 , the phosphate concentration was too low to ensure supersaturation with respect to struvite exceeding the critical value. Therefore, at a high mixing energy, the addition of phosphate to the solution at given mag-

nesium concentration delayed or completely prevented struvite formation depending on the concentration of the phosphate added for the adjustment of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ values. More experiments are needed at lower mixing energy (turbulence), i.e., at a lower airflow rate of 20 L min^{-1} and higher solution volumes for a more precise assessment of the effect of hydrodynamics on the precipitation of struvite.

3.2.2. Effect of ammonium concentration

To limit the inhibition effect of hydrodynamics on struvite precipitation (Section 3.2.1) experiments were carried out in which the airflow rate was 20 L min^{-1} , using ammonium concentration as variable. For all experiments, the predominant phase obtained was identified as struvite. The XRD pattern and the FTIR spectra of the collected solids are shown in Figs. 11 and 12, respectively. The precipitates obtained at low initial ammonium concentrations (18.93 and 37.87 mg L^{-1} corresponding to values of the molar ratio $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$ of $1/4$ and $1/2$, respectively) were strongly textured as suggested from the differences of the relative intensities of the XRD reflections in comparison with the reference material [29]. The difference in relative intensities was less pronounced for the precipitates obtained at higher ammonium concentrations, as e.g. in the case of 227.27 mg L^{-1} ($\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3} = 3$). On the other hand, the FTIR spectra of the precipitates obtained for different ammonium concentrations (Fig. 12) exhibited the characteristic PO_4^{3-} band at 1004.9 cm^{-1} and the characteristic NH_4^+ band at

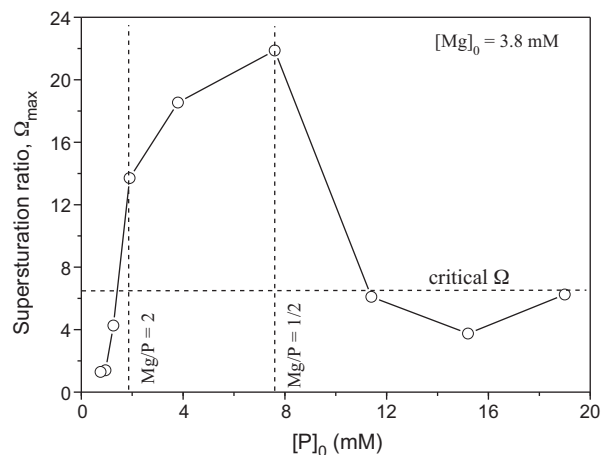


Fig. 10. Supersaturation ratio with respect to struvite as a function of the phosphate concentrations ($[\text{Mg}]_0 = 92.3 \text{ mg L}^{-1}$).

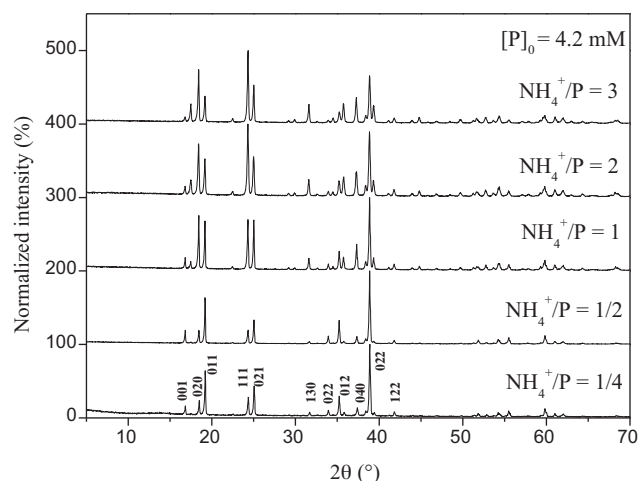


Fig. 11. XRD patterns of the precipitates obtained for different $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$ molar ratios ($[\text{Mg}]_0 = 130.2 \text{ mg L}^{-1}$).

2933.7 cm^{-1} . Similar spectra for struvite have been reported by Zhang et al. [5], Chauhan et al. [50] and Babic-Ivancic et al. [51]. In this series of experiments, the solutions were supersaturated with respect to both newberyite and struvite and the change of the supersaturation as a function of time may be seen in Fig. 13. It should be noted, however, that in all experiments newberyite was not detected to the analytical limits of the solid characterization techniques used. Abbona et al. [6] showed that struvite and newberyite crystallize simultaneously for $2 < \Omega_{\text{newberyite}}/\Omega_{\text{struvite}} < 4$. If $\Omega_{\text{newberyite}}/\Omega_{\text{struvite}} < 2$, struvite always crystallizes first whereas newberyite crystallizes first if $\Omega_{\text{newberyite}}/\Omega_{\text{struvite}} > 4$. In the present work, $0.05 < \Omega_{\text{newberyite}}/\Omega_{\text{struvite}} < 0.24$, so struvite was anticipated to crystallize first. At the end of struvite precipitation, the residual phosphate and magnesium concentrations in the solution were too low to ensure supersaturation with respect to newberyite.

The variation of pH and of the phosphate concentrations in the supersaturated solutions as a function of time for different values of the $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$ molar ratio at a fixed initial magnesium concentration of 92.3 mg L^{-1} compared well with the respective profiles obtained in experiments where the magnesium concentration was variable at fixed molar ratio $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3} (=1)$: because

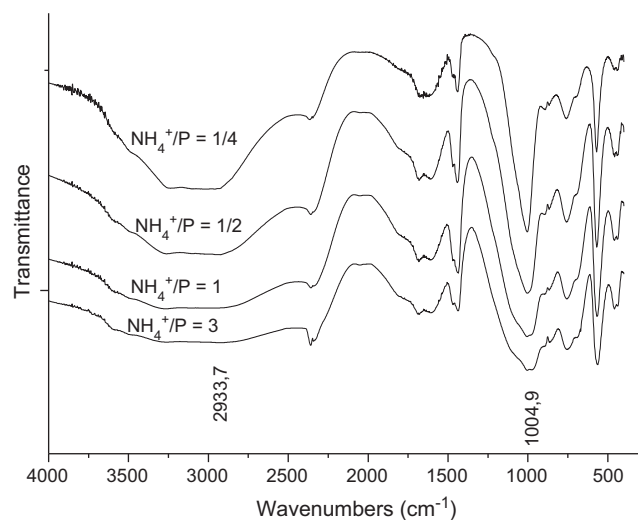


Fig. 12. FTIR spectra of the precipitates obtained for different values of the molar ratio $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$ ($[\text{Mg}]_0 = 130.2 \text{ mg L}^{-1}$).

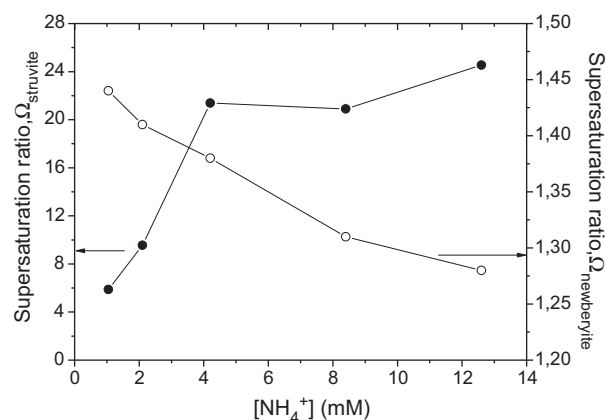


Fig. 13. Supersaturation ratios with respect to struvite and newberyite as a function of the initial ammonium concentration ($[\text{Mg}]_0 = 130.2 \text{ mg L}^{-1}$).

of carbonate removal from solution, pH increased to a maximum value depending on the ammonium concentration, followed by a decrease due to the precipitation of struvite. When the rate of precipitation became lower than the rate of CO_2 removal from the solution, the pH increased. At the same time, phosphorus concentration in solution remained constant up to t_n , past which it decreased because of struvite nucleation and growth. Finally, the phosphate concentration in solution remained constant suggesting that the formation of precipitate was completed. The different physico-chemical parameters obtained from the time dependence of pH and phosphate concentration are summarized in Table 2. For all experiments, the pH of struvite precipitation was in the range 8.2–8.6. As may be seen in Table 2, the induction time decreased significantly with increasing ammonium concentration. Moreover significant increase of the phosphorus removal was achieved, i.e., it increased from 21 to 75% when the ammonium concentration increased from 18.93 to 227.27 mg L^{-1} , respectively. These results are in agreement with reports by Zhang et al. [5], Pastor et al. [18] and Strateful et al. [38] suggesting that an excess of ammonium is beneficial for struvite precipitation. However, from the environment point of view, high ammonium concentration would generate enhanced effluent ammonium concentration. For example, the residual ammonium concentration in the solution increased from ~ 16 to $\sim 57 \text{ mg L}^{-1}$ when the initial ammonium concentration increased from 18.93 to 227.27 mg L^{-1} , respectively. Unlike the magnesium addition, the increase of ammonium concentration in the solution lowered the extent of crystallization of struvite in solution and enhanced the deposition of the crystallites on the reactor walls. For example, τ_{sol} decreased from 95 to 82% when ammonium concentration increased from 18.93 to 227.27 mg L^{-1} (Table 2).

Table 2

Induction time (t_n), precipitation pH, phosphate removal, precipitates mass fractions on the cell walls (τ_{wall}) and in the bulk solution (τ_{sol}) for different $\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$ molar ratios ($[\text{P}]_0 = 130.2 \text{ mg L}^{-1}$).

$\text{NH}_4^+/\text{H}_n\text{PO}_4^{n-3}$	t_n (min)	Precipitation pH	Phosphate removal (%)	τ_{sol} (%)	τ_{wall} (%)
1/4	40	8.6	21	95	5
1/2	20	8.5	50	92	8
1	19	8.6	67	85	15
2	12	8.3	76	71	29
3	12	8.2	75	82	18

4. Discussion

A number of different techniques, including mechanical and magnetic stirring [41,42], aeration [43], and ion exchange [44] have been used to precipitate struvite from synthetic or real wastewaters. These processes are already in full scale operation in several countries, in Japan [45], Canada, United States of America and Netherlands. Struvite may also be formed by electrochemical process [35,46]. However current and past literature, includes reports of laboratory scale experiments only, even though, the industrial electrolyzers developed for calcium carbonate formation could also be used for struvite precipitation [35]. In our earlier report [24], the carbonate removal technique, initially developed for the investigation of calcium carbonate [47], was applied to struvite precipitation. Precipitation of CaCO_3 by the removal of the dissolved carbonate technique is a good simulation of the natural scaling phenomenon in which precipitation takes place following the removal of the dissolved carbonate by the atmospheric air bubbled through the solutions. This technique has numerous advantages. First, compared to traditional techniques, the dissolved carbonate removal technique allows for high phosphate removal efficiency at a relatively short time [24]. Second, this technique allows for the easy measurement of the induction and crystal growth periods. Separation of these periods is very difficult at constant pH or when struvite formation is instantaneous. Finally, no chemicals were added to increase the solution pH, a fact contributing to cost reduction of the removal of phosphorus from wastewater. For example, a study conducted at the Lulu Island Wastewater Treatment Plant, using a struvite crystallizer and a CO_2 cascade stripper, showed that a high phosphorus removal efficiency of 90% was achieved and that the cascade stripper saved caustic usage of 86% [22].

In the present work, a low amount of calcium (20 mg L^{-1}) was added to the solution as CaCO_3 . This amount is comparable to that obtained after pretreatment of wastewaters and landfill leachate by, respectively, precipitation and autoclaving processes. Calcium is known to complicate the struvite precipitation through the formation of insoluble calcium phosphate salts [18,42], making the system hard to characterize chemically. In aqueous solutions containing phosphate ions, the presence of calcium could be responsible for the precipitation of a number of calcium phosphates, i.e., amorphous calcium phosphate, dicalcium phosphate dihydrate and hydroxyapatite. However, it was shown that the presence of magnesium and bicarbonate ions inhibited the formation of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) [48]. In the present work, we have investigated the effect of Ca on struvite precipitation by the dissolved carbonate removal technique. Fig. 14 shows the XRD diagrams of the precipitates obtained for different calcium concentrations. For a calcium concentration lower than 100.25 mg L^{-1} (magnesium concentration of 102.08 mg L^{-1}) mainly struvite was formed. In the range 100.25 – 148.37 mg L^{-1} , struvite co-precipitated with amorphous phase (shown in the respective XRD pattern by the pronounced background) and for 160.4 mg L^{-1} , mainly the amorphous phase was formed. These results are in good agreement with the results of Le Corre et al. [49]. Marti et al. [42] suggested that calcium could precipitate as both calcite and calcium phosphate when treating sludge digester liquors for phosphate removal through struvite crystallization. The presence of calcite was attributed to the high $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ ($=1.48$) and $\text{Ca}/\text{H}_n\text{PO}_4^{n-3}$ ($=2.34$) molar ratios. The calcium phosphate precipitated was an amorphous calcium phosphate. Therefore, the presence of Ca with low concentration of 20 mg L^{-1} ($\text{Ca}/\text{H}_n\text{PO}_4^{n-3} \approx 0.1$) did not affect the composition of the solid precipitate which consisted exclusively of struvite. Calcium however, is not the only foreign ion which affects struvite precipitation. In fact, the presence of potassium, chloride, sodium, carbonate and sulphate, among others, in real wastewater and landfill leachate could significantly affect the stru-

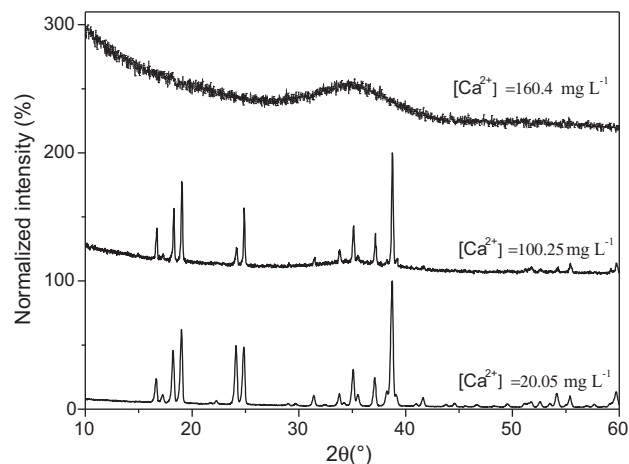


Fig. 14. XRD patterns of the precipitates obtained from supersaturated solutions in the presence of different calcium concentrations ($[\text{Mg}]_0 = 92.3 \text{ mg L}^{-1}$).

vite formation [34,36]. Clearly, further work is needed concerning struvite crystallization from real wastewater and landfill leachate.

In addition to the improvement of the phosphate removal efficiency, the presence of magnesium at high concentrations could be a solution, among others, to prevent undesired struvite scaling in WWTP. As already shown by the results of the present work, increase of magnesium concentration in the supersaturated solutions allowed for the recovery, from the bulk solution, of relatively high amounts of struvite, which could be easily collected by filtration to be used as fertilizer. However, provided that the molar ratio of $\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$ for the efficient phosphate removal is equal to 1.15:1:1 [5], there will be excess magnesium left unused which may increase the potential of struvite formation elsewhere in the WWTP. Moreover, higher magnesium concentrations affected the purity of the struvite precipitates. It should be noted that the highest phosphate removal was reached for initial values of the molar $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$, but the precipitate was mixed consisting of newberyite and cattite in addition to struvite. In order therefore to ameliorate phosphate removal efficiency through the precipitation of pure struvite in the bulk solution, the addition of magnesium should be controlled.

The results of the present work, have also shown that there is no optimal value for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio for struvite precipitation that could be determined independently of the initial concentrations of all three components (magnesium, ammonium and phosphate) but it should be optimized according to the initial magnesium and phosphate concentrations and operation conditions, i.e., hydrodynamic fluidization. In fact, for the same molar ratios $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$, obtained at a constant initial phosphate concentration and higher magnesium concentrations, or at a constant initial magnesium concentration, and varied phosphate concentrations, different results were obtained. For example, for $\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$, 92% of phosphate was removed increasing magnesium concentration at a fixed phosphate concentration. However, no precipitation was detected when this molar ratio was obtained by varying phosphate in solution at fixed magnesium concentration. More important, for equivalent magnesium and phosphate concentrations ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 1$), the results obtained depended on the initial concentrations used. From a scientific point of view, comparison between different results reported in the literature, the phosphate and magnesium concentrations should be taken into account, rather than the values of the $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ molar ratio. In the practice of struvite precipitation, the initial phosphate and magnesium concentrations should be determined to adjust the added magnesium concentration which leads to the

most efficient wastewater treatment for maximizing phosphorus recovery.

5. Conclusion

In the present work, the effect of magnesium, phosphate and ammonium concentrations on struvite precipitation by the carbonate removal technique was investigated. At a fixed phosphate concentration, the increase of magnesium concentration in solution to 510.4 mg L^{-1} ($\text{Mg}/\text{H}_n\text{PO}_4^{n-3} = 5$), decreased the precipitation pH and improved significantly the phosphate removal efficiency. However, this improvement led to the co-precipitation with struvite of other magnesium phosphates as well. Moreover, crystal deposition on the reactor walls was reduced (to 2%) while at the same time precipitation of struvite in the bulk solution was improved. The concentrations of the struvite constituent ions to be added in the supersaturated solutions in order to optimize phosphorus removal should be adjusted according to the initial phosphate and magnesium concentrations and operation conditions, i.e., hydrodynamic fluidization. The addition of phosphate to the solution at a fixed magnesium concentration of 92.3 mg L^{-1} delayed or completely suppressed struvite formation, depending on the added concentration. For values of the molar ratio $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ equal to 1/2, 1 and 2, ~32% of phosphate was removed. For $\text{Mg}/\text{H}_n\text{PO}_4^{n-3}$ higher than 2 or lower than 1/2, no precipitation was detected. For all experiments, struvite particle size, shape and purity were affected by the increase of magnesium or phosphate concentration. Excess of ammonium was found to favour struvite precipitation. Phosphorus removal increased from 21 to 75% upon increasing ammonium concentration from 18.93 to 227.27 mg L^{-1} . Unlike magnesium addition, the increase of ammonium concentration in the solution suppressed the crystallization of struvite in the bulk solution and enhanced adhesion on cell walls. Further experiments are needed which should focus on improving phosphate removal through struvite precipitation by magnesium addition without co-precipitation of other salts.

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