Ureolytic phosphate precipitation from anaerobic effluents

E. Desmidt, W. Verstraete, J. Dick, B. D. Meesschaert and M. Carballa

ABSTRACT

In this work, the elimination of phosphate from industrial anaerobic effluents was evaluated at lab-scale. For that purpose, the ureolytic method previously developed for the precipitation of Ca^{2+} from wastewater as calcite was adapted for the precipitation of phosphate as struvite. In the first part of the study, computer simulations using MAPLE and PHREEQC were performed to model phosphate precipitation from wastewater as struvite. The results obtained showed that relative high concentrations of ammonium and magnesium are needed to precipitate phosphate as struvite. The total molar concentrations ratio of Mg^{2+}:PO_4^{3-}-P:NH_4^+ required to decrease PO_4^{3-}-P concentrations from 20 to 6 mg PO_4^{3-}-P/l at pH 8.4-8.5 was estimated on 4.6:1:8. In the second part of the study, lab-scale experiments with either synthetic wastewater or the anaerobic effluent from a vegetable processing industry were carried out in batch and continuous mode. Overall, the continuous operation at a hydraulic retention time (HRT) of 2.4 h and an added molar concentration $[Mg^{2+}]$:$[PO_4^{3-}$-P]$:[NH_4^+]$ ratio of 1.6:1:2.3 resulted in a constant pH value in the reactor (around 8.5) and an efficient phosphate removal ($>$90%) to residual levels of 1–2 mg PO_4^{3-}-P/l. Different operational conditions, such as the initial phosphate concentration, HRT and the use of $CaCl_2$ or MgO instead of $MgCl_2$, were analysed and the performance of the reactor was satisfactory under a broad range of them. Yet, overall, optimal results (higher phosphate removal) were obtained with $MgCl_2$.

Key words | magnesium ammonium phosphate, modelling, phosphate removal, struvite, urea

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INTRODUCTION

The scarcity of freshwater resources has made the water reuse concept to become an essential component in increasing the reliability of water supply in terms of quality and quantity. Flanders counts about 6 million inhabitants and it is one of the most water stressed regions in Europe. As a result, the Flemish government has restricted the use of deep well water, and therefore, many industries are forced to treat and subsequently reuse their wastewaters. The problem is that the quality of these generated wastewaters does not allow their direct reuse in the production plant, and a pre-treatment is required prior to it.

In the case of food industries, mainly related to the production of frozen vegetables and pre-fried potato chips, the main problem lies in the presence of rather large amounts of phosphate in the wastewaters. The average phosphate concentrations measured in the frozen vegetables and pre-fried potato chips wastewaters are 5–55 and 50–90 mg PO_4^{3-}-P/l, respectively. This would result in its accumulation in the process water unless phosphate removal occurs prior to reuse.

The conventional method to remove phosphate from wastewaters is the addition of flocculants, such as ferric chloride and aluminium. The main problem is the high costs of these chemical flocculants. Therefore, in many cases, this process has been substituted by enhanced biological phosphorus removal (Alamdari & Rohani 2007).

Another alternative is the DHV crystalactor process (Morse *et al.* 1998), in which a fluidized bed crystallizer containing sand seed is used to remove phosphorus from wastewaters. By adding chemicals such as lime, calcium chloride, magnesium hydroxide or magnesium chloride, calcium or magnesium phosphates can be precipitated, respectively (Alamdari & Rohani 2007). Yet, this technology appears not to be applicable at small to moderate industrial scale.

Nowadays, the two most developed techniques for recovering phosphorus from wastewaters are based on the formation of calcium phosphates and struvite ($MgNH_4 PO_4 \cdot 6H2O$) (Pastor *et al.* 2008).

The ANPHOS®-process uses struvite formation as a method for phosphate removal (Colsen 2002). During this chemical process, the pH is firstly corrected to about 8.5 by air stripping, and secondly, MgO is provided as Mg^{2+} source to create the optimal conditions for struvite formation. Sand particles or previously formed struvite are often added to induce crystallisation. The reported phosphate recoveries during this process varied between 75% and 90% (Brekelmans 2005).

A new microbiological method to remove phosphate from wastewater by ureolytic precipitation of struvite (magnesium ammonium phosphate) has been recently described (Carballa *et al.* 2008). Ureolytic micro-organisms were previously used for the precipitation of calcium ions from wastewaters (Hammes *et al.* 2003*a*, *b*). The ureolytic sludge uses urea to increase the pH in the micro-environment of the sludge, thus promoting $CaCO_3$ precipitation. The reactor containing ureolytic sludge was fed with anaerobic effluent. Despite the fact that the effluent was already saturated in $CaCO_3$, the addition of urea to promote the hydrolytic activity was shown to be necessary for phosphate precipitation. Yet, the adoption of this technique to remove phosphate from anaerobic effluents by precipitation as struvite would require, apart from urea, the addition of a magnesium salt ($MgCl_2$ or MgO), since enough amounts of ammonium are usually already present in anaerobic effluents. Moreover, the hydrolysis of urea not only increases pH, a prerequisite for struvite precipitation, but it also supplies extra ammonium.

Gethke *et al.* (2006) used this ureolytic process to recover nutrients from human urine as struvite. Before the addition of MgO and urease, the urine was stored for a period of 8 months and the decomposition processes resulted in an increase of pH, ammonium and phosphate concentrations up to 9, 4700 mg NH_4^+-N/l and 400 mg PO_4^{3-}-P/l, respectively. The phosphate recovery during the ureolytic process accounted for 99%.

The techniques developed so far to recover phosphate from wastewaters as struvite are mainly chemically-based. In this work, the ureolytic-based phosphate precipitation was examined in more detail. The main advantage of this process is that this nano-precipitation occurs at the higher pH values occurring in the micro-environment of the ureolytic sludge compared to the pH values of the bulk water, which should favour struvite precipitation. Moreover, the ureolytic micro-organisms can act as nucleation seeds. This work differs with Gethke's study in the fact that the concentrations of nutrients in wastewaters are much lower than in urine.

MATERIAL AND METHODS

Computer simulations

Two different computer model systems, MAPLE (Scott 2001) and PHREEQC, were used to estimate the amounts of ammonium (dosed as urea) and magnesium and the optimal pH to precipitate phosphate as struvite from anaerobic effluents. The results obtained were subsequently implemented in different experiments.

Assuming that phosphate precipitates from the solution as struvite, MAPLE allowed the calculation of the equilibrium concentrations (as $p = -\log[]$) of ammonium, phosphate and magnesium. For that purpose, the constants of all the reactions that can occur, as well as the charge and mass balance of all species involved are needed.

PHREEQC allowed the calculation of the saturation indexes of the possible compounds which can be formed in the presence of the different phosphate derived ions ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}), magnesium and ammonium. The saturation index SI is defined as log (IAP/K_{sp}), where IAP is the Ion Activity Product and K_{sp} is the solubility product. Precipitation will occur when SI > 0. The input variables of this model are: the initial concentrations of

the different ions, the pH, the ionic strength of the medium and the reaction constants of all reactions that can occur.

Experimental set-up

A reactor of 3 l working volume was built according to BNB EN ISO 11733 and it was operated either as a Sequential Batch Reactor (SBR) or in a continuous mode coupled to a 2 l settler, depending on the experiment. Ureolytic sludge was obtained by adaptation (around 5–7 days) of a standard active sludge to urea (1–2 g/l) and peptone (1 g/l), using cycles of 24 h (23.5 h of reaction time + 0.5 h of feeding, settling and effluent discharge). When pH values and phosphate removal decreased, reactivation of the ureolytic sludge was performed according to this same procedure.

During the first experiment, the reactor was fed with synthetic wastewater, containing phosphate (20–30 mg PO_4^{3-}-P/l) and some peptone (0.5 g/l), while during the second experiment, the effluent of an anaerobic pre-purification reactor from a vegetable processing industry was used (5–55 mg PO_4^{3-}-P/l, 10–190 mg NH_4^+-N/l and 15–110 mg Mg^{2+}/l). $MgCl_2$ and urea were used as Mg^{2+} and NH_4^+ sources, respectively. The total cycle time in the SBR operation was 2 h (1.5 h of reaction time +0.5 h of feeding, settling and effluent discharge). During the continuous operation, a hydraulic retention time (HRT) of 2.4 h was applied. The reactor was not aerated and it was gently mixed with a mechanical stirrer. Total and volatile suspended solids concentrations in the reactor varied between 5 and 10 g/l and 3.5 and 5 g/l, respectively.
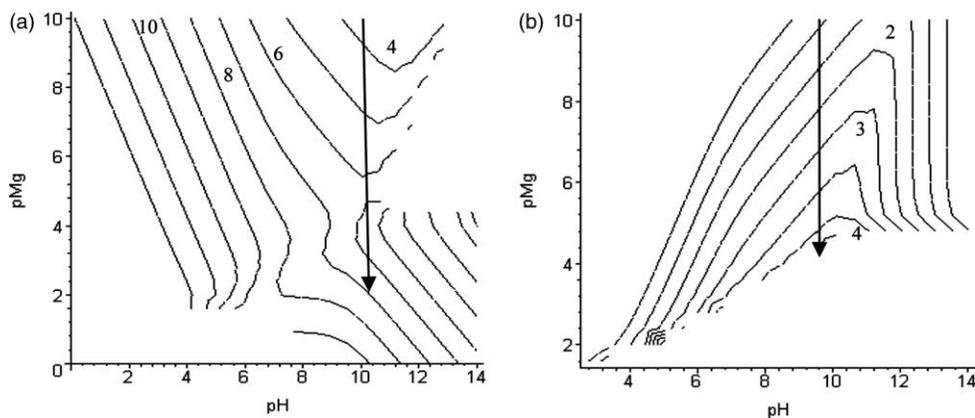
RESULTS AND DISCUSSION

Computer simulations

Figure 1 shows $p[PO_4^{3-}]$ and $p[NH_4^+]$ as a function of pH and $p[Mg^{2+}]$ obtained with MAPLE. It can be observed that the solubility of both phosphate (Figure 1a) and ammonium (Figure 1b) decreases at increasing magnesium concentrations. The arrow indicates that, at pH 9.2, the addition of magnesium until an equilibrium concentration of 10^{-2} and 10^{-4} M decreases the solubility of PO_4^{3-} and NH_4^+ to about 10^{-7} and 10^{-4} M, respectively, and thus, promoting struvite formation. This optimal pH for struvite formation coincides with the pK_a of ammonium obtained with PHREEQC (Figure 2a), which also shows that relatively higher amounts of ammonium than magnesium are required for struvite formation (Figure 2b).

Overall, from the results obtained with the models, the following molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio of 4.6:1:8 to be applied in the experiments was selected. As the industrial wastewaters already contain some NH_4^+ and Mg^{2+}, the required amounts for struvite formation would be lower than those calculated with the models.

Experimental section

Figure 3 shows the time course of pH, phosphate and ammonium concentrations during the reaction time in a preliminary experiment. It can be observed that the PO_4^{3-}-P concentration decreased to about 1 mg/l within the first 15 min of reaction, while the pH values and the
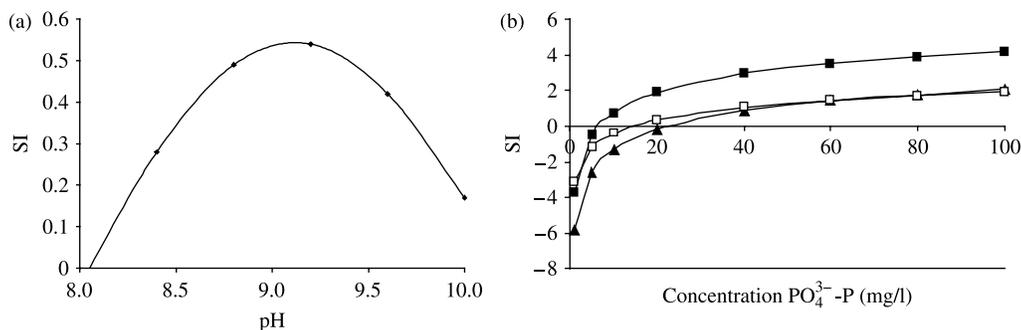

Figure 1 | $p[PO_4^{3-}]$ and $p[NH_4^+]$ as function of pH and $p[Mg^{2+}]$ obtained with MAPLE.

Figure 2 | (a) SI of struvite as a function of pH using a molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio of 4.6:1:8 and an initial $[PO_4^{3-}-P]$ of 20 mg/l; (b) SI of struvite (□), $Mg_3(PO_4)_2 \cdot 8H_2O$ (■) and $Mg_3(PO_4)_2 \cdot 22H_2O$ (▲) at pH 9.2 as a function of $[PO_4^{3-}-P]$ (mg/l) using a molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio of 4.6:1:8.

NH_4^+ concentration remained constant. The latter can be explained by the fact that the ammonium formed was simultaneously recovered as struvite, thus not rising the pH values in the bulk liquid. From 30 min on, both the pH and the NH_4^+ concentration increased up to 8.5 and 120 mg/l, respectively.

During the second experiment, an industrial anaerobic effluent containing around 22.5 mg PO_4^{3-}-P/l was treated in the same way. Initially, $MgCl_2$ and urea were added at a molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio of 4.6:1:12. However, these amounts of added Mg^{2+} and NH_4^+ could be decreased to 1.6 and 2.3, respectively, in the subsequent 2 months. Yet, taking into account the $Mg^{2+}(30-80 \text{ mg/l})$ and the $NH_4^+(0-60 \text{ mg/l})$ which were already present in the industrial effluent, the total molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio in the reactor was 4.6:1:5.2. During this phase, the effluent phosphate concentrations remained constant and low, between 0.5 and 0.7 mg PO_4^{3-}-P/l.

In the next phase, the reactor was operated in a continuous way with a HRT of 2.4 hours, but maintaining

the same added molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio of 1.6:1:2.3. This resulted in a constant pH in the reactor (around 8.5) and phosphate was efficiently removed to residual effluent levels of 1–2 mg PO_4^{3-}-P/l (removal efficiencies >90%). However, the added amounts of urea could not be lowered, because the reactor lost its potential for phosphate removal on day 3, when the added urea was decreased from 50 to 37.5 mg/l (Figure 4). This action probably resulted in a decrease of urea hydrolysis, and consequently, not giving rise to the pH levels and ammonium concentrations required for struvite precipitation.

In the next phases of this experiment, the influence of different operational conditions, such as initial phosphate concentration, HRT and the use of $CaCl_2$ or MgO instead of $MgCl_2$, were analysed (Figure 5), maintaining constant the total molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio at 4.6:1:5.2. At a HRT of 2.4 h, the increase of the initial phosphate concentration from 20 to 100 mg PO_4^{3-}-P/l resulted in a slight increase of the effluent levels, from 4 to 10 mg PO_4^{3-}-P/l
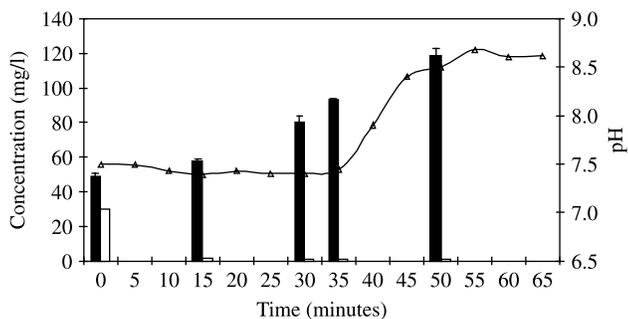

Figure 3 | Time course of pH (line), $[NH_4^+]$ (■) and $[PO_4^{3-}-P]$ (□) during the reaction time of the first preliminary experiment with synthetic wastewater (molar $[Mg^{2+}]:[PO_4^{3-}-P]:[NH_4^+]$ ratio of 3.2:1:27.5).
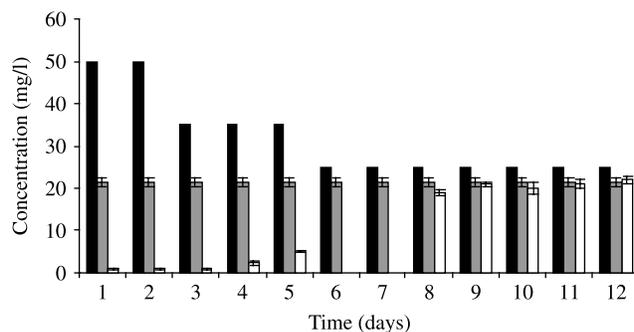

Figure 4 | Effect of different added amounts of urea on effluent phosphate concentrations during the treatment of industrial anaerobic effluent. (■) Urea; (▨) Phosphate in influent; and, (□) Phosphate in effluent.
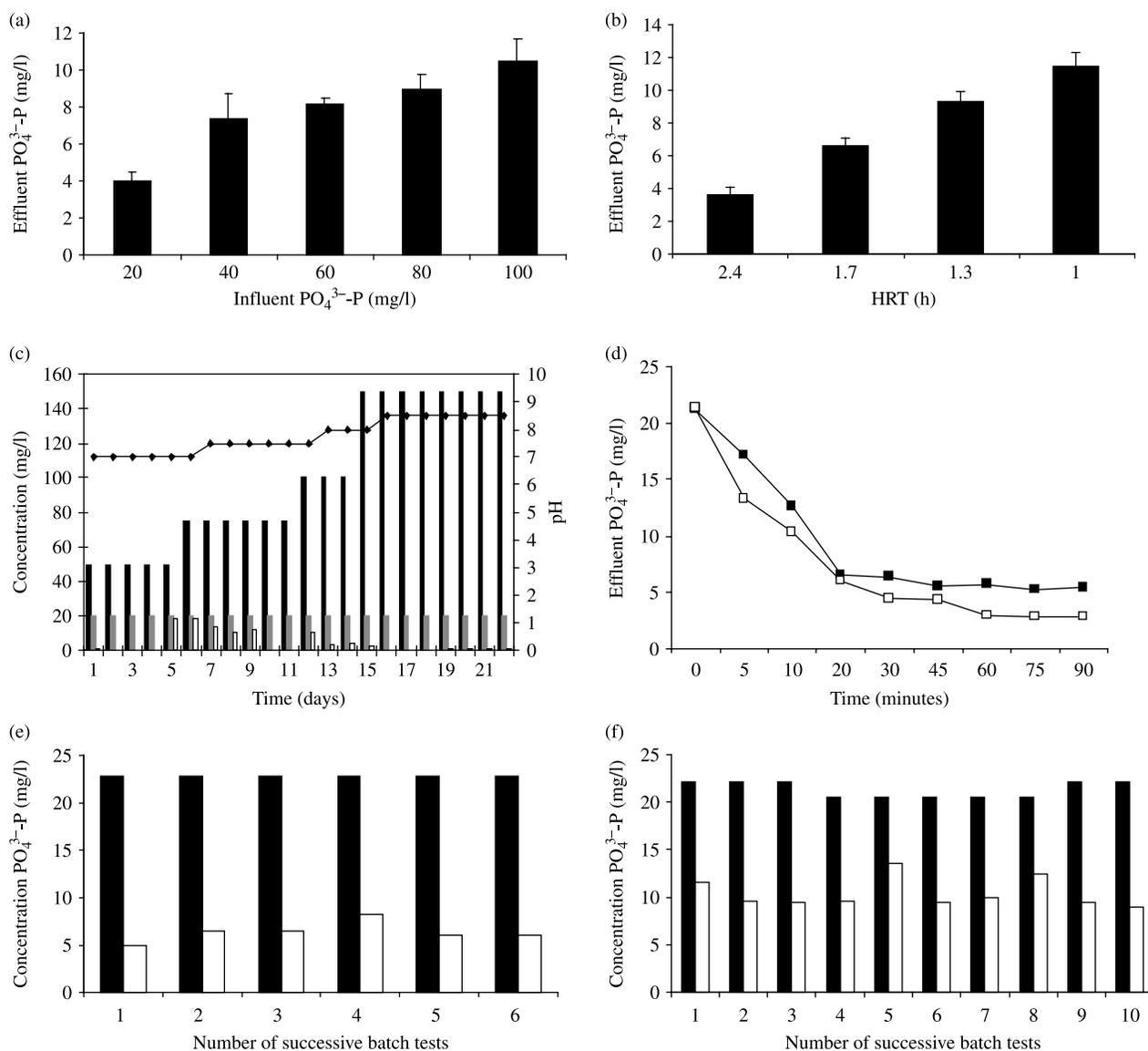
Figure 5 | (a) Influence of initial phosphate concentrations on residual phosphate levels in the effluent (HRT: 2.4 h); (b) Influence of HRT on the residual phosphate levels in the effluent (initial phosphate concentration: 20 mg PO_4^{3-}-P/l); (c) Influence of aeration on pH and phosphate removal (HRT: 2.4 h; (line) pH; (■) urea; (▨) influent phosphate concentrations; (□) effluent phosphate concentrations); (d) Influence of $CaCl_2$ (□) vs. $MgCl_2$ (■) on phosphate levels in the effluent (batch experiment: initial concentrations of $CaCl_2$ or $MgCl_2$: 3 mM; initial urea concentrations: 200 mg/l); (e) Influence of MgO on phosphate elimination at a total molar $[Mg^{2+}]:[PO_4^{3-}$-P]:$[NH_4^+]$ ratio of 4.6:1:8, ((■) influent concentrations, (□) effluent concentrations); and, (f) Influence of MgO on phosphate elimination at a total molar $[Mg^{2+}]:[PO_4^{3-}$-P]:$[NH_4^+]$ ratio of 4.6:1:5.2 ((■) influent concentrations, (□) effluent concentrations).

(Figure 5a). At an initial phosphate concentration of 20 mg PO_4^{3-}-P/l, the decrease in the HRT from 2.4 to 1 h resulted in an increase of the residual phosphate levels in the effluent, from 4 to 12 mg PO_4^{3-}-P/l (Figure 5b).

Aeration of the reactor resulted in enhanced nitrification, and consequently, pH values decreased from 8.5 to 7, which abolished almost completely the capacity for

phosphate removal (Figure 5c). By tripling the amount of urea added, both pH values and phosphate removal could be restored, thus indicating that the ureolytic activity of the sludge was the main driving force for the phosphate precipitation.

The use of $CaCl_2$ instead of $MgCl_2$ did not give rise to a significant improvement on phosphate elimination

(Figure 5d). In contrast, the use of MgO, which has basic properties, resulted in higher residual phosphate levels in the effluent, around 6 to 10 mg PO_4^{3-}-P/l (Figure 5e and f)? The pH was in this case around 8.8, and the higher the urea used, the lower the residual phosphate in the effluent was. These results fitted with those obtained with PHREEQC model at pH 9.2, assuming that only struvite precipitates, and with an initial phosphate concentration of 20 mg PO_4^{3-}-P/l and the two tested molar $[Mg^{2+}]$:$[PO_4^{3-}$-P]:$[NH_4^+]$ ratios of 4.6:1:8 and 4.6:1:5.2, respectively (data not shown).

Overall, the experimental results obtained for phosphate elimination are better than those predicted with the models for single struvite precipitation. This fact indicates that other precipitates are also likely to be formed during the process, most probably $Mg_3(PO_4)_2 \cdot 8H_2O$ according to Figure 2. Occasionally, during the continuous operation of the reactor, $Mg_2PO_4OH \cdot 6H_2O$ could be isolated, probably from the combination of $Mg_3(PO_4)_2 \cdot 8H_2O$ and $Mg(OH)_2 \cdot 4H_2O$, and thus indicating that pH values above 10 can be obtained in the micro-environment of the sludge flock.

CONCLUSIONS

This study shows that the ureolytic method previously developed for the precipitation of Ca^{2+} can be successfully applied for the continuous precipitation of phosphate from industrial anaerobic effluents. A pH higher than 8.5 is required and the use of $MgCl_2$ gave better results compared to the use of MgO. The use of computer models, such as MAPLE or PHREEQC, is very helpful to establish the operational conditions required for the desired results or to verify the experimental results obtained. Currently, research at pilot-scale is on-going.

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