

Economic Evaluation of the Precipitation of Phosphate as Struvite at Pilotscale

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Abstract A novel approach using ureolytic induced MAP formation, for the recovery of phosphate, has been economically evaluated. The ureolytic MAP crystallization has been tested on anaerobic effluent of a potato processing company in a pilot plant, with MgCl₂·6H₂O as magnesium source. The pilot plant showed a high phosphate removal efficiency of 82 ± 9 %, resulting in a final effluent concentration of 13 ± 7 mg/L PO₄-P. XRD analyses confirmed the presence of struvite in the precipitate. During operation pH and the molar magnesium : ammonium : phosphate ratio are the most important operational parameters influencing MAP crystallization. Results show that for high phosphate concentrations in wastewater (e.g. 100 mg/L PO₄-P) the ureolytic phosphate precipitation is a cost effective method (6.1 € kg⁻¹ P_{removed}). Moreover, the technique is competitive with the chemical phosphate precipitation of struvite (6.2 € kg⁻¹ P_{removed}).

Keywords: Phosphate removal; nutrient recovery; ureolytic activity

INTRODUCTION

Phosphorus is an important element, making a major contribution to agricultural and industrial development, but its release to natural water bodies is one of the main causes of eutrophication. It is desirable that water treatment facilities remove phosphorus from the wastewater before it is returned to the environment. In most countries, total removal or at least a significant reduction of phosphorus is obligatory, but is not always fulfilled.

In recent times two new processes have been developed for P precipitation from wastewater, the calcium phosphate crystallization process and the magnesium ammonium phosphate (MAP) crystallization process. (Doyle and Parsons, 2002). The recovered products can be used as the alternative of agricultural fertilizer or as the phosphate rock for phosphate industry (Li and Zhao, 2003; de-Bashan and Bashan, 2004).

Anaerobically treated wastewater mostly contains large amounts of phosphate and ammonium. For the recovery of phosphate as struvite an increase of pH and the addition of a magnesium source is necessary. When dealing with anaerobically treated wastewaters, pH increase can be achieved by simple air stripping. If air stripping does not suffice, additional alkaline reagent must be added, e.g. sodium hydroxide, although this alkaline addition can be combined with the supplementation of magnesium using either MgO or Mg(OH).

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An alternative process is the ureolytic MAP crystallization. In this process pH is increased by means of bacterial urease activity. Ureolytic activity decomposing urea in to ammonium leads to MAP formation when phosphate and Mg^{2+} -ions are present. (Meesschaert et al., 2007; Carballa et al., 2008; Desmidt et al., 2009).

MATERIALS AND METHODS

Description of the pilot plant

Ureolytic MAP crystallization was tested on anaerobically treated wastewaters in a pilot plant (figure 1). Influent was fed into a compressor-connected stripper by a centrifugal pump P1. $MgCl_2 \cdot 6H_2O$ (14.2 %) and urea (4%) were dosed with volumetric pumps P2 and P3 to the crystallization reactor. Influent flow rates to the stripper varied between 0.3 and 0.35 m^3h^{-1} , which resulted in a hydraulic retention time of around 0,7 hours. The effluent of the stripper flowed over to the crystallization reactor, provided with ureolytic sludge. The HRT varied between 2.9 and 3.3 hours. The effluent of the crystallisation reactor flowed to a settler, where separation between effluent and solids occurred. The heavy fraction of the struvite precipitate remained in the settler while the sludge and the smaller struvite crystals flowed over to the decantor and were recirculated to the crystallization reactor after precipitation.

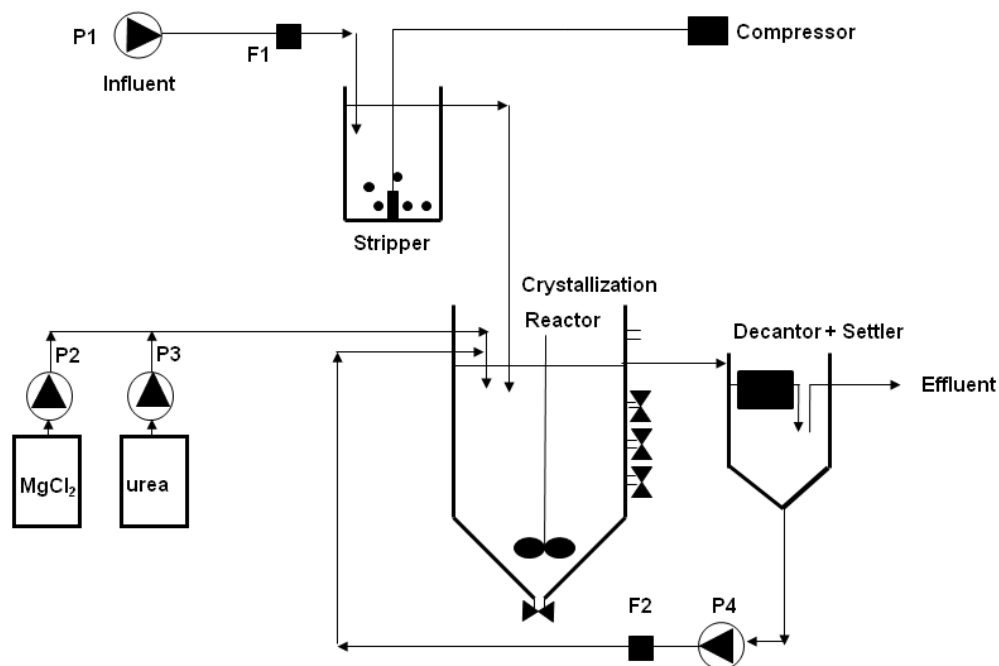


Figure 1. Scheme of the pilot plant used for ureolytic MAP crystallization

Wastewater characteristics

The pilot plant was fed with the effluent from an upflow anaerobic sludge bed (UASB) reactor from a potato processing industry. Table 1 shows the main characteristics of this wastewater, which corresponds with the influent of the MAP crystallizator.

Analytical methods

pH was measured with a pH meter (Mettler Toledo seven multi). Dissolved oxygen was measured with an oxygen meter Oxi 315 (WTW). Ammonium and magnesium were

determined with a Dionex DX-100 chromatograph equipped with a conductivity detector. Phosphate was measured with a Dionex series 4500i ion chromatography equipped with a conductivity detector. Dry matter content and its mineral fraction were determined according to standard methods (Greenberg et al, 1992). Urea was determined colorimetrically with diacetyl monoxime. XRD analyses were done by using a Stoe Stadi P unit with Cu K α radiation at 0.1541 nm with an image plate as detector.

Determination of the ureolytic activity

For the determination of the ureolytic activity 20 ml of sludge was taken from the crystallization reactor and washed several times with phosphate buffer by centrifugation during 15 minutes at 5000 g. After washing the sludge was suspended in 95 ml of salt solution (0.5 g KHCO₃ and 0.5 NaCl suspended in 330 ml tap water and 660 ml demineralised water) and 5 ml of a 2000 mg.L⁻¹ urea-nitrogen solution. The solution was incubated and shaken at 30°C. During 2 hours samples were taken and analyzed for ammonium by ion chromatography.

RESULTS AND DISCUSSION

The ureolytic MAP crystallization has been tested on anaerobic effluent of a potato processing company in a pilot plant, with a reactor volume of 1 m³, during several months. MgCl₂.6H₂O was used as magnesium salt during this process, because of the higher solubility compared to MgO and MgOH (Münch and Barr, 2001). During operation pH and the molar magnesium : ammonium : phosphate ratio are the most important operational parameters influencing MAP crystallization (Song et al., 2007).

The characteristics of the influent, stripper and effluent, during ureolytic MAP crystallization, of a potato processing wastewater are given in table 1.

Table 1. Characteristics of the influent, stripper and effluent obtained during MAP crystallization of a potato processing wastewater

Parameter	Influent	Stripper	Effluent
pH	7.41 ± 0.31	7.75 ± 0.27	8.04 ± 0.26
NH ₄ ⁺ (mg/L)	432 ± 76	415 ± 64	462 ± 66
Mg ²⁺ (mg/L)	48 ± 16	41 ± 16	130 ± 14
PO ₄ -P (mg/L)	99 ± 40	78 ± 30	13 ± 7
Inorganische Carbon IC (mg/L)	785 ± 165	765 ± 160	800 ± 145

From the results given in table 1 it is clear that some MAP-formation occurred in the stripper, thus by simple aeration of the influent. The pilot plant showed a high phosphate removal efficiency of 82 ± 9 %, resulting in a final effluent concentration of 13 ± 7 mg/L PO₄-P. During this period the added molar ratios of magnesium and urea-N were 2.0 ± 0,8 Mg.P⁻¹ and 2.4 ± 0.9 urea-N.P⁻¹ (phosphate concentrations in the influent). In the past the pilot plant has been running at higher pH 8.4 ± 0.2 (data not shown), which resulted in an even higher phosphate removal efficiency of 92 ± 7 % and a final effluent concentration of 5.9 ± 5.5 mg/L PO₄-P. During this period the added molar ratios of magnesium and urea-N were 2.1 ± 0.8 Mg.P⁻¹ and 3.3 ± 0.7 urea-N.P⁻¹. So, a higher ammonium : phosphate ratio also results in a higher phosphate removal efficiency.

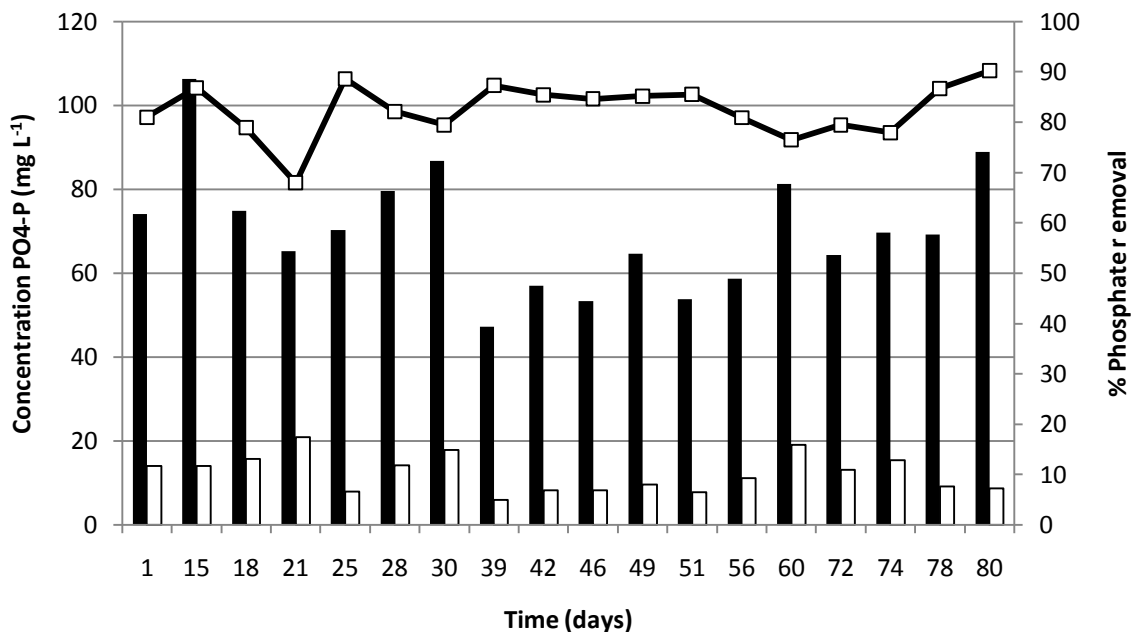


Figure 2. Phosphate concentration in influent (■), effluent (□) and phosphate removal (line) during ureolytic MAP crystallization

To evaluate the activity of the micro-organisms, urea concentration and ureolytic activity were tested during the operation. The mean value of the volatile suspended solids and specific ureolytic activity were respectively 7.8 g.L^{-1} and $0.30 \text{ g NH}_4\text{-N.g VSS}^{-1}\text{d}^{-1}$ (figure 3). This corresponds with an ureolytic activity of $0.056 \text{ mM urea.min}^{-1}$, which is comparable with the ureolytic activity determined by Hammes *et. al* during the microbial CaCO_3 precipitation (Hammes *et al.*, 2003). In addition no urea was found in the effluent of the treated wastewater. XRD analyses confirmed the presence of struvite in the precipitate.

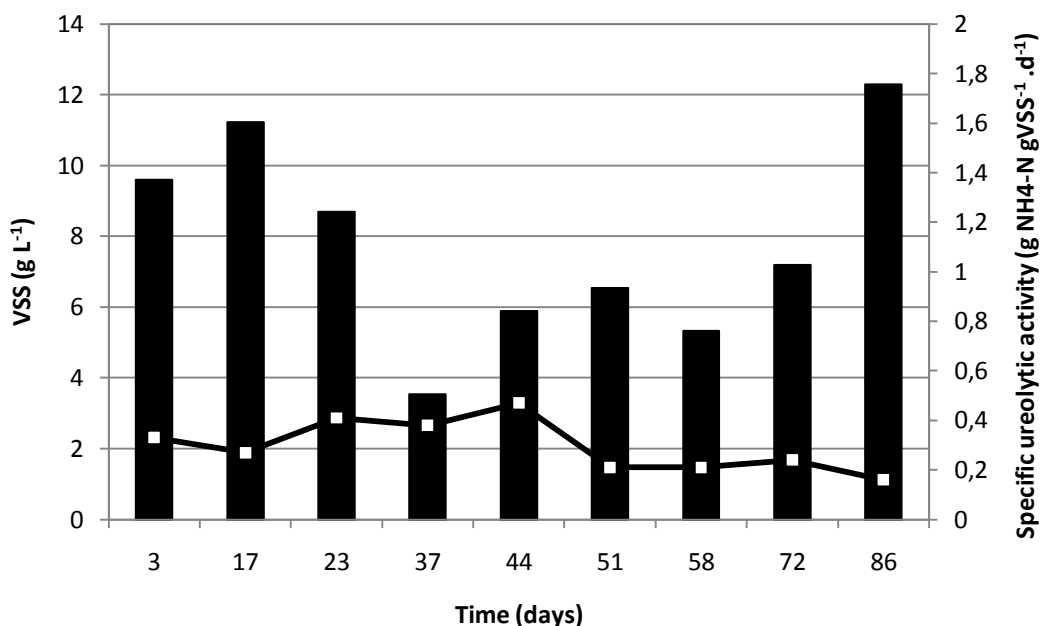


Figure 3. Specific ureolytic activity (line) and volatile suspended solids (VSS) (□) during ureolytic MAP crystallization

The cost for the ureolytic MAP crystallization according to an influent phosphate-phosphorus concentration of 100 mg/L is given in table 2 and is estimated at 6.1 € kg⁻¹ P_{removed}. The cost for struvite precipitation by air stripping and addition of MgCl₂ and NaOH is estimated at 6.2 € kg⁻¹ P_{removed} (Carballa et. al., 2008; personal communication). So, the ureolytic MAP crystallization is competitive with the chemical phosphate precipitation as struvite.

Table 2. Cost estimation of ureolytic and air stripping/MgCl₂/NaOH MAP crystallization (Carballa et. al., 2008; personal communication) according to influent phosphate-phosphorus concentrations of 100 mg/L.

	Ureolytic MAP crystallization	Air stripping/ MgCl₂/NaOH
MgCl ₂ (€ kg ⁻¹ P _{removed})	2.6	2.6
Urea (€ kg ⁻¹ P _{removed})	2.6	-
NaOH (€ kg ⁻¹ P _{removed})	-	3
Energy and sludge (€ kg ⁻¹ P _{removed})	0.9	0.6
Total (€ kg⁻¹ P_{removed})	6.1	6.2

CONCLUSIONS

Phosphate recovery by MAP crystallization is a alternative way of removing phosphate from wastewaters, especially for anaerobically treated wastewater. During operation pH and molar magnesium : ammonium : phosphate ratio are important. The optimal pH is around 8.5 although results show also a good removal efficiency at a pH of 8. Increasing the ammonium : phosphate ratio resulted in a better removal efficiency.

The ureolytic MAP crystallization requires, besides a magnesium source, the addition of urea. During operation no urea was found in the effluent, meaning complete hydrolysis of urea by the sludge, present in de crystallization reactor.

Results show that for high phosphate concentrations in wastewater (e.g. 100 mg/L PO₄-P) the ureolytic phosphate precipitation is a cost effective method. Moreover, the technique is competitive with the chemical phosphate precipitation as struvite (table 2).

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