RECOVERY OF PHOSPHORUS BY FORMATION OF STRUVITE WITH THE PHOSPAQ[™] PROCESS

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Abstract

This paper describes several case studies comprising Phospaq[™] technology for recovering phosphorus and nitrogen from sludge dewatering rejects waters and anaerobically treated industrial effluents by controlled precipitation of struvite.

Long term full-scale operational results of two full-scale Phospaq[™] installations are discussed in detail. Combining Phospaq[™] technology with Anammox® technology allows for extended removal of phosphorus and ammonium from nutrient (N & P) rich liquors.

The quality of the produced struvite is in compliance with European legislation for fertilisers. The struvite crystals have an average particle size of 0.7 mm and are used as raw material for producing bespoke agricultural fertilisers.

Keywords

Phosphorus, Struvite, MAP, Magnesium-ammonium-phosphate, Nutrient recovery, Fertiliser, Phospaq

Introduction

Recovery and removal of nutrients, especially phosphorus is of importance in preventing eutrophication. In addition recovery of phosphorus is of interest as it is a finite resource, which might become scarce in the medium term future.

Anaerobic treatment is effective in recovering energy from waste water in the form of biogas. As anaerobic treatment does not really remove nutrients, anaerobic effluents often still contain relatively high residual concentrations of phosphorus and nitrogen. Recovery of these nutrients can be achieved in a controlled manner using the Paques proprietary Phospaq[™] process. The Phospaq[™] reactor is a continuously aerated and therefore agitated reactor in which magnesium (Mg²⁺) is dosed to stimulate the controlled formation of magnesium-ammonium-phosphate (MAP or so called struvite). The chemical reaction can be described as follows (equation 1):

 $Mg^{2+} + NH_{4^{+}} + PO_{4^{3-}} \leftrightarrow MgNH_4PO_4 \cdot 6 H_2O$ (1)

The struvite crystallization is facilitated by the pH increase via stripping of carbon dioxide (CO₂) and addition of magnesium-oxide (MgO). The Phospaq[™] reactor is generally operated at a pH between 8 and 8.5. Dosing of MgO instead of MgCl₂ is preferred as it often shows to be more economical and eliminates the need for additional dosing of caustic soda (NaOH).

The Phospaq[™] reactor is equipped with a specially designed internal separator for retention of struvite crystals. Figure 1 shows pictures of struvite crystals collected from a Phospaq[™] reactor. The average size of the struvite crystals harvested from the Phospaq[™] reactors is 0.7 mm (Abma, *et al* 2010). Whereas the bigger crystals settle and are harvested from the bottom of the reactor, the smaller crystals are kept in suspension in the reactor by the aeration. The smaller crystals in suspension are used as nuclei for further crystallization of struvite.



Figure 1: Scanning Electron Microscopy (SEM) and optical microscopy pictures of struvite crystals (left and middle, respectively) and collected struvite (right), adapted from Abma *et al.* (2010).

The struvite is extracted from the bottom of the reactor and subsequently dewatered. The collected struvite has a dry matter content of 55 to 65%. During storage, the dry matter content increases over 70%.

Long term full scale experience has shown the Phospaq[™] process to be a reliable way to remove and recover phosphorus from industrial waste water. This is demonstrated by the following two case studies.

Case Study 1: Lomm WwTW (NL) – Industrial effluent

The Lomm WwTW in The Netherlands (figure 2) receives wastewater from a potato processing factory. After anaerobic treatment the wastewater is treated in a Phospaq[™] reactor for phosphorus recovery. Figure 4 shows a schematic representation of the process scheme at Lomm WwTW.



Figure 2: The Phospaq[™] reactor (left) and struvite collection (right) at Lomm WwTW



Figure 3: Process scheme at Lomm WwTW comprising anaerobic digestion (UASB) and Phospaq

As Table 1 shows, the Phospaq[™] reactor receives a load of about 120 kg P/d, of which approximately 75% is recovered as struvite. This corresponds to an overall struvite production of 720 kg per day.

Table 1: Influent and recovered phosphorus load of the Phospaq™ reactor at Lomm

	year 1	year 2
Influent load (kg P/d)	125	113
Recovered struvite (kg P/d)	94	85

Figure 4 presents long term (2 year) data on the concentrations of phosphate and ammonium in the influent and effluent of the Phospaq[™] reactor at Lomm. The phosphate concentration of the influent and effluent were 62 mgP/l and 15 mgP/l respectively. Achieving lower phosphate concentration is feasible however not economical as it would require disproportional amounts of MgO dosing. Operating at the current recovery efficiency is determined by economic considerations that include MgO consumption, struvite revenue and a reduction in phosphate discharge fees. The removed amounts of phosphorus did correspond with the stoichiometric composition of the struvite produced.



Figure 4: Phosphate concentration in the influent and effluent of the Phospaq[™] reactor at Lomm

Inspection of the Lomm Phospaq[™] reactor after two years of operation revealed that no significant amounts of struvite had precipitated onto the reactor internals and that struvite deposits were minimal.

Case Study 2: Olburgen WwTW (NL) - Sludge dewatering reject & industrial effluent

The Olburgen WwTW (figure 5) comprises anaerobic digesters, a Phospaq[™] reactor for phosphorus (P) recovery and Anammox[®] reactors for extended nitrogen (N) removal. The plant is operated by the DBFO company Waterstromen BV. The Olburgen WwTW treats a mixture of municipal sludge dewatering liquor and industrial effluent from a nearby food processing factory (Abma *et al.*, 2010). Figure 6 shows the process scheme, where the Phospaq[™] reactor recovers the phosphorus after anaerobic treatment.

The PhospaqTM reactor is equipped with a bespoke aeration system providing efficient mixing and enhancing stripping of CO_2 which is advantageous for struvite formation. In addition the aeration enhances residual BOD from the anaerobic treatment processes by biological oxidation. MgO is dosed to the reactor to further raise the pH and to achieve the desired P recovery. The struvite is harvested from the reactor and is used as a slow-release fertiliser (figure 5). The struvite quality meets EU requirements for use fertiliser use and has been tested for stimulating crops growth (Driessen *et al*, 2012).



Figure 5: The Phospaq[™] and ANAMMOX[®] reactors (left) and struvite collection (right) at Olburgen



Figure 6: Process scheme of the Olburgen STW comprising anaerobic digesters, Phospaq[™] reactors for P recovery and Anammox[®] for extended N removal

Table 2 presents the performance data of the Phospaq[™] reactor, showing improving performance over the years, reaching 150 kg P/d recovered after 3 years, corresponding to a daily struvite production of 1200 kg. The struvite was selectively removed from the reactor minimising any impurities.

Table 2: Performance data of the Phospaq[™] reactor at Olburgen

		year 1	year 2	year 3	year 4	year 5	
Influent load							
P (kg/d)		162	184	196	191	182	
COD (kg/d)		1583	1824	1635	-	-	
Removed load							
Recovered (ka/d)	Ρ	84	133	149	155	148	
COD (kg/d)		724	1224	918	-	-	

Table 3 presents the results of an analysis of the struvite produced at Olburgen. It shows that the values for heavy metals are well below the EU standards for fertilisers making it suitable to be applied as an agricultural fertiliser.

Table 3:	Heavy metal analysis of the struvite from the $\ensuremath{Phospaq^{\ensuremath{TM}}}$ at Olburgen
	(adapted from Abma et al., 2010)

	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As
EU standard (mg/kg P)	31	1875	1875	19	750	2500	7500	375
struvite product (mg/kg P)	0.9	17	42	<0.3	26	6.6	336	<6
Content compared to EL	J							
standard	3%	1%	2%	<2%	3%	<1%	4%	<2%

While phosphorus is removed in the PhospaqTM reactor by chemical precipitation, the majority of the ammonium is removed biologically in an Anammox[®] reactor. In the Anammox[®] reactor ammonium oxidizing bacteria convert part of the ammonium to nitrite ($NH_{4^+} + O_2 \rightarrow NO_2$) while anammox bacteria convert the residual ammonium and nitrite directly to nitrogen gas ($NH_{4^+} + NO_2^- \rightarrow N_2$). Equation 2 presents the simplified overall reaction:

$$1 \text{ NH}_{4^+} + 0.85 \text{ O}_2 \rightarrow 0.57 \text{ NO}_2^- + 0.43 \text{ NH}_{4^+} \rightarrow 0.44 \text{ N}_2 + 0.1 \text{ NO}_3^{-+} + \text{new biomass}$$
(2)

Figure 7 presents the phosphate and ammonium concentration in the influent of the Phospaq[™] reactor and effluent of the Anammox[®] reactor at Olburgen. Despite the high variations in the concentration of the influent, ranging from 50 to 140 mg/L, the phosphate concentration in the effluent remains relatively stable below 20 mg/L. While the average influent phosphate concentration was 78 mgP/L, the average effluent concentration was 14 mgP/L, resulting in an average removal of 82% over the last 2 years of operation.

The average ammonium concentration was 370 mgN/L, while the average effluent concentration was 29 mgN/L. Long term (2.7 years) operation of the Phospaq[™] and Anammox[®] process train has demonstrated an average ammonium removal efficiency above 92% at fluctuating loading conditions.



Figure 7: Phosphate (left) and ammonium (right) concentrations in the influent and effluent at Olburgen STW

In addition to these successful full scale applications for industrial waste waters, two more Phospaq[™] reactors are under construction for phosphate recovery from sludge dewatering liquors at municipal waste water treatment works.

Case study 3: Severn Trent Water (UK) - Sludge dewatering reject

In the UK, at Severn Trent Water's Stoke Bardolph STW, a Phospaq[™] reactor is being constructed to treat reject water from a sewage sludge digester (Morris & Jeffcoat, 2013). The capacity of the Phospaq[™] reactor is 550 kg P per day. After treatment of the sludge dewatering liquor by the Phospaq[™] reactor, the effluent is combined with a nutrient rich trade liquor and subsequently treated by an Anammox[®] reactor for the removal of nitrogen.

Case study 4: Waterboard De Dommel (NL) - THP Sludge dewatering reject

At Waterboard De Dommel in the Netherlands, a Phospaq[™] reactor for a load of 110 kg P/d will be constructed to treat the dewatering liquor of digested sludge pre-treated by a thermal hydrolysis process (THP). The Phospaq[™] reactor will decrease the phosphorus concentration prior to entering an Anammox[®] reactor and simultaneously remove remaining BOD after the digester, making the wastewater suitable for further treatment. The effluent of the Phospaq[™] reactor will be mixed with pre-THP-dewatering liquor and subsequently treated by the Anammox[®] reactor for removal of ammonia. The process scheme of the sludge treatment facility at the Waterboard De Dommel is shown in figure 8.



Figure 8: Process scheme of the THP sludge treatment plant at Waterboard De Dommel comprising anaerobic digestion, a Phospaq[™] reactor for P recovery and Anammox[®] for extended N removal.



Finally the treated (THP) sludge dewatering liquors will be return to the main WwTW (figure 9).

Figure 9: General overall process scheme of the WwTW at Waterboard De Dommel

Conclusions

The Phospaq[™] process has been successfully applied for removal of phosphorus on sludge dewatering liquors at municipal WWTPs as well as on industrial effluents.

Full scale references demonstrates long term reliable performance of the Phospaq[™] process.

Combining the Phospaq[™] process with the Anammox process allows for recovery of phosphorus and extended removal of nitrogen from nutrient rich liquors.

Recovered struvite quality meets EU requirements for use as fertiliser ingredient.

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