A Feasible Approach of Integrating Phosphate Recovery as Struvite at Waste Water Treatment Plants

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Abstract By the end of this century phosphate deposits with low concentrations of hazardous substances, first of all cadmium and uranium, will be totally exploited. As phosphates cannot be substituted for plant nutrition by other substances, usage of secondary phosphate materials is becoming more and more important. At the Institute of Environmental Engineering of RWTH Aachen University several approaches for phosphate recovery have been investigated and developed. The *PRISA* process (*P*hosphorus *R*ecovery by *ISA*) can be integrated into the sludge treatment of a municipal waste water treatment plant (wwtp). Related to the phosphorus inflow load to the wwtp, the process enables a recovery up to 40%. The recovered phosphate can be used either in agriculture or can be sold to the phosphate industry. The process can provide a sustainable sludge management in the future.

Keywords crystallisation; phosphate recovery; sewage sludge; struvite; waste water

INTRODUCTION

The phosphate-ore resources are finite and non-renewable. By the end of this century phosphate deposits with low concentrations of hazardous substances, first of all cadmium and uranium, will be totally exploited. As phosphates cannot be substituted for plant nutrition by other substances, usage of secondary phosphate materials is becoming more and more important. Sewage sludge is an alternative source with a high phosphate potential.

In Germany, approximately one third of the sewage sludge (approx. 2.5 million tons of dry matter per year) is still used in agriculture (Durth and Schaum, 2005; Statistisches Bundesamt, 2006). This recycling's main purpose is, of course, to utilise the nutrients contained in the sludge for fertilisation. But this possibility is going to be restricted by strict limit values for heavy metals and/or the implementation of limit values for additional (organic) substances. However, less sludge recycling in agriculture would mean that the phosphate compounds transferred into the sewage sludge during waste water treatment would no longer be available for plant fertilisation, and thus would have to be substituted by additional mineral fertilisers. It has to be examined to what extent it is possible to recycle valuable compounds of the sewage sludge already within the framework of waste water treatment and before sludge disposal.

At the Institute of Environmental Engineering (ISA) of RWTH Aachen University several approaches for phosphate recovery at waste water treatment plants (wwtp) have been investigated and developed. The processes have been examined in laboratory-scale and pilot-scale experiments. A promising process that is linked up with sludge treatment and process water treatment is described more precisely below. It was baptized the *PRISA process* (**P**hosphorus **R**ecovery by **ISA**). By integrating the process into a wwtp, non-renewable phosphate-ore deposits can be saved and huge environmental impacts in the phosphate-exploiting countries can be avoided.

METHODS

Experiments were carried out first in laboratory-scale (dissolution in 5 litre beakers) and afterwards in a pilot-scale wwtp (Q = 350 L/h) including a two-line sludge treatment composed of pre-thickener, anaerobic digestion and post-thickener. The first line (reference line) was operated in a conventional way and in the second line the recovery of phosphorus was investigated (PRISA line).

The pilot plant was fed with municipal wastewater. Instead of conventional primary treatment, the wastewater was pre-treated by a screen and a curved sieve (0.6 mm). The struvite crystallisation unit was operated in 50 L/h batch experiments.

DESCRIPTION OF THE PROCESS

The first step of the PRISA process is the acidification of excess sludge from enhanced biological phosphorus removal (Bio-P) in order to dissolve phosphates prior to anaerobic digestion (figure 1). Dissolution of phosphate takes place in the pre-thickener and is achieved basically by extension of the hydraulic retention time and periodical careful stirring of the sludge. External organic or inorganic acids are not used for acidification.

The thickened sludge is separated from the supernatant liquor which contains huge amounts of the phosphate that had been biologically bound before. Additionally, a small part of dissolved phosphate emerges from the hydrolysis of biomass. Thus, a considerable phosphorus load can be concentrated within this side-stream. It is particularly important to gain as much as possible of the phosphorus prior to sludge digestion, during which a certain amount of dissolved phosphate is fixed again to sludge particles.

Sludge digestion follows, where incrustations of tanks, aggregates and pipes as a result of spontaneous struvite crystallisation are no longer expected or at least diminished. Subsequently, the sludge enters the post-thickener and is dewatered mechanically. The supernatant liquor of the post-thickener and the filtrate are rich in ammonia and also contain some load of phosphate. Finally, the whole process water streams will be mixed in an equalising tank and solids will be removed by a cloth filter (figure 1). By dosing magnesium oxide (MgO) and after pH adjustment by caustic soda (NaOH), phosphate and ammonia precipitate as struvite (Magnesium-Ammonium-Phosphate – MAP) in the crystallisation reactor.
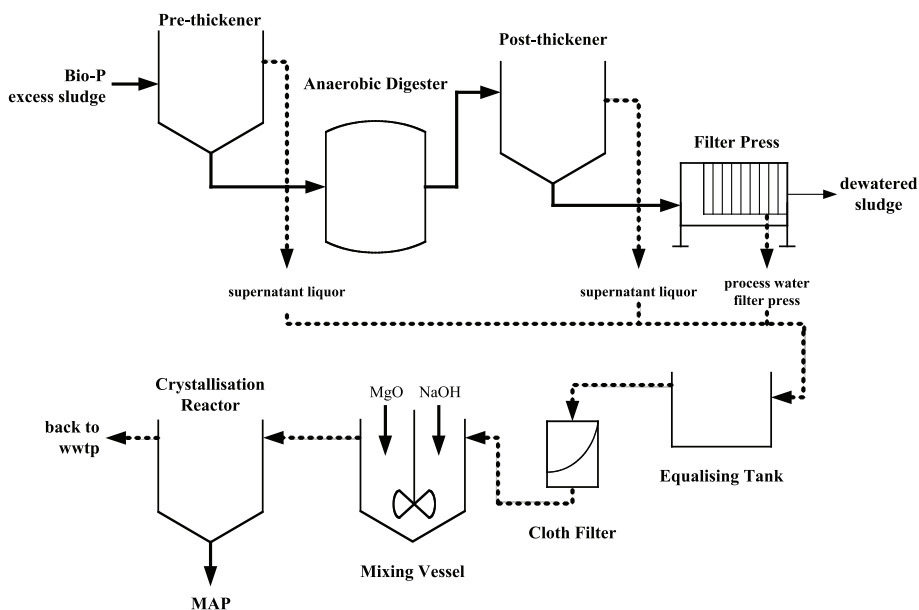

Figure 1. Flow sheet of the PRISA process

RESULTS AND DISCUSSION

Phosphate Dissolution

Figure 2 exemplifies the dissolution of phosphates in the pre-thickener. It is quite evident that with simple arrangements (variation of hydraulic retention time and periodical stirring) the phosphate concentration in the supernatant liquor can be increased significantly. In laboratory-scale experiment the sludge was stirred up once a day and then it settled down again. On the third day the dissolution of phosphate into the supernatant liquor was approximately 8 times higher compared to the regularly operated thickener.
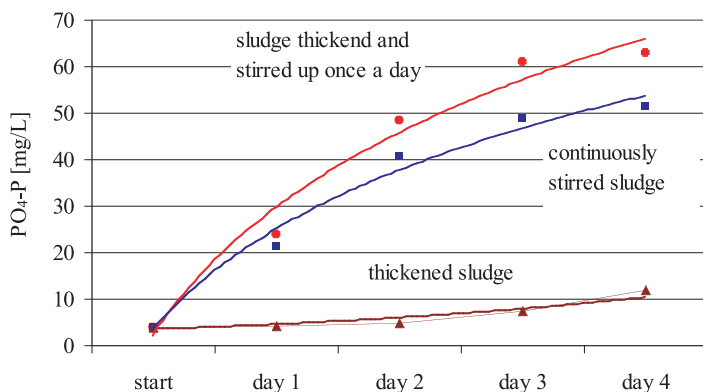

Figure 2. Dissolution of phosphate in laboratory-scale experiments

Subsequent pilot-scale experiments were carried out in order to optimise the dissolution of phosphate. Eleven phases with different hydraulic retention times and mixing conditions (stirring) of the sludge have been tested (table 1). As feed pure excess sludge (ES) and different mixtures of excess sludge and pre-treated waste water (PT-WW) have been used. Due to organic acids contained in the raw waste water it was expected that phosphate dissolution might be higher or faster using pre-treated waste water additionally.

Table 1. Experimental conditions, pre-thickener PRISA line

	Hydraulic Retention Time	Stirring	Feed
phase 1	2 days	once a day	ES
phase 2	2 days	twice a day	ES
phase 3	3 days	once a day	ES
phase 4	3 days	once a day	ES:PT-WW = 6.5 : 1
phase 5	3 days	once a day	ES:PT-WW = 4 : 1
phase 6	3 days	three times a day	ES:PT-WW = 4 : 1
phase 7	3 days	three times a day	ES:PT-WW = 9 : 1
phase 8	2 days	three times a day	ES:PT-WW = 8 : 1
phase 9	2 days	twice a day	ES:PT-WW = 8 : 1
phase 10	3 days	twice a day	ES:PT-WW = 9 : 1
phase 11	3 days	twice a day	ES

ES: excess sludge; PT-WW: pre-treated waste water

Success of phosphate dissolution (table 2) was calculated by equation 1.

$$PO_4 - P_{rec,PT} = \frac{Q_{PW-PT} \cdot c\,(PO_4 - P_{PW-PT}) \ - \ Q_{PT-WW} \cdot c\,(PO_4 - P_{PT-WW})}{Q_{ES} \cdot c\,(P_{total,ES})} \ [\%] \quad \text{(Equation 1)}$$

Q   flow [L]
c   concentration [mg/L]
PO4-P   phosphate
Ptotal   total phosphorus
index "rec, PT"   recovered in pre-thickener
index "PW-PT"   process water pre-thickener
index "ES"   excess sludge
index "PT-WW"   pre-treated waste water

Table 2. Release of phosphorus in pre-thickener 1 and 2; increase of arithmetic mean

		experimental conditions	arithmetic mean	increase
phase 1	pt 1	1 d HRT	4.5%	69%
	pt 2	2 d HRT, stirring once a day	7.6%	
phase 2	pt 1	1 d HRT	5.5%	225%
	pt 2	2 d HRT, stirring twice a day	17.9%	
phase 3	pt 1	1 d HRT	3.5%	551%
	pt 2	3 d HRT, stirring once a day	22.8%	
phase 4	pt 1	1 d HRT, ES:PT-WW = 6.5 : 1	4.0%	335%
	pt 2	3 d HRT, stirring once a day, ES:PT-WW = 6.5 : 1	17.4%	
phase 5	pt 1	1 d HRT, ES:PT-WW = 4:1	3.6%	336%
	pt 2	3 d HRT, stirring once a day, ES:PT-WW = 4:1	15.7%	
phase 6	pt 1	1 d HRT, ES:PT-WW = 4:1	5.2%	151%
	pt 2	3 d HRT, stirring three times a day, ES:PT-WW = 4:1	13.2%	
phase 7	pt 1	1 d HRT, ES:PT-WW = 9:1	6.0%	184%
	pt 2	3 d HRT, stirring three times a day, ES:PT-WW = 9:1	16.9%	
phase 8	pt 1	1 d HRT, ES:PT-WW = 8:1	5.1%	68%
	pt 2	2 d HRT, stirring three times a day, ES:PT-WW = 8:1	8.5%	
phase 9	pt 1	1 d HRT, ES:PT-WW = 8:1	5.2%	224%
	pt 2	2 d HRT, stirring twice a day, ES:PT-WW = 8:1	16.7%	
phase 10	pt 1	1 d HRT, ES:PT-WW = 9:1	1.9%	1059%
	pt 2	3 d HRT, stirring twice a day, ES:PT-WW = 9:1	21.6%	
phase 11	pt 1	1 d HRT	3.6%	476%
	pt 2	3 d HRT, stirring twice a day	20.8%	

pt: pre-thickener; HRT: hydraulic retention time

Good results were obtained in phase 3, 10 and 11, in each case at a hydraulic retention time of three days. In phase 3 no pre-treated waste water was added and the sludge was stirred once a day. According to equation 1 22.8% (table 2) of the P-content of the excess sludge became dissolved in the pre-thickener (reference 3.5%). The phosphorus load released from the sludge in pre-thickener 2 (PRISA line, pt 2) was approximately 6 times (551%) higher compared to the regularly operated thickener (pt 1). Figure 3 represents the dissolution of phosphate in the PRISA pre-thickener (pt 2) and in the reference pre-thickener (pt 1) in phase 3. Dissolution is mostly between 17% and 30%.
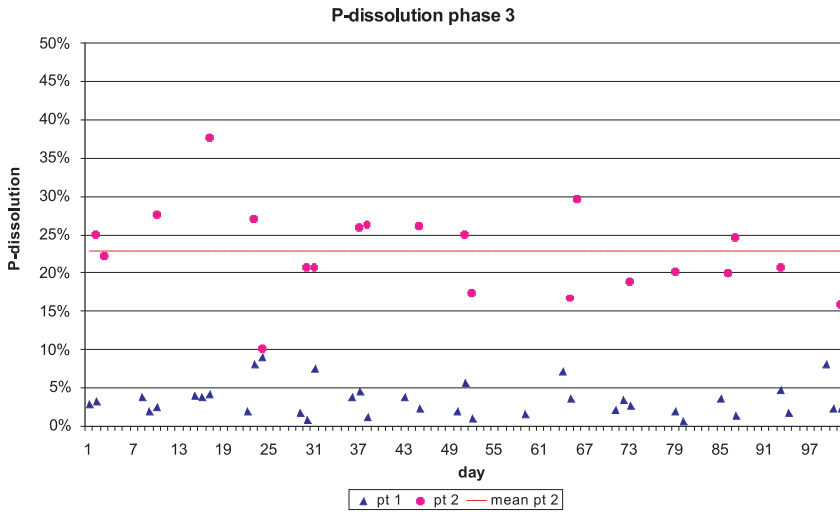
Figure 3. P-dissolution phase 3, pre-thickener 1 and 2

Also in phase 11, pre-treated waste water was not added. The sludge was stirred twice a day. 20.8% (table 2) of the P-content of the excess sludge became dissolved in pt 2 (reference 3.6%), which means an increase of 476% compared to pt 1. Figure 4 visualises that dissolution in phase 11 normally is between 15% and 25%.
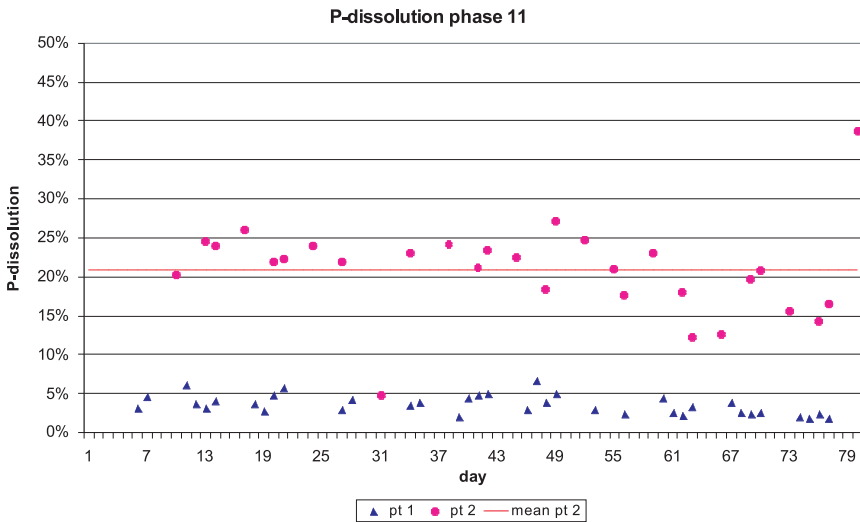

Figure 4. P-dissolution phase 11, pre-thickener 1 and 2

In phase 10 a ratio of excess sludge to pre-treated waste water of 9:1 was added and the sludge was stirred twice a day. 21.6% (table 2) of the phosphorus became dissolved in pt 2 (reference pt 1 1.9%) according to equation 1. The phosphorus load released from the sludge in pt 2 was more than 10 times (1059%) higher than in pt 1. Figure 5 shows the dissolution in phase 10, which normally is between 17% and 27%.
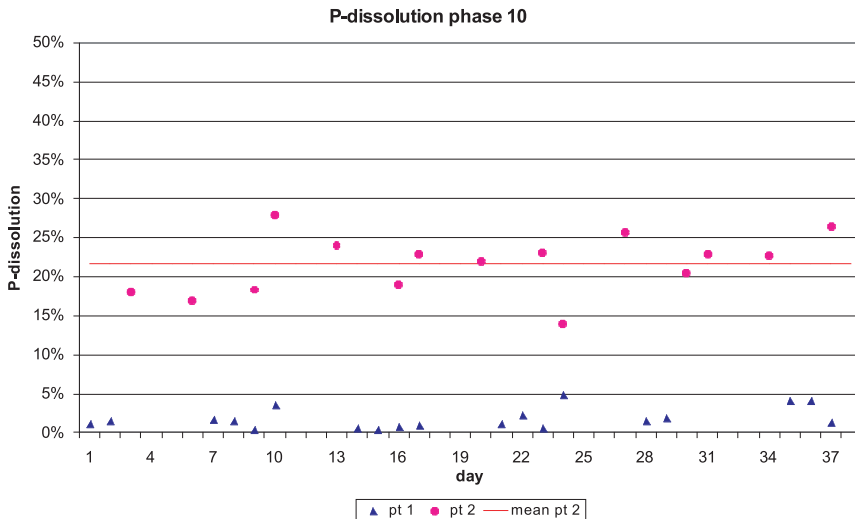
Figure 5. P-dissolution phase 10, pre-thickener 1 and 2

Stirring the sludge three times a day, results in low phosphate dissolution rates (table 2). For an effective dissolution longer repose intervals are necessary. Best results were obtained at a hydraulic retention time of three days. Stirring can be accomplished once or twice a day, respectively. Adding less than 10 Vol.-% of pre-treated waste water seems to be beneficial for the phosphate dissolution. A hydraulic retention time of 2 days is not as efficient as a 3-day thickening. Arranging a 2-day thickening, stirring twice a day is essential. In that case it's of no importance whether pre-treated waste water is added or not.

After anaerobic digestion the sludge is thickened again and dewatered using a centrifuge or a filter press. These process waters are rich in ammonia and also contain some load of phosphate (approx. 20% of the P-content of the digested sludge). These process waters are mixed with the supernatant liquor of the pre-thickener for the struvite crystallisation process.

Struvite Crystallisation

In an aqueous solution comprising magnesium, ammonium and phosphate, struvite precipitates if the pH value is approx. 9. In case of a molar ratio of 1:1:1 between the ions, theoretically a complete nutrient removal is possible (equation 2).

$$Mg^{2+} + NH_4^+ + PO_4^{3-} \rightarrow MgNH_4PO_4 \cdot 6\,H_2O \quad \text{(Equation 2)}$$

After all the process water streams (pre-thickener, post-thickener, filter press) have been mixed, magnesium oxide is added and after pH-adjustment phosphate and ammonia precipitate as struvite in the crystallisation reactor. Figure 6 represents results of the struvite crystallisation experiments. Amongst others, the degree of phosphorus crystallisation depends on the pH value. For the process water used in the pilot scale plant the pH > 9.2 and the molar Mg:N:P ratio of 1.5:6:1 led to a P-crystallisation of more than 90%.
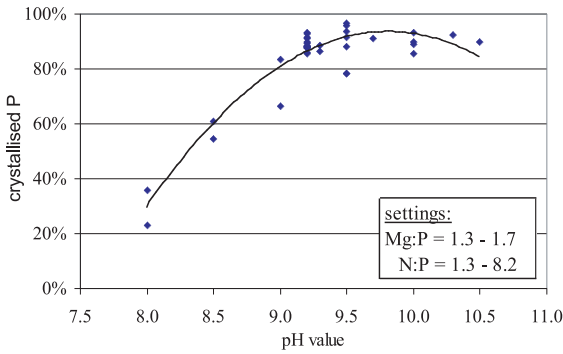
Figure 6. Dependence of struvite crystallisation on pH value

The effluent of the struvite crystallisation unit is re-circulated into the wwtp. Therefore, no limit values have to be met. As a positive side-effect, the nitrogen content of the recirculated water is reduced of 0.45 kg N/kg P, which is linked with the struvite crystallisation.

Product quality

The recovered struvite's fertilising effect was investigated from April to October 2004 and 2005, respectively. The fertilising effect of struvite-phosphorus was compared to a commercial phosphorus fertiliser. It became quite evident that the recycled phosphorus has the entirely same fertilisation effect as mineral fertilisers.

With regard to the discussion about the risk of heavy metals and other harmful substances (e.g. nonylphenol polyethoxylate, bisphenol A, oestrogens) in soils, extensive analysis of the struvite fertiliser have been made. In struvite organic compounds are contained in rather low concentrations compared to the average content in sewage sludge and are often even lower than the limit of detection.

Specific concentrations of all examined heavy metals (milligramme heavy metal per kilogramme phosphorus) bound into the recovered struvite are noticeably lower than in sewage sludge and are lower or in the range of the heavy metal concentrations of mineral fertilisers (figure 7). Especially, the concentrations of cadmium and chromium under-run the average content of these metals in tradable NPK-fertilisers. The slightly higher concentrations of the micro-nutrients copper and zinc present no obstacle for struvite utilisation for plant nutrition.
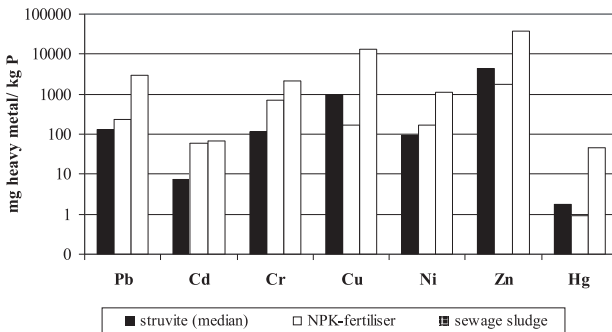

Figure 7. Heavy metal content of struvite, NPK fertiliser and sewage sludge; data fertiliser and sludge (Bannick, 2001)

CONCLUSIONS

The PRISA process can be easily integrated into existing wwtp's. As experiments in a pilot-scale wwtp have shown, by implementing this process up to 40% of the wwtp's phosphorus inflow load can be recovered. The necessary technology is not complicated and the process is easy to operate. The recycled struvite is an excellent plant fertiliser and contains very few hazardous substances. Thus, the applicability of phosphorus recycling by the PRISA process has been proven.

Within the context of resource protection the process can be recommended as possibility for sustainable sludge management in the future. Non-renewable phosphate-ore deposits can be conserved and huge environmental impacts in the phosphate-exploiting countries can be avoided.

ACKNOWLEDGMENT

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