

Is phosphorus recovery from waste water feasible?

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Abstract Phosphorus (P) recovery from waste water must become a predominant goal of all industrialised countries to face the finiteness of the resources of this essential nutrient. The induced crystallisation of calcium phosphate straight from the waste water phase applying tobermorite-rich waste materials from the construction industry as seed material proved to be a suitable method. In laboratory and pilot-scale experiments, P-loads of the crystallisation seeds of up to 13 % total P (P-tot) (30 % P₂O₅) were achieved. Recycling options of the generated products, both as substitute for phosphate rock and as a new fertiliser, were demonstrated. Indicative operating and investment costs for conversion of conventional waste water treatment plants (WWTP) designed for nutrient removal and P-precipitation with iron and aluminium reagents to the proposed new crystallisation technology for simultaneous P-removal and P-recovery were estimated.

Keywords Calcium phosphate; cost evaluation; crystallisation; phosphorus recycling; tobermorite; waste water

Introduction

Phosphorus is an essential nutrient, which cannot be substituted by any other element and is therefore a major component of fertilisers. However, extrapolating the current fertiliser consumption, the depletion of low-contaminated phosphate rock will become a severe problem within the next 30 to 100 years (ATV, 2003). Aiming at a sustainable development and at a preservation of natural resources, it is the goal of the European phosphate industry to replace up to 20 % of phosphate rock by recycling products within the upcoming ten years (Lijmbach, 2004). In this sense waste water treatment plants (WWTP) as important phosphate sinks should not only be used for phosphorus removal, but also for phosphorus recovery. According to state of the art technologies, phosphorus is transferred into the sewage sludge by precipitation and/or enhanced biological phosphorus removal (EBPR/Bio-P) to meet the effluent standards of WWTPs. Apart from unfavourable impacts on the water quality (increase of ion strength, loss of buffer capacity) also the sludge treatment and disposal costs resulting from this technology cannot be neglected.

Recovery of phosphorus from sewage sludge or its ash requires a mechanical, thermal and/or chemical digestion. Although the recovery potential of 40 % from waste water directly, compared to 90 % from sludge and ashes is considerably lower (ATV, 2003), phosphorus recovery straight from the water phase seems to be a reasonable technology taking the technical/chemical expenditure into account. In this case phosphorus is already mainly dissolved and just has to be scavenged by a suitable carrier. Several alternatives are conceivable:

(i) Precipitation of struvite (Heinzmann, 2001) (MAP, magnesium ammonium phosphate) from waste waters, requiring a constant stoichiometrical ratio of magnesium, ammonium and phosphorus of 1:1:1 (Ueno and Fuji, 2001).

(ii) Crystallisation of calcium phosphate: Most waste waters are supersaturated with respect to calcium phosphate compounds. However, spontaneous precipitation (homogeneous nucleation) of calcium phosphate seldom occurs. The fundamental idea of the crystallisation technology is to lower the interfacial energy by the supply of suitable seed material and thus to trigger the deposition of calcium phosphate compounds onto the seed material surfaces (mainly heterogeneous nucleation) in order to achieve equilibrium between Ca ions and phosphate.

Up to now crystallisation has been realised in pilot-scale (i) using sand in fluidised bed technology - the DHV Crystalactor® process - (Giesen, 1999) which requires an initial CO₂-stripping followed by an adjustment of the pH value to optimise the calcium phosphate precipitation, and (ii) using calcite in a stirring reactor (Donnert and Salecker, 1999), which also requires a pH adjustment. In addition, promising laboratory and pilot plant scale results were obtained in Japan by the use of tobermorite pellets as seed material for the deposition of phosphorus minerals in a fluidised bed (Moriyama *et al.*, 2001, 2003). This technology is mainly suitable for side stream Bio-P processes as the pH exceeds pH > 9.5.

The goal of this study was to develop a technology for phosphorus recovery, by which such complex pre-treatment steps as pH adjustment or CO₂ stripping for the crystallisation of calcium phosphate compounds may be avoided. This was realised by using tobermorite-rich construction waste material as seed material (Berg *et al.*, 2005). Another advantage of this tobermorite-rich seed material is the impassivity against the influence of the DOC compared to the application of calcite. Three technologies were tested and compared in pilot-scale with respect to their efficiency and economy using the waste water from a side-stream Bio-P process (Phostrip). The generated crystallisation products were analysed regarding their applicability as a secondary resource for the phosphate industry and/or as a new fertiliser.

Methodology

Two tobermorite-rich waste materials from the construction industry – seed A (grain size: 0.6 – 1.3 mm) and B (grain size: 0.5 – 1.5 mm) – were used. Seed B contained much lower initial concentrations of Fe, Cu and Zn compared to seed A, which was more favourable for a recycling process. Long-term fixed-bed column (20 – 100 l) and stirring reactor experiments (60 l) were carried out with the side-stream supernatant of the Phostrip process at a WWTP in Austria with a P concentration of about 25 mg l⁻¹ P. The suspended solids (SS) content was reduced to < 0.02 g l⁻¹ by means of an electro filtration device. Secondary effluent of the biological WWTP of the Forschungszentrum Karlsruhe - spiked to 25 mg l⁻¹ P by a NaH₂PO₄·H₂O (p.a. Merck) stock solution – was used for the development of the expanded bed technology (40 l) in pilot-scale without previous filtration.

For the fixed bed experiments the parameters filter velocity (FV: 0.5 m h⁻¹, 1.0 m h⁻¹, 1.5 m h⁻¹), the hydraulic retention time (HRT: 1 h, 2 h), the backwashing frequency (once, twice, thrice weekly) and the backwashing medium (air, tap water, filtrate, air/tap water mixture) were varied in order to investigate the influence of these parameters on the durability and efficiency of P-elimination, as well as on the P-yield of the generated products.

Batch experiments were carried out prior to long-term stirring reactor experiments to evaluate the influence of the following operating parameters on the P-elimination and -recovery: pre-treatment of the supernatant, solid/solution ratio (SSR), minimum stirring velocity (MSV) for a complete suspension and higher

stirring velocities (SV). The efficiency of continuous-flow experiments (HRT: 1 h, 2 h) was compared with a long-term discontinuous batch experiment using seed material B in the following cycle: feeding period 25 min., stirring period 120 min., sedimentation period 30 min. and a draining period of 45 min. per batch.

For the performance of the expanded bed experiments the SSR and HRT were optimised in preceding batch experiments. The efficiencies of seed materials A and B (5 wt-%) were compared in long-term continuous-flow experiments with an HRT of 20 min. in the unmoved seed bed.

The soluble reactive phosphorus (SRP) content and pH value of in- and outflow of all reactors were analysed according to relevant EU-DIN norms. The crystallisation products obtained were analysed for total phosphorus (P-tot), for their semi-quantitative chemical composition by XRF (Spectrace 500, Tracor) and for their mineralogical composition (calcium phosphate compounds formed) by XRD (powder diffractometry, Siemens D 5000).

Results and discussion

Fixed bed columns

The P-elimination efficiency of the fixed bed column increased with decreasing FV (Figure 1). Concerning FV, a value of 1.5 h and a concomitant HRT of 1 h proved to be an optimum, when the P content of the additionally obtained product is taken into account. Furthermore, P-elimination of 80 - 100 % could be maintained over a period of about 80 days.

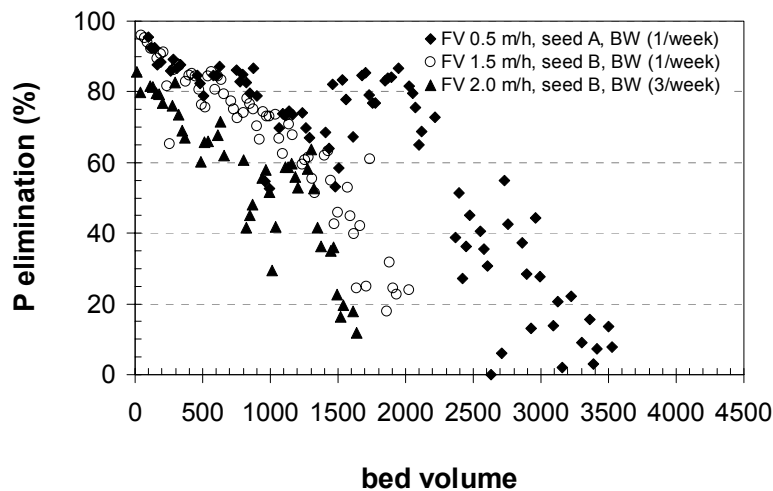


Figure 1 Influence of the filter velocity and the frequency of backwashing (BW) regarding the P-elimination efficiency of fixed bed experiments (HRT: 1 h).

Regular backwashing was necessary, at least once a week with an air/water mixture (Figure 1). The effectiveness of using tap water instead of filtrate for backwashing was not significant. Investigations of the seed material proved that the phosphorus once bound and deposited onto the seed surface was not released during backwashing. P-tot loads of the generated products of up to 10% P-tot were achieved, being favourable for a recycling by the phosphorus industry (Berg *et al.*, 2005), which requires similar properties for the substitutes of phosphate rock, i.e. apatite of a P content of about 10 - 13 % P-tot.

Stirring reactor

In continuous-flow experiments 60 – 70 % of P was eliminated over a period of only 150 h (Figure 2) with the P-rich supernatant (25 mg l^{-1}) applying an HRT of 2 hours. The following sudden drop was caused by the wash-out of highly efficient fine-grained seed material generated by mechanical abrasion during the stirring process. This loss of seed material amounted up to ~ 70 % within 240 h. However, it could be significantly reduced by discontinuous long-term batch technology. By that a constant P-elimination of 80 % during a time period of at least 30 days was achieved (Figure 2).

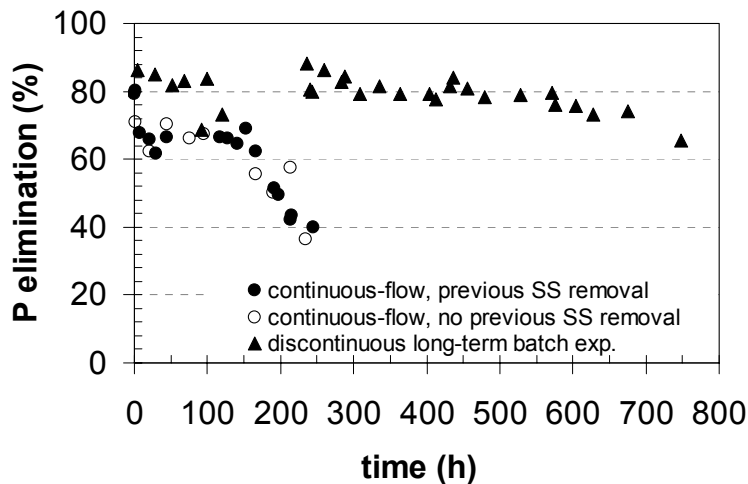


Figure 2 Comparison of discontinuous long-term batch (HRT: > 2 h) and continuous-flow stirring reactor experiments (HRT: 2 h) and impact of previous removal of suspended solids regarding the P-elimination efficiency of seed material B (5 wt- %); SS: Suspended solids.

The pre-treatment for the removal of SS did not improve the P-elimination efficiency (Figure 2). With respect to an optimum in P-elimination and P load, an SSR of 5 wt-% seemed to be optimal. The increase of the SV improved the P-elimination but concomitantly enhanced the abrasion and therefore the loss of seed material. The adjustment of the SV and a clearwater sedimentation zone above the suspension should help to minimise this effect.

Expanded bed reactor

Seed material B was more efficient compared to seed material A, eliminating 70 to 100 % P over 210 days (5100 bed volumes) versus 50 to 80 % over 150 days (3500 bed volumes) (Figure 3). The generated crystallisation products showed a P-tot content of 11 % (seed A) - 13 % (seed B), which is comparable to phosphate rock (natural apatite).

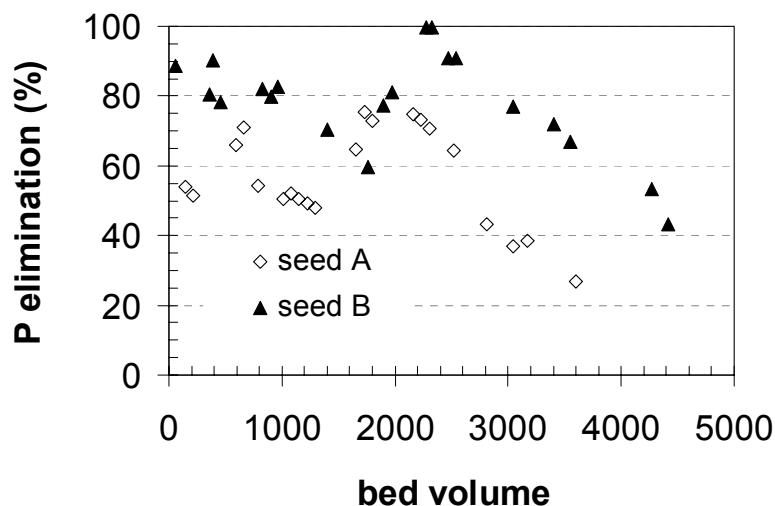


Figure 3 Comparison of the P-elimination efficiency of seed materials A and B (5 wt-%) in expanded bed experiments.

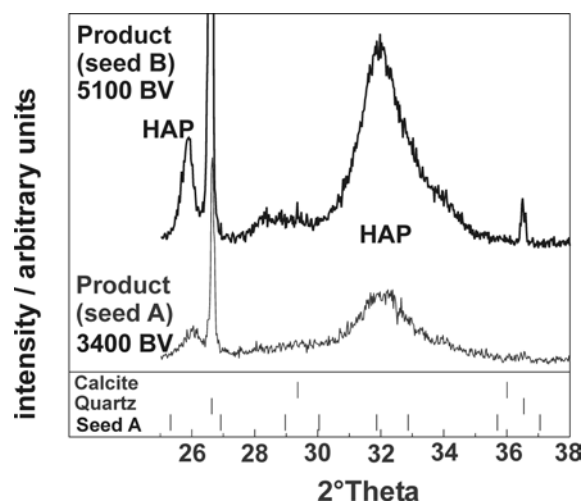


Figure 4 Formation of hydroxyl-apatite (HAP) on seed material A and B during crystallisation in expanded bed experiments; BV: bed volume.

XRD analysis showed distinct peaks of hydroxyl-apatite (HAP)-like compounds (Figure 4). This result was favourable for the recycling of the products.

Recycling of the crystallisation products

The results presented above indicated that a recycling of the P-rich crystallisation products by the phosphorus industry was promising, because the initial (0.1% Fe_2O_3 , 10 mg kg^{-1} Cu, Zn) and end concentrations of the P-rich products of seed material B with respect to Fe_2O_3 (0.3%), Cu (142 mg kg^{-1}) and Zn (15 mg kg^{-1}) generally met the requirements of the P-industry (1% Fe_2O_3 , 50 - 100 mg kg^{-1} Cu and Zn, respectively, Lijmbach, 2004). In contrast to phosphate rock, Cd and U contamination of the generated recycling products was below the detection limit of 0.3 mg kg^{-1} and 10 mg kg^{-1} , respectively. Therefore, the formation of pure recycling products is feasible with the crystallisation technology. Furthermore, it was assumed that the significant residual SiO_2 content of the products of about 30% already provided the SiO_2 aggregates necessary for the recycling process, which have to be added separately when using phosphate rock.

The fertilising efficacy of the recycling products can only be demonstrated fully by green-house and outdoor experiments. However, first hints were obtained by extraction experiments in order to characterise the chemical behaviour of the products. The results showed that the solubility in water was practically not detectable, which supported the mineralogical analysis of weak soluble apatite formation. Therefore, the application of the crystallisation products to low acid soils seemed to be favourable regarding the plant availability of phosphorus. Furthermore, the direct use of the recycling products as a fertiliser in ecological agriculture was promising, as silica favoured the supply of trace metals.

Cost evaluation

A cost model was compiled in order to create a benchmark with respect to investment and operating costs for the total process of phosphorus recovery. The model included all investments and running costs required for P-recovery in addition to a conventional state of the art WWTP designed for N- and C-elimination, such as (i) the Bio-P process (Phostrip), (ii) mechanical pre-treatment (electro-flotation) to remove SS, (iii) the crystallisation and (iv) solar drying of the generated calcium phosphate. Costs for investments, power and seed material (including transport), as well as operating costs were estimated and converted into yearly costs. Expenses for maintenance were assumed to cover a flat-rate of 0.5% of the investment costs per year. The monetary benefit of the model was the reduction in treatment and disposal costs for tertiary sludge, which was considerably lower than by conventional P-precipitation. A sales value for the product was not taken into account, but it was assumed that the generated products would be taken over by the phosphorus industry at the plant site free of charge (Lijmbach, 2004).

Costs for the crystallisation process were estimated with the help of supplier quotations on the base of design parameters as elaborated in the experiments and upscaled according to acknowledged models from Seyfried (1993), Günthert (2001) and Schröder (1998). The costs for the Phostrip process were published in Kaschka (2003). All costs were calculated for a plant of 45,000 population equivalents (PE) assuming a specific hydraulic load of $250 \text{ l PE}^{-1} \text{ d}^{-1}$ including extraneous water.

The results of the cost estimates are shown in Table 1. In that table costs were opposed the yearly costs for P-elimination by simultaneous iron precipitation (Novak, 2001; Paul, 2001). As can be seen, total costs for that process were determined by the costs for final disposal of the generated tertiary sludge. Note that also for the Phostrip process a tertiary sludge production was taken into account.

Costs of stirring reactor and expanded bed technology were in the same order of magnitude. However, the continuous-flow stirring reactor seemed to be the least cost solution concerning a large-scale application, supposed the loss of seed material can be reduced significantly. A further advantage of the stirring technology was that a subsequent reduction of SS was not mandatory. Economically, fixed bed filtration was not justifiable with respect to the extremely low applicable FV of only 0.5 m/h. The application of the crystallisation process in main stream (effluent) of a WWTP proved to be not economical under the given P concentration of typically only 6 - 10 mg l^{-1} P compared to side-stream process concentrations around 25 mg l^{-1} P.

Finally, it has to be remarked, that the high costs for P-recovery partly result from the fact that the recycling product can not achieve a real sales value as phosphate

rock substitute for the phosphate industry. A promising alternative to gain a market value from the generated products is their reuse as a new fertiliser. However, precondition would be to demonstrate fertilising efficacy.

Table 1 cost evaluation for Phostrip (bio-P side-stream), pre-treatment of the supernatant, P-recovery by crystallisation and solar desiccation of the generated products.

Process components	Annual costs (€ PE⁻¹ yr⁻¹)	
1. Phostrip (Bio-P side-stream)		0.79
2. Pre-treatment / Removal of SS		0.32
3. Crystallisation		
Fixed bed (upflow)		1.71
Stirring reactor, discontinuous batch		1.30
Stirring reactor, continuous-flow		1.10
Expanded bed	from	0.95
	to	1.24
4. Solar drying		0.09
Total costs	from	2.14
	to	2.90
Costs for simultaneous precipitation with iron precipitants		(€ PE⁻¹ yr⁻¹)
Agricultural reuse		1.55
Composting, disposal by suppliers		1.66
Landfill		1.73
Incineration		1.86
Assumptions for converting investment- and running costs into annual costs according to LAWA (1994)		(units)
<i>Interest calculation (% per yr)</i>		3
<i>Life-cycle of mechanical and technical equipment (yr)</i>		15
<i>Life-cycle of other components and assemblies (yr)</i>		30
<i>Period under consideration (yr)</i>		31

Conclusions

Phosphorus recovery from waste water by crystallisation is feasible from the chemical and mineralogical point of view. The use of tobermorite-rich waste materials as seed material for phosphorus recovery poses an additional recycling effect. The quality of the generated products is suitable to be reused according to a very low Cd and U contamination compared to phosphate rock. Possibly a new silicate-rich fertiliser could be developed. Concerning process engineering and cost-benefit optimisation, continuous-flow stirring reactor technology is a simple and efficient alternative at the current state of knowledge, if the loss of seed

material can be avoided. The expected increase of costs for phosphate rock and fertilisers due to the limitation of low-contaminated phosphate resources will promote the economy of phosphorus recovery processes in general.

References

- ATV (2003). ATV-DVWK team AK-1.1 "Phosphorrückgewinnung". Pinnekamp, J., Baumann, P., Buer, T., Cornel, P., Donnert, D., Goettlicher-Schmidle, U., Heinzmann, B., Jardin, N., Longdong, J., Mueller, J., Sothen, F. von, Temmink, H., Berg, U., Christian-Bickelhaupt, R., Schaum, C., Weidener, A. and Wichmann-Seidel, A. Phosphorrückgewinnung. *KA: Wasserwirtschaft, Abwasser, Abfall*, **50**, 805-814.
- Berg, U., Donnert, D., Ehbrecht, A., Weidler, P.G., Kusche, I., Bumiller, W. and Nüesch, R. (2005): Phosphate elimination and recovery from waste water by active filtration using crushed gas concrete, *Env. Technol.*, **26**(2), 219-229.
- Donnert, D. and Salecker, M. (1999). Elimination of phosphorus from wastewater by crystallisation. *Env. Technol.*, **20**(7), 735-742.
- Giesen, A. (1999). Crystallisation process enables environmental friendly phosphate removal at low costs, *Env. Technol.*, **20**(7), 769-776.
- Günther, F.W. (2001). *Investitionskosten der Abwasserversorgung*. Oldenbourg-Verlag.
- Heinzmann, B. (2001). Options for P-recovery from Waßmannsdorf Bio-P wwtp, Berlin. Implications for wwtp operation and phosphorus recovery potential at different locations in the Bio-P and sludge treatment process. 2nd international Conference on Recovery of phosphates, Noordwijkerhout, NL, 12.-13th March, 2001.
- Kaschka, E. and Donnert, D. (2003). Das Phostrip-Verfahren in Verbindung mit „Aktivfiltration“, ein wirtschaftlicher Weg zur P-Rückgewinnung. *Schriftenreihe WAR*, **147** (ISBN 3-932518-43-8), 101-128.
- LAWA (1994). *Leitlinien zur Durchführung von Kostenvergleichsrechnungen*. Report of Länderarbeitsgemeinschaft Wasser, München, Germany.
- Lijmbach, D. (2004). Phosphorus recycling in the phosphorus industry, Workshop of the ATV-AK 1.1 team "Phosphorrückgewinnung", 28th October, Weimar, Germany.
- Moriyama, K., Kojima, T., Minawa, Y., Matsumoto, S. and Nakamachi, K. (2001). Development of artificial seed crystal for crystallization of calcium phosphate. *Env. Technol.*, **22**(11), 1245-1252.
- Moriyama, K., Kojima, T., Koga, K., Takino, S. and Minawa, Y. (2003). Crystallisation process using calcium silicate hydrate for phosphorus removal. *Env. Engineering Res.*, **40**, 389-394.
- Novak, O. (2001). Expenditure on the operation of municipal wastewater treatment plants for nutrient removal. *Wat. Sci. Technol.*, **41**, 281-289.
- Paul, E., Laval, M.L., Sperandio, M. (2001). Excess sludge production and costs due to phosphorus removal. *Env. Technol.*, **22**(11), 1363-1372.
- Schröder, M. (1998): *Bewertung der Abwasserfiltration als Verfahrensschritt der kommunalen Abwasserbehandlung*. PhD thesis, RWTH Aachen, Germany.
- Seyfried, C.F. (1993). *Betriebstechnik, Kosten und Rechtsgrundlagen in der Abwasserreinigung*, 4th edn.
- Ueno, Y. and Fujii, M. (2001). Three years experience of operating and selling recovered struvite from full-scale plant. *Env. Technol.*, **22**(11), 1373-1381.