

Phosphorus Removal and Recovery from Waste Water by Tobermorite-seeded Crystallisation of Calcium Phosphate

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Abstract

Investigations were focussed on the development of a technology for phosphorus (P) recovery straight from waste water. Facing the finiteness of the natural resources of this essential nutrient, the declared goal must be the sustainable use of available phosphorus sinks such as waste water treatment plants (WWTP) for the generation of P-rock substitutes. A feasible method for simultaneous elimination and recovery of phosphorus from waste water proved to be the P-RoC process – the phosphorus recovery from waste water by induced crystallisation of calcium phosphate, applying tobermorite-rich waste compounds of the construction industry. The experiments were performed in fixed bed-, stirred- and expanded bed reactors in laboratory- as well as in pilot-scale. The efficiency and longevity of the P-RoC process was determined by the supply of Ca ions and the initial P concentration. Total P (P-tot) contents in the generated crystallisation products of up to 13 % P-tot (30 % P₂O₅) were achieved. Mineralogical investigations proved the formation of a hydroxy-apatite-(HAP) like coating onto the seed material's surface. Reuse options for the generated crystallisation products, such as substitute for phosphate rock or as new fertiliser, were assessed.

Keywords

Crystallisation; CSH; hydroxy apatite (HAP); fertiliser; phosphorus recovery; tobermorite

INTRODUCTION

In natural waters phosphorus concentrations as low as 10 µg/L P can already lead to eutrophication processes and to a deterioration of the water quality. On the other hand phosphorus is an essential nutrient for plants, which cannot be substituted by any other element, what makes it an indispensable fertiliser component in agriculture. Extrapolating the current fertiliser consumption, the depletion of low-contaminated phosphate rocks will become a serious problem within about 100 years (ATV, 2003). This fact implies the necessity of using phosphorus recycling products in the near future. State of the art WWTPs, serving as major sinks for phosphate, would offer a highly potential source for recycling of phosphorus.

Although the recovery potential from the waste water phase directly, is with 40 % considerably lower than 90 % recovery potential from sludge and ashes (ATV, 2003), phosphorus recovery straight from the liquid phase offers the noteworthy advantage that phosphate is already dissolved. By that, expensive and sophisticated mechanical, thermal and/or chemical processes for digestion of precipitated sludge or its ashes are not required, what makes processing cheaper and simpler. Phosphate has just to be scavenged, either by the precipitation of struvite (Heinzmann, 2001), requiring a constant stoichiometrical ratio of magnesium, ammonium and phosphorus (Ueno and Fuji, 2001), or by formation of calcium phosphate, e.g. by crystallisation. Though most waste waters are supersaturated with respect to calcium phosphate compounds, spontaneous precipitation

of calcium phosphate is kinetically inhibited. However, the supply of suitable seed material initiates the deposition of calcium phosphate compounds onto the seed material surfaces in order to achieve equilibrium between Ca ions and phosphate.

Crystallisation has already been realised in pilot-scale using sand as seed material (DHV Crystalactor® process, Giesen, 1999) and requiring CO₂-stripping followed by an adjustment of the pH value prior to the calcium phosphate precipitation. Calcite as seed material was applied in a stirred reactor (Donnert and Salecker, 1999), also requiring an adjustment of the pH value. Promising results were obtained in Japan by the application of tobermorite pellets as seed material in a fluidised bed reactor (Moriyama *et al.*, 2001, 2003). However, the pH value of the outflow in these experiments exceeded pH > 9.5, what required further treatment prior to discharge into natural water bodies.

The goal of this study was to develop a simple technology for phosphorus recovery from waste water, by which complex pre-treatment steps as pH adjustment or CO₂ stripping can be avoided. This was realised in the P-RoC process, (phosphorus recovery from waste water by crystallisation of calcium phosphate compounds), using tobermorite-rich construction industry waste grains as seed material (Berg *et al.* 2005, Berg *et al.*, in press). The new material proved to be more inured to dissolved organic matters than calcite (Donnert *et al.*, 2002).

Three technical process application variants – fixed bed-, stirred- and expanded bed reactor – applying two different tobermorite-rich calcium silicate hydrate (CSH) seed material types, were tested and compared in pilot-scale with respect to their efficiency in P-elimination and P-recovery. The experiments were conducted with two different waste waters, one from the WWTP of the Forschungszentrum Karlsruhe (effluent from the conventional activated sludge stage) and the other from a side-stream EBPR process (stripper supernatant from the Phostrip) in Austria. The generated crystallisation products were analysed regarding their applicability as a secondary resource for the phosphate industry and/or as a new fertiliser.

EXPERIMENTAL SECTION

Two tobermorite-rich waste materials from the construction industry – CSH seed material A (grain size: 0.6 - 1.3 mm) and seed material B (grain size: 0.5 - 1.5 mm) – were used in initial batch experiments in order to determine basic technical parameters, such as hydraulic retention time (HRT) and optimum solid / solution ratios (SSR). Seed material B was characterised by significantly lower background concentrations of Fe, Cu and Zn compared to seed material A, which was therefore considered to be more favourable for an application in a recycling process.

For the experiments in fixed bed column- (0.15 L) and stirred reactors (2.5 L) in laboratory scale, effluent from the biological WWTP of the Forschungszentrum Karlsruhe – spiked to a P-concentration of 10 mg/L P by a NaH₂PO₄·H₂O (p.a. Merck) stock solution – was used (Table 1). An HRT of 1 h was applied in the fixed bed reactors and of 1 h and 2 h, respectively, in the stirred reactors.

Pilot-scale long-term fixed-bed column- (10 - 100 L) and stirred reactor experiments (60 L) were carried out with the supernatant of the Phostrip process (Kaschka and Donnert, 2002) (with a characteristic P concentration of about 25 mg/L P) at the WWTP in Austria (Table 1). The influent was pre-treated by means of an electro-flotation device, in order to reduce the concentration of suspended solids (SS) to < 0.02 g/L. In the fixed bed reactor experiments, an HRT of 1 h was applied for both seed materials A and B. The efficiency of continuous-flow experiments in the

stirred reactor (material B, 5 wt-% SSR, HRT: 1 h, 2 h) was compared to a long-term discontinuous batch experiment. One batch cycle consisted of: a feeding period of 25 min, a stirring period of 120 min, a sedimentation period of 30 min and a draining period of 45 min (Table 1).

For the optimisation of the expanded bed application (40 L) in pilot-scale, the secondary effluent of the Forschungszentrum Karlsruhe was spiked to 25 mg/L P, corresponding to P-concentrations of the Austrian Phostrip process waters (see above). An HRT of 20 min in the unmoved seed bed, i.e. 26 min in the expanded bed was applied. The efficiencies of both seed materials A and B were compared using an SSR of 5 wt-%.

Table 1. Experimental setup of fixed bed-, expanded bed- and stirred reactor device in laboratory and pilot scale. HRT: hydraulic retention time; n.s.: not specified; SSR: solid solution ratio

	fixed bed		expanded bed	stirred reactor	
	laboratory	pilot	pilot	laboratory	pilot
Volume (L)	0.15	10 - 100	40	2.5	60
Seed	A, B	A, B	A, B	B	B
SSR (wt-%)	n.s.	n.s.	5	5	5
HRT (h)	1	1	0.3 ^a	1, 2	1, 2, ~4 ^b
P concentration (mg/L)	10 ^c	25 ^d	25 ^c	10 ^c	25 ^d

^a unmoved bed

^b long-term discontinuous batch experiment: feeding period 25 min, stirring period 120 min, sedimentation period 30 min and a draining period 45 min per batch cycle

^c spiked secondary effluent from WWTP of the Forschungszentrum Karlsruhe

^d Phostrip supernatant from a WWTP in Austria

The soluble reactive phosphorus (P) content and the pH value of the in- and outflow of all reactors were analysed. Additionally, analysis of the K_s value as well as of dissolved Ca and Mg concentrations was performed for in- and outflow of the fixed bed- and expanded bed reactor experiments 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 infrared spectroscopy (FTIR-ATR, Bruker IFS 66) and XRD (powder diffractometry, Siemens D 5000). Environmental Scanning Electron Microscopy (ESEM, Philips, The Netherlands) combined with EDX was applied to investigate the mineral's surface morphology. The fertilising properties according to the German fertiliser regulation (DüMV, 2003) were chemically assessed by elution (LUFÄ, 1999).

RESULTS

Fixed bed column reactor experiments

Tobermorite seed materials A and B behaved similar in the laboratory scale experiments conducted with an input concentration of 10 mg/L P. A constant P-elimination rate between 80 and 100 % could be maintained over a waste water throughput volume of about 3000 bed volumes (BV), before efficiency decreased steadily. In the pilot-scale experiments using Phostrip supernatant with a P concentration of 25 mg/L, P-elimination rates between 80 and 100 % could only be maintained over ~ 2000 BV for seed material A and over 800 BV for seed material B (Figure 1). However, a P-tot concentration of ~10 % could be detected in both seed materials. The formation of hydroxyl apatite-like compounds was confirmed by FTIR-ATR and XRD investigations.

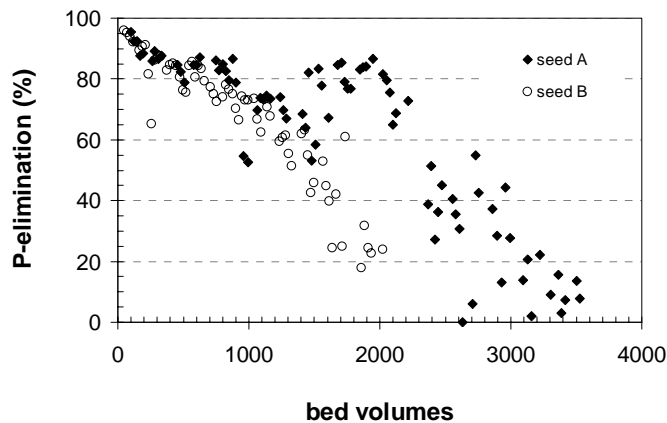


Figure 1. Pilot-scale experiments in fixed bed reactors comparing efficiency and longevity of P-elimination of the two crystallisation seed materials A and B; HRT: 1 h, initial P-concentration: 25 mg/L, Phostrip supernatant.

Stirred reactor experiments

In continuous laboratory scale experiments (10 mg/L P) a constant P-elimination efficiency of about 70 % (with HRT = 1 h) or 80 % (with HRT = 2 h) was observed over at least 24 h.

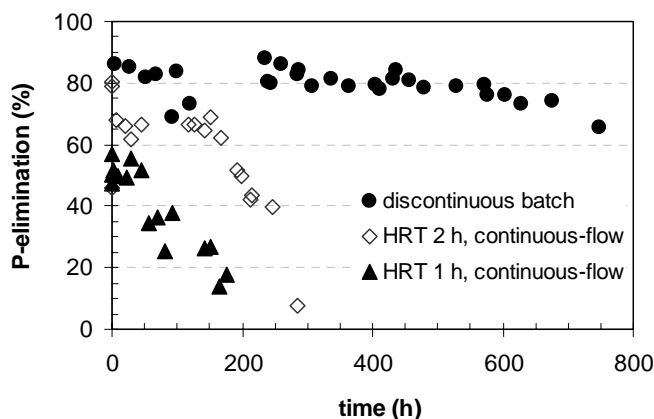


Figure 2. Pilot-scale experiments in stirred reactors comparing efficiency and longevity of P-elimination observed in continuous-flow experiments with an HRT of 1 and 2 h, and a discontinuous batch experiment using seed material B (5 wt-%). The experiments were conducted with Phostrip supernatant with an initial P-concentration of 25 mg/L P.

In analogous pilot-scale experiments using Phostrip waste water with 25 mg/L P, 50 to 60 % of P was eliminated over a period of about 48 h, followed by a continuous decrease in P-elimination efficiency (Figure 2). Doubling the HRT to 2 h led again to a 10 % improvement. A P-elimination of 60 to 70 % could be maintained over a period of about 150 h. The following significant declines were probably caused by the wash-out of highly efficient fine-grained seed material generated by mechanical abrasion due to 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 (Table 1). Thus, a constant P-elimination of 80 % could be maintained over a time period of at least 600 h (Figure 2).

Expanded bed experiments

Material B was more efficient than material A, eliminating 70 to 100 % P over about 4000 BV versus 50 to 70 % over about 3500 BV (Figure 3). The HRT applied was only 0.3 h in the unmoved bed, i.e. about 200 min in the whole reactor. Furthermore, shock loads could be reliably buffered. With a second reactor, limit values of < 1 mg/L P could be met. Considerable variations were caused by the depletion of waste water at weekends at the WWTP of the Forschungszentrum Karlsruhe. The efficiency of seed material B was similar in the expanded bed and the stirred reactors (Berg *et al.*, in press).

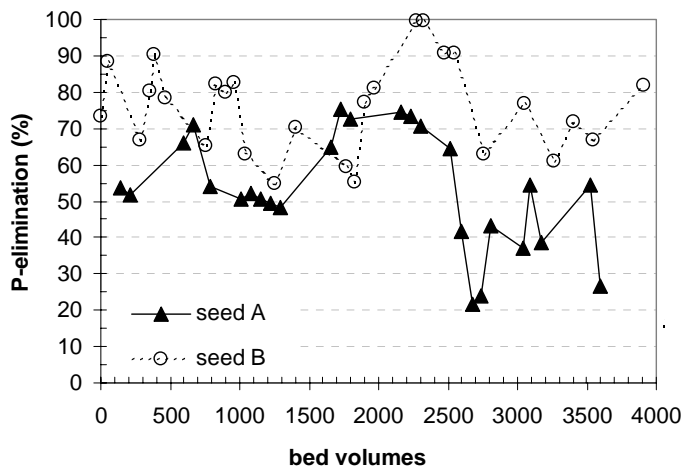


Figure 3. Pilot-scale experiments in expanded bed reactors comparing efficiency and longevity of P-elimination of the two crystallisation seed materials A and B; HRT: 0.3 h, initial P-concentration: 25 mg/L, WWTP Forschungszentrum Karlsruhe.

Generated crystallisation products showed a P-tot content of 11 % (seed material A) to 13 % (seed material B), which was comparable to phosphate rock (natural apatite). The formation of hydroxyapatite (HAP)-like compounds was proven by XRD and FTIR-ATR analysis (Figure 4). The HAP coated seed material A surface was visualised by ESEM (Figure 5) and verified by EDX analysis.

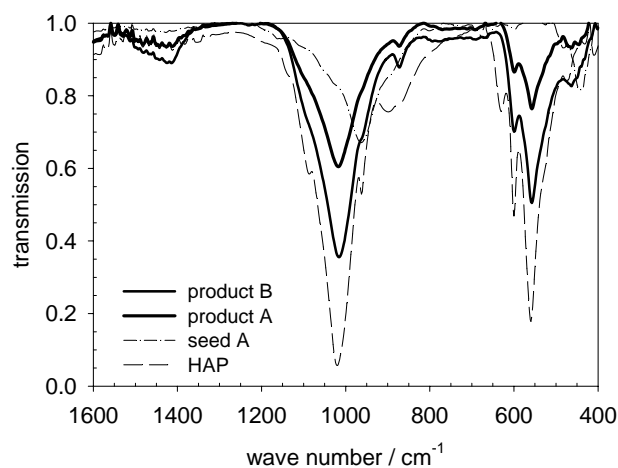


Figure 4. FTIR-ATR investigations on the generated recycling products from expanded bed reactor experiments. Hydroxyapatite (HAP) and the original seed material A were taken as a reference.

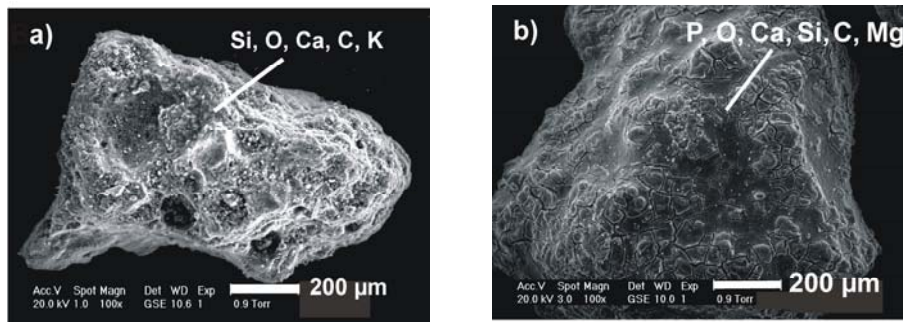


Figure 5. Surface morphology of a) the original seed material A and b) the generated product in expanded bed reactor experiments analysed by ESEM. The cracks were caused by the drying procedure. The chemical composition was analysed by EDX.

DISCUSSION

Effects of tobermorite seed material on the crystallisation of calcium phosphate

Initial Ca-release from the tobermorite-rich CSH and a simultaneous increase of the pH value triggered the crystallisation of calcium phosphate compounds. Therefore, the pH value could be used as a proxy for the longevity and efficiency of the seed material (Berg *et al.*, 2005, Berg *et al.*, in press). The shorter life-cycle of the crystallisation process of the pilot-scale fixed bed reactor experiments compared to the laboratory scale investigations could consequently be explained by the faster depletion of Ca ions due to the higher initial P concentration of 25 mg/L in the pilot-scale experiments compared to 10 mg/L in the laboratory scale investigations (Berg *et al.*, in press). Accordingly, for both experimental set-ups the same P-tot yield was achieved.

Additionally, loss of smallest (and therefore most reactive) CSH grains in the stirred reactor experiments contributed considerably to a continuous decrease in the P-elimination efficiency. However, an optimised clear water sedimentation zone above the suspension zone should help to minimise this loss of finest grains.

Quality of the generated products

The products obtained met the requirements of the P-industry (Schipper, 2001, Lijmbach, 2004). In particular the use of seed material B was promising, since its heavy metal concentrations were significantly lower compared to those of seed material A (Table 2). The iron content of the generated product using seed material B met the requirements of the phosphorus industry, too. Restrictions remain regarding the enrichment of Zn onto the seed materials during the crystallisation process. Even though limit values set by the phosphorus industry on the maximum tolerable Zn content were exceeded also in case of applying seed material B, the content was still lower than the one normally found in natural phosphate rock. (apatite ref., Table 2). Taking the natural content of P-rock regarding Cd and/or U into consideration, it was feasible to generate purer substitutes for P-rock by crystallisation with the P-RoC process. However, the recycling products have to be dried prior to their delivery to the phosphate industry. A solar drying step would be conceivable.

Furthermore, investigations regarding the use of the crystallisation material as a new fertiliser were undertaken. It was shown that due to the high silica content and the low water solubility the fertilising properties of products originating from seed material A were comparable to “Thomas-phosphate”. In former times “Thomas-phosphate” was a by product in steel production and widely applied as a fertiliser in ecological agriculture and on low acid soils. Therefore, the licensing of the

seed material as a new fertiliser seems to be feasible. However, only greenhouse and field experiments will be able to prove the plant availability of the generated nutrients.

Table 2. Chemical properties of the original seed materials A and B, natural P-rock (apatite ref.) and the generated recycling products from the half-scale fixed bed reactor experiments compared to the requirements for its reuse as a substitute for natural P-rock in the phosphate industry.

	SiO ₂	Fe ₂ O ₃	P ₂ O ₅	Zn	Cu	Cd	U
	(%)			(mg/kg)			
seed A (original)	53	1.0	0.05	85	22	<0.3	<10
product A	28	1.1	23	143	30	<0.3	<10
seed B (original)	56	0.1	0.03	9	8	<0.3	<10
product B	34	0.3	25	142	15	<0.3	<10
P-rock (apatite ref.)	4.0	0.3	30	240	30	17	72
Requirements of P-industry (NL)	supply	0.4-<1.0	≥23	50-100	50-100	-	-

CONCLUSIONS

Two different tobermorite-rich waste compounds were used as seed material for the crystallisation of calcium phosphate from municipal waste water. Three different process engineering technologies in laboratory and pilot scale have been applied within the frame of the development of the P-RoC process. With a circumvention of a loss of the finest fraction of the seed material, the stirred reactor seemed to represent the optimal method from the technological and economical point of view. The P-removal efficiency was comparable to the one of the expanded bed reactor. The optimisation of the stirred reactor process will be focus of further investigations.

Both seed materials were highly effective in elimination and recovery of phosphorus. The longevity of the crystallisation of HAP-like calcium phosphate compounds was controlled by the supply of calcium ions and the initial P concentration. A maximum P-tot content of the crystallisation products of up to 13 % P-tot was achieved, being fairly similar to natural P-rock. Especially the products generated from seed material B met the requirements of the P-industry as a phosphate rock substitute. The product generated was less Cd and U contaminated than natural phosphate rock itself. The fertilising properties were promising and will be subject of further studies.

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