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Phosphate removal from waste water by a seeding approach using novel seeding material

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ABSTRACT

A seeding concept was successfully applied for water treatment application, in particular to phosphate removal from wastewater. Here, several different seeding materials based on hydroxylapatite and fluoroapatite were synthesized and the P-removal capabilities were tested in a test water system. Besides high chemical stability, the fluoroapatite seeding material successfully and repeatedly removes >95% of phosphorous from the test water. A small pilot test was carried out, showing that also in continuous operation the seeds have high removal capacity of >90%.

Keywords: Seeding; Water treatment; Phosphorous removal; P recovery; Hydroxylapatite; Fluoroapatite; Accelerated crystallization

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1. Introduction

The removal and recovery of phosphorous from waste water streams before discharge has gained growing interest among researchers in the last decade. Since the availability of phosphorus in natural and surface waters is one the leading cause for phytoplankton growth, controlling the discharge of phosphorous compounds by municipal and industrial waste water plants is essential in the prevention of eutrophication of lakes and natural waters [1–3]. Several strategies to remove phosphorus from waste water are applied, P is removed, for example, by biological processes (incorporation of P into cell biomass with subsequent removal from the process as a result of sludge wasting, so called conventional biological P-elimination [4]), but mainly by chemical/physical removal by means of phosphate precipitation. Generally, phosphate precipitation involves the addition of lime or coagulant, such as aluminum and iron salt or organic polymers [5]. Disadvantage of these methods are the necessity of pH increase for enhanced phosphate removal, high amounts of salts are needed (typically overdosing of coagulants) as well as potential contaminant incorporation into sludge due to impurities of the used salts, which are typically byproducts from industrial productions. Recent developments include phosphate recovery by e.g. MAP (magnesium ammonium phosphate or struvite) crystallization, which uses magnesium and ammonium salts for controlled precipitation [6]. However, also here, an

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equimolar dosage of the salt is necessary to archive a 1:1:1 ratio of Mg^{2+}, NH_4^+, and PO_4^{2-} [1].

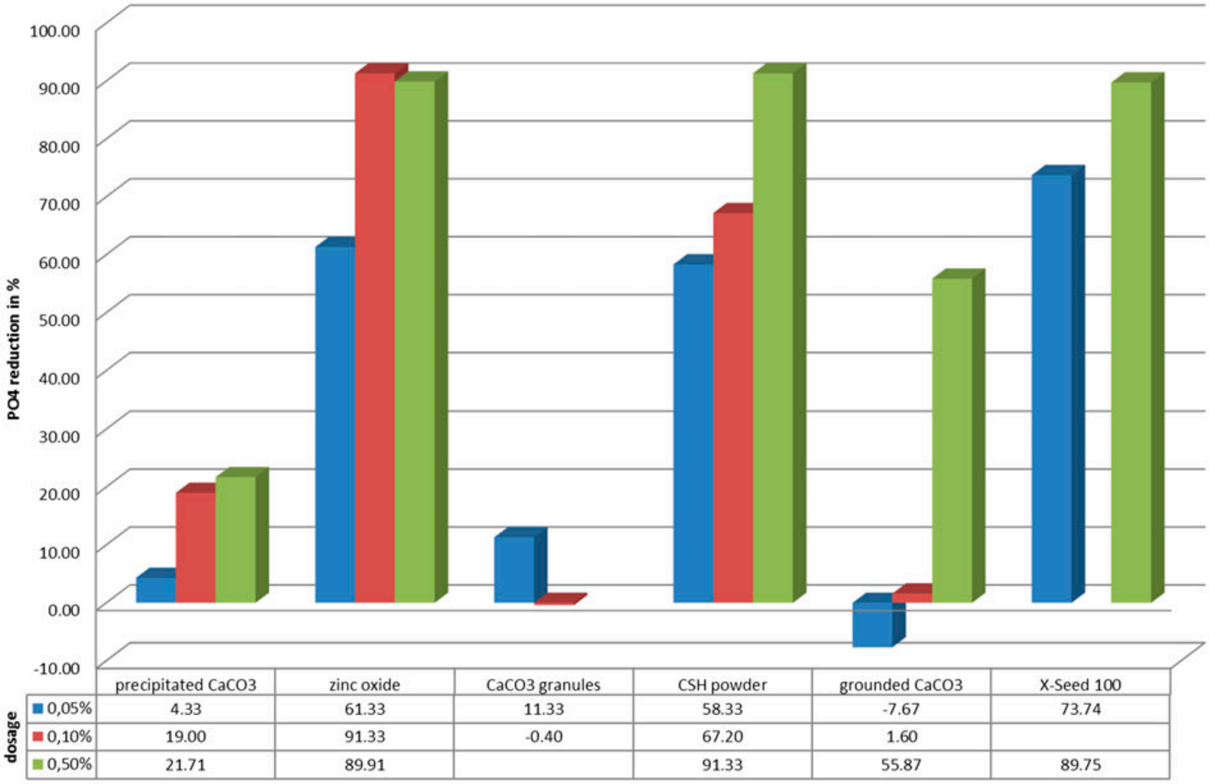
An alternative approach to effectively remove phosphorus from waste water is the so-called "seed crystal induced crystallization" [7]. Waste water usually is supersaturated with calcium phosphate compounds, but due to kinetic limitations, spontaneous precipitation on rare occasions occurs. The "seed crystal induced crystallization" method is based on the addition of seed crystals to such high or low supersaturated solutions. This leads to a change of the equilibrium of calcium and phosphate, lowers interfacial energies, and thus triggers precipitation phosphate onto the seed crystal surface [8]. Advantages of this method are the low dosage of active seed material required (substoichiometric amounts) compared with the standard coagulant dosage and no pH adjustment is necessary during precipitation [9]. Whereas several seed materials have been evaluated in detail including sand [10], calcite [7], tobermorite-rich crushed gas concrete [11,12], blast furnace [13], and xonolite [14], it turned out that the physicochemical properties of the seed crystals is crucial for an efficient P removal, especially in a waste water with a low phosphorus concentration [2]. We present our efforts towards a novel seeding material which showed increased phosphorus removal in both lab scale as well as small pilot scale. We also compare the new material with already available seeding material such as precipitated calcium carbonate (pcc), silica, or calcium silicate hydrate (main part of crushed concrete) with respect to both efficiency as well as kinetic considerations. Our findings show that tailor-made design of seeding crystals allow increased P removal of more than 96% already within the first hour of experiment, and thus opens the door for new efficient ways of P removal and recovery.

2. Results and discussion

2.1. Different seeding materials and tailor-made seeds

The phosphate removal capacity of several available seeding materials was investigated. The phosphate removal of the different seeding materials after stirring for 20 h is shown in Fig. 1.

While pcc, calcium carbonate granules, and also grounded calcium carbonate do not show good phosphate reduction even with a very high dosage of 0.5w%, precipitated zinc oxide, calcium–silicate–hydrate (C–S–H) powder, as well as commercial available X-Seed



	precipitated CaCO3	zinc oxide	CaCO3 granules	CSH powder	grounded CaCO3	X-Seed 100
🟦 0,05%	4.33	61.33	11.33	58.33	-7.67	73.74
🟥 0,10%	19.00	91.33	-0.40	67.20	1.60	
🟩 0,50%	21.71	89.91		91.33	55.87	89.75

Fig. 1. Overview of P removal of several seeding materials at different dosages.

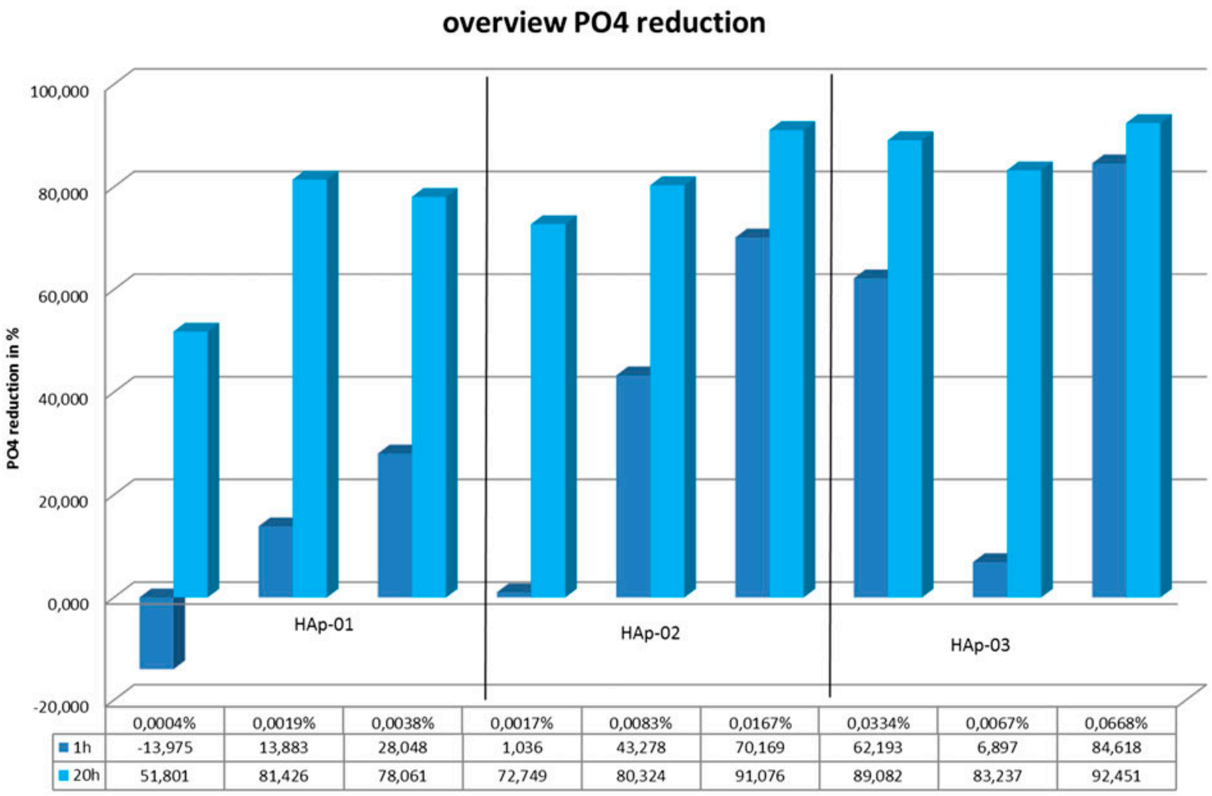
100 suspension show ~90% phosphate reduction at 0.5w% dosage. Nevertheless, lower dosages significantly reduce phosphate removal capacity; only for zinc oxide, a similar reduction capacity could be observed for 0.1w% dosage. One possible explanation might be the pH of the resulting solution after seed addition. Whereas for $CaCO_3$, the pH stays around 8.4 after 20 h, C–S–H powder and X-Seed increased the pH to values >9.5, which might explain the good P removal values for this material. However, for zinc oxide, no such pH increase could be observed, indicating that the pH effect is not the reason, but more important the nature of the seeding material is essential for the observed phosphate removal. Since it is known that crystal growth is favorable on surfaces similar to the growing crystal morphology (epitaxy), we decided to synthesize specific seed material based on hydroxyapatite, $Ca_5(PO_4)_3(OH)$. Fig. 2 shows the result of different synthesized hydroxyapatite (HAp) seeding materials which were applied as suspensions.

It is interesting to note that even very low amounts of this epitaxial seeding materials (down to 0.002w%) show similar removal capacity after 20 h compared with zinc oxide with a 20-fold higher dosage or lower dose efficiency. Again, the pH was not affected by the addition of the seeding material and stayed close to the starting value of 7.8. With this tailor-made material, P removal of ~90% could be achieved within 20 h at a dosage of 0.02%. We also tried to investigate the mechanism of precipitation in detail. Generally, two different mechanisms are possible: (1) the seed crystals lower the surface energy and the phosphate starts to crystallize on the seed crystal surface and (2) partial dissolution of the seed crystals increase the calcium and/or phosphate concentration locally, which increases supersaturation and thus induces crystallization.

For this purpose, we tried to use a calcium selective electrode to follow the calcium amount in the solution. Unfortunately, due to no significant and detectable changes of the calcium content in the system during seed addition and precipitation, we could not exclude or strengthen any of the two possible mechanisms at this stage.

2.2. New seed generation

As industrial and municipal waste water do not vary only in their water composition but also in their pH value, (from 4–5 up to 11) and as hydroxyapatite



	0,0004%	0,0019%	0,0038%	0,0017%	0,0083%	0,0167%	0,0334%	0,0067%	0,0668%
■ 1h	-13,975	13,883	28,048	1,036	43,278	70,169	62,193	6,897	84,618
■ 20h	51,801	81,426	78,061	72,749	80,324	91,076	89,082	83,237	92,451

Fig. 2. P removal of different synthesized hydroxyapatite samples after 1 and 20 h stirring time at different dosages.

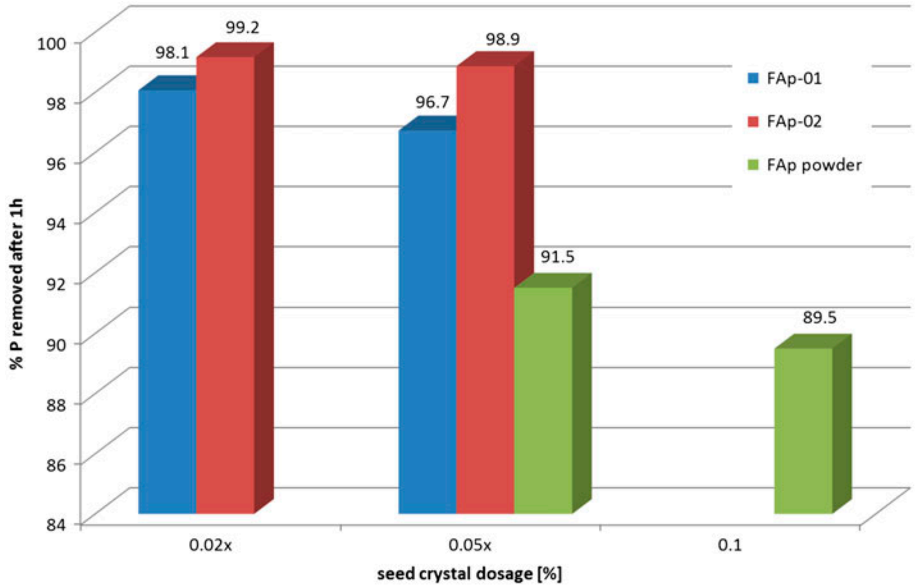


Fig. 3. P removal efficiency of different synthesized FAp samples after 1 h at different dosages.

starts to dissolve under acidic conditions (pH < 7) [15], the use of HAp cannot be considered in all waste water, but only in basic waste waters. We, therefore, decided to use an isotype, but more pH-stable seeding material, namely fluorapatite, $Ca_5[(PO_4)_3F]$ (FAp). This material is more acid resistant than hydroxyapatite as well as less soluble, but should show similar removal capacity. The results of the phosphate removal tests for different FAp samples are summarized in Fig. 3. We tested two different FAp suspensions with active content of ~14% as well as a dried FAp powder. As expected, the suspensions showed higher P removal values than the powder, which is most likely due to lower agglomeration which might take place in the drying step. In comparison to the HAp seed crystals, the new synthesized FAp seed crystals showed almost complete removal (>95%) in the first hour even for the low dosage of 0.028 and 0.027w%, respectively. Higher dosages (0.056 and 0.053%) do not improve the recovery, but stays at a similar lever within the error of experiment. For the dried FAp powder, the removal is also very high—around or close to 90% at 0.05w% dosage.

In order to have a closer look on the kinetics of P removal by FAp seed crystals, we did time-dependent tests with our material. We, therefore, performed P removal tests with our FAp suspensions as well as with the FAp powder, took samples every 2–3 min, and analyzed them for their P content. The results are shown in Fig. 4. As already known from the previous experiments, the FAp powders showed a somehow slower P removal rate compared with the respective FAp suspensions. Also, a higher dosage of 0.1w% increases the P removal rate being almost at its maximum after only 15 min. However, in both cases, even for the powders at low dosages of 0.05w%, the P removal is ~85% after only 15 min and reached its maximum at ~60 min. Thus, a residence time of ~1 h is sufficient for the performance tests.

2.3. Efficiency of P removal

In order to elucidate the phosphate removal efficiency of our new seed material in more detail, we used two different approaches to test our seed crystals activity. In the first approach, schematically shown in Fig. 5, we prepared a standard beaker test, we added the FAp seeding material in quantities of 0.05 and 0.1w% related to mass of water used, and stirred it for 1 h, and then we measured the residual P content to analyze the P removal efficiency. Then, 15 ppm of phosphate was added by addition of 1 ml of a concentrated phosphate stock solution, the suspension was stirred again for 1 h, and the residual P content was measured. This procedure was repeated four times until a total amount of 75 ppm phosphate was added to the standard solution. The results of this approach are summarized in Table 1.

Here, one has to distinguish between two different phosphate removal values: the overall P removal and the phosphorous removal in each step. The overall P removal is based on a total addition of 75 ppm

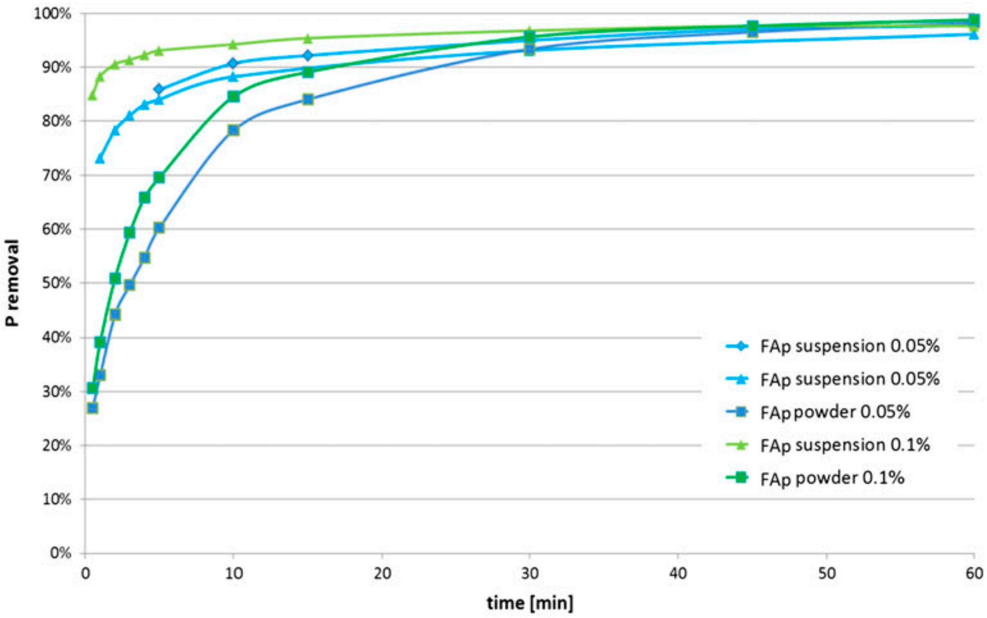


Fig. 4. Time-dependent P removal tests with different FAp samples. The squares represent powder samples which were dried and applied as powders, whereas the triangles represent FAp suspensions.

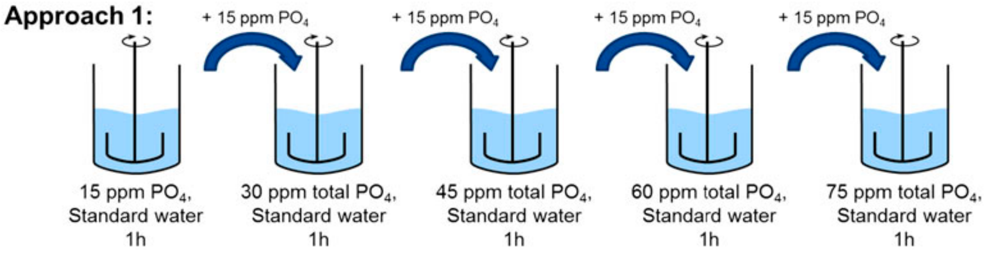


Fig. 5. Schematic description of the first approach to test seed activity. After adding the seed crystals to the standard solution and stirring for 1 h, 15 ppm of phosphate was added as a stock solution and stirred for 1 h. This step was repeated four times.

Table 1
Results of the addition of PO_4 stock solution to the standard test solution and P removal values for two seed crystal dosages of FAp seeds

Seed dosage [%]	PO_4 added [ppm]	PO_4 in solution after addition (measured PO_4 + added PO_4)	Measured PO_4 [ppm]	Overall PO_4 removal [%]	PO_4 removal in each step [%]
0.05	15	15	0.82	94.5	94.5
0.1	15	15	0.3	98.0	98.0
0.05	30	15.82	3.39	78.6	88.7
0.1	30	15.3	1.16	92.4	96.1
0.05	45	18.39	6.2	66.3	86.2
0.1	45	16.16	2.5	84.5	94.4
0.05	60	21.2	9.6	54.7	84.0
0.1	60	17.5	4.9	72.0	91.8
0.05	75	24.6	12.8	48.0	82.9
0.1	75	19.9	7.28	63.4	90.3

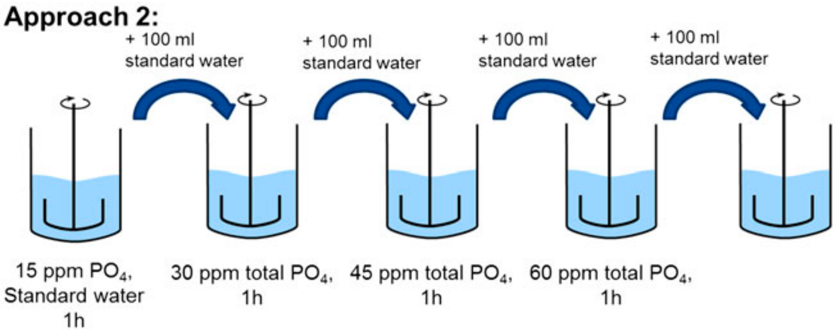


Fig. 6. Schematic description of the second approach to test seed activity. After adding the seed crystals to the standard solution and stirring for 1 h, 100 ml of standard test water was added and further stirred for 1 h. This step was repeated four times.

Table 2
Results of the addition of 100 ml standard test water to the seed crystal containing test solution and P removal values for two seed crystal dosages of FAp seeds

Seed dosage [%]	PO_4 added [ppm]	PO_4 in solution after addition (measured PO_4 + added PO_4)	Measured PO_4 [ppm]	Overall PO_4 removal [%]	PO_4 removal in each step [%]
0.05	15	15	0.75	95.0	95.0
0.1	15	15	0.27	98.2	98.2
0.05	30	15.75	1.72	89.1	94.3
0.1	30	15.27	0.66	95.7	97.8
0.05	45	16.72	2.48	85.2	94.5
0.1	45	15.66	1.36	91.3	97.0
0.05	60	17.48	2.92	83.3	95.1
0.1	60	16.36	1.84	88.8	96.9
0.05	75	17.92	3.2	82.1	95.7
0.1	75	16.84	2.28	86.5	97.0

phosphate and starts at 94.5w% (for 0.05w% dosage) after the seed addition, going down to 78.6w% after the first phosphate addition until it reaches only 48.0% at the end of the experiment. A similar trend is observed for the 0.01w% dosage, although the remaining P removal stays at 63.4w%. This can be explained by the fact that we only added phosphate and, therefore, depletion of calcium in our test water occurs; thus, no further crystallization of calcium phosphate can take place. For the higher dosage, more surface is present, and thus slightly more phosphate can additionally adsorb on the crystals; hence, the remaining P removal is higher.

In contrast to that one can calculate the P removal based on the actual present P content in the solution after each phosphate addition. This simply corresponds to the added phosphate amount in each step (15 ppm) plus the residual phosphate after the following 1 h stirring period (e.g. 1.16 ppm). If calculating the P removal based on this values, the removal capacity of the seed crystals for each individual step also decreases, but in the final step, it is still very high with 82.9w% (dosage 0.05w%) and 90.3w% (dosage 0.1w%).

Since in the aforementioned approach we deplete our test solution with calcium, we added in the second approach not the phosphate stock solution but 100 ml of test water which originally was used for the beaker tests (i.e. 100 ml of a solution containing 80 ppm calcium, 12.5 ppm magnesium, 15 ppm phosphate, and 250 ppm bicarbonate for each addition, see Fig. 6).

Similar to the first approach, we also observed a decline in P removal, which, however, is less pronounced compared with the phosphate addition only, starting from 95% (0.05w% addition) or 98.2% (0.1w% dosage, see Table 2). The final P removal considering a total P content of 75 ppm was 82.1% and 86.5%, respectively. Taking the P removal of each individual step into account, we do not observe a significant decline in P removal capacity (always stays in the range of 95–97% for all dosages). This shows on the

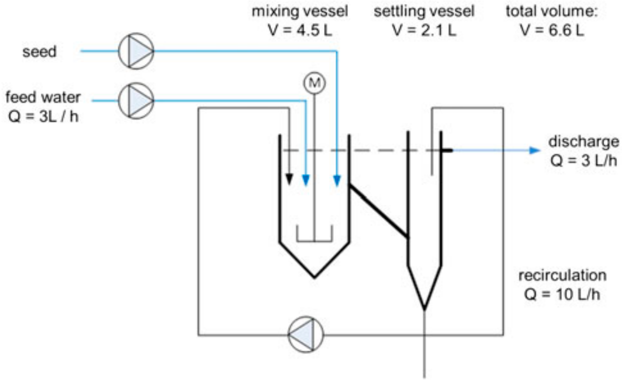


Fig. 7. Schematic drawing of the small pilot plant setup used for testing different seed crystals in P removal.

one hand that depletion of calcium reduces significantly the efficiency of the seed crystal induced P removal. On the other hand, a high P removal is allowed, since we used only a fixed amount of seed crystals. The dilution of the original seed crystals (by five times) does in this case still allow a very high P removal. One possible explanation might be that additional crystals are formed during precipitation of calcium phosphates in each step; thus, the overall seed crystal concentration increases over time.

2.4. Small pilot plant test trial

A small pilot test system was set up to test if continuous addition of the seed material allows continuous P removal. The setup is schematically shown in Fig. 7.

First, 4.5 l of the artificial waste water (also used in the beaker tests) was added into the mixing vessel. Then, new artificial waste water as feed water was added to the mixing vessel with a flow rate of 3 l/h. In this stream, the FAp seeding crystal solution was added with a concentration of 0.05w%. The solution passed into the settling tank via an overflow valve and was recirculated into the mixing vessel at 10 l/h. Finally, the discharge was collected every 30 min and analyzed. Two different seeding materials were tested: the new FAp suspension as well as a commercial pcc. The results of the P removal are summarized in Fig. 8.

After an induction phase of around 2 h, the FAp suspension showed a constant P removal of ~96% for an additional 2 h. The induction phase can be explained by the fact that the seed crystal concentration at the beginning is rather low (dosing seed crystals into 4.5 l of water), whereas after 2 h, the desired concentration of the seed crystals are obtained in the system. In contrast to that the similar test with pcc did not show any P removal even after 3.5 h of experimental time.

2.5. Summary

We have shown that P removal can be achieved via seed crystal-induced crystallization of calcium phosphates even in low supersaturated waters. Here, the nature (i.e. morphology as well as chemical

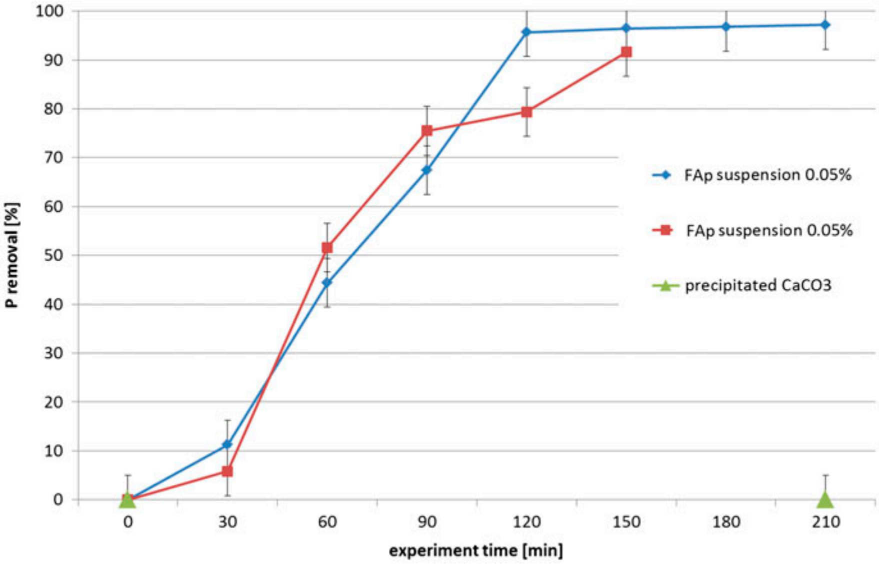


Fig. 8. Results of the small pilot test for two FAp samples and precipitated $CaCO_3$. After ~2 h, the P removal is ~96% for the FAp suspensions at 0.05% dosage, whereas for precipitated $CaCO_3$, no removal could be observed.

nature) of the seeding material is essential for their performance. While calcium carbonate does not show good P removal capacity, zinc oxide and C–S–H (e.g. crushed concrete) offer a certain alternative for P removal technologies. Nevertheless, epitaxial seed crystals such as hydroxyapatite or, due to their lower solubility and chemical inertness, fluorapatite allow much higher seeding efficiencies. A P removal capacity of up to 95% within the first hour at very low dosages (0.02w%) are proofed. We also showed that seeds can be used multiple times for waste water purification, with a P removal performance remaining higher than 90%. Furthermore, the water composition is crucial for this approach since depletion of one of the necessary compounds such as calcium leads to a loss in efficiency. The general concept, however, can be applied also in small pilot scale where we showed P removal after an induction period of more than 96% with only 0.05w% of seed crystal addition. More experiments to optimize seed crystal dosage as well as further elucidations of the working mechanism will be part of ongoing research.

3. Experimental setup

3.1. Hydroxyapatite seed synthesis

In a typical synthesis for hydroxyapatite, 69.2 g phosphoric acid (85w%), H_3PO_4, was diluted with 489.6 g water. This solution was then poured into a slurry containing 74.1 g calcium hydroxide, $Ca(OH)_2$, and 100 g of a sodium hydroxide solution (50w%), NaOH, in 450 g of water.

The resulting slurry contains 10.1w% of hydroxyapatite and has a solid content of 15.1w%. The formation of hydroxyapatite was ensured by powder XRD.

3.2. Fluorapatite seed synthesis

In a stirred 1 l glass reactor, 78.4 g diammonium phosphate, $(NH_4)_2HPO_4$, and 7.3 g ammonium fluoride, NH_4F, were dissolved in 750 g water.

A second solution containing 234.1 g calcium nitrate tetrahydrate, $Ca(NO_3)_2{\cdot}4H_2O$, in 250 g water was dosed by means of a peristaltic pump during 7 min during stirring into the reactor.

Subsequently, 24.7 g of an ammonia solution (32w%) was added directly to the reactor during stirring.

The formation of fluorapatite was ensured by powder XRD.

3.3. Phosphate removal batch experiments

All experiments were performed by batch experiments using synthetic solutions. Briefly, stock solutions from reagent grade KH_2PO_4 (200 mg/l PO_4^{3-}), $CaCl_2{\cdot}2H_2O$ (200 mg/l Ca^{2+}), $MgCl_2{\cdot}6H_2O$ (1,000 mg/l Mg^{2+}) and $NaHCO_3$ (2,000 mg/l HCO_3^-) were prepared by dissolving the respective amounts of salts in deionized water and stirring until all solids are dissolved. Then, the test solution was prepared by adding the desired amounts of stock solution into 50 ml of DI water to reach a concentration of 80 ppm Ca^{2+}, 12.5 ppm Mg^{2+}, 250 ppm HCO_3^- and 15 ppm PO_4^{3-}. The pH of the solution was adjusted to pH 8 ± 0.1. While stirring the test solution with a magnetic stirrer (~300 rpm), the respective amount of seed material (powder or dispersion) was added under stirring. Samples of these solutions were taken after e.g. 1 h, filtered through a 0.22 μm syringe filter, and diluted by a factor of 10 to allow orthophosphate determination.

3.4. Determination of soluble phosphate salts (orthophosphate)

To determine the soluble phosphate (orthophosphate) content, a spectrophotometric method was used. This method is based on quantification of the green complex formed between Malachite Green, molybdate, and free orthophosphate. The rapid color formation from the reaction can be measured on a spectrophotometer at 620 nm. For more detailed information see e.g. [16]. Briefly, 440 mg malachite green was dissolved in 360 ml of 20% sulfuric acid. Then, 10 ml of this solution was mixed with 2.5 ml of a 7.5w% ammonium molybdate solution and 200 μl of a 11% TWEEN 20 solution. 2.5 ml of the mentioned malachite-molybdate solution was added to 10 ml of an orthophosphate-containing solution. After 10–15 min, the UV/vis extinction at 620 nm was measured and the respective amount of orthophosphate in the test solution was determined.

3.5. Phosphate removal small pilot plant test

A small pilot plant (total volume 6.6 l) according to the schematic presented (Fig. 7) was set up. Briefly, into a mixing tank with a volume of 4.5 l, synthetic feed water with a concentration of 80 ppm Ca^{2+}, 12.5 ppm Mg^{2+}, 250 ppm HCO_3^- and 15 ppm PO_4^{3-} was added continuously with 3 l/h. Additionally, the seeding material was added continuously into the mixing tank as a suspension in the desired dosage (0.05w%). Under moderate stirring (~300 rpm) the solutions were mixed via an overflow valve, the solution was then passed into a settling tank ($V = 2.1$ l), and was recirculated into the mixing tank with a flow of 10 l/h.

The discharge was collected and samples were taken every 30 min for their orthophosphate analysis.

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