P-Recovery from sewage by seeded crystallisation in a pilot plant in batch mode technology

A. Ehbrecht, S. Schönauer, T. Fuderer and R. Schuhmann

ABSTRACT

P-Recovery from actual sewage by P-RoC-technology (Phosphorus Recovery by Crystallisation of phosphate mineral phases from waste- and processwater) was studied in a pilot scale. Therewith the practicability of the pilot plant was tested and the quality of the so generated products was investigated.

Key words | batch technology, calcium phosphates, crystallisation, pilot plant, P-Recovery

INTRODUCTION AND OBJECTIVE

The increasing use of fertilisers and the finite nature and contamination of natural phosphorus resources (WAFD and GFST, 2006) necessitates a sustainable technology for P-recovery. Because of sewage being an important nutrient sink, the crystallisation of phosphate mineral phases e.g. calcium phosphate (Ca-P) triggered by a reactive substrate represents a promising method of P-Recovery from waste- and processwater.

In P-RoC-technology, P-elimination and -recovery occurs in one singular step without the addition of chemicals except for the reactive substrate (Berg et al. 2007). P-RoC-technology was applied within the Federal Ministry of Education and Research funded initiative ‘Recycling management of plant nutrients, particularly phosphorus’ in bench- and semi-technical scale with model sewage on the basis of clarifier effluent spiked with P-stock solution (Ehbrecht et al. 2009a). The influence of grain size of the substrate, a Calcium-Silicate-Hydrate (CSH), and the reactivity of the CSH-substrate on the P-elimination (Ehbrecht et al. 2008) had been shown in kinetic experiments in bench-scale units and semi-technical experiments.

The objective of this study was to test the practicability of P-RoC-technology in pilot scale with actual sewage.

MATERIALS, METHODS AND PRELIMINARY WORK

The crystallisation experiments can be carried out in stirred-reactor- or in fluidized-bed-technology. Preliminary experiments have shown a higher efficiency of P-elimination by use of a stirred reactor. This is due to a higher turbulence at the particle surfaces of the reactive substrate which causes a greater renewal of the boundary surfaces. That implies a higher reactivity concerning the crystallisation process. Kinetic information had been obtained in short-term experiments in bench-scale units configured as stirred reactor (Figure 1).

At first the Ca-content and the content of dissolved organic carbon (DOC) of the wastewater were of interest, because both can have an influence on the Ca-P-crystallisation: DOC can delay the crystallisation of Ca-P (van der Houwen et al. 2003 and Alvarez et al. 2004) and Ca is needed as reactant for the crystallisation of Ca-P. Therefore, tap water, distilled water and clarifier effluent were spiked with 50 mg/L P as well as 5 wt.-% of the reactive substrate and were applied in a short term experiment of about 24 h. In Figure 2 the P-elimination over a time period of 2 h is presented, with tap water clearly showing the highest P-elimination. This can be explained by the absence of DOC and the higher Ca-concentration compared to distilled water. The P-elimination of clarifier effluent was the lowest which is caused by the existing DOC with a concentration of nearly 20 mg/L. Yet regarding the P-elimination after 2 h, the differences of all experiments are only marginal.

In contrast to the bench-scale experiment, the substrate from the semi-technical experiments (Figure 3) is not idle but used due to the number of batches.
This way the particle surface could be coated by organics Ehbrecht and Schuhmann (2009b) as a certain organic load of the sewage diminishes the P-elimination by crystallisation of Ca-P. Therefore we investigated several model waters consisting of tap water with different contents of a purchasable humic material (Fulvital WSP 80®) all spiked with 50 mg/L P in a semi-technical plant. The results are shown in Figure 4: The P-elimination decreases with increasing DOC-concentration. But there seems to exist a limiting DOC-concentration at which the substrate reacts in the same way.

Another eventuality could be a Ca-P-coating of the product particle (Berg et al. 2006). To confirm this assumption, an ESEM picture was prepared Figure 5. The hypothesis could not be confirmed because Ca-P was detected completely in the product particle (Ehbrecht et al. 2009a). Thus the semi-technical experiments were configured as a stirred tank reactor with a reaction time of 2 h. Thereby a high turbulence with a high renewal of the boundary surface is given so that reactive surfaces will be produced over a longer time range.

The reaction mechanisms can be described as follows: The contact of the CSH-particles with water involves solution processes, causing an increase of the pH-value and a release of Ca. Due to this, a shift of the chemical equilibrium occurs in favor of the P-containing product. LM-micrographs show a kind of framework consisting of amorphous silica with areas of phosphate mineral phases.

In summary the bench-scale and semi-technical experiments result in the following procedural information for a further scale-up: The application of actual sewage demands a stirred reactor and a hydraulic retention time of 2 h.

The P-RoC pilot plant (Figure 6) is an automatically working research unit enclosed in a container which can be relocated.

The batch volume is 800 L, working with 750 L in discontinuous mode of operation. The operating water levels in the reactor are adjusted by filling-level meters. A centrifugal pump feeds the P-RoC-reactor with influent. The system can operate automatically 24 h due to the process measuring and control technology (pmc-t). Stirring time can be changed according to the quantity and properties of the seed material. Settling time can also be timed variable. The mixing unit is a
so called Intermig agitator in centre position. An Intermig agitator enables an intensive mixing due to up- and down-flow. Stirring rate is adjustable as well. The system is equipped with data logger KM2000 for logging pH-value and electrical conductivity from the influent and in the reactor. Data can be logged in variable intervals. A cycle was run in 3 hours mode Table 1.

The pilot plant was operated with a sidestream of a municipal sewage plant in Husum (Northern Germany) with an average P-concentration of 25 mg/L in the range of 20–40 mg/L and with centrifuge effluent from a sewage plant in Eberstadt (Southern Germany) with an average P-concentration of 50 mg/L in the range of 40–100 mg/L. Important hydrochemical parameters like pH-value and electrical conductivity were measured automatically by sensors. The determination of o-P was carried out according to DIN EN ISO 6878. Solid samples were taken in certain intervals. One part of solid analysis was used in order to evaluate the content of total phosphorus (TP) via acid digestion by microwave according to DIN EN 13346. The identification of the mineral phases of the reactive substrate and the generated products was done by X-Ray diffraction (XRD) with the X-Ray Diffractometer D 5000 (Siemens).

**RESULTS AND DISCUSSION**

In order to evaluate the proceeding of the crystallisation the P-concentration was plotted against the reaction time. In Figure 7 the P-concentrations of the influent and the effluent of the four experiments are demonstrated, carried out with actual sewage of a side-stream of the WWTP from Husum at different times.

The variation of the P-concentration of the influent can be attributed to the periodical discharge of sewage from a slaughterhouse. It can be noticed that the variation of the P-concentration of the influent was buffered by the crystallisation reaction. The four curves of the effluent are nearly congruent. This can be interpreted as reproducibility of the crystallisation of phosphate mineral phases by P-RoC-technology.
In Figure 8 the P-elimination against reaction time is displayed to compare the four experiments. P-elimination occurs in one field of values.

The diagram with the pH-value plotted against the reaction time (Figure 9) seems to be very similar to this graph: the four curves are nearly congruent.

An interesting point is that the end of the crystallisation reaction coincides with a decrease of the pH-value of the effluent to the pH-value of the influent. This means that the pH-value can be assigned to an easy monitoring of the crystallisation of phosphate mineral phases and therefore to identify the end of the crystallisation reaction.

In addition to the observations named above, a more detailed examination of the results from the municipal sewage plant in Eberstadt will be specified in the following. In (Figure 10) the P-concentration of the influent is arranged in a higher range compared to the influent of Husum. But again P-concentration of the effluent slowly increases.

A closer examination of Figure 11 reveals that P-elimination fluctuates around 30% after a reaction time of 200 h.

The explanation for this observation can be found in Figure 12:

The pH-value decreases after 200 h to a value lower than 8. Crystallisation of phosphate mineral phases takes places more efficiently at pH-values greater than a pH-value of 8 (Hong et al. 2004).
In summary, Table 2 shows the differences in sewage composition. The pH-value of the influent of Husum varies between 7.0 and 7.3 whereas the pH-value of the centrifuge influent varies between 7.8 and 8.1.

The results of X-Ray Diffraction (XRD) from the solid samples are shown in Figure 13. The most important information that can be obtained from the XRD pattern is that the product generated with actual sewage from a sidestream of the municipal sewage plant of Husum mainly consists of less crystalline and very small hydroxylapatite-like Ca-P-phases (Tadic et al. 2001 and Furutaka et al. 2006). In contrast to this, the product generated with centrifuge effluent, consists of struvite, a low soluble and valuable fertiliser (De-Bashan & Bashan 2004).

<table>
<thead>
<tr>
<th>Dissolved matter [mg/L]</th>
<th>Husum</th>
<th>Eberstadt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO$_4^{3-}$-P</td>
<td>25–30</td>
<td>45–70</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>85–110</td>
<td>30–39</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>9–11</td>
<td>25–35</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.1</td>
<td>55–250</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>105–120</td>
<td>115–140</td>
</tr>
<tr>
<td>K$^+$</td>
<td>38–45</td>
<td>200–220</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>135–172</td>
<td>600–710</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>45–57</td>
<td>3–12</td>
</tr>
<tr>
<td>DOC</td>
<td>5–10</td>
<td>80</td>
</tr>
</tbody>
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Of main interest – as well as the identification of the generated mineral phases – is the P-content of the product. In Table 3 the theoretical P-content (calculated by the P-elimination) is opposed to the analysed P-content (measured after hot acid digestion of the product according to DIN EN ISO 6878).

The differences can be explained by the inhomogeneity of the sample taken for the analysis. Due to the reaction mechanism the product consists of generated P-containing mineral phases and residual mineral phases, both in diverse grain sizes. Particularly the smallest grains can be attributed to the generated P-containing mineral phases.

### CONCLUSION AND OUTLOOK

It had been shown that the semi-technical experiments can be transferred to pilot-scale with a consideration of the boundary conditions of the actual sewage. Particularly with regard to P-elimination of the sewage and P-content of the generated products, the results from the experiments with the pilot plant can be assessed by the reaction kinetics of bench-scale and semi-technical experiments. Due to the operation in batch mode, the pilot plant can presently be applied in partial current or sidestream as compliance with limiting values in the effluent of municipal sewage plants [RaAwVwV] cannot be ensured.

The next step of course is a full-scale application. Considering the waste water stream and the capacity of the pilot plant, a full-scale application is technically feasible at a biogas plant for example by fermentation of pig slurry. Furthermore, P-RoC-technology in continuous mode is a very interesting challenge.

The efficiency of P-elimination depends on the P-bonding of the influent of a municipal sewage plant (Jenkins et al. 1971) and of the P-bonding at the generated product (Brushite, HAp, Struvite). We aim a load examination to draw up a balance sheet.
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REFERENCES


