# Task 3.1 – P-recovery from LFD via struvite crystallisation

## Objective

The objective of Task 3.1 was to evaluate the applicability of struvite crystallisation for recovering phosphate from liquid fraction of digestate (LFD). Optimal operational conditions were determined through lab-scale tests using synthetic phosphate solution and real digestate. The efficiency of phosphate recovery was assessed, and composition of the recovered products were analysed using X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX).

## Set-up/Parameters

Initially, batch flask tests (Set-1) were conducted using LFD obtained from the SELEDA's Biogas Plant in Babaeski, Turkiye. Magnesium chloride ($MgCl_2.6H_2O$) was used as the Mg source, and the Mg:P molar ratio was adjusted to 2 based on preliminary findings. After adding the Mg source, the flasks were stirred for 1 hour using an orbital shaker and samples were taken at intervals for pH and phosphate analyses.

After flask tests, the next experiments (Set-2) were conducted using an up-flow reactor with a total volume of 4.5 L and an active volume of 3.5 L (Figure 1) using the LFD obtained from SELEDA and the same Mg:P molar ratio. The LFD was recirculated using a peristaltic pump with an upflow velocity of 20 cm/min for 24 hours. Samples were collected at specific time intervals throughout the experiment, and phosphate concentration and pH were monitored.

Figure 1. Laboratory scale upflow reactor.

Another batch experiment (Set-3) was conducted using the LFD obtained from the laboratory scale anaerobic digester operated in Task 2.2. The same set-up shown in Figure 2 was used. These experiments were performed with and without pH adjustment with the Mg:P molar ratio set to 1.

After completing the laboratory-scale batch experiments, a pilot-scale upflow reactor was installed at SELEDA's Biogas Plant in Babaeski, Turkiye. SELEDA is one of the SMEs in the User Group of the BiODEN Project. In each experiment, the pilot reactor operated for 6-8 hours, receiving a continuous feed of LFD at a rate of 160-180 L/h. The upflow velocity was adjusted to 1800-2000 L/h with the help of internal recirculation. Figure 3 illustrates the schematic of the pilot set-up.

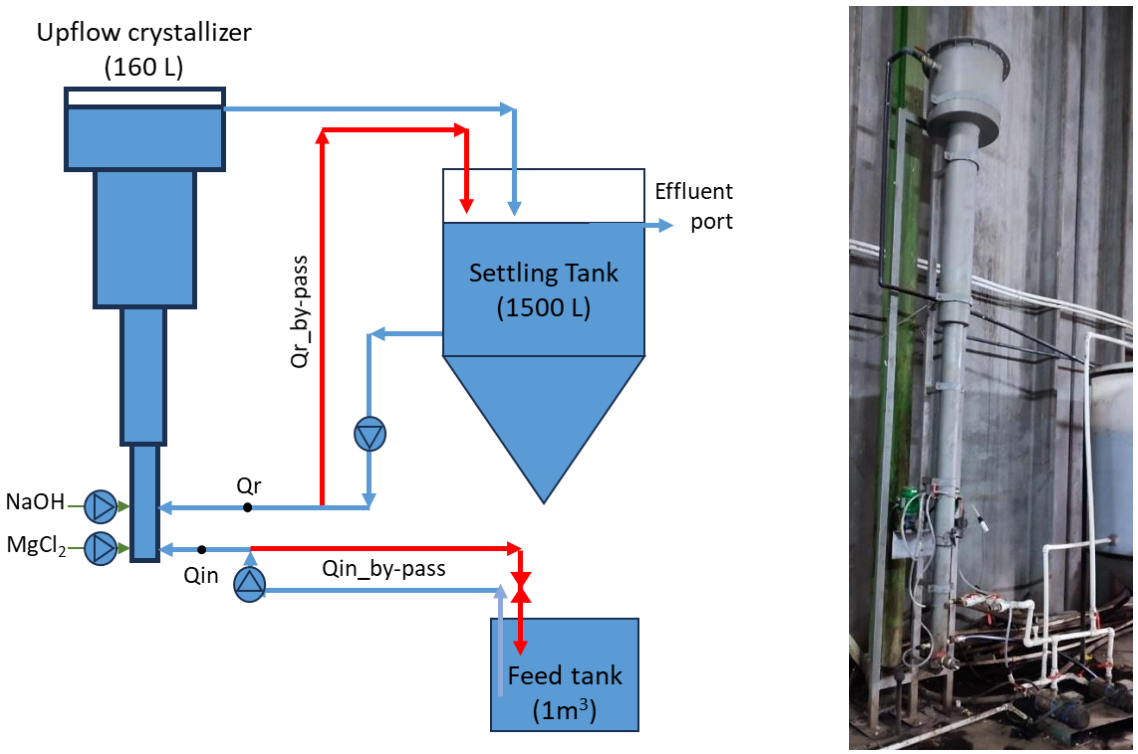


Figure 2. Pilot scale upflow reactor and struvite crystallisation system.

## Results

The results of the batch flask-type struvite tests, conducted without pH adjustment and with the Mg:P molar ratio set to 2, using the LFD obtained from SELEDA's Biogas Plant, are presented in Table 1. Because of the low phosphate concentration in SELEDA's LFD and the constraints of continuously stirred batch type tests, the phosphate removal remained below 70% in 60 minutes.

Table 1. Results of batch flask tests conducted using LFD obtained from SELEDA (set-1).

| | Test -1 (no pH adjustment) | | | Test-2 (no pH adjustment) | | |
|---|---|---|---|---|---|---|
| Time, minute | mgP/L | % P removal | pH | mgP/L | % P removal | pH |
| 0 | 64 | 0% | 7,9 | 64 | 0% | 7,9 |
| 30 | 23 | 64% | 8,6 | 29 | 54% | 8,6 |
| 60 | 20 | 69% | 8,8 | 22 | 65% | 8,7 |

In the second set of experiments, conducted under the same conditions as the flask tests but with continuous recirculation in an up-flow reactor, struvite formation was more successful due to the up-flow effect. This led to higher phosphorus removal compared to the flask tests (Table 2). The phosphate removal exceeded 70% in 120 minutes.

Table 2. Results of batch upflow reactor tests conducted using LFD obtained from SELEDA (set-2).

| | Test-3 (no pH adjustment) | | | Test-4 (no pH adjustment) | | |
|---|---|---|---|---|---|---|
| Time, minute | mgP/L | % P removal | pH | mgP/L | % P removal | pH |
| 0 | 63,7 | 0% | 7,9 | 63,7 | 0% | 7,9 |
| 30 | 25,8 | 59% | 8,1 | 16,2 | 75% | 7,9 |
| 60 | 22,0 | 65% | 8,1 | 16,1 | 75% | 8,0 |
| 120 | 19,4 | 70% | 8,3 | 15,2 | 76% | 8,1 |
| 240 | 19,4 | 70% | 8,4 | 15,2 | 76% | 8,3 |
| 1440 | 18,1 | 72% | 9,0 | 14,1 | 78% | 8,9 |

In the third set of experiments, the whole digestate obtained from a lab-scale AD fed with chicken manure was used under the same conditions. The higher phosphate content of this digestate led to an increase in phosphate removal efficiency (Table 3). Without pH adjustment, the pH increased up to 9.1 due to the recirculation effect resulting in 80% phosphate removal. By adjusting the pH to 9.4, the removal efficiency reached 86%.

Table 3. Results of batch upflow reactor tests conducted using digestate obtained from lab-scale AD (set-3).

| | Test - 5 (no pH adjustment) | | | Test - 6 (pH adjusted to 9.4) | | |
|---|---|---|---|---|---|---|
| Time, minute | mgP/L | % P Removal | pH | mgP/L | % P removal | pH |
| 0 | 230 | 0% | 8.6 | 230 | 0% | 9.4 |
| 30 | 48 | 79% | 8.8 | 39 | 83% | 9.4 |
| 60 | 47 | 79% | 8.9 | 38 | 83% | 9.4 |
| 120 | 45 | 80% | 9.1 | 33 | 86% | 9.4 |

Lastly, the pilot-scale upflow struvite system operated by continuous feeding of SELEDA's LFD with a flow rate of 160-180 L/h. Three consecutive experiments were conducted by keeping the pH at 9.1-9.2 by dosing NaOH as needed. The results presented in Table 4, were obtained. After 350 min of continuous feeding of LFD and supplementation of $MgCl_2$ at Mg:P molar ratio of 2, the $PO_4$-P concentration decreased to below 14 mg/l, achieving an 82% removal efficiency. The efficiency obtained was attributed to the upflow velocity (160-180 L/h) provided by internal recirculation and keeping the pH above 9.

Table 4. Results of continuous flow pilot-scale tests conducted using LFD obtained from SELEDA.

| | Test - 7 (pH adjusted to 9.1-9.2) | |
|---|---|---|
| Time, minute | mgP/L | % P removal |
| 0 | 76.1 ± 4.1 | - |
| 10 | 44.1 ± 13.7 | 42.0% |
| 20 | 33.4 ± 8.4 | 56.1% |
| 30 | 20.8 ± 2.6 | 72.7% |
| 40 | 15.6 ± 3.2 | 79.5% |
| 50 | 27.8 ± 2.7 | 63,5% |
| 110 | 17.7 ± 9.7 | 76,7% |
| 170 | 15.7 ± 7.6 | 79,4% |
| 230 | 14. 9 ± 5.6 | 80,4% |
| 290 | 17.6 ± 6.9 | 76,9% |
| 350 | 13.7 ± 3.9 | 82,0% |

After each experiment, the chemical precipitates were sampled, dried, and analyzed by using XRD and SEM-EDX. The analyses revealed that the predominant component of the precipitates is $MgNH_4PO_4$ (Struvite) as illustrated in Figure 3. The SEM-EDX analyses of the crystals (Figure 4) are consistent with the XRD findings, showing the presence of Mg and P, which supports the conclusion of struvite formation.

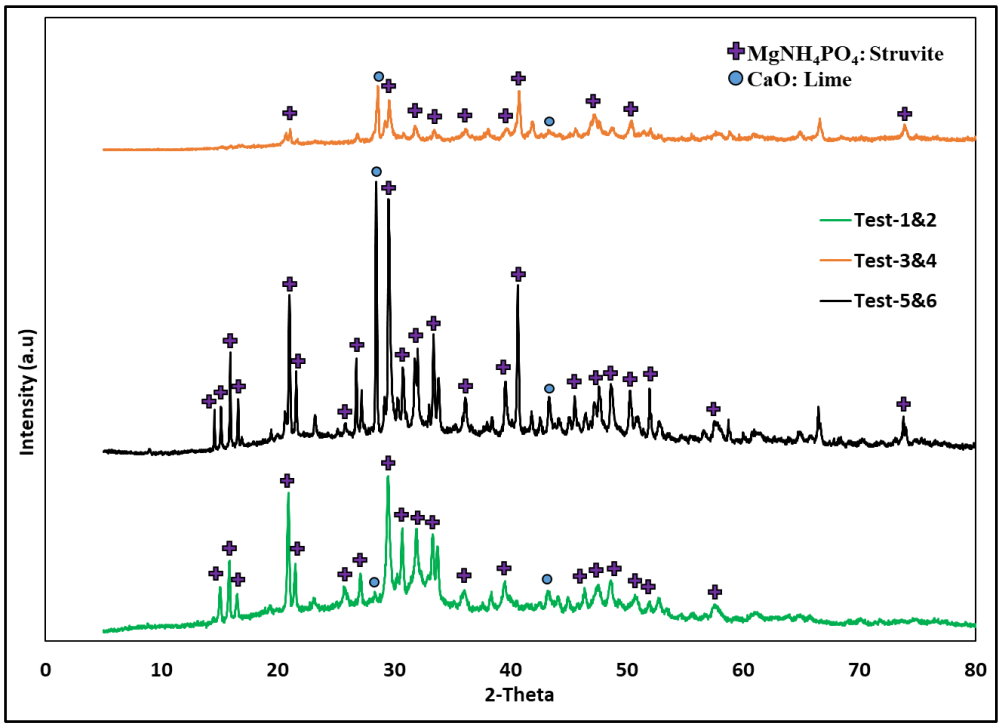


Figure 3. Results of XRD analysis.

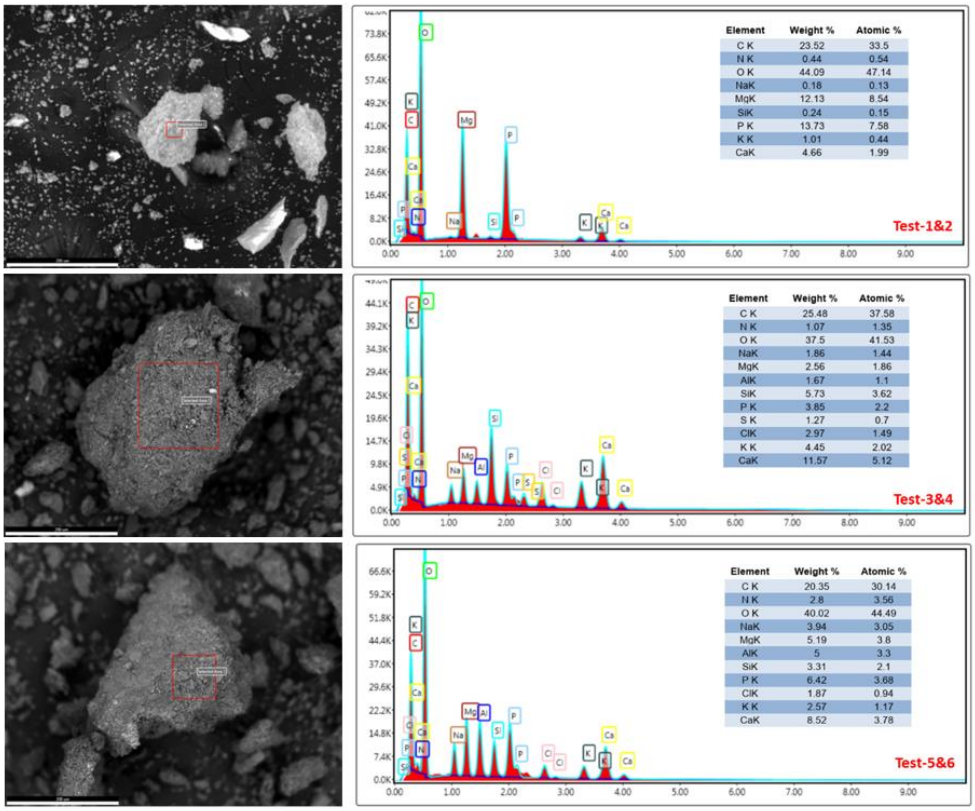


Figure 4. Results of SEM-EDX analysis.

## Conclusions/Remarks

- Slightly over 80% of the phosphate was removed from liquid fraction of digestate (LFD) through struvite crystallization in a pilot-scale continuously fed, upflow reactor.
- The key parameters affecting the P-romoval were determined to be pH, Mg:P molar ratio, up-flow velocity, reactor type and continuous feeding mode.
- Although many publications in the literature state the contrary, the substantial amount of particulate and soluble organics in LFD did not significantly hinder the struvite formation.

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**More information about the project:** check out the project website.
**Project partners:** Biogas-E, KU Leuven, Ghent University, Marmara University, VCM, OSTIM
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