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Calcium phosphates recovery from digester supernatant by fast precipitation and recrystallization

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Abstract

Conditional solubility of dicalcium phosphate dihydrate (DCPD) and hydroxyapatite (HAp) in digester supernatant was determined as a function of pH and was compared to its conditional solubility in distilled water. Conditional solubility of both substances in digester supernatant at pH > 5-6 was higher than their conditional solubility in pure water due to the presence of impurities, and this influence is more significant for HAp. Amorphous CaP was precipitated through a fast precipitation process from digester supernatant with initial total phosphate concentration 0.008 mol/L and 0.015 mol/L and Ca/P ratios 2 and 5 respectively. The amorphous CaP can be subsequently recrystallized into crystalline CaP. Obtained amorphous products have Ca/P ratio > 1, which allow performing the recrystallization process without further Ca dosing into the system. Batch recrystallization of the amorphous products resulted in crystallization of HAp, DCPD or their mixture depending on the conditions of the process. Maximum achieved P-recovery was 69.5 %. The increase of phosphate concentration and the addition of seeding decreased the yield of the process but promoted crystallization of DCPD. The increase of Ca/P ratio had a positive effect on the total P-recovery. Compared with the direct batch crystallization of CaP from digester supernatant, the two-step process with fast precipitation and recrystallization significantly improved the color of the obtained products.


1 Introduction

According to the Mineral Commodity Summaries 2016, mine production of phosphate rock worldwide in 2015 was 223 thousand tons, while the remaining reserves are approximately 69 million tons
At the same time, quality of the phosphorus reserves is decreasing, as a consequence the costs of the mining process are increasing [2]. Thus, phosphorus recovery (P-recovery) from wastewater is of the great interest in the last decades due to the importance of finding sustainable sources of phosphorus for industrial use and fertilizers production. It is possible to recover phosphorus from sewage sludge (SS) at different stages of its treatment, from a liquid phase produced during sludge digestion – digester supernatant (DS), as well as from the sewage sludge ash (SSA) [3-5]. Airprex process has been developed for P-recovery as struvite directly from an SS after digestion. It allows the recovery of phosphorus of 7% in the sludge input [6]. More technologies that are implemented nowadays at the wastewater treatment facilities are using DS as an input material: Crystalactor (producing magnesium ammonium phosphate (MAP)/CaP/MgP), Phosphaq (granulated MAP), Pearl (Crystal green fertilizer product containing 99.9% MAP in pellets), P-REX (mixture of HAp and MAP) [4, 5, 7-9]. Some of the technologies are using different processes for phosphorus leaching from the SS/SSA with further crystallization of phosphorus compounds from obtained concentrate. As examples of the technologies for leaching SS, there are Gifhorn and Stuttgart processes with further MAP production with 45-49% of P-recovery [4, 10]. Usually, obtained products can only be used as a fertilizer, which allows partially refund the costs of the treatment process and to decrease costs associated with the disposal of sludge. In our previous work the conceptual design of a crystallization process for recovery of high purity calcium phosphate from SSA has been reported [11].

This study is focused on P-recovery by calcium phosphate crystallization from DS, as all the phosphorus presented in this phase is in a dissolved state and concentration of it is the highest compared to all the other streams (up to 400 mg PO₄³⁻-P/L) [4]. Obtaining a pure high-quality CaP, which can be used in industry, can increase costs refund at WWTPs. However, development of the crystallization technology for producing high quality product from DS is challenging due to the presence of a wide range of different impurities and its inconsistent composition. Temperature and pH are few of the key process parameters that influence the nature of the final product. Tsuge et al. established the landscape of CaP formation during reactive crystallization of
equimolar calcium nitrate and potassium phosphate of 10 mmol/L at different temperatures in the range of 15 – 50 °C and initial solution pH in the range of 5 – 9 [12]. They reported that at pH lower than 5.5 no precipitation was happening, pure DCPD crystallized at pH < 7 and temperature 10 – 25 °C, and pure HAp crystallized at pH > 7 and temperature 38 – 50 °C. At the intermediate conditions, the product of crystallization was octacalcium phosphate (OCP) or the mixtures of OCP with DCPD or HAp. CaP crystallization from an artificial system that mimics DS in terms of PO₄³⁻ and NH₄⁺ content at different Ca/P ratios was previously conducted to study the influence of Ca/P and N/P ratio on the metastable zone and nature of the obtained product at room temperature [13]. It showed that at the studied conditions pure DCPD was crystallized when nucleation pH was 5.5 – 6.5 and pure HAp was crystallized at initial pH > 6.8 for both studied N/P ratios (10 and 20). Higher N/P ratio resulted in the higher nucleation pH that influenced the nature of the product. It was also discovered that the presence of ammonia affects the kinetics of crystal growth as well [13].

During anaerobic digestion of SS biodegradable organic compounds are transformed into biogas, while those which are non-biodegradable remain in the sludge. Among non-biodegradable compounds, there are humic substances (HS). HS are proven to be removed from wastewater by biosorption on activated sludge instead of biodegradation; therefore, some part of them can be released to DS [14]. Moreover, organic polymers are often used during wastewater treatment to enhance the effectiveness of coagulation and to produce denser sludge. Residuals of these polymers can be present in the DS as well. Presence of these substances in DS can have a significant effect on further phosphorus recovery process. In our previous study it has been observed that the presence of polymers in DS significantly influence the crystal size and shape of struvite at low supersaturation levels [15]. Amjad reported that presence of polyacrylic acid (PAA) at the concentration of 50 ppm inhibits calcium phosphate precipitation for more than 95% for at least 20 h [16]. It was also reported that various HS inhibit the crystal growth of both DCPD and HAp [17, 18]. Song et.al reported that the Ca consumption for CaP precipitation was increased with the addition of HS and the removal of HS from the solution took place simultaneously with CaP precipitation [19]. This removal of HS was explained
by its adsorption on the surface of formed CaP. Apart from the inhibiting effect on CaP crystallization, HS can have a negative effect on the final product color and purity. Our recent study of CaP crystallization from DS reported that the obtained product was with a dark brown color. At the SEM images of the obtained samples, dark spots could be seen which are believed to be HS absorbed on the surface of the crystals [20].

Therefore, for the improvement of the products quality and of the phosphorus recovery rate, it is essential to determine how is the solubility of calcium phosphates affected by the impurities present in DS. It is also important to reduce the effect of the present organic compounds on the crystallization process. The aim of this research is to study if this improvement can be achieved by using a two-step crystallization process where at the first stage fast precipitation of amorphous CaP is done at high supersaturation, which is created by a high pH and Ca/P ratio. It was decided perform the precipitation within a short time of about 15 min in order to reduce the adsorption of the organic contaminants on the surface of the solid product. During the second stage, obtained amorphous products can be re-crystallized into different crystalline calcium phosphates forms depending on the conditions of the process.

2 Experimental Methods

2.1 Materials

Aaby WWTP located in Aarhus, Denmark provided digester supernatant. Selective composition of digester supernatant is given in Tab. 1.

Table 1. Concentrations of selected ions in digester supernatant

<table>
<thead>
<tr>
<th>Parameter</th>
<th>[PO₄³⁻]ₗ₀ₓ</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Suspended solids</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, mol/L</td>
<td>0.008</td>
<td>0.050</td>
<td>0.003</td>
<td>164</td>
<td>7.8 – 8.0</td>
</tr>
</tbody>
</table>

In order to remove suspended solids, digester supernatant was filtrated using vacuum filtration with Munktell filter paper (grade 3). Initial total phosphate concentration in digester supernatant was 0.008 mol/L. Experiments were done with two different [PO₄³⁻]ₗ₀ₓ concentrations: 0.008 mol/L and 0.015 mol/L. NH₄H₂PO₄ was used to increase total phosphate concentration in digester supernatant when
needed. Reagent grade CaCl$_2$ was used for the preparation of the 1M solution for dosing Ca. 2M standard NaOH, 23% NaOH, and 37% HCl solutions were used for pH adjustment during experiments. Control samples for FT-Raman analysis were reagent grade DCPD and HAp. All chemicals were purchased from Sigma Aldrich and were used without further purification. All experiments were done at room temperature.

### 2.2 Determination of conditional solubility of DCPD and HAp in digester supernatant

The conditional solubility of DCPD and HAp in digester supernatant was measured with the isothermal method. Excess amounts of commercial reagent grade DCPD and HAp was suspended in digester supernatant at different starting pH in the range of 1 – 13. The suspension was kept under mixing for 24 hours to attain the solid-liquid equilibrium. After that the pH was measured and the suspension was filtrated and the liquid sample was analyzed with ion chromatography. pH were measured with combination electrode. It was calibrated using IUPAC buffer solutions (pH 4.00 and 7.00) at room temperature before each experiment and stored in a 3M KCl solution between measurements. The conditional solubility of both compounds was calculated using the equation:

$$\log P_s = \log ([Ca^{2+}]_{\text{tot}}^* \cdot [PO_4^{3-}]_{\text{tot}}^*)$$  \hspace{1cm} (1)

Where $[Ca^{2+}]_{\text{tot}}^*$ and $[PO_4^{3-}]_{\text{tot}}^*$ are the total concentration of phosphate and calcium in the aliquots of digester supernatant. Graphs of $\log P_s$ versus final pH were plotted and compared to the solubility of DCPD and HAp in distilled water [21].

### 2.3 Analysis of liquid phase

Ion chromatography was used to determine concentrations of calcium and total phosphate in the liquid phase. The ion chromatography was equipped with a 761 SD Compact IC with an 813 Compact Autosampler by Metrohm. A column for cations analysis is Metrosep Cation 4 (6.1010.000) and the eluent is 1.7 nM Nitric acid/0.70 mM dipicolinic acid. A column for anions analysis is Metrosep A Supp 5 - 150 (6.1006.520) and the eluent is 3.2 mM Na$_2$CO$_3$/1.0 mM NaHCO$_3$ + 10 % acetone.
2.4 Analysis of crystalline products

The solid products were characterized with Raman spectroscopy and X-ray diffractometer. A Bruker MultiRAM FT-Raman Spectrometer equipped with 1064 nm laser at 100 – 400 mW laser power (depending on the color of the crystalline product) was used in the present work. Baseline correction of spectra was done using CrystalSleuth software.

A Rigaku Miniflex 600 X-ray diffractometer with a Cu source of X-rays and a Ni filter was used for the PXRD analysis with following settings: voltage – 40 kV, current – 15 mA, speed –10°/min, step size – 0.02, 2θ range: 2 – 70°. A demo version of Match! Ver.3. was used with a COD-Inorg database to analyze the peaks of the PXRD patterns.

EI Quanta 200ESEM at the low vacuum mode was used to make Scanning Electron Microscope (SEM) images of the obtained crystalline products. Specimen chamber was set up at pressure of 30 Torr to prevent charging.

2.5 Batch crystallization experiments

2.5.1 Precipitation stage

Precipitation experiments were done in 4 repetitions. Two initial concentrations of total phosphate in digester supernatant were used: 0.008 mol/L and 0.015 mol/L. A 1L glass reactor was filled with filtrated digester supernatant. An overhead magnetic agitator was set up to 100 rpm. Certain amount of NH₄H₂PO₄ was weighed and dissolved in digester supernatant, for the experiments when initial [PO₄³⁻]tot concentration was increased to 0.015 mol/L. Thereafter, 1M CaCl₂ solution was dosed into the system using a peristaltic pump with the feed rate 45 mL/min to create the target Ca/P ratio. Two Ca/P ratios were tried at the stage of precipitation: 2 and 5. Turbidity measurements during precipitation were done using a Crystal Eyes turbidity probe. After 15 minutes solid and liquid phases were separated by vacuum filtration using an Advantec Glass Fiber filter (pore size 0.45 µm). The product was dried and weighted and the liquid phase was analyzed for the total phosphate and calcium concentrations. All mass measurements were done using Mettler Toledo Analytical Balances (±0.0001
Phosphate content in the obtained products was determined by the difference of the initial and final concentrations of $[\text{PO}_4^{3-}]_{\text{tot}}$ in the liquid phase.

### 2.5.2 Recrystallization stage

It was decided to do recrystallization by dissolving the amorphous products in order to obtain total phosphate concentrations 0.005 mol/L (for the initial 0.008 mol/L) and 0.01 mol/L (for the initial 0.015 mol/L). For the recrystallization, 1L of distilled water was poured into the reactor and its pH was adjusted to 0.9 – 1.0 by adding 37 % HCl. Needed amount of amorphous product was weighted and dissolved in this water for 2 hours with mixing set up at 250 rpm. After dissolution a non-dissolved part (organic compounds which are not soluble at pH<2) was filtrated using the Advantec Glass Fiber filter.

Recrystallization experiment was done with and without DCPD seeding. The pH value of solution was increased by dosing 23% NaOH solution until nucleation, which was detected using the turbidity probe. For the seeding experiment, 0.5 g (±0.001 g) of DCPD seeds was added to the solution before nucleation. Experiment lasted for 2 hours with the continuous turbidity measurement. During this time, the pH was monitored and kept stable using 2M NaOH solution. Thereafter, solid and liquid phases were separated and analyzed. Recrystallization experiments with and without DCPD seeding were repeated twice.

The yield of P-recovery was calculated for precipitation and recrystallization using an equation:

$$P_{\text{rec}} = \frac{P_{\text{in}} - P_{\text{fin}}}{P_{\text{in}}} \cdot 100 \%,$$

(2)

where $P_{\text{rec}}$ represents the % of phosphorus recovered from the liquid phase; $P_{\text{in}}$ is the initial concentration of total phosphate; $P_{\text{fin}}$ is the concentration of total phosphate in the liquid phase after the experiment. The total P-recovery rate was calculated by multiplication of the yield for precipitation and recrystallization processes:

$$P_{\text{rec}}^{\text{tot}} = P_{\text{rec}}^{\text{prec}} P_{\text{rec}}^{\text{recryst}}.$$

(3)
3 Results and Discussion

3.1 Influence of the composition of digester supernatant on conditional solubility of DCPD and HAp

Functions of conditional solubility of DCPD and HAp versus pH of digester supernatant are presented in Fig. 1.a and Fig.1.b, respectively, together with their solubility in distilled water. Conditional solubility data for distilled water (experimental and modeled with the use of PHREEQC software) were retrieved and modified from our previous work [21].

Fig. 1. The conditional solubility of two CaP phases in digester supernatant and distilled water vs. pH: a. DCPD; b. HAp.

The conditional solubility of HAp is affected by the presence of different impurities in digester supernatant more significantly than the solubility of DCPD. For the pH values above 5.8 the conditional solubility of HAp increased dramatically, while at pH below 5.8 the conditional solubility of HAp decreased by the presence of impurities in DS. The conditional solubility of DCPD in DS slightly increased at the pH higher than 4.8 compared to its conditional solubility in distilled water. This increase could be attributed to the presence of various impurities as well as the different ionic strength in DS compared to that in distilled water. At this stage it is impossible differentiate further the effects of every individual species due to the complex nature of DS, however, the effects of certain group of substances, e.g., humic compounds, on the conditional solubility of CaP will be investigated in our
future work. The increase of conditional solubility can have a negative effect on the P-recovery yield when calcium phosphates crystallizations are conducted at the pH range of 5 – 7.

3.2 Precipitation of amorphous product from digester supernatant

No pH control was done during precipitation of amorphous product from digester supernatant. At the initial pH of digester supernatant of 7.8 – 8.0 a high supersaturation was created by the addition of CaCl₂ for Ca/P ratios 2 and 5. Precipitation began at the beginning of Ca dosing and was detected by the significant turbidity change. According to the turbidity measurements after 15 minutes of precipitation maximum of P-recovery was achieved for all experiments as no more turbidity change could be observed. Filtration of these amorphous products was rather slow due to the small particles size as well as the presence of organic compounds with polymeric structure, which blocked the filter.

P-recovery rate for the precipitation stage depends on the initial total phosphate concentration in digester supernatant and the used Ca/P ratio, as illustrated in Fig.2.

![Fig. 2. The P-recovery rate by fast precipitation from digester supernatant.](image)

High degree of phosphorus removal from digester supernatant by precipitation were obtained due to the rather high operation pH (7.8 – 8.0). For precipitation with the initial concentration of total phosphate 0.008 mol/L, P-recovery increases from 74.0 % to 93.7 % with the increase of Ca/P ratio from 2 to 5. For the initial concentration of total phosphate 0.015 mol/L, P-recovery approaches a high level with Ca/P ratio at 2 (93.2%) and doesn’t change significantly with increasing Ca/P ratio to 5 (increases to 94.9%). All obtained solids were analyzed with Raman and did not show any peaks in the spectra. Therefore, they were characterized as amorphous calcium phosphate.
3.3 Recrystallization of the amorphous products

The amounts of amorphous products, which need to be dissolved in distilled water, were calculated based on the content of phosphate in the solid phase. Target concentrations of solutions were 0.005 and 0.01 mol/L for initial total phosphate concentrations during precipitation stage of 0.008 and 0.015 mol/L, respectively. After 2 hours of dissolution at pH 0.9 – 1.0 part of the solid phase was not dissolved and it was considered to be the organic matter which is not soluble at pH < 2. Total phosphate and calcium concentrations in the solutions after amorphous products dissolution were determined with IC and Ca/P ratio was calculated. For all dissolved samples Ca/P ratio was > 1. Therefore, it was decided to conduct recrystallization without any further Ca dosing into the system. Experimental conditions and the description of the products obtained at the recrystallization stage are presented in Tab. 2.

Table 2. Parameters and results of the recrystallization experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>P&lt;sub&gt;i&lt;/sub&gt; for prec. stage, mol/L</th>
<th>Ca/P for prec. stage</th>
<th>P&lt;sub&gt;i&lt;/sub&gt; for recryst. stage, mol/L</th>
<th>Ca/P for recryst. stage</th>
<th>Addition of DCPD seeds</th>
<th>Obtained product (first product is a major)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.008</td>
<td>2</td>
<td>0.005</td>
<td>1.49 (±0.07)</td>
<td>–</td>
<td>HAp+DCPD</td>
</tr>
<tr>
<td>2</td>
<td>0.008</td>
<td>5</td>
<td>0.005</td>
<td>1.77 (±0.25)</td>
<td>–</td>
<td>HAp</td>
</tr>
<tr>
<td>3</td>
<td>0.008</td>
<td>2</td>
<td>0.005</td>
<td>1.49 (±0.07)</td>
<td>+ 0.5 g</td>
<td>DCPD+HAp</td>
</tr>
<tr>
<td>4</td>
<td>0.008</td>
<td>5</td>
<td>0.005</td>
<td>1.77 (±0.25)</td>
<td>+ 0.5 g</td>
<td>DCPD+HAp</td>
</tr>
<tr>
<td>5</td>
<td>0.015</td>
<td>2</td>
<td>0.010</td>
<td>1.07 (±0.09)</td>
<td>–</td>
<td>DCPD+HAp</td>
</tr>
<tr>
<td>6</td>
<td>0.015</td>
<td>5</td>
<td>0.010</td>
<td>1.62 (±0.19)</td>
<td>–</td>
<td>DCPD+HAp</td>
</tr>
<tr>
<td>7</td>
<td>0.015</td>
<td>2</td>
<td>0.010</td>
<td>1.07 (±0.09)</td>
<td>+ 0.5 g</td>
<td>DCPD</td>
</tr>
<tr>
<td>8</td>
<td>0.015</td>
<td>5</td>
<td>0.010</td>
<td>1.62 (±0.19)</td>
<td>+ 0.5 g</td>
<td>DCPD</td>
</tr>
</tbody>
</table>

Depending on the initial concentration of total phosphate and Ca/P ratio for the recrystallization experiment, two different phases were obtained: DCPD and HAp. Raman spectra and XRPD pattern of the selected samples are show in Fig. 3.a and b.
DCPD and dicalcium phosphate anhydrous (DCPA) have an intense peak at 986 cm$^{-1}$ at the FT-Raman spectra. Discrimination between DCPD and DCPA can be done by the peak at 880 cm$^{-1}$ that is characteristic for DCPD while for DCPA this peak is shifted to 897 cm$^{-1}$. The peaks at low Raman shifts (141 cm$^{-1}$, 174 cm$^{-1}$, 207 cm$^{-1}$, 380 cm$^{-1}$) can also prove the appearance of DCPD. The peaks at 11.68° and 20.8° at the PXRD pattern can also verify the presence of DCPD.

When the quality of the spectra is low it is complicated to discriminate between HAp and OCP. Both of them have the strong peak at 961 cm$^{-1}$. These phases can be distinguished using the PXRD patterns. Due to the low crystallinity of the samples that had a peak on the FT-Raman spectra at 961 cm$^{-1}$, PXRD patterns of these samples didn’t have any intense peaks. At the same time, OCP should have a strong peak at 4.85°. Therefore, when this peak was absent in the PXRD pattern, these samples were characterized as HAp [22].

With the increase of total phosphate concentration in the solution from 0.005 to 0.01 mol/L, the major product becomes DCPD instead of HAp. This can be explained by the fact that with the increase of concentration nucleation starts at lower pH, which can result in crystallization of DCPD. When no seeding was used in the experiments, the recrystallization, conducted at total phosphate concentration 0.005 mol/L, yielded the main product as HAp for both Ca/P ratios (some minor amount of DCPD were present in the sample No.1). For the experiments with initial total phosphate concentration 0.01 mol/L, the major product was DCPD with some minor amounts of HAp. For all experiments with the use of seeding, DCPD was the major product. But for the total phosphate concentration of 0.005
mol/L, minor amounts of HAp were also present in the samples. At the same time, for higher total phosphate concentration (0.01 mol/L) the product was pure DCPD. This proves that both total phosphate concentration in the solution and application of seeding can affect the nature of the crystallized phase. SEM images of selected samples after recrystallization are presented in Fig. 4.a – 4.d.

![SEM images of selected samples](image)

**Fig. 4.** SEM images of the selected samples:

a. $P_{in}^{recryst} = 0.005$ mol/L, Ca/P = 1.49, without seeding (HAp+DCPD);

b. $P_{in}^{recryst} = 0.005$ mol/L, Ca/P = 1.49, with seeding (DCPD+HAp);

c. $P_{in}^{recryst} = 0.010$ mol/L, Ca/P=1.62, without seeding (DCPD+HAp);

d. $P_{in}^{recryst} = 0.010$ mol/L, Ca/P=1.62, with seeding (DCPD);

e. DCPD crystals crystallized directly from DS at Pin=0.016 mol/l and Ca/P=2 [20].

For the comparison of crystal color/purity in terms of adsorption of humic/organic compounds on their surface, the SEM image of the crystals obtained during direct batch crystallization from DS in our previous work is also presented at the figure 4.e [retrieved from 20]. On this image, dark spots on the surface of crystals can be observed, that gave the crystals dark brown color. When the precipitation/recrystallization process was applied, the amount of humic/organic compounds that can be adsorbed on the surface of the crystals decreased and no dark spots can be observed on the surface of recrystallized products (Fig. 4.b – 4.d). The color of obtained samples was light beige.

Initial concentration of total phosphate in the solution affected the phosphorus recovery rate as well as the seeding. These data are illustrated in Fig. 5.
P-recovery was significantly higher for lower initial total phosphate concentration during recrystallization. The maximum P-recovery that was achieved at this stage was 81.7 % for the concentration of total phosphate 0.005 mol/L and Ca/P=1.49 without seeding. For the total phosphate concentration 0.01 mol/L the highest achieved P-recovery rate was 54.9 %. In general, for all experimental conditions, P-recovery decreased with the use of DCPD seeding. In most of the cases with the increase of Ca/P ratio P-recovery rate increases except for the non-seeding conditions at the lower total phosphate concentration. Lower Ca/P ratio can be an explanation of the lower P-recovery for the P concentration at approximately 0.01 mol/L.

### 3.4 Influence of the experimental parameters on total phosphorus recovery and yield of the target products

The maximum achieved total P-recovery for the two-stage precipitation/recrystallization process was 69.5 %. It was achieved for the initial total phosphate concentration at precipitation stage of 0.008 mol/L (0.005 mol/L at recrystallization stage) and Ca/P ratio 5 (Ca/P=1.77 at recrystallization stage) without seeding (Fig. 6.a). For the initial total phosphate concentration of 0.015 mol/L at the precipitation stage (0.01 mol/L during recrystallization), maximum overall P recovery was 54.9 %. It was achieved at the higher Ca/P ratio without seeding as well. The decrease of initial Ca/P ratio decreases the overall P-recovery rate for both initial concentrations and with/without seeding. Application of
seeding decreased the P-recovery as well, as it significantly influences the P-recovery at the recrystallization stage. This can be explained by the promotion of DCPD crystallization instead of HAp, while DCPD has higher solubility at the tested conditions.

![Fig. 6. Total phosphorus recovery from digester supernatant by two-stage precipitation/recrystallization process for: a. Initial total phosphate concentration at precipitation stage 0.008 mol/L; b. Initial total phosphate concentration at precipitation stage 0.015 mol/L.](image)

**4 Conclusions**

The conditional solubility of both target phases (DCPD and HAp) is affected by the presence of impurities in digester supernatant. The conditional solubility of DCPD slightly increases at pH higher than 5 and for HAp it significantly increases at pH higher than 5.8. Therefore, crystallization of CaP directly from DS is not feasible due to the low initial total phosphate concentration (0.008 mol/L) of the DS used in the present work. It was proved that with the creation of high supersaturation by the addition of Ca and slightly alkaline pH (7.8 – 8.0) it is possible to recover amorphous product with up to 94.9 % of P-recovery, which depends on the initial total phosphate concentration in digester supernatant and Ca/P ratio. By dissolving the amorphous product in distilled water at pH 0.9 – 1.0 it was possible to recrystallize it into the crystalline product. It was shown that the amount of Ca in the amorphous product was enough for the recrystallization of CaP without any further Ca dosing into the system. It was studied that during recrystallization stage both the increase of the total phosphate concentration and the addition of DCPD seeding can promote crystallization of DCPD instead of HAp. During recrystallization stage with lower total phosphate concentration (0.005 mol/L) without
seeding, HAp was the major product. At higher total phosphate concentration (0.01 mol/L) with DCPD seeding, it became possible to crystallize pure DCPD. At the same time, it was discovered that P-recovery decreases when DCPD seeds are added. In most of the cases, the mixture of DCPD and HAp was produced. Therefore, it might be concluded the optimization of the recrystallization stage is needed in order to obtain pure phase instead of their mixtures. It was proved that the combination of fast precipitation and further recrystallization of the obtained amorphous products allow improving the purity of the products in terms of the crystals color compared to the direct crystallization from DS.

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References


