Dynamic and equilibrium precipitation of struvite from the concentrated cellulosic ethanol stillage

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ABSTRACT

The phosphate rock mineral is the main source of P-fertilizer production. It is estimated to become depleted in next century. Thus, the recovery of phosphorus from waste streams has attracted great interest. The cellulosic ethanol production is seen as more and more important in future. During the production of cellulosic ethanol, the phosphorus element is released from lignocellulosic biomasses and ends up dissolved as phosphate ions in the stillage stream. In this study, the struvite (MgNH₄PO₄ · 6H₂O) recovery from the concentrated cellulosic ethanol stillage (ES) was conducted under room conditions with an initial pH at 7–9. The effect of Mg²⁺, PO₄³⁻/C₀, and Ca²⁺ during struvite precipitation tests was investigated. The optimized pH value for struvite recovery is estimated at 8.5, by which 85% of PO₄³⁻ and 46% of Mg²⁺ are removed from the liquid stream. The mass fraction of struvite in recovered crystal sample reaches 82 wt.%. The economic evaluation of struvite recovery from ES was also investigated. This work proves that the struvite is potentially to be recovered with high purity from the concentrated cellulosic ethanol stillage.

Key words: crystallization of calcium-phosphate salts, humic acid-like organic compounds, stillage of cellulosic ethanol, struvite recovery

HIGHLIGHTS

- The struvite recovery from cellulosic ethanol production process requires only dosage of sodium hydroxide.
- Struvite is recovered from feed stream comprising extreme high concentration of TOC and TDS.
- The struvite with high purity is recovered from concentrated cellulosic ethanol stillage.

INTRODUCTION

Cellulosic ethanol is considered as one of the preferred alternatives to fossil fuel; around 194 million m³/year cellulosic ethanol could be potentially produced from crop residuals (Kim & Dale 2004; Sims et al. 2010; Gupta & Verma 2015; Karimi Alavijeh & Yaghmaei 2016). During the production of cellulosic ethanol, the PO₄³⁻ is released from the lignocellulosic biomass and ends up transfer red in the stillage as dissolved phosphates. The production yield of cellulosic ethanol from the dry wheat straw is estimated at around 180 g/kg. That results the concentration of phosphorus in the form of phosphate (PO₄³⁻-P) up to 270 mg/L in stillage (Liao et al. 2004; Hu et al. 2017; Mohapatra et al. 2017). The corresponding discharge of stillage would sum up to 3.9 billion cubic meters per year. Assuming a total recovery of PO₄³⁻-P from cellulosic ethanol stillage, around 6.9 million tons of phosphate rocks could benefit (Gupta & Verma 2015). P is a nutrient element, comprising raised eutrophication potential for natural water systems at aqueous concentration higher than 75 μg/L (Dodds & Smith 2016). It is sustainable to recover overabundant P from cellulosic ethanol stillage as fertilizers in agriculture sectors.

P-fertilizers are heavily invested in the agriculture sector. According to the statistics by USGS (United States Geological Survey), about 44.5 million tons of P₂O₅ were used in production of P-fertilizer in 2016 (Jasinski 2017). That was about half of the worldwide phosphate rock (30–40 wt.% P₂O₅) consumption, which is estimated at 263 million tons in 2016.
(Jasinski 2017). The P₂O₅ consumption in agriculture sector is expected to grow in the next years. It is supposed to reach 70 million tons in 2030 (López-Arredondo et al. 2014). Phosphate rock minerals have been forecasted to become depleted within the next 100 years, which will cause a worldwide big challenge for agriculture (Karabegovic et al. 2013). Thus, the recovery of phosphorus from waste streams has attracted great interest.

Typically, there are two chemical precipitation methods for the recovery of phosphorus (P) from aqueous streams, aiming at the production of either magnesium ammonium phosphate hexahydrate MgNH₄PO₄·6H₂O (MAP/struvite) or calcium phosphate (Ca-P) (Desmidt et al. 2015; Daneshgar et al. 2018). The struvite could be precipitated as solid hydrate salt from liquid stream with a molar ratio of Mg²⁺:NH₄⁺:PO₄³⁻ at 1:1:1, according to Equation (1) \( n = 0, 1 \) or 2 (Le Corre et al. 2009). Compared to calcium phosphate fertilizers, struvite is known as providing a better bioavailability to plants (Melia et al. 2017).

\[
Mg^{2+} + NH_4^+ + H_nPO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+ \quad (1)
\]

Currently there are numbers of researchers and industry players engaged in P-recovery from waste liquids (Desmidt et al. 2015). Several full-scale processes such as ANPHOS, PHOSPAQ, NuResys, Phosnix or Ostara Pearl were developed for struvite recovery from liquid stream. The anaerobic digested wastewater, dewatering liquid from sludge digestion or industry wastewater, which contain 60–900 mg/L PO₄₃⁻-P, were successfully utilized in struvite recovery with a recovery rate of P up to 80–90% (Desmidt et al. 2015). Nevertheless, as Mg²⁺ is widely dosed in feed stream for the recovery of struvite, the cost of magnesium can contribute up to 75% of the total production cost (Ashley 2009). Moreover, the dissolved calcium in the aqueous solution can compete with magnesium, which could lead to the precipitation of unexpected crystals, such as hydroxyapatite, whitlockite, octacalcium phosphate or monenite (Daneshgar et al. 2019b). Thus, the mass fraction of struvite in recovered crystals is strongly influenced by the concentration of calcium (Li et al. 2016).

In this study, the evaporation concentrated cellulosic ethanol stillage (ES) is utilized in struvite recovery tests. The ES was collected from a pilot-scale cellulosic ethanol production plant with the following production steps in Figure 1. The hydrolysate was firstly produced from the input material wheat straw through the steam explosion followed by biological hydrolysis. The hydrolysate was then fermented by introduced strains. After removing undissolved organic materials by microfiltration, the stream was distilled to gain highly concentrated ethanol. To reduce the effluent volume as well as to gain reusable process water, the stillage stream was further evaporated. All previously dissolved compounds in the stillage stream were concentrated by a factor of around 10 after evaporation. The ES samples were taken from the neutralized concentrated stillage stream with initial pH around 6. After collection, the samples were stored at 6 °C.

Against the backdrop of current research landscape, this is the first time to recover struvite from a liquor stream comprising high concentrations of TDS as well as TOC. The dynamic precipitation tests (DP-tests) and equilibrium precipitation tests (EP-tests) are conducted to investigate the contribution of specific ions to struvite crystallization. Moreover, the economy of struvite recovery from ES has been investigated.

**METHODS**

**Materials**

The ES samples were collected from a pilot-scale cellulosic ethanol production plant with the following production steps in Figure 1. The hydrolysate was firstly produced from the input material wheat straw through the steam explosion followed by biological hydrolysis. The hydrolysate was then fermented by introduced strains. After removing undissolved organic materials by microfiltration, the stream was distilled to gain highly concentrated ethanol. To reduce the effluent volume as well as to gain reusable process water, the stillage stream was further evaporated. All previously dissolved compounds in the stillage stream were concentrated by a factor of around 10 after evaporation. The ES samples were taken from the neutralized concentrated stillage stream with initial pH around 6. After collection, the samples were stored at 6 °C.

Owing to different sampling times, ES 1 and ES 2 are differently composed, as shown in Table 1. For the precipitation tests, the ES is utilized without further pretreatment. The organic compounds in ES are suggested to be composed of 55% humic acid-like organic compounds (HAOC), 16.4% soluble microbial byproduct-like materials and 19.6% fulvic acid-like materials. The organic mass fraction of carboxylic acids and alcohols in ES could reach 20.4% and 71.3%, respectively (Shan et al. 2015, 2016).
The sodium hydroxide (Sigma-Aldrich >98%) is used in the form of solution at concentration 4 mol/L to alkalize the ES samples. The magnesium ammonium phosphate hexahydrate powder (NH₄MgPO₄ · 6H₂O) (>98%, 13478-16-5) with equivalent spherical diameter at 4.7–15.2 μm is purchased from Alfa Aesar and seeded as crystal nuclei in feed stream during DP-tests.

Experimental design
The purpose of DP-tests is to investigate the effect of ions such as Mg²⁺, Ca²⁺, NH₄⁺ and PO₄³⁻ on struvite crystallization. During these tests, the ES 1 is filled in a glass beaker and agitated by magnetic stirrer at ambient conditions (T = 25 ± 2 °C, P = 1 bar). The MAP (NH₄MgPO₄ · 6 H₂O) is then seeded as nuclei at mass ratio 1 g/kg in feed stream. The test sequence started after adjustment of the initial pH value to 7, 7.5, 8, 8.5 and 9, respectively. For detection of the concentrations of dissolved Mg²⁺, NH₄⁺, PO₄³⁻ and Ca²⁺, the feed stream is sampled at given time after centrifugation at 3,000 rpm for 5 min. Through utilization of struvite nuclei in feed stream, the struvite could be more rapidly crystallized from stream through particle growth of struvite crystals. That conforms to an actual crystallization system, by which the nuclei are always presented in mother liquor.

The EP-tests are conducted at 25 °C in a closed Schott bottle. The ES 2 is filled into a Schott bottle, which is then flooded full of N₂ gas. Through NaOH dosage simultaneously with agitation by magnetic stirrer, the initial pH value of feed stream is adjusted to 7, 7.5, 8, 8.5 or 9, respectively. The feed stream is then set calmly at 25 °C for 120 hours. Through filtration by sieve with pore size at 55 μm, the inorganic precipitates are separated from feed stream. To remove the residual feed stream from inorganic precipitates, the samples are blown at least for 30 seconds by dry air. For the further characterization of the recovered inorganic precipitate, the samples are dried at least 24 hours in a desiccator at ambient condition. The content of crystals

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**Figure 1** | Flow sheet of the cellulosic ethanol production and discharge of evaporation concentrated cellulosic ethanol wastewater (ES).

**Table 1** | Compositions of ES streams

|          | ES 1    | ES 2    |
|----------|---------|---------|
| pH       | 6.5     | 5.95    |
| TOC [g/L]| 227     | 175     |
| Ortho-PO₄³⁻ [mg/L] | 1,321 | 1,486 |
| NH₄⁺ [mg/L] | 958.9 | 1,443 |
| Mg²⁺ [mg/L]  | 2,536 | 2,476 |
| Ca²⁺ [mg/L]  | 1,819 | 1,893 |
| Na⁺ [g/L]   | 44      | 35      |
| K⁺ [g/L]    | 26      | 30      |
| Cl⁻ [g/L]   | 4.25    | 4.9     |
| SO₄²⁻ [g/L] | 34    | 24      |
| Total dissolved salts [g/L] | 115 | 101 |
in crystalline samples is detected by XRD. The mass fraction of ions in crystalline samples is detected by atomic absorption spectroscopy (AAS) through the dissolution of a sample of crystal in desalinated water.

### Analytical methods

The dissolved cations Na\(^+\), K\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) in the liquid samples are detected by AAS with model 900AA from Perkin Elmer-AAS-PinAAcle\(^\text{TM}\). The dissolved anions Cl\(^-\) and SO\(_4\)\(^{2-}\) are detected via ion chromatography (IC) 790 Personal from Metrohm, using Metrosep anion dual 2 75/4 column. The PO\(_4\)\(^{3-}\)-P and NH\(_4\)\(^+\) are detected by flow injection analysis (FIA) FOSS FIA Star 5000. The phase compositions in the crystalline samples are detected under ambient condition by X-ray-diffractometer (XRD) (Rigaku SmartLab 3 kW) from company Rigaku Europe SE with scanning rate at 0.5°/min ranging from 10° to 85° then evaluated by the International Centre for Diffraction Data (ICDD).

The TOC is detected through thermal catalytic oxidation process at 850 °C with Analytik Jena multi N/C 3100. The organic compositions in aqueous samples are separated by size exclusion chromatography (SEC column) (Toyopearls HW-50S from Tosoh Bioscience, Tokyo/Japan) through eluent solution and subsequently detected by organic carbon detection (LC-OCD), which is supplied by DOC-Labor Dr Huber Karlsruhe (Germany).

### Calculation

The removal efficiency \(E_{i,t}\) as well as the recovery efficiency \(R_i\) of inorganic ions are calculated according to the following equations:

\[
E_{i,t} = \frac{c_{i,0} - c_{i,t}}{c_{i,0}} \times 100\%
\]

\[
R_i = \frac{m_{i,\text{recovery}} \cdot w_i}{c_{i,0} \cdot V_{total}} \times 100\%
\]

where the \(E_{i,t}\) is the removal efficiency of ion \(i\) (%) at reaction time \(t\), \(c_{i,0}\) and \(c_{i,t}\) are the concentration of ion \(i\) (mg/L) in ES at the beginning of test and at the reaction time \(t\). \(R_i\) is the recovery efficiency of ion \(i\) (%), \(m_{i,\text{recovery}}\) is the mass of recovered crystal sample, \(w_i\) is the mass fraction of the ion in recovered crystal sample, \(V_{total}\) is the total volume of ES in recovery test.

### RESULTS AND DISCUSSION

#### Consumption of NaOH in DP-tests

During DP-tests, NaOH solution is provided to adjust initial pH value of ES stream to 7, 7.5, 8, 8.5, 9, respectively as well as to keep the pH value constant during the crystallization process. The main organic compounds in ES; stream are carboxylic acids and alcohols. The acids, such as propionic acid and lactic acid, might be mainly contained in ES; their pKa values are 4.8 and 3.9 (Lee et al. 1994; Narendranath et al. 2001; Couallier et al. 2006; Shan et al. 2015). The 2-pentanol and 3,5-dimethylphenol are main carboxylic alcohols in ES; their pKa values are 17.8 and 10.6 (Huyskens & Tack 1975). Owing to the high TOC concentration in the ES stream at around 200 g/L, the pH of ES is well buffered by organic species. The NaOH consumption for alkalization and for keeping pH constant during crystallization are listed in Table 2. With an initial pH at 7–9, the NaOH consumption of alkalization reaches 3.9–9.3 g for each liter of ES stream. That is much higher than the NaOH consumption to keep the pH value of ES stream constant. With initial pH at 7–9, it reaches 0.4–1.2 g for each liter of ES stream. The ratio of NaOH consumption on alkalization of ES stream reaches around 91, 78, 79, 86 and 89% of total consumption in tests with initial pH at 7, 7.5, 8, 8.5 and 9, respectively. With initial pH at 8, the consumption ratio of NaOH in crystallization process is highest.

**Table 2** | NaOH consumption in DP-tests on alkalization or crystallization

| Initial pH | 7  | 7.5 | 8  | 8.5 | 9  |
|-----------|----|-----|----|-----|----|
| NaOH - Alk. [g/L] | 3.9 | 5.1 | 6  | 7.6 | 9.3 |
| NaOH- Cry. [g/L]  | 0.4 | 1.4 | 1.6 | 1.2 | 1.2 |
| Total NaOH [g/L]  | 4.3 | 6.5 | 7.6 | 8.8 | 10.5 |
Contribution of Mg$^{2+}$ and PO$_4^{3-}$ in DP-tests

As shown in Figure 2, the relative mass concentrations of Mg$^{2+}$ and PO$_4^{3-}$ decrease in the tests at all investigated initial pH values. This indicates a corresponding precipitation of crystals containing these ions. In the test with an initial pH at 7, the relative mass concentration of Mg$^{2+}$ in ES is almost not decreased in first 30 min. However, the relative mass concentration of PO$_4^{3-}$ increases from 92% to 100% between 15 and 30 min. Although the NaOH is dosed into ES with a concentration of 3.9 g/L during alkalization, it is supposed to be totally consumed by the organic buffer-systems. Owing to low concentration of available OH$^-$ in the feed stream, the saturation index of struvite might be lower than 0. Thus, the seeded struvite is dissolved into ES, leading to the increase of PO$_4^{3-}$ concentration in ES. After continued dose of OH$^-$ into ES stream, the PO$_4^{3-}$ and Mg$^{2+}$ might be precipitated after a reaction time of 30 min. The final decrement of PO$_4^{3-}$ and Mg$^{2+}$ (removal rate of PO$_4^{3-}$ and Mg$^{2+}$) reaches 25 and 19% at a reaction time of 120 min, respectively.

With initial pH higher than 7.5, a high concentration of NaOH is rapidly dosed in ES during alkalization step, which can lead to the precipitation of Mg(OH)$_2$ from ES stream. The concentration of Mg$^{2+}$ in ES is also continuously decreased through crystallization of struvite; consequently the saturation index of struvite in ES is decreased. In the tests with initial pH at 7.5 and 8, the saturation index of Mg(OH)$_2$ in feed stream might be lower than 0 after struvite precipitation. The precipitated Mg(OH)$_2$ can be redissolved into ES to contribute Mg$^{2+}$ and OH$^-$ to ES stream. That leads to an increase of Mg$^{2+}$ concentration in ES, correspondingly with a higher saturation index of struvite in ES stream. After further precipitation of struvite from ES, the relative mass concentration of PO$_4^{3-}$ in ES is further decreased; however, the relative mass concentration of Mg$^{2+}$ is slightly increased or kept same. Thus, with initial pH at 7.5 or 8, the relative mass concentration of Mg$^{2+}$ and PO$_4^{3-}$ reaches 37 and 67, or 39 and 81% in 45 min, and the final relative mass concentration of Mg$^{2+}$ and PO$_4^{3-}$ at reaction time 120 min reaches 35 and 69, or 38 and 81%.

With initial pH at 8.5 or 9, the NaOH with the concentration of 7.6 or 9.3 g/L is dosed in ES stream. The concentration of OH$^-$ is higher than that in feed stream with initial pH at 7.5 or 8. Thus, the saturation index of Mg(OH)$_2$ after struvite precipitation could be higher than 0. Thus, the precipitated Mg(OH)$_2$ could not be redissolved into feed stream, and the relative mass concentration of Mg$^{2+}$ in ES is not increased after a reaction time of 45 min. The relative mass concentration of Mg$^{2+}$ and PO$_4^{3-}$ reaches 43 and 76, or 43 and 74% in 45 min, and the final relative mass concentration reaches correspondingly 43 and 83, or 43 and 78%.

As shown in Figure 2, the Mg$^{2+}$ is removed in 15 min more rapidly in the test with initial pH at 8.5 or 9 than that with initial pH at 8. The relative mass concentration of Mg$^{2+}$ in tests with initial pH at 8.5 or 9 reaches 43% at reaction time 120 min; however, 1.7 g more NaOH is consumed for each liter of ES stream in the test with initial pH at 9. The highest removal rate of Mg$^{2+}$ is determined to be the same at 43%. The other Mg$^{2+}$ species in ES might be tightly combined with organic compounds.

Figure 2 | The relative mass concentration of struvite relevant ions Mg$^{2+}$, PO$_4^{3-}$ and NH$_4^+$ in ES during DP-tests with initial pH values at 7–9.
and not able to be precipitated from ES after NaOH dosage. The optimized NaOH dosage for PO\textsubscript{4}{3−}-P recovery is determined at 7.3 g per liter of ES stream, corresponding with an initial pH at 8. The removal rate of PO\textsubscript{4}{3−}-P from ES reaches around 80% after a reaction time of 120 min.

The molar ratios of the removed Mg\textsuperscript{2+}:PO\textsubscript{4}{3−} during DP-tests are shown in Figure 3. The highest molar ratio reaches 1.68 in the test with initial pH at 7.5 at reaction time of 15 min. It decreases to around 1.25 at the reaction time of 120 min. That could be owing to the precipitation of Mg(OH)\textsubscript{2} at the beginning of the test and then being partly redissolved in ES. The molar ratio of Mg\textsuperscript{2+}:PO\textsubscript{4}{3−} reaches the lowest in the test with initial pH at 8, which ranges from 1.00 to 1.22. Thus, the Mg\textsuperscript{2+} is mainly contained as struvite in inorganic precipitates. It is reported that the crystal Mg\textsubscript{3}PO\textsubscript{4}·22 H\textsubscript{2}O is usually precipitated from feed stream at pH higher than 9 (Le Corre et al. 2009). With initial pH at 8.5 or 9, the molar ratio of Mg\textsuperscript{2+}:PO\textsubscript{4}{3−} is similarly high at 1.24–1.43. Besides struvite, a low amount of Mg\textsubscript{3}PO\textsubscript{4}·22 H\textsubscript{2}O or Mg(OH)\textsubscript{2} might be precipitated from ES.

**Contribution of NH\textsubscript{4}{+} in DP-tests**

As shown in Figure 2, the relative mass concentration of NH\textsubscript{4}{+} in ES decreases rapidly after NaOH addition in the test with initial pH at 8. It confirms the removal of NH\textsubscript{4}{+} from ES as a crystallization of struvite. With initial pH at 8.5, the Mg\textsubscript{3}PO\textsubscript{4}·22 H\textsubscript{2}O might be precipitated from ES. However, the removal rate of PO\textsubscript{4}{3−}-P and Mg\textsuperscript{2+} is higher and the removal rate of NH\textsubscript{4}{+} is much lower than that in tests with other initial pH values. Another probable reaction of NH\textsubscript{4}{+} in feed stream is shown in Equation (4). At pH value higher than 10.5, the conversion of NH\textsubscript{4}{+} to NH\textsubscript{3} in feed stream is accelerated (Hao et al. 2008). The NaOH consumption in the test with initial pH 9 is up to 10.5 grams per liter of ES stream, and the NH\textsubscript{4}{+} in ES is transferred to NH\textsubscript{3} and escapes from ES stream. Thus, the relative mass concentration of NH\textsubscript{4}{+} in ES after reaction with initial pH at 9 is much lower than that with initial pH at 8.5.

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} \] (4)

**Influence of HAOC on precipitation of crystals in DP-tests**

As shown in Figure 4, the relative mass concentration of Ca\textsuperscript{2+} in ES increases to higher than 100% in tests. For the detection of Ca\textsuperscript{2+} concentration in ES, the sample is prepared through centrifugation at 3,000 rpm for 5 min. The large molecular organic compounds are separated in precipitate phase. The Ca\textsuperscript{2+} could combine with HAOC through complex bonds and aggregate into large organic molecules. It can be separated from ES stream after the centrifuge. Thus, the concentration of dissolved Ca\textsuperscript{2+} in ES is obviously lower than the total concentration of Ca\textsuperscript{2+} in ES.

Although the Ca\textsuperscript{2+} is combined with HAOC in ES, the complex bonds between Ca\textsuperscript{2+} and HAOC could be broken up under alkaline condition, consequently with a precipitation of Ca(OH)\textsubscript{2}. With initial pH at 8–9, the relative mass concentration of Ca\textsuperscript{2+} in ES decreases rapidly in 5 min after alkalinization. The OH\textsuperscript{−} is continuously consumed by pH-buffer systems in ES, the precipitated Ca(OH)\textsubscript{2} could redissolve into ES stream and contribute OH\textsuperscript{−} to ES stream. The aggregation tests of humic acids and Ca\textsuperscript{2+} ion show that, after increasing Ca\textsuperscript{2+} concentration in feed stream of humic acids, the variation of zeta potential is stabilized within 2 min (Kloster et al. 2013). There are high concentrations of HAOC in ES, and the dissolved Ca\textsuperscript{2+} is rapidly combined with HAOC.

![Figure 3](http://iwaponline.com/wst/article-pdf/84/12/3859/980010/wst084123859.pdf)

**Figure 3** | Molar ratio of removed Mg\textsuperscript{2+} and PO\textsubscript{4}{3−} during DP-tests with initial pH at 7.5–9.
There are two roles in aggregation processes: (1) the Ca\(^{2+}\) ion decreases the repulsive forces between carboxylic acid molecules by decreasing their zeta potential, and (2) formation of calcium bridges between two approaching molecules (Kloster et al. 2013). After redissolving of Ca(OH)\(_2\), the Ca\(^{2+}\) ions are combined with HAOC compounds, which are small molecules. That could not be removed from ES stream by centrifuge. Therefore, the relative mass concentration of Ca\(^{2+}\) in ES is, owing to dissolution of Ca\(^{2+}\) from large molecular aggregations, higher than 100%.

As shown in Figure 4, the relative mass concentration of Ca\(^{2+}\) in ES decreases rapidly in tests with initial pH at 7–9 at reaction time of 2–15 min. Although the highest removal rate of Ca\(^{2+}\) is determined as 22% with initial pH at 8, the Ca(OH)\(_2\) is crystallized very rapidly from ES stream, and the highest removal rate of Ca\(^{2+}\) after dosage of NaOH solution could not be exactly detected. With initial pH at 7, the OH\(^-\) is consumed by pH buffer systems. The HAOC combined Ca\(^{2+}\) could not be released into ES stream. Thus, the relative mass concentration of Ca\(^{2+}\) is almost constant after redissolving of Ca(OH)\(_2\). Moreover, as reported by Zhou, the humic acid could impede the precipitation of struvite (Zhou et al. 2015). However, the impediment effect is dramatically decreased at higher mass ratio of Mg : P. The mass ratio of Mg: P in ES is at around 2:1. However, the TOC concentration is high at around 200 g/L, and the struvite is rapidly precipitated from ES stream.

Crystal habits of recovered struvite from EP-tests

The NaOH consumption and inorganic precipitate yield of the EP-tests are displayed in Table 3. The NaOH consumption in EP-tests reaches 3.5–9.2 grams per liter of ES stream with initial pH at 7–9. After crystallization process, the pH value of feed stream decreases correspondingly from 7–9 to 7.0–8.3, and the yield of inorganic precipitate reached 0.3, 1.3, 3.4, 9.8 and 0.5 grams per liter of ES stream, respectively.

Struvite is structurally held together in regular PO\(_4^{3-}\) tetrahedra, distorted Mg(H\(_2\)O)\(_6^{2+}\) octahedra and NH\(_4^+\) groups through hydrogen bonding. The crystal habit of struvite is determined by its orthorombic system. The structure of struvite varies with regard to its developed forms as equant, wedge-shaped, short prismatic or thick tabular (Abbona & Franchini-Angela 1990). As shown in Figure 5, the recovered inorganic precipitates are tabular in structure, which is typical for crystallization of struvite under a decreasing supersaturation condition.

The agglomeration of crystal is positively correlated to the zeta-potential value at the slipping plane of individual crystals. The zeta-potential value at the slipping plane of struvite is negative, it increases with higher pH values (Zhang et al. 2016). The agglomeration trend of struvite is lower at higher initial pH values. Thus, the length of struvite crystal reaches longer than

| Initial pH | 7 | 7.5 | 8 | 8.5 | 9 |
|---|---|---|---|---|---|
| Final pH | 7.0 | 7.2 | 7.7 | 8.0 | 8.3 |
| NaOH dosage [g/L] | 3.5 | 4.6 | 5.9 | 7.3 | 9.2 |
| Crystal yield [g/L] | 0.3 | 1.3 | 3.4 | 9.8 | 0.5 |
500 μm (Figure 5(a)–5(c)) in EP-tests with initial pH at 7–8. With initial pH at 8.5, the length of recovered crystalline sample is short at around 150 μm (Figure 5(d)). With initial pH at 9, the length of precipitated crystals is shorter than 55 μm; thus, the inorganic precipitates are not able to be separated by sieving.

**Characteristic of recovered crystalline samples**

**Crystallographic identity of recovered samples**

The displayed XRD patterns of recovered inorganic precipitate samples in Figure 6 show a good conformity to standard syn. struvite reflection pattern (PDF#15-0762). Only a few unknown reflections with very low intensity are present. Thus, the recovered inorganic precipitate is detected as struvite with a very low mass fraction of other unknown impurity.

The mass fraction of struvite in inorganic precipitates is reported to depend strongly on mass ratio of Ca\(^{2+}\) : Mg\(^{2+}\) in feed stream (Li et al. 2016). With a mass ratio lower than 0.45:1, the Ca\(^{2+}\) has no influence on the crystallization of magnesium phosphate crystals. For the given mass ratio of Ca\(^{2+}\) : Mg\(^{2+}\) at 0.73 : 1 in ES, the mass fraction of struvite in precipitated crystal is expected to be 73%. However, the calcium phosphate crystals are not present in recovered samples.

As shown in Figure 7, the mass fractions of Ca\(^{2+}\) in recovered samples are all low at around 0.1%; almost no calcium phosphate crystals are contained in recovered crystalline samples. The precipitation of calcium phosphate crystals is totally prevented by high concentration of HAOC compounds in the ES stream (Song et al. 2006). The mass fraction of Mg\(^{2+}\)
and \( \text{PO}_4^{3-} \) in recovered inorganic precipitate are found to be highest in recovered sample with initial pH at 7.5, reaching 40 and 11%, respectively. They are higher than the mass fractions of \( \text{Mg}^{2+} \) and \( \text{PO}_4^{3-} \) in pure struvite crystal, which are 39 and 10%. The deviation could be explained by crystal water loss of struvite \((\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O})\).

### Composition of organic compounds in recovered inorganic precipitates

The inorganic precipitates are separated from ES stream by filtration. With a smaller particle size of inorganic precipitate, the ES stream between precipitates is more difficult to remove by filtration. Thus, as shown in Figure 7, the mass fraction of dissolved organic carbon (DOC) in recovered inorganic precipitates with initial pH at 8.5 is around two-fold higher than that in recovered sample with initial pH at 8 or 7.5. The recovery yield of inorganic precipitate is low in the test with initial pH at 7.5; the organic compounds on surface of sieve filter were mixed in recovered inorganic precipitate. Although the length of crystal in recovered inorganic precipitate is also longer than 500 \( \mu \text{m} \), the mass fraction of DOC in sample is high at 22%.

To decrease the mass fraction of organic compounds in recovered inorganic precipitates, it is helpful to know the composition of organic compounds in precipitates. According to reference literature, the cellulosic ethanol wastewater is comparable to wastewater from paper industry regarding the production process: both the cellulosic ethanol production and paper production utilize lignocellulosic materials as input material, and a heat treatment process in their production process is required. The organic compounds in paper wastewater are divided into five groups: biopolymers (BP), humic acid (HA), building blocks (BB), low molecular weight acids (LA) and low molecular weight neutrals (LN) (Kliaugaïtë et al. 2013). The same classification is utilized in characterization of organic compositions in this work.

The original ES sample as well as the recovered inorganic precipitate after dissolution are analyzed by LC-OCD. As shown in Figure 8, the x-axis is the retention time of LC-OCD, and the y-axis shows the relative value of response signals (Response signal/DOC) with unit \((\text{L/mg})\). During EP-test, the small molecular organic compounds BB and LA are probably aggregated to BP and HA. The BP and HA are more easily aggregated at higher initial pH value. Thus, the relative response signals of BP and HA are the highest in recovered inorganic precipitate with initial pH at 8.5. The relative response signal of LN in recovered inorganic precipitate is higher than that in original ES sample; the crystals show a selective adsorption ability of LN. Although the LN could be more easily adsorbed on crystal with a larger specific surface area (smaller particle size), the relative response signal of LN in recovered inorganic precipitate with initial pH 8.5 is obviously lower than that in other crystal samples. The relative mass concentration of LN is diluted by residual ES stream in inorganic precipitate.

### Economic evaluation

The recovery efficiency and removal efficiency of ions after EP-tests are calculated through Equations (2) and (3). As shown in Figure 9, the relative mass concentration of \( \text{PO}_4^{3-} \) in recovered inorganic precipitate (>55 \( \mu \text{m} \)) or in total precipitate reaches

![Figure 7](http://iwaponline.com/wst/article-pdf/84/12/3859/980010/wst084123859.pdf)

Figure 7 | Compositions in recovered inorganic precipitate and in struvite sample.
65% or 85% in EP-test with initial pH at 8.5. Considering the struvite in ES, which has crystal size smaller than 55 μm, the expected recovery efficiency of PO$_4^{3-}$ could reach 85% (equal to removal rate of PO$_4^{3-}$-P). The inorganic precipitate with mass fraction of struvite at about 82% (24 wt.% P$_2$O$_5$) is successfully recovered from ES in EP-test with initial pH at 8.5. Compared to the Phosnix process, the struvite is recovered from ES stream with a much shorter retention time (Desmidt et al. 2015). Although the expected recovery yield of PO$_4^{3-}$-P is comparably similar, the crystal size of recovered struvite is slightly lower.

The market price of struvite is correlated to the phosphorus price; as the price of phosphorus ranges from 0.38 to 0.46 €/kg, the price of struvite is estimated at 0.1–0.12 €/kg (Peng et al. 2018). The NaOH with a worldwide price of 0.45 $/kg (0.39 €/kg) is the only consumed chemical in struvite recovery in this study (Huang et al. 2018). With an initial pH of 8.5, the expected struvite recovery yield is estimated at 10.5 g/L, corresponding to a benefit of 1.16 €/ton. During the test, 7.3 g/L NaOH is dosed into feed to adjust the initial pH from 5.95 to 8.5. After precipitation test the pH value decreases from 8.5 to 8.0. As shown in Table 3, the pH difference of 5.95–8.0 conforms to a NaOH dosage of 5.9 g/L. Thus, through reflowing of the alkalized stillage for neutralization, the NaOH consumption for struvite recovery is decreased to 1.4 g/L. That corresponds to a cost of 0.55 €/ton.

**Figure 8** | The relative response signal of organic compounds in ES sample or recovered crystal samples from EP-tests with initial pH at 7.5–8.5.

| PO$_4^{3-}$ | Ca$^{2+}$ | Mg$^{2+}$ | ES stream | <55 μm | >55 μm |
|------------|----------|----------|-----------|--------|--------|
| PH 7       | 89%      | 76%      | 64%       | 35%    | 85%    |
| PH 7.5     | 95%      | 64%      | 72%       | 37%    | 95%    |
| PH 8       | 72%      | 95%      | 73%       | 37%    | 87%    |
| PH 8.5     | 85%      | 72%      | 72%       | 37%    | 95%    |
| PH 9       | 82%      | 80%      | 87%       | 48%    | 87%    |

**Figure 9** | The relative concentrations of PO$_4^{3-}$, Ca$^{2+}$ and Mg$^{2+}$ in ES stream, recovered inorganic precipitate and precipitate after EP-tests with initial pH at 7–9 for a reaction time of 5 days.
The cost of struvite recovery depends on the phosphate concentration. For the feed with an initial $PO_4^{3-}$-P concentration of 1,000 mg/L, the main cost is from chemicals consumption with a relative cost of 86% (Ashley 2009). The energy consumption in this work may be higher than the cost of struvite recovery from other feeds. At beginning of process, the NaOH should be dosed into feed and homogeneously mixed. Instead of seeding pure struvite nuclei into feed, the precipitate should be sedimented through a side-stream precipitation reactor and refilled into reactor (Daneshgar et al. 2019a). After sedimentation, a filtration may be required to further remove the organic compounds from precipitate. However, owing to its low cost of chemicals, the struvite recovery from ES has a high economic potential. To evaluate the accurate economy of struvite recovery from ES, it may be possible to construct a pilot-scale plant.

CONCLUSIONS

ES stream is a high comprising of organic and inorganic compounds. The ionic activity coefficients in ES are strongly impeded by its high ionic strength and high concentration of dissolved organic compounds. Owing to the high mass fraction of humic acids-like compounds, which could bridge to $Ca^{2+}$ through complex bonds, the precipitation of calcium phosphate is totally prevented in our tests. The HAOC can be potentially utilized to prevent the precipitation of calcium phosphate during struvite recovery process.

The optimized pH value for struvite recovery from ES stream is determined at pH 8.5, with an expected recovery yield of phosphate at 85%. The mass fraction of struvite in recovered precipitate is around 82% (24 wt.% P$_2$O$_5$). The crystal size of recovered inorganic precipitate can be enlarged through multiple dosage of NaOH in feed stream. With a larger particle size, the mass fraction of organic compounds in recovered precipitate could be decreased. However, owing to selective adsorption of LN on crystals, the mass fraction of LN in recovered inorganic precipitates might not be obviously decreased.

Through reflowing of alkalized ES stream for neutralization, the NaOH consumption of struvite recovery could be reduced to 0.55 €/ton, which is much lower than the value of recovered struvite (1.16 €/ton). Although a pilot-scale plant should be constructed to observe a complete economic evaluation of struvite recovery, owing to a low consumption of chemicals, the struvite recovery from ES has a high economic potential.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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