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# Use of side stream-based $MgSO_4$ as chemical precipitant in the simultaneous removal of nitrogen and phosphorus from wastewaters

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## ABSTRACT

Wastewaters and agricultural sludges can contain high concentrations of phosphate and ammonium- or nitrate–nitrogen, which run off easily to waterways causing eutrophication in water bodies. However, it is possible to precipitate phosphate and ammonium as struvite and use it as recycled fertilizer. In this research, $MgSO_4$ solution obtained by treating fly ash (FA) or dolomite (DOL) with sulfuric acid was used as a precipitant for simultaneous phosphorus and nitrogen removal from synthetic $(NH_4)_2HPO_4$ solution. Precipitation experiments were performed at room temperature (20°C ± 2°C) using different molar ratios Mg:P:N (1.1-2:1-2:1-2) and precipitation times (4–24 h). The pH was adjusted to 9.0 and kept constant. In all cases, there were only minor changes in the removal of both ammonium and phosphate after 4 h of reaction time. Highest ammonium removal percentages after the 4 h test were 79.5% for $MgSO_4$ 1.3:1:1, DOL 1.1:1:1, and DOL 1.3:1:1. Highest ammonium removal percentages (75.5%) for FA based $MgSO_4$ solution were achieved using molar ratios Mg:P:N 2:1:1 and 1.1:2:2. Also, the highest phosphate removal percentages were achieved with these samples (97% for MgSO4 1.3:1:1, 93.3% for DOL 1.3:1:1, 89.8% for DOL 1.1:1:1, 84.5% for FA 2:1:1, and 82.5% for FA 1.1:2:2) Struvite was the only formed precipitation product in all cases as was confirmed by X-ray diffraction. Results indicate that fly ash and DOL based $MgSO_4$ solutions performed quite well compared to commercial $MgSO_4$ salt and they have great potential in the ammonium and phosphate precipitation.

*Keywords:* Dolomite; Fly ash; Struvite; Ammonium; Phosphate; Precipitation

## 1. Introduction

Wastewaters and agricultural sludges can contain large amounts of phosphorus and nitrogen, which run off easily to waterways causing eutrophication in water bodies. Ammonium nitrogen ($NH_4$) volatilizes easily as ammonia gas at alkaline conditions, which reduces the efficiency of nitrogen fertilizers. Haber–Bosch reaction used for the production of nitrogen fertilizers causes large amounts of greenhouse gas emissions, as the process consumes high amounts of natural gas [1]. The exploitable phosphate resources will be significantly depleted during the following decades meaning that expensive mining technology is needed. Also, the quality of the remaining rock phosphate reserves is decreasing meaning, for example, higher Cd and U concentrations [2,3]. There is a vast need to find alternative, recycled fertilizers for a more sustainable future. It has been estimated that there is enormous economic potential in the recycled fertilizer market. In Finland alone, the market size would be around 0.5 billion € annually [4]. Also, in the summer of 2019, the European Commission released a revision of the EU's fertilizer production regulation [5]. The new regulation will be applied from the 16th of July 2022 and it opens the European wide market also

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for recycled fertilizers. European Commission has nominated the STRUBIAS group to determine the criteria on how struvite, biochar and ash-based fertilizer products will be accepted for the EU fertilizer market [6]. The STRUBIAS group's final report was recently published and these materials would soon be added to the annexes of fertilizer production regulation [7].

One answer to the recycled fertilizer market would be to precipitate ammonium and phosphate simultaneously from nutrient containing wastewaters as a phosphate mineral called struvite ($NH_4MgPO_4·6H_2O$). Struvite solubility to water is only 0.2 g/L (0°C) so it is a slow-release fertilizer [8,9]. Struvite fertilizers are also easy to manufacture and handle, and they are odorless [10].

Even though the most common motive for struvite precipitation is the fertilizer use, other motives do exist. Especially since struvite precipitation can occur spontaneously if wastewater contains all of the ions needed for the precipitation. This can cause large problems in anaerobic digesters as magnesium, phosphate and ammonium ions are released during digestion [11]. Struvite precipitates in pipes, pumps, etc. causing clogging of the system. However, by precipitating struvite in a controlled manner these problems can be avoided.

Commercial Mg salts such as $MgCl_2$, $MgSO_4$, MgO and $Mg(OH)_2$ are commonly used precipitants in struvite precipitation [12]. Due to the relatively high price of these commercial salts, and since magnesium is listed in the European Union's critical raw material list, alternative magnesium sources should be preferred instead of commercial salts [13]. For these reasons, several authors have studied various inexpensive Mg-sources for struvite precipitation, including brucite [14], seawater [12,15], magnesite [16], bottom and fly ash [17,18], dolomite (DOL) [19,20], and MgO-saponification wastewater [21].

DOL is a carbonite mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$) and it is used, for example, as a soil improver to increase the pH of acidic soils [22]. Fly ash is a fine-grained, inorganic residue that is left behind after combustion at a thermal power plant. Depending on the fuel used, it mostly contains calcium, magnesium, aluminum, and silicon oxides in varying proportions [23]. Even though both fly ash and DOL are potential precipitants for struvite precipitation [17,19,20,24] the high Ca concentration they contain can cause the phosphate ions to precipitate as hydroxyapatite preventing struvite formation [17,19,25], therefore it would be best to first precipitate Ca as insoluble $CaSO_4$ and transform the Mg ions to soluble $MgSO_4$ [26].

In this research, the $MgSO_4$ solution was manufactured from DOL or fly ash, which was then used for the simultaneous precipitation of ammonium and phosphate from synthetic $(NH_4)_2HPO_4$ solution. The effects of precipitant dosing and precipitation time on the removal efficiency of ammonium and phosphate were studied.

## 2. Materials and methods

DOL was provided by a Finnish lime quarry. It was a small-sized (<3 mm) fraction that is leftover as the DOL is sieved to desired size-fractions. The demand for these small particle sizes is very limited and it is mostly considered as a waste fraction for the lime quarry. Fly ash came from a Finnish 3 MW power plant that uses a fluidized bed combustion technique. The fuel used during sampling was peat and the ash sample was collected directly from the ash silo.

First DOL or fly ash (50 g) was treated with 2 M sulfuric acid (250 mL) for 90 min using a magnetic stirrer and a stirring speed of 500 rpm. The precipitate was settled for 30 min after treatment and then filtered through 2–5 μm pore size filter paper. Liquid ($MgSO_4$ solution) was collected and stored in glass bottles. During this treatment, Ca and Mg oxides/carbonates react with $H_2SO_4$ to form insoluble $CaSO_4$ [Eq. (1)] and soluble $MgSO_4$ [Eq. (2)].

$$Ca^{+}(l) + SO_4^{-}(l) \rightarrow CaSO_4(s) \tag{1}$$

$$Mg^{+}(l) + SO_4^{-}(l) \rightarrow MgSO_4(l) \tag{2}$$

The procedure used for the precipitation is based on previous studies [17,19]. Precipitation experiments were performed at room temperature (20°C ± 2°C) using different molar ratios Mg:P:N (1.1-2:1-2:1-2) and precipitation times (4–24 h). Ammonium phosphate $(NH_4)_2HPO_4$ solution (100–200 mg/L $NH_4^+$ and 1.05–2.1 g/L $PO_4^{3-}$) was prepared from ammonium chloride ($NH_4Cl$) and potassium hydrogen phosphate ($KH_2PO_4$) salts. In the experiments, $MgSO_4$ solution was added to 1.6 L of the ammonium phosphate solution while stirring the solution by overhead stirrer at a constant speed (1 min 450 rpm, then 50 rpm), the pH was adjusted to 9.0 and kept constant by using HCl and /or NaOH. Water samples were taken in the beginning, and then after every half an hour until the end of the experiments. They were filtered (0.45 μm) before analyzing. Two experiments with commercial $MgSO_4$ was conducted using molar ratio 1.3:1:1 to do a comparison with commercial chemicals. In these tests 5.7 g of $MgSO_4·7H_2O$ was first dissolved to 10 mL of deionized water, otherwise, the procedure was the same as in other experiments. Ammonium concentration was measured from the water samples with the use of $NH_4$-selective electrode (Hach Lange Intellical ISENH4181, United States), phosphate concentration was measured by ion chromatography (IC; Methrohm 761 Compact IC, Switzerland), and magnesium, calcium, and harmful element concentrations by inductively coupled plasma (ICP; Perkin Elmer Optima 5300 DV, United States). The precipitate was dried at room temperature and analyzed using an X-ray diffractometer (XRD; Rigaku SmartLab 9 kW, Japan) and scanning electron microscope (SEM; Carl Zeiss Sigma FESEM, Germany). DOL and fly ash were analyzed using X-ray fluorescence Bruker AXS S4 Pioneer, United States).

## 3. Results and discussion

### 3.1. Raw materials and $MgSO_4$ solution

The main components of the DOL and fly ash were CaO, MgO and $SiO_2$ (Table 1). The other components in DOL consisted mainly of $CO_2$. Concentrations of harmful elements are low (Table 2) and they are clearly under the limit values of Finnish fertilizer legislation [27]. Therefore, these raw materials could be used for forest fertilization

Table 1
Main components (XRF) of the dolomite and fly ash

| | Dolomite | Fly ash |
|---|---|---|
| CaO (%) | 37.9 | 36.9 |
| MgO (%) | 16.5 | 14.2 |
| $SiO_2$ (%) | 10.4 | 17.7 |
| $Al_2O_3$ (%) | 3.1 | 8.1 |
| FeO (%) | 3.5 | 8.9 |
| $P_2O_5$ (%) | 0.1 | 1.6 |
| $K_2O$ (%) | 1.1 | 0.5 |
| $Na_2O$ (%) | 0.2 | 0.5 |
| $TiO_2$ (%) | 0.3 | 0.3 |
| MnO (%) | 0.1 | 0.3 |
| Others (%) | 26.8 | 11.0 |

Table 2
Harmful element contents (XRF) and a comparison to the limit values of Finnish fertilizer decree [27]

| | Dolomite | Fly ash | Limit value field/ forest fertilizers |
|---|---|---|---|
| As (ppm) | <10 | <10 | 25/40 |
| Cd (ppm) | <10 | <10 | 1.5/25 |
| Cr (ppm) | 50 | 20 | 300 |
| Cu (ppm) | 40 | 100 | 600/700 |
| Ni (ppm) | 80 | 80 | 100/150 |
| Pb (ppm) | <10 | 140 | 100/150 |
| Zn (ppm) | 20 | 80 | 1,500/4,500 |

in Finland. It remains uncertain if they could also be used for field fertilization since Cd concentration was below the detection limit value (10 ppm) of the XRF equipment. The Pb concentration in fly ash exceeded the limit value for field fertilizers. However, the limit values of Finnish fertilizer decree are for nitric acid digestion, which is usually lower than the total concentrations measured by XRF [28]. In practice, the results obtained with XRF tend to overestimate the actual bioavailability of these elements.

The Mg, Ca and harmful element concentrations of the $MgSO_4$ solutions are presented in Table 3. Only less than 500 mg/L of the Ca was soluble even though fly ash (FA) and DOL contained 36.9% and 37.9% of Ca (Table 1). The Mg leached more easily from the FA than from the DOL, since the leaching efficiencies for magnesium were 84.7% (FA) and 47.4% (DOL). Concentrations of harmful elements in the DOL based $MgSO_4$ were mostly the only minor. However, in the FA based $MgSO_4$ solutions concentrations of As, Cu, and Zn were elevated. The limit values for Cu and Zn in fertilizers are quite high in the Finnish legislation and they are also considered micronutrients [29], therefore their concentration should not be problematic. The same goes for Ni, which is also slightly elevated in both $MgSO_4$ solutions. Also As seems to be quite mobile in FA. The As concentration in FA based $MgSO_4$ solution could cause problems in fertilizer use if it is co-precipitated to struvite. For this reason, it would be best to use FA that contains as little as possible As. This could be achieved, for example, by avoiding peat and using wood as a fuel at the power plant since peat tends to contain more As than wood [30].

### 3.2. Ammonium removal

Ammonium removal percentages of the different samples are presented in Fig. 1. The precipitation experiment was continued for 24 h with FA based $MgSO_4$ solution when the molar ratio Mg:P:N was 1.1:2:2. However, there was a clear drop in the removal percentage at the end of the experiments. Therefore, the lengths of the experiments were reduced to 4–6 h. Others found that when calcined, powdered DOL [19] was used as a precipitation agent after being dissolved to water, the contact time needed was at least 24 h. The same finding was made with FA in another study [17]. This is due to the low solubility of MgO to water. In this study, Mg was already dissolved by using sulphuric acid and therefore shorter reaction time was adequate. The highest removal percentage (83.5%) was achieved with commercial $MgSO_4$ after 30 min of reaction time. After the 4 h test removal percentage for $MgSO_4$ 1.3:1:1, DOL 1.1:1:1 and DOL 1.3:1:1 was 79.5%. Highest removal percentages (75.5%) for FA based $MgSO_4$ solution were achieved using molar ratios Mg:P:N 2:1:1 and 1.1:2:2. Since there was excess ammonium present in the latter case, in practice as much ammonium that was possible to be bound by magnesium was precipitated. Therefore, the excess amount of ammonium seems to favor the struvite formation. With FA 1.1:1:1 the removal percentage was 73.5% and with FA 1.3:1:1 70. With FA (Mg:P:N = 1.6:1:1) and DOL based $MgSO_4$ solutions (Mg:P:N = 1.6:1:1 and 2:1:1), the removal percentages were 59%, 62%, and 63.5% respectively. In all cases, there was only a minor change in the removal percentages after 4 h. Pesonen et al. [19] reported similar removal percentages calcined DOL. Myllymäki et al. [17] reported nearly 100% ammonium removal but some of the ammonium was evaporated as ammonia gas due to high pH. Also, shorter contact times (2–4 h) have been used in other studies [18,20]. Chen et al. [20] reported around 90% removal for ammonium when calcined DOL was used as a precipitation agent but the initial ammonium concentration was very high (2,000 mg/L) in their study. Therefore, the final ammonium concentration (around 200 mg/L) was still very high at the end of the experiments. Sakthivel et al. [18] reported less than 15% ammonium removal as the initial ammonium concentration was around 2,500 mg/L. As the $NH_4^+$ removal efficiency was better or equal with smaller Mg-molar ratios (1.1 and 1.3) than with the higher (1.6 and 2), based on precipitant consumption alone, the lower dosage, especially Mg:P:N = 1.1:1:1 should be preferred. FA and DOL based $MgSO_4$ solutions perform almost as well as the commercial $MgSO_4$ salt but the reaction seems to be slower. It is known that ions of, for example, Al, Ca, K, and Na can hinder struvite formation [31]. In this case, the concentration of Ca (Table 3) was elevated, which could be the reason for the slower reaction.

### 3.3. Phosphate removal

Phosphate removal percentages of the different samples are presented in Fig. 2. Phosphate reduction was very fast

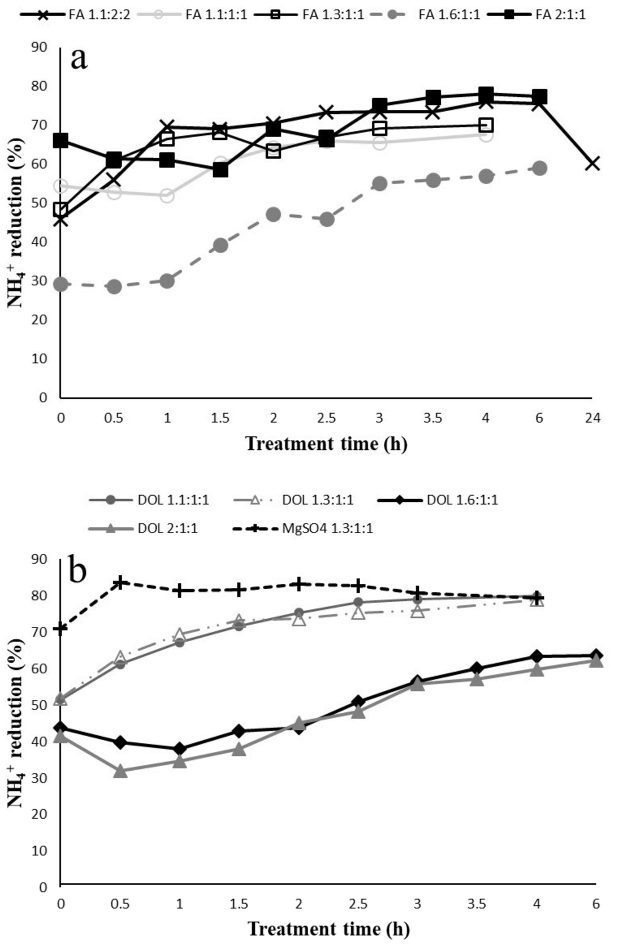

Fig. 1. Ammonium removal percentages with fly ash (FA; a) and dolomite (DOL; b) based $MgSO_4$ solutions, and commercial $MgSO_4$ using different molar ratios of Mg:P:N. The pH during all treatments was 9.0.

with commercial $MgSO_4$ and FA based $MgSO_4$ solution when the molar ratio was Mg:P:N 2:1:1. The same observation was made also for ammonium removal. The reduction percentage was 84.5% after the 6 h experiment for FA 2:1:1 and 97% for $MgSO_4$ 1.3:1:1. With FA 1.3:1:1, FA 1.1:1:1, and FA 1.6:1:1, the removal percentages were 78.7%, 72%, and 56% respectively. For FA 1.1:2:2 phosphate was measured only before and after the 24 h experiment and the removal percentage was 82.5%. The removal percentages were lower than the ones reported for fly ash (over 99%) by Myllymäki et al. [17]. Also, Sakthivel at al. [18] obtained 99% phosphate removal with bottom ash. However, the initial phosphate concentration was in this case only 187 mg/L. For DOL the removal percentages were 93.3% for DOL 1.3:1:1, 89.8% for DOL 1.1:1:1, 71.9% for DOL 2:1:1, and 70.9% for DOL 1.6:1:1. It should be noted that the result for DOL 2:1:1 is based on a single experiment due to difficulties when analyzing the first sample. The phosphate removals were better than the ones reported for calcined DOL (around 60%) by Pesonen et al. [19]. Overall, the phosphate removals are comparable to the ammonium removal percentages and DOL performed almost as good as commercial $MgSO_4$ in phosphate removal. As was concluded with ammonium removals, it would be best to use the molar ratios Mg:P:N 1.1-1.3:1:1 due to the smaller Mg wastage.

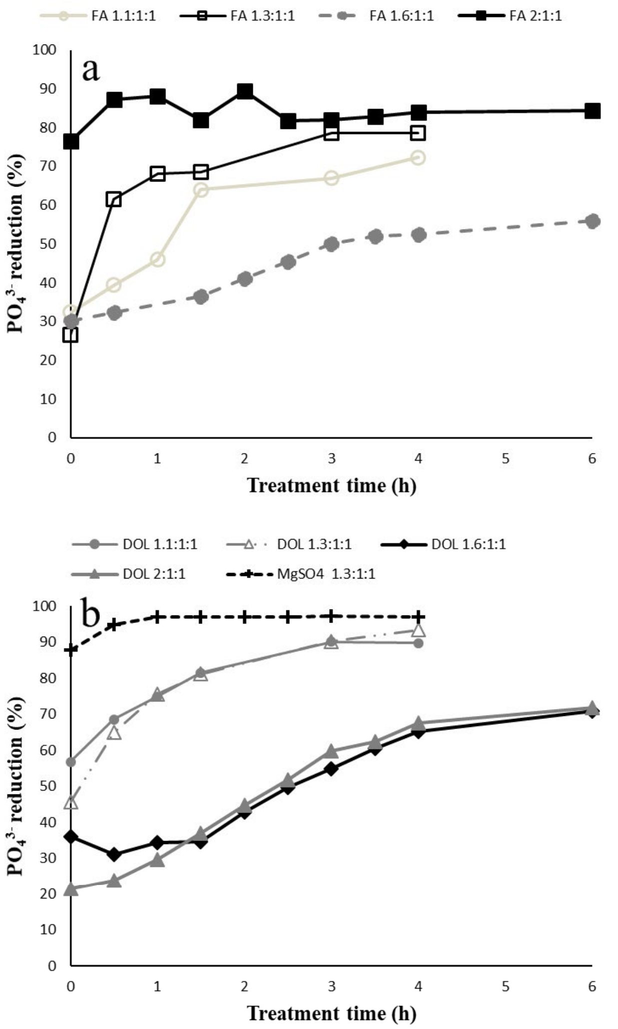

Fig. 2. Phosphate removal percentages with fly ash (FA; a) and dolomite (DOL; b) based $MgSO_4$ solutions, and commercial $MgSO_4$ using different molar ratios of Mg:P:N. The pH during all treatments was 9.0.

### 3.4. Characterization of the precipitate

X-ray diffraction (XRD) diffractograms of the precipitates are presented in Fig. 3. Even though there were clear differences in the ammonium and phosphate removal percentages (Figs. 1 and 2), all peaks were associated with struvite. However, the intensities of some peaks seem to be reversed: the main struvite peak should be the one at around 21° and around 33° should be a smaller peak but in Fig. 3 the intensities of these peaks are the other way around in all other tests than FA 1.1:2:2 and $MgSO_4$ 1.3:1:1. This could be due to the growth of the crystal structure [32]. In Fig. 4, the struvite crystals are elongated stick-like structures, but in Fig. 5 the shapes are more varied and there is very fine precipitate on the surface of the larger struvite crystal. Shape and surface structure of the struvite crystals are similar in

Table 3
Mg, Ca and harmful element concentrations (ICP) of the $MgSO_4$ solutions

| | FA based $MgSO_4$ | DOL based $MgSO_4$ |
|---|---|---|
| Ca (mg/L) | 483 | 494 |
| Mg (mg/L) | 14,500 | 9,430 |
| As (mg/L) | 0.08 | 3.94 |
| Cd (mg/L) | 0.01 | 0.10 |
| Cr (mg/L) | 0.64 | 0.97 |
| Cu (mg/L) | 0.59 | 3.41 |
| Ni (mg/L) | 1.21 | 1.81 |
| Pb (mg/L) | 0.04 | 0.14 |
| Zn (mg/L) | 1.32 | 2.79 |

both FA (Figs. 4a and c) and DOL (Figs. 4b and d). Pesonen et al. [19] reported also $CaCO_3$ as calcined DOL was used as a precipitation agent. Myllymäki et al. [17] found several Ca-containing compounds such as CaO and calcium phosphate hydrate ($CaHPO_4{\cdot}2H_2O$) and no struvite was found. Also, Chen et al. [20] found $CaCO_3$ in addition to struvite. In addition to these compounds, Sakthivel at al. [18] found also $SiO_2$ and $(Mg_{0.129}Ca_{0.871})CO_3$ as fly ash was used as a precipitation agent. The pre-treatment with $H_2SO_4$ used here prevents the formation of these other unwanted Ca-compounds, which reduce the purity of the struvite formed. Therefore, the $H_2SO_4$ treatment would be preferred if these side-streams are used as precipitation agents.

Yields of the formed struvite are presented in Table 4. The calculation was based on the theoretical maximum amount of struvite that could be formed with corresponding molar ratios. The best yield was obtained with commercial $MgSO_4$ salt (90.4%). The best yields for both DOL and FA

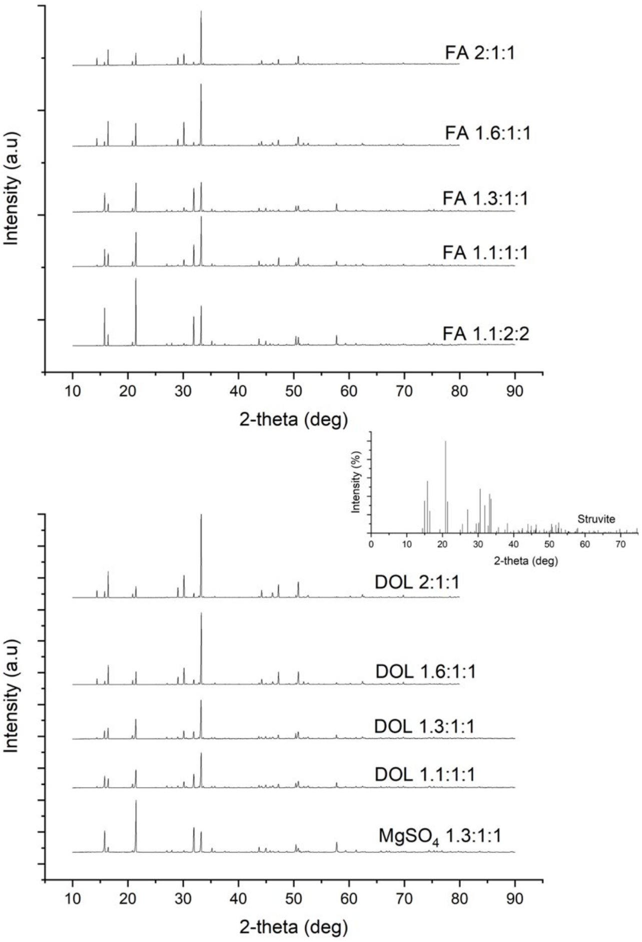

Fig. 3. (a) XRD diffractograms of the precipitates and (b) intensities of the standard struvite peaks.

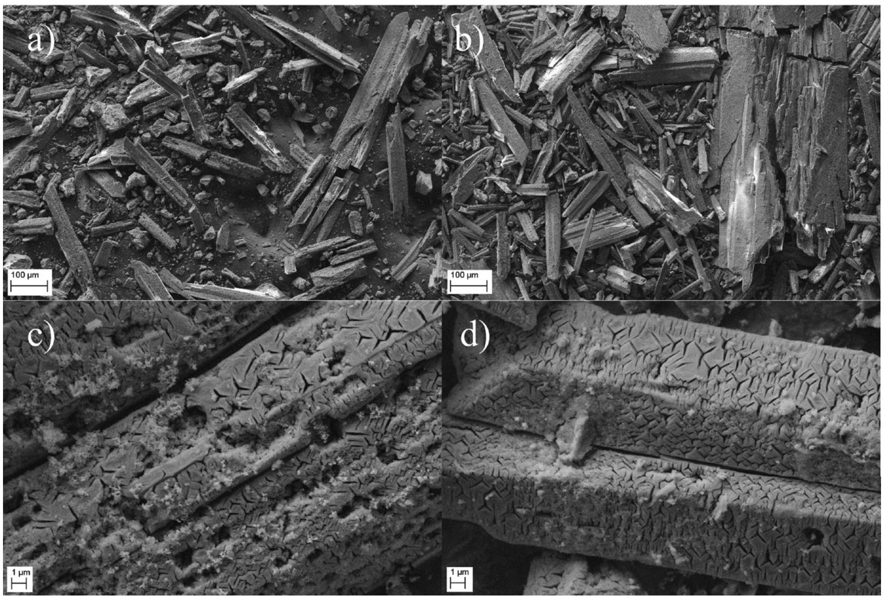

Fig. 4. Scanning electron microscopy images of the precipitates after 6 h experiments (Mg:P:N 1.6:1:1): (a and c) FA; (b) and c) DOL. The bars indicate 100 µm length in (a and b) and 1 µm length in (c and d).

Table 4
Yields of the formed struvite for the corresponding molar ratios. Yield calculation was based on the theoretical maximum amount of struvite that could be formed with corresponding molar ratios

| Sample | Yield (%) |
|---|---|
| FA 1.1:2:2 | 70.2 |
| FA 1.1:1:1 | 58.3 |
| FA 1.3:1:1 | 71.3 |
| FA 1.6:1:1 | 46.5 |
| FA 2:1:1 | 55.2 |
| DOL 1.1:1:1 | 73.8 |
| DOL 1.3:1:1 | 77.5 |
| DOL 1.6:1:1 | 54.1 |
| DOL 2:1:1 | 45.7 |
| $MgSO_4$ 1.3:1:1 | 90.4 |

Yield = (total mass of the precipitate/theoretical mass of struvite formed) × 100

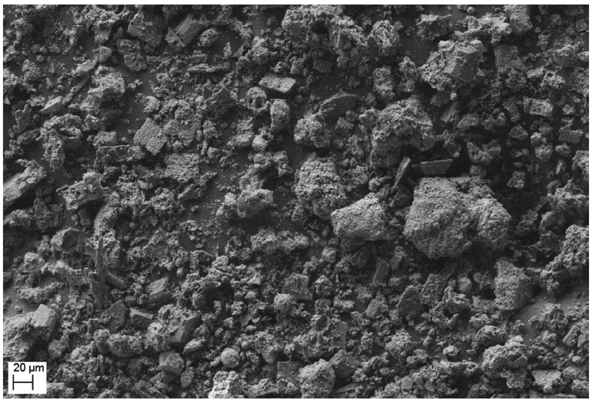

Fig. 5. Scanning electron microscopy image of the precipitate after 24 h experiment (FA; Mg:P:N 1.1:2:2). The bar indicates 20 µm length.

were obtained with molar ratio 1.3:1:1, 77.5% for DOL and 71.3% for FA. Otherwise, the yields were 70.2% for FA 1.1:2:2, 58.3% for FA 1.1:1:1, 46.5% for FA 1.6:1:1, 55.2% for FA 2:1:1, 73.8% for DOL 1.1:1:1, 54.1% for DOL 1.6:1:1, and 45.7% for DOL 2:1:1. The yields are somewhat lower than the phosphate removal percentages suggest. However, the order of magnitude is the same with both. A small part of struvite crystals is accumulated on the surfaces of the precipitation reactor (incl. stators and mixing blade). A precipitate was collected, it was decanted to a Buchner funnel and the remaining precipitate was collected with a spoon from the reactor. Therefore, the amount of collected precipitate is slightly smaller than the actual yield would be which explains the difference with phosphate removals.

## 4. Conclusions

In this research, $MgSO_4$ solution obtained by treating fly ash or DOL with sulfuric acid was used as a precipitant for simultaneous phosphate and ammonium removal from synthetic $(NH_4)_2HPO_4$ solution. The purpose of the sulfuric acid treatment was to remove CaO from the precipitant solution since low CaO concentration is better suited for struvite precipitation. DOL contained 37.9% CaO and 16.5% MgO, and fly ash contained 36.9% CaO and 14.2% MgO. Only less than 500 mg/L of the Ca was left in the $MgSO_4$ solution. The Mg leached more easily from the fly ash than from the DOL (14500 mg/L vs. 9430 mg/L) even though DOL contained more Mg. Harmful element contents of the $MgSO_4$ solutions were generally low especially in the case of DOL. However, As was quite mobile in the case of FA, which could cause problems fertilizer use if it is co-precipitated to struvite. Precipitation experiments were performed at room temperature (20°C ± 2°C) using different molar ratios Mg:P:N (1.1-2:1-2:1-2) and precipitation times (4–24 h). In all cases, there was only minor changes in the removal of both ammonium and phosphate after 4 h of reaction time. Highest ammonium removal percentages after the 4 h test were 79.5% for $MgSO_4$ 1.3:1:1, DOL 1.1:1:1, and DOL 1.3:1:1. Highest ammonium removal percentages (75.5%) for FA based $MgSO_4$ solution were achieved using molar ratios Mg:P:N 2:1:1 and 1.1:2:2. Also the highest phosphate removal percentages was achieved with these samples (97% for $MgSO_4$ 1.3:1:1, 93.3% for DOL 1.3:1:1, 89.8% for DOL 1.1:1:1, 84.5% for FA 2:1:1, and 82.5% for FA 1.1:2:2). Struvite was the only formed precipitation product in all cases as was confirmed by XRD. The best yield was obtained with commercial $MgSO_4$ salt (90.4%). The best yields of struvite for both DOL and FA were obtained with molar ratio 1.3:1:1, 77.5% for DOL and 71.3% for FA. Results indicate that fly ash and DOL based $MgSO_4$ solutions performed quite well compared to commercial $MgSO_4$ salt and they have great potential in the ammonium and phosphate precipitation. However, more tests with authentic wastewaters should be conducted. Also, solubility tests and growth tests in greenhouses and fields should be performed to confirm the suitability for fertilizer use.

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