

Use of sidestream based MgSO₄ as chemical coagulant in the simultaneous removal of nitrogen and phosphorus from wastewaters

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Abstract: Phosphorus as phosphate and nitrogen as ammonium or nitrate are the main nutrients in wastewaters and agricultural sludges. They runoff easily to waterways and cause eutrophication in water bodies. However, ammonium and phosphate could be precipitated simultaneously and used as recycled nutrients. In this research, MgSO₄ solution obtained by treating fly ash or dolomite with sulfuric acid was used as a coagulant for simultaneous phosphorus and nitrogen removal from synthetic (NH₄)₂HPO₄ solution. Precipitation experiments were performed at room temperature (20 ± 2 °C) using different molar ratios Mg:P:N (1.1-1.6:1-2:1-2) and precipitation times (6 – 24 h). The pH was adjusted to 9.0 and kept constant. In all cases, there was only a minor changes in the removal of both ammonium and phosphate after 4 hours of reaction time. Highest ammonium removal percentages (75.5 %) were achieved for fly ash based MgSO₄ solution using molar ratios Mg:P:N 1.6:1:1 and 1.1:2:2. Also the highest phosphate removal percentages was achieved with these two molar ratios (84.5 % for 1.6:1:1 and 82.5 % for 1.1:2:2). Struvite was the only formed precipitation product in all cases as was confirmed by XRD. Results indicate that fly ash and dolomite based MgSO₄ solutions have great potential in the ammonium and phosphate precipitation from synthetic samples.

Keywords: dolomite; fly ash; struvite; ammonium; phosphate; precipitation

1. Introduction

Wastewaters and agricultural sludges can contain large amounts of phosphorus and nitrogen, which runoff easily to waterways causing eutrophication in water bodies. Ammonium nitrogen (NH₄) volatilizes easily as ammonia gas at alkaline conditions, which reduces the efficiency of nitrogen fertilizers. Also, the production of nitrogen fertilizers by using the energy-intensive Haber-Bosch reaction causes large amounts of greenhouse gas emissions, as production consumes high amounts of natural gas [1]. The exploitable phosphate resources will be significantly depleted during the following decades and the remaining rock phosphate reserves are characterized by decreasing quality (higher Cd and U concentrations) and more expensive mining technology [2–4]. There is a vast need to find alternative, recycled fertilizers for more sustainable future. It has been estimated that there is an enormous economic potential in the recycled fertilizer market. In Finland alone, the market size would be around 0.5 billion € annually [5]. In addition, the European Union's fertilizer directive is currently under revision and the use of bio-based and recycled fertilizers will be encouraged in the revised directive [6].

One answer to recycled fertilizer market would be to precipitate ammonium and phosphate simultaneously from nutrient containing wastewaters as a phosphate mineral called struvite (NH₄MgPO₄ · 6H₂O). Struvite

solubility to water is only 0.2 g/L (0 °C) so it is a slow-release fertilizer [7,8]. Struvite fertilizers are also easy to manufacture and handle, and they are odorless [9].

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 [10]. 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 [11]. Due to the relatively high price of these commercial salts, and since magnesium is listed in European Union's critical raw material list, alternative magnesium sources should be preferred instead of commercial salts [12].

Dolomite is a carbonate mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$) and it is used e.g. as a soil improver to increase the pH of acidic soils [13]. 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 [14]. Both fly ash and dolomite could be potential precipitants for struvite precipitation [15–18]. High Ca concentration can cause the phosphate ions to precipitate as hydroxyapatite preventing struvite formation [17–19], therefore it would be best to first precipitate Ca as insoluble $CaSO_4$ and transform the Mg ions to soluble $MgSO_4$ [20].

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

2. Materials & Methods

Dolomite was provided by a Finnish lime quarry. It was small sized (<3 mm) fraction that is leftover as the dolomite 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 fluidized bed combustion technique. The fuel used during sampling was peat and the ash sample was collected directly from the ash silo.

First dolomite 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. 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 $CaSO_4$ and soluble $MgSO_4$.

Precipitation experiments were performed at room temperature (20 ± 2 °C) using different molar ratios Mg:P:N (1.1-1.6:1-2:1-2) and precipitation times (6 – 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 minute 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.

Ammonium concentration was measured from the water samples with the use of NH_4 -selective electrode, phosphate concentration was measured by ion chromatography (IC) and magnesium and calcium concentration by inductively coupled plasma (ICP). Precipitate was dried at room temperature and analyzed using x-ray diffractometer (XRD) and scanning electron microscope (SEM).

3. Results & Discussion

3.1 Raw materials and MgSO_4 solution

Main components of the dolomite and fly ash were CaO , MgO and SiO_2 (Table 1). The other components in dolomite consisted mainly of CO_2 . Concentrations of harmful elements are reasonably low (Table 2) and they are clearly below the limit values of Finnish fertilizer decree i.e. dolomite and fly ash could be used as a forest fertilizer in Finland. Cd concentration was below the detection limit value of the XRF equipment, therefore, it cannot be stated with certainty if the Cd concentration is also below the limit for field fertilizers. The Pb concentration in fly ash exceeded the limit value for field fertilizers. It should be noted though, that the limit values of Finnish fertilizer decree are for nitric acid digestion. XRF measures the total concentration of the elements and the concentrations obtained with nitric acid digestion are typically clearly lower than the total concentrations [9]. Therefore, the results obtained with XRF overestimate the actual availability of these elements.

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

	CaO (%)	MgO (%)	SiO₂ (%)	Al₂O₃ (%)	FeO (%)	P₂O₅ (%)	K₂O (%)	Na₂O (%)	TiO₂ (%)	MnO (%)	Others (%)
Dolomite	37.9	16.5	10.4	3.1	3.5	0.1	1.1	0.2	0.3	0.1	26.8
Fly ash	36.9	14.2	17.7	8.1	8.9	1.6	0.5	0.5	0.3	0.3	11.0

Table 2 Harmful element contents (XRF) and a comparison to the limit values of Finnish fertilizer decree [22]

	As (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Dolomite	<10	<10	50	40	80	<10	20
Fly ash	<10	<10	20	100	80	140	80
Limit value field/forest fertilizers	25/40	1.5/25	300	600/700	100/150	100/150	1500/450 0

The Mg and Ca 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 dolomite (DOL) contained 36.9 % and 37.9 % of Ca (Table 1). The Mg leached more easily from the FA than from the DOL.

Table 3 Mg and Ca concentrations (ICP) of the MgSO_4 solutions

Sample	Mg (mg/L)	Ca (mg/L)
FA based MgSO_4	14500	483
DOL based MgSO_4	9430	494

3.2 Ammonium removal

Ammonium removal percentages of the different samples are presented in Fig. 1. The precipitation experiment was continued for 24-hours with FA based MgSO_4 solution when the molar ratio Mg:P:N was 1.1:2:2. However, there was clear drop in the removal percentage at the end of the experiments. Therefore, the lengths of the experiments were reduced to 6 hours. Highest removal percentages (75.5 %) were achieved for FA based MgSO_4 solution using molar ratios Mg:P:N 1.6:1:1 and 1.1:2:2. Since there was excess ammonium present in the latter case, in practise all of the ammonium was precipitated. Ammonium removal was very fast with FA (Mg:P:N = 1.6:1:1). With FA (Mg:P:N = 1.3:1:1) and DOL based MgSO_4 solutions (Mg:P:N = 1.3:1:1 and 1.6:1:1, 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 hours.

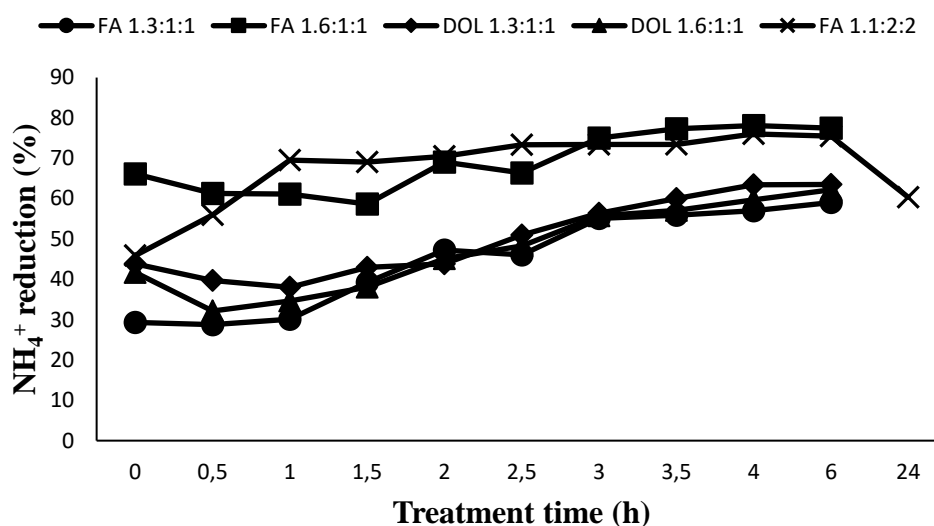


Fig. 1 Ammonium removal percentages with fly ash (FA) and dolomite (DOL) based MgSO_4 solutions using different molar ratios of Mg:P:N

3.3 Phosphate removal

Phosphate removal percentages of the different samples are presented in Fig. 2. Also phosphate reduction was very fast with FA based MgSO_4 solution when the molar ratio was Mg:P:N 1.6:1:1. The reduction percentage was 84.5 % after the 6-hour experiment. With the other samples, the removal percentages rose more linearly with increasing precipitation time. The reduction percentages were 71.9 % for DOL based MgSO_4 solution (Mg:P:N = 1.6:1:1) and 56.0 % for FA based MgSO_4 solution (Mg:P:N = 1.3:1:1). The result for DOL 1.6:1:1 is based on a single experiment due to difficulties when analyzing the first sample. For FA 1.1:2:2 phosphate was measured only before and after the 24-hour experiment. The removal percentage was 82.5 %.

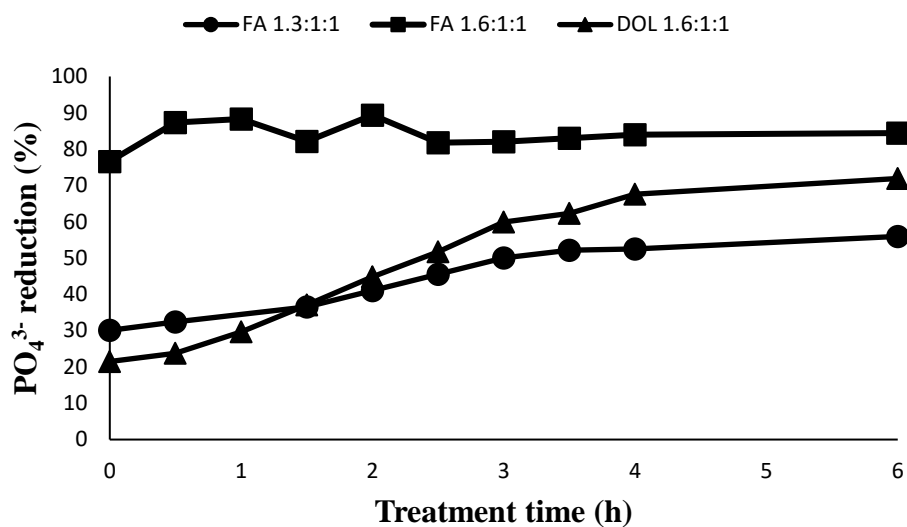


Fig. 2 Phosphate removal percentages with fly ash (FA) and dolomite (DOL) based $MgSO_4$ solutions using different molar ratios of Mg:P:N

3.4 Characterization of the precipitate

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 seems to be reversed in the top picture: the main struvite peak should be the one at around 21 degrees and at around 33 degrees should only be a small peak, but in Fig. 3 the intensities of these peaks are the other way around. This could be due to the growth of the crystal structure [23]. 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 both FA Fig. 4 (a) and c) and DOL Fig. 4 (b) and d).

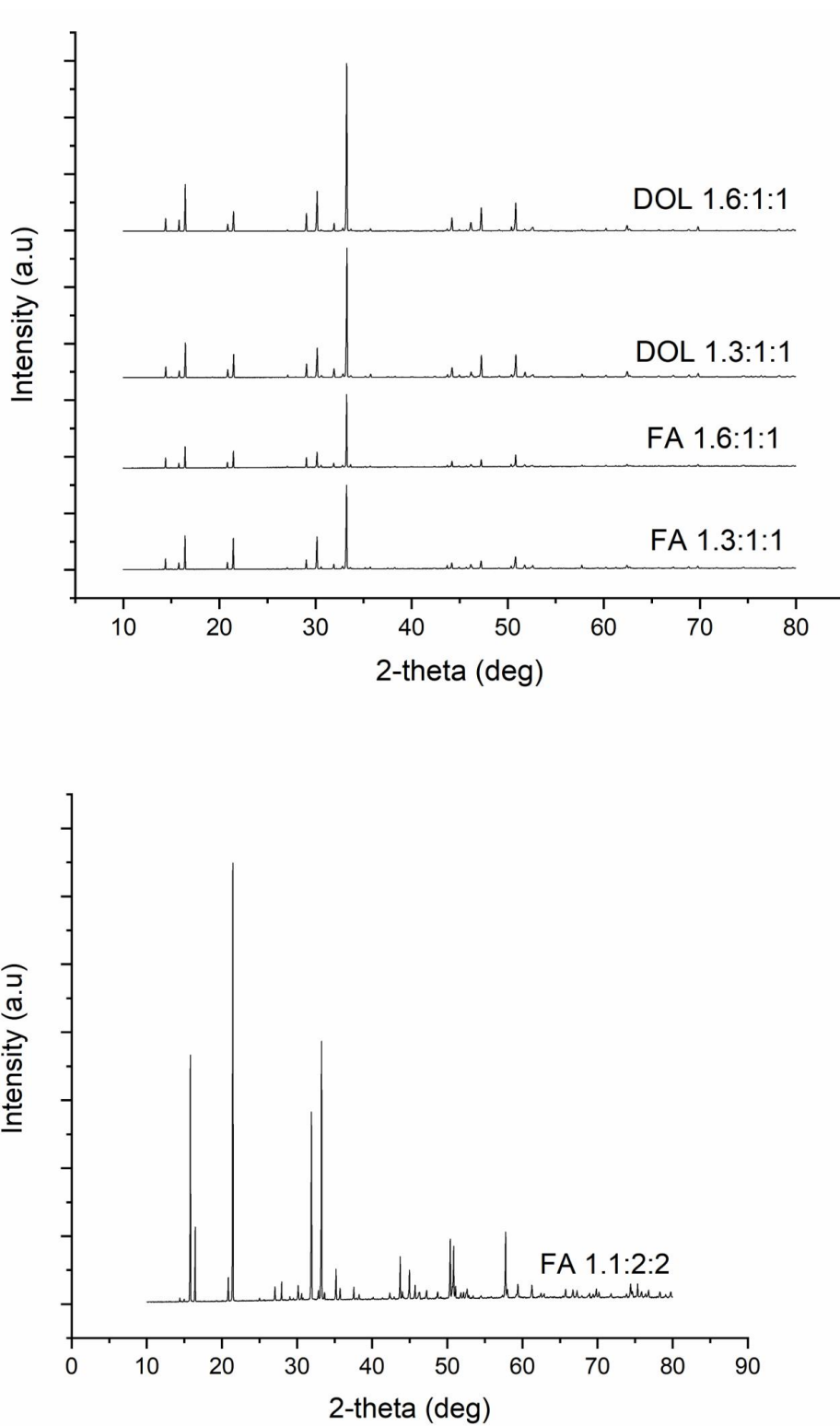


Fig. 3 XRD diffractograms of the precipitates after the 6-h (top picture) and 24-hour (bottom picture) experiments

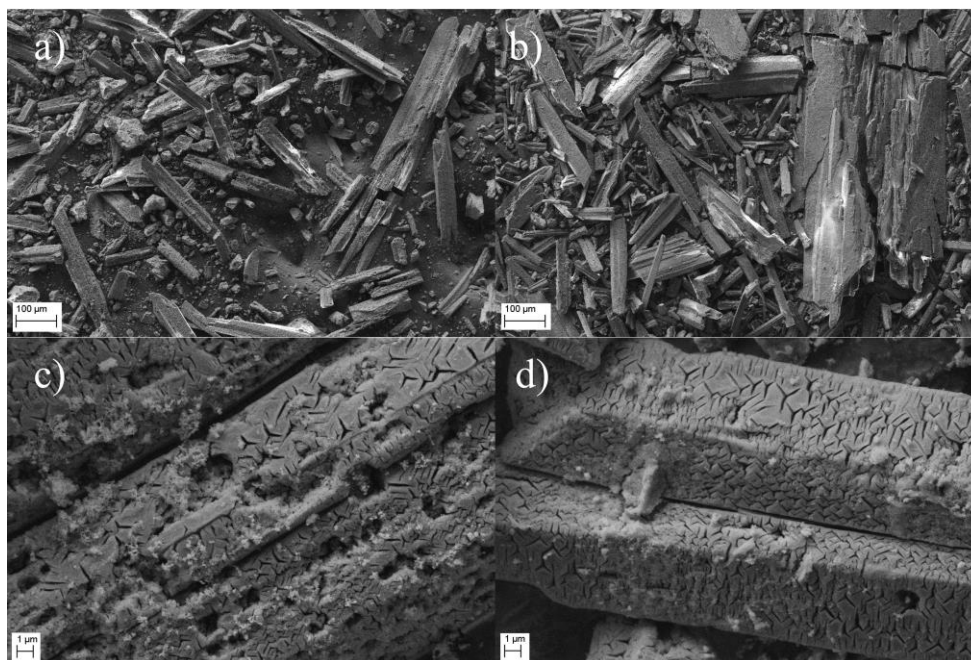


Fig. 4 SEM images of the precipitates after 6-hour experiments (Mg:P:N 1.3:1:1): a) and c) FA; b) and c) DOL. The bars indicate 100- μ m length in a) and b) and 1- μ m length in c) and d)

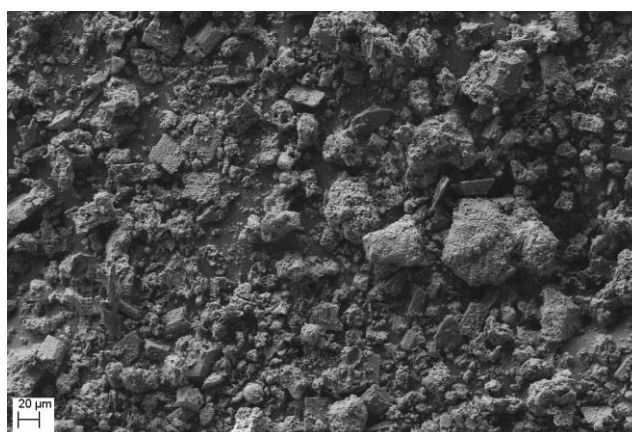


Fig. 5 SEM image of the precipitate after 24-hour experiment (FA; Mg:P:N 1.1:2:2). The bar indicate 20- μ m length

Yields of the formed struvite are presented in Table 4. Calculation was based on the theoretical maximum amount of struvite that could be formed with corresponding molar ratios. The yield in FA 1.1:2:2 was 125.4 % (6-hour precipitation), but since there was no other products found in the XRD analysis, some of the phosphate or ammonium is probably adsorbed on the struvite crystals. This is supported also by the ammonium and phosphate removal percentages, since excess ammonium and phosphate was present in the solution. Similar observation was made also previously when calcined dolomite was used for struvite precipitation [17]. Otherwise, the yields were 67.2 % for FA 1.3:1:1, 79.7 % for FA 1.6:1:1, 78.4 % for DOL 1.3:1:1, and 65.8 % for DOL 1.6:1:1. For FA 1.3:1:1, the yield was better than expected by the phosphate removal percentage, possibly due to the same reason than with FA 1.1:2:2.

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

	FA 1.3:1:1	FA 1.6:1:1	FA 1.1:2:2	DOL 1.3:1:1	DOL 1.6:1:1
Yield (%)	67.2	79.7	125.4	78.4	65.8

4. Conclusions

In this research, MgSO₄ solution obtained by treating fly ash or dolomite with sulfuric acid was used as a coagulant for simultaneous phosphate and ammonium removal from synthetic (NH₄)₂HPO₄ 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. Dolomite 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 MgSO₄ solution. The Mg leached more easily from the fly ash than from the dolomite (14500 mg/L vs. 9430 mg/L) even though dolomite contained more Mg. Precipitation experiments were performed at room temperature (20 ± 2 °C) using different molar ratios Mg:P:N (1.1-1.6:1-2:1-2) and precipitation times (6 – 24 h). In all cases, there was only a minor changes in the removal of both ammonium and phosphate after 4 hours of reaction time. Highest ammonium removal percentages (75.5 %) were achieved for FA based MgSO₄ solution using molar ratios Mg:P:N 1.6:1:1 and 1.1:2:2. Since there was excess ammonium present in the latter case, in practise all of the ammonium was precipitated. Also the highest phosphate removal percentages was achieved with these two molar ratios (84.5 % for FA 1.6:1:1 and 82.5 % for FA 1.1:2:2). Struvite was the only formed precipitation product in all cases as was confirmed by XRD. However, yields of the precipitate were higher than expected for FA when Mg:P:N was 1.1:2:2 or 1.3:1:1 possibly because some of the phosphate or ammonium was adsorbed on the struvite crystals. Results indicate that fly ash and dolomite based MgSO₄ solutions have great potential in the ammonium and phosphate precipitation from synthetic samples. 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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