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STRUVITE PRECIPITATION FROM THE LIQUID FRACTION OF THE DIGESTATE OF A MUNICIPAL WASTE BIOGAS PLANT

Currently, municipal waste biogas plant digestate is treated both as an alternative fertilizer and as a potential source of water. In practice, before advanced purification technologies, the liquid fraction of the digestate is subjected to pretreatment, aiming also at recovering the dissolved nutrients and making them into a concentrated fertilizer, e.g., by struvite precipitation. In this study, the possibility of struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitation from the liquid fraction of municipal digestate was determined. In the experiments, $MgCl_2$ and NaH_2PO_4 were added to the treated solution as a complementary source of magnesium and phosphorus. Their doses were chosen to achieve the most favorable conditions for controlling struvite precipitation. The results obtained confirmed the possibility of struvite precipitation from the liquid fraction of municipal digestate. The process realized for pH 9.0, temperature 20–23 °C, molar ratio N:Mg:P = 5.13:1:1 and 1:1.1:1.1, reaction time 5 min with a stirring rate of 160 rpm, provides a high efficiency of struvite precipitation from the liquid fraction of digestate. From the viewpoint of process economics (less amount of reactants added with similar process efficiency), a molar ratio of N:Mg:P = 1:1.1:1.1 was found to be optimal for the reaction of precipitation.

1. INTRODUCTION

The operation of any type of biogas plant is connected with the production of large amounts of digestate, which is one of the products of the reaction of processing organic substances. This amount corresponds approximately to the weight of the substrates used in the fermentation process. The digestate contains many organic and inorganic compounds,

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which can be used among others as a fertilizer for plants. For the components separated from the digestate to meet all quality requirements allowing it to be used, for example, in agriculture, it is necessary to treat it using advanced physicochemical methods.

Often, before more advanced treatment technologies are applied, the liquid fraction of the digestate is pre-treated to recover the dissolved nutrients and to produce a concentrated fertilizer. This can be achieved, among other things, by precipitating struvite, which is a hydrated ammonium magnesium phosphate ($MgNH_4PO_4 \cdot 6\ H_2O$). Precipitation of struvite under controlled conditions is advisable also since it can precipitate both in the technological installations and in the pipelines, causing operational problems for the biogas plant.

The reactions that occur during struvite precipitation are:

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+,\ \ n = 0,\ 1 \text{ or } 2$$

Struvite is a mineral with a crystalline structure, characterized by a white transparent or semi-transparent color with a vitreous luster, an uneven fracture, good to poor cleavage, a Mosh scale hardness of 2, and a specific gravity of 1700 kg/m^3 [1]. Precipitated struvite can be a valuable fertilizer that has many potential applications in agriculture and horticulture. Its precipitation depends on many parameters. The most important of these are pH, temperature, Mg:P molar ratio, reaction time, and the presence of impurities (e.g., suspended solids) and other ions (e.g., calcium ions).

Struvite is well soluble in acidic solutions and very poorly soluble in alkaline media. Therefore, its precipitation can be controlled by pH and supersaturation as the activity of NH_4^+ and PO_4^{3-} ions depends on pH [2]. There are many reports in the literature regarding the effect of pH on the precipitation efficiency of struvite [3–5]. According to [2, 5] struvite can crystallize in the pH range from 5.3 to 11.0, while according to [6] the optimum pH for struvite precipitation should be 9.5. The authors [6] suggest that the highest efficiency of struvite precipitation from digestion leachate can be achieved in the pH range 8.2–8.6. On the other hand, Zeng and Li [7] consider that the minimum pH value necessary for struvite precipitation from digestate should be 8.0, while the optimum is in the range of 8.5–9.5.

The molar ratio of Mg^{2+}, NH_4^+ and PO_4^{3-} ions is of great importance in struvite formation. This ratio should be determined experimentally for each solution to ensure maximum precipitation of struvite crystals [8]. With favorable magnesium ion concentration, struvite can be recovered at 97%. A P:Mg ratio of 1:1.05 is considered the most favorable. On a technical scale, this ratio should be kept between 1:1.1 and 1:1.6, while the P:N ratio should be at least 1:1 [9]. The effect of temperature on struvite crystallization is ambiguous. While temperature has less effect on struvite precipitation than, for example, pH, it can contribute to struvite dissolution [5]. According to [10], at high temperatures, struvite dissolution is more intense than its precipitation and dissolution is faster at 35 °C than at 25 °C. Also, other authors [3, 11] confirm the fact that struvite

solubility increases proportionally with increasing temperature. Hanhoun et al. [12], however, showed that the solubility of struvite increased with increasing temperature up to 35 °C but decreased rapidly with further increase in temperature.

The reaction time is not insignificant for the efficiency of struvite precipitation from the solution. According to [13], struvite precipitation occurs very quickly. The authors observed the appearance of struvite crystals as early as a few minutes after the magnesium compound was fed into the treated solution.

The inhibitory effect on struvite precipitation may be due to the presence of some contaminants in the liquid fraction of the digestate. Taddeo et al. [14] showed that the efficiency of struvite precipitation was inversely proportional to the concentration of suspended solids. At a leachate suspension concentration of 0.8 g/dm^3, the crystallization efficiency and the share of struvite in the precipitate were 94 and 76%, respectively. However, when the amount of suspended solids was increased 7 times, these values decreased to 61 and 48%.

Table 1

Recommended struvite precipitation conditions [3, 4, 21]

Parameter	Range	Optimal value
pH	5.3–11.5	8–9
Temperature, °C	20–47	20–30
Stirring intensity, min^{-1}	30–300	100–250
Reaction time, min	15–240	60–120
Molar ratio Mg:P	1.1:1–2:1	1.1:1–1.2:1
Molar ratio N:P	1:1–3:1	1:1
Molar ratio Ca:Mg	<1.5:1	<1

According to Le Corre et al. [15] and Barbosa et al. [16], the crystallization rate of struvite is significantly affected by the presence of calcium and carbonate ions in the digestate. The presence of calcium ions in the digestate can also lead to the formation of other compounds such as hydroxyapatite $Ca_5(PO_4)_3OH$ [17]. In addition, dolomite $CaMg(CO_3)_2$, magnesite $MgCO_3$, or huntite $CaMg_3(CO_3)_4$ may precipitate. According to Kabdasli et al. [18], the presence of sodium, calcium, carbonate, and sulfate ions affects the induction time of struvite crystals, their size, and morphology. When the molar proportion of Ca: Mg is above 1, the phosphate ions present in the solution are precipitated as calcium phosphate [14]. According to [2], the presence of Ca^{2+} in a solution with pH > 9.5 increases the amount of additives (Ca_3PO_4 and $CaHPO_4$) in the precipitate. Battistoni et al. [19] are of a different opinion, considering that the presence of calcium ions in the leachate accelerates struvite formation, but only at low pH. At a molar ratio of Mg:P > 1.5, 70% struvite content in the precipitate can be achieved [20]. Table 1 shows the recommended parameters for struvite precipitation.

Other less common methods of struvite precipitation are CO_2 elimination or electrochemical processes using a magnesium anode. The former is based on increasing the pH value by desorption of CO_2 during aeration. This method allows the recovery of a large amount of phosphorus (about 78%) in a relatively short time. It has also been shown [22] that the use of an anode as a source of magnesium allows for the recovery of struvite from the supernatant of digested sludge from wastewater treatment plants as well as from aqueous solutions.

Since uncontrolled struvite precipitation in installations of biogas plants treating municipal waste may cause many problems, e.g., increase of hydraulic resistance due to blocking of transport pipelines, mechanical damage to pumps, increase in operating costs associated with the removal of the above-mentioned hazards, an attempt was made to determine the possibility of struvite precipitation from the liquid fraction of municipal biowaste to improve its quality at the leachate pretreatment stage.

2. MATERIALS AND METHODS

The subject of this study was the liquid fraction of digestate from a waste biogas plant processing the organic fraction of municipal waste located in the Polish waste management facilities in the Lower Silesia Province (50°53′15.5″N 17°23′28.0″E). This fraction was separated from the digestion pulp by using sedimentation centrifuges. The characteristics of the test solution are presented in Table 2. Physicochemical analysis of tested solution was conducted according to Standard Methods for the Examination of Water and Wastewater, 23rd Edition.

Table 2

Properties of the test solution

Parameter	Value range
pH	7.2
Temperature, °C	20–23
Conductivity, mS/cm	20.4
Dry residue, mg/dm³	55 230
Alkalinity, mmol/dm³	142
Total hardness, mval/dm³	740
COD, mg O_2/dm³	11 450
BOD_5, mg O_2/dm³	3600
DOC, mg C/dm³	4210
NH_4^+-N, mg /dm³	776
NO_2^--N, mg/dm³	5.8
NO_3^--N, mg/dm³	below the level of detection

Table 2

Properties of the test solution

PO_4^{3-}, mg/dm³	21.4
SO_4^{2-}, mg/dm³	40
P, mg/dm³	21.4
Na, mg/dm³	1920
K, mg/dm³	2070
Ca, mg/dm³	420
Mg, mg/dm³	235
Cl, mg/dm³	2246
Fe, mg/dm³	3.1
Mn, mg/dm³	3.9
Cu, mg/dm³	0.096
Zn, mg/dm³	0.780
Li, mg/dm³	6
Hg, mg/dm³	0.0036
Co, mg/dm³	0.137
Ni, mg/dm³	0.250
Ba, mg/dm³	0.235
As, mg/dm³	0.0005
Cr, mg/dm³	0.220
Pb, mg/dm³	0.025
Cd, mg/dm³	0.001
Mesophilic bacteria, CFU/cm³	$1.11 \cdot 10^8$
Thermophilic bacteria, CFU/cm³	$1.63 \cdot 10^4$
Particle size distribution: d_{10}–d_{50}–d_{90}, µm	1.9–12.3–76.4

The ratio of N:Mg:P in the test solution was 40.1:14.2:1, hence there was a need to dose Mg and P compounds to ensure optimum proportion of these components for struvite precipitation. In the experiments, two chemical reagents were used, $MgCl_2$ as a magnesium supplement and NaH_2PO_4 as a phosphorus supplement. Some authors [7, 17] recommend the application of $MgCl_2$ as a source of Mg because this compound has a high solubility, which makes the reaction time required to dissolve Mg^{2+} in solution shorter than when using other magnesium supplements such as $MgSO_4$ or MgO. Besides, due to the large excess of ammonium nitrogen in relation to magnesium and phosphorus concentrations, the application of phosphorus sources must also be ensured [23]. The doses of magnesium and phosphorus salts were chosen to achieve the most favorable conditions for struvite precipitation, according to literature data. Table 3 shows the characteristics of the reagents used in struvite precipitation.

In the present study, struvite precipitation reactions were carried out at pH 9.0. The solution sample, 500 cm³ in volume, was set on a Velp Scientifica FC6S mechanical stirrer. $MgCl_2$ and NaH_2PO_4 (Chempur, Poland) were then dosed into the sample. The

doses of the reactants were set so that the molar ratios of N:Mg:P were: 5.13:1:1 (solution A), 1:1:1 (solution B), 2:1:1 (solution C), and 1:1.1:1.1 (solution D). The temperature of the solutions was 20–23 °C. After dispensing the appropriate amount of reactants, the pH was adjusted to 9.0 using 0.1 M NaOH. According to the literature, such parameters of the process (temperature and pH) are favorable for struvite precipitation. The samples were then stirred for 5 min at a stirring rate of 160 rpm, followed by 30 min sedimentation.

Table 3

Characterization of the chemical reagents used in the struvite precipitation [24, 25]

Property	$MgCl_2$	NaH_2PO_4
Molar mass, g/mol	95.211	119.98
Color	colorless to white	white to colorless
Odour	odourless	n.a.
pH	5–6.5 (5%, 20 °C)	4–4.5 (5%, 20 °C)
Density, g/cm^3	1.57 (20 °C)	1.91 (20 °C)
Solubility in water, g/dm^3	2430 (20 °C)	n.a.

Additionally, samples A and D, were further investigated to analyze and identify the precipitate formed. Images of the formed crystals were taken using an Axio Imager.M1m optical microscope (Zeiss) in transmitted light mode and using a JSM-6610LV scanning electron microscope (JEOL) after coating the samples with carbon using a JEC-530 automatic coating machine (JEOL).

To confirm that the crystals obtained after chemical precipitation are struvite, FTIR measurements were performed. They were carried out using a Vertex 70V spectrometer (Brucker) in the wavenumber range 4000–400 cm^{-1} with a resolution of 2 cm^{-1}. The samples were ground in an agate mortar, then a small amount (1 wt. %) was mixed with an excess of KBr powder (99 wt. %) and again ground to a homogeneous consistency. Pellets with a diameter of 13 mm were prepared from the mixture. IR spectra of each sample were then recorded using a spectrometer. Analysis of the powder diffraction data was performed using ReX 0.8.3[3].

The particle size distribution of the obtained struvite crystals was carried out by laser diffraction using a Mastersizer 2000 particle size analyzer equipped with a HydroMu dispersing device (Malvern Instruments, Ltd.). In the device, solid particles whose size distribution is to be determined are added to a glass vessel containing water. It is equipped with a stirrer and a pump, thus ensuring mixing, circulation and pumping of the analysed diluted particle suspension through the measuring chamber of the apparatus. Moreover, it is possible to generate ultrasound in the dispersing unit, which ensures breaking up particle aggregates.

[3]The software free for personal and non-commercial use is available at https://www.rexpd.org

3. RESULTS

It was found that after the addition of Mg and P compounds to the samples, and after pH correction, the solution became cloudy, which indicated the beginning of the precipitation of sludge (Fig. 1). It was observed that the amount of precipitate from solution D (Fig. 1b) was greater than that from solution A (Fig. 1c). This is probably the result of the proportion of precipitating reagents used. Moreover, the precipitate in solution D was light brown, while the precipitate in solution A was much darker. Besides, the remaining supernatant is also much lighter than the raw liquid fraction of the digestate.

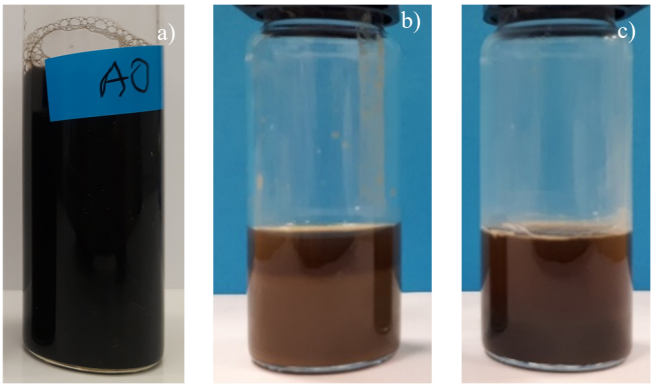

Fig. 1. Raw solution (a) and samples after precipitation:
sample D – N:Mg:P 1:1.1:1.1 (b), and sample A – N:Mg:P 5.13:1:1 (c)

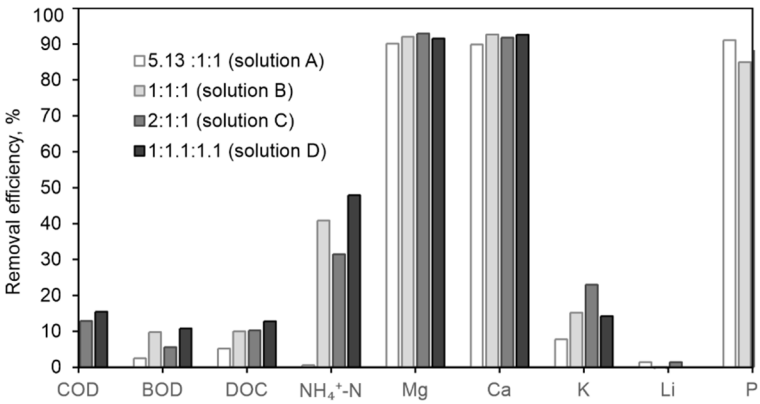

Fig. 2. Removal efficiency of different compounds as a function of N:Mg:P molar ratio in solution during struvite precipitation

The removal efficiency of selected pollutants from the samples of the liquid fraction of digestate, for which the chemical precipitation process was carried out by dosing the

salts of $MgCl_2$ (as an external source of magnesium) and NaH_2PO_4 (as an external source of phosphorus) is presented in Fig. 2. Irrespective of the applied N:Mg:P molar ratio, a low degree of organic compounds removal was observed. COD, BOD_5 and DOC concentrations decreased up to 15% as compared to the concentrations in the initial sample.

NH_4^+-N concentrations in treated digestate samples decreased but showed high variability. It was observed that NH_4^+-N removal efficiency was dependent on the amount of dosed magnesium and phosphorus supplements and ranged from 0 (for N:Mg:P = 5.13:1:1) to 48% (for N:Mg:P = 1:1.1:1.1). Both in-house studies and literature reports [2–5, 8, 9] did not clearly indicate a specific quantitative effect of ammonium nitrogen removal depending on the process operation parameters. These differences may have been caused by different qualitative characteristics of the leachate. The observed effect of NH_4^+-N reduction may be partly due to the desorption of NH_3, which at pH 9 can account for about 30% of the ammonium nitrogen in solution.

The efficiency of magnesium and calcium elimination from the liquid fraction of digestate was practically independent of the molar ratio adopted. Despite external dosing of the magnesium compound, the concentrations of magnesium ions in the supernatant varied in the range of 16.6–23.1 mg/dm^3 and were much lower than the initial Mg content. A similar situation was observed for calcium ion concentrations in the samples after chemical precipitation (from 30.8 to 42.3 mg/dm^3). The presence of Ca^{2+} in the solution at pH above 9.5 promotes the formation of Ca_3PO_4 and $CaHPO_4$, among others [2]. In the experiments conducted, pH was lower, hence the amount of these types of salts should not be significant. Another factor favoring the precipitation of struvite was the maintenance of an appropriate Ca:Mg ratio. According to [26], the value of this ratio should be below 1 and this value was maintained in the experiments conducted. This reduced the risk of hydroxyapatite precipitation and favors struvite formation.

It was also observed that potassium concentrations after the precipitation decreased by a maximum of 22% as compared to the concentration in the initial sample. On the other hand, the concentrations of phosphorus ions in the treated samples of the digestate decreased significantly and showed considerable variability depending on the amount of reagents added at appropriate molar ratios. The highest phosphorus precipitation efficiency (91%) was observed when the reactants were dosed at a molar ratio of 5.13:1:1. Probably such conditions were most suitable for the precipitation of potassium struvite.

At all N:Mg:P molar ratios analyzed, a negligible removal of Li and an increase in Na ion concentration could be observed, which is completely understandable due to the dosing of the phosphorus source in the form of NaH_2PO_4 into the treated digestate liquid.

Taking into account the best removal effects of selected contaminants in the chemical precipitation process and the amount of sludge formed that should potentially contain struvite, the sludge from samples A and D, i.e., obtained at N:Mg:P 5.13:1:1 and 1:1.1:1.1 molar ratios was subjected to in-depth investigation for the identification of the sludge formed and its analysis.

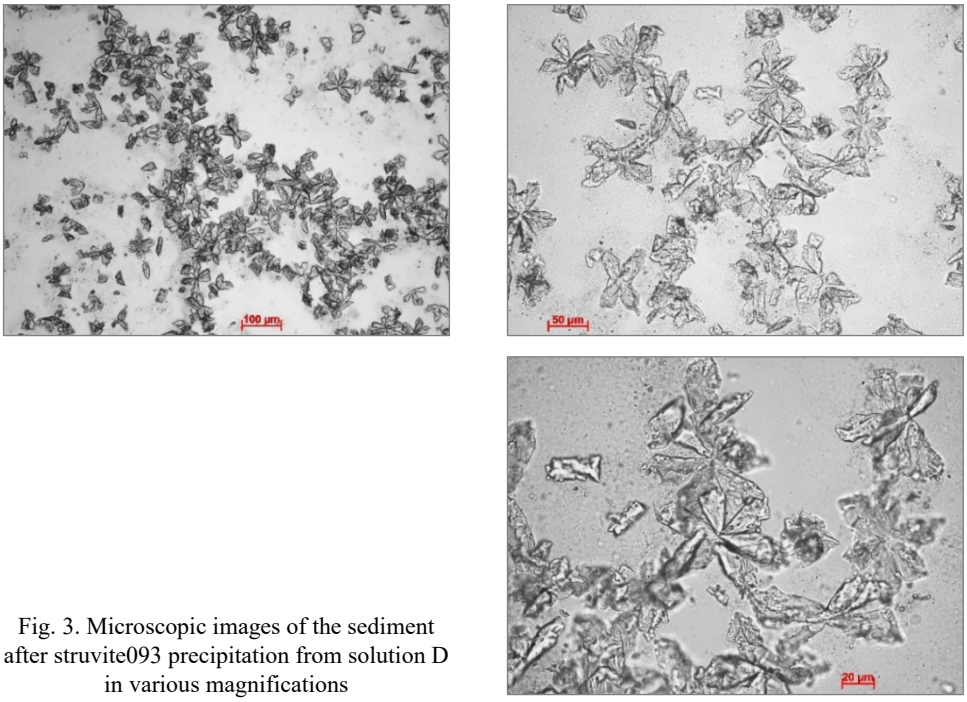

Fig. 3. Microscopic images of the sediment after struvite093 precipitation from solution D in various magnifications

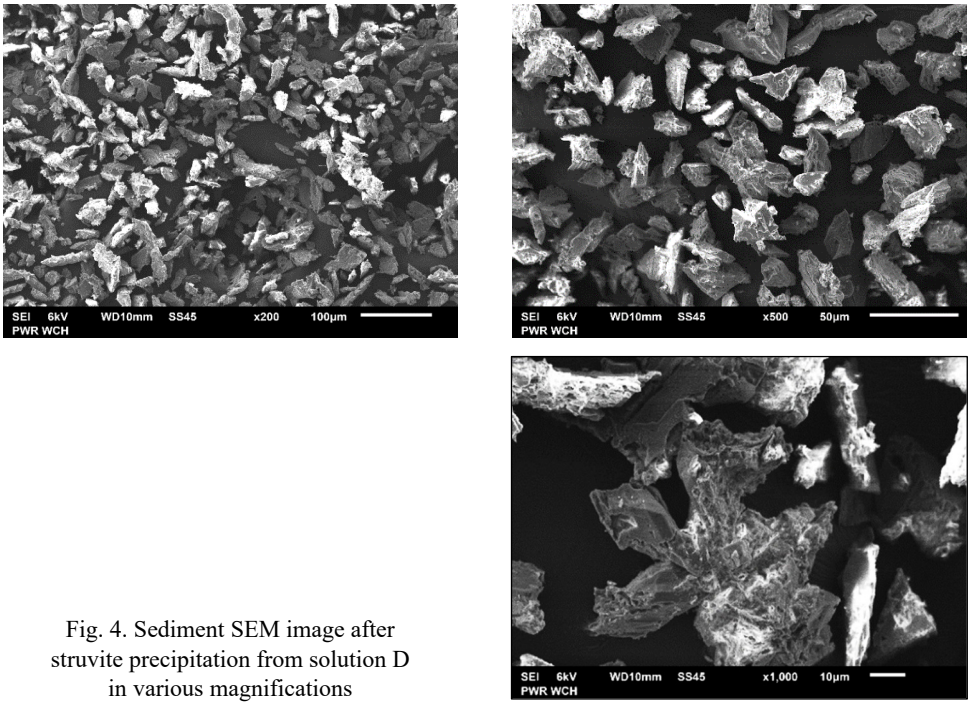

Fig. 4. Sediment SEM image after struvite precipitation from solution D in various magnifications

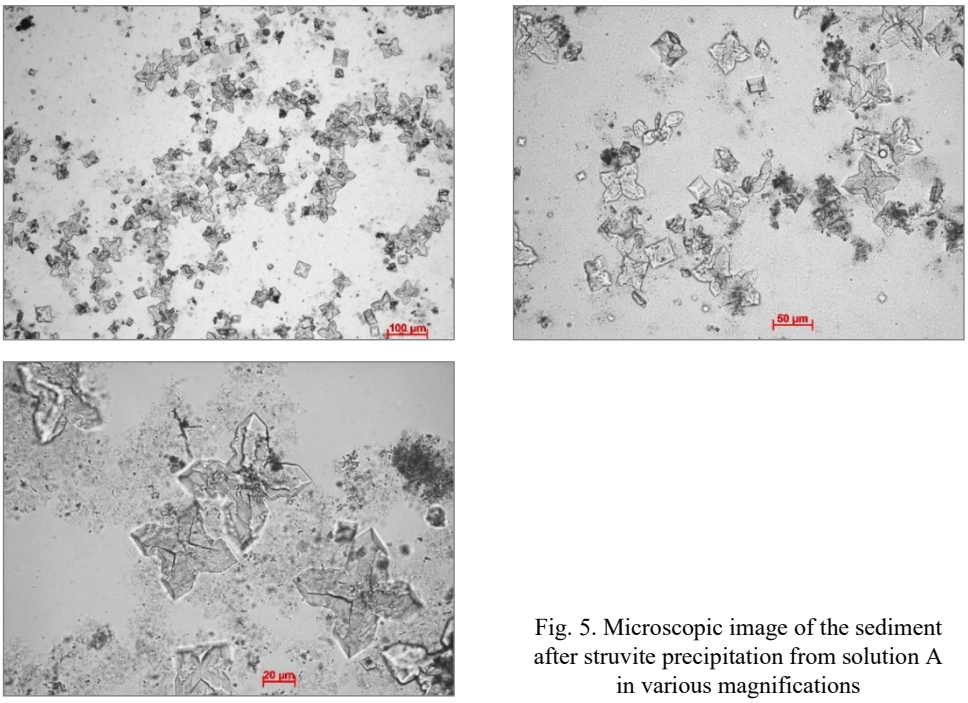

Fig. 5. Microscopic image of the sediment after struvite precipitation from solution A in various magnifications

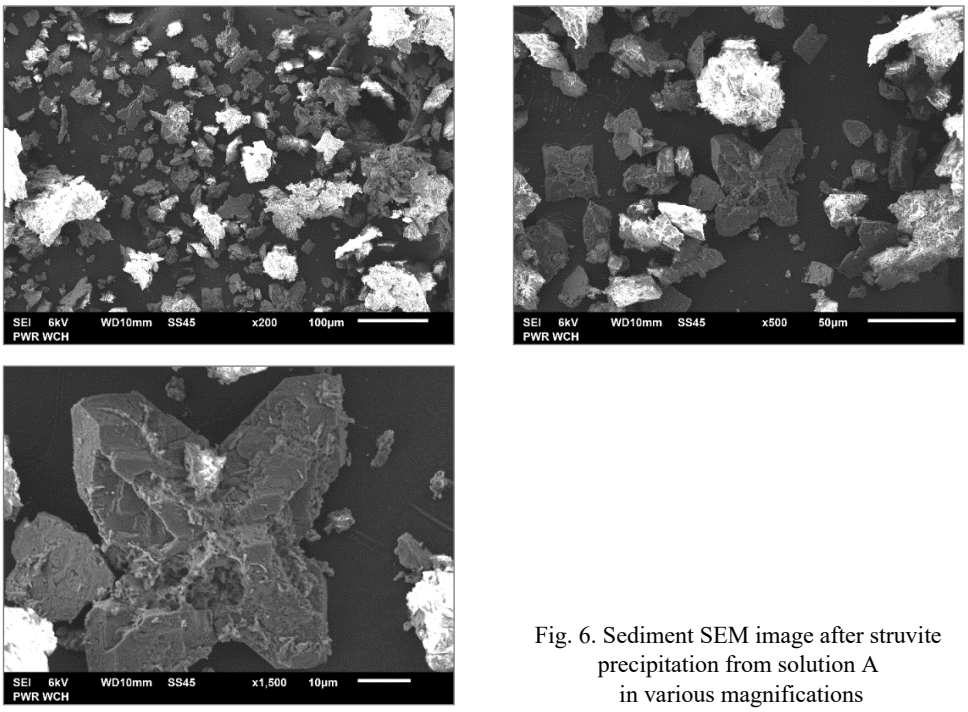

Fig. 6. Sediment SEM image after struvite precipitation from solution A in various magnifications

Struvite can take different crystal forms. The morphological variability of struvite crystals may depend on factors such as supersaturation, growth kinetics, pH, specific gravity, and the presence of moderators or inhibitors [27]. As shown in the microscopic images of both samples (Figs. 3 and 4), the precipitate obtained after dosing with $MgCl_2$ and NaH_2PO_4 at a molar ratio of 1:1.1:1.1 (sample D) is composed of dendritic crystals consisting of 4–6 coffin-like segments. Four segment crystals are X-shaped. They are quite fragile because on SEM images, where the sediment had been previously filtered and dried, they are not so numerous or they have cracked. In the literature [28], examples of branched or taking X-shape struvite structures can be found. Scientists attribute it, among others, to heterogeneous supersaturation distribution in the surroundings of the crystals, which may lead to their growth in one or two planes giving this type of elongated or branched structures. The presence of various additives such as biopolymers in the reaction medium is also important.

In the case of the precipitate obtained after dosing with $MgCl_2$ and NaH_2PO_4 at a molar ratio of 5.13:1:1 (sample A, Figs. 5 and 6), finer prism-like crystals and larger crystals (quadragonal structures) are seen to transform into small x-shaped structures (inscribed in a square). Li et al. [28] report that the striations and indentations left on quadrangular tabular structures suggest that these structures are composed of four arrowhead-shaped crystals. Consequently, the quadrangular tabular structure is almost 4 times larger than the arrowhead-shaped structure, confirming that an assembly process may be occurring. In addition, the optical microscope and SEM images (Figs. 3–6) also sho a large amount of organic matter and microorganisms in the analyzed precipitates.

The FTIR spectra of struvite crystals precipitated from the liquid fraction of the digest (Fig. 7) are consistent with the values reported in the literature. The absorption occurring between 3500 and 3250 cm^{-1} is due to O–H and N–H stretching vibrations and suggests the presence of hydration water. The weak band appearing at 2364 cm^{-1} can be attributed to the H–O–H stretching vibrations of the water molecule cluster. The band at 1435 cm^{-1} is due to asymmetric H–N–H bending vibrations. The vibrations located in the region of 1000 and 460 cm^{-1} are characteristic of the phosphate group. The strongest band at 1005 cm^{-1} is due to the asymmetric stretching vibrations of the phosphate group. The bands at 872 and 759 cm^{-1} are associated with the H-ion ammonium-water bond and H-water-water bond, and the bands at 570 and 460 cm^{-1} are attributed to the P-O bend and PO_4^{3-} mode, respectively. Thus, the FTIR spectra indicate the presence of hydration water, N-H bending and stretching, and P-O bending and stretching [27].

By analyzing the particle size distribution of the precipitates, it was found (Fig. 8) that the precipitate in solution D is characterized by slightly larger particles of struvite crystals that easily crack when the sample is sonicated. The diameter defining 90% of the particle population (d_{90}) is reduced from 90 μm to 60 μm and the diameter of the larger particle fraction shifts to the left. In contrast, the precipitate in solution A shows greater stability in crystal size, with d_{90} changing by only about 5 μm after sonication of the sample (Table 4).

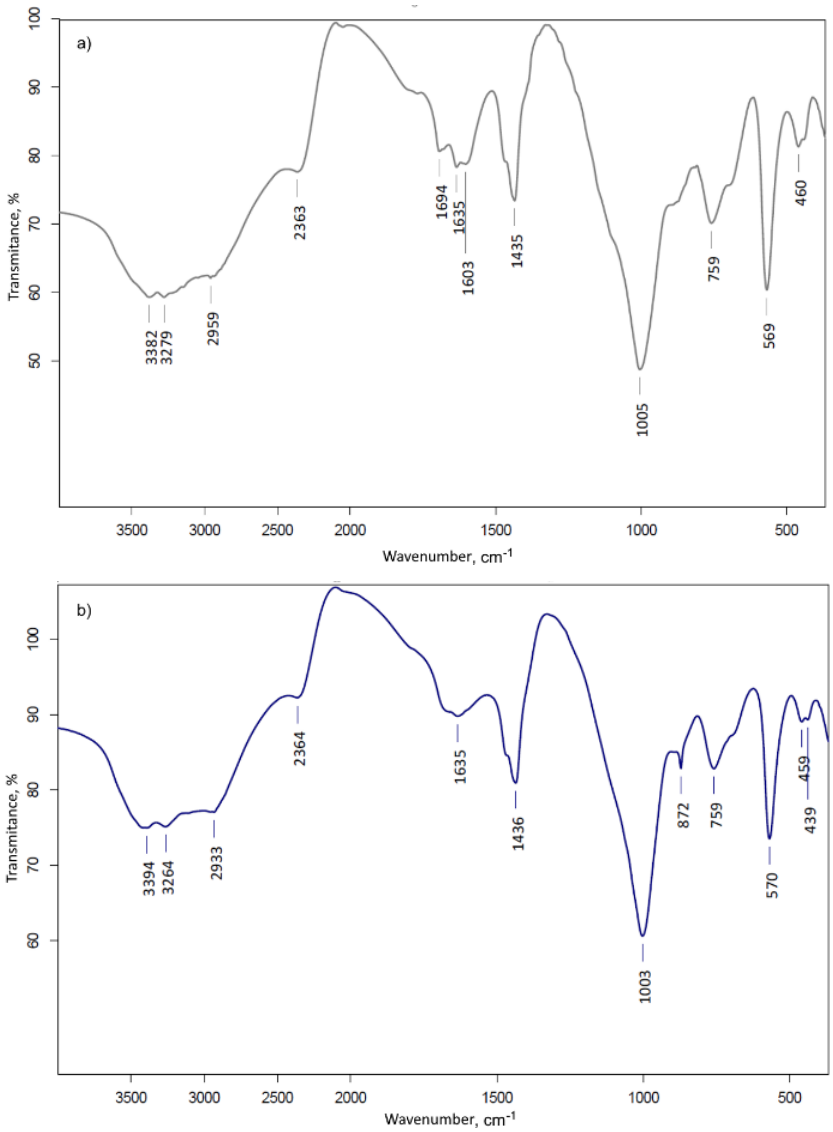

Fig. 7. FTIR spectrum of struvite crystals precipitated
from the digestate liquid fraction in solution D (a) and solution A (b)

The finer fraction present in the sediment size distributions are the particles found in the raw liquid digestate. For the precipitate in solution D it is in the range of 0.4–4 µm and for the precipitate in solution A it is in the range from 0.4 µm and merges with the medium particle fraction with an average diameter of about 4 µm and then transitions to the coarser particle fraction.

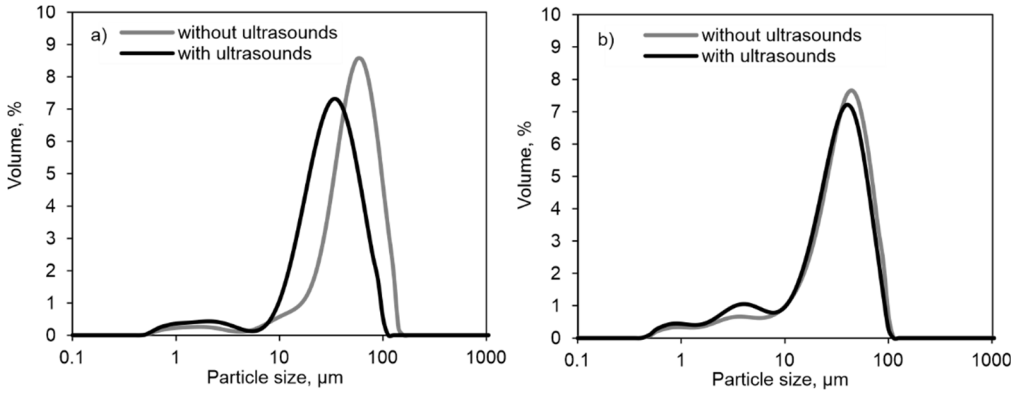

Fig. 8. Particle size distribution in solution D (a) and solution A (b)

Table 4

Particle size distribution as d_{10}, d_{50} i d_{90} values of the sediment of the analyzed solutions [μm]

Precipitate		d_{10}	d_{50}	d_{90}
In solution D	without ultrasounds	17.43	49.11	89.53
	with ultrasounds	10.82	29.13	59.88
In solution A	without ultrasounds	6.22	33.53	64.81
	with ultrasounds	3.72	29.66	59.56

4. SUMMARY

The study confirmed the possibility of struvite precipitation from the liquid fraction of municipal digestate. Irrespective of the applied N:Mg:P molar ratio, a slight removal of organic compounds, magnesium and calcium ions, lithium, and sodium from the purified solution was observed. On the other hand, the concentrations of phosphorus ions in the treated leachate were significantly reduced and showed considerable variability depending on the amount of reagents added at appropriate molar ratios. It was confirmed that struvite can take various crystalline forms. The microscopic images taken confirm that the precipitate obtained after the addition of an appropriate amount of $MgCl_2$ and NaH_2PO_4 is struvite. Also, the FTIR spectra of the obtained struvite crystals are in agreement with the literature reports. The particle size distribution shows that the precipitate obtained at the N:Mg:P ratio of 1:1.1:1.1 is characterized by slightly larger particles of struvite crystals, which crack when the sample is sonicated. In contrast, the precipitate separated from solution at an N:Mg:P ratio of 5.13:1:1 shows greater stability in crystal size, with only a slight leftward shift in the size distribution of the largest particles and an increase in the volume of the mean fraction after sonication of the sample. The precipitation procedure under the utilized experimental conditions, i.e., pH 9.0, temperature

20–23 °C, molar ratio N:Mg:P = 5.13:1:1 or 1:1.1:1.1, reaction time 5 min with a stirring rate of 160 rpm, ensures high efficiency of struvite precipitation from the digestate. From the point of view of process economics (less amount of reactants added with similar process efficiency), the molar ratio of N:Mg:P = 1:1.1:1.1 was found to be the best among those tested.

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