A proposal of low-cost technology for nutrient recovery from leachate of anaerobic digester at a biological wastewater treatment plant

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Abstract. Removal of nutrients from wastewater with simultaneous recovery of phosphorus (P) and nitrogen (N) in the form assimilable by plants is possible by the precipitation of ammonium magnesium phosphate (struvite). This method benefits environmental protection but has not been widely implemented in Wastewater Treatment Plants (WWTPs). One of the reasons is the high costs of available technologies. The aim of the work is to investigate the low-cost methods of reduction and recovery of nutrients from wastewater. It involves the precipitation of struvite from phosphate-rich leachate from WWTP fermentation chambers. The reaction was carried out in the prototype of a simple horizontal reactor, ensuring the possibility of collecting sediment in the funnel. A cheap waste magnesium salt was used to precipitate the struvite, which significantly reduced the costs of its acquisition. The reduction of P exceeded 80% in most of performed tests in leachate waters. The precipitant removed from the reactor has the character of sludge with a significant degree of hydration (85%). After drying, it is a dusty powder with an average P content of 40% and a total N content of 8% and a trace of heavy metals. It was proposed to mix the obtained aqueous form of struvite sediments with compost produced from excessive sludge, without drying it. Studies have shown that one percent of struvite admixture in compost results in an increase of P and N content by 13% and 2.7%, respectively.

1. Introduction
Removal of nitrogen (N) and phosphorus (P) from sewage is one of the priorities of Wastewater Treatment Plants (WWTPs). The nutrient concentration in the treated wastewater, allowed by the standards, is 10 g/m³ of nitrogen and 1 g/m³ for phosphorus. It is difficult and expensive to achieve and maintain these parameters. Phosphorus removal in WWTPs, most often takes place through the biological incorporation into the sludge biomass and the chemical precipitation-assisted process. As a result of these processes sewage sludges containing phosphorus are obtained. Chemical precipitation guarantees an effective reduction of phosphate concentration but, at the same time, generates low-use sediments which are discharged from the system together with the excessive sludge. The precipitate binds phosphorus in a form difficult to access for plants when iron compounds are used as a coagulant [1]. The mixture of iron phosphate and digestate, after composting, is supplied to the soil, increasing the accumulation of permanently bonded phosphorus in it. Sparingly soluble inorganic compounds
may be present in the soil for many years but they are not available to plants and have very low effect on soil fertility [2]. Phosphorus present in sludges (preliminary and excessive) is not completely removed with them. Part of them is released into the leachate during fermentation and dewatering of sludges. This leachate is returned to the beginning of the process as an additional phosphorus charge of the biological part. It increases the cost of reagents using for precipitation. Thus, it is reasonable to separate this additional load from leachate. Significant amounts of phosphorus and nitrogen compounds are released during the biomass disintegration in the fermentation chambers. The presence of magnesium ions in the wastewater causes uncontrolled precipitation of the ammonium magnesium phosphate (struvite) in the digestate discharging pipes. Under such circumstances, numerous operational problems, such as pipe obstructions, valve immobilization, increased hydraulic losses and thus increased operating costs in the WWTP. Struvite precipitated in a controlled manner from post-fermentation effluent through the addition of magnesium compounds (in a reactor adapted for this) protects the biological part of the WWTP against the occurrence of the above mentioned negative phenomena.

In wastewater treatment plants controlled phosphorus precipitation in the form of struvite, which is a compound with very good fertilizing properties, is increasingly used [3]. The applied struvite precipitation technologies allow for 90% reduction of phosphorus and 40% nitrogen reduction in leachate [4,5]. The resulting product is characterized by a high degree of purity. It is devoid of a significant part of harmful organic micro-contaminants (i.e. pharmaceuticals, personal care products, etc.) present in the leachate [6,7]. The advantages of struvite also includes the fact that crystallizing does not bind heavy metals present in the solution. Crystallization of struvite is an ecological process that removes and allows recovery of phosphorus and nitrogen from wastewater. Due to the content of two nutrients and slow release into the soil, precipitated crystals have very desirable fertilizing properties. For many plants, it is profitable that it also contains magnesium. For this reason, a number of technologies have been developed to recover struvite from phosphorus and nitrogen rich sewage streams (e.g. liquid manure, post-fermentation leachate) [4,8]. Struvite obtained using advanced technologies, produced as a fertilizer on an industrial scale, takes the form of several millimeter pellets. This form is enabled by long-lasting, cyclic precipitation of struvite in the reactor, allowing the crystals to merge into larger agglomerations [9,10]. The disadvantage of available industrial technologies is the high cost of installation. They also require high leachate flows and therefore are not profitable for small and medium WWTPs. Despite the range of technologies available, the struvite precipitation method is not applicable in many countries. The reasons for the lack of native technology should be seen in the lack of legal regulations regarding the management of generated waste, lack of economic studies and the absence of full analysis needed for process description.

The struvite precipitation from a solution is influenced by a number of factors such as pH, of phosphate, magnesium and ammonium ions concentrations, as well as the presence of the other ions constituting impurities (e.g. Ca²⁺, Na⁺, SO₄²⁻). They significantly affect the homogeneity and structure of the obtained crystals [4,11]. The pH range from 7.5 to 9.5 is recommended for struvite precipitation [12]. In neutral medium (pH from 7 to 7.5), typical for post-fermentation leachate, in addition to struvite, other less favourable phosphorus compounds may precipitate [13,14]. Leachate alkalization is associated with a significant increase in the costs of the phosphorus removal process and also with the need to use concentrated solutions, e.g. NaOH. From an economic point of view, it is important to use a magnesium-containing reagent for the precipitation of struvite that is cheap and at the same time ensures high process efficiency. The cost of magnesium salt should be lower than the cost of iron coagulants, so that it becomes competitive with preparations commonly used in sewage treatment plants. The most commonly used magnesium source is MgCl₂, MgO or Mg(OH)₂ [15]. It is possible to use cheap substances such as magnesium chloride-rich waste generated during the exploitation of some halite - rock salt deposits [16,17]. The efficiency of the phosphate ion binding process in the form of struvite and the degree of purity of the obtained product also depends on the molar ratio of [Mg²⁺] : [NH₄⁺] : [PO₄³⁻]. However, these parameters are difficult to control, because in leachate
mentioned proportions change dynamically, depending on the fermentation chamber feed, especially if sludge co-fermentation with organic waste is carried out in the WWTP.

The low-cost solution leading to the reduction and recovery of nutrients from wastewater, which does not require expensive installations, is proposed in this work. The assumption is to precipitate struvite in the form of aqueous sediment, and then utilize it by mixing with the compost produced in WWTP from fermented sludge. A number of parameters published in the literature ensuring the efficiency of struvite precipitation is based on studies using synthetic wastewater. The results obtained in the laboratory are significantly modified after the application of a specific technology. For this reason, the research have been conducted in the pilot-scale reactor using the leachate acquired directly from the fermentation chambers of the WWTP.

2. Materials and methods

2.1. Struvite precipitation – tests in the pilot-scale reactor

The horizontal 150 dm$^3$ pilot-scale reactor, equipped with a mixer and a screw conveyor for removing sludge was constructed for the purposes of the research [Figure 1]. The reactor is similar to a sand scrubber, where struvite crystals settle at the bottom of the reactor, from where they are discharged in the form of sludge. In each test series, the reactor was cyclically filled with digestate. Five struvite precipitation series, three for leachates without pH correction (Series 1-3) and two for leachates alkalized with 4M NaOH to pH = 8.5 (Series 4 and 5), were performed. Each series consisted of 6 cycles of reactor filling and struvite precipitation, after which the sludge deposited in the reactor was discharged. The cycle consisted of 30 minutes of reaction, during which the reagents were mixed, and 30 minutes of struvite sedimentation. A saturated road salt solution containing MgCl$_2$ was used as the precipitation agent. Phosphate phosphorus (PO$_4$-P) content in initial leachate, after the first precipitation cycle and in the total leachate from the whole series after 24 hours was tested for each series.

![Figure 1. Pilot-scale reactor for struvite precipitation](image)

2.2. Laboratory tests

The optimal reaction time of struvite precipitation from leachate was determined on the basis of tests conducted in laboratory conditions, in a reactor with a capacity of 1 dm$^3$. After 30 min of mixing the
leachate with precipitant, the content of phosphate phosphorus (PO$_4$-P) in the supernatant liquid was measured. The measurement was made after 0.5 h; 1h, 2h and 24 hours from the start of the reaction. The concentrations of ammonium and phosphates were measured in commercial Merck tests (Spectroquant® 114752; 114542 114729 and 114543, respectively). All colorimetric analyses were performed using a Spectroquant Vega 400 spectrophotometer (Merck). The magnesium content in the saturated road salt solution was determined by titrating the solution with EDTA.

The hydrated struvite sludge obtained in the reactor, after drying at T = 105 °C, was examined for the content of: dry mass (d.m.) volatile suspended solids (VSS), total phosphorus (Pog), ammonia nitrogen (N-NH$_4$) and total nitrogen (Nog) and metal content (Mg, Ca, Cr, Zn, Cd, Cu, Ni, Pb). The tests were carried out in the laboratory accredited within physical and chemical tests of wastewaster and sewage sludge. Microscopic examination of the struvite crystals was performed in an optical microscope Nikon Alphaphot-2YS2 at magnification and 1: 160 and 1:400. The sedimentation time, in the Imhoff cone, was made for: 1) sand with grain size of 0.1 mm, 2) primary sludge, 3) struvite crystals obtained from leachate.

3. Results and discussion

The conditions for struvite precipitation in the reactor were determined. For this purpose, the struvite sedimentation time and phosphate content in the supernatant liquid were measured. The study of the struvite settling in the Imhoff cone showed that the minimum time allowing the majority of precipitated struvite to settle down is 0.5 h. The results of previous research have shown that in order to precipitate struvite from an aqueous solution, enriched by phosphate and ammonium salts, such conditions should be fulfilled: pH in the range from 8.5 to 9.5, PO$_4$-P content higher than 200 g / m$^3$ and twice excess ammonium nitrogen content in relation to phosphate phosphorous content are preferred [17]. The reaction time of struvite precipitation from aqueous solutions extended from 1h to 24h resulted in an increase in the reduction of phosphorus compounds (by about 10%).

The tests were repeated, replacing the aqueous solutions with real leachate. The laboratory tests of phosphorus removal from the leachate showed that the optimal time for the process of struvite precipitation is 1 hour. Shorter time does not allow effective phosphorus removal, while extending the reaction time to 2 hours does not significantly increase phosphorus reduction in the leachate. The struvite precipitation cycle can be completed one hour after the start of the reaction applying a half hour mixing time of the reagents followed by a half hour settling time. The struvite precipitation tests in the reactor were carried out for leachate without alkalization (pH = 7.5) (Series 1-3) and for leachate after pH correction to 8.5 (Series 4 and 5). Neutralization of the leachate to the optimum struvite reaction (pH = 9.5) increases the operating costs of the treatment plant and requires the use of a large amount of aggressive reagent (4M NaOH) while the yield increases by only about 10% compared to the yield obtained at pH 8.5. For this reason, tests for high pH values have been dropped.

Percentage analysis of the solution used in the study showed that it contains 12% (by weight) of magnesium. Based on previous studies [17], it is proved that this solution added in an amount of 2.5 dm$^3$ to 1m$^3$ of leachate effectively precipitates phosphates. At this stage of research, this dose of magnesium salt was used. The magnesium content in the solution after the struvite precipitation was not determined. Tests carried out in the model reactor show that under the assumed conditions of struvite precipitation, at least 80% of the phosphates contained in the solution are removed (Table 1). The exception is the test in which the low initial concentration of phosphate ions in the leachate was noted (Series 2). This confirms earlier observations that high phosphate concentration in leachate is one of the key conditions for the profitability of phosphorus removal by struvite precipitation.
Table 1. The phosphorous (PO₄-P) reduction in investigated leachates – tests in the reactor.

| SERIE | Leachate parameters | Reaction parameters | Reduction PO₄-P [%] |
|-------|---------------------|---------------------|---------------------|
|       | pH                  | PO₄-P [g/m³]        | NH₄-N [g/m³]        | pH after 1 h | after 24 h |
| 1     | 7.5                 | 247                 | 440                 | 7.5         | 81         | 79         |
| 2     | 7.4                 | 128                 | 400                 | 7.4         | 63         | 59         |
| 3     | 7.5                 | 215                 | 440                 | 7.5         | 80         | 67         |
| 4     | 7.5                 | 220                 | 410                 | 8.5         | 90         | 91         |
| 5     | 7.5                 | 282                 | 440                 | 8.5         | 93         | 90         |

The struvite removed from the reactor is the fine crystalline precipitate with a high degree of hydration (85%). Some of the crystals remain on the walls and reactor stirrer. Designing a full-size device the need to remove deposits should be taken into account. Steel with increased corrosion resistance should be used for its construction. It is advisable to leave some struvite crystals in the reactor after each cycle (about 1/3 of the obtained product) to facilitate crystallization during subsequent fillings. An average of 0.45 kg of dry struvite mass (approximately 3 kg of hydrated sediment) was obtained for each cubic meter of leachate tested (excluding series 2). This is 50% of the amount of struvite that results from theoretical calculations. Low efficiency results from the need to leave some of the sludge in the reactor and the presence of other phosphorus compounds in the crystalline sediment. Figure 2 shows the forms of struvite obtained after drying of the deposits discharged from the reactor.

![Figure 2](image)

The structure of struvite does not show significant differences depending on reaction pH. For both pH values, the struvite after drying (at 105° C) is in the form of fine crystalline dust (Fig. 2 a, b).
Microscopic images (2 c, d, e) show a significant content of organic matter in struvite crystals, especially when they are precipitated without pH correction (pH = 7.5). The crystals obtained at lower pH had a larger size (in the range of 0.03mm to 0.2mm). The presence of organic matter in the struvite is confirmed by the results of the chemical composition analysis of the obtained sediments (see Table 2).

Table 2. The results of chemical analysis of struvite sediments precipitated in reactor.

| SERIE | VSS [% d.m.] | Pog [% d.m.] | Nog [% d.m.] | NH4-N [% d.m.] | Mg [% d.m.] | Ca [g/kg d.m.] | Cu [g/kg d.m.] | Cr [g/kg d.m.] | Zn [g/kg d.m.] | Ni [g/kg d.m.] | Pb [g/kg d.m.] | Cd [g/kg d.m.] |
|-------|-------------|-------------|-------------|---------------|------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1,3   | 23.7        | 42.4        | 8.4         | 3.15          | 15         | 1.1            | 8.0           | 62            | 20            | 24            | 5.3           | 0.62          |
| 4,5   | 26.5        | 35.5        | 7.1         | 1.22          | 13         | 1.9            | 8.5           | 43            | 63            | 17            | 30            | 3.54          |

The fermentation sludge residue constitute about 25% of the dry weight of the resulting struvite sediment. Some organic particles are embedded in struvite crystals. The content of heavy metals in obtained struvite is comparable with results reported in the literature [9]. The heavy metal content in struvite is similar to the values determined in the fermentation sludge when it is precipitated from leachate with a pH of 7.5. Crystallization at a higher pH causes a partial purification of the struvite crystals from their admixture. The precipitates also have a high phosphorus content. The weight ratio between the elements forming dehydrated struvite (MgNH4PO4), resulting from the molecular weight of this compound, should be N: Mg: P = 1: 1.7: 2.2, respectively. In the obtained sediments the proportion between nitrogen and magnesium is maintained, whereas phosphorus content is twice as much as indicated by the chemical composition. Some phosphorus may come from organic matter, however, this result indicates that other phosphorus compounds (e.g. calcium phosphate) precipitate with struvite.

Drying and separating the precipitated struvite from organic contaminants and possible further actions leading to its utilization as a pure agricultural fertilizer would involve a high processing cost. In the case of WWTP utilizing post-fermentation sludge by compost production, struvite obtained in the form of hydrated waste salt can be utilized by mixing it with digestion sludge intended for composting. In the compost pile, phosphorus is present in the form of various organic and mineral fractions. The largest amount of this element is found in organic particles of digestate and in mineral deposits from phosphate precipitation with iron compounds. Precipitating part of the phosphorus with magnesium salt the amount of iron salt used is reduced. Thus the percentage of practically insoluble iron phosphate in the fertilizer is limited. Studies have shown that mixing 100g (d.m.) of struvite precipitated from leachate with 10kg (d.m.) of compost produced in WWTP caused an increase in phosphorus and nitrogen content of 13% and 2.7%, respectively to the initial values (the compost used was characterized by parameters: d.m. = 40 %, VSS = 57%, Pog = 2.5% and N og = 3.2%). It should be mentioned that the content of metals determined in struvite sludge does not exceed the values allowed for organic compost. Thus, mixing the sludge containing struvite with the material intended for the composting in the WWTP will increase its fertilizer value.

Typical devices designed for the treatment plant can be adapted as a struvite precipitation reactor to reduce the production costs of the installation. For this purpose, the sedimentation times of different substances were compared in the Imhoff cone: fine crystalline struvite, sand particles and flocs of the primary sludge. The relationship: 2min. / 4min. / 30min. was obtained, respectively for particles: sand / struvite / primary sludge. This measurement is helpful in estimating the size of the reactor settling tank and the hydraulic load calculation for the struvite precipitation reactor. In this reactor, to avoid sedimentation of organic matter present in the leachate, there should be so-called turbulent movement.
Assuming a load of WWTP as 50,000 People Equivalent, the volume of the struvite precipitation reactor should not exceed 20 m$^3$. The reactor should be equipped with a funnel for precipitation of struvite and automatic systems for: pH adjustment, dosing magnesium salts and removing struvite. Steel with increased corrosion resistance should be used for their construction.

4. Summary
The method used enables a 90% reduction of phosphorus from leachate and reduces the load on the biological part of the sewage treatment plant by increasing nitrogen throughput. The pH of leachate introduced into the reactor, must be constantly controlled and adjusted by dosing the NaOH solution (to optimal pH range 7.5 - 9.5). The effluents should contain at least 200 mg / dm$^3$ phosphorus in the form of phosphate (P-PO$_4$) and twice the nitrogen value in the form of ammonium ion (N-NH$_4$). After stabilizing the pH, the solution of the magnesium salt is dosed to the leachate with stirring (the magnesium content should be adjusted depending on the expected concentration of phosphates) to obtain magnesium ammonium phosphate (struvite). For the proposed cyclic reactor, a 30-minute mixing period and a 30-minute crystal sedimentation time can be assumed. The resulting struvite crystals (size 0.03 - 0.2 mm) drop by gravity to the bottom of the reactor. Approximately 20-30% of the obtained crystals should be left in the reactor as nuclei in the next batch of leachate in order to facilitate crystallization. The obtained struvite crystals can be removed from the reactor as hydrated sediment. The struvite takes up a small volume and can be removed periodically, every few months. The upper layer should be drained continuously or cyclically (depending on the type of the reactor). The obtained sediment can be mixed with compost or drained and granulated.

The struvite precipitation process is very fast, therefore the retention time in the tank could be shortened to 1-1.5 hours. The proposed method allows not only to remove nutrients from wastewater, but also to recover them in the form of a compound with very desirable fertilizing properties. Struvite is precipitated using cheap waste material (magnesium salt), which allows to minimise the use of ferric coagulant for this purpose. Removing part of the nitrogen from the biological part of WWTP is associated with a significant reduction in energy consumed for its oxidation. Phosphorus compounds co-precipitating along with struvite at low pH (e.g. CaPO$_4$, MgHPO$_4$), despite the fact that they do not have such favourable fertilizing properties as struvite, are an environmentally more beneficial form of phosphorus than the currently formed iron phosphate.

The presented studies are of preliminary nature. The development of a technology that could be implemented in WWTP requires extended analyzes, including the selection of magnesium dose, so that it does not remain in the solution discharged from the reactor. It should also specify where in the WWTP process line the installation should be located to ensure the highest efficiency of phosphorus removal and reduce the side effects of the process. The proposed technology requires individual adaptation to each wastewater treatment plant. The dimensions of the reactor and its operation depend on the effluent parameters and WWTP capacity. Systematic measurement of PO$_4$-P and NH$_4$-N content in leachate is also required, as these are variable values. Moreover, the proposed method of struvite precipitation is possible to use in all facilities containing concentrated sewage, ammonium nitrogen and phosphates, such as municipal landfills, lagoons with liquid manure, fermentation chambers and composting plants.

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