Inżynieria i Ochrona Środowiska 2018, 21(2), 183-190
Engineering and Protection of Environment
https://ios.is.pcz.pl/

p-ISSN 1505-3695
e-ISSN 2391-7253
DOI: 10.17512/ios.2018.2.6

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Precipitation of Sediments Containing Struvite from Supernatant Liquid

Wytrącanie osadów zawierających struwit z cieczy nadosadowej

Sewage sludge management is a problem that remains topical, with particular emphasis placed on preventing its storage. One of the possibilities of using sewage sludge is recovery of biogenic elements: phosphorus and nitrogen. Municipal sewage sludge may contain significant amounts of phosphorus compounds. According to different sources, the content of phosphorus in dry mass of sewage sludge sources ranges from 2.62% (for dewatered sewage sludge) to 7.6% (for dried sewage sludge). The most favourable forms of phosphorus that are bioavailable to plants are calcium phosphates and struvite $(NH_4)Mg[PO_4]\cdot 6H_2O$. Struvite crystals contain two important macroelements necessary for the growth and development of plants: phosphorus and nitrogen. Phosphorus compounds in struvite, with content of 58% (P_2O_5), are released into soil solution gradually. For economic reasons, the technologies of struvite recovery from sewage sludge are not yet widely used while research studies are aimed to optimize the process of its precipitation.

The aim of the present study was to determine the most favourable concentrations of Mg^{2+}, NH_4^+ ions needed to precipitate sediments containing struvite. The research consisted in the precipitation of struvite sediments from the supernatant liquid of digested sewage sludge. The tests were performed at variable ion concentrations: Mg^{2+} in the form of a solution of $MgSO_4\cdot 6H_2O$, ions of NH_4^+ in the form of NH_4Cl. The solutions were made using distilled water. A constant pH = 9 was maintained, whereas the reaction temperature was 20÷22°C. The highest mass (6.43 g/250 ml of the supernatant liquid) of precipitates was obtained for concentrations of 150 mg NH_4^+/dm^3 and 60 mg Mg^{2+}/dm^3.

Keywords: **phosphorus, struvite, sewage sludge, sewage sludge management**

Introduction

Technological advances and increasing population lead to an increasing amount of sewage produced, and, consequently, sewage sludge. Consequently sewage sludge management is becoming an important problem that has to be addressed [1]. It is estimated that about 20% of sludge is reused in agriculture [2]. The factor limiting the use of sewage sludge in nature or agriculture is the increased content of heavy metals and pathogens [1]. One alternative to sewage sludge management is offered by recovery of biogenic elements. Table 1 shows the content of total nitrogen and total phosphorus in various types of sewage sludge.

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Table 1. **Selected parameters of individual types of sewage sludge [3]**

Parameters/ unit	Sludge type				
	Raw		Digested		
	From mechanical treatment	Biological	Poor	Medium	Very well
pH	5÷7	6÷7	6.5÷7	6.8÷7	7.4÷7.8
Total nitrogen % N in d.m.	2÷7	1.5÷5.0	1÷5	1÷3.5	0.5÷2.5
Total phosphorus % P in d.m.	0.4÷3	0.0÷1.5	0.3÷0.8	0.3÷0.8	0.3÷0.8

The most beneficial forms of phosphorus which are bioavailable for plants as fertilizers are calcium phosphates and struvite $(NH_4)Mg[PO_4]\cdot 6H_2O$, containing 58% of P_2O_5. Struvite was discovered in 1845. It is a mineral containing phosphate, ammonium and magnesium ions in its composition. It is characterized by a transparent/semi-transparent white colour with a glassy gloss. The Mohs hardness is 2. The reaction (1) presents obtaining of the compound [1]:

$$Mg + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4\cdot 6H_2O \qquad (1)$$

The use of struvite as a granular fertilizer seems to be environmentally friendly due to its low solubility. However, recovery technologies for this mineral are not yet widely used for economic reasons. There are ongoing studies aimed to optimize the process of struvite precipitation [3, 4].

Struvite sediments may precipitate in sewage treatment plants. Anaerobic conditions, especially those observed in pipelines and devices that are installed after the fermentation chamber, are particularly favourable for struvite precipitation [5]. In addition, struvite may be present in sludge from animal production (anaerobic fermentation) and in agricultural waste after biological treatment. The process of precipitation of struvite deposits is influenced by: pH, temperature, and concentration of ammonium and phosphate ions in the solution. In addition, mole ratio of magnesium, ammonium and phosphate ions required for the formation of struvite is: 1 mole Mg^{2+}, 1 mole NH_4^+: and 1 mole (PO_4^{3-}). Table 2 presents factors affecting the process of struvite precipitation.

Table 2. **Factors affecting precipitation of struvite sediments [6]**

pH < 7	•**no precipitation**
increased temperature	•**$MgHPO_4\cdot 3H_2O$**
pH > 10	•**$Mg_3(PO_4)_2\cdot 4H_2O$**
pH > 10 excess of Mg^2	•**$Mg(OH)_2$**
excess of NH_4^+	•**$MgNH_4PO_4\cdot 6H_2O$**
excess of PO_4^{3-}	•**$MgNH_4PO_4\cdot 6H_2O$ and other phosphates**

The aim of the research was to determine the most favourable concentration of Mg^{2+}, NH_4^+ ions needed to precipitate sediments containing struvite.

1. Material and methods

1.1. Research procedure

The research consisted in the precipitation of struvite from supernatant liquid of digested sewage sludge. The digested sludge was centrifuged, whereas further examinations were performed for supernatant liquid (solution above the sludge). The salt solutions used in the study ($MgSO_4 \cdot 6H_2O$, NH_4Cl) were prepared based on distilled water. The tests were performed for Mg^{2+} (20, 30, 40, 60, 80 mg/dm^3) and NH_4^+ ion concentrations (100, 150, 200 mg/dm^3). The same reaction conditions were maintained during the experiment: temperature of 20÷22°C and constant pH = 9. The pH value was determined based on literature data which shows that precipitation of struvite sediments can be observed over a wide range of concentrations of ammonium and phosphate ions at a given concentration of magnesium ions [7, 8]. Figure 1 shows the experimental design used in the present study.

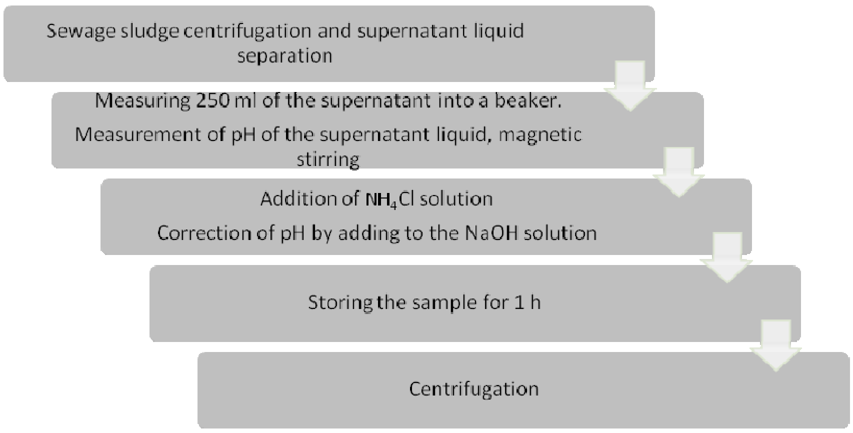

Fig. 1. Experimental design

1.1.1. Physicochemical analyses

The following physicochemical indices were determined: dry matter [9], ammonium nitrogen concentration [10], concentration of: total phosphorus, phosphates [10] and available phosphorus [11], total organic carbon [10], heavy metals concentration [12] using ICP-Mass Spectrometry (Optima 200 DV), and pH [13]. An XRD X-ray diffractometer (Bruker D8 Advance) was used to examine composition of precipitated deposits. All analyses were performed in triplicate. The results are presented in tables and figures as arithmetic means with standard deviations.

1.2. Substrates for testing

The substrate used for testing was digested sewage sludge from the WARTA municipal sewage treatment plant in Częstochowa, Poland. Table 3 presents a general characterization of digested sewage sludge used in the study.

Table 3. **Results of the physicochemical analysis of the substrate**

Index		Unit	Result
Dry matter		%	2.6 ±0.14
Residue on ignition		%	1.6 ±0.12
Loss on ignition		%	1 ±0.12
Water content		%	97.4 ±0.14
Ammonium nitrogen		mg/dm^3	770 ±1.41
Phosphates PO_4^{3-}		mg/dm^3	48.7 ±0.21
Total phosphorus		mg/dm^3	35.9 ±0.21
Available phosphorus		mg/dm^3	30.1 ±0.18
Total organic carbon		mg/dm^3	240.47 ±0.15
Heavy metals	Cadmium (Cd)	mg/kg	0.18 ±0.02
	Chromium (Cr)	mg/kg	5.88 ±0.05
	Copper (Cu)	mg/kg	4.54 ±0.02
	Nickel (Ni)	mg/kg	4.59 ±0.02
	Lead (Pb)	mg/kg	2.18 ±0.23
	Zinc (Zn)	mg/kg	27.9 ±0.24
	Calcium (Ca)	mg/kg	5799.5 ±0.20
pH		–	7.5

The content of dry matter in sediments was 2.6%, of which ca. 60% were mineral substances. A pH value of 7.5 indicates a well-stabilized test substrate. The content of phosphorus in the form of phosphates in the supernatant liquid of the substrate was 49 mg PO_4^{3-}/dm^3. The content of heavy metals did not exceed the standards contained in the Regulation of the Minister of the Environment as of 6 February 2015 on municipal sewage sludge, item 257 [14]. The risk of presence of the substances interfering with the process of struvite formation declines with the decreasing amount of metals in the substrate. Calcium content in the substrate has an effect on the struvite precipitation process. At a specific pH, its high concentrations can lead to precipitation of calcium hydrogen phosphates.

2. Results and discussion

2.1. Sludge precipitation

Table 4 shows the effect of NH_4^+ and Mg^{2+} ion concentrations in precipitation solutions on the amount of sediments obtained from 250 ml of supernatant liquid.

Table 4. **Mass of precipitated sediments [g] at varying concentrations of NH_4^+ and Mg^{2+}**

Mg^{2+} [mg/dm^3]	NH_4^+ [mg/dm^3]	Sediment mass [g]
20	100	3.287
	150	**4.397**
	200	3.903
30	100	3.845
	150	**4.098**
	200	3.244
40	100	5.134
	150	**5.980**
	200	5.251
60	100	5.325
	150	**6.433**
	200	4.046
80	100	4.948
	150	**6.258**
	200	3.878

The highest efficiency was obtained for the concentration of ammonium ions of 150 mg NH_4^+/dm^3 regardless of the change in the concentration of magnesium ions. Figure 2 shows changes in the mass of obtained sediments in relation to the change in the variable concentration of magnesium ions.

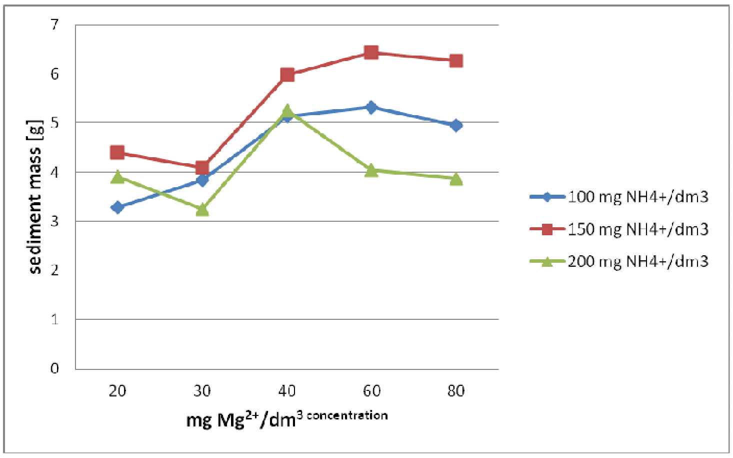

Fig. 2. Change in the mass of precipitated sediment vs. the change in the concentration of Mg^{2+} and mg NH_4^+/dm^3 ions

The results lead to the conclusion that the concentration of Mg^{2+} ions of 60 mg/dm^3 was the most favourable since the highest mass of sediments was obtained: 5.33 g. A test with concentration of 80 mg Mg^{2+}/dm^3 was performed to verify whether higher concentration of Mg^{2+} would lead to the increase in mass. The test showed that the increase in the concentration of these ions in the solution did not improve the precipitation process. At concentrations of 100 mg NH_4^+/dm^3 and 80 mg Mg^{2+}/dm^3, the mass of ammonium magnesium phosphate began to decrease insignificantly. With the concentration of ammonium ions of up to 150 mg/dm^3 and the concentration of 100 mg of NH_4^+/dm^3, sediment mass increased to 60 mg NH_4^+/dm^3, reaching its maximum at 6.26 g. After exceeding the concentration of 60 mg Mg^{2+}/dm^3, a decrease in the mass of precipitated sediments was observed. Distribution of mass of precipitates for the concentration of ammonium ions of 200 mg NH_4^+/dm^3 is similar to the previous cases. A significant decline in mass was found for the concentration of Mg^{2+} ions of 30 mg/dm^3. An increase to 40 mg Mg^{2+}/dm^3 was observed, followed by a decrease in the precipitated mass of sediments. Excessive concentration of magnesium ions did lead to the increase in the mass of precipitated sediments.

2.2. Analysis of the composition of precipitated sediments

The sediments precipitated from the supernatant liquid were characterized by a large variety of composition. The XRD analysis revealed presence of calcium compounds in precipitates. However, the atomic percent of connections, including struvite, is small and amounts to less than 0.9% for supernatant liquor of the sewage sludge. Furthermore, the study revealed the presence of calcium, zinc and magnesium oxides (with their content of less than 1%) and metal salts. This analysis did not provide unambiguous information about the composition of the precipitates.

Spectra obtained during tests showed that sediments precipitating in wastewater treatment plants commonly termed struvite are actually a mixture of various compounds, which consist of ions present in solutions [9, 10]. Given that the composition of the supernatant liquid is very diverse and varies over time, deposits are characterized by significantly different compositions. The literature data show that an increase in the efficiency of recovery of the compound can be achieved by sequential extraction and struvite precipitation [11].

Summary and conclusions

The study presents the results of the precipitation tests for phosphorus compounds in the form of struvite from the supernatant liquid from digested sewage sludge. The findings of the study lead to the following conclusions:

1. Precipitation of phosphorus compounds in the form of struvite from sewage sludge represents an alternative method of reuse of supernatant liquor from sewage sludge digestion process. The products obtained can be used as fertilizers.
2. During precipitation of sediments from supernatant liquor from digested sewage sludge, the highest yield (6.43 g/250 ml of supernatant) was found for ion configuration of Mg^{2+}: 60 mg/dm^3, and NH_4^+: 150 mg/dm^3. Further increase in ion

concentration to 80 mg Mg^{2+}/dm^3 and 200 mg NH_4^+/dm^3 in the solution did not improve the efficiency of sediment precipitation.

3. The composition of the precipitated sediments was very diverse, with the struvite content of 0.9%. Furthermore, the XRD analysis revealed the content of calcium, magnesium and zinc compounds in the form of oxides and metal salts (calcium phosphates). The obtained results confirmed that sequential extraction is needed to increase the efficiency of struvite recovery from the supernatant liquid.

Acknowledgements

The research was financed by the project No. BS/MN-401-310/17.

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Streszczenie

Zagospodarowanie osadów ściekowych jest tematem wciąż aktualnym, szczególny nacisk kładzie się na przeciwdziałanie ich składowaniu. Jedną z możliwości zagospodarowania

osadów ściekowych jest odzysk pierwiastków biogennych: fosforu i azotu. Komunalne osady ściekowe mogą zawierać znaczne ilości związków fosforu. Zawartość fosforu w suchej masie osadów ściekowych według różnych źródeł mieści się w zakresie od 2,62% (dla odwodnionych osadów ściekowych) do 7,6% (dla suszonych osadów ściekowych). Najkorzystniejszymi formami fosforu biodostępnymi dla roślin są fosforany wapnia oraz struwit $(NH_4)Mg[PO_4]\cdot 6H_2O$. Kryształy struwitu zawierają dwa ważne makroelementy niezbędne dla wzrostu oraz rozwoju roślin, tj. fosfor oraz azot. Związki fosforu w struwicie, stanowiące 58% (P_2O_5), uwalniane są do roztworu glebowego stopniowo. Ze względów ekonomicznych technologie odzysku struwitu z osadów ściekowych nie są jeszcze powszechnie stosowane, a prowadzone badania mają na celu zoptymalizowanie procesu jego wytrącania.

Celem badań było określenie najkorzystniejszego stężenia jonów Mg^{2+}, NH_4^+ niezbędnych do wytrącenia osadów zawierających struwit. Przeprowadzone badania polegały na wytrącaniu osadów struwitu z cieczy nadosadowej przefermentowanych osadów ściekowych. W badaniach zastosowano roztwory o zmiennym stężeniu jonów: Mg^{2+} w postaci roztworu $MgSO_4\cdot 6H_2O$, jonów NH_4^+ w postaci NH_4Cl. Roztwory sporządzono, wykorzystując wodę destylowaną. Utrzymywano stałą wartość pH = 9 oraz temperaturę reakcji wynoszącą 20÷22°C. Na podstawie przeprowadzonych badań największą masę (6,43 g na 250 ml cieczy nadosadowej) wytrąconych osadów uzyskano dla stężeń 150 mg NH_4^+/dm^3 i 60 mg Mg^{2+}/dm^3.

Słowa kluczowe: fosfor, struwit, osady ściekowe, zagospodarowanie osadów ściekowych