

TREATMENT OF HIGH-STRENGTH WASTEWATER
FROM AMMONIUM AND PHOSPHATE IONS
WITH THE OBTAINING OF STRUVITE*Yurii Tulaydan¹, Myroslav Malovanyy¹, Viktoria Kochubei¹*, Halyna Sakalova¹*

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Abstract. This work reviews the main methods of nitrogen and phosphorus removal from wastewater. The method of simultaneous removal of highly concentrated nitrogen and phosphorus was analyzed by physical and chemical precipitation, forming struvite, a by-product of magnesium ammonium orthophosphate hexahydrate. Laboratory investigations were conducted on the test solutions with the concentrations of ammonium nitrogen, phosphates, ions of magnesium and calcium corresponding to the ones of relevant elements in wastewater of swine complexes located in Lviv region, Ukraine. The analyses were done at various molar ratios of magnesium and phosphate ions and at various pH values. The comparative thermal analysis of chemical precipitation products and pure struvite was performed. The optimal conditions were identified to experience the maximum efficiency of simultaneous removal of ammonium nitrogen and phosphate ions from wastewater, forming $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Recommendations on the use of the obtained product as a fertilizer were elaborated.

Keywords: nitrogen, phosphorus, physical and chemical precipitation of magnesium ammonium orthophosphate hexahydrate (struvite), fertilizer, thermal analysis.

1. Introduction

Excessive nitrogen and phosphorus that enters natural water bodies from wastewater can lead to eutrophication – a rapid growth of algae causing an imbalance in the ecological system of a water body [1].

In Ukraine, particularly in Lviv region, the largest sources of nitrogen and phosphorus pathways into surface water are agriculture (fertilizers, manure, sewage) [2], and municipal wastewater. Especially difficult is a situation requiring wastewater, having high concentration of

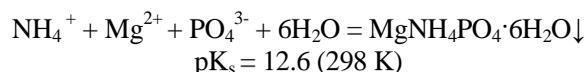
ammonium nitrogen, phosphates and organic matter from swine complexes equipped with wash water of manure disposal, to be discharged into open water bodies.

In view of a tendency for a sharp increase in the number of swine complexes, a burning question arises as to reduction of a load on the ecosystem by introducing new cost-effective technologies for wastewater treatment of nitrogen and phosphorus. At present a lot of methods for removing nutrients from wastewater are known. For removal of nitrogen compounds, most often a biological treatment method is employed [3], in which the extraction of free nitrogen is facilitated by bacteria. Wastewater treatment of phosphates requires both biological methods with the use of phosphate-accumulating organisms and non-biological methods, including precipitation, coagulation, flocculation, and separation [3-4].

Despite their widespread application, the methods described have certain disadvantages. Nutrient removal requires significant energy costs for bacterial viability. In the case of chemical precipitation of phosphates, inert compounds are formed with no further use.

In the recent years, the method of chemical precipitation for treating nitrogen and phosphorus-containing wastewater has been most widely used [5-11]. The product of precipitation is magnesium ammonium orthophosphate hexahydrate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite) [12]. Struvite is a soft crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations [13].

Magnesium ammonium orthophosphate hexahydrate forms according to the reaction shown below [14]:



Struvite is a soft mineral with Mohs hardness from 1.5 to 2 and low specific gravity of 1.7. It is readily soluble in acid [15].

Struvite can be used as a concentrated fertilizer containing three nutrients at the same time. Due to the presence of water-insoluble nitrogen, it is distinguished with its permanency. Magnesium ammonium orthophos-

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phate can be used for manufacturing foam extinguishers and in metal phosphate coating.

As the amount of swine complexes tends to increase in Ukraine, the purpose of the work has been to develop the method for treating high-strength wastewater from ammonium and phosphate ions with the obtaining of struvite. This was confirmed by performing the complex thermal analysis of precipitation products of test swine wastewaters.

2. Experimental

To maintain the experiment integrity, it was decided to conduct investigations on test solutions. This allowed eliminating the effect of suspended particles, organic matters, proteins, fat, and metal ions, which are present in the real-life piggery wastewaters, on struvite formation. A wastewater sample was taken in September 2015 from the drains of the two active pig farms located in Zolochiv district, Lviv region, Ukraine. As sampling was completed, the samples were stored at 280 K for 24 h in a 2 l glass vessel for the sedimentation of solid particles. After sedimentation, aliquots were collected at the top of the vessel and then passed through a vacuum filter. The analyses were made according to the procedures [16-18]. The analysis results are shown in Table 1.

A more detailed chemical analysis of wastewaters for the presence of other elements except Ca^{2+} ions was not conducted as their effect on struvite formation is negligible [16].

Swine wastewaters had a large excess of ammonium nitrogen while the content of Mg^{2+} ions was not enough for the formation of struvite. The Mg:P initial molar ratio of swine wastewater I was 0.94:1 and of swine wastewater II, 0.87:1.

For running the investigations, the test solutions were prepared, whose compositions corresponded to those of actual piggery wastewaters. Concentrated solutions, including ammonium chloride (NH_4Cl) with the $\text{NH}_4^+\text{-N}$ concentration of 5500 mg l^{-1} , sodium hydrogen phosphate (Na_2HPO_4) with the $\text{PO}_4^{3-}\text{-P}$ concentration of 9500 mg l^{-1} , magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) with the

Mg^{2+} concentration of 2400 mg l^{-1} , calcium chloride (CaCl_2) with the Ca^{2+} concentration of 2800 mg l^{-1} , were used for the preparation of the test solution. The standard solutions were prepared by using chemically pure reagents.

The investigations were carried out at a room temperature using the method of chemical precipitation. Precipitation was performed in 100 ml glass flasks. The solution of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) with the Mg^{2+} concentration of 2400 mg l^{-1} was used as precipitant. For identifying the optimal conditions of precipitation of ammonium nitrogen and phosphates, the investigations were performed at various Mg:P molar ratios of 1:1, 1.1:1, 1.2:1, 1.3:1, and 1.4:1 and at various pH 7, 8, 9, 10, 10.5, and 11 of the reaction mass which was determined by adding 10% NaOH. The pH of the reaction mass was measured through the pH meter Hach SensIon 2 electrode 51935-00.

The reaction mass was mixed at 350 rpm for a 1-minute period (rapid mixing, reaction time), then at 20 rpm for 30 min (slow mixing, formation of flocculi). The obtained suspension was sedimented for 1 h. After that, the suspension was filtered through a blue ribbon ashless filter. The resulting filtrate was analyzed on the content of residual ions using the photoelectrocolorimeter FEC-56 M according to the procedures for photometrical determination of ammonium ions by Nessler's reagent in wastewater (KND 211.1.4.030-95) [17] and photometrical determination of phosphate ions in wastewater (KND 211.1.4.030-95) [18]. The product of physical and chemical precipitation has been formed as fine solid-phase particles. It resembles a white finely dispersed powder. High dispersity of the product under investigation is ascribed to its precipitation conditions [19].

The thermal analysis of precipitation products was done on a Q-1500 D derivatograph of system F. Paulik, J. Paulik and L. Erdey by registration of both an analytical signal of mass loss and thermal effects *via* the computer. The samples were analyzed in a dynamic mode at the heating rate of 10 K/min up to 1073 K under atmosphere of air. The weight of the samples was equal to 200 mg. Al_2O_3 was used as a standard.

Table 1

Concentration of pollutants in wastewaters of the real-life pig farms

Name	pH	Mg^{2+} , mg l^{-1}	$\text{NH}_4^+\text{-N}$, mg l^{-1}	$\text{PO}_4^{3-}\text{-P}$, mg l^{-1}	Ca^{2+} , mg l^{-1}
Swine wastewater I	7.1	49.1	320.6	67.2	139
Swine wastewater II	6.9	54.3	180.4	79.1	146

3. Results and Discussion

3.1. Analysis of Chemical Precipitation Results

For the identification of optimal parameters of simultaneous removal of nitrogen and phosphorus from the test solutions, a series of investigations were undertaken at various values of pH and Mg:P molar ratios. The efficiency of nitrogen and phosphorus removal was established by the relation (1):

$$j = \frac{a_j - a_k}{a_j} \cdot 100\% \quad (1)$$

where a_j indicates the initial concentration of ions in water; a_k is the concentration of residual ions after the formation of struvite.

The objective of investigations was to identify conditions under which phosphate ions are maximally

removed from wastewaters, featuring simultaneous removal of a certain amount of NH_4^+ -N ions necessary for struvite formation. Wastewater containing NH_4^+ -N ions could be further treated with the use of biological methods.

As shown in Figs. 1-4, the experimental dependencies of residual ionic concentrations on pH solutions were obtained at various Mg:P molar ratios. For each cluster of points the polynomial trend lines were plotted, displaying the average residual ionic concentrations at different pH values.

The maximum efficiency of removing phosphate ions (96.6 %) from the test solutions A (Fig. 1) is observed at the pH of 9 and the Mg:P molar ratio of 1.4:1. During chemical precipitation, the PO_4^{3-} -P concentration is decreasing from an initial value of 67.2 $\text{mg}\cdot\text{l}^{-1}$ to the residual one of 2.3 $\text{mg}\cdot\text{l}^{-1}$.

The maximum efficiency of removing phosphate ions (94.7 %) from the test solutions B (Fig. 2) equals to the pH of 9 and the Mg:P molar ratio of 1.4:1. The PO_4^{3-} -P concentration during removal is dropping from 79.1 to 4.2 $\text{mg}\cdot\text{l}^{-1}$.

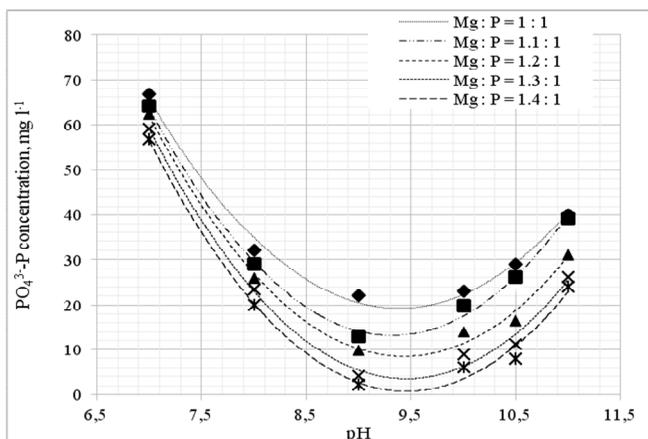


Fig. 1. Concentration of PO_4^{3-} -P after precipitation in the test solutions A (swine wastewater I) at various pH values

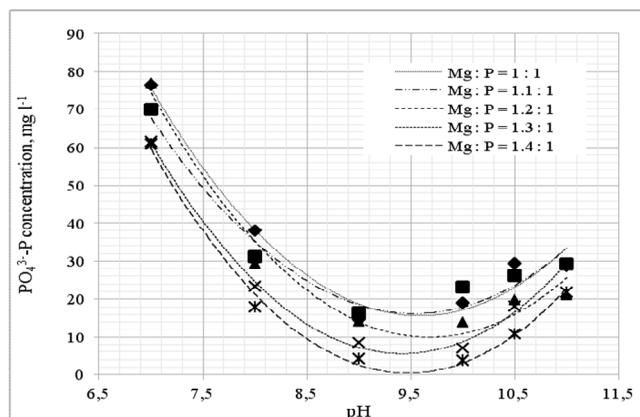


Fig. 2. Concentration of PO_4^{3-} -P after precipitation in the test solutions B (swine wastewater II) at various pH values

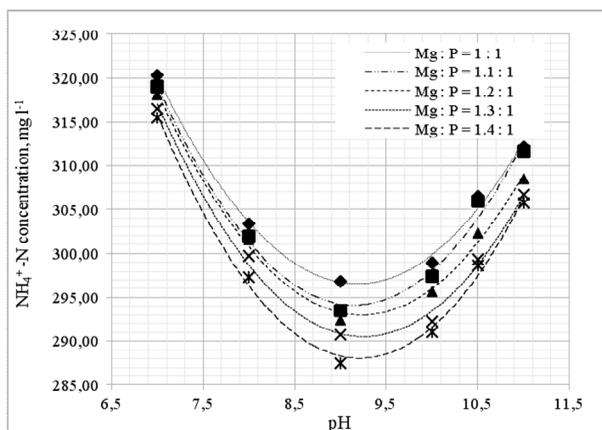


Fig. 3. Concentration of NH_4^+ -N after precipitation in the test solutions A (swine wastewater I) at various values of pH

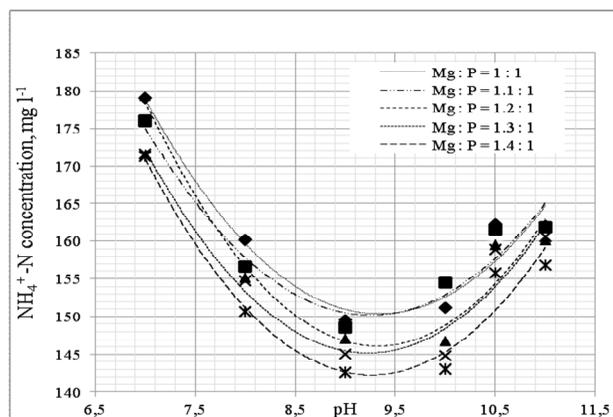


Fig. 4. Concentration of NH_4^+ -N after precipitation in the test solutions B (swine wastewater II) at various values of pH

The experimental data obtained reveal that the maximum removal of phosphate ions correlates with the pH of 9–10. A further increase in the alkalinity of a medium is not preferable. This can lead to the release of NH_3 known as air pollutant. Apart from this, highly alkaline wastewaters are not used as nitrogen-rich fertilizers for the irrigation of fields.

The increase in magnesium ions in the test solutions promotes a rise in PO_4^{3-} -P removal efficiency at any pH values. Thus, at the pH of 9 the increasing content of magnesium ions in the test solution A enables the residual ionic concentration to be decreased from 22.1 (Mg:P = 1:1) to 2.3 $\text{mg}\cdot\text{l}^{-1}$ (Mg:P = 1.4:1). The concentration of PO_4^{3-} -P in the test solution B at the pH of 9 appears to fall from 16.2 (Mg:P = 1:1) to 4.2 $\text{mg}\cdot\text{l}^{-1}$ (Mg:P = 1.4:1).

The increase in alkalinity and the content of magnesium ions similarly affects the removal of ammonium nitrogen from the test solutions. However, the removal efficiency of NH_4^+ -N at the pH of 9 and 10 is much lower than that of PO_4^{3-} -P at the same values of pH (Figs. 3 and 4). A reasonable explanation to this is a great excess of ammonium nitrogen with respect to phosphate ions in the initial test solutions.

The maximum recovery of ammonium nitrogen is achieved at the pH of 9 and the Mg:P ratio of 1.4:1. For the test solution A, it amounts to 10.3 % and for the test solution B – to 21 %. Hence, during chemical precipitation the concentration of NH_4^+ -N in the test solution A is decreasing from initial 320.6 $\text{mg}\cdot\text{l}^{-1}$ to remaining 287.5 $\text{mg}\cdot\text{l}^{-1}$ while in the test solution B – from initial 180.4 $\text{mg}\cdot\text{l}^{-1}$ to remaining 142.6 $\text{mg}\cdot\text{l}^{-1}$.

Hence, the objective set for the investigations is attained. The maximum removal of phosphate ions with the partial removal of NH_4^+ -N ions is achieved. Since the removal efficiency of ammonium nitrogen is quite low, it seems reasonable to use the proposed chemical precipitation technique in combination with other methods of wastewater treatment, for example with biological treatment. The application of biological wastewater treatment makes sense if the concentrations of ammonium nitrogen are less than 150 $\text{mg}\cdot\text{l}^{-1}$ [20]. As the NH_4^+ -N concentration increases, the rate of biochemical oxidation of pollutants is decreasing and biological treatment of wastewater in general is inhibited. That is why, when the initial concentration of NH_4^+ -N ions is over 150, these ions are additionally diluted with other domestic sewage prior to biological treatment in order to make NH_4^+ -N concentration lower than 150 $\text{mg}\cdot\text{l}^{-1}$.

The devised technique ensures more efficient (>94 %) simultaneous recovery of phosphate ions and less efficient (10–20 %) recovery of ammonium nitrogen. A greater amount of magnesium ions in the initial test

solution A in comparison with the initial test solution B gives rise to a more effective recovery of phosphate ions from this solution and produces better conditions for struvite formation. The maximum recovery of ammonium nitrogen and phosphate ions from the test solutions A and B is observed when the pH of 9–10 is reached, under which conditions struvite is minimally soluble.

The investigation results showed that the optimal Mg:P ratio for struvite formation is of 1.4:1 while struvite contains these elements in equal quantities. A required excess of Mg^{2+} ions can be explained by a possible occurrence of by-products from chemical precipitation in the presence of the ions in question, particularly of magnesium hydroxide.

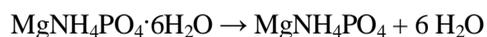
3.2. Thermal Analysis of Precipitation Products

For conducting the thermal analysis the chemical precipitation products of the test solution A were taken. They were produced under the most optimal conditions of struvite formation – at the Mg:P ratio of 1.4:1 and at various pH values of 7, 9, 10.

The differences in the chemical composition of the chemical precipitation products were confirmed by the investigation of their thermal stability, as compared to the stability of a chemically pure crystalline $\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.997 %).

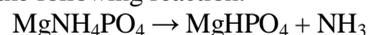
The thermogram recorded for a pure crystalline hydrate sample is depicted in Fig. 5. It includes the TG, DTG, and DTA curves. The TG and DTG curves represent the mass loss of the sample when heated and the rate of mass loss. The DTA curve refers to a variation in the temperature difference between the sample and the standard substance and describes the value and type of a thermal effect.

Thermolysis of the pure crystalline sample occurs in three stages. The first stage takes place in the temperature range of 293–473 K. It is accompanied by the intensive mass loss ($\Delta m = 44.02$ %), corresponding to the decomposition of six molecules of crystal-bonded water given by the reaction:



Within this temperature range the DTA curve exhibits the endothermic effect with the maximum at 422 K.

The second stage of thermolysis occurs in the temperature range of 473–608 K, followed by the appearance of the endothermic effect on the DTA curve with the maximum at 513 K. The weight loss ($\Delta m = 6.92$ %) at this stage is ascribed to the release of ammonium by the following reaction:



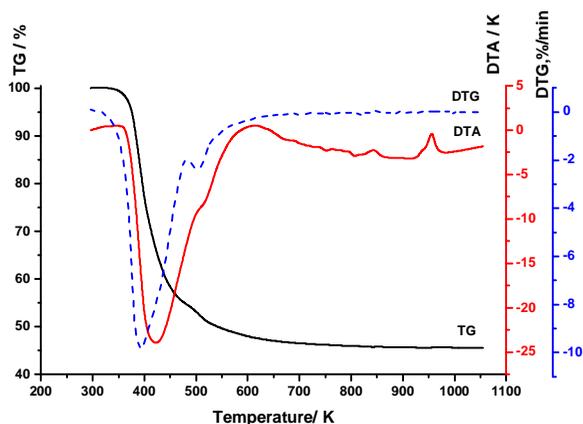


Fig. 5. Thermogram for pure crystalline hydrate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$

The third stage happens in the temperature region of 608–946 K, exhibiting the decomposition of hydrogen phosphate magnesium into pyrophosphate and water by the reaction:



This process is accompanied by a gradual weight loss ($\Delta m = 3.67\%$) and by the appearance of endothermic effect on the DTA curve. The total sample mass loss upon decomposition is 54.61%.

Figs. 6-7 show the comparison of thermogravimetric (TG) curves with that of differential thermogravimetric (DTG) of both chemical precipitation products at the pH = 7, pH = 9, pH = 10 and the sample of pure crystalline hydrate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Table 2 includes the results of the TG curves processing.

Table 2

Results of thermogravimetric analysis of the chemical precipitation products

Sample	Stage	Temperature range, K	Mass loss, %
pH = 7	I	293–473	43.24
	II	473–613	6.08
	III	613–913	2.65
	I–III	293–913	51.97
pH = 9	I	293–473	41.77
	II	473–633	9.06
	III	633–993	2.05
	I–III	293–993	52.88
pH = 10	I	293–493	42.66
	II	493–613	4.33
	III	613–913	1.73
	I–III	293–913	48.72

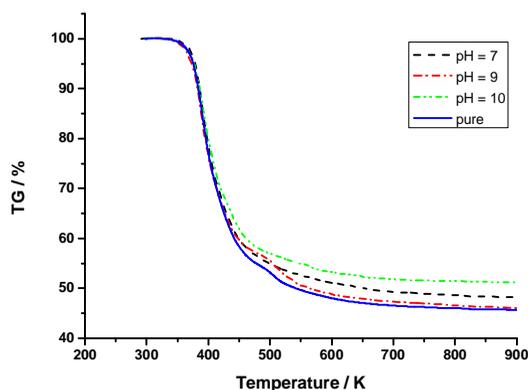


Fig. 6. Comparison of the TG curves of the chemical precipitation products with crystalline hydrate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$

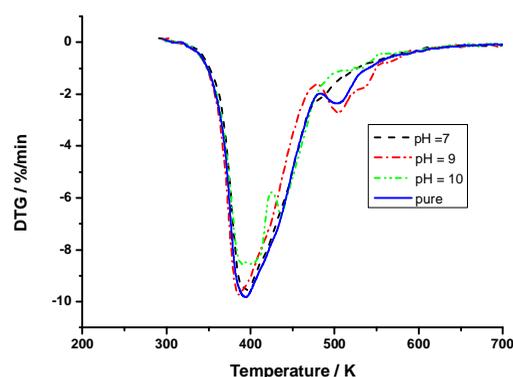


Fig. 7. Comparison of the DTG curves of the chemical precipitation products with crystalline hydrate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$

A similarity of the TG and DTG curves for the products of chemical precipitation and pure crystalline hydrate indicates that they resemble each other in their chemical composition. The chemical precipitation product at the pH of 9 seems to bear the closest resemblance to the sample of pure crystalline in terms of mass loss and total mass loss upon completion of

the process. Partial unconformity of mass losses between this sample and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ at various stages of thermolysis (Table 2) indicates that a small amount of impurities such as magnesium hydroxide and Ca-phosphates might exist in this sample. A thermogram of the precipitation product at the pH of 9 is presented in Fig. 8.

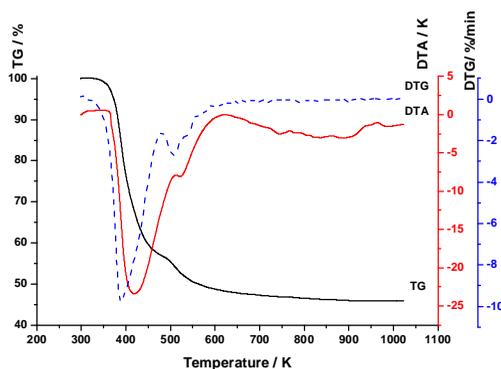


Fig. 8. Thermogram of the precipitation product at pH =9

Based on the data obtained from the thermal analysis, one can assert that the presence of the Ca^{2+} ions in the samples does not significantly affect the formation of struvite. This can be explained by the fact that the Mg^{2+} ions kinetically suppress the formation of Ca-phosphates [21–22].

4. Conclusions

The applicability of the chemical precipitation of ammonium nitrogen and phosphate ions as a slightly soluble, finely dispersed compound called struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) was proved. The investigation results of the test solutions, the chemical composition of which conforms to that of swine wastewaters, revealed that the pH values of 9 and 10 correspond to the maximum recovery of phosphates ions. A further increase in the alkalinity of the medium is not preferable. This can lead to the release of NH_3 known as air pollutant. The maximum recovery of ammonium nitrogen is achieved at the pH of 9 and the Mg:P ratio of 1.4:1. Struvite synthesis demonstrates that ammonium nitrogen is not completely released. For the wastewater post-treatment from this pollutant, it is feasible to use the methods of biological treatment. The behavior of resulting precipitate when heated allows for the conclusion about the product's stability in the temperature range (273–343 K) of its industrial application as a compound fertilizer. Thus, the product of wastewater treatment can be used on an industrial scale. High dispersity of the product formed facilitates the processes of drying and granulation.

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ОЧИЩЕННЯ ВИСОКОЗАБРУДНЕНИХ СТОКІВ СВИНОФЕРМ ВІД ЙОНІВ АМОНІЮ ТА ФОСФОРУ ІЗ ОТРИМАННЯМ ВИСОКОДИСПЕРСНИХ ЧАСТОЧОК СТРУВІТУ. ТЕРМІЧНИЙ АНАЛІЗ ПРОДУКТІВ ОСАДЖЕННЯ

Анотація. В роботі розглянуто основні методи вилучення сполук Нітрогену та Фосфору із стічних вод. Проаналізовано метод одночасного вилучення Нітрогену та Фосфору у великих концентраціях внаслідок фізико-хімічного осадження з утворенням побічного продукту магнію-амонію ортофосфату, так званого струвіту. Лабораторні дослідження проводились на модельних розчинах, в яких концентрація амоній-, магній-, кальцій- та фосфат-іонів відповідала концентрації відповідних елементів в стоках свинокомплексів, розміщених в Львівській області України. Аналізи проводились при різному молярному співвідношенні іонів магнію і фосфат-іонів та значеннях рН. Проведений порівняльний термічний аналіз продуктів хімічного осадження та чистого струвіту. Встановлені оптимальні умови, за яких спостерігається максимальна ефективність одночасного вилучення іонів амонію та фосфат-іонів зі стоків з утворенням $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Розроблені рекомендації щодо застосування отриманого продукту як мінерального добрива.

Ключові слова: Нітроген, Фосфор, фізико-хімічне осадження, магнію-амонію ортофосфат (струвіт), добриво, термічний аналіз.