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EXTRACTION OF NITROGEN AND PHOSPHORUS FROM THE WASTEWATER OF MUNICIPAL TREATMENT FACILITIES

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Abstract
The article presents a new solution to reduce the load of phosphorus and nitrogen on urban wastewater treatment plants, based on the use of semi-burnt dolomite to extract these elements from sludge waters. The efficiency of the proposed method is compared with existing purification technologies using the example of the Minsk wastewater treatment plant. The methods for determining the concentrations of phosphate phosphorus and ammonium nitrogen in model and real wastewater samples are described in detail. The analysis of model data simulating various pollution scenarios made it possible to evaluate the efficiency of phosphorus and nitrogen extraction using various reagents. The study takes into account all key return flows of wastewater treatment plants, including silt ponds, water after compaction of activated sludge and fugate after sludge dewatering. Daily material balances for total nitrogen and total phosphorus have been developed for a comprehensive assessment. Experimental studies with fugate obtained after dehydration of sediment with pretreatment with polyelectrolyte have confirmed the effectiveness of semi-burnt dolomite for the extraction of phosphorus and nitrogen, which opens up prospects for obtaining phosphorus-containing fertilizers. The dependence of the degree of extraction of phosphates and ammonium nitrogen on factors such as pH and the initial ratio of concentrations of these elements in the return streams was revealed. The results obtained indicate the high efficiency of using semi-burnt dolomite to reduce the load on wastewater treatment plants and create conditions for the production of environmentally friendly fertilizers. This scientific research is of high practical importance and contributes to the development of resource-saving and environmentally friendly wastewater treatment technologies.

Keywords: extraction, ammonium nitrogen, phosphate phosphorus, wastewater treatment plants, liquid fraction from mechanical sludge dewatering, return flows, semi-burnt dolomite.

ИЗВЛЕЧЕНИЕ АЗОТА И ФОСФОРА ИЗ ИЛОВЫХ ВОД КОММУНАЛЬНЫХ ОЧИСТНЫХ СООРУЖЕНИЙ

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Реферат
В статье представлено новое решение для снижения нагрузки фосфора и азота на городские очистные сооружения, основанное на применении полуобожженного доломита для извлечения этих элементов из иловых вод. Проведено сравнение эффективности предлагаемого метода с существующими технологиями очистки на примере Минской очистной станции. Подробно описаны методики определения концентраций фосфора фосфатного и азота аммонийного в модельных и реальных пробах сточных вод. Анализ модельных данных, имитирующих различные сценарии загрязнения, позволил оценить эффективность извлечения фосфора и азота при использовании различных реагентов. В исследовании учтены все ключевые возвратные потоки очистных сооружений, включая иловые пруды, воду после уплотнения активного ила и фугат после обезвоживания осадка. Для комплексной оценки разработаны суточные материальные балансы по общему азоту и общему фосфору. Экспериментальные исследования с фугатом, полученным после обезвоживания осадка с предварительной обработкой полиэлектролитом, подтвердили эффективность полуобожженного доломита для извлечения фосфора и азота, что открывает перспективы получения фосфорсодержащего удобрения. Выявлена зависимость степени извлечения фосфатов и аммонийного азота от факторов, таких как pH и исходное соотношение концентраций этих элементов в возвратных потоках. Полученные результаты свидетельствуют о высокой эффективности применения полуобожженного доломита для уменьшения нагрузки на очистные сооружения и создания условий для производства экологически чистого удобрения. Данное научное исследование имеет высокое практическое значение и вносит вклад в разработку ресурсосберегающих и экологически безопасных технологий очистки сточных вод.

Ключевые слова: извлечение, азот аммонийный, фосфор фосфатный, очистные сооружения, фугат, возвратные потоки, полуобожженный доломит.

Introduction

Currently, nitrogen and phosphorus are indispensable elements for plant growth and form the basis of mineral fertilizers, the demand for which is constantly increasing under conditions of intensive agriculture. The sole source of phosphorus for fertilizer production is non-renewable phosphate and apatite ores, which will lead to its future scarcity [1].

Municipal wastewater treatment plants (WWTPs) play a crucial role in ensuring the environmental safety of water bodies. A key indicator of their efficiency is the degree of reduction in the content of nitrogen and phosphorus compounds in wastewater. The excessive influx of these elements into water bodies leads to eutrophication, disrupting the ecological balance and deteriorating water quality [2].

Traditional methods of wastewater treatment for biogenic elements do not always provide sufficient efficiency. In particular, sludge water generated during the thickening and mechanical dewatering of sewage sludge (filtrate) contains significant concentrations of nitrogen and phosphorus [3]. Returning to the inlet chamber, it increases the load on the wastewater treatment plant and reduces the quality of treatment.

Therefore, the development of effective methods for extracting biogenic elements in a usable form from sludge water is a pressing task. This will not only reduce environmental pollution but also create an opportunity for the production of valuable fertilizers.

1 Principal methods for phosphorus removal from wastewater

The elevated phosphorus concentration in municipal wastewater, significantly exceeding that found in natural water bodies, is a primary driver of eutrophication and consequent water quality degradation. Municipal wastewater exhibits approximately 250 times higher phosphorus levels

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compared to natural environments. Phosphorus enters WWTPs via the sewerage system. Principal sources of phosphorus in municipal wastewater include human waste products and phosphate-based detergents [4].

Various methods exist for phosphorus removal from wastewater, broadly categorized into three groups: chemical, physico-chemical, and biological [5]. Chemical methods rely on the application of chemical reagents to bind phosphorus and render it insoluble. Physico-chemical methods encompass processes such as precipitation, coagulation, flotation, and adsorption, all aimed at phosphorus removal through insolubilization. Biological methods utilize microorganisms to absorb phosphorus from wastewater and incorporate it into their biomass [6].

Currently, a widely employed method involves the extraction of phosphorus from sludge water as a complex ammonium, magnesium, and orthophosphoric acid salt – the sparingly soluble compound $MgNH_4PO_4$ (struvite) – which can subsequently be utilized as a fertilizer [7]. This method facilitates the simultaneous removal of nitrogen and phosphorus, enhancing its ecological and economic viability.

Research into struvite recovery from wastewater and its application as fertilizer is ongoing globally. Technological schemes for struvite extraction have been developed for various sources, including municipal wastewater, steel mills, tanneries, coking processes, landfill leachate, livestock and dairy farms, and blackwater from decentralized treatment systems. Research into struvite's application as a fertilizer has spanned nearly two decades [8, 9].

In global wastewater treatment practices, various technologies are employed for the removal of nitrogen and phosphorus compounds. These include:

1. The University of Cape Town process. This process design minimizes nitrate inflow to the anaerobic treatment zone, thereby enhancing the efficiency of biological phosphorus removal.
2. The A2/O process. This represents a modification of the A/O process, incorporating a dedicated denitrification zone. Effective phosphorus removal using this configuration is limited to wastewaters exhibiting high concentrations of organic compounds.
3. The Bardenpho process. This five-stage process includes an additional denitrification/nitrification step compared to the A2/O process, mitigating the adverse effects of nitrate within the anaerobic zone under conditions of incomplete denitrification [10].

Separate technologies are employed for the treatment of sludge water, targeting either nitrogen or phosphorus extraction. Phosphorus recovery technologies include Phostrip, Ostara PEARL, and PRISA, while nitrogen removal is achieved using BABE, CANON, and DEMON processes. Phosphorus removal efficiencies may reach 85 %, while nitrogen removal rarely exceeds 30 % [11–13].

The application of semi-burnt dolomite (calcined at 600–750°C) represents a promising approach for phosphorus adsorption. Prior research has demonstrated its high effectiveness in removing phosphate phosphorus from wastewater treatment plant return streams [14].

The present investigation aims to assess the efficiency of nitrogen and phosphorus extraction from sludge water under operational wastewater treatment plant conditions using a range of reagents. The following objectives will be pursued:

1. Conduct a compositional analysis of return flows from the Minsk wastewater treatment plant and establish a mass balance for nitrogen and phosphorus.
2. Determine the extraction efficiency of nitrogen and phosphorus from sludge water at the operational wastewater treatment plant using various reagents.
3. Quantify the yield of phosphorus-containing products resulting from phosphorus extraction from sludge water at the treatment plant.

2 Materials and methods

Model waters containing phosphate phosphorus and ammonium nitrogen and silt waters formed at the Minsk treatment plant during compaction and mechanical dewatering of sediment (fugate) were used as research objects.

Model wastewater containing ammonium and phosphate ions at specified concentrations was obtained by mixing solutions of K_2HPO_4 and NH_4Cl in terms of phosphate and ammonium ion in certain ratios. The concentrations of ammonium nitrogen and phosphate phosphorus were assumed to be similar to their content in the streams that have developed and are predicted in the streams of wastewater treatment plants.

To determine the composition of the return flows of the Minsk treatment plant with determination of the concentration of ammonium nitrogen (NH_4^+) and phosphate phosphorus (PO_4^{3-}), samples of fugate, silt waters from ponds and after silt compactors were used, which were selected on 04/24/2024.

$MGSO_4{\cdot}7H_2O$, semi-burnt dolomite (firing temperature – 700–750 °C), CaO were used as reagents for the extraction of phosphate phosphorus and ammonium nitrogen.

Magnesium sulfate is a water-soluble fine powder of white or light gray color. It is obtained by the interaction of magnesite with sulfuric acid, followed by filtration, crystallization and drying of the product in a drying drum. Magnesium sulfate 7-aqueous is used in agriculture as a fertilizer and in the production of synthetic detergents, as a technological raw material in the chemical, metallurgical, pulp and paper, textile industries, in the production of building materials and other industries [15].

The concentration of phosphate phosphorus was determined by photometric method with ammonium molybdate, and ammonium nitrogen was determined by photometric method using Nessler reagent [16, 17].

3 Nitrogen and Phosphorus Extraction from Wastewater Sludge Using Semi-burnt Dolomite

To establish the established distribution of nitrogen and phosphorus throughout the wastewater treatment plant's material flows, in addition to the routinely monitored concentrations in the influent and effluent wastewater streams, the concentrations of ammonium nitrogen (NH_4^+) and phosphate phosphorus (PO_4^{3-}) were determined in the return flows. These return flows included the return from sludge ponds, sludge water after thickening of excess activated sludge (EAS), and the fugate after cake dewatering.

The concentrations of ammonium nitrogen and phosphate phosphorus in the return flows from the Minsk wastewater treatment plant are presented in Table 1.

Table 1 – Ammonium nitrogen and phosphate phosphorus concentrations in return flows from the Minsk wastewater treatment plant

Return flow	Concentration, mg/dm³			
	ammonium nitrogen		phosphorus phosphate	
	minimum value	maximum value	minimum value	maximum value
From sludge ponds	10,5	535	14,1	143
After sealing the EAS	2,6	29,1	7,0	131
Fugate	26,8	73,2	63,3	191

Analysis of Table 1 reveals a substantial variation and wide range in ammonium nitrogen and phosphate phosphorus concentrations within the return flows of the Minsk wastewater treatment plant. The highest concentrations of both nutrients are observed in the return flow from sludge ponds, indicating a significant load on the treatment plant due to the transfer of these nutrients from the sludge deposited in the ponds into the sludge water.

Based on the data obtained during the analysis of the composition of return flows and wastewater at the entrance and exit from the treatment facilities, the material balances of total phosphorus and nitrogen for the Minsk treatment plant per day were compiled.

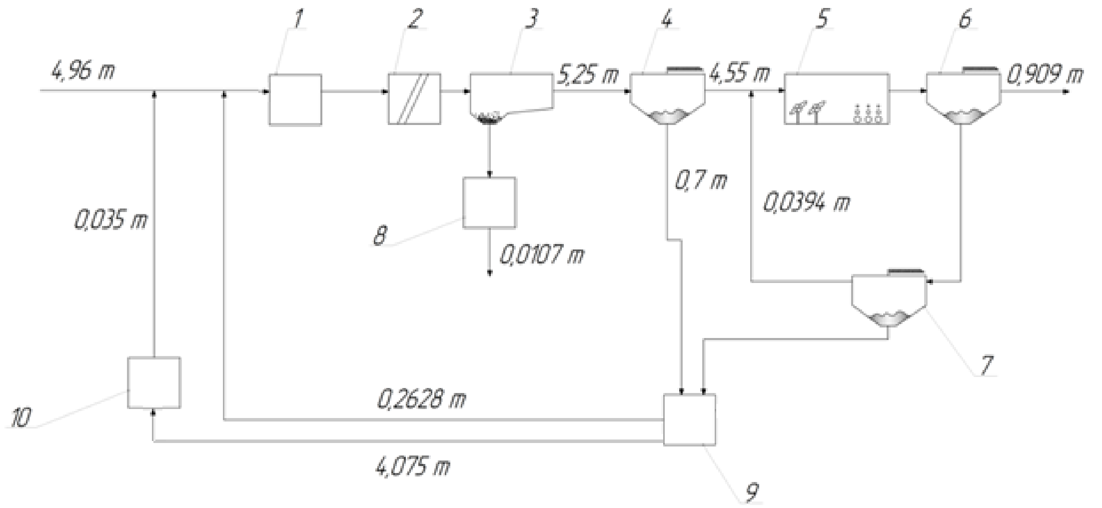
The daily material balance for total phosphorus is shown in Figure 1.

Figure 2 illustrates the daily mass balance for total nitrogen.

The analysis of material balances shows that the nitrogen and phosphorus content in the return streams has a significant effect on the composition of wastewater entering the aeration tank. Given that sediments placed on silt ponds are not used, it is possible to estimate how much nitrogen and phosphorus are annually withdrawn from circulation at wastewater treatment plants.

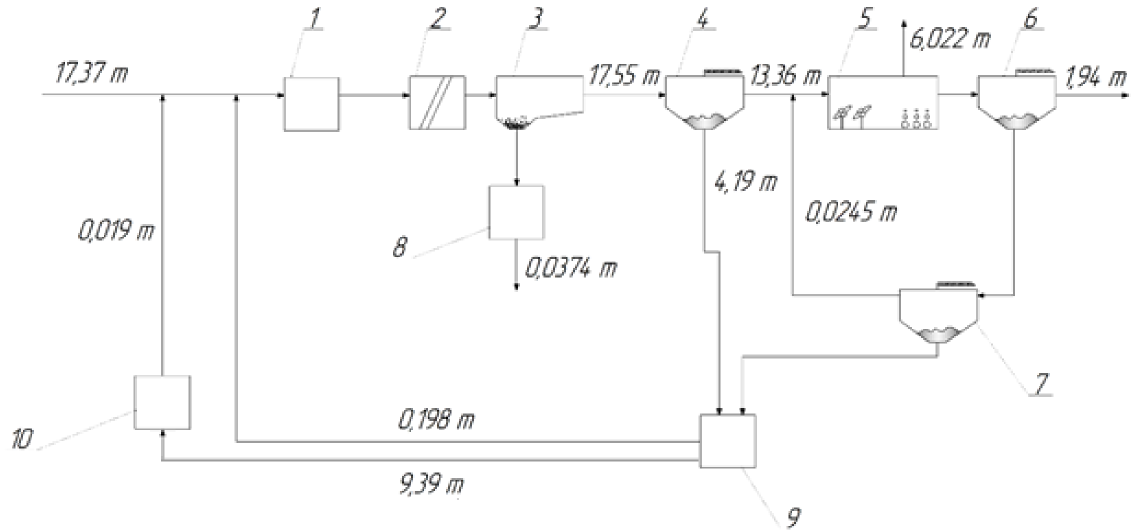
For effective biological treatment, a BOD (biological oxygen demand):N:P ratio of 100:5:1 is required [18]. Significant deviations from this ratio will reduce the overall efficiency of water treatment.

It is important to note that the nitrogen and phosphorus concentrations in the return flows significantly exceed those in the influent wastewater, substantially increasing the load on the treatment plant. The use of a biogas complex for sludge stabilization will further increase the load on the aeration tank with respect to these compounds.



1 – influent chamber; 2 – screens; 3 – grit chambers; 4 – primary clarifiers; 5 – aeration tanks; 6 – secondary clarifiers; 7 – sludge thickeners; 8 – grit storage areas; 9 – sludge treatment facility; 10 – sludge ponds

Figure 1 – Daily mass balance of total phosphorus in return flows at the Minsk wastewater treatment plant



1 – influent chamber; 2 – screens; 3 – grit chambers; 4 – primary settling tanks; 5 – aeration tank; 6 – secondary settling tanks; 7 – sludge thickeners; 8 – grit storage areas; 9 – sludge treatment facility; 10 – sludge ponds

Figure 2 – Daily mass balance of total nitrogen in return flows at the Minsk wastewater treatment plant

To study the efficiency of extraction of ammonium and phosphate ions from sludge waters, studies have been conducted on model wastewater. The model wastewater contained ammonium and phosphate ions in concentrations corresponding to their content in the streams of the Minsk treatment plant. Published data were used to account for the concentrations of these elements in sludge waters after the introduction of the biogas complex [19].

This study investigated three options for ammonium and phosphate ion removal, differing in the type of reagents used: $MgSO_4 \cdot 7H_2O$, partially semi-burnt dolomite, and CaO.

The results of the studies are presented in Table 2.

Analysis of the results presented in Table 2 shows that the use of semi-burnt dolomite (700 °C) provides the most effective phosphorus removal (over 90 %) from the model wastewater. Ammonium nitrogen removal efficiency is also quite high (70–80 %) with this method. The use of $MgSO_4 \cdot 7H_2O$ results in lower ammonium removal (around 60 %), but higher phosphorus removal (around 85 %). The addition of CaO provides the lowest removal efficiency for both phosphorus and ammonium.

It is important to note that when the ratio of ammonium and phosphate ions in the model wastewater is changed (samples 4–6), a decrease in phosphorus removal efficiency is observed when using $MgSO_4 \cdot 7H_2O$ and CaO. Meanwhile, the use of semi-burnt dolomite (700 °C) maintains a high degree of phosphorus removal.

Samples 1–3 of the model wastewater contained ammonium nitrogen and phosphate phosphorus in ratios similar to those found at the Minsk Wastewater Treatment Plant. Samples 4–6 reflected the concentrations of these substances in the digestate after anaerobic digestion.

The results from the model wastewater studies were used to select the optimal conditions for removing nitrogen and phosphorus from the digestate produced at the Minsk wastewater treatment plant. This digestate is the byproduct of sludge dewatering with a prior polymer conditioning. The initial concentrations of ammonium nitrogen and phosphate phosphorus in the digestate were 45 mg/dm³ and 131 mg/dm³, respectively.

Depending on the type and concentration of reagents, the removal efficiency of ammonium nitrogen varied from 37.7 % to 96.6 %, and phosphate phosphorus from 57.1 % to 99.5 %. Increasing the nitrogen removal efficiency was achieved by adding phosphate to concentrations stoichiometrically appropriate for the formation of magnesium ammonium phosphate. Nitrogen and phosphorus were removed as a part of the sludge, separated from the sludge water by settling for 30 minutes after reagent addition and mixing.

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Currently, a reconstruction project is underway at the Minsk Wastewater Treatment Plant. This project aims to increase the depth of dephosphorization/denitrification and construct an anaerobic digestion sludge treatment block. The project will be implemented in stages over 5–6 years [20].

Given this, a crucial task for the Minsk Wastewater Treatment Plant is now ensuring nitrogen and phosphorus removal from the sludge water. This will not only improve the overall treatment efficiency for these compounds but also create a valuable fertilizer.

Table 2 – Results of studies on model wastewater

Model water No.	Reagents	Ammonium ion concentration (mg/dm³)		Removal efficiency (%)	Phosphate phosphorus concentration (mg/dm³)		Removal efficiency (%)	pH	
		before	after		before	after		before	after
1	$MgSO_4 \cdot 7H_2O$	40	16,4	59	150	21,8	85,5	9,4	9,4
	semi-burnt dolomite (700 °C)		4,27	89,3		1,61	98,9	7,2	9,6
	CaO		28,2	29,5		11,9	92,1	7,2	8,5
2	$MgSO_4 \cdot 7H_2O$	50	5,78	89,4	200	40,2	79,9	10,4	9,9
	semi-burnt dolomite (750 °C)		8,47	78,1		7,68	91,2	7,2	9,3
								9,3	9,8
	CaO		41,2	17,6		50,9	74,6	7,2	8
3	$MgSO_4 \cdot 7H_2O$	60	16,2	73	250	47,4	81,0	9,76	9,5
	semi-burnt dolomite (700 °C)		18,3	64,5		24,3	85,3	7,1	8,2
								8,2	8,6
	CaO		43,1	28,2		38,8	84,8	7,1	8,0
4	$MgSO_4 \cdot 7H_2O$	640	255	60,2	370	6,2	98,3	9,7	9,5
	semi-burnt dolomite (700 °C)		351	40,2		1,04	94,7	6,3	8,5
								8,5	8,96
	CaO		568	11,3		139	62,5	6,3	7,7
5	$MgSO_4 \cdot 7H_2O$	540	221	59,1	320	19,9	93,8	9,54	9,54
	semi-burnt dolomite (700 °C)		125	71,8		3	94,1	6,96	9,5
								9,5	9,86
	CaO		521	3,5		101	68,5	6,93	7,9
6	$MgSO_4 \cdot 7H_2O$	740	289	61	420	7,32	98,3	9,45	9,4
	semi-burnt dolomite (700 °C)		2,6	95,6		3,41	95,2	6,84	10,2
								10,2	11,8
	CaO		517	30,1		122	71	6,75	7,8

Conclusion

This study confirmed the effectiveness of removing nitrogen and phosphorus compounds from wastewater treatment plant sludge water using semi-burnt dolomite and $MgSO_4 \cdot 7H_2O$.

The efficiency of ammonium nitrogen and phosphate phosphorus removal depends on several factors, including pH, the initial nitrogen-to-phosphorus ratio in the water, and the type of reagents used. The best results for simultaneous nitrogen and phosphorus removal from the Minsk Wastewater Treatment Plant digestate were achieved using an additional phosphate source (NaH_2PO_4).

Using this nitrogen and phosphorus removal process from the Minsk Wastewater Treatment Plant digestate, up to 0.26 tons of total phosphorus and up to 0.19 tons of total nitrogen per day can be recovered as a phosphorus- and nitrogen-containing fertilizer (up to 2 tons total).

When removing nitrogen and phosphorus from the digestate of digested sludge, up to 1.672 tons of total phosphorus and up to 2 tons of total nitrogen per day can be recovered as a phosphorus- and nitrogen-containing fertilizer (up to 13 tons total).

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