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PHYSICO-CHEMICAL AND TECHNOLOGICAL STUDY OF COMPLEX HETEROGENEOUS PROCESSES OF NITROGEN COMPOUNDS IN BIOLOGICAL WASTEWATER TREATMENT PLANTS IN THE REPUBLIC OF MOLDOVA

145.01. Ecological Chemistry

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CONCEPTUAL FRAMEWORK OF THE RESEARCH

Currently, the Republic of Moldova is facing a serious situation regarding the protection of the aquatic environment. This is largely due to the insufficient treatment of domestic wastewater and discharges from small industries into wastewater treatment plants located in rural areas. The situation has arisen as a result of multiple factors: human, financial, and technogenic. Since 2005–2006, service providers for the design and construction of small and medium-sized block-type wastewater treatment plants (WWTPs) for rural areas have entered the market. However, the operation of these WWTPs is left to managers who often lack fundamental knowledge in analyzing changes in wastewater pollution characteristics and in adapting operational methods to maintain pollutant removal efficiency.

Given the accelerated process of association with the European Union, it has become imperative to harmonize environmental protection legislation with the provisions of EU directives (EU Directive 91/271, 1991). The requirements of this Directive, as well as partially harmonized national legislation (Government Decision No. 950, 2013; Law No. 272, 2013), regarding the treatment of wastewater from anthropogenic agglomerations, include a clear strategy for removing biogenic substances from wastewater. The removal of nitrogen and phosphorus compounds, which are the main contributors to water eutrophication and aquatic ecosystem degradation, is a major and pressing issue for the Republic of Moldova, considering its limited hydrographic network and increasing aridization trends.

According to the Environmental Protection Inspectorate's statistical data (EPI Yearbook, 2020), out of 271 wastewater treatment plants in Moldova, only 211 are operational, and of these, only 29 perform adequate treatment for the removal of carbon compounds (BOD_5) and suspended solids. This includes the treatment plants in the municipalities of Chisinau and Balti. It is important to note that among the 29 functional treatment plants, only a few effectively ensure the removal of nitrogen compounds, which has significantly contributed to the worsening eutrophication of water bodies in the country.

Nitrogen is a biogenic element, and its role in biological wastewater treatment processes is critical. One of the current environmental trends is anthropization, associated with an increase in the concentration of both inorganic and organic nitrogen species. Elevated concentrations of these biogenic species lead to the excessive growth of aquatic flora in lakes and rivers, followed by their decomposition, which results in oxygen consumption and a deficit of dissolved oxygen in the water. At the same time, the transformation of toxic nitrogen species (such as amines, nitrosamines, ammonium ions, nitrites) into molecular nitrogen gas in aquatic environments can help reduce the anthropogenic pressure on lakes and rivers receiving treated wastewater discharges.

Since most urban settlements in the Republic of Moldova are small (≤ 2,000 PE) and medium-sized (≤ 15,000 PE)—with the exception of municipalities like Chisinau and Balti—modern nitrogen removal technologies, which are complex and require additional equipment and external carbon sources (such as methanol, ethanol, glycerol, and acetates), are not widely applicable. Therefore, there is a need to explore new technological approaches in wastewater treatment to minimize the environmental impact of these biogenic substances on aquatic ecosystems (Ungureanu, 2005; Visnevschi, 2021).

Purpose of the Work: The aim of this research is to optimize wastewater treatment processes through kinetic modeling, with a focus on deepening the understanding of pollutant removal mechanisms and implementing original technological solutions to reduce the concentrations of nitrogen compounds that have a significant negative impact on aquatic ecosystems.

Research Objectives:

* To develop and optimize technological schemes for nitrogen compound removal in order to improve biological treatment systems.
* To conduct thermodynamic and physico-chemical studies of complex heterogeneous processes that reduce highly toxic inorganic nitrogen species.
* To perform kinetic modeling of parameters influencing the fixation and separation of organic nitrogen compounds to minimize their negative effects on treatment processes.

Research Hypothesis: The application of kinetic modeling and thermodynamic analysis in the optimization of biological treatment technologies, combined with the implementation of innovative treatment schemes, will enable the effective reduction of both inorganic and organic nitrogen compounds in wastewater, contributing to improved effluent quality and protection of aquatic ecosystems.

Methodology Summary and Justification of Selected Research Methods: The physico-chemical study of the dynamics of inorganic nitrogen species was carried out using a combination of theoretical approaches and instrumental techniques, including: thermodynamics of complex heterogeneous processes, kinetic modeling of biochemical processes, chemical analysis of parameters such as COD (Cr), BOD_5, ammonium ions, nitrites, nitrates, total nitrogen, and UV-Vis spectroscopy.

Scientific Impact of the Work: The study contributes to the development of a theoretical and practical framework for optimizing the removal of nitrogen compounds from wastewater by integrating kinetic modeling and thermodynamic analysis. It provides significant insights into the mechanisms of biological treatment and proposes innovative technological solutions tailored to the specific conditions of the Republic of Moldova. The results will serve as a scientific foundation for modernizing wastewater treatment plants, reducing environmental impact on aquatic ecosystems, and promoting sustainable water resource management in line with European Union requirements.

Social Impact: The research supports the improvement of the ecological status of aquatic environments, reduces river eutrophication, enhances fish growth conditions, and contributes to the professional training of wastewater treatment plant operators by involving young researchers in complex interdisciplinary environmental studies.

Applied Value: The method developed for nitrogen compound removal at treatment plants, described in two of the author's patents, along with the use of modified kinetic equations to estimate the pollutant removal potential in wastewater, represents an essential step in optimizing wastewater treatment.

Implementation of Scientific Results: This method has been successfully implemented at two biological wastewater treatment plants in the towns of Causeni and Cricova, allowing for advanced treatment without the use of external carbon sources (the industrial-scale implementation certificate of the author’s patent in Causeni is attached).

1. CHARACTERISTICS OF DOMESTIC WASTEWATER AND NITROGEN COMPOUND REMOVAL TECHNOLOGIES

.1 Variation in the Composition of Domestic Wastewater

In the context of urbanization and sustainable development, the management of lomestic wastewater has become an increasingly complex challenge. Domestic wastewater ›rimarily consists of "grey water" (originating from household activities such as washing and ›athing) and "black water" (originating from toilets). Water-saving efforts and changes in :onsumption behavior can significantly alter the characteristics of this wastewater, particularly n terms of the carbon : nitrogen : phosphorus (C : N : P) ratio (Nsavyimana et al., 2020).

With water conservation and changes in consumer behavior gaining momentum, esource-saving has become a top priority in many regions—especially in areas facing water carcity or where water use represents a financial burden, such as the Republic of Moldova. Modern policies and technologies promote the efficient use of water resources. These include he installation of water-efficient appliances (e.g., automatic washing machines for clothes and lishes, low-flow faucets and showers, dual-flush toilets), as well as initiatives encouraging esponsible water usage (e.g., installing water meters). As a result, the total volume of vastewater generated decreases, and its physico-chemical characteristics are altered.

Traditionally, domestic wastewater maintained a relatively stable C : N : P ratio, :orresponding to an average water consumption of 200 L/person/day between 1980 and 2000. This ratio enabled efficient biological treatment processes. However, changes in water use and he implementation of water-saving measures (Table 1.1) have led to a shift in the balance ›etween grey water and black water, which directly affects the composition of collected and reated wastewater in the Republic of Moldova.

Table 1.1 Effects of water conservation on the characteristics of domestic wastewater

Study	COD_{Cr} mgO_2/L	*N* total mg /L	*P* total mg /L
Smith, 2020	900	70	15
Liu and Wang, 2019	960	75	17
Zhang and Zhao, 2019	1000	80	20

According to data provided by the Environmental Investigation Laboratory regarding ›ollutant and nutrient concentrations in the influents of wastewater treatment plants from various urban localities, these changes are clearly evident (Table 1.2). They reflect global trends ›ut do not comply with the requirements set forth by the current legislation in the Republic of Moldova.

Table 1.2 Pollutant and nutrient concentrations in the influent of wastewater treatment plants in the Republic of Moldova

City	Population (thousands of inhabitants)	COD_{Cr}, mgO_2/L	Total nitrogen, mg /L	Total phosphorus, mg /L
MAC according to GD 950/2013		350	30	5
Donduseni	7,100	997,7	88,4	10,1
Cricova	10,670	930,5	81,4	9,7
Causeni	15,940	560,4	76,5	9,9
Chisinau	532,510	618,8	65,7	20,4
Ocnita	7,250	1022,1	63,1	11,6
Cantemir	3,430	1109,5	109,2	9,27
Basarabeasca	8,470	996,6	74,6	9,63
Stefan Voda	3,850	819,8	74,4	7,89

Biological and chemical treatment processes (Table 1.3) must be adjusted to cope with higher concentrations of pollutants and to ensure compliance with environmental standards. Nitrification and denitrification processes require adaptations to handle elevated levels of nitrogen and carbon compounds. In addition, high concentrations of phosphorus and nitrogen compounds may require additional treatment steps to prevent exceeding legal limits (Government Decision No. 950, 2013). Water-saving measures** and changes in consumption behavior have a significant impact on the characteristics of domestic wastewater, particularly in terms of the C\:N\:P ratio. These changes directly influence wastewater treatment processes and necessitate adjustments to ensure both efficiency and compliance with environmental standards. Understanding these changes and adapting treatment processes accordingly is essential for the sustainable management of water resources and for protecting the environment (Visnevschi, 2024).

Table 1.3 Methods for the removal of inorganic nitrogen compounds from wastewater

Biological processes	Chemical processes	Physical processes
Bacterial Biomass Assimilation	Chlorination at the critical point	Air stripping
Conventional nitrification-denitrification	Chemical precipitation	Reverse osmosis
Hybrid nitrification-denitrification	Ion exchange of NH_4^+	

1.2 Methods and technologies for nitrogen compound removal using biological processes

Bacterial Biomass Assimilation

In the assimilation process, nitrogen is used as a nutrient by microorganisms involved in treatment processes. It is assimilated from ammonium ions (NH_4^+) and incorporated into the cell mass to create new, living cellular material. The greater the biomass production, the higher the nitrogen removal rate, ranging from 10% to 30% (Dima et al., 2002).

Nitrification

Nitrification is an autotrophic biological process in which nitrogen compounds are converted into nitrites and nitrates. The energy required for biomass development is derived from the oxidation of ammonia compounds. Typically, the number of nitrifying bacteria is low, their growth rate is slow, and their reproduction depends on many factors.

Denitrification

Denitrification is a biochemical process in which nitrates and nitrites are reduced to molecular nitrogen (N_2) or nitrous oxide (N_2O), depending on various factors, and it occurs under anoxic conditions. This process is triggered as a stress response in aerobic microorganisms that, deprived of oxygen, are forced to obtain it from nitrates and nitrites in the wastewater flow. Denitrification is carried out by facultative aerobic autotrophic and heterotrophic bacteria such as *Nitrococcus dinitrificans, Thiobacillus, Nitrobacter, Pseudomonas, Acromobacter, and Micrococcus* (Dima et al., 2002).

Simultaneous Nitrification/Denitrification (SND) in sludge flocs

Simultaneous nitrification and denitrification (SND) in sludge flocs involves both processes occurring within the same floc structure. The microstructure of sludge flocs naturally creates zones with distinct oxygen and anoxic conditions. SND is a promising method for biological nitrogen removal. Compared to conventional nitrogen removal processes, SND is cost-effective because it requires few or no external carbon sources, making it a revolutionary approach for municipal wastewater treatment. SND removal systems and mechanisms are linked to functional microorganisms and enzymes within the flocs and biofilms, especially at low C/N ratios. Creating stable aerobic and anoxic conditions in flocs and optimizing dissolved oxygen (DO) levels are key challenges in SND (James et al., 2023; Van et al., 2023).

Anammox – PN/Anammox process

Anaerobic ammonia oxidation (anammox) is one of the most innovative alternative methods for removing ammoniacal nitrogen from wastewater (Jetten et al., 2001; Sepeli et al., 2024). Under anaerobic conditions, this process directly converts ammonia and nitrites into nitrogen gas. To supply nitrites for anammox, two strategies can be used: nitrite can be produced in a separate aerated reactor and then fed into an anoxic anammox reactor, or it can be generated in a single-stage system with limited dissolved oxygen (Holmes et al., 2019; Sepeli et al., 2024).

Comammox

The discovery of *Nitrospira comammox* bacterial communities in soil (Wang et al., 2019), freshwater (Palomo et al., 2018), and wastewater treatment systems (Daims et al., 2015) has enabled the directed use of these organisms for nitrogen removal not only via traditional multi-step nitrification-denitrification methods. This process occurs due to the enzymatic activity of these communities in a single step (Zhu et al., 2022).

n-DAMO process

The n-DAMO (nitrate/nitrite-dependent anaerobic methane oxidation) process allows nitrogen removal from wastewater through the oxidation of methane by nitrites and nitrates (Ettwig et al., 2010). When coupled with anammox or comammox processes, it offers several advantages:

a) energy savings from reduced aeration;
b) elimination of greenhouse gas N_2O emissions;
c) independence from C/N ratio (Liu et al., 2019).

Feammox

A recently discovered method, feammox (Zhang et al., 2015), involves ammonium oxidation coupled with Fe(III) as an electron acceptor. It is applicable in wastewater treatment systems with low C:N ratios and can be integrated with other nitrogen removal technologies. The final products of feammox reactions are N_2, NO_2^-, and NO_3^- (Zhu et al., 2021).

Sulfammox

This process is based on the oxidation of NH_4^+ and reduction of SO_4^{2-} under strictly anaerobic conditions, initially discovered in seabed sediments (Fdz-Polanco et al., 2001) in marine and oceanic waters. Sulfammox was first proposed for the removal of SO_4^{2-} and NH_4^+ in a fluidized bed anaerobic reactor used for treating vinasse. Sulfammox is gaining growing interest, but practical research and applications remain limited (Liu et al., 2024).

1.3 Methods and technologies for nitrogen compound removal using physico-chemical processes

Recovery of nitrogen and phosphorus from wastewater through struvite crystallization

Struvite formation in wastewater effluents is an alternative to conventional phosphorus removal techniques commonly used in the wastewater treatment industry. This process has become increasingly appealing due to its potential advantages over traditional biological or chemical phosphorus removal methods (Povar et al., 2024).

2. MATERIALS AND METHODS FOR THE EVALUATION AND MODELLING OF BIOLOGICAL WASTEWATER TREATMENT PROCESSES

2.1 Study area

The developed process and installation were implemented on a wastewater treatment line at the Causeni wastewater treatment plant, designed for an influent flow rate of 1,200 cubic meters per day. The installation includes a homogenization tank, four consecutive aeration basins with gravity flow, and a secondary clarifier. Each aerated compartment has a volume of 200 m^3. The final aeration basin is equipped with a biofilter block covering an area of 30 m^2, a stripping system, and a post-aeration zone with fine turbulence, with a volume of 120 m^3.

The recirculated flow from the secondary clarifier is pumped into the first aerated compartment. The total volume of the aeration basins is 800 cubic meters. The treatment plant is operated and monitored via a SCADA (Supervisory Control and Data Acquisition) system, which provides real-time data on key parameters throughout the investigation period (January 2024 – August 2024), highlighting critical components and stages of the process.

2.2 Methods for determining the physico-chemical parameters of water quality

To estimate the intensity of the oxidation processes of organic compounds, ammonia oxidation, and nitrate reduction to molecular nitrogen within the treatment plant, investigations were carried out on key physico-chemical water quality parameters (COD_{Cr}, DO, NH_4^+–N, NO_2^-–N, NO_3^-–N, and pH) using samples collected from reference points along the technological flow. Various analytical methods were developed to ensure precise and reliable determination of these parameters.

COD_{Cr} measures the amount of oxygen required to oxidize both organic and inorganic compounds in a water sample. The most commonly used method is the potassium dichromate method, according to ISO 6060:1989. The amount of dichromate consumed is determined by titration to calculate COD_{Cr}. UV–Vis spectroscopy was used for rapid and reliable COD_{Cr} determination with minimal sample preparation (Chen et al., 2019), at the treatment plant, using a multiparameter photocolorimeter and a thermoreactor for sample heating ("Hanna Instruments Multiparameter Photocolorimeter, ±1000 mV").

Dissolved Oxygen (DO) is a vital indicator of water quality, crucial for sustaining aquatic life. The Winkler method, described in ISO 5813:1983, remains the gold standard for DO measurement. This method involves adding reagents that react with dissolved oxygen to form an iodine precipitate, which is then titrated with sodium thiosulfate. For continuous online DO monitoring, optical sensors are used. Optical sensors, based on phosphorescence technology, offer significant advantages, including reduced calibration needs and minimal interference from other chemicals (Wei et al., 2019).

To estimate ammoniacal nitrogen, the phenate method was used. According to ISO 7150–1:1984, ammonia reacts with phenate to form a colored complex, which is measured spectrophotometrically at 640 nm.

Nitrites are determined using the Griess–Ilosvay method, in accordance with ISO 13395:1996. Nitrites react with sulfanilic acid and N-(1-naphthyl)ethylenediamine to form a red azo dye, which is measured spectrophotometrically at 540 nm.

To determine nitrates, the cadmium reduction method was used, as described in ISO 7890–3:1988. Nitrates are reduced to nitrites using cadmium granules, and the resulting nitrites are quantified using the Griess–Ilosvay method. The determination of ammoniacal nitrogen, nitrites, and nitrates was performed using the UV-2005 SELECTA spectrophotometer.

2.3 Kinetic modelling of nitrification and denitrification processes

The modelling of biochemical processes involving suspended microflora or biofilm-based systems is widely used globally to predict the influence of various factors that affect and determine the efficiency of a given process or technology. Unfortunately, in the Republic of Moldova, the prediction, design, and evaluation of wastewater treatment systems through modelling are not commonly applied.

The most widely used models in the field of activated sludge treatment are the Activated Sludge Models (ASM) developed by the international association IAWQ Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment (Henze et al., 2006). These models describe the biochemical processes involved in biological treatment, including organic matter oxidation, nitrification, denitrification, hydrolysis, phosphorus removal, and bacterial lysis, taking into account the factors that influence and inhibit these processes.

At the core of biochemical process modelling are equations describing the growth and development of bacterial biomass based on a consumable substrate, according to the Monod equation (1942–1948). This equation expresses the specific growth rate and the substrate consumption rate as a function of bacterial biomass increase (active sludge biomass) and mortality rate (represented by the coefficient β) (Henze et al., 2008).

$$\rho_{j,s} = \frac{1}{Y_{j,max}}\left(\mu_{max}\frac{S}{Ks+S} - \beta \right) X_B$$

To fully estimate the progression of processes within the technological flows at wastewater treatment plants, it is necessary to consider both external factors such as temperature, pH, and inhibitory pollutants in the wastewater, which cannot be controlled by operators and internal factors such as dissolved oxygen (controlled during operation), the dose of activated sludge, and the variation in sludge age, determined by the ratio of recycled to excess sludge volume.

The formulas that incorporate all the key factors in the kinetic modelling of nitrification processes in suspended activated sludge systems can be expressed as follows:

$$\rho_{NH4,s} = \frac{1}{Y_{NH4,max}} \cdot$$

$$\mu_{NH4,20C,max}\, e^{\chi 1(t-20)} \text{x}\left(\frac{S_{NH_4}}{K_{s,NH_{4},A1}+S_{NH_4}} \frac{S_{NO_2}}{K_{s,NO_{2},A2}+S_{NO_2}} \frac{S_{O_2}}{K_{s,O_{2},A1}+S_{O_2}} \frac{K_{pH}}{K_{pH1}+(10^{pH,opt-pHi}-1)} - \beta \right) \cdot X_{Ba}$$

2.4 Methodology for the thermodynamic study of struvite crystallization from domestic and industrial wastewater

To determine the optimal thermodynamic conditions for struvite crystallization an essential process in the recovery of nitrogen and phosphorus compounds from domestic and industrial wastewater a structured methodology was applied, including the following steps (Povar & Spinu, 2016; Povar & Rusu, 2012):

Development of a thermodynamic database: A comprehensive database was compiled containing equilibrium constant values for the chemical species involved in the studied systems (both synthetic and real wastewater), as well as the stoichiometry of relevant compounds. This database was based on the authors' own experimental data and validated literature sources. It also included solubility constants directly relevant to the design and optimization of ammonium and phosphate ion recovery processes.

Definition of the chemical equilibrium model: An advanced chemical model was selected, capable of rigorously describing the nature, composition, and stability of both soluble and insoluble chemical species present in the analyzed homogeneous and heterogeneous systems. The model accounts for complex interactions between system components and the influence of environmental parameters (pH, total/analytical concentrations of system components, temperature) on the formation of struvite ($MgNH_4PO_4 \cdot 6H_2O$).

Construction of the mathematical model and development of a simulation tool: A complex mathematical model of the equilibrium systems was developed, based on mass balance equations, the laws of mass action and thermodynamic equilibrium. The model integrates the formation of all possible soluble and insoluble ionic species (Mg^{2+}, NH_4^+, PO_4^{3-}).

Calculation of the total Gibbs free energy of the global struvite crystallization process.

Validation of the model and theoretical results: The reliability of the simulation results was assessed by comparing them with an extensive set of experimental data from the literature. This approach enables validation of the proposed chemical and mathematical model, providing a solid foundation for experimental planning and optimization of the struvite crystallization process aimed at nutrient recovery from domestic and industrial wastewater.

3. INNOVATIVE METHOD OF BIOLOGICAL WASTEWATER TREATMENT WITH SIMULTANEOUS NITRIFICATION AND DENITRIFICATION

3.1 Implementation and monitoring of the innovative biological wastewater treatment method with simultaneous nitrification and denitrification.

In this study, the developed innovation introduces an advanced system based on biological processes that utilize natural mechanisms to efficiently treat municipal wastewater without negatively impacting the environment. The developed process and installation were implemented on a wastewater treatment line at the Causeni treatment plant, with a designed flow rate of 1,200 m^3 per day. The installation includes a homogenization tank, four consecutive aeration basins with gravitational flow, and a secondary clarifier. In the advanced technological process, the detachment of the biological film is achieved through intense air stripping from a fixed bed introduced into the treatment system as a submerged biofilter compartment composed of structured polymeric configurations with an extended surface area. These structured polymeric configurations act as support for the attachment and development of the biological film, which enhances the oxidation of organic substances and the nitrification processes.

In the oxygen-deficient inner layer (depending on the substance diffusion function), the process reduces nitrates to nitrogen. For the detachment of the developed biofilm, the filter block is equipped with a separate system for intensive air aeration. Due to the movement in slow turbulent currents in the fine-bubble post-aeration zone, the detached biological film from the fixed support forms cocoon-like conglomerates of attached microflora (Figure 3.1). These microorganism cocoon conglomerates, recirculated upstream of the secondary clarifier via return pumps, perform simultaneous oxidation and reduction functions, depending on the treatment phase, in accordance with the technological flow (Povar et al. 2024; Visnevschi and Povar 2025).

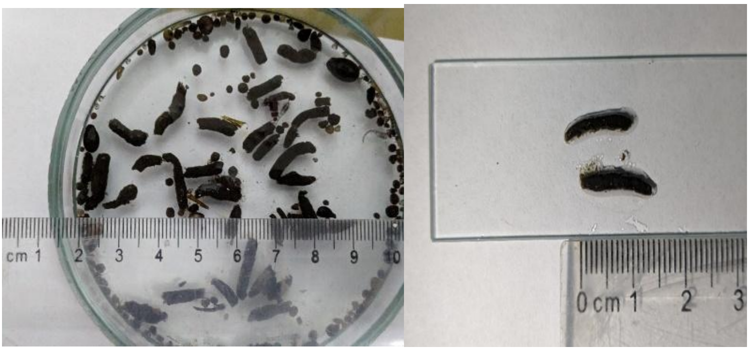

Figure 3.1 Cocoon-like microbial aggregates collected from the technological cycle flow at the experimental line of the WWTP and cross-section of a cocoon

As a result of the prolonged circulation time within the treatment system (aeration–clarification–aeration), the aggregated microflora cocoons formed through the lysis and hydrolysis of bacterial mass within the intercellular content under anaerobic conditions serve as a carbon source necessary as a consumable donor for the denitrification process. The developed purification process eliminates the aforementioned disadvantages by using conglomerated microbial carriers in the form of biological film cocoons, thus removing the need for external carbon source injection. The carbon required for denitrification comes from the lysis and hydrolysis of microorganisms within the intercellular space, ensuring an anaerobic environment over an extended period to maintain the structural integrity of the cocoons.

The installation developed in this study (Figure 3.2) consists of: a single-block biological reactor (1) with a fine-bubble aeration system (2), a biofilter block (3) made of structured polymeric configurations with a fixed surface, a separate block for intensive aeration (4) using perforated pipes with hole diameters of 4–6 mm, a slow-turbulence aeration zone for cocoon formation (5), a secondary clarifier (6) for sedimentation-based separation of activated sludge mixed with formed cocoons, and one or more recycling pumps, either air-driven or hydraulic (7), for recirculating the mixture of activated sludge and cocoons upstream of the single-block reactor.

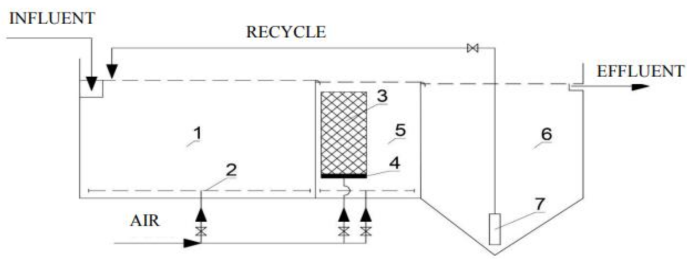

Figure 3.2 Principal diagram of the installation with biological film detached from a fixed support, developed in this study

The installation is equipped with a submerged biofilter block made of structured polymeric configurations for the attachment and development of the biological film, featuring a separate aeration system with medium to large bubble stripping at an intensity of 10–14 m^3/m^2 for film detachment. The formation of microbial cocoon conglomerates is ensured by the downstream zone of the biofilter block, which is equipped with a slow aeration system producing fine bubbles, where fine turbulences create the hydrodynamic shapes of the cocoons (Figure 3.1).

The compartments with the biofilter block and the post-aeration zone with fine turbulence for cocoon formation can be integrated into newly built plants as well as into existing bioreactors undergoing reconstruction to increase the efficiency of organic and biogenic substance removal (nitrogen, phosphorus) by increasing the concentration of microbial biomass and utilizing internal carbon sources from the intercellular space, without the need for injecting an external source.

The sizes of the developed cocoons ranged between 2 mm and 16 mm in length and 1.5–2.5 mm in diameter, with a microbial conglomerate density reaching up to 58 g/L, approximately 20 times higher compared to the activated sludge concentration in the bioreactor (Visnevschi 2024).

3.2 Kinetic calculation of the nitrification and denitrification potential in the continuous technological flow of the Causeni wastewater treatment plant

To estimate the potential for ammonium oxidation in the technological flow of the newly constructed wastewater treatment plant in the city of Causeni, the equation for determining the nitrification rate in suspended activated sludge systems was used, applied using the ASM kinetic model (Henze et al. 2006) and the mass balance equation (3.1) for the wastewater recycling treatment system:

$$Q_i \cdot S_{NH4,i} - \rho_{NH4,s} \cdot V = Q_e \cdot S_{NH4,e} + Q_{ex} \cdot S_{NH4,ex} \qquad (3.1)$$

where Q_i, Q_e, Q_{ex} represents the influent, effluent, and excess sludge flow rates in the system, in m³/day, and $S_{NH4,i}, S_{NH4,e}, S_{NH4,ex}$ are the respective concentrations of N-NH_4, in g/m³.

Then, the equation for estimating the ammonium oxidation potential, derived in the thesis, in the wastewater treatment process of the treatment plant is as follows:

$$S_{NH4,i} = \frac{V}{Qi} \cdot \frac{1}{Y_{NH4,max}} \cdot \mu_{NH4,20C,max}\, e^{\chi(t-20)} \cdot \left(\frac{S_{NH4,e}}{K_{S,NH_{4,A}}+S_{NH4,e}} \frac{S_{O_2}}{K_{S,O_{2,A}}+S_{O_2}} \frac{K_{pH}}{K_{pH}+(10^{pH,opt-pHi}-1)} - \beta\right) \cdot X_{Ba} + S_{NH4,e} \qquad (3.2)$$

For the calculation of the 3-D diagram and the numerical table estimating the ammonium oxidation potential in the technological flow, the stoichiometric coefficients and constants from equation (3.2) for each process and substrate, derived from ASM1 (Henze et al. 2006), as well as the operating parameters of the treatment plant, were used.

By substituting the operational parameters of the studied plant into equation (3.2), with Qi = 1200 m³/zi, V = 800 m³, MLSS (Mixed Liquor Suspended Solids) = 2000 g/m³ and $NH4^+$ = 2,0 g/m³, the data are graphically represented in a 3D diagram (Fig. 3.3). The study produced a series of 3D diagrams based on variable values of operational parameters.

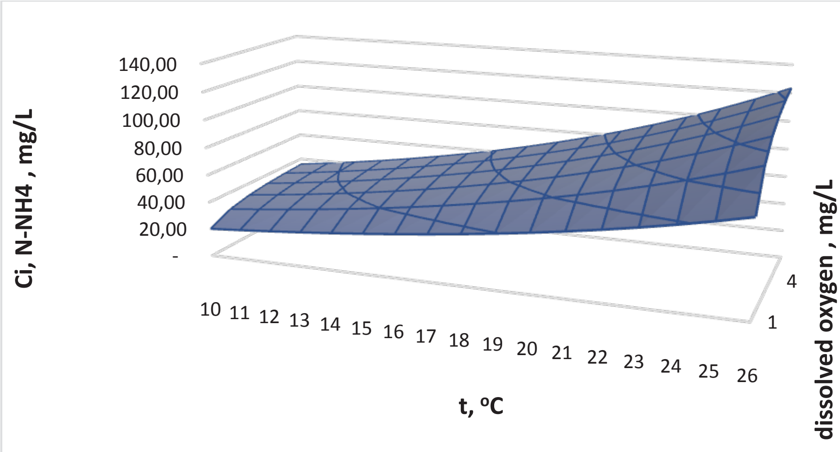

Figure 3.3 3-D diagram for estimating the ammonium oxidation potential in the process flow of the wastewater treatment plant

To demonstrate the simultaneity of the nitrification and denitrification processes in wastewater within a single aerated flow of the Causeni wastewater treatment plant, without separating oxic and anoxic zones, the efficiency of each process was calculated at different temperatures.

Table 3.1 Calculation of the simultaneous nitrification efficiency (Eff% N-NH4) and denitrification efficiency (Eff% N) in the wastewater treatment process at different temperatures, based on experimentally determined physicochemical parameters, for the Causeni wastewater treatment plant

Nr.	Temp.	COD_{Cr} influent	COD_{Cr} effluent	$N\text{-}NO_3$ effluent	$N\text{-}NO_2$ effluent	$N\text{-}NH_4$ influent	$N\text{-}NH_4$ effluent	Eff $N\text{-}NH_4$	Eff N
	°C	gO_2/m^3	gO_2/m^3	g/m^3	g/m^3	g/m^3	g/m^3	%	%
1	9.1	462	109.3	42.9	6.8	82.5	16.5	80.0	19.8
2	10.2	535.7	118.2	36.5	4.6	65.7	2.26	96.6	34.0
3	15.1	522.6	116.4	42.5	0.05	70.4	0.66	99.1	38.6
4	15.9	556.8	93.1	12.1	0.19	49.5	2.41	95.2	70.2
5	17.3	616.2	99.1	1.65	8.11	103.3	7.9	92.4	82.9
6	17.6	488.3	73.2	16.7	0.11	69.0	0.72	98.9	74.1
7	20.8	493.7	96.6	5.32	0.03	65.3	0.43	99.3	91.1
8	20.4	341.1	29.5	6.3	0.11	61.2	0.62	98.8	88.6
9	25.4	622.5	64	13.4	0.45	79.8	0.94	98.8	81.5

From Table 3.1, it is evident that nitrification reaches an efficiency of up to 99.3%. Simultaneously, denitrification occurs at rates ranging between 19.9% and 91.1%, which is fundamentally correlated with the temperatures of the treated wastewater. The data presented in Table 3.1 indicate that the presence of conglomerated microbial cocoons in the activated sludge within the technological flow initiates and intensifies the nitrification and denitrification processes under continuous aeration conditions, due to the functioning of the biological film within the cocoons. To evaluate the processes occurring in each separate compartment, or by sampling from the influent, the mixed influent sample and recycled sludge after the first aeration compartment (basin), after the second aeration compartment, after the third aeration compartment (there being three successive ones), after the biofilter unit, and from the effluent, a concentration profile of all estimated elements across the entire technological flow can be constructed. The denitrification process is evident from the sloped phases of nitrification (ammonium oxidation following the decrease in $N\text{-}NH_4$ concentration) and denitrification from the sloped phases of nitrate reduction (decrease in $N\text{-}NO_3$ concentration), which takes place based on the consumption of carbon as a substrate source for the process from the COD_{Cr} available in the first aeration tank and more pronounced in the subsequent compartments. This is due to the consumption of substrate formed inside the conglomerated microbial cocoons through bacterial lysis in the anaerobic intercellular zone, the carbon source from the wastewater (COD_{Cr}) already being oxidized in compartments 1 and 2 (Povar et al. 2024; Visnevschi and Povar 2025).

The technical challenge addressed by the developed wastewater treatment installation and process lies in its ability to operate without the need to introduce additional floating carriers (such as sand, activated carbon particles, resin, etc.) for the attachment and development of the biofilm environment, and without requiring the introduction of an external carbon source to ensure the denitrification process. The biological treatment process for municipal wastewater with simultaneous nitrification and denitrification is characterized by the use of conglomerated cocoons of the biological film, which increases the biomass concentration of microorganisms and utilizes an internal carbon source from the intercellular space, without the need for external injection. This is due to the lysis and hydrolysis of microorganisms in the intercellular space, ensuring an anaerobic environment sustained by the cocoons. In these central zones, where oxygen and nitrates are practically absent, anaerobic processes such as fermentation and bacterial lysis occur. These processes contribute to the breakdown of complex organic materials into simpler compounds that can be utilized by other microorganisms in the outer layers. This ensures enhanced efficiency in the removal of organic and biogenic compounds from the wastewater.

As a result, there is an increase in the degree of purification of organic and biogenic substances, simplifying equipment and construction configurations, allowing integration into existing structures, and reducing the volumes of waste generated in the biological treatment process.

4. ESTIMATION OF THE IMPACT OF URBANIZATION AND THE TREATMENT POTENTIAL IN THE REPUBLIC OF MOLDOVA

4.1 Optimization of nitrification processes through the use of kinetic equations in suspended sludge treatment systems

This work proposes an innovative and practical approach for wastewater treatment plant operators, suggesting the use of kinetic equations developed for nitrification processes in conventional suspended sludge treatment systems. In other words, the calculation results provide the possibility to estimate the treatment potential of the analyzed plant in order to adjust operational parameters (dissolved oxygen in the aeration basin, sludge dosage, and influent flow) with the aim of intensifying the process and achieving the expected or planned results.

The derived equation (3.2) allows simulation of different operational scenarios and adjustment of process parameters to maximize pollutant removal efficiency. The simulations enable rapid testing of numerous operating scenarios without physical intervention in the process to identify optimal operating conditions, such as the optimal dissolved oxygen concentration, sludge dosage, or recirculation rate.

To validate the proposed equation for adapting the operational parameters of a functional treatment plant, experimental results were compared with calculated ones. This calculation utilized technical data including the volume of aeration tanks, operational data such as influent flow rate, dissolved oxygen concentration in the aeration tanks, activated sludge dosage, as well as physicochemical parameters of the influent and effluent of the plant. The study area included the treatment plants of Chisinau municipality and the city of Cricova.

Verification and validation of equation (3.2) and the kinetic model applied for simulating the nitrification process in activated sludge were evaluated based on mean absolute error, mean relative error, and the coefficient of determination R^2. The results indicate a mean absolute error of 3.454 mg/L and a mean relative error of 5.70%, reflecting an acceptable accuracy in predicting oxidized ammonium concentrations. However, the coefficient of determination R^2 value of 0.709 suggests a moderate to good correlation between modeled and experimental values, indicating that the model captures 71% of the variability of the actual process (Mehrani et al., 2021).

These results indicate that the model is usable for operational and predictive purposes, and to increase the accuracy of estimates in the context of wastewater treatment in the Republic of Moldova, calibration is necessary; research and investigations on this segment are ongoing based on a broader database (Mehrani et al., 2022).

By applying this kinetic equation, operators can modulate and adjust critical operational parameters of the plant, such as dissolved oxygen concentration in the aeration tanks, activated sludge dosage, as well as influent and sludge recycle flow.

In conclusion, the use of kinetic equation (3.2) for nitrification processes represents an advanced and necessary strategy for wastewater treatment plant operators, providing them with a valuable tool to improve treated water quality and comply with current legal requirements. This approach not only enhances the operational performance of treatment plants but also contributes to the protection of water resources and reduction of environmental pollution.

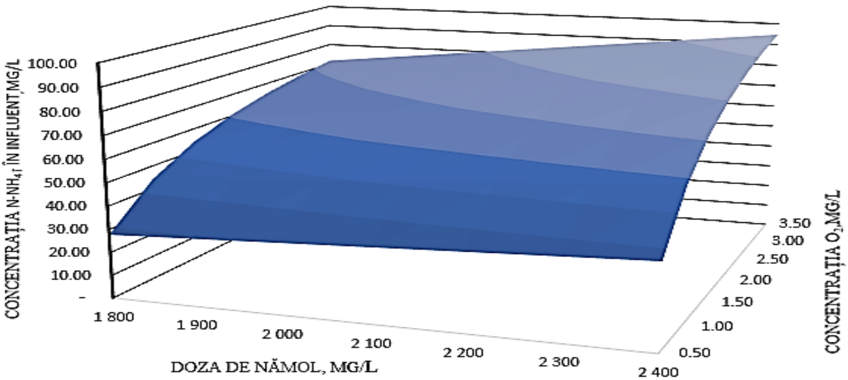

Figure 4.1 3-D diagram of the N-NH4 concentration in the influent of the treatment plant and simulation of possible operational variations to achieve an effluent $NH4^+$ result of 2.0 mg/L at a wastewater temperature of 20°C and a hydraulic retention time θ = 0,7.

Table 4.1 Tabular application for selecting a suitable scenario to achieve the desired result in the treatment process with the plant's individual characteristics, such as hydraulic retention time θ = V/Qi = 0,7 and wastewater temperature of 20°C.

DO\dose	**1 800**	**1 900**	**2 000**	**2 100**	**2 200**	**2 300**	**2 400**
0.50	27.81	29.27	30.73	32.19	33.65	35.11	36.57
1.00	44.20	46.57	48.93	51.30	53.67	56.04	58.41
1.50	54.03	56.94	59.86	62.77	65.69	68.60	71.52
2.00	60.58	63.86	67.14	70.42	73.70	76.98	80.25
2.50	65.26	68.80	72.34	75.88	79.42	82.96	86.50
3.00	68.77	72.50	76.24	79.97	83.71	87.44	91.18
3.50	71.50	75.39	79.27	83.16	87.04	90.93	94.82

Given that 3D diagrams (e.g., Figure 4.1) can be constructed according to equation (3.2) for different wastewater temperatures as well as for different hydraulic retention times, it is possible to present the values of N - $NH4^+$ potentially treated up to the standard by modifying the operational parameters using a tabular method. The use of tabular forms (e.g., Table 4.1) enables the selection of a suitable scenario to achieve the desired result in the treatment process with the individual characteristics of the plant, such as the hydraulic retention time $\theta = \frac{V}{Qi}$ and the wastewater temperature being an external factor that influences the intensity of ammonium oxidation in the treatment process.

4.2 Derivation and use of the calculation equation for the ammonium oxidation potential in the treatment process of the wastewater treatment plant

The second kinetic equation, which will be derived below, allows for the verification and adjustment of design parameters (aeration basin volume and influent flow rate) and operational parameters (sludge dosage and dissolved oxygen in the aeration basins) to achieve results in accordance with the current legislative standards (Government Decision 950, 2013) for plants under design or resizing.

The equation for estimating the ammonium oxidation potential in the treatment process of the plant for the influent ammonium ion concentration is rewritten as follows:

$$S_{NH4,i} = \frac{V}{Q_i} \cdot \frac{1}{Y_{NH4,max}} \cdot \mu_{NH4,20C,max}\, e^{\chi(t-20)} DN \cdot \delta b \cdot \eta a \cdot \left(\frac{S_{NH4,ie}}{K_{s,NH_{4,A}} + S_{NH4,e}} \frac{S_{O_2}}{K_{s,O_{2,A}} + S_{O_2}} \frac{K_{pH}}{K_{pH} + (10^{pH,opt-pHi} - 1)} - \beta \right) + S_{NH4,ie} \quad (4.7)$$

Using mathematical methods, the equation for estimating the ammonium oxidation potential in the treatment process of the plant for the ammonium ion concentration in the effluent is expressed as:

$$:S_{NH4,ie} = \frac{S_{NH4,i} - a - b - c \pm \sqrt{\left(S_{NH4,i} - a - b - c\right)^2 + 4b\left(S_{NH4,i} - c\right)}}{2}. \quad (4.8)$$

This is the general solution for $S_{NH4,e}$ in terms of the constants *a, b, c*, and the variable $S_{NH4,i}$. It can be easily solved using Excel.

By solving this equation with multiple variations of θ = V/Qi and the NH_4^+ concentration in the plant influent, 3-D diagrams can be constructed to estimate the NH_4^+ concentration in its effluent. For example, (Figure 4.2) the 3-D diagram is constructed for a wastewater temperature of 15°C, the minimum average monthly temperature in the climatic zone.

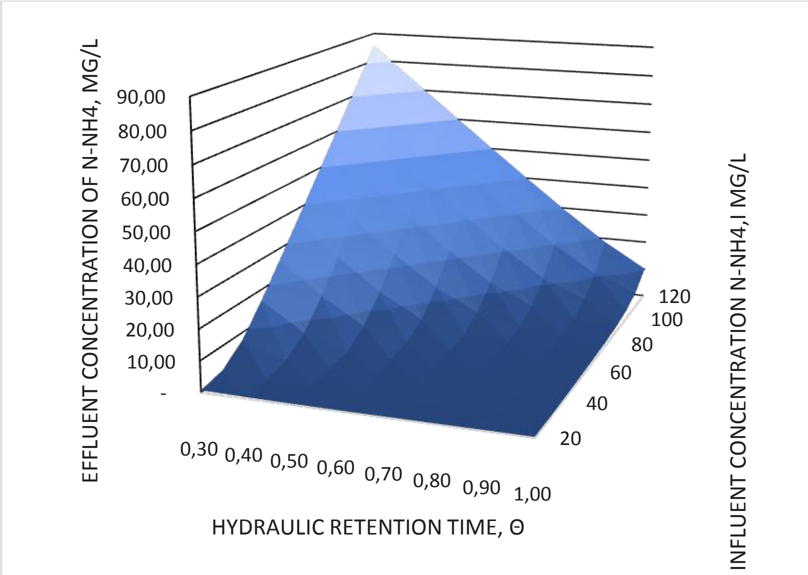

Figure 4.2 3-D diagram of the N-NH_4 concentration, mg/L, in the effluent of the treatment plant depending on the N-NH_4 concentration, mg/L, in the influent and the hydraulic retention time θ 1/day at a wastewater temperature of 15°C, sludge dose of 2000 mg/L, and dissolved oxygen of 2.0 mg/L.

The tabular forms derived from these 3-D diagrams can be applied to calculate technological parameters during the design stage and to estimate baseline values necessary to maintain the ammonium oxidation process and reduce the negative ecological impact caused by the uncontrolled release of ammonium ions into the aquatic environment.

Based on these applications and data from the project specifications for designing and constructing a wastewater treatment plant for a locality—where influent flow and N-NH_4 concentration, as well as the average monthly wastewater temperature during the cold period, are provided—it is possible to size:

The volume of the aeration tanks $V = \theta \cdot Qi$, which impacts the capital construction costs;

The dissolved oxygen concentration—this value is included in the technological calculation of the air demand for the treatment process and dictates the selection of blower equipment;

The sludge dose—this value is included in the technological calculation for the secondary sedimentation process and dictates the type, design, and dimensions of the secondary clarifier.

This equation is a valuable tool for designers, allowing them to size and optimize the infrastructure of treatment plants according to the specifics of the locality and the composition of the wastewater.

5. THERMODYNAMICS OF THE PROCESS OF REMOVING NITROGEN AND PHOSPHORUS COMPOUNDS FROM WASTEWATER IN THE FORM OF STRUVITE

5.1 Conceptual thermodynamic analysis of the struvite crystallization process

An innovative thermodynamic methodology was used to explore complex chemical equilibria, taking into account the intricate reactions in multicomponent systems, both homogeneous and heterogeneous, under experimental settings. This innovative approach involves a comprehensive examination of the thermodynamic conditions that govern various processes through general thermodynamic characteristics.

A thermodynamic analysis of the chemical composition of wastewater was performed to establish the optimal conditions for struvite precipitation. Using selected thermodynamic data for relevant species, the thermodynamic stability domains of the solid phase and the distribution of soluble and insoluble chemical species were investigated as a function of solution pH and various total reactant concentrations in the analyzed homogeneous and heterogeneous mixtures. The process of constructing heterogeneous diagrams involves several key steps:

Thermodynamic determination of the mineral stability zone. This involves calculating the Gibbs energy values for the examined process of struvite formation using the equation:

$$\Delta G_S = -RTln\frac{C^r_{Mg}}{C^0_{Mg}} - RTln\frac{C^r_{NH4}}{C^0_{NH4}} - RTln\frac{C^r_{PO4}}{C^0_{PO4}}.$$

The diagrams constructed in this study, which illustrate the variation of total Gibbs energy, simplify the identification of the solid phase stability zone depending on the initial composition of multicomponent systems. The calculation of $\Delta G_S\ (pH)_{c_i}$ for the overall struvite precipitation-dissolution process depending on the chemical composition reveals that the pH range of its thermodynamic stability depends on the chemical composition of the heterogeneous mixture (Povar & Rusu 2012; Povar & Spinu 2014; Povar & Spinu 2016b; Zinicovscaia et al. 2018).

Calculation of the partial molar fractions (f_i) of all species containing the magnesium ion in the thermodynamic stability area of the mineral established in the previous step.

Using mass balance equations, three specific cases of the heterogeneous system were examined (Povar & Rusu 2012):

a) If the solid phase consists of $MgNH_4PO_4 \cdot 6H_2O$, the three mass balance (MB) equations, taking into account the possible equilibria in solution for both cations and anions, are (from the stoichiometry of the solid phase, $Mg^{2+} : NH_4^+ : PO_4^{3-} = 1 : 1 : 1$, it follows that $\Delta C_{Mg^{2+}} = \Delta C_{PO_4^{3-}} = \Delta C_{NH_4^+}$):

$C^0_{Mg^{2+}} = \Delta C_{MgNH_4PO_4} + [Mg^{2+}] + [MgOH^+] + [Mg(OH)_2] + [MgPO_4^-] + [MgHPO_{4(aq)}] + [MgH_2PO_4^+] = \Delta C_{MgNH_4PO_4} + C^r_{Mg^{2+}}$

$C^0_{PO_4^{3-}} = \Delta C_{MgNH_4PO_4} + \sum_{j=0}^{j=3}[H_jPO_4^{j-3}] + \sum_{n=0}^{n=2}[MgH_nPO_4^{2+n-3}] = \Delta C_{MgNH_4PO_4} + C^r_{PO_4^{3-}}$

$C^0_{NH_4^+} = \Delta C_{MgNH_4PO_4} + [NH_4^+] + [NH_3]$

Thus, a system of three equations with four unknowns is obtained: $\Delta C_{MgNH_4PO_4}$, $[Mg^{2+}], [PO_4^{3-}]$ and $[NH_4^+]$.

The fourth unknown, the equilibrium concentration $[Mg^{2+}]$, is calculated from the solubility product value of $MgNH_4PO_4 \cdot 6H_2O_{(S)}$:

$$[Mg^{2+}] = K_{S(MgNH_4PO_4 \cdot 6H_2O)}[NH_4^+]^{-1}[PO_4^{3-}]^{-1}.$$

The equilibrium concentration $[NH_3]$ is calculated from the dissociation constant logK_d = - 9.25.

The equilibrium concentration $[NH_3]$ is calculated from the dissociation constant logK_d = - 9.25 of the reaction: $NH_4^+ = NH_3 + H^+,\ K_d = \frac{[NH_3][H^+]}{[NH_4^+]}$, $[NH_3] = \frac{K_d[NH_4^+]}{[H^+]}$.

b) A more complex case is examined, investigating two solid phases that include both $MgNH_4PO_4 \cdot 6H_2O_{(S)}$ and $Mg(OH)_{2(S)}$. The simultaneous presence of these two phases has not been previously investigated in the mass balance (*MB*) equations according to the approach developed earlier (Povar & Rusu 2012; Povar et al. 2022; Povar et al. 2024). The addition of multiple solid phases increases the number of unknown parameters, leading to greater model complexity. This explains why many published studies have focused exclusively on struvite precipitation, a single solid phase. The three mass balance equations take the following form:

$C^0_{Mg^{2+}} = \Delta C_{MgNH_4PO_4} + \Delta C_{Mg(OH)_2} + C^r_{Mg^{2+}}$,

$C^0_{PO_4^{3-}} = \Delta C_{MgNH_4PO_4} + \sum_{j=0}^{j=3}[H_jPO_4^{j-3}] + \sum_{n=0}^{n=2}[MgH_nPO_4^{2+n-3}] = \Delta C_{MgNH_4PO_4} + C^r_{PO_4^{3-}}$,

$C^0_{NH_4^+} = \Delta C_{MgNH_4PO_4} + NH_4^+ + NH_3$.

In this case, a system of three equations with five unknowns is obtained: $\Delta C_{MgNH_4PO_4}$, $\Delta C_{Mg(OH)_2}$, $[Mg^{2+}], [PO_4^{3-}]$, and $[NH_4^+]$.

The fourth unknown, the equilibrium concentration of the magnesium ion $[Mg^{2+}]$, is calculated from the solubility product value of $Mg(OH)_{2(S)}$:

$$Mg(OH)_{2(S)} + 2H^+ = Mg^{2+} + 2H_2O,\quad K_{S(Mg(OH)_2)} = [Mg^{2+}][H^+]^{-2}$$

The fifth unknown, the equilibrium concentration of the ammonium ion, is calculated using the expression obtained from the combination of two solubility products:

$$[NH_4^+] = \frac{K_{S(MgNH_4PO_4 \cdot 6H_2O)}}{K_{S(Mg(OH)_2)}[H^+]^2[PO_4^{3-}]}.$$

c) The solid phase is present only in the form of $Mg(OH)_2(s)$. The mass balance equations are expressed as follows:

$$C^0_{Mg^{2+}} = C^r_{Mg^{2+}} + \Delta C_{Mg(OH)_2},$$

$$C^0_{PO_4^{3-}} = \sum_{n=0}^{n=2} [MgH_nPO_4^{2+n-3}] = C^r_{PO_4^{3-}}.$$

In this case there are two equations and three unknowns: $\Delta C_{Mg(OH)_2}$, $[Mg^{2+}]$and $[PO_4^{3-}]$. The equilibrium concentration of $[Mg^{2+}]$ is calculated from the solubility product of $Mg(OH)_{2(S)}$. The ratio between the amount ΔC_{Me} and the total concentration of the metal ion $C^0_{Me^{n+}}$ actually represents the degree of metal ion precipitation γ, which is a key criterion in the precipitation process (Povar & Spinu 2016a).

To complete the diagram for a homogeneous aqueous solution, the partial molar fractions are calculated using the equations commonly used for constructing conventional species distribution diagrams.

To simulate the short-term precipitation of solid phases based on experimental results, the following insoluble species were considered: struvite $MgNH_4PO_4 \cdot 6H_2O_{(S)}$, brucite $Mg(OH)_{2(S)}$, newberyite $CaHPO_{4(S)}$, and monetite $CaHPO_{4(S)}$. In the presence of potassium and sodium ions, the formation of insoluble species $MgKPO_4 \cdot 6H_2O_{(S)}$ and $MgNaPO_4 \cdot 6H_2O_{(S)}$ was also accounted for.

Using the developed thermodynamic approach to model the precipitation process—with a range of relevant variables such as initial concentrations in the liquid phase and the solid struvite phase—showed very good agreement with experimental data. The optimal conditions for struvite precipitation were determined to be pH 9.0–9.5, and equimolar ratios of the struvite components: $C^0_{Mg^{2+}} < C^0_{PO_4^{3-}} = C^0_{NH_4^+}$.

In conclusion, the experimental findings closely aligned with the model's predictions regarding ammonium recovery efficiency, struvite crystal formation, and the required alkaline dosing. The thermodynamic modeling results elucidated the mechanisms of struvite crystallization associated with precipitation reactions and prevailing conditions.

GENERAL CONCLUSIONS

1. An industrial-scale implementation was carried out—based on a single-author patent (Visnevschi 2024)—of a new biological treatment technology at Causeni (Annex 3). This system uses biological-film cocoon carriers to increase microbial biomass concentration and utilize an internal carbon source, eliminating the need for external carbon addition. The technology sustains an anaerobic core while maintaining cocoon structural integrity, resulting in improved effluent quality (Subchapter 3.1).
2. The industrially implemented treatment scheme with simultaneous nitrification–denitrification enables nitrification efficiencies of up to 99.3%. At the same time, denitrification ranges from 19.9% to 91.1%, significantly reducing nitrogen compound concentrations in effluent compared to conventional methods used in Moldova. This demonstrates superior performance and reduces anthropogenic impacts on aquatic ecosystems (Subchapter 3.2).
3. For the first time in Moldova, existing and author-derived kinetic equations were introduced to simulate and optimize wastewater biological treatment processes. These equations allow real-time adjustment of critical parameters like dissolved oxygen and activated sludge dosage ensuring maximum treatment efficiency and reducing operating costs.
4. The use of modified kinetic equations to model biochemical processes in treatment plants via 3-D diagrams and tables enables more precise performance prediction and more efficient optimization of operational parameters than conventional kinetic models. This results in lower effluent nitrogen concentrations (Subchapters 4.1 & 4.2).
5. The thesis developed an innovative approach to optimize wastewater treatment by formulating a thermodynamic methodology that investigates complex equilibria in both homogeneous and heterogeneous multicomponent systems, offering an integrated thermodynamic perspective—an unprecedented contribution.
6. An advanced theoretical framework was created for studying struvite and other poorly soluble compound precipitation. Based on original mass-balance equations and formal thermodynamic analysis, it accurately estimates core parameters affecting struvite crystallization (pH, chemical composition). Optimal struvite precipitation occurs at pH 9.0–9.5 and equimolar reactant ratios $C^0_{Mg^{2+}} < C^0_{PO_4^{3-}} = C^0_{NH_4^+}$, governing N and P removal and enabling more efficient tertiary treatment design (Subchapter 5.2).

RECOMMENDATIONS

1. Revise Government Decision 950/2013 to reflect anthropogenic changes in domestic water usage, which cause significant variations in influent wastewater parameters and loads, directly affecting organic and biogenic removal efficiency.
2. Wastewater treatment plants in Moldova should adopt the kinetic models proposed in this thesis to monitor and optimize nitrification and denitrification processes in real time, ensuring effective treatment and reducing operational costs.
3. Expand the adoption of biological-film cocoon carriers in treatment plants to intensify simultaneous nitrification–denitrification. These carriers provide an internal carbon source and promote anaerobic conditions, removing the need for external carbon and reducing a major operational expense while enhancing process efficiency.
4. Apply the thermodynamic methodology developed here to optimize nutrient precipitation and recovery in Moldovan treatment plants as a tertiary step. This enables accurate, no-cost estimation of optimal conditions for forming and separating compounds like struvite and helps mitigate water pollution by inorganic and organic substances.

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ADNOTARE

La teza cu titlul **"Studiul fizico-chimic și tehnologic al proceselor eterogene complexe ale compușilor azotului în stațiile biologice de epurare din Republica Moldova"**, înaintată de către candidatul – **VISNEVSCHI Alexandru,** pentru conferirea titlului științific de doctor în științe chimice la specialitatea **-145.01. Chimia ecologică**

Chisinau 2025

Structura tezei constă din introducere, cinci capitole, concluzii generale și recomandări, bibliografie din 221 de titluri, 4 anexe, 118 pagini text de bază, 18 figuri, 27 tabele. Rezultatele obținute au fost publicate în 20 articole științifice, inclusiv 2 brevete de invenție și 3 articole în reviste cu factor de impact.
Cuvinte cheie: ape uzate, stații de epurare, azot anorganic, nitrificare, denitrificare, modelare cinetică, termodinamica cristalizării struvitului.
Scopul lucrării: Optimizarea proceselor de epurare a apelor uzate prin modelare cinetică, cu aprofundarea mecanismelor de eliminare a poluanților, și valorificarea soluțiilor tehnologice originale în vederea reducerii concentrațiilor compușilor de azot cu impact negativ semnificativ asupra ecosistemelor acvatice.
Obiectivele cercetării: Elaborarea și optimizarea schemelor tehnologice de eliminare a compușilor de azot pentru îmbunătățirea sistemelor de epurare biologică, prin studii termodinamice și fizico-chimice ale proceselor eterogene complexe care reduc speciile anorganice de azot cu toxicitate ridicată, precum și modelarea cinetică a parametrilor care influențează fixarea și separarea compușilor organici ai azotului, pentru minimalizarea efectelor negative asupra proceselor de epurare.
Noutatea și originalitatea științifică: In premieră a fost elaborată și implementată pe scară industrială o schemă tehnologică de epurare cu nitrificarea și denitrificarea simultană mai eficientă și în special de reducere a speciilor azotului ca element de impact antropic major, și utilizarea ecuațiilor cinetice modificate în lucrare ale proceselor biochimice. Metodologia teoretică inovatoare, aplicată pentru prima dată asupra apelor uzate, explorează echilibre chimice complexe în sistemele multicomponente, atât omogene, cât și eterogene, folosind o abordare termodinamică originală care analizează interacțiunile chimice complexe și condițiile termodinamice reale pentru setări experimentale.
Semnificația teoretică: Utilizarea pentru prima dată a analizei termodinamice originale asupra apelor uzate a permis o examinare unitară a interacțiunilor chimice complexe, oferind o înțelegere profundă a influenței pH-ului și compoziției chimice asupra proceselor reale în apele uzate. Dezvoltarea unui cadru termodinamic specific pentru sistemele de recuperare a nutrienților din apele uzate, bazat pe echilibrele de precipitare, hidroliză și formare a complecșilor, facilitează estimarea eficienței proceselor de cristalizare a mineralelor, având aplicații directe în optimizarea tratamentului fizico-chimic al apelor uzate. Lucrarea contribuie la perfecționarea strategiilor de nitrificare și denitrificare simultană a apelor uzate.
Valoarea aplicativă: Aplicarea metodei elaborate pentru eliminarea compușilor azotului în stațiile de epurare, descrisă în două brevete ale autorului, împreună cu utilizarea metodelor de estimare a potențialului de eliminare a poluanților din apele uzate prin ecuații cinetice modificate, constituent pas esențial în optimizarea epurării apelor uzate.
Implementarea rezultatelor științifice: Această metodă a fost implementată cu succes la două stații de epurare biologică în or. Causeni și or. Cricova, permițând o epurare mai avansată fără utilizarea surselor externe de carbon (actul de implementare pe scară industrială a brevetului mono autor în or. Causeni se anexează).

ANNOTATION

Of the thesis entitled **"Physico-Chemical and Technological Study of Complex Heterogeneous Processes of Nitrogen Compounds in Biological Wastewater Treatment Plants in the Republic of Moldova".** Presented by the candidate **VISNEVSCHI Alexandru,** for obtaining the degree of Doctor in Chemical Sciences with specialty – **145.01. Ecological chemistry.**

Chisinau, 2025

Thesis Structure: The thesis consists of an introduction, five chapters, general conclusions and recommendations, a bibliography of 221 titles, 4 appendices, 118 pages of main text, 18 figures, and 27 tables. The results obtained have been published in 20 scientific articles, including: two patents; 3 articles in journals with impact factor.
Keywords: wastewater, treatment plants, inorganic nitrogen, nitrification, denitrification, applied kinetic modeling, thermodynamics of struvite crystallization.
Purpose of the Work: Optimization of wastewater treatment processes through kinetic modeling, with a deeper understanding of pollutant removal mechanisms, and the exploitation of original technological solutions in order to reduce the concentrations of nitrogen compounds with significant negative impact on aquatic ecosystems.
Research Objectives: Development and optimization of technological schemes for nitrogen compound removal to improve biological treatment systems, through thermodynamic and physico-chemical studies of complex heterogeneous processes that reduce high-toxicity inorganic nitrogen species, as well as kinetic modeling of parameters influencing the fixation and separation of ammoniacal nitrogen organic compounds, with the aim of minimizing negative effects on treatment processes.
Scientific Novelty and Originality: For the first time, an innovative technological scheme for more efficient simultaneous nitrification and denitrification, particularly for minimizing nitrogen species as a major anthropogenic impact element, has been developed. The pioneering theoretical methodology applied to wastewater explores complex chemical equilibria in both homogeneous and heterogeneous multi-component systems using a comprehensive thermodynamic approach that analyzes chemical interactions and general thermodynamic conditions in experimental settings.
Theoretical Significance: The use of advanced thermodynamic analysis for the first time on wastewater allows for a unified examination of chemical interactions, providing a detailed understanding of the influence of pH and chemical composition on processes in aqueous solutions. The development of a specific thermodynamic framework for nutrient recovery systems based on precipitation facilitates the estimation of precipitation process efficiency and the formation of stable complexes, with direct applications in optimizing wastewater treatment. The work contributes to the refinement of simultaneous nitrification and denitrification strategies.
Practical Value: The application of the developed nitrogen removal method in wastewater treatment plants in the Republic of Moldova, as described in two author patents, one of which, monoauthor, was implemented on the industrial scale, together with the use of methods for estimating pollutant removal potential through kinetic equations, represents a crucial step in optimizing wastewater treatment.
Implementation of scientific results: This method was successfully implemented at two biological treatment stations in Causeni and Cricova, allowing a more advanced purification without the use of external carbon sources (the act of implementation on an industrial scale of the single-author patent in Causeni is attached).

АННОТАЦИЯ

Диссертация **«Физико-химическое и технологическое исследование комплексных гетерогенных процессов соединений азота на станциях биологической очистки сточных вод Республики Молдова»,** представленная **ВИШНЕВСКИЙ Александру** на соискание степени доктора химических наук по специальности **– 145.01. Экологическая химия**

Кишинев, 2025

Структура диссертации: Диссертация состоит из введения, пяти глав, общих выводов и рекомендаций, библиографии из 221 наименований, 4 приложений, 118 страниц основного текста, 18 рисунков и 27 таблиц. Полученные результаты опубликованы в 20 научных статей, включая: 2 патента; 3 статьи с импакт фактором,

Ключевые слова: сточные воды, очистные сооружения, неорганический азот, нитрификация, денитрификация, прикладное кинетическое моделирование, термодинамика кристаллизации струвита.

Цель работы: Оптимизация процессов очистки сточных вод путем кинетического моделирования с более глубоким пониманием механизмов удаления загрязняющих веществ и использованием оригинальных технологических решений с целью снижения концентраций соединений азота, оказывающих существенное негативное воздействие на водные экосистемы.

Задачи исследования: Разработка и оптимизация технологических схем удаления соединений азота для улучшения систем биологической очистки путем термодинамических и физико-химических исследований сложных гетерогенных процессов, которые уменьшают концентрации высокотоксичных неорганических форм азота, а также кинетическое моделирование параметров, влияющих на фиксацию и разделение азотсодержащих органических соединений, с целью минимизации негативных эффектов на процессы очистки.

Научная новизна и оригинальность: Впервые разработана инновационная технологическая схема для более эффективной одновременной нитрификации и денитрификации, особенно для минимизации видов азота как основного антропогенного фактора воздействия. Новаторская теоретическая методология, примененная к сточным водам, исследует сложные химические равновесия в однородных и гетерогенных многокомпонентных системах, используя комплексный термодинамический подход, который анализирует химические взаимодействия и общие термодинамические условия в экспериментальных установках.

Теоретическое значение: Использование разработанного термодинамического анализа для сточных вод впервые позволяет провести единую оценку химических взаимодействий, предоставляя детальное понимание влияния pH и химического состава на процессы в водных растворах. Разработка термодинамической базы для систем восстановления питательных веществ посредством осаждения способствует более точной оценке эффективности процессов осаждения и образования стабильных комплексов, с прямыми приложениями в оптимизации очистки сточных вод. Работа способствует совершенствованию стратегий одновременной нитрификации и денитрификации.

Практическая ценность: Применение разработанного метода удаления азота на станциях очистки сточных вод в Республике Молдова, как это описано в двух патентах автора, один из которых, моноавторский, внедрен на производственном уровне, вместе с использованием методов оценки потенциала удаления загрязняющих веществ посредством кинетических уравнений, представляет собой важный шаг в оптимизации очистки сточных вод.

Внедрение научных результатов: Этот метод был успешно внедрен на двух станциях биологической очистки в Каушанах и Крикова, позволяющий провести более глубокую очистку без использования внешних источников углерода (акт внедрения в промышленном масштабе единого авторского патента в Каушанах прилагается).

VISNEVSCHI Alexandru

Physico-chemical and technological study of complex heterogeneous processes of nitrogen compounds in biological wastewater treatment plants in the Republic of Moldova

145.01. Ecological chemistry

Summary of the PhD thesis in chemical sciences

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