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The Impact of Temperature on the Removal of Nitrogen Compounds in Activated Sludge System

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

Introduction: The temperature, as one of the essential factors affecting the growth and survivability of all microorganisms, may have an impact on them in two opposite directions: the change in the temperature (its increase and decrease) may have a positive impact on the growth rate or may lead to the irreversible inactivation and degradation of the components. It influences on the efficiency of biological wastewater treatment carried out by microorganisms.
Aims: This paper presents the results of test performed in the model activated sludge system. The impact of temperature on the nitrogen compounds removal processes was investigated, within the temperature ranging between 10 and 37°C.
Methodology: The evaluation of the temperature impact on the processes of removal of nitrogen compounds was made on the basis of the laboratory tests conducted in the activated sludge system. The system was supplied with synthetic wastewater in the composition approximated that of the typical household wastewater. Each value of analyzed parameters (TKN, N-NH_4, N-NO_3, BOD_5, COD, X) was determined as the average of the values measured in the following nine days. The formulations of ASM Models were used to calculate the kinetic parameters of transformations of the nitrogen compounds in the activated sludge process.
Results: The degree of removal of total nitrogen from the wastewater within the temperature range

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between 10 and 34°C was at the level of 75.5-90.6% (12.5-4.8 gN/m^3), and at the temperature of 37°C, it amounted to 71.8% (14.4 gN/m^3). The highest efficiency of overall nitrogen removal was observed within the temperature range from 10°C to 22°C and from 32°C to 35°C. Temperature coefficient values Θ was different in various temperature ranges.

Conclusion: It was determined that the assumption of an exponential increase in the rate of biochemical reactions together with an increase in the temperature does not take into account the changes of the physiological condition of microorganisms. The activity of the bacteria does not change exponentially together with the increase in temperature, but rather demonstrates the minimum and maximum values. Temperature coefficient value Θ can be regarded as a constant only within a strictly defined temperature range, characteristic for the respective groups of microorganisms.

Keywords: Temperature coefficient; nitrification; denitrification; activity of bacteria.

ABBREVIATIONS

A - Arrhenius coefficient
K_{O2}, K_{NH4}, K_{NO3}, K_F *- saturation constant*
k_{dA} *and* k_{dH}*- biomass self-oxidisation coefficient*
E - activation energy
S - substrates concentration
U - substrate uptake rate
X_H *- heterotrophic biomass*
X_A *- autotrophic biomass*
X_i *- inactive part of active sludge mass*
X_r *- recycled sludge concentration*
X_e *- concentration of a total suspension in sewage outflow*
Y - efficiency of microorganism growth
Y_A *and* Y_H *- nitrificant and denitrificant efficiency growth*
Q - sewage inflow
Q_{w} *– recycled sludge*
Q_e *– sewage outflow*
q_A^{max} *and* q_H^{max} *- maximum substrate uptake rate*
V_k *- volume of bioreactor*
HRT- hydraulic retention time
SRT - age of activated sludge
Θ *- temperature coefficient*
μ_A^{max} *and* μ_H^{max} *- maximum nitrificant and denitrificant growth rate*
η_D *- share of denitrificants in the biomass of heterotrophies*
ρ - load of activated sewage sludge
[kg d.o.m.· d] - kg dry organic matter · day

1. INTRODUCTION

The works on the selection of the highly efficient technology of removal of nitrogen compounds from wastewater have been conducted for many years in scientific-research centres. They concentrate on nitrification and denitrification processes, which run simultaneously with the bio-oxygenation processes of organic substances, most often with the use of active sludge biomass.

The simplified stoichiometric model of the process of wastewater treatment, including the biochemical transformation of nitrogen compounds can be put down in the form of formulas:

Oxidation of organic carbon

$$C_{org} + O_2 \longrightarrow CO_2 + \Delta(\text{heterotrophs}) + \text{energy} \tag{1}$$

Amonification

$$N_{org} \longrightarrow NH_4^+ \tag{2}$$

Nitrification

$$\begin{aligned} NH_4^+ + O_2 &\xrightarrow{\text{Nitrosomonas}} NO_2^- + \Delta(\text{autotrophs}) + \text{energy} \\ NO_2^- + O_2 &\xrightarrow{\text{Nitrobacter}} NO_3^- + \Delta(\text{autotrophs}) + \text{energy} \end{aligned} \tag{3}$$

Denitrification

$$NO_3^- + C_{org} \longrightarrow N_2 + CO_2 + \Delta(\text{heterotrophs}) + \text{energy} \tag{4}$$

In general, it is assumed that the active sludge biomass comprises:

1. heterotrophic biomass X_H, which covers all organisms that decompose the organic substances and are responsible for ammonification and denitrification;
2. autotrophic biomass X_A, covering mainly nitrificants. Due to the fact that no nitrites are singled out as a separate substance in the technological evaluation of the nitrification process, the division into organisms that oxidise ammonia nitrogen to nitrites (*Nitrosomonas*) and those that conduct the second phase of oxidisation to nitrates (*Nitrobacter*) is unnecessary.
3. the inactive part of active sludge mass X_i, which constitutes the sum of a part of biologically neutral suspended matters at the supply of sewage to the system, and the neutral mass produced as a result of biomass atrophy [1].

The share of the respective groups of microorganisms in the bacterial culture depends on the conditions inside the activated sludge chamber. Above all, the changes occurring in the activated sludge flocs, including the effect of removal of nitrogen compounds from wastewater, are affected, by the temperature, pH and environment alkalinity, aeration, mixing, nutrients and toxic substances (inhibitors).

The temperature, as one of the essential factors affecting the growth and survivability of all microorganisms, may have an impact on them in two opposite directions: the change in the temperature (its increase and decrease) may have a positive impact on the growth rate or may lead to the irreversible inactivation and degradation of the components. The final result will be the inhibition of the growth or death of the given cell [2,3]. The studies of the dependencies of the growth rate on the temperature show that the point or the narrow range, in which the cell growth is the highest, is achieved for each species of microorganisms taking part in the wastewater treatment process. This is the optimal temperature. Different optimal temperature ranges correspond to the development of different organisms. The minimum and maximum temperatures determine the possible limits of the cell growth and development. These three points often referred to as cardinal temperatures, are not fixed values for the respective microorganisms, but can be subject to a shift as a result of changes in other factors, as well as to the adaptive ability of the microorganisms. For instance, the *Zooglea ramigera* bacteria, which impact the formation and the structure of an activated sludge floc, occur within the temperature range between 10 and 40°C, and their optimal growth takes place within the temperature range between 28 and 30°C [4,5].

In principle the temperature of household wastewater in the moderate climate ranges between 10 and 20°C. It follows from the above that the household wastewater temperature conditions the development of the activated sludge organisms within the temperature range optimal for psychrophilic bacteria [6].

The equations analogous to the dependencies used in the description of the impact of temperature on the kinetics of simple chemical reactions are used for the description of the temperature impact on the processes of biochemical degradation of organic substances as well as oxygenation and reduction of nitrogen compounds with the participation of activated sludge microorganisms [7].

Arrhenius, described the relationship between the reaction rate constant *k* and temperature *T* by the following equation [8]:

$$k = A \cdot e^{-E/R \cdot T'} \tag{5}$$

The Arrhenius equation is true for the majority of simple chemical reactions and the *E* coefficient has a clearly specified physical sense only for them. For complex reactions, the Arrhenius equation may be fulfilled when the total speed of the process is equal to the speed of the stage which is the slowest. In case of treatment of the wastewater with the use of activated sludge, equation (5) may be expressed in the following form:

$$k_t = k_{20} \cdot \Theta^{(T-20)} \tag{6}$$

In spite of elaborating upon other relationships in the subsequent years, at present, equation (6) is used most frequently in determining the impact of temperature on the processes of biological treatment of wastewater with the use of activated sludge.

The higher the value of temperature coefficient is, the greater the impact of temperature on the rate of degradation, and therefore, the biodegradability of substrates, is.

The value of temperature coefficient set for the processes run in different technological conditions was specified in Table 1.

The values of the temperature coefficient were specified in Table 2 for the nitrification and denitrification processes, running with the participation of the activated sludge microorganisms.

The studies conducted by Schroeder and Friedman [9] proved that equation (6), may be used only to a limited extent in order to specify its impact on the kinetics of the biological wastewater treatment. The application of this equation to describe the impact of temperature on kinetics of the process of nitrogen removal from wastewater gives results which deviate significantly from the reality. These differences are a result of the dependence of the temperature coefficient values on the type of substrates and the adaptive ability of the respective groups of bacteria to the given wastewater treatment temperature. Not only does an increase in the temperature affect the rate of biochemical reactions (metabolism), but also the physiological condition (structure) of the microorganisms.

The mathematical relationships presently used to interpret the experimental studies (including equation (6)) do not consider the impact of temperature on the type and properties of substrates and the series of other parameters and phenomena such as the ones mentioned below:

- Fluid viscosity,
- The value of surface tension
- The concentration of dissolved oxygen,
- The kinetics of gas exchange between the gas-liquid-gas phases,
- The course of the process of mixing the content of the activated sludge chamber,
- The solubility of nutrients (substrates),
- The sedimentation of suspended matter, including activated sludge flocs, which may also impact the speed of the course of the process significantly.

The problem of proper determination and assumption of the temperature coefficient values becomes significant at the stage of designing the volume of activated sludge chambers. The calculated maximum rate of nitrificant growth depends on this value, and in turn, this parameter affects the age of the activated sludge, and thus the capacity of the wastewater treatment facilities. This issue is of standing importance, especially in the technology of treatment of wastewater with enhanced temperature and in warm climate.

Table 1. The value of temperature coefficient Θ for different biochemical processes

Process		Factor Θ	References
activated sludge			[10]
load	a) > 0,5 kg BOD_5/ kg d.o.m. d	1.0	
	b) < 0,5 kg BOD_5/ kg d.o.m. d	1.0-1.04	
aerobic ponds		1.035	[11]
anaerobic ponds		1.070-1.080	[12]
nitrification process		1.120	[7]
denitrification process		1.060-1.130	[13]
anaerobic digestion of sewage sludge		1.013	[14,15]
		1.066	[16]
		1.07	[17]

Table 2. The values of temperature coefficient Θ for the nitrification and denitrification processes

Process	Temperature, °C	Sample	Factor Θ	References
Nitrification	4-10	synthetic wastewater	1.165	[18]
	5-20	municipal wastewater	1.12	[19]
	7-15	municipal and industrial	1.02	[20]
	2-6	wastewater	1.4	
	4-25	dry mass of sewage sludge		[21]
		(mg/dm^3)	1.129	
		3200	1.061	
		1200	1.028	
		430		
Denitrification	4-10	synthetic wastewater	1.132	[18]
	5-20	municipal wastewater	1.15	[19]
	7-15	municipal and industrial	1.06	[20]
	2-6	wastewater	1.30	

2. METHODOLOGY

2.1 Scope of the Test

The evaluation of the temperature impact on the processes of removal of nitrogen compounds was made on the basis of the tests conducted in the activated sludge system. The activated sludge used in the tests was collected from the municipal sewage treatment plant and adapted to the operation in the system for 2 weeks. The temperature range between 10 and 37°C was changed every 3°C, in time intervals required as the adaptation period of the activated sludge microorganisms (7-14 days).

The system was supplied with synthetic wastewater in the composition approximated that of the typical household wastewater. The organic contamination was modelled with the use of starch (100 g/m^3), glucose 240 (g/m^3) and sodium glutaminate (250 g/m^3), and the ammonium chloride (95 g/m^3) was used as the source of non-organic nitrogen. Micronutrients were the salts of zinc, manganese, molybdenum and copper. The batch of wastewater with the volume of 5 dm^3 was prepared every day. The physico-chemical parameters of the synthetic wastewater were specified in Table 3. The characteristic quotients for the prepared synthetic wastewater were as follows: $P/BOD_5 = 0.035$, $N/BOD_5 = 0.156$, $COD/BOD_5 = 2.26$.

The test station consisted of:

- The denitrification chamber with the volume of $V = 2.52\ dm^3$
- The nitrification chamber with the volume of $V = 4.21\ dm^3$
- The secondary clarifier with the volume of $V = 1.9\ dm^3$
- The feed tank with the volume of $V = 5\ dm^3$.

Table 3. Physico-chemical properties of synthetic wastewater

	Parameter	Unit	Value
1.	pH	-	7.3
2.	Alkalinity	$mval/dm^3$	4.5
3.	Total solids	g/m^3	1132
4.	Dissolved substances	g/m^3	818
5.	Total suspension	g/m^3	314
6.	Organic suspension	g/m^3	269
7.	COD	$g\ O_2/m^3$	736
8.	BOD_5	$g\ O_2/m^3$	326
9.	$N\text{-}NH_4^+$	$g\ N\text{-}NH_4/m^3$	31
10.	$N_{org.}$	$g\ N/m^3$	20
11.	Phosphates	$g\ PO_4^{3-}/m^3$	35

The gravity wastewater flow (4 dm^3/d) was provided for in the system. Hydraulic retention time, calculated in relation to the volume of the nitrification and denitrification chamber, respectively, for the relevant processes was equal to 1.05 and 0.63d. Sludge retention time depends on temperature. It was from 18.7d (10°C) to 12.7 d (37°C).

The required oxygen concentration in the nitrification chamber equal to 1.5 mgO_2/dm^3 was ensured by the fine bubble-diffused aeration of wastewater. The sludge-wastewater mixture was kept in constant motion in the activated sludge chambers by low speed mixers. The external recirculation of activated sludge (in order to obtain the constant biomass concentration in the system) amounted to 100%, and the internal recirculation used to intensify the denitrification process amounted to 200% in relation to the average daily wastewater flow. The following measurements were performed in the activated sludge chambers by means of the Multiline P4 WTW meter: temperature, oxygen concentration and oxygen reduction potential. The constant required temperature of the sludge-wastewater mixture in the system was kept by means of the thermostating system, which consisted of: a thermostat, a contact thermometer, a water jacket and thermal insulation.

Within the framework of the analytic process control 90 series of determinations were performed. The physico-chemical properties of the wastewater discharged from the system, the process parameters in the activated sludge chambers, the activity of the activated sludge and its morphological composition were examined.

The activated sludge from the microscopic examinations was collected from the aeration chamber. The following elements were analysed during the observation: resilience, appearance, structure and size of the flocs, existence of organic compounds, composition of flocs and in particular, the number of protozoans, rotifers and nematodes, *Zooglea* and *Treponema Pallidum*. The microscopic analysis of the activated sludge aimed at determination of the changes in the population of microorganisms at the time of the tests and depending on the temperature of running the wastewater treatment process. The observations were made by means of the optic microscope, performing five analyses at a given temperature in 2-days intervals.

The analyses of the quality of raw and treated wastewater were performed in accordance with the applicable standards (Standard Methods for the Examination of Water and Wastewater APHA) [22].

2.2 Methodology of Calculations

The parameters of kinetics of the nitrification and denitrification processes were determined on the basis of the following results of measurements and calculations: wastewater flow, concentration of substrate at the supply and discharge (in reference to the TKN - nitrification, nitrate nitrogen - denitrification), biomass concentration, oxygen and age of sludge and substrate uptake rate. The maximum growth rate of *Nitrobacter* is much greater than the maximum growth rate of *Nitrosomonas*. In the established conditions of the wastewater treatment process, the nitrites do not accumulate in the biological treatment system in great quantity. The growth value of the nitrificants may be determined only when the limited growth value of the nitrification bacteria, leading to the transformation of ammonia nitrogen into nitrites, is taken into account.

While determining the kinetic parameters of the nitrification and denitrification processes, it was assumed that:

- The growth rate of nitrificants and denitrificants in the activated sludge chamber was not limited by the concentration of phosphorus and alkalinity;
- The process of assimilation of ammonia, nitrite and nitrate nitrogen may be omitted in the description of the nitrification and denitrification process kinetics;
- The growth rate of the denitrificants may be determined only when the limited growth rate of denitrification bacteria, leading to the transformation of nitrate nitrogen into free nitrogen, is taken into account.

The following formulations were used to calculate the kinetic parameters of transformations of the nitrogen compounds in the activated sludge process (ASM Model) [23]:

$$Y = \frac{(Q_w \cdot X_r + Q_e \cdot X_e)}{(S_o - S_e) \cdot Q_e} \qquad \text{[kg d.o.m./kg]} \qquad (7)$$

It must be noticed that depending on the assumed substrate (e.g. BOD_5, TKN, $N\text{-}NO_3$) we will receive the value of parameter *Y* expressed in [kg d.o.m/ kg BOD_5] or [kg d.o.m./kg $N\text{-}NH_4$], [kg d.o.m./ kg $N\text{-}NO_3$]. The same remark refers to such parameters as U, r_{su}:

$$U = \frac{Q}{V_k} \cdot \frac{S_o - S_e}{X} \qquad \text{[kg/kg d.o.m.}\cdot\text{d]} \qquad (8)$$

$$r_{su} = \frac{S_o - S_e}{HRT} \qquad [\text{kg/m}^3\cdot\text{d}] \qquad (9)$$

$$q_A^{max} = \frac{U_A}{\left(\frac{S_{NH_4,e}}{K_{NH_4} + S_{NH_4,e}}\right) \cdot \left(\frac{S_{O_2}}{K_{O_2} + S_{O_2}}\right)} \quad [\text{kg/kg d.o.m.} \cdot \text{d}] \quad (10)$$

$$q_H^{max} = \frac{U_H}{\left(\frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}}\right) \cdot \left(\frac{S_{NH_4,e}}{K_{NH_4} + S_{NH_4,e}}\right) \cdot \left(\frac{S_{O_2}}{K_{O_2} + S_{O_2}}\right) \cdot \left(\frac{S_{ChZT}}{K_F + S_{ChZT}}\right)} \quad [\text{kg/kg d.o.m.} \cdot \text{d}] \quad (11)$$

$$\mu_r = Y \cdot U \quad [d^{-1}] \quad (12)$$

$$\mu_r^{net} = \frac{1}{SRT} \quad [d^{-1}] \quad (13)$$

$$k_d = \mu_r - \mu_r^{net} \quad [d^{-1}] \quad (14)$$

$$\mu_A^{max} = \frac{\mu_A^r}{\left(\frac{S_{NH_4,e}}{K_{NH_4} + S_{NH_4,e}}\right) \cdot \left(\frac{S_{O_2}}{K_{O_2} + S_{O_2}}\right)} \quad [d^{-1}] \quad (15)$$

$$\mu_H^{max} = \frac{\mu_H^r}{\left(\frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}}\right) \cdot \left(\frac{S_{NH_4,e}}{K_{NH_4} + S_{NH_4,e}}\right) \cdot \left(\frac{S_{O_2}}{K_{O_2} + S_{O_2}}\right) \cdot \left(\frac{S_{ChZT}}{K_F + S_{ChZT}}\right)} \quad [d^{-1}] \quad (16)$$

In equations (10), (11), (15), (16), the values of saturation constants were assumed in accordance with the guidelines included in the study of the mathematical model of wastewater treatment in the activated sludge process.

The percentage of X_A and X_H in the activated sludge biomass belongs to one of the basic parameters necessary to determine the kinetic coefficients of the processes of organic compound biooxygenation and nitrogen compound removal from the wastewater.

The mass of autotrophies X_A was calculated on the basis of the percentage share of the nitrification bacteria in the activated sludge biomass depending on quotient $\Delta BOD_5/\Delta TKN$ [24]. The inactive part of activated sludge biomass X_i was determined from a relationship included in (17), taking into account the fraction of the biologically neutral organic suspensions at the wastewater supply (without the share of neutral mass produced as a consequence of biomass atrophy, which ranges between 0.5% and 6% of biomass depending on the temperature) [25]:

$$X_i = 0{,}6 \cdot TS \cdot \alpha SRT, \quad [\text{kg d.o.m./m}^3] \quad (17)$$

The mass of heterotrophies X_H, capable of denitrification was calculated from equation (18), assuming the share of denitrificants in the biomass of heterotrophies: $\eta_D = 0{,}6$ [1]:

$$X_H = \eta_D (X - X_A - X_i), \quad [\text{kg d.o.m./m}^3] \quad (18)$$

In each of the tested temperatures, determinations of X_{smo} were made on the basis of three samples during nine consecutive days. The mean results of determinations were the basis for calculations of the mass of heterotrophies X_H, autotrophies X_A, and part of the inactive mass of activated sludge X_i.

3. RESULTS

3.1 Microscopic Observations

Within the whole temperature range, the activated sludge flocs were rounded, brown, strong and with compact structure (internal structure of the flocs contained few perforations). Because of the content of filamentous bacteria, the activated sludge was classified into category 1 (the filamentous bacteria occurred in small quantity) [26].

Within the temperature range between 10°C and 28°C, an increase in the number of protozoans was observed. Above the temperature of 28°C, their number was decreased and at the temperature of 37°C, they occurred sporadically. The activated sludge contained anchored ciliates - *Vorticella* and *Opecularia*, as well as *Carchesium*, *Epistilis*, and *Aspidisca*, crawling among the flocs, which confirmed the correct course of the sewage treatment process. Flagellates in the tested activated sludge occurred sporadically. Within the temperature range between 10 and 13°C, a group of *Rhizopoda* appeared. The microorganisms from the group of rotifers, regarded as bioindicators of the correct wastewater treatment process, occurred within the whole temperature range. Above the temperature of 34°C, a sudden reduction in the number of all the species of microorganisms was observed.

3.2 The Concentrations of Nitrogen Compounds in the Treated Wastewater

The course of changes in the quantity of organic nitrogen, ammonia nitrogen, nitrite nitrogen and overall nitrogen in the treated wastewater, depending on the temperature of tests, was presented in Fig.1.

The changes in the concentrations of all the nitrogen forms in the treated wastewater, depending on the temperature in which the process was run, confirmed the proper course of the nitrification and denitrification processes.

The course of changes in the concentrations of the overall nitrogen and nitrate nitrogen in the wastewater treated within the temperature range between 10 and 34°C, was comparable. The nitrate nitrogen concentrations ranged between 1.27 and 7.80 $gN\text{-}NO_3/m^3$, with the maximum at the temperature of 28°C. The concentrations of organic nitrogen, ammonia nitrogen and nitrite nitrogen did not show clear changes in relation to the temperature increase within the tested range of values. The sudden increase in the concentration of the ammonia nitrogen and organic nitrogen at the temperature of 37°C was an exception. Observed increase of the concentration of ammonia nitrogen in temperatures above 34°C, was due of microorganisms death and hydrolysis process occurring organic nitrogen contained in the body proteins.

The ammonia nitrogen was oxidised to a high and comparable extent (85.7-91.9%). Its concentration in the treated wastewater changed within the range from 2.50 to 4.42 $g\ N\text{-}NH_4/m^3$. At the temperature of 37°C, the concentration of ammonia nitrogen at the discharge was several times higher and amounted to 11.0 $gN\text{-}NH_4/m^3$ (degree of removal 64.5%).

The degree of removal of the organic nitrogen, within the temperature range between 10 and 34°C was kept at the level from 94.5% to 100% (concentration ranging between 0.0 and 1.02 gN_{org}/m^3), and fell to 91% (1.83 gN_{org}/m^3) at the temperature of 37°C.

The degree of removal of total nitrogen from the wastewater within the temperature range between 10 and 34°C was at the level of 75.5-90.6% (12.5-4.8 gN/m^3), and at the temperature of 37°C, it amounted to 71.8% (14.4 gN/m^3). The highest efficiency of overall nitrogen removal was observed within the temperature range from 10°C to 22°C and from 32°C to 35°C.

3.3 The Kinetic Parameters of Nitrogen Compound Transformations in the Activated Sludge Process

The result of the mathematical analysis of the measuring data was the determination of basic dependencies of basic kinetic parameters on the temperature of wastewater treatment and then the determination of temperature coefficient values. The values of the kinetic parameters of the nitrification and denitrification processes were calculated within the tested temperature range from 10 to 37°C, in 3°C intervals. Within the framework of the conducted tests, the dependencies of the following parameters on the temperature were determined from equations 7-16:

- efficiency of microorganism growth (Y),
- substrate uptake rate (U), referred to the total activated sludge biomass;
  and
- maximum nitrificant and denitrificant growth rate (μ_A^{max} and μ_H^{max});
- nitrificant and denitrificant efficiency growth (Y_A and Y_H);
- biomass self-oxidisation coefficient (k_{dA} and k_{dH});
- maximum substrate uptake rate (q_A^{max} and q_H^{max}) referred to the biomass of

denitrification autotrophies and heterotrophies.

The calculations were included in Table 4.

4. DISCUSSION

The effect of the biological processes can be evaluated through the analysis of the wastewater treatment expressed by the degree of component removal (in %) or on the basis of a change of the value kinetic parameters. At present, the dependencies determined for the enzymatic reactions are assumed for the purpose of description of the biochemical reactions taking place in the biological wastewater treatment processes. In the model of enzymatic reactions from which, among other things, the Monod equation and equation (6) follow, it is assumed that the biochemical processes are simple reactions catalysed by enzymes. The fact that the relevant transformations may occur only inside the cellular structures of microorganisms, and thus, beyond the analysed solution (the living environment of the microorganisms) is not taken into account.

The presented results of tests and the determined dependencies of the kinetic coefficients on the temperature take into consideration both the species composition and the quantity of microorganisms, as above all, the temperature, considering the lack of inhibitors, determines the development of microorganisms.

The optimal function by means of which it is possible to describe the changes in the determined kinetic parameters of the nitrification and denitrification processes together with an increase in temperature, is the polynomial. The statistical studies of the dependencies between the variables demonstrated that within the tested temperature range, it is the sixth order polynomial. The degree of fitting of the determined functions expressed in percentage by means of correlation coefficient R^2 (specifying the dependency between the measuring values and their equivalents on the best fit curve) reached values within the range between 96 and 99%.

Such a correlation coefficient proved the significant compliance of the best fit curves (sixth-order polynomial) with the course of the experimentally determined functions. However, on the basis of the obtained results, it is not possible to determine unambiguously the physical sense of the respective constants of this polynomial. The description of the determined dependencies of the kinetic coefficients on temperature by means of the exponential function in the form of:

$$k_2 = k_1 \cdot \Phi^{(T_2 - T_1)} \qquad (6)$$

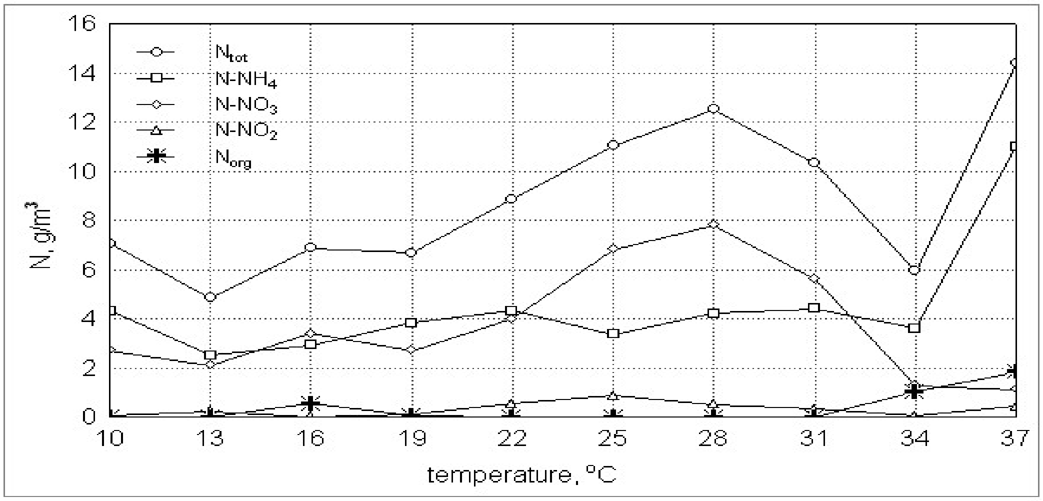

Fig. 1. Changes of various forms of nitrogen in the treated wastewater within the temperature range of 10 - 37°C

Table 4. Experimentally determined values of kinetic coefficients of nitrification and denitrification

T	q_H^{max}	q_A^{max}	Y_H	Y_A	k_{dH}	k_{dA}	μ_H^{max}	μ_A^{max}
°C	kg N-NO_3 /kg d.o.m.·d	kg N-NH_4 /kg d.o.m.·d	kg d.o.m./ kg N-NO_3	kg d.o.m./ kg N-NH_4	d^{-1}	d^{-1}	d^{-1}	d^{-1}
10	0.62	0.54	1.88	0.26	0.09	0.004	1.16	0.14
13	0.93	0.69	1.78	0.26	0.10	0.005	1.66	0.18
16	1.21	0.72	1.86	0.26	0.11	0.007	2.26	0.19
19	1.26	0.69	1.85	0.26	0.11	0.006	2.34	0.18
22	0.73	0.71	2.15	0.27	0.12	0.005	1.56	0.19
25	0.39	0.78	2.30	0.28	0.13	0.005	0.89	0.22
28	0,36	0.74	2.35	0.28	0.13	0.005	0.85	0.21
31	0.40	0.61	2.23	0.27	0.11	0.003	0.89	0.16
34	1,13	0.61	1,91	0.26	0.10	0.004	2.16	0.16
37	0.47	0.65	2.29	0.28	0.13	0.005	1.07	0.18

Table 5. Temperature coefficient values for the nitrification and denitrification processes

No.	Parameter(1)	Temperature range of using the equation	Temperature coefficient Θ	The degree of fit the appointed function to the experimental curves, R^2
1	μ_A^{max}	10-25°C	1.02	0.76
		25-34°C	0.96	0.89
2	μ_H^{max}	10-19°C	1.08	0.91
		19-28°C	0.89	0.93
		28-37°C	1.17	0.78
3	q_A^{max}	10-25°C	1.02	0.65
		25-34°C	0.97	0.81
4	q_H^{max}	10-19°C	1.09	0.89
		19-28°C	0.86	0.93
		28-37°C	1.21	0.82
5	k_{dA}	10-16°C	1.10	0.99
		16-31°C	0.96	0.80
		31-37°C	1.09	0.99
6	k_{dH}	10-28°C	1.02	0.97
		28-34°C	0.95	0.92

(1) *Kinetic parameters in the determined temperature ranges must be calculated on the basis of the following equation:* $k_2 = k_1 \cdot \Phi^{(T_2 - T_1)}$*, assuming values* k_1 *and* T_1 *from the temperature range of the equation application.*

The degree of fitting of the determined functions, expressed by means of correlation coefficient R^2 was assumed as the criterion of selection of the temperature ranges, in which the dependencies of the studied kinetic parameters on the temperature can be described by equation (6). In most cases, it reached the values ranging from 80% to 99% (the degree of fitting was lower for three functions and amounted to 0.65, 0.76 and 0.78). Such a degree of correlation proves the great compliance of the best fit curves with the course of the experimentally determined functions.

Table 5 specifies temperature coefficient values Θ for the nitrification and denitrification processes in separated temperature ranges, as well as the values of the degree of fitting of the determined functions to the value of the experimentally determined parameters.

Temperature coefficient values Θ are different in various temperature ranges, but they also depend on the method of wastewater treatment. While analysing the collected literature data (Tables 1 and 2), it can be noticed that most of the authors provide different values of this coefficient as well as very broad and diversified temperature ranges for their application, e.g. Streeter and Phelps 2-40°C (Θ =1.047), Randall 5-45°C (Θ =1.05) and Malina 4-31°C (Θ =1.0) [14]. The different temperature coefficient values for the same process are given depending on the wastewater treatment conditions:

- for wastewater treatment in the activated sludge process at BTS < 0.5 kg BOD_5/kg of d.o.m. 1.0÷1.04 [27],
- for the nitrification process 1.12 [23], 1.103 [18] i 1.08-1.1 [24],
- for the denitrification process, the range of values from 1.06 to 1.13 [1] and from 1.14 to 1.16 [24].

In these cases, the temperature ranges for their application are not specified and the same temperature coefficient values are used to determine the values of different kinetic parameters.

The analysis of experimentally determined temperature coefficient values Θ (Table 5) allows a conclusion to be drawn that they assume different values for different temperature ranges and for respective kinetic parameters. For instance, according to the literature data, value Θ for μ_A^{max}, within the temperature range between 10 and 37°C amounts to 1.103 [28], 1.08-1.1 [24] or 1.12 [23]. It follows from the conducted tests that coefficient value Θ is not a constant value, independent of the temperature within the range between 10 and 37°C. Its value, in the separated temperature ranges amounted to: 1.02 (10-25°C) and 0.96 (25-34°C) (Table 5). The determined value of the temperature coefficient within the temperature range between 10 and 25°C was lower than the one given in literature by 0.06 [5], and within the temperature range between 25 and 37°C, it was lower by 0.12. Similar changes in the value of temperature coefficients were confirmed for the respective analysed kinetic coefficients of the nitrification and denitrification processes.

Fig. 2 presents the experimental curve that depicts the changes in the value of the maximum growth rate for the nitrificants in the temperature function determined on the basis of tests, as well as the theoretical curves determined on the basis of equation (6). The following values were assumed for the calculations:

- variant I: temperature coefficient Θ equal to 1.08, maximum nitrificant growth rate $\mu_A^{max20^\circ C}$= 0.3 d^{-1} [25],
- variant II: temperature coefficient Θ equal to 1.103, maximum nitrificant growth rate $\mu_A^{max20^\circ C}$= 0.6 d^{-1} [23].

While comparing the above curves, which describe the changes in the value of the same parameter in the temperature function, the occurrence of the correlation between experimentally obtained values μ_A^{max} and those determined on the basis of equation (6) was confirmed only within the temperature range from 10 to 16°C. Within this temperature range, the course of changes in values μ_A^{max} determined in an experiment was practically the same as the one calculated theoretically on the basis of the parameters assumed in variant I.

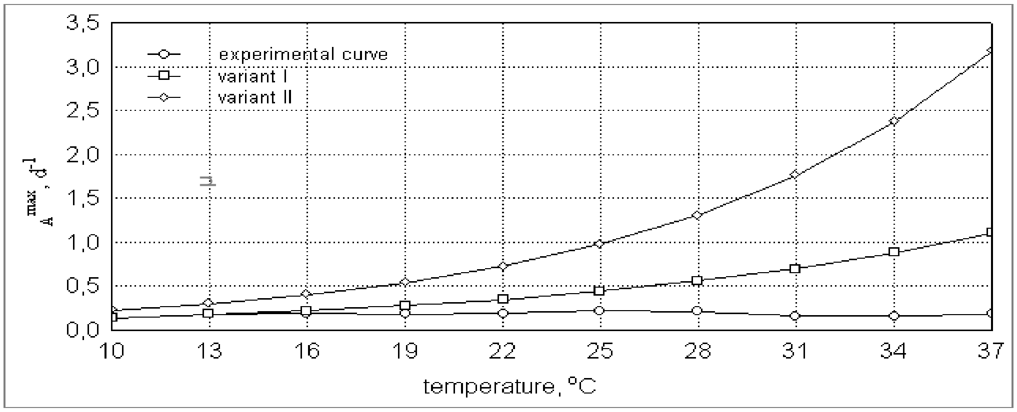

Fig. 2. Changes in parameter value μ_A^{max}

The values of maximum nitrificant growth rate calculated in variant II were higher than those determined in the experiment. In this area (standard temperatures for municipal sewage), value μAmax increased exponentially together with an increase in temperature. Within higher temperatures, the experimental curve is significantly different from the curves determined on the basis of equation (6).

The theoretical curves do not reflect the occurrence of areas of lower activity of the selected bacterial cultures. In case of formulation of equations, a tacit assumption was made that the activity of bacterial cultures increases together with the temperature or at least remains constant, which does not reflect the reality. It can be concluded that equation (6) is applicable to a limited extent and may be used in a strictly specified range of low temperatures (up to about 16°C).

4. CONCLUSION

While analysing the results of the studies and the conducted computational simulations, it may be noticed that the integration of removal of carbon and nitrogen compounds from the wastewater takes place in the process of wastewater treatment by means of the low-loaded activated sludge [29].

It can be concluded that the determined values of kinetic coefficients were conditioned by the variable activity of the bacteria at different temperatures (activity of relative psychrophiles at the temperature between 20 and 32°C) and did not have the form of the monotonic exponential function. Above the temperature of 16°C, the curve representing the course of changes in the value of parameter μ_A^{max}, determined on the basis of the results of the studies, deviated from the hypothetical curve determined on the basis of equation (6). The equation does not reflect the occurrence of temperature ranges with a higher or lower activity of microorganisms of the activated sludge sufficiently. The temperatures were determined within the range between 10 and 37°C, and coefficients Θ related to these temperature ranges do not depend on the temperature set within these ranges. Their values in these ranges were specified for the analysed kinetic parameters of transformations of the nitrogen compounds in the activated sludge process.

The temperature coefficient value is taken into account during the dimensioning of the activated sludge chambers and affects their computational volume. The correct assumption of values Θ may impact a decrease in investment and operational costs of process facilities of wastewater treatment plants. This problem is of great significance, particularly in the case of technology of sewage treatment with an enhanced temperature and in warm climate.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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