



Improving efficiency of nitrogen removal from municipal wastewater in modified A2O technological system – case study

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Received 8 March 2021; Accepted 26 April 2021

ABSTRACT

Results of qualitative examination of municipal wastewater purified in a modernized A2O (Anaerobic/Anoxic/Oxic) treatment system have been presented in this paper. The tests were performed on the real system. Primary organic contamination indicators such as BOD₅, COD_{Cr} and nitrogen compounds were analyzed. The test results were compared with those achieved before modernization. Thanks to the implementation of aerobic conditions modification in chambers and due to separation of the final denitrification stage, improvement of total nitrogen removal efficiency was achieved. Considering significant increase and fluctuations of total nitrogen concentration in wastewater supplied to the wastewater treatment plant (from 54 to 238 mg N_{tot}/dm³), the average concentration in treated wastewater did not exceed 6.7 mg/dm³, whereas the average annual final total nitrogen concentration before modernization was 9.0 mg/dm³. Efficiency of total nitrogen removal increased to 94% and efficiency of removal of organic compounds expressed by BOD₅ and COD_{Cr} as well as total phosphorus (98%–99%), was maintained at a similar level. The test results were subjected to statistical analysis and mutual correlations between particular pollutant elements, with particular consideration of nitrogen compounds, were determined. To evaluate these correlations the stepwise regression procedure was applied. Corrected coefficient of determination R² was used here to develop a model describing the process of total nitrogen removal from wastewater taking into account the variables that were strongly correlated with the dependent variable and, at the same time, the least correlated between themselves.

Keywords: Nitrogen removal; Municipal wastewater; A2O system; Post anoxic zone; Municipal wastewater treatment plant; BOD; COD; Effectiveness; Correlation; Multiple regression module; Stepwise regression procedure

1. Introduction

Highly efficient technological systems used for municipal wastewater treatment that ensure effective removal of biogenic compounds are based on a multi-phase process of activated sludge with separate oxic, anoxic, and anaerobic zones [1–4]. The most employed technological systems comprise circulation ditches, Johannesburg plug-flow systems, UTC (University of Cape Town system),

MUTC (modified-UCT system) as well as three-phase A2O and five-phase Bardenpho systems (biological process for removing phosphorus and nitrogen developed by James Barnard) [5]. The A2O system, which is considered as a fundamental one, is composed of three consecutive reactors: anaerobic, anoxic, and aerobic [6]. Bardenpho's five-phase technological system guarantees, thanks to the application of pre-emptive and final denitrification, in purified wastewater total nitrogen concentration at the level below

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5 mg $N_{\text{tot}}/\text{dm}^3$ [2,7,8]. The closing oxygen zone of Bardenpho system guarantees effective implementation of phosphorus in phosphobacteria cells; phosphorus is released into the wastewater in the pre-anaerobic chamber. Municipal wastewater treatment systems should be operated in a way that would assure compliance with legal requirements pertaining to purified wastewater quality [9,10].

1.1. Legal regulations

The principal legal rule that applies thereto in the majority of EU countries makes conditional the values of the admissible wastewater quality indicators upon wastewater treatment plant size expressed by PE indicator (Population Equivalent). Generally, a rule applies that the higher load of pollutants supplied to the wastewater treatment plant, the lower are the values of admissible pollutant concentrations in purified wastewater. Legal norms pertaining to admissible values of organic impurities indicators COD_{Cr} and BOD_5 , total suspended solids, total nitrogen, and total phosphorus in purified wastewater are considered as fundamental [11]. The admissible values applicable in particular European Union countries vary significantly. For example, the admissible value of COD_{Cr} in purified wastewater indicated in the French legislature is 125 mg O_2/dm^3 , whereas German laws provide for 75 mg O_2/dm^3 for wastewater treatment plants of Population Equivalent >100,000 PE. The admissible total nitrogen concentration for big wastewater treatment plants (>100,000 PE) is 13 mg/ dm^3 (Germany) and 10 mg/ dm^3 (France) respectively [12]. When influence of process conditions on nitrogen removal efficiency is considered, the purified wastewater temperature aspect is considered. Polish legislature applicable before 2015 provided for a temperature criterion in biological chambers, which in the case of temperature below 12°C, put no obligation on wastewater treatment plant operators to maintain fixed admissible total nitrogen value. Currently, for a wastewater treatment plant below and above 100,000 PE, the admissible total nitrogen value N_{tot} in wastewater effluents drained into waters is 15 and 10 mg/ dm^3 , respectively [13]. The remaining purified wastewater quality indicators take into account wastewater temperature, pH, BOD_5 and COD_{Cr} as well as the concentration of total suspended solids and total phosphorus.

1.2. Problems with nitrogen removal

In normal operational practice maintaining of admissible total nitrogen concentrations in purified wastewater often makes a significant challenge for the practice in terms of the possibility of implementation of new solutions pertaining to nitrogen removal from main and side streams such as CANON, ANNAMOX, and SHARON [14]. One of the main problems associated with total nitrogen to be maintained at the admissible level in purified wastewater may be an insignificant susceptibility of wastewater to biological decomposition identified as a ratio of BOD_5 and total nitrogen indicators [15,16]. This indicator may also be influenced by overloading or underloading

of the wastewater treatment plant with pollutant load. Literature provides that the condition of correct conduct of the denitrification process is the value of $\text{COD}_{\text{Cr}}/N_{\text{tot}}$ ratio exceeding 5 in the inflowing wastewater [17].

1.3. Scope and novelty of the research

Currently performed intense research work in laboratory scale pertaining to increase of efficiency of nitrogen removal from the main and side stream (supernatants from digestion process of sewage sludge) of a wastewater treatment plant prove a need to perform such research also in full technological scale [2,18–20]. Research works in full technological scale in real terms on operated wastewater treatment technological systems are not performed frequently, however, they are important from the point of view of plant operation and allow to evaluate the efficiency of adopted solution for given specific case featuring specific characteristic of raw wastewater as well as properties originating also from specific features of the sewerage system used to collect wastewater from given town/city supplied to the wastewater treatment plant [21]. Experience gained from real objects may also provide recommendations for design of new or modification of the already existing wastewater treatment systems. Therefore, the objective of this work was to analyze the qualitative wastewater changes with particular consideration of total nitrogen after the implementation of technological modifications into the A2O wastewater treatment system in real terms. Application of statistical analysis to elaborate test results allowed for the finding of significant relationships between the analysed wastewater pollutants.

2. Methodology of research

2.1. A2O technological system before modification

Said wastewater treatment plant has been in operation since 1995 in Koszalin City located in the northern part of Poland. The Population Equivalent PE for it is 279,030. Purified wastewater is discharged into River Dzierżęcinka, which flows into Lake Jamno. Municipal wastewater being a mix of household and industrial wastewater from the city flows into the wastewater treatment plant. Furthermore, wastewater is supplied by a gully emptier fleet from those areas in which there are no sewerage systems. The share of such sewage in the total volume of wastewater is approximately 1%. The design average daily throughput of the plant is 36,000 m^3/d , whereas the maximum hourly throughput is 5,000 m^3/h . As of 2002, the plant has been operating in A2O arrangement. The following devices are incorporated into the technological arrangement of the mechanical and biological wastewater treatment plant: step screens, sand trap, pre-settlement tanks PST_n , A2O biological reactors (2 pcs.) and secondary settlement tanks SST (2 pcs.). The biological reactor comprises anaerobic chamber AC 1,500 m^3 , anoxic (denitrification) chambers DC_n and ANC – featuring total volumetric capacity of 6,000 m^3 and oxic chambers (nitrification) – NC_n – 5,000 m^3 . The total volumetric capacity of a single reactor

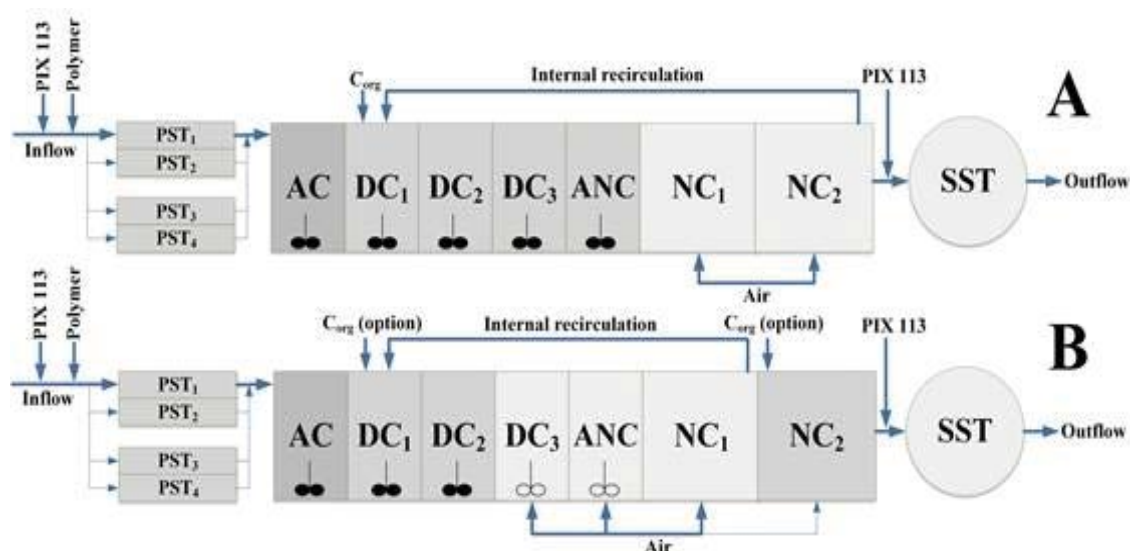


Fig. 1. Wastewater treatment plant before (A) and after (B) modification diagram: AC – anaerobic chamber, DC_n and ANC – anoxic chambers, NC_n – oxia chamber (nitrification), PST_n – pre-settlement tanks, SST – secondary settlement tank.

is approximately 12,500 m³. Fig. 1A shows an arrangement of the wastewater treatment system existing in the described wastewater treatment plant. A system of internal recirculation of wastewater rich in nitrogen (V) rich from NC₂ nitrification chamber to DC₁ denitrification chamber has been designed. To support the heterotrophic denitrification process supplementation of an external organic carbon source to DC₁ denitrification chamber has been provided (A2O).

To remove phosphates from wastewater there is a possibility, in the technological system, to add chemical reagents (PIX 113) and to proceed with chemical removal of phosphorus both through initial and final precipitation. Sludge is subjected to psychrophilic fermentation in an open digestive chamber then sludge is mechanically dehydrated. Dehydrated sludge is then directed to a low-temperature belt conveyor drying facility combined with two electro-osmotic dehydrators systems. Right from putting the plant into normal operation values of indicators of raw and purified wastewater quality were systematically analyzed. In the initial operational period, wastewater purification efficiency was high and purified wastewater quality indicators complied with legal requirements.

As of 2017 reduced influx of raw wastewater and increased concentrations of organic compounds, suspended solids, phosphorus, and total nitrogen in raw wastewater were noted. At the same time increase of total nitrogen concentration in purified wastewater was noted. At that period increase of pollutant concentrations level, including total nitrogen concentration in raw wastewater, could be caused by an uncontrolled discharge of industrial wastewater, which was often loaded with mineral and organic nitrogen compounds because apart from clear increase of total nitrogen in the influx also clear increase of other regulated indicators of raw wastewater quality were noted. Furthermore, it was determined that introduction (recirculation) of sludge

liquids coming from sludge treatment processes to the stream of wastewater inflowing to the biological part could have impact on increase of nitrogen load in raw wastewater. On the other hand, high sludge liquid loading with pollutants was influenced by hydraulic and mass overload of the gravity thickeners to which mixed sewage sludge, initial, and surplus sludge were directed. Overcharging of gravity thickeners was observed particularly during temperature decrease periods and when surplus sludge was removed from the treatment system (recirculation degree regulation). In such case higher loading of overflow channels with mixed sludge slurry was observed. This might have impact on quality of raw wastewater, and consequently cause increase of total nitrogen level in purified wastewater. At the same time, to reduce phosphorous compounds concentrations in sludge liquids a chemical reactor (accelerator) was used to which wastewater from overflows of gravity thickeners and liquids separated in dehydration of sludge digested in sedimentation centrifuges were supplied. Thus phosphates were precipitated in sludge liquids before the liquids were supplied to pre-settlement tanks. There was also a possibility of simultaneous phosphate precipitation in biological reactors before the secondary settlement tanks and at the final stage of sewage sludge treatment.

Increase of concentration of organic compounds expressed by BOD₅ and COD_{Cr} noted at that period with simultaneous decrease of raw wastewater resulted in increase of organic pollutants charge entering part of the biological treatment facility. Furthermore, the proportion between the content of those compounds and total nitrogen concentration changed thus having impact on interference of nitrogen biological compounds transformation. Due to hydraulic underload of the wastewater treatment plant only one out of four pre-settlement tank chambers was used. The average time of wastewater retention exceeded 1 h. All pre-settlement tank chambers were operated periodically, i.e. in the event

of influx of rainwater to the plant. Hydraulic underload and increasing trend in total nitrogen concentration variation in raw and purified wastewater was the cause of commencement of the action to modify the wastewater treatment process.

2.2. Modification of A2O technological system

As problems associated with maintaining of total nitrogen concentration in purified wastewater were diagnosed, in 2019 some attempts to increase nitrogen removal efficiency were made. This consisted in change of the aeration system and abandonment of wastewater aeration in the last chamber NC_2 . The changes introduced in the wastewater treatment technological system are presented in Fig. 1B. Thus, the final denitrification in the already existing A2O system was sectioned out. Assurance of anaerobic conditions (concentration of dissolved oxygen below $0.1 \text{ mg O}_2/\text{dm}^3$) for the final denitrification process in biological reactors was achieved by limitation of influx of compressed air to two NC_2 chambers located at the end part of the biological reactors [21–24]. In order to assure proper volumetric capacity of the aerobic (nitrification) zone, which was reduced due to final denitrification, volumetric capacity of the preceding denitrification zone was reduced by supply of air to ANC and DC_3 chambers [25–27]. In these chambers (ANC and DC_3) the existing wastewater fine-bubble aeration system was used. However, the disk diffusers with EPDM membranes that were in use, provided oxygen concentration at the variable level from 0.2 to $1.5 \text{ mg O}_2/\text{dm}^3$ depending on pollutant load volume in raw wastewater flowing into the wastewater treatment plant. It was found that despite relatively low oxygen concentration in the nitrification zone, proper conditions for oxidation of ammonium nitrogen to nitrates (V) occurred in the chamber ANC and DC_3 [28,29].

It appears from the literature data that the ammonium nitrogen oxidation process proceeds with intermediate origination of hydroxylamine and its oxidation to nitrate nitrogen (III) proceeds using oxygen originating from water molecules and the nitrification process may proceed at lower than stoichiometric concentration of dissolved oxygen [30]. It's been considered that this zone may be treated as a pre-nitrification zone. In NC_1 chamber oxygen concentration was equal to $1.5 \text{ mg O}_2/\text{dm}^3$. The internal recirculation system was also modified. The internal recirculation flow was being performed before the modernization using pumps located at NC_1 and NC_2 . In the classic A2O arrangement the influx to the internal recirculation is located at the end of the nitrification zone i.e. to the last oxic chamber NC_2 . But in the modified A2O arrangement the internal recirculation influx is accomplished from NC_1 chamber. External and internal recirculation flow in the modified A2O arrangement was above 100% and 400%, respectively. The technological parameters of the biological process were set at the level: the BOD load of activated sludge was equal to $0.13 \text{ kg BOD/kg}_{\text{d.m.o}}$ (low-loaded activated sludge), the BOD load of bioreactor – $0.59 \text{ kg BOD/m}^3 \text{ d}$. The hydraulic load of bioreaktor was $0.81 \text{ m}^3/\text{m}^3 \text{ d}$ ($0.13 \text{ m}^3/\text{m}^2 \text{ h}$) on average. The concentration of activated sludge in bioreaktor and the age of activated sludge was equal to 4.5 kg/m^3 at 18 d, respectively.

2.3. Wastewater sampling

In order to check which change in wastewater purification had taken place, with particular consideration of nitrogen compounds, concentration of selected raw and purified wastewater indicators was monitored. At the period from January to August 2020, during operation of the modified A2O technological system, samples for testing were being taken, on average, once per week. The samples were being taken using automatic Liquistation CSF 48 Endress+Hauser station. Frequency of sampling and analyses performed was adjusted to the frequency of wastewater analyses before the modernization. During the period of 2015–2019 (before modification) samples of raw and purified wastewater were also being taken, on average, once per week. This allowed to compare the results and indicated the impact of performed modernization on the change of concentrations and indicators values as well as the efficiency of wastewater treatment. In this paper, average monthly test results achieved from 33 average daily raw wastewater samples and 33 average daily purified wastewater samples are presented versus the test results of 2015–2019 period. Simultaneously, also the volume of surplus sludge was being determined.

2.4. Analytical methodology

Samples of wastewater taken for testing were analyzed in accredited wastewater testing laboratory located at “JAMNO” wastewater treatment plant. Particular indicators of quality of purified and raw wastewater were being determined using mainly standard research methods in accordance with Polish standards (PN): pH (PN-ISO 10523:2012), temperature (PN-77/C-04584:1977), COD_{Cr} (bichromate method PN-ISO 15705:2005), BOD_5 (manometric method, PN-EN 1899-1:2002 and PN-EN 1899-2:2002) this method was used also to determine ammonium nitrogen N-NH_4 (PN-ISO 5664:2002), and nitric nitrogen(V) N-NO_3 (PN-82 C-04576-08:1982), Kjeldahl nitrogen N-N_{Kj} (titration method PN-EN 25663:2001), nitric nitrogen (III) N-NO_2 (PN-EN 25777:1999), total nitrogen N_{tot} (PN-73/C-04576.14:1973), total phosphorus P_{tot} (PB-16:2014 ed. 4), total suspended solids TSS (PN-EN 872:2007 + Ap1:2007), easily settling suspended solids ESSS (PN-72/C-04559:1972), chlorides (PN-ISO 9297:1994). The test methods uncertainty was defined at $\alpha = 95\%$ level of confidence. The organic nitrogen N_{org} concentration based on the values of N-N_{Kj} and N-NH_4 was calculated.

2.5. Statistical methods

Physicochemical and biological processes that occur during municipal wastewater purification are complex. They have nonlinear character due to frequent process disturbances caused by high quantitative and qualitative (chemical composition) variability of raw wastewater flowing into wastewater treatment plant [31]. Therefore, development of a universal mathematical model dealing with all mutual correlations between wastewater qualitative indicators is not easy. However, advanced statistical and numerical methods allow for development of a highly reliable model. To evaluate the measures of examined result

sets STATISTICA package – (multiple regression module) was used at the first stage of the analysis [1,32]. At the second stage the stepwise regression procedure was applied as an element of an auxiliary procedure. In our calculations we used previously corrected coefficient of determination R^2 , which allows to find the best possible model taking into account variables that are strongly correlated with the dependent variable and, at the same time, the least correlated between them. To develop the model, the results of raw and purified wastewater testing from the period after the modernization i.e. from January to August 2020 were used.

3. Results

3.1. Wastewater quality tests

Table 1 presents a comparison of concentrations and pollutant loads fed with raw wastewater to the wastewater treatment plant in 2020 and design assumptions pertaining to wastewater supplied to the biological part of the plant. In subsequent years of plant operation decrease of raw wastewater was observed and in 2020 the average daily wastewater influx was at 21,262 m³/d level, so it was by 43% lower than the assumed value (36,000 m³/d).

At the same time, an increase of concentrations of the analyzed wastewater quality indicators trend was observed. However, variations of those concentrations were not adequate to the reduced wastewater stream. Organic compounds concentrations in that period were approximately two-fold higher than the assumed ones, which proves influx of those pollutants from additional sources.

Tables 2 and 3 show the results of tests performed during the January–August 2020 period for raw and purified wastewater, respectively. Apart from concentration values for the analyzed pollutants. Table 3 contains also the effectiveness of analyzed pollutants removal during the wastewater treatment processes.

This scope comprises the following physicochemical indicators: nitrogen compounds (N-NH₄, N-NO₂, N-NO₃, N-N_{Kj}, BOD₅, COD_{Cr}, P_{tot}, TSS, ESSS, chlorides, pH, and wastewater temperature. Apart from concentration values for the analyzed pollutants, Tables 2 and 3 contain also loads of pollutants in raw and purified wastewater, respectively.

The analysis results indicate that raw wastewater featured increased (compared with the assumed value) content of organic compounds (COD_{Cr}, BOD₅) and ammonium nitrogen N-NH₄ as well as Kjeldahl nitrogen. Comparison of the pollutant loads flowing into the wastewater treatment plant with the designed loads leads to a conclusion that during the research period, as well as in the previous years (2005–2019), the plant was overloaded with organic pollutants load expressed by COD_{Cr} and total suspended solids with simultaneous underloading with nitrogen and phosphorus loads (Tables 1 and 2).

During the March–June period, increased concentrations of ammonium ions were recorded. This could be related both to the ammonification process and inhibition of the nitrification process (the inhibition by *Nitrobacters* and *Nitrosomonas* activity). According to literature data [30] by un-ionized ammonia and un-ionized nitrous acid the inhibitory concentrations of the nitrification process ranged from 0.1 to 150 mg/dm³ and 0.2 to 2.8 mg/dm³, respectively. The inhibition was not permanent and could be relieved by adjusting operational conditions.

In Table 3, the same way as in Table 2, results of the determination of quality indicators for purified wastewater performed within the same period (January–August 2020) are presented. Table 3 shows also the highest admissible values (HAV) of particular quality indicators that apply in Polish legislature [13]. During the research period and in the previous year's said wastewater treatment plant was insignificantly underloaded with easily biodegradable compounds (BOD₅), which is one of the main factors having impact on efficiency of biological nitrogen removal. The ratio between this indicator and total nitrogen content increased to 5.9 whereas an assumption was made for 5.4. Therefore, simultaneous variations of biodegradable compounds and total nitrogen should not have any significant impact on the efficiency of the biological nitrogen removal process (Table 3). In the tested case, during the period from July to August 2020 (Table 2), the average value of COD_{Cr} appeared to be at 1,558.6 mgO₂/dm³ level with average total nitrogen level amounting to 119.4 mg N_{tot}/dm³, which means that COD_{Cr}/N_{tot} ratio was beneficial as it amounted to 13. At the same time, BOD₅ concentration amounted to 708 mg/dm³, therefore, BOD₅/COD_{Cr} ratio amounted to 0.45 (design assumption – 0.55). As it appears from the literature,

Table 1

Average concentration and load values for fundamental pollutant indicators in raw wastewater in 2020 and design assumptions for theoretical loads after the pre-settlement tanks

Indicator	Concentration	Design load	Concentration during I–VIII 2020 period (design concentration %) average value	Load during I–VIII 2020 period (design load %) average value
	mg/dm ³	kg/d	mg/dm ³	kg/d
BOD ₅	380	15,200	708 (186%)	14,681 (97%)
COD _{Cr}	690	27,600	1,559 (226%)	32,258 (117%)
TSS	290	11,600	920 (317%)	19,565 (169%)
N-N _{Kj}	70	2,800	119 (170%)	2,447 (87%)
N-NH ₄	37	1,480	53 (143%)	1,092 (74%)
P _{tot}	14	560	19 (136%)	374 (67%)

Table 2
Average monthly indicators for raw wastewater quality and pollutant load in 2020

Indicator	Unit	Value	I	II	III	IV	V	VI	VII	VIII	Monthly average
Average monthly flow rate	m ³ /d	36,000	25,844	27,265	23,307	18,081	18,980	18,393	19,824	18,424	21,262
COD _{Cr}	mg O ₂ /dm ³	690	1,073.3	891.8	2,151.6	2,309.3	2,226.0	1,362.8	1,132.8	1,321.0	1,559
COD Load	kg/d	27,600	27,738.4	24,314.9	50,147.3	41,754.5	42,249.5	25,066.0	22,456.6	24,338.1	32,258
BOD ₅	mg O ₂ /dm ³	380	510.0	412.5	976.0	1,043.3	827.5	606.0	630.0	655.0	708
BOD ₅ Load	kg/d	15,200	13,180.4	11,246.8	22,747.6	18,863.9	15,706.0	11,146.2	12,489.1	12,067.7	14,681
N–NH ₄	mg/dm ³	37	44.2	33.6	49.6	64.4	57.4	58.9	54.4	60.2	53
N–NH ₄ Load	kg/d	1,480	1,142.3	916.1	1,156.0	1,164.4	1,089.5	1,083.3	1,078.4	1,109.1	1,092
N–N _{Kj}	mg/dm ³	70	86.6	67.4	126.6	193.0	153.0	120.0	90.8	116.5	119
N–N _{Kj} Load	kg/d	2,800	2,238.1	1,837.7	2,950.7	3,489.6	2,903.9	2,207.2	1,800.0	2,146.4	2,447
N–NO ₂	mg/dm ³	–	0.14	0.25	0.16	0.12	0.14	0.18	0.14	0.17	0.20
N–NO ₂ Load	kg/d	–	3.70	6.79	3.61	2.21	2.68	3.26	2.78	3.11	3.52
N–NO ₃	mg/dm ³	–	0.25	0.25	0.25	0.25	2.30	0.25	0.25	0.25	0.50
N–NO ₃ Load	kg/d	–	6.46	6.82	5.83	4.52	43.65	4.60	4.96	4.61	10.18
N _{tot}	mg/dm ³	–	86.7	67.7	126.7	193.0	153.5	120.0	90.9	116.5	119
N _{tot} Load	kg/d	–	2,240.7	1,845.8	2,953.0	3,489.6	2,913.4	2,207.2	1,802.0	2,146.4	2,450
N _{org}	mg/dm ³	–	42.4	33.8	77.0	128.6	95.6	61.1	36.4	56.3	66
N _{org} Load	kg/d	–	1,095.8	921.6	1,794.6	2,325.2	1,814.5	1,123.8	721.6	1,037.3	1,354
P _{tot}	mg/dm ³	14	9.6	6.8	19.8	37.7	20.5	19.1	12.3	23.5	19
P _{tot} Load	kg/d	560	248.1	185.4	461.5	681.7	389.1	351.3	243.8	433.0	374
TSS	mg/dm ³	290	566.7	342.5	1,264.0	1,966.7	1,061.5	780.0	515.0	865.0	920
TSS Load	kg/d	11,600	14,645.8	9,338.3	29,460.0	35,559.9	20,147.3	14,346.5	10,209.4	15,936.8	19,565
ESSS	cm ³ /dm ³	–	16.7	18.0	55.6	109.3	46.4	34.4	20.5	31.0	42
Chlorides	mg/dm ³	–	228.0	123.8	149.3	194.3	205.3	168.0	249.3	364.5	210
pH	–	–	7.4	7.5	7.4	7.4	7.1	7.3	7.3	7.3	7.3
Temperature	°C	–	12.2	10.6	12	13.9	14.1	17.7	18.7	19.7	14.9

Table 3
Average monthly quality indicators for purified wastewater quality and pollutant load in 2020

Indicator	Unit	NDS	I	II	III	IV	V	VI	VII	VII	Monthly average	Removal %
Average monthly flow rate	m ³ /d	36,000	25,844	27,265	23,307	18,081	18,980	18,393	19,824	18,424	21,262	–
COD _{Cr}	mg O ₂ /dm ³	125	28.8	30.2	32.6	35.7	31.4	32.7	33.3	36.1	32.9	97.9
COD _{Cr} Load	kg/d	4,500	744.3	823.4	759.8	645.5	596.0	601.5	660.1	665.1	687.0	97.9
BOD ₅	mg O ₂ /dm ³	15	4.6	4.0	4.8	5.8	6.1	4.9	2.8	5.4	4.8	99.3
BOD ₅ Load	kg/d	540	118.9	109.1	111.9	104.9	115.8	90.1	55.5	99.5	100.7	99.3
N–NH ₄	mg/dm ³	10	1.8	2.2	1.9	3.2	2.7	0.5	0.9	1.2	1.7	96.8
N–NH ₄ Load	kg/d	360	46.5	60.0	44.3	57.9	51.2	9.2	17.8	22.1	38.6	96.5
N–N _{Kj}	mg/dm ³	–	4.1	4.4	4.1	5.5	5.6	3.8	2.6	3.0	4.1	96.5
N _{Kj} Load	kg/d	–	106.0	120.0	95.6	99.4	106.3	69.9	51.5	55.3	88.0	96.4
N–NO ₂	mg/dm ³	1	0.14	0.19	0.20	0.17	0.05	0.05	0.07	0.10	0.12	–
N–NO ₂ Load	kg/d	36	3.5	5.0	4.7	3.0	0.9	1.0	1.4	1.8	2.7	–
N–NO ₃	mg/dm ³	10	2.7	2.3	2.8	2.3	1.3	2.8	2.9	3.5	2.6	–
N–NO ₃ Load	kg/d	360	69.8	62.7	65.3	41.6	24.7	51.5	57.5	64.5	54.7	–
N _{tot}	mg/dm ³	10	6.9	6.9	7.1	7.9	6.9	6.5	5.5	6.6	6.8	94.3
N _{tot} Load	kg/d	360	178.3	188.1	165.5	142.8	131.0	119.6	109.0	121.6	144.5	94.1
N _{org}	mg/dm ³	–	2.3	2.2	2.2	2.3	2.9	3.3	1.7	1.8	2.3	96.5
N _{org} Load	kg/d	–	59.4	60.0	51.3	41.6	55.0	60.7	33.7	33.2	49.4	96.4
P _{tot}	mg/dm ³	1	0.5	0.3	0.3	0.4	0.4	0.5	0.5	0.4	0.4	97.8
P _{tot} Load	kg/d	36	12.9	8.2	7.0	7.2	7.6	9.2	9.9	7.4	8.7	97.7
TSS	mg/dm ³	35	6.8	4.0	6.8	5.3	8.1	3.5	3.9	7.1	5.7	99.4
TSS Load	kg/d	1,260	175.7	109.1	158.5	95.8	153.7	64.4	77.3	130.8	120.7	99.4
pH	–	6.5–9.0	7.2	7.2	7.2	7.2	7.1	7.1	7.1	7.1	7.2	–
Temperature	°C	35	12.2	10.8	12.4	14.6	14.9	19.0	19.6	20.9	15.6	–

NDS – The highest permissible concentration

the organic substrate is the most easily degradable when this ratio exceeds 0.5 [33]. This confirms the thesis about influx of industrial wastewater into the plant. Values of BOD_5/N_{tot} at 5.4 and BOD_5/P_{tot} at 27.1 level assure correct course of biological processes. The COD_{Cr} and total phosphorus content proportion appeared to be 82 at that period, which assured good conditions for phosphorus removal. According to literature data, if COD_{Cr}/P_{tot} ratio exceeds 50, efficiency of this process is high and phosphorus concentration in purified wastewater should not exceed 2 mg/dm³ [30]. This has been confirmed by the results obtained as the final phosphorus concentration did not exceed 0.5 mg/dm³.

Furthermore, reduction of phosphorus content in purified wastewater was achieved also due to increase of the external recirculation degree up to approximately 200% and curtailment of the active sludge period of retention in the secondary settlement tanks. Earlier research work performed by the co-author have indicated that at low variations of organic compounds concentrations as well as concentrations of nitrogen compounds in raw wastewater and following preliminary precipitations of phosphates, high efficiency of removal of those compounds in the pre-settlement tank can be achieved. Reduction of BOD_5 , COD_{Cr} and nitrogen loads in the pre-settlement tank was 70%, 50% and 30%, respectively [34]. It can be assumed, with a high degree of probability, that qualitative composition of mechanically purified wastewater, assuming maximum reduction of pollutant loads, was beneficial for the biological stage of biogenic substances removal ($BOD_5/N_{Kj} = 6.2$). An assumption has been made in literature that susceptibility of wastewater (raw or mechanically purified) to biodegradation, including biological nitrogen removal through denitrification, proceeds correctly if BOD_5/N_{Kj} ratio exceeds 4 [15]. Fig. 2 illustrates the efficiency of wastewater treatment with regard to five fundamental legally fixed pollutant indicators during the pre-modernization (2015–2019) and post-modernization (2020) periods.

During the 2015–2019 period efficiency of removal of organic compounds expressed by total indicators COD_{Cr} and BOD_5 was high and amounted, on average, to 99.5 and 98.2%, respectively. Equally high was the efficiency

of removal of total suspended solids (98.2%) and total phosphorus (97.8%). Efficiency of total nitrogen removal was relatively high (91.6%) on an average but systematic increase of total nitrogen concentration in purified wastewater was observed. This was a reason for planning and performance of the modernization operation described in paragraph 2 of this paper. Due to said alterations, efficiency of removal of organic compounds and total phosphorus was maintained at a similar level. However, efficiency of removal of total nitrogen increased by several percentage points whereas efficiency of total suspended solids removal increased insignificantly. Fig. 3 illustrates relationships between values of the tested BOD_5 , $N-NH_4$, $N-N_{Kj}$, $N-NO_2$, $N-NO_3$, N_{tot} and total suspended solids versus temperature in 2020. Impact of temperature in particular seasons (12.4°C and 18.7°C) on quality of purified wastewater after modification of the technological system is significant and pertains, in particular to the concentrations of nitrates and total nitrate. It is a typical phenomenon associated with activity of nitrification and denitrification microorganisms.

Those differences, depending on wastewater temperature, amount to approximately to 0.7 mg/dm³. The lowest total nitrogen concentrations in purified wastewater (7.2 mg/dm³ on average) were noted at wastewater temperature below 13°C. At higher wastewater temperature (average 18.7°C) total nitrogen concentration amounted on average to 6.5 mg/dm³. In both cases the total nitrogen removal degree was satisfactory. It should be underlined that in said period raw wastewater manifested high variability in total nitrogen concentration (67.7–193.0 mg/dm³– Table 2). The nitrogen compound's transformation intensity depending on temperature is described in literature. It appears therefrom that the most favorable temperature for phosphorus removal, nitrification and denitrification processes is in excess of 20°C [35]. Figs 4 and 5 illustrate average total nitrogen concentrations in raw and purified wastewater that occurred after modernization of the technological system (2020) and in the previous period (2015–2019).

Research of raw wastewater performed at the wastewater treatment plant during 2015–2019 period has shown

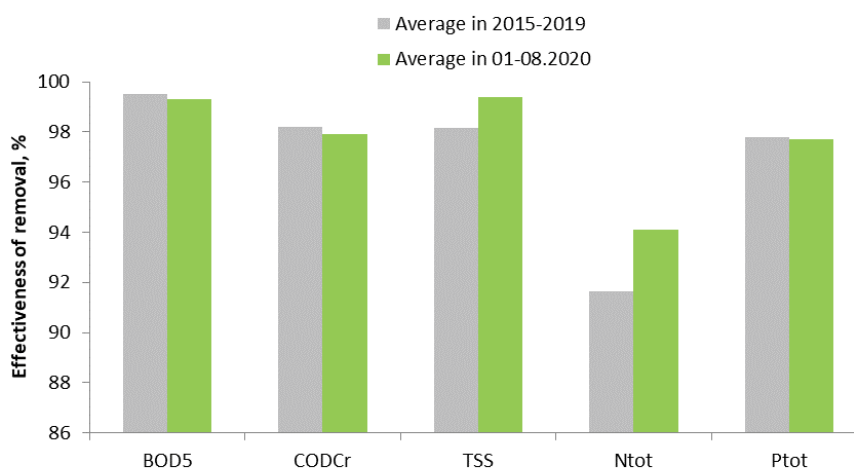


Fig. 2. Wastewater treatment efficiency during 2015–2019 and January–August 2020 periods.

that total nitrogen concentration was higher compared to the designed value amounting to $70 \text{ mg N}_{\text{tot}}/\text{dm}^3$ (Fig. 2). This pertained, in particular, to 2018–2019 period (Fig. 4). Concentration of these compounds in wastewater treated during 2015–2017 period did not exceed the admissible value ($10 \text{ mg}/\text{dm}^3$) but a rising trend of those compounds concentrations was noted [11,36].

Increase of total nitrogen in recent years was caused by increased load of those pollutants delivered from industrial plants or/and an increase caused by internal recirculation of sediment supernatant to raw wastewater stream flowing

into the plant. Variations in nitrogen concentrations in raw wastewater were noted and during 2016–2019 period this had a rising trend (Fig. 4). Modification of A2O system and sectioning off of the final denitrification allowed for firm reduction of total nitrogen in purified wastewater (by 41% on average). Increase of the total nitrogen load reduction resulted from the final denitrification to classic A2O technological system at expense of reduction of the pre-emptive denitrification zone. It should be assumed in design practice (maintaining certain degree of safety) that the denitrification zone size should make 30% of the total

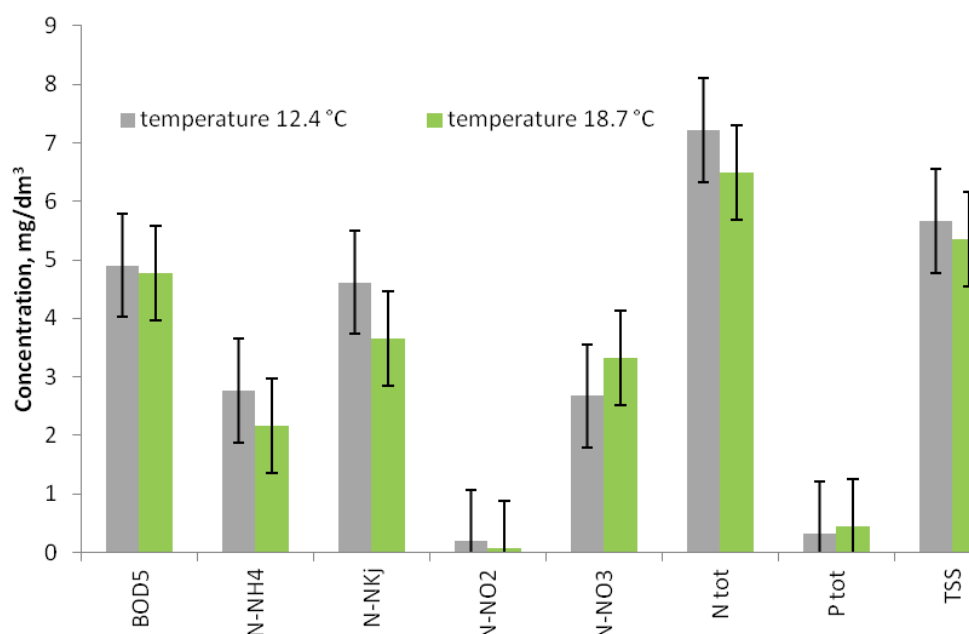


Fig. 3. Average concentration of selected quality indicators of purified wastewater within the researched period depending on the average wastewater temperature.

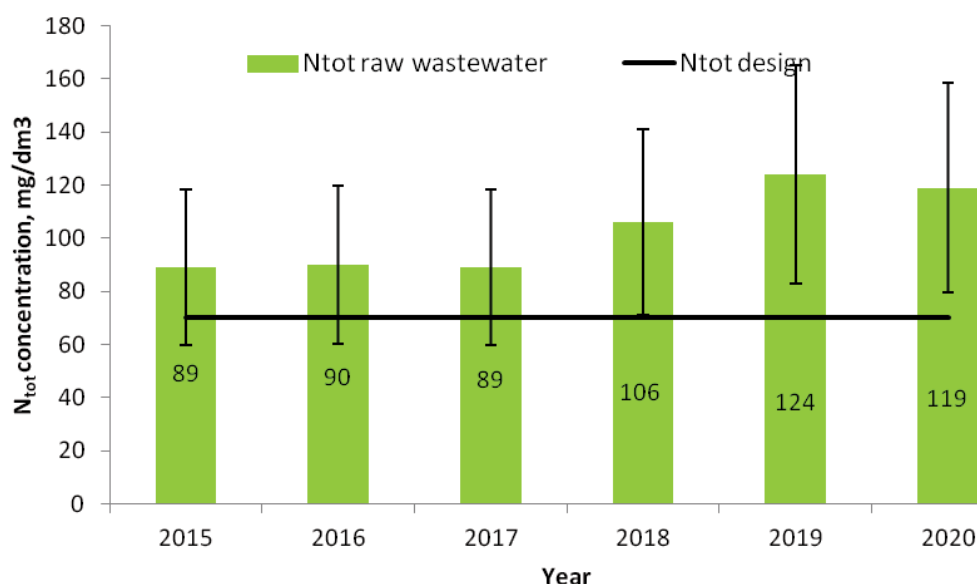


Fig. 4. Annual average total nitrogen N_{tot} concentrations in raw wastewater during 2015–2020 period versus the designed value amounting to $70 \text{ mg}/\text{dm}^3$.

volumetric capacity of the biological reactor [37]. In the researched case the volumetric capacity of the pre-emptive denitrification zone in classical A2/O arrangement was approximately 50% (Fig. 1). Reduction of the pre-emptive denitrification zone due to modification of the technological arrangement from approximately 50% to approximately 25% was, from the design point of view, an admissible operation that had no significant impact on total nitrogen removal efficiency in this part of the technological system. Additionally, due to the low throughput of the oxygen supplying devices (aeration grates) in DC₃ and ANC concentration of dissolved oxygen was relatively low remaining within 0.2 to 1.5 mg/dm³ limits. Therefore, an assumption can be made, that in this part of the modified A2O system beneficial conditions for the course of simultaneous nitrification and denitrification (SND) may exist [9,33,38].

In the modified A2/O technological system not only significant results of nitrogen compounds removal but also total suspended solids removal were achieved compared to plant operation periods in the preceding years (Table 2 and Fig. 2). Increase of the total suspended solids removal degree in the modified technological system by 1.2% compared to previous years can be explained by the effect of both reductions of nitric nitrogen concentration as well as molecular oxygen in the closing denitrification zone in sludge directed to the secondary settlement tanks. Decrease of nitric nitrogen due to secondary denitrification before the secondary settlement tanks limits the possibility to drag out active sludge flocs in the secondary settlement tanks [2,4]. It was proved that decrease of molecular oxygen content in the chambers performing final denitrification has impact on improvement of active sludge particles sedimentation in the secondary settlement tanks. This phenomenon is specific for biological wastewater treatment systems in which BIOGRADEX technology is employed. This technology is based on degassing of active sludge flocs before the secondary settlement tanks [3]. This technology, which

is employed in, among other places, Wastewater Treatment Plant in Czeszochowa, allowed for reduction of total suspended solids in purified wastewater from 13.8 to 5.6 mg/dm³ [39]. Insignificant decrease of COD_{cr}, BOD₅, and total phosphorus load reduction degree in modified A2O system may result from influence of final denitrification in which phosphorus is re-released from active sludge cells including possible extracorporeal secretion of organic polymer substances EPS. It was noted that removal of gas from active sludge may lead to release of extra-cellular polymer substances, which cause increase of COD_{cr} [40]. Figs. 6 and 7 illustrate forms of occurrence of mineral and organic nitrogen compounds that make total nitrogen N_{tot} components in raw and purified wastewater analyzed in 2020.

Nitrogen occurred in raw wastewater mainly in organic form and as ammonium nitrogen whereas in purified wastewater share of nitrates, particularly nitrates (V), increased. In Table 4 results of the annual average volume of surplus sludge removed from the wastewater treatment system were set out in the aspect of total nitrogen concentration in raw and purified wastewater. Surplus sludge volumes removed from the wastewater treatment system during 2015–2020 were increasing systematically and in 2020 amounted to 337,156 m³/y. The wastewater treatment system modification, despite increase of excess sewage sludge volumes, had no impact on the nitrogen compounds removal efficiency. The average total nitrogen concentration in purified wastewater in that period amounted to 6.7 mg/dm³ (Table 4).

3.2. Statistical analysis of results

3.2.1. Determination of correlation coefficients

Table 5 contains coefficients of correlation between particular parameters of pollutants occurring in raw and purified wastewater, thus selected significant linear correlation coefficients are set out.

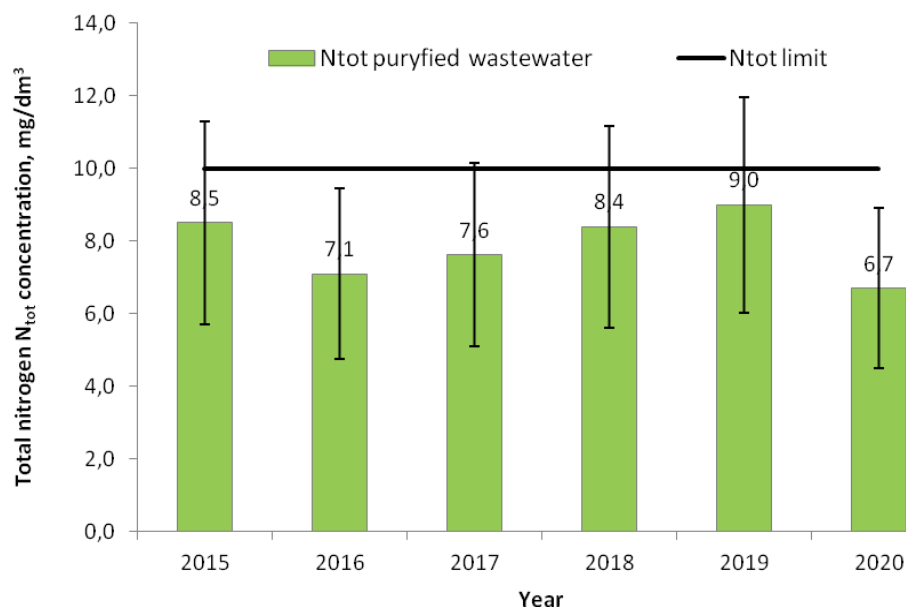


Fig. 5. Annual average total nitrogen N_{tot} concentrations in purified wastewater from 2015 to August 2020.

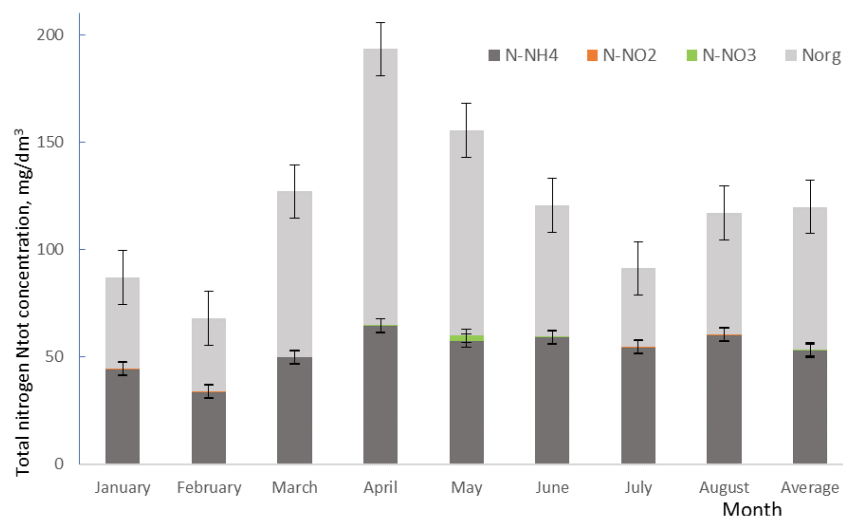


Fig. 6. Monthly average total nitrogen N_{tot} concentrations taking into account mineral and organic components in raw wastewater during the period from January to August 2020.

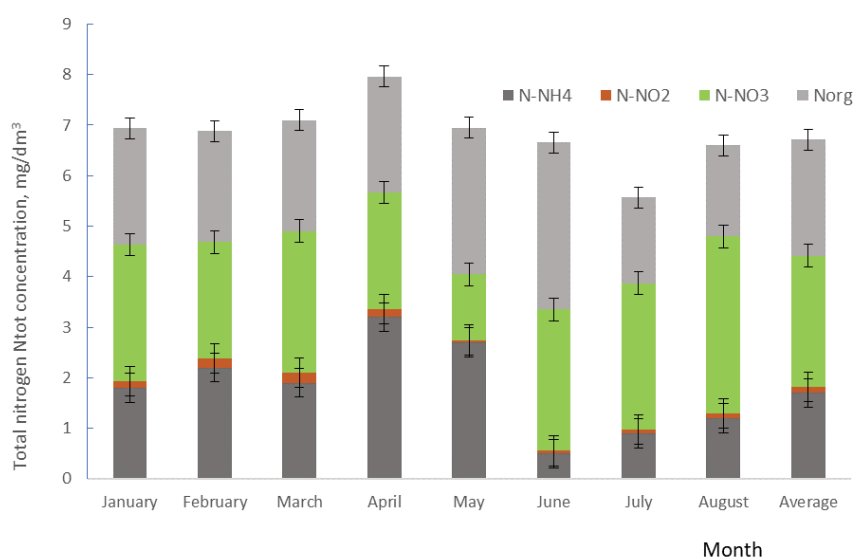


Fig. 7. Average monthly total nitrogen N_{tot} concentrations taking into account mineral and organic components in purified wastewater during the period from January to August 2020.

Having analyzed the processes occurring during wastewater treatment, independent variables used to develop a multiple regression model explaining the highest percentage of variability of total nitrogen variable (purified wastewater) were selected [32,40,41]. Correlations for the variables were calculated using Tables 2 and 3 marked for raw and purified wastewater respectively. The values of the correlation coefficients between the analyzed indicators are diversified. It was because they were calculated on the basis of the results obtained under real conditions. The quality of the wastewater flowing into the wastewater treatment plant varied with time. Additionally, the intensity of the nitrification, ammonification, and denitrification processes at changing temperatures was varied. It was determined that there is a clear positive total nitrogen correlation with values of COD_{Cr} , BOD_5 , total phosphorus, and total suspended

solids TSS. For example, a high correlation $r = 0.78$ was noted for COD_{Cr} parameter in purified wastewater and total phosphorus in raw wastewater (Table 5. and Fig. 8).

Positive correlation $r = 0.76$ was noted also between BOD_5 indicator in purified wastewater and organic nitrogen in raw wastewater (Fig. 9). Strong correlation $r = 0.72$ was determined between total nitrogen in purified wastewater and total suspended solids in raw wastewater (Fig. 10). Each time particular graphs in Figs. 8–10 were supplemented with histograms categorized in terms of particular groups of nitrogen and phosphorus compounds. Particular correlations indicated in those figures illustrate categorized scatter plots with regression lines. Histograms of the variable distribution were also inserted to illustrate the frequency of occurrence of given parameter/component in both types of waste (raw and purified).

Table 4

Excess sewage sludge volumes removed in 2015–2020 period in the aspect of average annual total nitrogen concentrations in raw and in purified wastewater

Year	Excess sewage sludge volume m ³ /y	Total nitrogen N _{tot} concentration – average value mg/dm ³	
		Raw wastewater	Purified wastewater
2015	191,475	89	9.7
2016	208,783	90	9.0
2017	266,178	89	9.9
2018	255,320	106	10.7
2019	274,835	124	11.4
2020	337,156	119	6.7

Table 5

Values of correlation coefficients r (significant for $p < 0.05$; column: indicators tested in raw wastewater; table row: indicators tested in purified wastewater)

Variable	COD _{Cr}	BOD ₅	N–NH ₄	N–N _{Kj}	N–NO ₂	N–NO ₃	N _{tot}	N _{org}	P _{tot}	TSS
COD _{Cr}	0.38	0.69	0.61	0.66	0.08	–0.47	0.60	0.27	–0.31	0.49
BOD ₅	0.54	0.54	0.51	0.47	0.18	–0.23	0.53	0.06	–0.27	0.38
N–NH ₄	0.78	0.49	–0.02	0.07	–0.49	0.07	0.09	0.17	0.37	0.16
N–N _{Kj}	0.58	0.75	0.55	0.62	–0.06	–0.35	0.62	0.29	–0.07	0.32
N–NO ₂	–0.33	–0.29	–0.18	–0.14	0.27	0.07	–0.10	0.03	–0.46	–0.41
N–NO ₃	–0.19	0.50	0.40	0.56	–0.48	–0.81	0.07	0.43	–0.06	0.56
N _{tot}	0.58	0.75	0.55	0.62	–0.06	–0.36	0.62	0.30	–0.07	0.32
N _{org}	0.47	0.77	0.68	0.74	0.08	–0.45	0.73	0.31	–0.20	0.34
P _{tot}	0.78	0.68	0.42	0.42	0.02	–0.06	0.58	0.11	–0.08	0.22
TSS	0.58	0.66	0.60	0.58	0.24	–0.21	0.72	0.12	–0.22	0.29
ESSS	0.56	0.59	0.64	0.62	0.28	–0.27	0.74	0.13	–0.24	0.14
Chlorides	0.50	0.10	–0.30	–0.49	–0.41	0.51	–0.32	–0.47	0.37	0.37
pH	–0.15	–0.39	0.07	–0.13	0.83	0.39	0.28	–0.36	–0.34	–0.44
Temperature	0.64	–0.10	–0.65	–0.62	–0.71	0.51	–0.59	–0.13	0.56	–0.16

3.2.2. Stepwise regression

The objective of this analysis was, at the first stage, definition of the statically significant impact of particular components (independent variables) on total nitrogen concentration in wastewater. To describe relationships between particular variables an estimator of the coefficient of correlation between examined parameters was used. For this purpose t-Student test was used to verify the hypothesis that the correlation coefficient differs significantly from “0”. At the second stage impact of selected variables (COD_{Cr}, BOD₅, total phosphorus and total suspended solids) on the independent variable, which was the total nitrogen concentration in purified wastewater, was examined [41]. At that time a progressive stepwise regression procedure was applied. Multiple regression equations obtained from further steps were being evaluated based on the value of corrected determination coefficient R^2 and Mallows’s statistics. Significance of regression equations in subsequent steps was being evaluated by application of Fischer F test, which means that at least one regression coefficient differed from zero. It allows to find a correlation between

particular variables using the estimator of coefficient of correlation between tested parameters as correlation r . Consequently, four models taking into account selected significant parameters specific for examined wastewater were developed. Corrected coefficients of determination R^2 calculated for regression equations in subsequent steps (Table 5) were: 0.44, 0.54, 0.76, and 0.78. These statistics determine what part of dependent parameter variability can be explained using the developed model. Statistical significance of regression coefficients b_i was also examined for $i = 1, 2, 3, 4$. To select the best possible set of independent variables the progressive stepwise regression was applied. Calculation results are shown in Tables 6–11, in which the following marking of particular variables was adopted: S_{raw} – COD_{Cr} of raw wastewater mg O₂/dm³; B_{raw} – BOD₅ of raw wastewater mg O₂/dm³; P_{tot} – total phosphorus mg/dm³; TSS – total suspended solids mg/dm³; WW_{pur} – purified wastewater.

Analysed regression Eqs. (1)–(4):

$$\text{Step 1. } S_{\text{raw}} \cdot N_{\text{tot}} = b_0 + b_1 \times \text{TSS}_{\text{tot}} \quad (1)$$

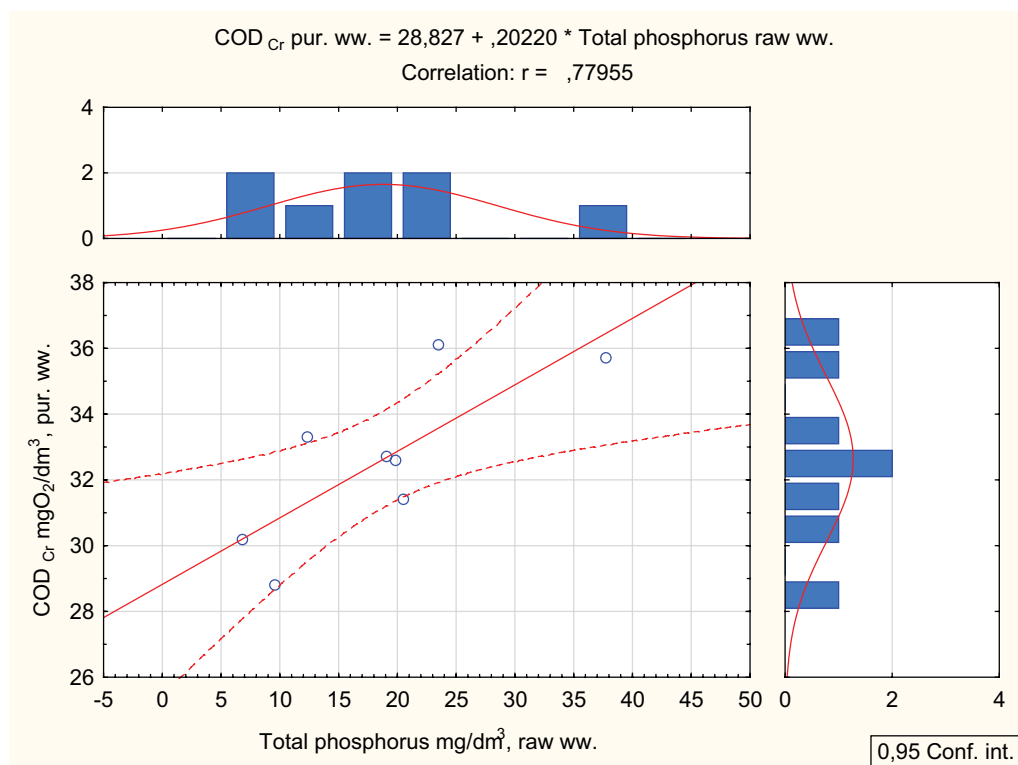


Fig. 8. Categorized scatter plot with regression line for COD_{Cr} indicator in purified wastewater and total phosphorus P_{tot} in raw wastewater. The correlation was tested for the monthly average.

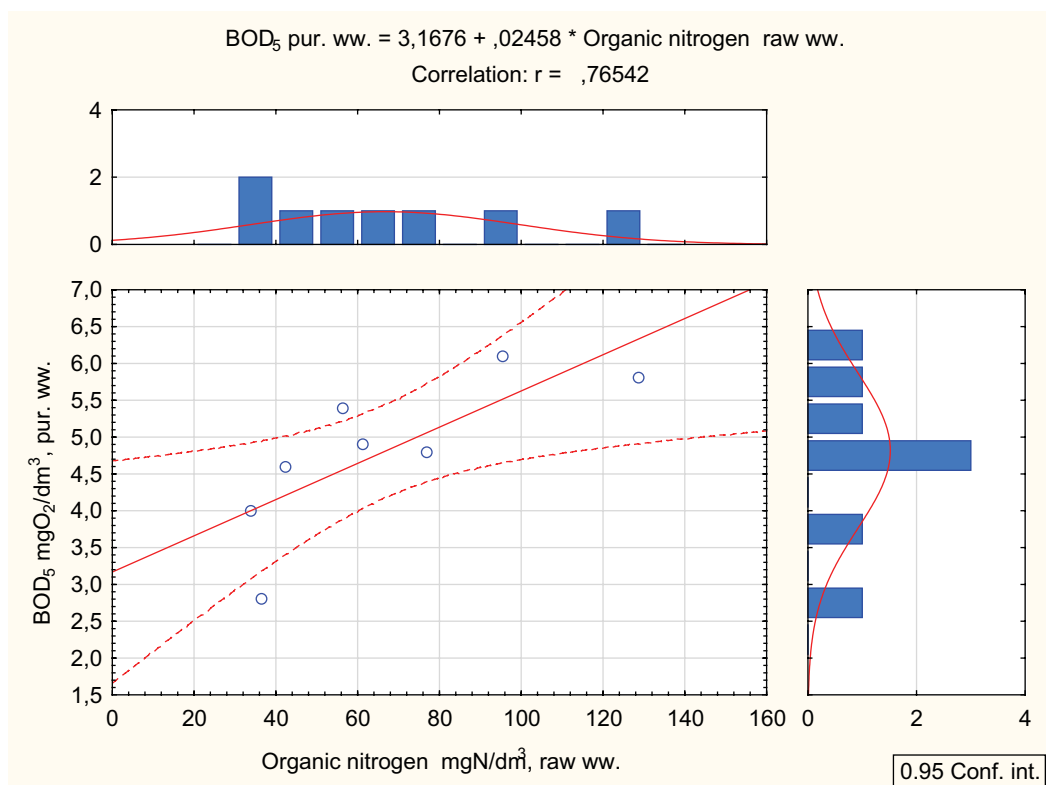


Fig. 9. Categorized scatter plot with regression line for BOD_5 indicator in purified wastewater and organic nitrogen N_{org} in raw wastewater. The correlation was tested for the monthly average.

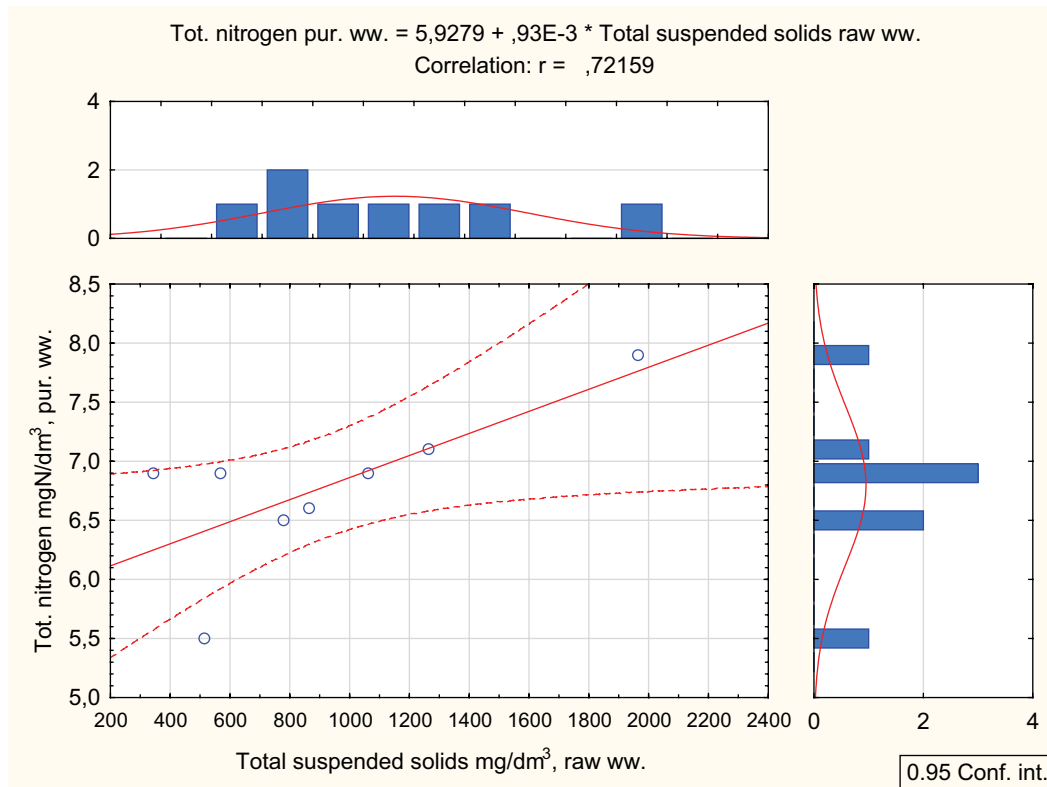


Fig. 10. Categorized scatter plot with regression line for total nitrogen N_{tot} in purified wastewater and total suspended solids TSS in raw wastewater. The correlation was tested for the monthly average.

Table 6
Sequence of addition of explanatory variables

Variable	Step 1.	Step 2.	Step 3.	Step 4.
Total suspended solids TSS	X	X	X	X
BOD ₅		X	X	X
Total phosphorus P_{tot}			X	X
COD _{Cr}				X

$$\text{Step 2. } S_{\text{raw}} \cdot N_{\text{tot}} = b_0 + b_1 \times \text{TSS} + b_2 \times B_{\text{raw}} \quad (2)$$

$$\text{Step 3. } S_{\text{raw}} \cdot N_{\text{tot}} = b_0 + b_1 \times \text{TSS} + b_2 \times B_{\text{raw}} + b_3 \times P_{\text{tot}} \quad (3)$$

$$\text{Step 4. } S_{\text{raw}} \cdot N_{\text{tot}} = b_0 + b_1 \times \text{TSS} + b_2 \times B_{\text{raw}} + b_3 \times P_{\text{tot}} + b_4 \times \text{WW}_{\text{pur}} \quad (4)$$

The regression equations obtained from the first and third steps are statistically significant. Documentation for the course of the progressive stepwise regression analysis is contained in Tables 8–11. Consolidated listing of that analysis is presented in Table 12.

To compare the models obtained from further steps also Mallows's statistics C_p was used (5). If regression models are being compared, a lower value of Mallows's statistics C_p in subsequent steps means better regression model. Table 13 contains the results of variance analysis calculated for particular regression steps. They were used

Table 7
Summary: regression results in subsequent steps

Statistics	Step 1.	Step 2.	Step 3.	Step 4.
	Value			
Multiple R	0.72	0.82	0.93	0.95
Multiple R ²	0.52	0.67	0.87	0.91
Corrected R ²	0.44	0.54	0.76	0.78
F	6.52	5.06	8.55	7.20
ρ	0.04	0.06	0.03	0.07
Estimation standard error	0.50	0.46	0.33	0.31

to calculate Mallows's C_p (5) statistics for each regression step presented in Table 14.

$$C_p = \frac{\text{SSR}(p)}{\text{MSR}(k)} - [n - 2(p + 1)] \quad (5)$$

where n – number of observations, p – number of subsequent variables setting the reduced model.

SSR(p) – sum of rests of the reduced model based on p subsequent variables, MSR(k) – mean square of rests of full model (k independent variables).

The best regression model for the data contained in Tables 1 and 2 justifying variability of total nitrogen in

Table 8

Summary of dependent variable regression: Total nitrogen – purified wastewater step 1

$$N_{\text{tot pur}} = 5.927934 + 0.000934 \times \text{TSS}_{\text{raw}} \pm 0.50$$

N = 8		Summary of dependent variable regression: Total nitrogen – raw wastewater $R = 0.72159467$ $R^2 = 0.52069887$ Corrected $R^2 = 0.44081535$ $F(1.6) = 6.5182$ $p < 0.04331$ Estimation std. error: 0.50153				
	b^*	Std. error (with b^*)	b	Std. error (with b)	$t(6)$	p
Free term			5.927934	0.380518	15.5786109	0.000004
$\text{SS}_{\text{tot raw}}$	0.721595	0.282637	0.000934	0.000366	2.55308172	0.043310

Table 9

Summary of dependent variable regression: Total nitrogen – purified wastewater step 2

$$N_{\text{tot pur}} = 7.0204 + 0.0022 \times \text{TSS}_{\text{raw}} - 0.0032 \times B_{\text{raw}} \pm 0.46$$

N = 8		Summary of dependent variable regression: Total nitrogen – raw wastewater $R = 0.81802032$ $R^2 = 0.66915724$ Corrected $R^2 = 0.53682014$ $F(2.5) = 5.0565$ $p < 0.06296$ Estimation std. error: 0.45645				
	b^*	Std. error (with b^*)	b	Std. error (with b)	$t(5)$	p
Free term			7.020376817	0.80737342	8.695328	0.00033283
TSS_{raw}	1.710140	0.70832217	0.002213844	0.00091695	2.414353	0.06053784
$\text{BOD}_{5 \text{ raw}}$	-1.060980	0.70832217	-0.00320831	0.0021419	-1.497878	0.19443275

Table 10

Summary of dependent variable regression: Total nitrogen – purified wastewater step 3

$$N_{\text{tot pur}} = 7.7757 + 0.0045 \times \text{TSS}_{\text{raw}} - 0.0047 \times B_{\text{raw}} - 0.0956 \times P_{\text{tot raw}} \pm 0.33$$

N = 8		Summary of dependent variable regression: Total nitrogen – raw wastewater $R = 0.93011536$ $R^2 = 0.86511458$ Corrected $R^2 = 0.76395051$ $F(3.4) = 8.5516$ $p < 0.03254$ Estimation std. error: 0.32585				
	b^*	Std. error (with b^*)	b	Std. error (with b)	$t(4)$	p
Free term			7.77576579	0.65604573	11.852475	0.00029012
TSS_{raw}	3.464787	0.88628699	0.004485305	0.00114733	3.909329	0.0174037
$\text{BOD}_{5 \text{ raw}}$	-1.556861	0.54589929	-0.00470780	0.00165075	-2.851919	0.04630589
$P_{\text{tot raw}}$	-1.378136	0.57169433	-0.09562382	0.03966778	-2.410617	0.07350565

Table 11

Summary of dependent variable regression: Total nitrogen – purified wastewater step 4

$$N_{\text{tot pur}} = 7.8429 + 0.0043 \times \text{TSS}_{\text{raw}} - 0.0064 \times B_{\text{raw}} - 0.0871 \times P_{\text{tot raw}} + 0.0008 \times \text{TSS}_{\text{raw}} \pm 0.31$$

N = 8		Summary of dependent variable regression: Total nitrogen – raw wastewater $R = 0.95169073$ $R^2 = 0.90571525$ Corrected $R^2 = 0.78000224$ $F(4.3) = 7.2046$ $p < 0.06828$ Estimation std. error: 0.31458				
	b^*	Std. error (with b^*)	b	Std. error (with b)	$t(3)$	p
Free term			7.842876325	0.63609334	12.329757	0.00114926
TSS_{raw}	3.296751	0.8683007	0.004267776	0.00112405	3.796785	0.03207462
$\text{BOD}_{5 \text{ raw}}$	-2.131634	0.73039068	-0.00644587	0.00220864	-2.918485	0.06157163
$P_{\text{tot raw}}$	-1.256055	0.5622686	-0.08715304	0.03901376	-2.233905	0.11159101
$\text{COD}_{\text{Cr raw}}$	0.663036	0.58335166	0.000772959	0.00068006	1.136597	0.3382816

Table 12
Summary list: regression coefficients and assessment of their significance

Dependent variable	Step 1.		Step 2.		Step 3.		Step 4.	
	b_i	p	b_i	p	b_i	p	b_i	p
Free term	5.927	0.000	7.020	0.000	7.776	0.000	7.842	0.001
TSS _{raw}	0.001	0.043	0.002	0.060	0.004	0.017	0.004	0.032
BOD _{5 raw}			−0.003	0.194	−0.005	0.046	−0.006	0.061
P _{tot raw}					−0.096	0.073	−0.087	0.111
COD _{Cr raw}							0.000	0.338

Table 13
Variance analysis. Data to be used to calculate Mallows's C_p statistics

Result	Variance analysis: Total nitrogen – purified wastewater step 1				
	Sum (square)	df	Mean (square)	F	p
1.	1.639551	1	1.639551	6.518226	0.043310
2.	1.509199	6	0.251533		
3.	3.148750				
4.	52.1%				
Result	Variance analysis: Total nitrogen – purified wastewater step 2				
	Sum (square)	df	Mean (square)	F	p
1.	2.107009	2	1.053504	5.056460	0.062958
2.	1.041741	5	0.208348		
3.	3.148750				
4.	66.9%				
Result	Variance analysis: Total nitrogen – purified wastewater step 3				
	Sum (square)	df	Mean (square)	F	p
1.	2.724030	3	0.908010	8.551600	0.032539
2.	0.424720	4	0.106180		
3.	3.148750				
4.	86.5%				
Result	Variance analysis: Total nitrogen – purified wastewater step 4				
	Sum (square)	df	Mean (square)	F	p
1.	2.851871	4	0.712968	7.204627	0.068283
2.	0.296879	3	0.098960		
3.	3.148750				
4.	90.6%				

1 – Sum square justified by regression. 2 – Sum square of rests, 3 – Total sum square. 4 – Variability of independent variable justified by the model (sum square justified by regression/total sum square \times 100%)

Table 14
Mallows's C_p calculations

SSR(p)	MSR(k)	SSR(p)/MSR(k)	n	p	$n-2(p+1)$	C_p	Step
1.509199	0.098960	15.2506	8	1	4	11.3	1
1.041741	0.098960	10.5269	8	2	2	8.5	2
0.424720	0.098960	4.2919	8	3	0	4.3	3
0.296879	0.098960	3.0000	8	4	−2	5.0	4

Table 15 contains statistics to assess matching of the model with statically significant regression equations (the first and third step).

Table 15

List of statistics used for assessment of matching of the model for statistically significant regression equations (the first and third step)

Step	Mallows's C_p statistics	Corrected determination coefficient R^2	Number of variables	Number of statistically significant variables
1	11.3	0.44	1	1
3	4.3	0.76	3	2

purified wastewater is the regression equation from the third step taking the following form Eq. (6):

$$N_{\text{tot pur}} = 7.7757 + 0.0045 \times \text{TSS}_{\text{raw}} - 0.0047 \times B_{\text{raw}} - 0.0956 \times P_{\text{tot raw}} \pm 0.33 \quad (6)$$

4. Summary

The analysis of test results for raw and purified wastewater from 2015 to 2019 period indicated increase of total nitrogen concentration in raw and purified wastewater. This required taking action to modernize the wastewater treatment plant operation. Following modification of the technological arrangement, during analyses performed from January to August 2020 efficiency of the alterations was confirmed results in form of considerable reduction of total nitrogen compounds concentration (94%) in purified wastewater confirmed correctness of the system modification [36]. The modification consisted in change of oxic conditions sequence in particular chambers A and B of the biological reactor and on change of location of the internal recirculation place from NC1 instead of NC2 chamber. In the researched case no external source of carbon was dosed as efficiency of nitric nitrogen removal was sufficient. Additional alterations were channelled to improvement of phosphorus removal efficiency.

The reduction of phosphorus amount in purified wastewater was achieved (98%) due to increase of the external recirculation degree up to approximately 200% level and shortening of active sludge retaining period in the secondary settlement tanks. Increased efficiency of nitrogen compounds removal allows to maintain total nitrogen concentration values in purified wastewater complying with legal requirements pertaining to purified wastewater. The system modernization had no significant impact on organic compounds removal efficiency, which remained at 98%–99% level. Based on the legal regulations analysis pertaining to norms provided for total nitrogen in purified wastewater it is necessary to verify Polish legislature with relation to regulations that apply in European Union member states. The requirements regarding admissible total nitrogen concentrations in purified wastewater in other EU states are adjusted to climate conditions, in particular, to temperature in the biological chamber. In the currently applicable Polish legislature, it is necessary to maintain total nitrogen concentration in purified wastewater at the same time irrespective of temperature. However, it is a well-known fact that at a temperature below 12°C speed of nitrification and denitrification processes clearly decreases.

Therefore, admissible values and requirements pertaining to efficiency of total nitrogen removal from

municipal wastewater in Poland should take into account variable temperatures. Application of statistical analysis to elaborate test results allowed for finding of significant relationships between particular wastewater components. Significance of the models was additionally proved based on the Mallows's statistics [42,43]. The multiple regression applied to assess mutual relation between particular components of raw and purified wastewater assured taking into account several factors (COD_{Cr} , BOD_5 , total phosphorus, and total suspended solids). Statistical calculations allowed for selection of a model describing mutual relationships between those components [44]. Those variables explain properly 86.5% of the dependable variable variance. For this purpose, the so-called progressive stepwise regression was used. The highest values of the corrected determination coefficient ($R^2 = 0.76$) and the least value of Mallows's statistics ($C_p = 4.3$) were attained. In the third step regression equation impact of the analyzed indicators (P_{tot} , TSS, BOD_5 in raw wastewater) on the variable, which was total nitrogen in purified wastewater, was significant. At the same time, the determination coefficient R^2 increases from 0.54 to 0.76. In the third step, Mallows's C_p reached the lowest value 4.3, which proves the correct selection of the model originating from the third step. The statistical procedures that were applied, used to select independent variables in the regression analysis, complied with the condition of use of the most reliable and statistically significant model.

Acknowledgements

The research was funded both by the scientific subvention of Municipal Water Supply and Sewage Systems Ltd., Koszalin University of Technology, and Czestochowa University of Technology.

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