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Denitrifcation rate in the mainstream deammonification

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ABSTRACT

The conventional processes of biological nitrogen removal based on nitrification and denitrification does not fit properly into the concept of the circular economy. As the alternative one should consider the deammonification process, which is a combination of partial nitrification (nitritation) and Anammox processes. It consists of removing ammonium nitrogen from wastewater under anaerobic conditions by a group of autotrophic microorganisms. The result is a significant reduction in oxygen demand, while there is no a need for organic compounds that can be converted into biogas in digesters. The deammonification process can be successfully used to treat leachate from the sludge management of WWTP. Currently, research works focus on the use of this process for wastewater treatment in the mainstream of WWTP. This type of research, on a pilot scale, was also carried out at Gdańsk WWTP~~s~~. The aim of the presented research was the analysis of the possibility of a simultaneous removal of nitrates, generated during the mentioned deammonification process. The dissolved organic compounds present in the mechanically and chemically treated wastewater can be used in the denitrification process. The efficiency of the process has been determined by performing conventional denitrification rate tests (NUR). The average values of NUR 1 (2.75 mg NOx / gvss · h) and NUR 2 (1.05 NOx / gvss · h) were close to the values typical for mechanically treated municipal sewage. It has been shown that the denitrification process can cause an increase of total nitrogen removal efficiency in the process of deammonification of municipal wastewater. The amount of available organic compounds was sufficient to carry out the denitrification process of nitrates produced during the deammonification process.

***Keywords*:** Anammox, denitrifcation, conventional denitrification rate tests, NUR, deammonification

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1. INTRODUCTION

Nitrogen is a crucial element for all organisms to live. The earth's atmosphere consist of the major amount of nitrogen approximately 78%. Moreover, nitrogen may occur in the environment not only in a gas form, but also in organic forms such as urea, uric acid amino acids or inorganic forms such as nitrates, nitrites, and ammonium. The cycle of transformations between the particular forms of nitrogen is important for the environment. This is one of the most important circulations occurring in nature. The presence of nitrogen, as well as phosphorus and organic compounds in the water environment, e.g. an increase in the amount of discharged wastewater, may lead to the adverse changes and phenomena, e.g. eutrophication.

Currently, the removal of nitrogen from wastewater is based on biological transformations in the nitrification/denitrification process. However, it should be noticed that these processes may turn out to be insufficient for difficult wastewater for example reject water from sludge dewatering. Moreover, some types of wastewater e.g. digestate are characterized by the lack of easily degradable organic carbon, which is necessary to carry out the denitrification process.

The necessity of adding an external carbon source and large energy inputs, connected with aeration in the nitrification process, leads to an increase in the operating costs of the WWTPs. An alternative to the conventional processes may be the process of anaerobic ammonia oxidation discovered at the beginning of the 20th century, called the Anammox process. It consists of the anaerobic oxidation of ammonium nitrogen with nitrites to nitrogen gas. T

herefore, two processes are needed to remove nitrogen: nitritation and Anammox. In the nitritation process, ammonia is partially oxidized to nitrites under aerobic conditions. Then in anaerobic stage, ammonia is oxidized with the previously formed nitrites to nitrogen gas. The process describes the chemical reaction (1):

$$NH_4{}^+ + 1{,}32NO_2{}^- + 0{,}066\,HCO_3{}^- + 0{,}13\,H^+ \rightarrow 1{,}02\,N_2 + 0{,}26\,NO_3{}^- + 0{,}066\,CH_2O_{0{,}5}N_{0{,}15} + 2{,}03\,H_2O \quad (1)$$

The typical diagrams, showing this process, don't take into account the production of nitrate. However, according to the general reaction, the deammonification process can produce 0.44 g of N_2 using 1 g NH_4-N and about 0.11 g of NO_3-N. (Fig. 1)

Comparing the deammonification process to the conventional nitrification/denitrification system, it is possible to notice many advantages. The special advantage of the process is reducing the oxygen demand (by almost 60%), which reduces the operating costs of the WWTPs incurred in aeration process. An important fact is also the lack of consumption of the organic compounds. However, the bacteria responsible for this process are characterized with very slow cell division time (c.a 100 days). The deammonification process is successfully used for the purification of reject water from WWTPs digesters.

Currently, research works focus on the use of the process to treat wastewater in the mainstream. The researches were also carried out in the Gdańsk WWTP at the pilot scale. The aim of the mentioned research was the analysis of the possibility of simultaneous removal of nitrates, generated during the deammonification process, in a denitrification process using dissolved organic compounds present in wastewater after primary mechanical and chemical treatment. The idea of research is shown in Figure 2.

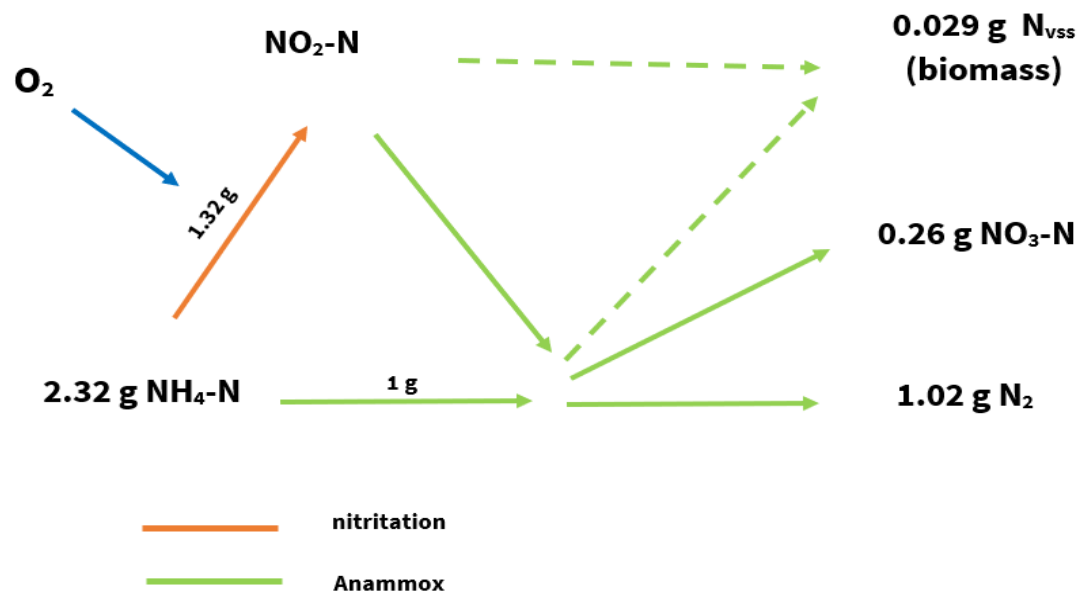

Figure 1. Modified scheme of nitrogen transformation in the deammonification process

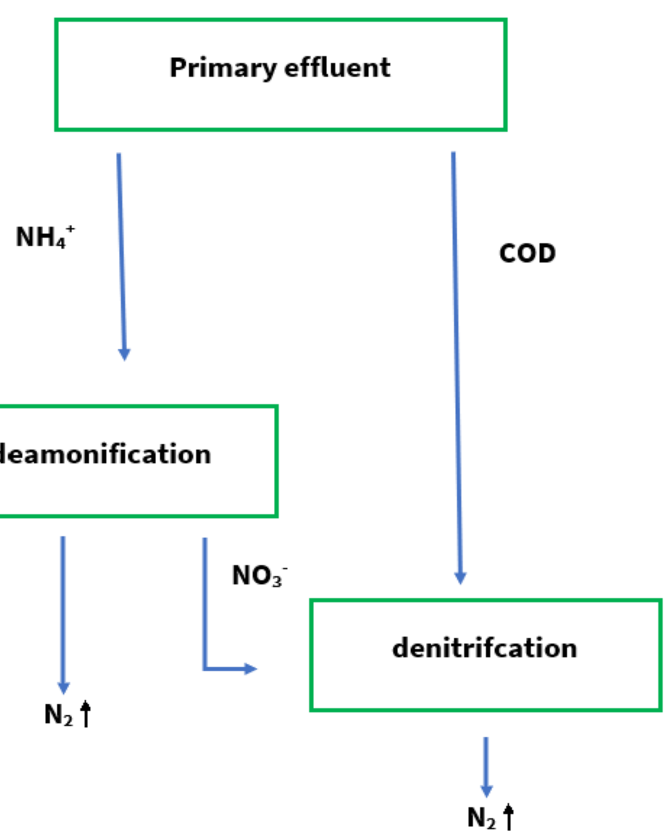

Figure 2. The idea of research.

2. MATERIALS AND METHODS

2. 1. Sampling

The research was conducted on the pilot-scale at the Gdańsk WWTP. The technological system of wastewater treatment includes preliminary chemical precipitation of organic compounds, removal of nitrogen in the deammonification process and cleaning of wastewater in the hydrophytic bed. In April 2018, two samples were taken to conduct laboratory tests. The samples of different capacities were collected from two different points (Figure 3):

- A - wastewater after primary mechanical and chemical treatment (1 L),
- B – wastewater from bioreactor with the K5 fittings (3.5 L).

After sampling, they were immediately transported to the laboratory of the Department of Water and Wastewater Technology, Faculty of Civil and Environmental Engineering, Gdansk University of Technology, where the denitrification rate was tested.

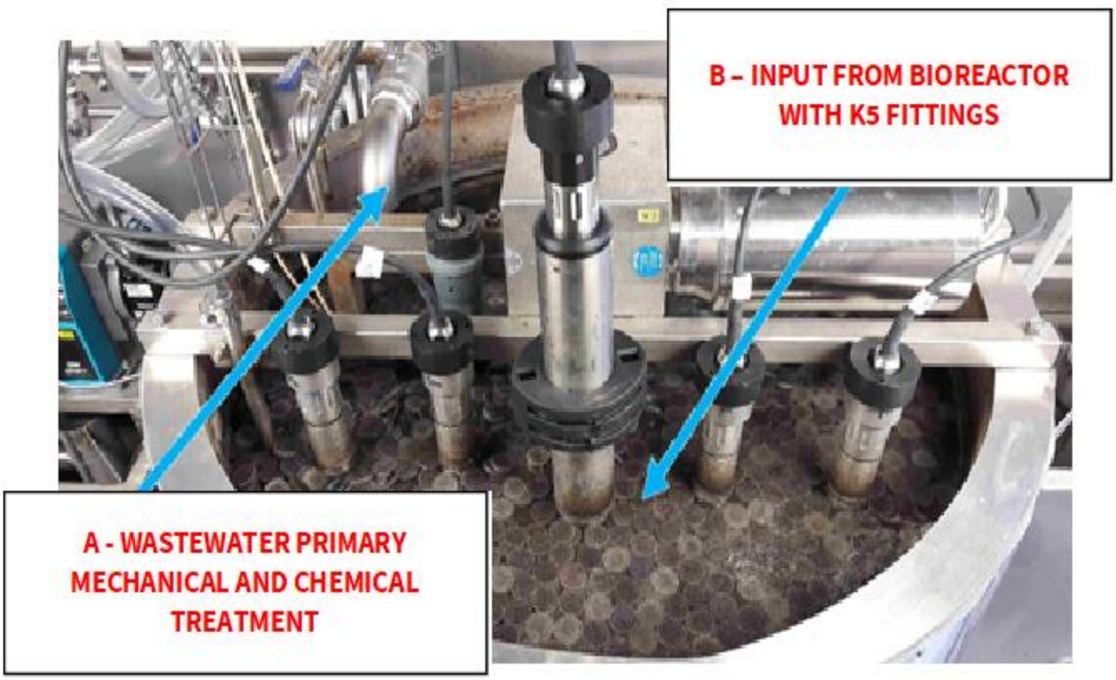

Figure 3. Sampling points

2. 2. Methodology of the conventional denitrification rate measurand

The research was carried out in a batch reactor with a capacity of 4 L. The reactor is made of organic glass (plexiglass), equipped with an aeration system (air pump and aeration grate) and a mechanical agitator. The agitator was set at 200 rpm. The reactor temperature was set to the same value as at the time of sampling at the research station at Gdańsk WWTP. About 3.5 L of bioreactor feed and about 0.5 L of mechanically and chemically treater wastewater were introduced into the reactor. Three research series were identified during the research. They were characterized with different test run conditions (Table 1):

- different temperature,
- dosing of the external source of nitrates (potassium nitrate).

Table 1. Conditions of research series

Date / series	Temperature [°C]	External source of nitrates
12.04.2018, series I	13.30	yes
19.04.2018, series II	16.90	no
19.04.2018, series III	16.90	yes

Samples were collected at specific intervals. The first sample of approx. 50 mL were taken after approx. 2 minutes from the start of the reactor operation. Subsequent samples were collected at predetermined time intervals (after 20, 40, 60, 90, 120, 150 and 180 minutes), the sampling time was adjusted to the current rate of nitrate removal. Each sample was filtered under vacuum through a filter made of fiberglass with 1.2 μm pores size (Whatman GF / C), using a filtration kit. Chemical parameters were defined in the filtered samples.

The following analyses were made (used Hach cuvette tests):

- ammonium nitrogen,
- nitrates and nitrites nitrogen,
- orthophosphates phosphorus,
- COD.

The total nitrogen (TN) concentrations were determined using a TOC analyser (TOC-VCSH) coupled with a TN module (TNM-1) (SHIMADZU Corporation, Kyoto, Japan). Catalytic thermal decomposition/chemiluminescence methods conformed to the American Society for Test Method's (ASTM) D5176 procedure, are adopted for TN measurement. Samples containing nitrogen are introduced into an oxygen-rich combustion tube with a platinum catalyst at a temperature of 720 °C. Bound nitrogen is then converted to nitrogen monoxide (NO), further oxidized to nitrite (NO_2^-) in the presence of ozone, and is then detected by a chemiluminescence detector. TN concentrations in the range of 0.1 to 4000 mg/L can be measured. The concentration of organic nitrogen (ON) was determined based on the difference between total nitrogen and the sum of the concentrations of inorganic nitrogen forms (NH_4-N, NO_2-N, and NO_3-N).

2. 3. Calculating the rate of the denitrfication process

Figure 4 shows the typical variation of COD and NO_3-N concentrations during the conventional denitrification test. There are two rates of the denitrification process. The first, marked as NUR1, is associated with the use of easy and slowly degradable organic compounds, the second marked as NUR2, is related only to slowly degradable organic compounds.

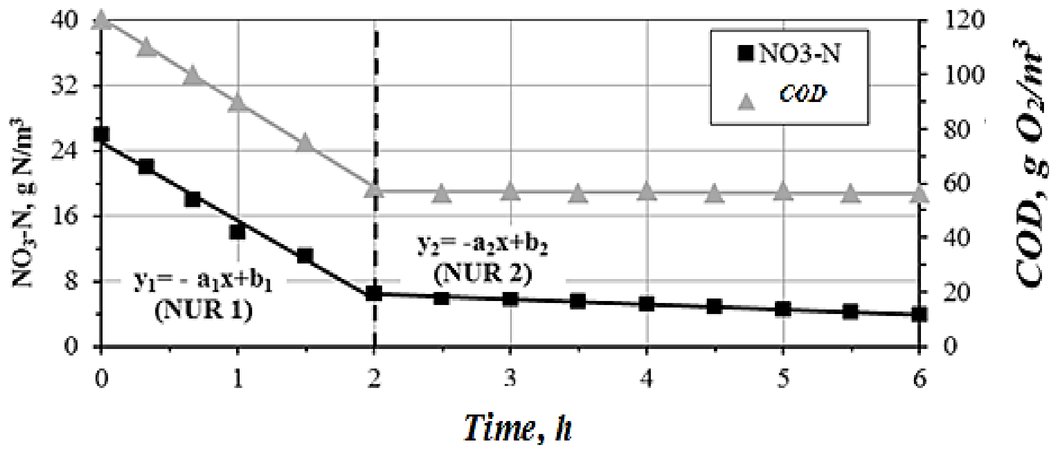

Figure 4. Typical changes of nitrate and COD concentration during conventional denitrification test (NUR).

The denitrification rate (NUR 1 and NUR 2) were calculated using the formula 2:

$$NUR = \frac{a}{X_{OC}} \qquad \left[\frac{gN}{kg_{vss}} \cdot h\right] \tag{2}$$

where:
X_{OC} – concentration of organic fraction of activated sludge, kg_{vss}/m^3
a – slope of the trend line of in nitrate concentration changes occurring in the measurements of NUR 1 (a_1) or NUR 2 (a_2).

3. RESULT / EXPERIMENTAL

3. 1. Result in wastewater and bioreactor efficiency

Figure 5 shows the technological diagram of the research pilot scale installation. Table 2 presents the results of pollutant concentrations for mechanically treated wastewater in the main streams (called as inflow, point A Fig. 5) and for first stage mechanical-chemical treatment (called outflow point B, Fig. 5). The tests at the Gdańsk WWTP was conducted twice a week. The results were collected between April 10 and April 25, 2018, i.e. during the sampling period of denitrification rate test (April 12 and 19).

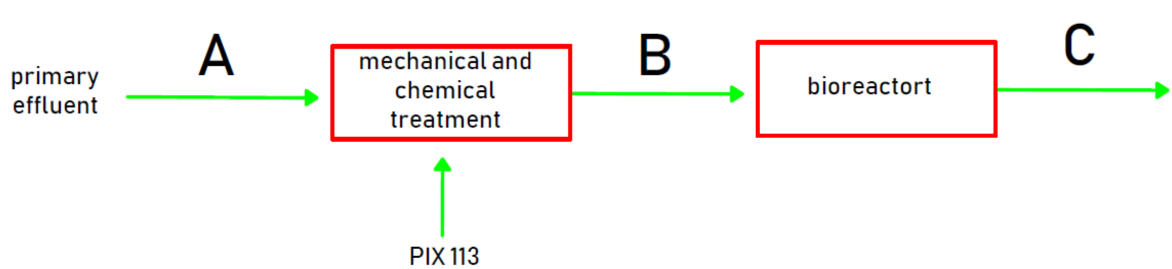

Figure 5. Technological diagram of the research bioreactor.

Table 2. Concentration of COD, TN and TP in primary effluent and after mechanical-chemical pretreatment.

Date	INFLOW (POINT A)			OUTFLOW (POINT B)		
	COD [mg O_2/L]	TN [mg N/L]	TP [mg P/L]	COD [mg O_2/L]	TN [mg N/L]	TP [mg P/L]
10.04.2018	680	82	10,4	447	86	9,2
12.04.2018	668	88	10,0	451	86	9,2
17.04.2018	753	96	12,1	461	92	9,8
19.04.2018	654	92	11,2	451	91	9,7
25.04.2018	657	92	11,2	440	91	9,5
26.04.2018	648	88	10,0	383	85	8,9
average	**676.7**	**89.7**	**10.8**	**438.8**	**88.5**	**9.4**
SD	**39.10**	**4.82**	**0.83**	**28.19**	**3.15**	**0.34**

Analysing the COD concentration at mobile research installation on the inflow and outflow from the first stage of mechanical-chemical treatment signalised a significant reduction of organic compounds. The average value of COD at the inflow was 676.7 mg O_2/L, and the average value in the outflow was 436.9 mg O_2/L. The average level of efficiency of organic compounds (determined as COD) by means of chemical precipitation is about 35%. This means that the dosage of PIX113 gives a high efficiency in removing organic compounds. The range of COD variability in the outflow in terms of the conventional wastewater treatment system can be stated to be relatively low. However, these are still high values of COD in wastewater that feed the deammonification process, as in the research station. This indicates a high content of organic compounds that may contribute to the development of heterotrophic bacteria with much higher growth rate in relation to the autotrophic bacteria (e.g. Anammox bacteria).

The nitrate and nitrite concentrations were extremely low. Therefore, nitrogen in the ammonium form dominates in wastewater. The ratio of TN to COD is 0.2, therefore the technological system should ensure stable conditions for the denitrification process. Taking into account total (amount of) nitrogen, the impact of the chemical and mechanical treatment is relatively low. Average concentration of TN at the inflow is 89.7 mg N/L (SD 4.8 mg N/L), and the average value at the outflow is 88 mg N/L (SD 3.3 mg N/L). Removal efficiency of nitrogen compounds are obtained at the pretreatment level of only 1.9%. In case of total phosphorus concentration, it was found that its concentration is kept within a narrow range. Based on studies, the values of TP has been reported to range 10.80 mg P/L for inflow, (SD 0.8 P/L) to 9.3 mg P/L for outflow (SD 0.4 P / L). The average removal efficiency was about 14%.

The calculated COD /P ratio equals to 47.53 and indicates the presence of a sufficient amount of organic matter to implement the biological phosphorus removal.

Figure 6 shows the percentage of removal efficiency of organic pollutants (presented by COD), TN and TP in the deammonification bioreactor. It is presented that the efficiency of TN reduction is high (over 70%), which may mean that in Anammox process takes in the system. In addition to the relatively high efficiency of nitrogen removal, the study has confirmed very high removal efficiency of COD (over 90%). The aim of the sampling was to verify if such a high efficiency of nitrogen removal results from the process of deammonification or from classical nitrification - denitrification. An extremely low reduction was observed for phosphorus, an average of 25%.

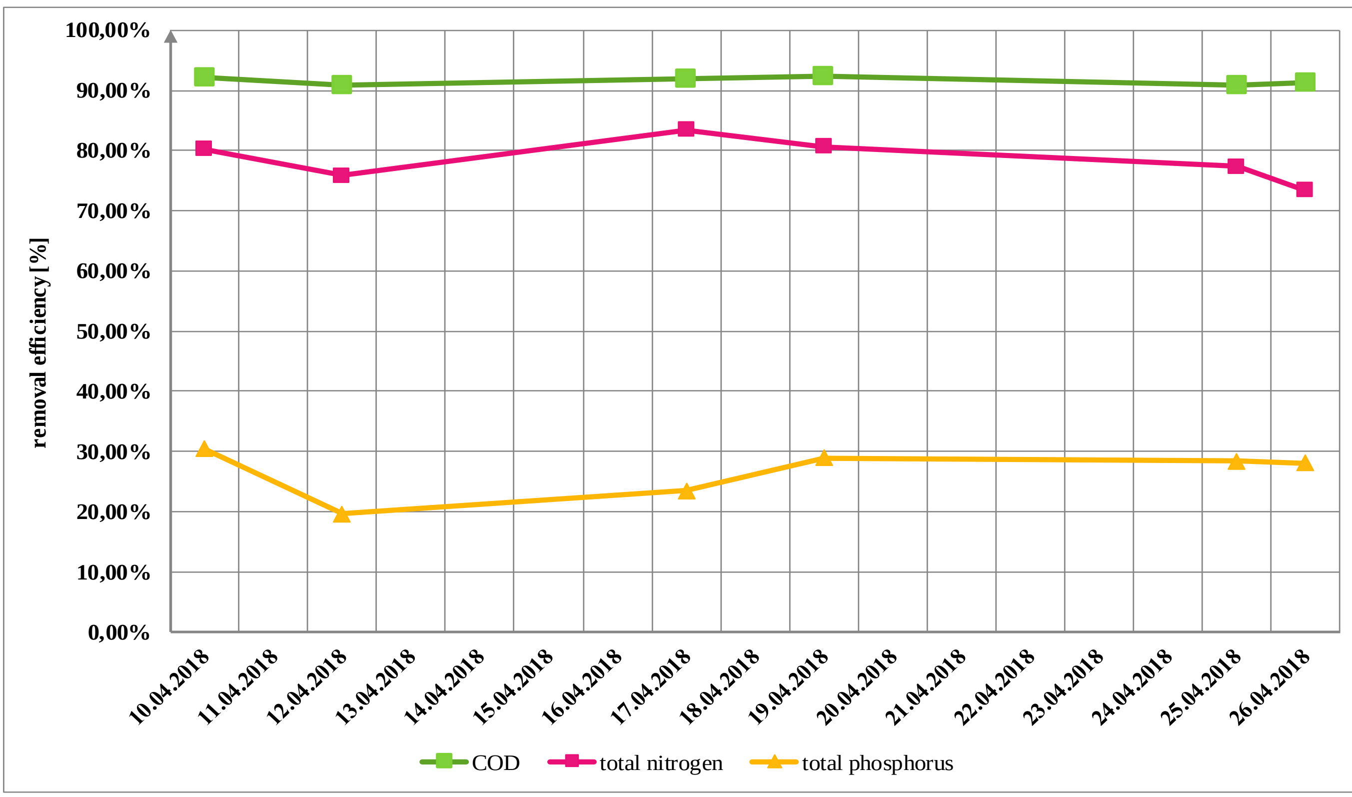

Figure 6. The removal efficiency of organic pollutants, total nitrogen and total phosphorus in the bioreactor.

An important element of wastewater quality assessment is the assessment of biogenic compounds. Effective removal of pollutants in municipal wastewater occurs for the ratio of TN to COD below 0.1, and the ratio of COD to TP above 12.5. The proportion of carbon to nitrogen and phosphorus (COD: N: P) is also important for the biomass increment. The average values of these ratios were TN/COD > 0.2 and COD / TP > 47.5. The TN/COD ratio indicates that the efficiency of nitrogen removal in conventional nitrification - denitrification processes may not be sufficient to achieve low nitrogen concentration in treated wastewater. This is confirmed by the COD: TN : TP, ratio of 100: 20.0: 2.1. The analysis of these proportion in terms of the deammonification process, may lead to the conclusion that process unfavourable. The ratio of

COD to TN for the denitrification proceed without disturbances, to TN should remain between 5 and 10. Table 3 shows the ratio of COD to TN for the individual test series. It is noticeable that the ratio for each of the three series varies between 0.75 and 1.89. This means that there is not enough organic carbon in the wastewater and the denitrification process is only a supplement to the deammonification process.

Table 3. Ratio of COD to TN for the samples of wastewater.

Parameter	Series I	Series II	Series III
COD [mg O_2/L]	69.60	46.1	30.2
TN. [mg N/L]	65.89	24.38	40.16
COD/TN	1.05	1.89	0.75

3. 2. Conventional denitrification rate

Table 4 presents the output parameters for tests, i.e. the current status of parameters in the bioreactor registered by the mobile research installation. Two most important parameters crucial to perform the tests are the temperature in the bioreactor and the concentration of the total suspension solids (TSS).

Table 4. Output parameters for bioreactor.

Date	Temperature [°C]	Concentration of TSS [mg/L]
12.04.2018	13.30	1438
19.04.2018	16.90	1258

The first series of the test lasted three hours. In the beginning, 500 mg of potassium nitrate (KNO_3) was added to the bioreactor, to increase the nitrogen nitrate concentration by 20 mg N/L. During the test 5 samples were collected at intervals of 20 min. Further measurements were discontinued due to the small decrease in NO_3-N concentration that was discovered after three hours. The second and third series of tests took place 7 days after the first series. The temperature in the bioreactor was slightly higher - 16.90 °C. In turn, the concentration of TSS dropped to 1258 mg/L. The research was divided into two steps. The first steps (of series II) consisted on checking the effect of studies without the addition of potassium nitrate. There were collected 6 samples. The last sample was taken 100 minutes after the start of the reactor's operation. Due to an extremely low concentration of NO_3-N (0.98 mg N/L) further measurements were discontinued and a series III started. The second step of the test, called series III, included the addition of 503 mg of KNO_3 to the reactor after completion of the second series to increase the nitrate nitrogen concentration by 20 mg NO_3-N/L. This series lasted 2 hours. After this time, studies were discontinued due to small decrease of NO_3-N concentrations. Two denitrification rates were observed during the research with mechanically-chemically treated wastewater. Analysing the denitrification rate of the I series, it has been found that the NUR 1 value is disproportionately high. This may be caused by the disturbing proportion of COD to TN, which amounted to 1.05 for the first series. To verify these results, the denitrification rate of series I was recalculated, taking into account the values of the oxidized forms of nitrogen (NO_x-N), i.e. the sum of nitrates and nitrites. During the research, a small decrease in nitrates and a large increase in nitrite were observed. The recalculation was aimed at checking the rates of the denitrification process taking into account both oxidized forms of nitrogen and at confirming previously submitted outcomes.

The results are presented in Table 5.

Table 5. NUR values for three series of tests.

Date/series	NUR 1 [mg NOx-N/gvss·h]	NUR 2 [mg NOx-N/g_{vss}·h]	Temperature [°C]
12.04.2018, series I	1.20	0.4	13.30
19.04.2018, series II	4.30	1.7	16.90
19.04.2018, series III	3.50	0.7	16.90

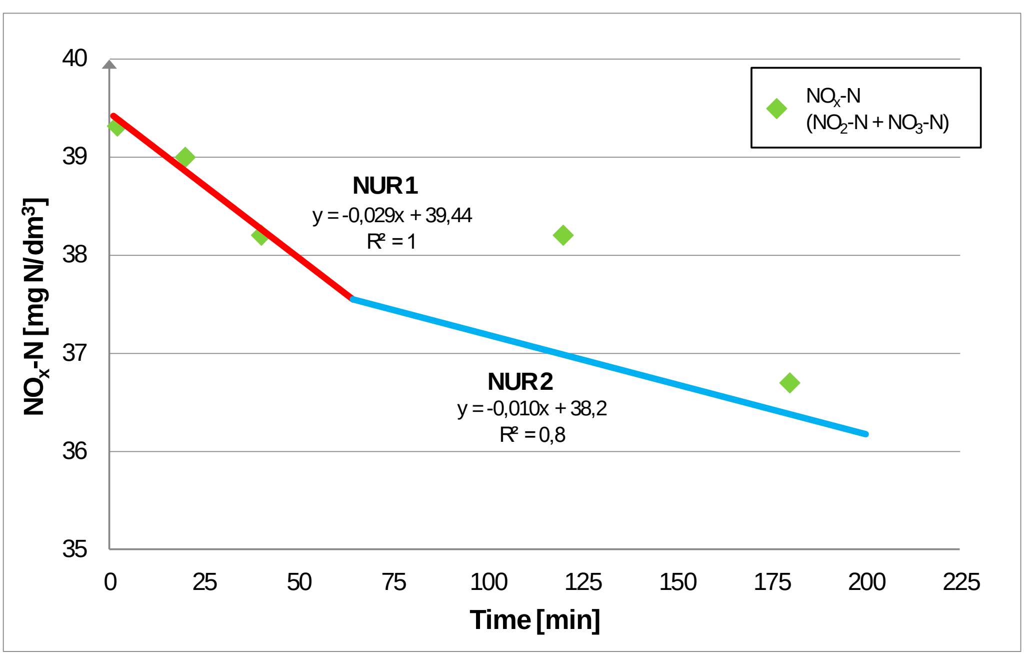

Figure 7. Denitrification rate (NUR) for series I.

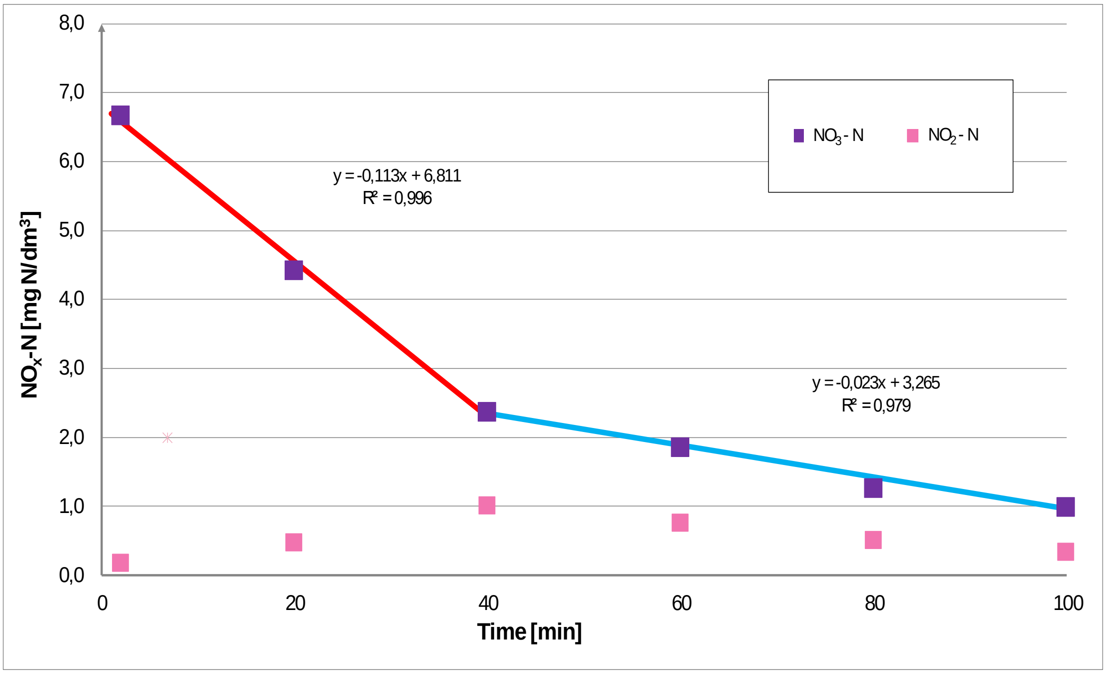

Figure 8. Denitrification rate (NUR) for series II.

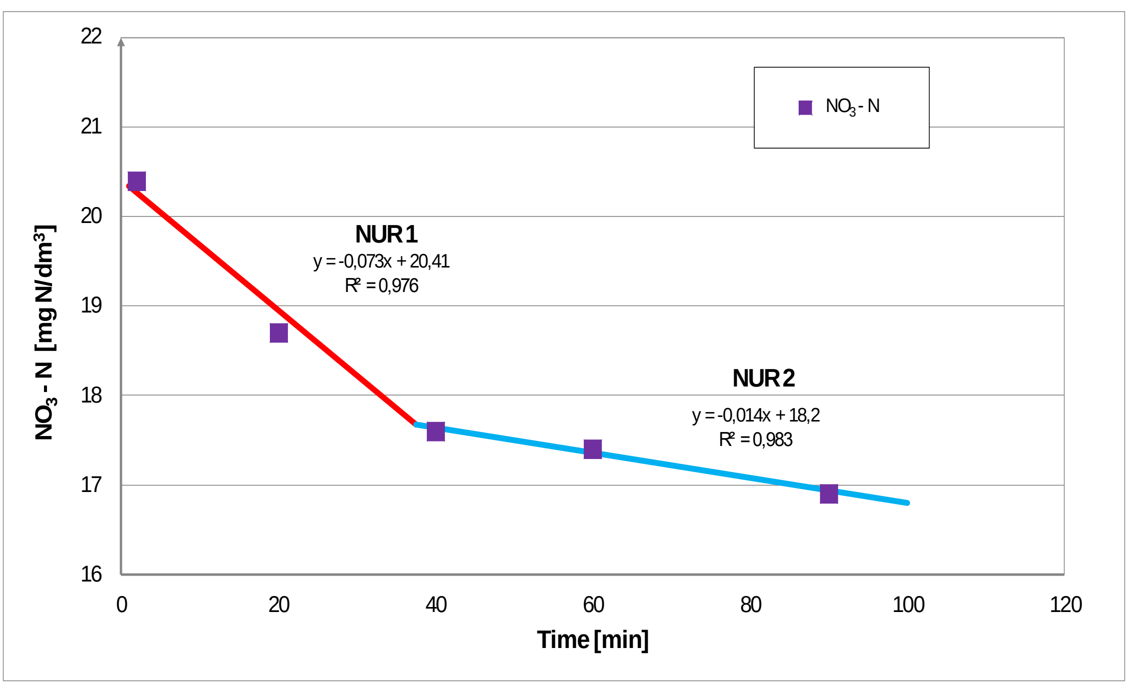

Figure 9. Denitrification rate (NUR) for series III.

The denitrification rates (NUR 1 and NUR 2), shown during all three series of tests, equal to the rates described in the literature for primary treated wastewater. Analysing the course of the chart for series I (Fig. 7), it was found that the wastewater contains a significant amount of easy degradable organic compounds, which was consumed by the denitrifying bacteria in the first 60 minutes of the test. A decrease in nitrate concentration was observed which may be indicative of a significant amount of slowly degradable organic compounds.

A similar situation occurs in the examination of series II (Fig. 8) and series III (Fig. 9). During the series II, denitrifying bacteria used all easy degradable organic compounds. It was characterized by a large decrease in nitrates, however, it wasn't associated with the increase in nitrites as in the series I. After about two hours no nitrates was found. Then it was decided to carry out the series III of research. In this case, 503 mg of potassium nitrate was added, which was an additional source of nitrate nitrogen, but no significant decrease in nitrate was noted. This may be due to the fact that despite the addition of an additional source of nitrates, the denitrifying bacteria had too few easy degradable organic compounds and had to use slowly degradable organic compounds, which affected the reduction of the NUR 1 and NUR 2 rates comparing to the II series.

4. CONCLUSIONS

The paper presents the results of a conventional denitrification rate (NUR) for samples collected at mainstream deammonification process in pilot scale in Gdańsk WWTP. The presented research aimed to evaluate the efficiency of the denitrification process occurring in the bioreactor. For this purpose, three tests wastewater from a pilot bioreactor were made. The test was carried out in April, and the samples were taken at regular intervals of 7 days. During the research, three research series were identified, each characterized by different conditions during the research. For series I, the reactor temperature was 13.7 °C, and at the beginning of the test, potassium nitrate was added to the reactor, as an additional source of nitrates for denitrifying bacteria. For series II and III, the temperature was 16.9 °C, also in the case of series III potassium nitrate was added to the reactor. The results and conclusions of studies on tests can be presented as follows:

1) The denitrification rates (NUR 1 and NUR 2), shown during all tree series of tests, equal to the rates described in the literature for primary treated wastewater. In the case of series I, due to a large amount of total nitrogen about the amount of organic compounds, calculations were made for the oxidized forms of NOx-N. As a result, obtained values similar was to those obtained in series II and III.
2) It was found that there is a denitrification process in the bioreactor. However, the amounts of organic compounds in the inflow wastewater are not sufficient to remove the entire nitrogen load.
3) It was not determined whether nitrogen is reduced only in the deammonification process or in the denitrification process. However, the amount of organic compounds supplied to the bioreactor is sufficient to carry out the denitrification process of nitrates produced in the process of deammonification
4) Due to the limited availability of organic compounds in treated wastewater, the denitrification process can only be a supplement to the deammonification process carried out in the bioreactor.

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