

SIMULTANEOUS NITRIFICATION AND DENITRIFICATION IN AN SBR WITH A MODIFIED CYCLE DURING REJECT WATER TREATMENT

KATARZYNA BERNAT*, DOROTA KULIKOWSKA, MAGDALENA ZIELIŃSKA,
AGNIESZKA CYDZIK-KWIATKOWSKA, IRENA WOJNOWSKA-BARYŁA

University of Warmia and Mazury in Olsztyn, Department of Environmental Biotechnology
ul. Słoneczna 45G, 10-709 Olsztyn, Poland

*Corresponding author's e-mail: bernat@uwm.edu.pl

Keywords: Anaerobic sludge digester supernatant, SBR, simultaneous nitrification and denitrification (SND).

Abstract: In this study, the dependence between volumetric exchange rate (n) in an SBR (Sequencing Batch Reactor) with a modified cycle and simultaneous nitrification and denitrification (SND) efficiency during the treatment of anaerobic sludge digester supernatant was determined. In the SBR cycle alternating three aeration phases (with limited dissolved oxygen (DO) concentration up to 0.7 mg O₂/L) and two mixing phases were applied. The lengths of each aeration and mixing phases were 4 and 5.5 h, respectively. Independently of n , a total removal of ammonium was achieved. However, at $n = 0.1$ d⁻¹ and $n = 0.3$ d⁻¹ nitrates were the main product of nitrification, while at $n = 0.5$ d⁻¹, both nitrates and nitrites occurred in the effluent. Under these operational conditions, despite low COD/N (ca. 4) ratio in the influent, denitrification in activated sludge was observed. A higher denitrification efficiency at $n = 0.5$ d⁻¹ (51.3%) than at $n = 0.1$ d⁻¹ (7.8%) indicated that n was a crucial factor influencing SND via nitrite and nitrate in the SBR with a low oxygen concentration in aeration phases.

INTRODUCTION

Supernatant from anaerobic sludge digesters (reject water) is characterized by a high ammonium concentration (up to 2.3 g N-NH₄/L) and a low COD to total nitrogen ratio (COD/N). Biological treatment of these wastewaters can be proceeded by a separate treatment in a side stream [8] or in the main stream of wastewater treatment plant (WWTP). However, during the treatment in the side stream, only the degree of oxidation of nitrogen is changed, and the removal of this pollutant is not observed. Although this intervention lowers the input ammonia nitrogen load, an additional organic carbon source for denitrification has to be applied. Therefore, reject water is most often treated together with municipal wastewater.

Despite the fact that the anaerobic sludge digesters supernatant constitutes about 0.5–2.0% of total WWTP flow rate it contributes to 15–20% of the nitrogen load in raw wastewater. This causes a drop in the COD/N ratio in the influent and, consequently a decrease

of nitrogen removal effectiveness in conventional denitrification. Organic compounds in wastewater may be efficiently used as carbon source for denitrification, even at a higher ammonium concentration in the influent if appropriate operating conditions are applied. Simultaneous nitrification and denitrification (SND) is one of the possibilities of reducing carbon requirements for nitrogen elimination. Some studies showed that nitrification and denitrification occur concurrently in a single reactor under aerobic conditions [14, 17]. The efficiency of SND depends mainly on the oxygen concentration, the availability of organic carbon and the floc size. Pochana and Keller [15] proved that SND is promoted by a low dissolved oxygen concentration ($< 2 \text{ mg O}_2/\text{L}$) and a large floc size. Other authors stated that the improvement of nitrogen removal from municipal wastewater via SND can be achieved by the adjustment of the aeration length in the SBR, leading to limited oxidation of organic substrates that act as electron donors for denitrification [16].

Our research focused on the simultaneous nitrification and denitrification during the treatment of anaerobic sludge digester supernatant with a low COD/N ratio. For this kind of wastewater nitrogen removal via SND is advantageous, since it lowers the required amount of organic carbon for nitrate reduction as compared to the sequential nitrification and denitrification. The supernatant was treated in the SBR with a modified cycle mode – each of the three aeration phases lasted only 4 h and they were separated with 5.5-h mixing phases. The air supply in the aeration phases was adjusted to attain the low DO concentration of $0.7 \text{ mg O}_2/\text{L}$. Such a low DO in the aeration phases should additionally promote ammonia oxidation to nitrites and, consequently, SND via nitrites and nitrates. Besides, the relationship between SND and volumetric exchange rate, one of the key parameters in SBR designing, was investigated.

MATERIALS AND METHODS

Process configuration

The experiment was carried out in three SBRs, each with a working volume of 5 L, that were operated in parallel. Before each series, the reactors were seeded with a sludge from a municipal wastewater treatment plant (WWTP) with SND. The reactors were equipped with a stirrer with a regulated rotation speed (50 rpm) and a controlled air supply system. Air was supplied by porous diffusers placed at the bottom of the tank. The amount of air entering the SBRs was automatically adjusted to a stable set-point of $0.7 \text{ mg O}_2/\text{L}$. The reactors were operated at about 8 pH and $20 \pm 2^\circ\text{C}$.

Experiment organization

During the experiment, the mixture of anaerobic sludge digester supernatant and synthetic wastewater composed similarly to municipal sewage was introduced to the reactors (30:70, v/v). The use of synthetic wastewater was aimed at maintaining a constant COD/N ratio in the SBR influent. The SBRs were operated at a different volumetric exchange rate (n) of $n = 0.1 \text{ d}^{-1}$ (series 1), $n = 0.3 \text{ d}^{-1}$ (series 2), $n = 0.5 \text{ d}^{-1}$ (series 3).

The SBRs were operated in a 24 h cycle mode. Each cycle consisted of the eight following phases: filling, I aeration, I mixing, II aeration, II mixing, III aeration, settling and decantation. The lengths of the filling phase (0.25 h), settling (0.5 h) and decantation (0.25 h) were stable for each series. The lengths of each aeration and mixing phase were 4 and 5.5 h, respectively (Tab. 1).

Tab. 1. SBR cycle mode in series 1–3

Phases	The length of the SBR phases (h)
Filling	0.25
I aeration	4
I mixing	5.5
II aeration	4
II mixing	5.5
III aeration	4
Settling	0.5
Decantation	0.25

Characteristics of the influent

Anaerobic sludge digester supernatant was obtained from open digesters of the WWTP in Olsztyn, Poland. The average values of pollutant concentrations in synthetic wastewater and anaerobic sludge digester supernatant are presented in Tab. 2. The organic nitrogen comprised 35% of the total Kjeldahl nitrogen (TKN).

Tab. 2. Pollutant concentrations in synthetic wastewater and anaerobic sludge digester supernatant

Component	Unit	Average concentration	
		wastewater	supernatant
Organics (COD)	mg COD/L	600±32.5	1390±242.3
Ammonia	mg N-NH ₄ /L	76±5.2	585±65.3
Total Kjeldahl nitrogen	mg N _{TKN} /L	85±7.4	692±93.5
Volatile fatty acids	mg VFA/L	nd	300±27.2

nd – not determined

Synthetic wastewater used in this study was prepared according to Coelho *et al.* [5], with some modifications, and contained: CH₃COONa, urea, NH₄Cl (concentrations given in Tab. 2), Na₂HPO₄·12H₂O – 46.2 mg /L, NaCl – 10.1 mg/L, KCl – 4.7 mg/L, CaCl₂·2H₂O – 4.7 mg/L, MgSO₄·7H₂O – 16.7 mg/L, NaHCO₃ – 243.3 mg/L, Na₂CO₃ – 162.2 mg/L; and FeCl₃·6H₂O, ZnSO₄, MnSO₄·H₂O and CuSO₄ < 0.2 mg/L.

Analytical methods

Daily measurements of pollutant concentrations in the effluent included: COD, TKN, ammonium, nitrites and nitrates. The activated sludge was analyzed for total suspended solids (TSS) and volatile suspended solids (VSS). The analyses were performed according to APHA [1].

At established effluent parameters, periodic sampling and measurements of COD and nitrogen compounds were performed in the reactor working cycle. COD and ammonium removal rates were determined.

RESULTS AND DISCUSSION

In the influent, the COD and TKN concentrations were 855 mg COD/L and 220 mg N/L, respectively, resulting in a COD/N ratio of ca. 4. Organic nitrogen comprised 17.4% of the total nitrogen, the rest of nitrogen was in the form of ammonium. In series 1–3, a change of the volumetric exchange rate from 0.1 d⁻¹ to 0.5 d⁻¹ caused an increase in a substrate to biomass ratio (C_0/X_0) from 0.037 to 0.095 mg COD/mg VSS, and from 0.007 to 0.021 mg TKN/mg VSS. At the $n = 0.1$ d⁻¹ and $n = 0.3$ d⁻¹, nitrates were the main nitrification products, and their concentrations reached 108.2 and 87.5 mg NO₃-N/L, respectively. Nitrite concentrations were ≤ 0.5 mg NO₂-N/L. At the highest volumetric exchange rate (0.5 d⁻¹) nitrites and nitrates in the effluent were present at the 1:1 ratio (Fig. 1).

Changes of the ammonium, nitrites and nitrates concentrations in the SBR cycle are shown in Fig. 1. The ammonium oxidation proceeded according to zero-order kinetics, i.e. linear changes in ammonium concentration with time were observed, and it was expressed by the equation:

$$r_{\text{NH}_4\text{-N}} = -k_{\text{NH}_4\text{-N}} \quad (1)$$

The ammonium concentration after time t was calculated as:

$$C_{\text{NH}_4\text{-N}} = -k_{\text{NH}_4\text{-N}} \cdot t + C_{0,\text{NH}_4\text{-N}} \quad (2)$$

where:

- $r_{\text{NH}_4\text{-N}}$ – the rate of ammonium removal [mg N-NH₄/(L · h)],
- $k_{\text{NH}_4\text{-N}}$ – the constant rate of ammonium removal [mg N-NH₄/(L · h)],
- $C_{\text{N-NH}_4}$ – the ammonium concentration after time t (mg N-NH₄/L),
- t – time (h),
- $C_{0,\text{N-NH}_4}$ – the ammonium concentration at the beginning of SBR cycle (mg N-NH₄/L).

It was shown that, independently of the n , ammonium was removed during I and II aeration phases. At the highest n of 0.5 d⁻¹ (series 3), a significant increase in the ammonium concentration at the beginning of the SBR cycle to ca. 90 mg N-NH₄/L resulted in only about 66% of ammonium oxidation efficiency in the I aeration phase. However, a complete oxidation (ammonium concentration in the effluent < 1 mg N-NH₄/L) occurred in the II aeration phase. The overall efficiency of ammonium oxidation in series 1–3 was 96.0–97.5%.

The values of constant rates of ammonium removal increased parallelly with the increasing n ; however, all the values obtained in the I aeration phase were higher than those noted in the II aeration phase. The rates of ammonium removal in the I aeration phase varied from 1.17 mg N-NH₄/(g VSS·h) at $n = 0.1$ d⁻¹ (series 1) to 5.12 mg N-NH₄/(g VSS·h) at 0.5 d⁻¹ (series 3) (Tab. 3).

In the current research, the highest ammonium oxidation rate was observed at the highest n values and it resulted from the availability of the substrate. Similar nitrification rate (6.16 mg N-NH₄/(g VSS·h)) under alternating anaerobic/aerobic conditions was obtained in SBR by Dytczak *et al.* [7]. The rate was higher than the one observed under strictly aerobic conditions (2.95 mg N-NH₄/(g VSS·h)), since rapid-nitrifiers such as

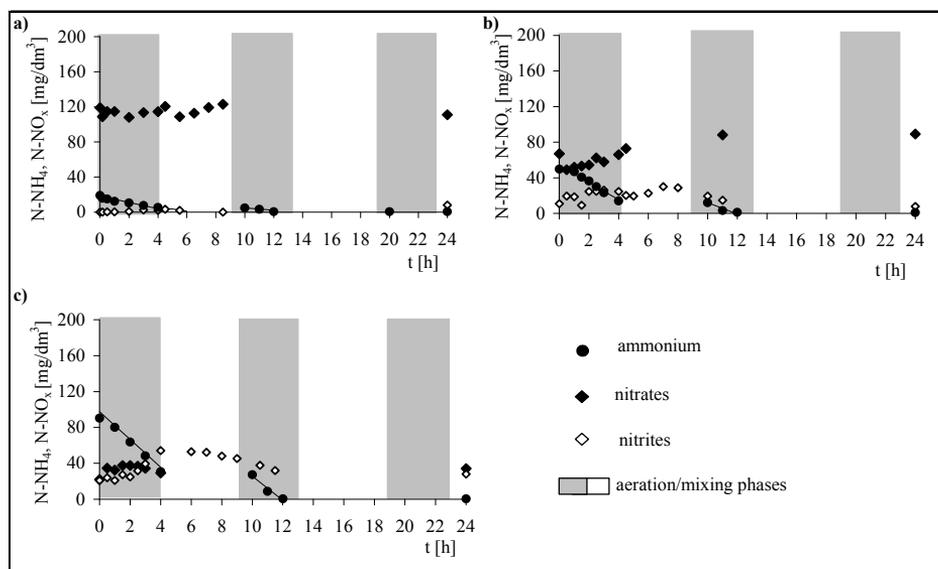


Fig. 1. Concentration of ammonium, nitrites and nitrates in the SBR cycle; a) series 1, b) series 2, c) series 3

Tab. 3. Ammonium removal rates in series 1–3

Series	Reaction rate $r_{\text{NH}_4\text{-N}}$ [mg/L·h]		Reaction rate $r_{\text{NH}_4\text{-N}}$ [mg/g VSS·h]	
	I aeration	II aeration	I aeration	II aeration
Series 1	3.7	2.84	1.17	0.88
Series 2	9.56	6.4	2.09	1.40
Series 3	15.47	13.37	5.12	2.59

Nitrosomonas and *Nitrobacter* (79.5% of the nitrifying population) dominated in the alternating reactor, while the dominance of slower nitrifiers such as *Nitrosospira* and *Nitrospira* (78.2%) was noted in the strictly aerobic reactor [6]. Ling Chen [11] studied the nitrification rate as a function of the total ammonium concentration, with and without the interaction of organic matter, in floating bed, fluidized sand and submerged bio-cube filters. They showed that for the wastewater with the C/N ratio > 1 , the nitrification rate was 10.42 mg N/(g VSS·h). A further increase in the C/N from 1 to 6 did not influence the rate of ammonium oxidation. In our research, at the COD/N ratio of ca. 4, there were twofold to tenfold lower values of nitrification rate in the I aeration phase.

The current study proved that, independently of the n , ammonium oxidation was not accompanied by a stoichiometric production of nitrites and nitrates in the SBR working cycle (even taking into account the use of ammonium for biomass synthesis) (Fig. 1). Some studies have shown that this indicated SND that occurs under aerobic conditions with a low dissolved oxygen concentration [14, 18, 9]. In our study, at the oxygen concentration of 0.7 mg O_2/L in the aeration phase, the SND efficiency was determined

using the assumption that TKN influent, including ammonium generated from organic nitrogen in ammonification, may be oxidized to nitrites and/or nitrates and simultaneously denitrified during aeration and mixing phases, as well as used for biomass production.

SND efficiency (E_{SND}) was calculated according to Chiu *et al.* [4]:

$$E_{SND} = \left(1 - \frac{NO_x^-}{NH_4^+}\right) \cdot 100$$

where:

NO_x^- – the sum of nitrites and nitrates remaining after the SBR cycle,

NH_4^+ – the ammonium oxidized in the SBR cycle.

In our study, with the increasing n , the efficiency of SND increased from 7.8% ($n = 0.1 \text{ d}^{-1}$) to 50.3% ($n = 0.5 \text{ d}^{-1}$). At the $n = 0.3 \text{ d}^{-1}$, the effectiveness of SND was 41.5%. The literature data showed that one of the factors influencing SND is the composition of wastewater, particularly the C/N ratio. According to Chiu *et al.* [4], at the C/N = 6.3 in a synthetic wastewater with sodium acetate, a rapid carbon deficit occurred that resulted in the unbalanced and inefficient SND (1.02%) in the SBR cycle. In the system operated with the initial C/N = 11.1, the equilibrium between nitrification and denitrification was reached, causing the optimal removal of nitrogen (98.7%) and carbon without leaving any nitrites in the effluent. As our research proved, at the COD/N ratio of ca. 4 that is considered as unfavorable to achieve the effective nitrogen elimination, the efficiency of SND equaled 50.3%.

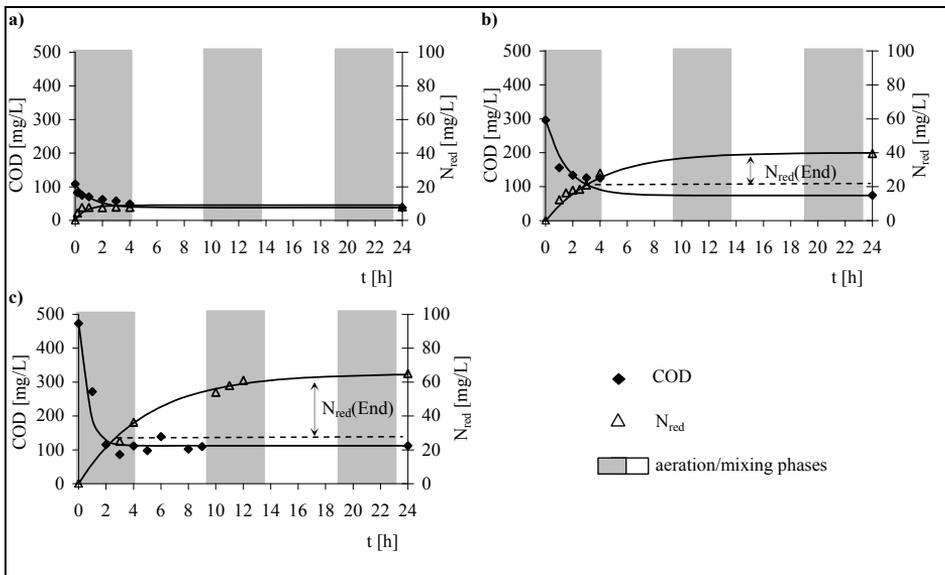


Fig. 2. COD removal and nitrogen reduction due to denitrification during the SBR cycle; N_{red} – nitrogen reduced in the SND, $N_{red}(End)$ – nitrogen reduced as a result of SND with the internal carbon source: (a) series 1, (b) series 2, (c) series 3

As shown in Fig. 2, during the first 4 h of the SBR cycle the concentrations of organic carbon compounds over time decreased to the values noted in the effluent. It can be assumed that COD removal resulted from its oxidation, denitrification and biomass production. In series 1, with the low initial concentration of organic compounds in the reactor (100 mg COD/L), a part of the organic compounds became oxidized and used for the growth (the coefficient of biomass yield Y equaled 0.56 g VSS/g COD). The rest of the organic compounds was utilized for denitrification; the calculated amount of reduced nitrogen reached ca. 8 mg N_{red}/L . In series 1, the overall efficiency of the nitrogen removal through denitrification and the biomass growth was 11.2%. At higher initial COD concentrations in the reactor (about 300 and 500 mg COD/L at the $n = 0.3$ and 0.5 d^{-1} , respectively) the values were significantly higher and equaled 0.66 and 0.76 g VSS/g COD at the $n = 0.3$ and 0.5 d^{-1} , respectively. It is known that the high rate of biomass production (Y) results from cell division and the intracellular storage. The last is induced by a low oxygen concentration [12]. In our research, the high values of Y obtained under the low DO level and the alternating mixing and aeration phases suggested the presence of stored substances in the biomass that may be used in denitrification. The use of intracellularly stored substrates as a carbon source for endogenous denitrification was shown by Bernat *et al.* [2].

Our results indicated that the amount of reduced nitrogen was 43.5 and 59.6 mg N_{red}/L at the $n = 0.3$ and 0.5 d^{-1} , respectively. About 70% (series 2) and 50% (series 3) of the total reduction were achieved during the first 4 h of the cycle; at that time a loss of an external source of organic carbon was also noted (Fig. 2). In the following hours of the SBR cycle, the further reduction of the oxidized forms of nitrogen proceeded, however, no loss of external carbon source was observed and this suggested that bacteria used the stored substances. According to Third *et al.* [16], the nitrification and denitrification rates should be approximately equal to obtain complete SND. As autotrophic nitrification is slow, SND requires slowly biodegradable organic substrates, such as internal storage polymers. The internal carbon source is degraded much slower than a soluble substrate and can be used as an electron donor for denitrification if no external substrate is available [10, 13, 3]. The ability of heterotrophs to rapidly remove the soluble substrate and store it as a slowly degradable polymer represents a convenient opportunity to preserve reducing power for SND.

CONCLUSION

At the low oxygen concentration of 0.7 mg O_2/L in the aeration phase there was a total loss of ammonium in the SBR cycle. At the $n = 0.1$ and 0.3 d^{-1} , nitrates were the product of nitrification, while at the $n = 0.5 \text{ d}^{-1}$ both nitrates and nitrites were formed in the reactor. Under all experimental conditions denitrification was obtained. The process proceeded most efficiently at the $n = 0.5 \text{ d}^{-1}$, indicating that the high n , stimulating a high concentration gradient in the SBR working cycle, was a crucial factor promoting SND.

Higher concentrations of COD in the reactor induced by the increasing n , the modified SBR cycle and the low DO in the aeration phases may favor the storage of organic compounds that can comprise a source of carbon for the reduction of oxidized nitrogen forms. The presence of nitrites and nitrates in the effluent at the $n = 0.5 \text{ d}^{-1}$ indicated

that the treatment of wastewater with low COD/N ratio requires, despite observed SND, the supply of external carbon addition. The application of the proposed technological solution allows for the reduction of the amount of the external carbon source introduced into the system to obtain complete denitrification.

ACKNOWLEDGEMENTS

We are grateful for the financial support of the Ministry of Scientific Research and Information Technology of Poland (Project No. N523 084 32/3351).

REFERENCES

- [1] APHA-AWWA-WEF. (1992). Standard methods for the examination of water and wastewater. 18th Edition.
- [2] Bernat, K., Wojnowska-Baryła, I., & Dobrzyńska, A. (2010). Organics (COD) removal in dependence on loading of volatile fatty acids (VFA), *Archives of Environmental Protection*, 36, 93–105.
- [3] Beun, J.J., Paletta, F., & van Loosdrecht M.C.M. (2001). N removal in a granular sludge sequencing batch airlift reactor, *Biotechnology Bioengineering*, 75, 82–92.
- [4] Chiu, Y.C., Lee, L.L., Chang, C.N., & Chao A.C. (2007). Control of carbon and ammonium ratio for simultaneous nitrification and denitrification in a sequencing batch bioreactor, *International Biodeterioration and Biodegradation*, 59, 1–7.
- [5] Coelho, M.A.Z., Russo, C., & Araújo O.Q.F. (2000). Optimization of a sequencing batch reactor for biological nitrogen removal, *Water Research*, 34, 2809–2817.
- [6] Dytczak, M.A., Londry, K.L., & Oleszkiewicz J.A. (2008 a). Activated sludge operational regime has significant impact on the type of nitrifying community and its nitrification rates, *Water Research*, 42, 2320–2328.
- [7] Dytczak, M.A., Londry, K.L., & Oleszkiewicz J.A. (2008 b). Nitrifying genera in activated sludge may influence nitrification rates, *Water Environmental Research*, 80, 388–396.
- [8] Gut, L., Plaza, E., Treala, J., Hultaman, B., & Bosander J. (2005). Combined partial nitritation/Anammox system for treatment of digester supernatant. Nutrient management in wastewater treatment processes and recycle streams, *IWA Specialized Conference*, 19, 149–159.
- [9] Holman, J.B., & Wareham D.G. (2005). COD, ammonia and dissolved oxygen time profiles in the simultaneous nitrification/denitrification process, *Biochemical Engineering Journal*, 22, 125–133.
- [10] Jones, W.L., Schroeder, E.D., & Wilderer P.A. (1990). Denitrification in a batch wastewater treatment system using sequestered organic substances, *Research Journal Pollution Control Federation*, 62, 259–267.
- [11] Ling, J., & Chen S. (2005). Impact of organic carbon on nitrification performance of different biofilters, *Aquacultural Engineering*, 33, 150–162.
- [12] Majone, M., Dircks, K., & Beun J.J. (1999). Aerobic storage under dynamic conditions in activated sludge processes. The state of the art, *Water Science and Technology*, 39, 61–73.
- [13] Majone, M., Massaniso, P., & Ramadori R. (1998). Comparison of carbon storage under aerobic and anoxic conditions, *Water Science and Technology*, 38, 77–84.
- [14] Münch, E.V., Lant, P., & Keller J. (1996). Simultaneous nitrification and denitrification in bench-scale sequencing batch reactors, *Water Research*, 30, 277–284.
- [15] Pochana, K., & Keller J. (1999). Study of factors affecting simultaneous nitrification and denitrification (SND), *Water Science and Technology*, 39, 61–68.
- [16] Third, K.A., Gibbs, B., Newland, M., & Cord-Ruwisch R. (2005). Long-term aeration management for improved N-removal via SND in a sequencing batch reactor, *Water Research*, 39, 3523–3530.
- [17] Zeng, R.J., Lemaire, R., Yuan, Z., & Keller. J. (2003). Simultaneous nitrification, denitrification and phosphorus removal in a lab-scale sequencing batch reactor, *Biotechnology Bioengineering*, 3, 170–178.
- [18] Zhao, H.W., Mavinic, D.S., Oldham, W.K., & Koch F.A. (1999). Controlling factors for simultaneous nitrification and denitrification in a two-stage intermittent aeration process treating domestic sewage, *Water Research*, 33, 961–970.

NOMENCLATURE

- C_{N-NH_4} – Ammonium concentration after time t (mg N-NH₄/L)
 $C_{0,N-NH_4}$ – ammonium concentration at the beginning of SBR cycle (mg N-NH₄/L)
 E_{SND} – SND efficiency (%)
DO – dissolved oxygen concentration (mg O₂/L)
 k_{NH_4-N} – constant rate of ammonia removal [mg N-NH₄/(L·h)]
 n – volumetric exchange rate (d⁻¹)
 r_{NH_4-N} – rate of ammonium removal [mg N-NH₄/(L·h)]
 NO_x^- – sum of nitrites and nitrates remaining after the SBR cycle
 NH_4^+ – ammonium oxidized in the SBR cycle
 t – time (h)

SYMULTANICZNA NITRYFIKACJA I DENITRYFIKACJA W SBR ZE ZMODYFIKOWANYM CYKLEM PRACY PODCZAS OCZYSZCZANIA WÓD NADOSADOWYCH

W prezentowanych badaniach określono wpływ stopnia wymiany objętościowej (n) SBR ze zmodyfikowanym cyklem pracy na efektywność symultanicznej nitryfikacji i denitryfikacji (SND) podczas oczyszczania wód nadosadowych. Cykl pracy SBR składał się z naprzemiennie występujących trzech faz napowietrzania (limitowane stężenie tlenu do 0,7 mg O₂/L) oraz dwóch faz mieszania. Długość każdej z faz napowietrzania i mieszania wynosiła odpowiednio 4 i 5,5 h.

Niezależnie od stopnia wymiany objętościowej uzyskano całkowite usunięcie azotu amonowego. Przy $n = 0,1$ d⁻¹ i $n = 0,3$ d⁻¹ głównym produktem nitryfikacji był azot azotanowy (V), podczas gdy przy $n = 0,5$ d⁻¹ w ściekach oczyszczonych występował zarówno azot azotanowy (III) jak i (V). W założonych warunkach technologicznych, pomimo niekorzystnego ilorazu ChZT/N w dopływie (ok. 4), w osadzie czynnym uzyskano denitryfikację. Przy stopniu wymiany objętościowej $n = 0,5$ d⁻¹ efektywność denitryfikacji wynosiła 51,3% i była kilkukrotnie wyższa niż przy $n = 0,1$ d⁻¹ (7,8%), co wskazuje, że w warunkach ograniczonego dostępu do tlenu w fazie napowietrzania czynnikiem decydującym o uzyskaniu symultanicznej nitryfikacji i denitryfikacji był stopień wymiany objętościowej.