

# Removal of Organics and Nitrogen from Municipal Landfill Leachate in Two-Stage SBR Reactors

D. Kulikowska\*, E. Klimiuk

Faculty of Environmental Sciences and Fisheries, University of Warmia and Mazury in Olsztyn,  
Oczapowskiego St. 5, 10-957 Olsztyn Poland

Received: 5 May 2003

Accepted: 14 November 2003

## Abstract

The aim of this study was to investigate efficiency of ammonium nitrogen removal from municipal landfill leachate in activated sludge in two-stage SBR reactors. Treated leachate contains low concentrations of organic substances measured as chemical oxygen demand (COD) – 757 mg O<sub>2</sub>/dm<sup>3</sup> and high concentrations of ammonium – 362 mgN<sub>NH<sub>4</sub></sub>/dm<sup>3</sup>.

Nitrification was studied in two parallel, aerated SBR reactors with two different hydraulic retention times (HRT), 3 and 2 days, respectively. We have found that 2 days HRT was sufficient to achieve complete nitrification. In the effluent ammonium, nitrite and nitrate nitrogen concentrations were 0.08 mgN<sub>NH<sub>4</sub></sub>/dm<sup>3</sup>, 0.04 mgN<sub>NO<sub>2</sub></sub>/dm<sup>3</sup> and 320 mgN<sub>NO<sub>3</sub></sub>/dm<sup>3</sup>, respectively. The ammonium nitrogen removal rate was 20.2 mgN<sub>NH<sub>4</sub></sub>/dm<sup>3</sup>·h.

The effluent from aerobic reactors (HRT 2 days) was fed to the anoxic SBR reactors. An external carbon source (methanol) was added to promote denitrification. In the anoxic reactor, at a methanol dosage 3.6 mg COD/mg N<sub>NO<sub>3</sub></sub> and HRT of 1 day complete denitrification was achieved with nitrate nitrogen residual concentrations of 0.9 mgN<sub>NO<sub>3</sub></sub>/dm<sup>3</sup>. The maximum denitrification rate was 48.4 mgN<sub>NO<sub>x</sub></sub>/dm<sup>3</sup>·h.

The highest values of the yield methanol coefficient  $Y_{m/N-NO_x}$  were determined for dosages 3.6 mg COD/mg N<sub>NO<sub>3</sub></sub> and 5.4 mg COD/mg N<sub>NO<sub>3</sub></sub>, the lowest for 1.8 mg COD/mg N<sub>NO<sub>3</sub></sub>.

**Keywords:** landfill leachate, activated sludge, sequencing batch reactor (SBR), nitrification, denitrification, methanol.

## Introduction

Leachate from landfills is a potential environmental hazard as surface and groundwater contamination. In order to minimize the negative influence on the environment, leachate must be treated to remove organic compounds and nitrogen before being discharged.

The leachate chemical composition may differ markedly depending on age and maturity of the landfill site. In leachate from the acid-phase landfill, more than 95% of the dissolved organic carbon content of 20,000 mg DOC/dm<sup>3</sup> consisted of volatile fatty acids and only 1.3% of high molecular weight compounds. In methanogenic-phase landfill in leachate, however, there are no volatile acids, and 32%

of the DOC content of 2,100 mg/dm<sup>3</sup> consisted of high molecular weight compounds [1]. According to Artiola-Fortuny and Fuller [2] in methanogenic-phase leachate more than 60% of the DOC is humic-like material.

Biological methods are highly effective in treating leachate from the young landfills containing a large amount of readily biodegradable organic acids [3]. However, their contents decrease rapidly in the following 2-3 years exploitation of landfill. For this reason for leachate treatments are recommended to be multistage systems that include biological and physicochemical processes [4, 5].

The main source of nitrogen in leachate are proteins. According to Jokela et al., [6] percentage of proteins in municipal solid waste is 0.5% of dry weight. The hydrolysis of the polypeptide chain is disadvantageous in

---

\*Corresponding author; e-mail: dorotak@uwm.edu.pl

energetic terms and this is apparently the reason for the slow kinetics of protein hydrolysis that in turn causes slow ammonium releasing. Therefore the mature leachate contains relatively high concentration of ammonium [7]. In activated sludge, nitrogen removal from leachate can be achieved by biosynthesis, ammonia stripping and denitrification [8, 9, 10].

In the activated sludge, however, the nitrification process is slow and may be inhibited by metals and hazardous materials [11, 12], high concentrations of ammonium nitrogen [13] and high concentrations of organic substances, especially volatile fatty acids [14]. When treating leachate characterized by low levels of biodegradable organics, a supplementary source of organic carbon is required to ensure adequate denitrification.

In the presented experiment SBR reactors were used. It is stated that high and low floc loading conditions are continuously repeated in the SBR operating cycle. The existence of substrate concentrations gradient in initial and end of aeration phases results in stratification of activated sludge flocs and promotes the nitrification and denitrification rates [15]. An additional advantage is the possibility for technological modifications during the process since very significant changes in the chemical composition of leachate can occur during the time of the landfill operation [16]. This research seeks to determine organic removal efficiency, rates of nitrification and denitrification and yield methanol coefficient in the denitrification process. The highest nitrogen removal rates are expected for design parameters that are similar to the landfill site where this work was studied.

## Materials and Methods

### Leachate Feed

The leachate used in this study was collected from a municipal landfill located in Wysieka (near Bartoszyce), which has been in operation since 1996. The leachate had the typical characteristics of a mature landfill. The biochemical oxygen demand ( $BOD_5$ ) and chemical oxygen demand (COD) were  $105 \text{ mgO}_2/\text{dm}^3$  and  $757 \text{ mgO}_2/\text{dm}^3$ , respectively. The ammonium nitrogen concentration of the leachate was  $362 \text{ mgN}_{\text{NH}_4}/\text{dm}^3$  (Tab. 1). This low (0.14)  $BOD_5/\text{COD}$  clearly indicated that the leachate was low in biodegradability. For that reason methanol was added to the anoxic reactor as a carbon source for denitrification.

The leachate was delivered 1-2 times per month to the laboratory and stored at  $4^\circ\text{C}$ .

### Process Configuration and System Design

A post denitrification process was carried out in this study. The laboratory treatment two-stage system consisted of an aerobic SBR-N (nitrification) and anoxic SBR-D (denitrification) sequencing batch reactors. The system was operated at room temperature.

Table 1. Landfill leachate characterization.

Parameter	Raw leachate	Aerobically treated leachate	
		SBR 1-N (HRT 3d)	SBR 2-N (HRT 2d)
COD ( $\text{mg O}_2/\text{dm}^3$ )	757	386	394
$BOD_5$ ( $\text{mg O}_2/\text{dm}^3$ )	105	5.6	8.4
Organic nitrogen ( $\text{mgN}_{\text{org}}/\text{dm}^3$ )	35	32	33.2
Ammonium nitrogen ( $\text{mg N}_{\text{NH}_4}/\text{dm}^3$ )	362	0.07	0.08
Nitrate nitrogen ( $\text{mg N}_{\text{NO}_3}/\text{dm}^3$ )	n.d.	323	320
Nitrite nitrogen ( $\text{mg N}_{\text{NO}_2}/\text{dm}^3$ )	n.d.	0.02	0.04

n.d. — not detected

Table 2. The operation conditions in nitrified reactors.

Operation conditions	SBR 1-N	SBR 2-N
Hydraulic retention time (HRT) (d)	3	2
Volumetric exchange rate (%)	33	50

### Nitrification

Two identical SBR reactors worked at 3 days HRT (SBR 1-N) and 2 days HRT (SBR 2-N) in parallel to treat the mature leachate from sanitary landfill. The total volume of each reactor was  $6 \text{ dm}^3$ . Both reactors were operated in a 24-h cycle mode, at 0.25, 20.5, 3 and 0.25 hours for the feed, aeration, settle and decant, respectively. Dissolved oxygen was supplied using porous diffusers, placed at the bottom of aerobic reactors. The operation conditions for the aerated SBR reactors were listed in Table 2.

### Denitrification

Leachate from SBR 2-N was subsequently fed into four SBR reactors (SBR 1-D – SBR 4-D) that were operated in parallel in a 12-h cycle mode and differed in methanol dosage (Tab. 3). Duration phases time was 0.25; 10; 1.5 and 0.25 hours for the feed, mixing, settle and decant, respectively. The operation conditions in denitrified reactors were listed in Table 3.

### Analytical Method

The daily measured parameters were chemical oxygen demand (COD), ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, volatile suspended solids (VSS) and total suspended solids (TSS) in the mixed reactor content and settled effluent. The analyses were carried out according to the methodology described by Hermanowicz et al., [17].

Table 3. The operation conditions in denitrified reactors.

Operation conditions	SBR 1-D	SBR 2-D	SBR 3-D	SBR 4-D
Hydraulic retention time (HRT) (d)	1	1	1	1
Volumetric exchange rate (%)	50	50	50	50
Methanol dosage (mg COD/mg N <sub>NO<sub>3</sub></sub> )*	1.8	3.6	5.4	7.3

\*methanol dosage per nitrate concentration at the beginning of the SBR reactor operating cycle

## Results

### Organics Removal and Nitrification

Organic compounds removal and nitrification were tested at HRT 3d and at HRT 2d. It was shown that organics elimination efficiency (expressed as COD) was adequately 51% and 49%. Their average concentrations in the effluent were 386 mgO<sub>2</sub>/dm<sup>3</sup> and 394 mgO<sub>2</sub>/dm<sup>3</sup>, respectively (Tab. 1). Relatively low effectiveness, although long leachate retention time, could be the result of high concentration of slowly or non-biodegradable organics in the leachate. This is confirmed by low BOD<sub>5</sub>/COD (0.14) in raw leachate.

Ammonium nitrogen removal rate and nitrification rate were described by zero-order kinetics and defined by the following differential equation:

$$r_N = \pm \frac{dC_N}{dt} = \pm k_N \quad (1)$$

The solution for this could be fitted to the experimental data according to (2):

$$C_N = C_{0,N} \pm k_N \cdot t \quad (2)$$

sign (-) means ammonium concentration decrease and sign (+) means nitrate concentration increase.

where:

$r_N$  - ammonium removal rate or nitrification rate (mg N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup>·h or mg N<sub>NO<sub>3</sub></sub>/dm<sup>3</sup>·h),

$k_N$  - constant of ammonium removal rate or nitrification rate (mg N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup>·h or mg N<sub>NO<sub>3</sub></sub>/dm<sup>3</sup>·h),

$C_N$  - ammonium nitrogen or nitrate nitrogen concentration after time  $t$  (mg N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup> or mg N<sub>NO<sub>3</sub></sub>/dm<sup>3</sup>),

$t$  - time (h),

$C_{0,N}$  - ammonium nitrogen or nitrate nitrogen concentration at the beginning of the aeration phase (mg N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup> or mg N<sub>NO<sub>3</sub></sub>/dm<sup>3</sup>).

The values of ammonium removal rate estimated from equation (2) in both reactors were comparable 20.1 mg N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup>·h (HRT 3d) and 20.2 mg N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup>·h (HRT 2d). This means that the rate of ammonium removal was independent of HRT (Figs.1a, 2a). However, in SBR 1 (HRT 3d) nitrite was not detected (Fig. 1b), where-

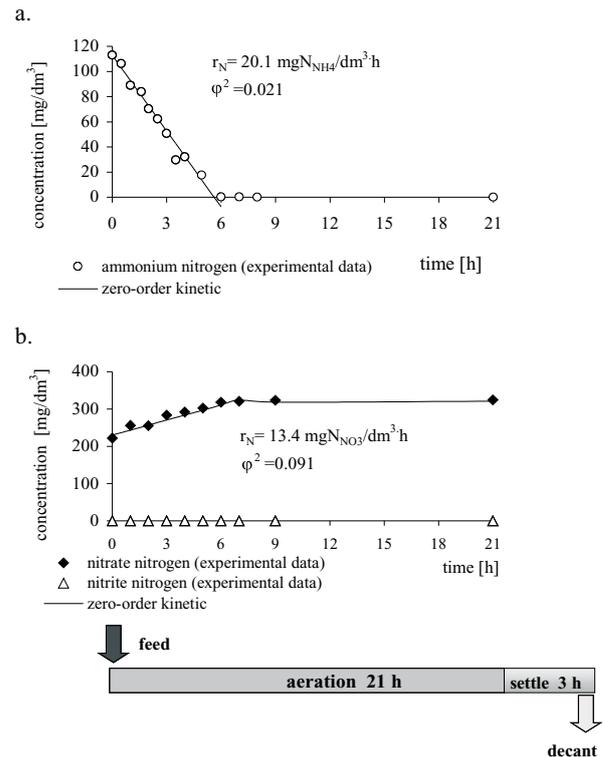


Fig. 1. Concentrations profiles in leachate of ammonium nitrogen (a), nitrate nitrogen and nitrite nitrogen (b) during aerobic conditions and reaction rates described by zero-order kinetics at HRT 3d (SBR 1-N).

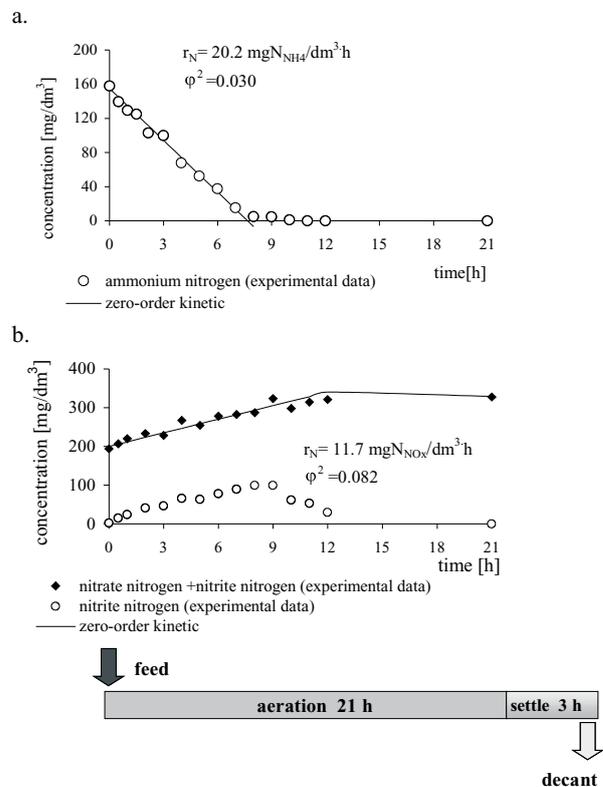


Fig. 2. Concentrations profiles in leachate of ammonium nitrogen (a), nitrate nitrogen and nitrite nitrogen (b) during aerobic conditions and reaction rates described by zero-order kinetics at HRT 2d (SBR 2-N).

as in SBR 2-N (HRT 2d) ammonium oxidation to nitrate was due to nitrite accumulation (Fig. 2b). The highest nitrite nitrogen concentration (99.7 mg  $N_{NO_2}/dm^3$ ) was observed after 7 h of the experimental cycle.

Nitrification rate in SBR 1-N was 13.4 mg $N_{NO_3}/dm^3 \cdot h$  (Fig. 1b) and was 1.5-times lower than the rate of ammonium removal. The rate of I and II phases nitrification in SBR 2-N (estimated from the dependence of sum of nitrite nitrogen and nitrate nitrogen concentrations versus time) was 11.7 mg  $N_{NO_3}/dm^3 \cdot h$  (Fig. 2b).

The ammonium consumed for biomass assimilation, ammonia stripping and nitrification were calculated in the cycle. Figure 3 show the data worked out on the basis of nitrogen balance. The yield coefficient of activated sludge ( $Y_{obs}$ ) was apparently low, due to low readily biodegradable organics concentration and long sludge age ( $Y_{obs} = 0.28$  mg VSS/mg COD in SBR 1-N and 0.36 mg VSS/mg COD in SBR 2-N). It was estimated that nitrogen used for the biomass growth was 3.3 mg N/ $dm^3$  (SBR 1-N) and 6.2 mg N/ $dm^3$  (SBR 2-N) (on the basis determined by Kulikowska [18] the yield coefficients  $Y_{obs}$  and nitrogen content in activated sludge – 9.5 mgN/100 mg VSS). It was adequately 2.9% and 3.9% of nitrogen removed from leachate. Nitrogen loss as the result of stripping calculated according to Balmelle et al., [19] was 4.6% (SBR 1-N) and 7.2% (SBR 2-N). Non-balanced nitrogen loss did not exceed 3% in both reactors (Figs. 3a, b).

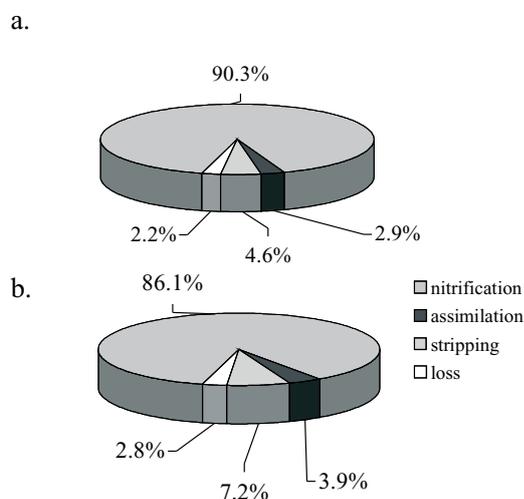


Fig. 3. Ammonium nitrogen balance during SBR reactor operating cycle; a. SBR 1-N (HRT 3d) b. SBR 2-N (HRT 2d).

It was observed that nitrification was highly stable, the average concentrations of ammonium nitrogen and nitrate nitrogen were 0.07 mg $N_{NH_4}/dm^3$  and 323 mg $N_{NO_3}/dm^3$  in SBR 1-N and 0.08 mg $N_{NH_4}/dm^3$  and 320 mg $N_{NO_3}/dm^3$  in SBR 2-N (Figs. 4 a, b). In SBR 1-N, where nitrite accumulation was not observed, the time after that there was ammonium oxidation to nitrate made up approximately 30% of the aeration phase. The time necessary for ammonium oxidation through nitrite and nitrate was two-

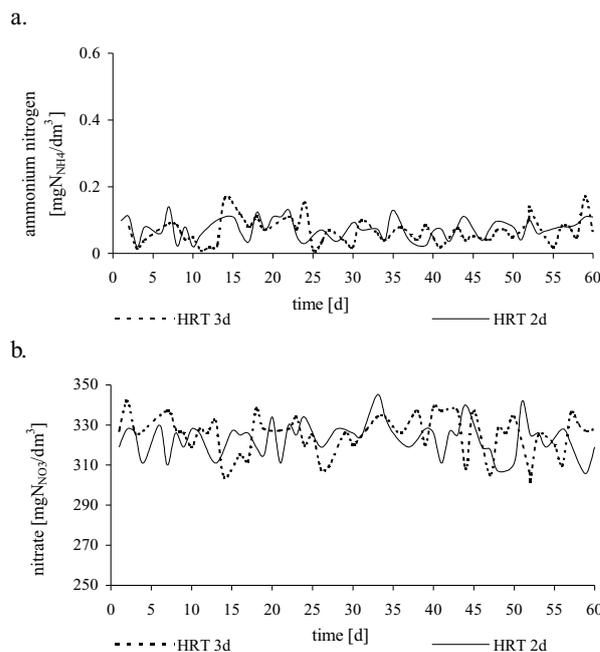


Fig. 4. Concentration of ammonium nitrogen (a) and nitrate nitrogen (b) in the effluent from SBR reactors (steady conditions).

fold longer in SBR 2-N. It should be emphasized that the nitrification rate – 20mg  $N_{NH_4}/dm^3 \cdot h$  and HRT 2d can be the basis for a safe SBR design in leachate treatment.

### Denitrification

Effluent from SBR 2-N was fed to four anoxic reactors operated in parallel, differed in methanol dosage. In the SBR reactors methanol dosage values ranged from 1.8 mg COD/mg  $N_{NO_3}$  (SBR 1-D) to 7.3 mg COD/mg  $N_{NO_3}$  (SBR 4-D) (Tab. 3).

The methanol consumption and nitrate reduction rate in the SBR cycle were described by zero-order kinetics. Methanol removal rate ( $r_m$ ) values are presented in Figure 5. From the obtained results it follows that the highest COD elimination rate – 182.1 mgCOD/ $dm^3 \cdot h$  was achieved in SBR 3-D, the lowest one – 115 mg COD/ $dm^3 \cdot h$  in SBR 1-D. It should be noticed that the value of methanol dosage 1.8 mg COD/mg  $N_{NO_3}$  was insufficient to completely nitrate reduction (denitrification efficiency was 67.2%). In SBR 3-D and SBR 4-D the increase in organics concentration in the effluent was observed, which indicates the incomplete use of methanol for nitrate reduction.

The nitrate reduction rate ( $r_{N-NO_3}$ ) was calculated directly from the dependence nitrate nitrogen concentration versus time (3).

$$r_{N-NO_3} = - \frac{dC_{N-NO_3}}{dt} \quad (3)$$

where:

$r_{N-NO_3}$  - nitrate reduction rate (mg  $N_{NO_3}/dm^3 \cdot h$ ),

$C_{N-NO_3}$  - nitrate nitrogen concentration in the anoxic phase after time  $t$  (mg  $N_{NO_3}/dm^3$ ),

$t$  - time (h).

The data obtained are presented in Figure 5. From the results it can be concluded that nitrite was the intermediate of nitrate reduction to molecular nitrogen detected to accumulate significantly. The maximum nitrite accumulation is visible lower than the initial nitrate concentration, which indicates that they were simultaneously reduced. The nitrate reduction rate was higher than nitrite one, especially when methanol concentration increased.

Denitrification rate ( $r_{N-NO_x}$ ) was expressed as dependence sum of the nitrite nitrogen and nitrate nitrogen concentrations versus time (4):

$$r_{N-NO_x} = - \frac{dC_{(N-NO_x)}}{dt} \quad (4)$$

where:

$r_{N-NO_x}$  - nitrate reduction rate (mg  $N_{NO_x}/dm^3 \cdot h$ ),  
 $C_{N-NO_x}$  - sum of the nitrite nitrogen and nitrate nitrogen concentrations in the anoxic phase after time  $t$  (mg  $N_{NO_x}/dm^3$ ),  
 $t$  - time (h).

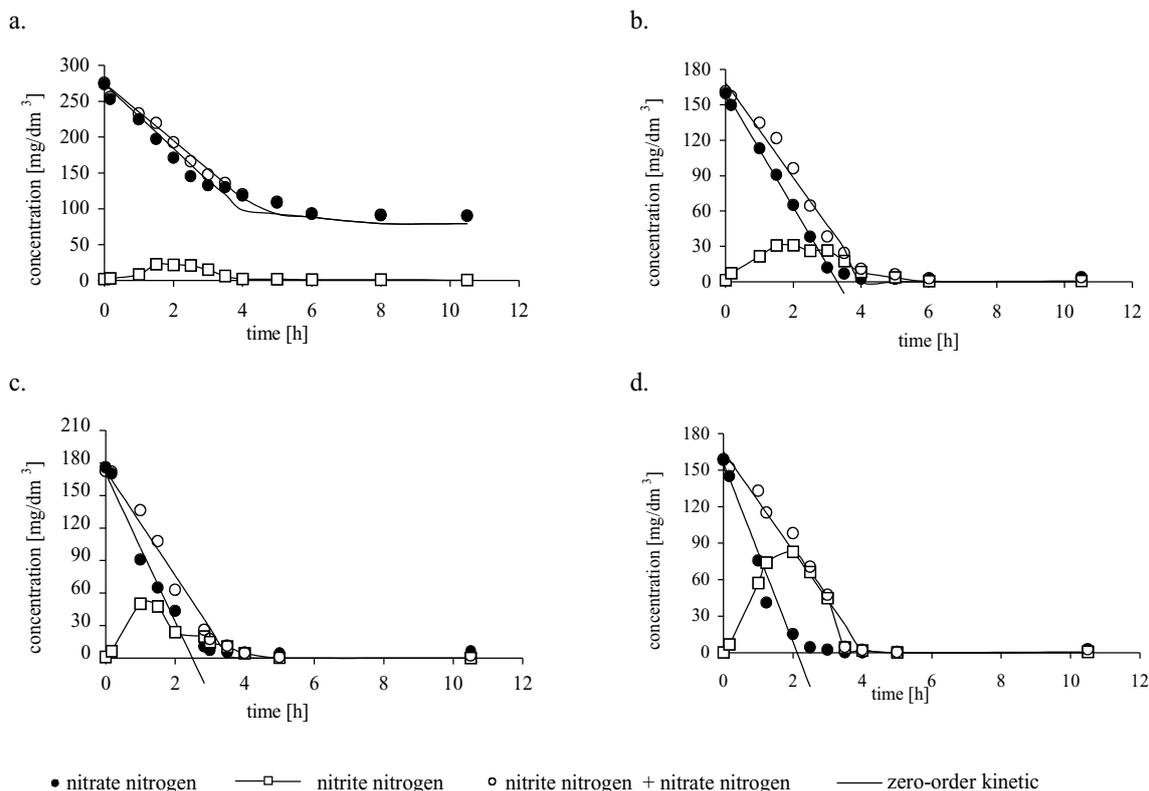
The highest denitrification rate  $r_{N-NO_x}$  - 48.4 mg  $N_{N-NO_x}/dm^3 \cdot h$  was observed for methanol dosage 5.4 mg COD/mg  $N_{NO_3}$ . In other series the values of  $r_{N-NO_x}$  were about 1.2-fold lower (Figs. 5a, b, c, d).

Then, yield coefficient nitrogen removal from leachate  $Y_{N-NO_x/N-NO_3}$  was calculated as the ratio of denitrification rate  $r_{N-NO_x}$  and nitrate reduction rate  $r_{N-NO_3}$  (after Almeida et al., [20]). The value  $Y_{N-NO_x/N-NO_3}$  ranged from 0 to 1 depending on the relative rate of sum nitrite and nitrate reduction at nonlimiting concentration of nitrite and nitrate. The plot of  $Y_{N-NO_x/N-NO_3}$  versus the concentration of methanol was linear (Fig. 6) and can be described by the following equation:

$$Y_{N-NO_x/N-NO_3} = -0.057 \cdot C_m + 1 \quad (5)$$

where:

$C_m$  - methanol dosage per nitrate concentration at the beginning of the SBR reactor operating cycle (mg COD/mg  $N_{NO_3}$ ).



methanol dosage ( $C_m$ ) (mg COD/mg $N_{NO_3}$ )	$r_m$ (mg COD/ $dm^3 \cdot h$ )	$\phi^2$	$r_{N-NO_3}$ (mg $N_{NO_3}/dm^3 \cdot h$ )	$\phi^2$	$r_{N-NO_x}$ (mg $N_{N-NO_x}/dm^3 \cdot h$ )	$\phi^2$
1.8	115	0.027	45	0.011	39.9	0.015
3.6	145	0.03	48.2	0.048	40.2	0.018
5.4	182.1	0.07	68.1	0.052	48.4	0.055
7.3	137	0.048	73.4	0.058	40.4	0.040

Fig. 5. Concentration of nitrite nitrogen, nitrate nitrogen and sum of nitrite nitrogen and nitrate nitrogen versus time and straight line described by zero-order kinetics (a. SBR 1-D; b. SBR 2-D; c. SBR 3-D; d. SBR 4-D). The table includes the methanol dosage ( $C_m$ ), methanol removal rate ( $r_m$ ), nitrate reduction rate ( $r_{N-NO_3}$ ) and denitrification rate ( $r_{N-NO_x}$ ) described by zero-order kinetics and the goodness coefficient  $\phi^2$ .

The ratio of the methanol removal rate ( $r_m$ ) and nitrate removal rate ( $r_{N-NO_3}$ ) or denitrification rate ( $r_{N-NO_x}$ ) to express  $Y_{m/N-NO_3}$  and  $Y_{m/N-NO_x}$  (yield methanol coefficient):

$$Y_{m,N-NO_3} = \frac{r_m}{r_{N-NO_3}} \tag{6}$$

or

$$Y_{m,N-NO_x} = \frac{r_m}{r_{N-NO_x}} \tag{7}$$

where:

- $r_m$  - methanol removal rate (mg COD/dm<sup>3</sup>·h),
- $r_{N-NO_3}$  - nitrate removal rate (mg N<sub>NO<sub>3</sub></sub>/dm<sup>3</sup>·h),
- $r_{N-NO_x}$  - denitrification rate (mg N<sub>NO<sub>x</sub></sub>/dm<sup>3</sup>·h).

The correlation between  $Y_{m/N-NO_3}$  and  $Y_{m/N-NO_x}$  and methanol dosage is shown in Figure 7. The values of  $Y_{m/N-NO_3}$  ranged from 1.87 mg COD/mg N<sub>NO<sub>3</sub></sub> (SBR 4-D) to 2.98 mg COD/mg N<sub>NO<sub>3</sub></sub> (SBR-2D). The values of  $Y_{m/N-NO_x}$  for the dosages 3.6 mg COD/mg N<sub>NO<sub>3</sub></sub> (SBR 2-D) and 5.4 mg COD/mg N<sub>NO<sub>3</sub></sub> (SBR 3-D), for almost all the time points were on the same level. It corresponded with the stoichiometric methanol dosage - 2.47 mgCH<sub>3</sub>OH/mg N<sub>NO<sub>3</sub></sub> (calculated by McCarty et al., [21]), which converted on COD was 3.6 mg COD/mg N<sub>NO<sub>3</sub></sub>. One of the reasons why lower than stoichiometric values

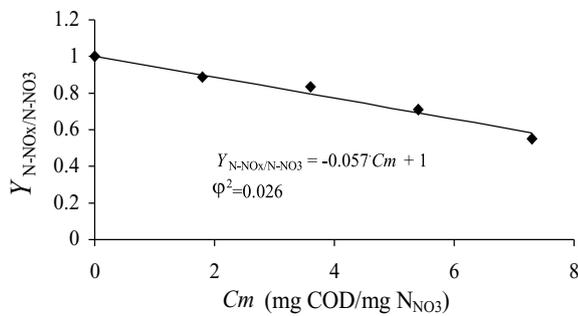


Fig. 6. The ratio between denitrification rate and nitrate reduction rate ( $Y_{N-NO_x/N-NO_3}$ ) versus methanol dosage ( $C_m$ ).

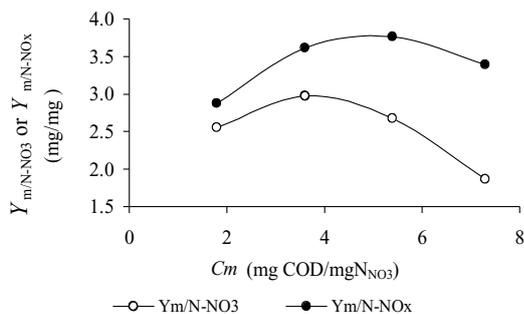


Fig. 7. Yield methanol coefficients ( $Y_{m/N-NO_3}$  and  $Y_{m/N-NO_x}$ ) versus methanol dosage ( $C_m$ ).

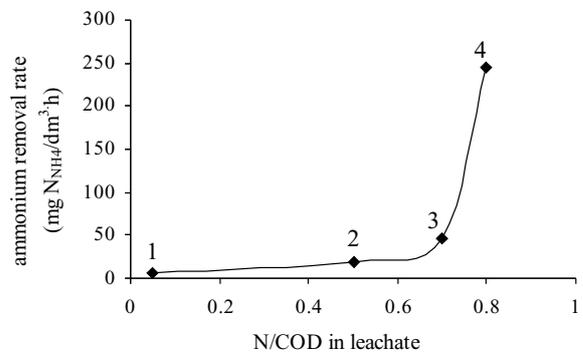
of  $Y_{m/N-NO_x}$  at the methanol dosage 1.8 mg COD/mg NO<sub>3</sub> (SBR 1-D) and 7.3 mg COD/mg N<sub>NO<sub>3</sub></sub> (SBR 4-D) were achieved might be due to the fact that not only molecular nitrogen but also nitrogen oxides appeared after denitrification.

### Discussion

Leachate with low BOD<sub>5</sub>/COD, ratio used in this study, was collected from landfill, which has been operated for 6 years. It is obvious that correspondingly with the decrease in BOD<sub>5</sub>/COD ratio there is a decrease in treatment effectiveness. In the presented experiment effluent contained high organics concentration (about 390 mg O<sub>2</sub>/dm<sup>3</sup>). It was about 50% of their contents in the influent. Barbusiński et al., [22] indicated that during the treatment of leachate from completely stabilized, 50-year old landfill of industrial wastes at BOD<sub>5</sub>/COD 0.05, the value of COD removal efficiency was 7.5%.

In this research, ammonium concentration did not exceed 0.08 N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup> in the effluent and stable nitrification were obtained at the leachate hydraulic retention time (HRT) 2d. An effluent of similar quality with 0.1 mg N<sub>NH<sub>4</sub></sub>/dm<sup>3</sup> Zaloum and Abott [23] have been observed at the retention time of 3.2 d but at four-fold lower nitrogen concentration. For raw leachate containing high concentration of organic substances (12 760 mgCOD/dm<sup>3</sup>) and nitrogen (218 mgN/dm<sup>3</sup>) it is necessary to extend HRT to 20 d. According to Robinson and Carville (after Lo 1996) [24] in SBR reactors, although the favourable N/COD ratio for the nitrification (1.08), in order to obtain high effectiveness of the process (99.8 %), the hydraulic retention time must not to be shorter than 20 d. Comparing nitrification rate obtained in the presented experiment with the results of the other authors (Fig. 8) it should be noted that leachate composition, especially N/COD ratio in the treated leachate determined the process.

The research reported that under aerobic conditions over 90% (SBR 1-N) and 86% (SBR 2-N) of nitrogen was nitrified. The nitrogen amount for biosynthesis, stripping



1 - Yalmaz, Öztürk [25]	3 - Yalmaz, Öztürk [25]
2 - our experiment	4 - Doyle et al., [28]

Fig. 8. Ammonium removal rate versus N/COD in treated leachate (according to some authors).

and the nitrogen loss did not exceed 10% (SBR 1-N) and 14% (SBR 2-N). Results in the literature indicate that in the leachate both the use of nitrogen for biosynthesis [8] and the nitrogen loss caused by ammonia stripping [9] are diversified and in extreme cases can achieve almost 100%.

In our experiments methanol and nitrate concentrations decreased near linearly with time. Similarly, Timmermans and van Haute [26] indicated that in pure culture of *Hyphomicrobium* sp. the denitrification rates have been described with zero-order kinetics with respect to the carbon source and nitrate. It was showed that nitrate reduction rate ( $r_{N-NO_3}$ ) depended on methanol dosage and it ranged from 45 to 73.4 mg  $N_{NO_3}/dm^3 \cdot h$ , whereas the denitrification rate ( $r_{N-NO_x}$ ) was almost on the same level of approximately 42.2 mg  $N_{NO_x}/dm^3 \cdot h$ .

Data in literature indicate that accumulation of nitrite is strongly affected by species composition culture, oxygen and substrate concentrations. Loukidou and Zouboulis [27] indicated that the rate of denitrification depends on the supply of an adequate concentration of carbon source for denitrifying microorganisms. Doyle et al., [28] during the investigations in SBR reactors under anoxic conditions proved that denitrification rate depends on carbon source. In cases of acetate and methanol the rates were adequately 1.5-times (16.25 mgN/dm<sup>3</sup>·h) and 1.7-times (14.58 mgN/dm<sup>3</sup>·h) lower in comparison to maltose (25 mgN/dm<sup>3</sup>·h). In our experiment, at the optimal methanol dosage (3.6 mg COD/mg  $N_{NO_3}$ ), denitrification rate ( $r_{N-NO_x}$ ) was 40.2 mg  $N_{NO_x}/dm^3 \cdot h$ .

In presented researches the highest yield methanol coefficients  $Y_{m/N-NO_x}$  were obtained for dosages 3.6 mg COD/mg  $N_{NO_3}$  and 5.4 mg COD/mg  $N_{NO_3}$ . Lower values of the coefficient for dosages 1.8 mg COD/mg  $N_{NO_3}$  and 7.3 mg COD/mg  $N_{NO_3}$  may indicate that nitrogen oxides were the products of denitrification. Itokawa et al., [29] reported nitrous oxide production in high-loading biological nitrogen removal process under low COD/N ratio condition. In steady-state operation, 20-30% of influent nitrogen was emitted as  $N_2O$  in the bioreactors with influent COD/N ratio less than 3.5.

In our experiment methanol demand was about 3.6 mg COD/mg  $N_{NO_3}$ . Literature data concerning external carbon source demanding for denitrification are not unambiguous. From the investigations carried out by Grabińska-Loniewska [30] in activated sludge it results that methanol demanding for denitrification was 3.03 g  $CH_3OH/g N_{NO_3}$  (4.48 mg COD/mg  $N_{NO_3}$ ). Christensson et al., [31] compared methanol demanding of activated sludge and pure denitrifying cultures isolated from activated sludge. They indicated that methanol demand was on a similar level (4.45 and 4.1 g COD/g  $N_{NO_3}$ ). Doyle et al., [28], studying leachate treatment in SBR reactors under anoxic conditions, found that for complete nitrate reduction the COD/ $N_{NO_3}$  ratio should be higher than 7.

### Conclusions

The results of the study can be summarized as follows:

1. Complete nitrification in the SBR was possible at

leachate hydraulic retention time 2d, the average ammonium concentration in the effluent 0.08 mg  $N_{NH_4}/dm^3$ . Determined ammonium removal rate was on the level of 20 mg  $N_{NH_4}/dm^3 \cdot h$ ,

2. The yield coefficient nitrogen removal from leachate ( $Y_{N-NO_x/N-NO_3}$ ) depending on methanol dosage was linear with  $k$  coefficient - 0.057,
3. Determined yields methanol coefficient  $Y_{m/N-NO_x}$  was 3.6 mg COD/mg  $N_{NO_x}$  and was in accordance with theoretical demand, which indicates that the final denitrification product was molecular nitrogen. A lower than theoretical yield coefficient for dosages 1.8 mg COD/mg  $N_{NO_3}$  and 7.3 mg COD/mg  $N_{NO_3}$  indicates that the products of denitrification may be nitrous oxides.

### References

1. HARMSSEN J. Identification of organic compounds in leachate from a waste tip. *Wat. Res.*, **17** (6), 699, **1983**.
2. ARTIOLA-FORTUNY J., FULLER W. H. Humic substances in landfill leachates: I. Humic acid extraction and identification. *J. Environ. Qual.* **11**, 663, **1982**.
3. TIMUR H., ÖZTURK I., ALTINBAS M., ARIKAN O., TUYLUOGLU B. S. Anaerobic treatability of leachate: a comparative evaluation for three different reactor systems. *Wat. Sci. Technol.*, **1-2** (42), 287, **2000**.
4. ALBERS H., KRÜCKEBERG G. Combination of aerobic pre-treatment, carbon adsorption and coagulation. Landfilling of waste: leachate. Elsevier applied science. London and New York, 305, **1992**.
5. LEITZKE O. Landfill treatment by photochemical wet oxidation. *Roczn. PZH*, **1** (47), 125, **1996** (in Polish).
6. JOKELA J. P.Y., KETTUNEN R. H., SORMUNEN K. M., RINTALA J. A. Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. *Wat. Res.*, **36**, 4079, **2002**.
7. KNOX K. Leachate treatment with nitrification of ammonia. *Wat. Res.*, **7** (19), 895, **1985**.
8. ROBINSON H. D., MARIS P. J. The treatment of leachates from domestic wastes in landfills I. Aerobic biological treatment of a medium – strength leachate. *Wat. Res.*, **11** (17), 1537, **1983**.
9. MARTTINEN S. K., KETTUNEN R. H., SORMUNEN K. M., SOIMASUO R. M., RINTALA J. A. Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates. *Chemosphere*, **46**, 851, **2002**.
10. ABUFAYED A. A., SCHROEDER E. D. Performance of SBR/denitrification with a primary sludge carbon source. *Journal WPCF* **5** (58), 387, **1986**.
11. ANTONIOU P., HAMILTON J., KOOPMAN B., JAIN R., HOLLOWAY B., LYBERATOS G., SVORONOS S. A. Effect of temperature and pH on the effective maximum specific growth rate of nitrifying bacteria. *Wat. Res.*, **1** (24), 97, **1990**.
12. FDZ – POLANCO F., VILLAYERDE S., GARCIA P. A. Temperature effect on nitrifying bacteria activity in biofilters: activation and free ammonia inhibition. *Wat. Sci. Technol.*, **11** (30), 121, **1994**.
13. LI X. Z., ZHAO Q. L. Inhibition of microbial activity of activated sludge by ammonia in leachate. *Environment International*, **8** (25), 961, **1999**.

14. TAKAIT., HIRATA K., YAMAUCHI K., INAMORI Y. Effects of temperature and volatile fatty acids on nitrification-denitrification activity in small-scale anaerobic-aerobic recirculation biofilm process. *Wat. Sci. Technol.*, **6** (35), 101, **1997**.
15. WANNER J. Activated sludge bulking and foaming control. A Technomic Publishing Company, Inc. Lancaster, Pennsylvania. **1994**.
16. IRVINE R. L., WILDERER P. A., FLEMMING H-C. Controlled unsteady state processes and technologies – an overview. *Wat. Sci. Technol.*, **1** (35), 1, **1997**.
17. HERMANOWICZ W., DOŻAŃSKA W., DOJLIDO J., KOZIOROWSKI B. Physicochemical research of water and wastewater. Arkady. Warszawa. **1999** (in Polish).
18. KULIKOWSKA D. Efficiency of municipal landfill leachate treatment in SBR reactors. Doctor's thesis. Wydział Inżynierii Środowiska, Politechnika Warszawska. **2002** (in Polish).
19. BALMELLE B., NGUYEN K. M., CAPDEVILLE B., CORNIER J. C., DEGUIN A. Study of factors controlling nitrite build-up in biological processes for water nitrification. *Wat. Sci. Technol.*, **5-6** (26), 1017, **1992**.
20. ALMEIDA J. S., REIS M. A., CARRONDO M. J. Competition between nitrate and nitrite reduction in denitrification by *Pseudomonas fluorescens*. *Biotechnology and Bioengineering*, **46**, 476, **1995**.
21. MCCARTY P. L., BECK L., AMANT P. S. Biological denitrification of wastewater by addition of organic materials. Proceedings of the 24<sup>th</sup> Industrial Waste Conferene, Purdue University. **1969**.
22. BARBUSIŃSKI K., KOŚCIELNIAK H., MAJER M. Treatment of underground water from industrial landfill. V Ogólnopolskie Sympozjum Naukowo-Techniczne "Biotechnologia Środowiskowa". **1997** (in Polish).
23. ZALOUM R., ABBOTT M. Anaerobic pretreatment improves single sequencing batch reactor treatment of landfill leachates. *Wat. Sci. Technol.*, **1** (35), 207, **1997**.
24. LO I. Characteristics and treatment of leachates from domestic landfills. *Environment International*, **4** (22), 433, **1996**.
25. YALMAZ G., ÖZTÜRK I. Biological ammonia removal from anaerobically pre-treated landfill leachate in sequencing batch reactors (SBR). *Wat. Sci. Technol.*, **3** (43), 307, **2001**.
26. TIMMERMANS P., VAN HAUTE A. Denitrification with methanol. Fundamental study of the growth and denitrification capacity of *Hyphomicrobium* sp. *Wat. Res.*, **17**, 1249, **1983**.
27. LOUKIDOU M. X., ZOUBOULIS A. I. Comparison of two biological treatment processes using attached-growth biomass for sanitary landfill leachate treatment. *Environmental Pollution*, **111**, 273, **2001**.
28. DOYLE J., WATTS S., SOLLEY D., KELLER J. Exceptionally high-rate nitrification in sequencing batch reactors treating high ammonia landfill leachate. *Wat. Sci. Technol.*, **3** (43), 315, **2001**.
29. ITOKAWA H., HANAKI K., MATSUO T. Nitrous oxide production in high-loading biological nitrogen removal process under low COD/N ratio condition. *Wat. Res.*, **3** (35), 657, **2001**.
30. GRABIŃSKA-LONIEWSKA A. Effect of some carbon sources on biocenosis during nitrogen removal in denitrification. Wydawnictwa Politechniki Warszawskiej, Warszawa. **1990** (in Polish).
31. CHRISTENSSON M., LIE E., WELANDER T. A comparison between ethanol and methanol as carbon sources for denitrification. *Wat. Sci. Technol.*, **30**, 83, **1994**.