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ANALYSIS OF THE NITRIFICATION PROCESS IN A CASCADE SYSTEM WITH MOVING BED BIOFILM

The effectiveness of the nitrogen removal depends on the rate and the extent of nitrification. The aim of this research was to estimate the efficiency of the nitrogen removal in a cascade system with two stages of denitrification, step-feed and moving bed biofilm (Kaldnes carriers). In this paper, a part of the results concerning nitrification are discussed. A rate of nitrite and nitrate production in nitrification reactors reached $0.41 \text{ kg N-NO}_x^-/\text{m}^3\text{d}$ ($2 \text{ g N-NO}_x^-/\text{m}^2\text{d}$ and $0.53 \text{ g N-NO}_x^-/\text{g d.m.o.d}$). Nitrification effectiveness exceeded 80% for an ammonia nitrogen load of up to $0.3 \text{ kg N-NH}_4^+/\text{m}^3\text{d}$. A permanent drop of this parameter was visible for a greater ammonia nitrogen load.

1. INTRODUCTION

The effectiveness of the nitrogen removal depends on the rate and the extent of the nitrification process, which depends on a large number of factors. The processes of mass transport play an important role in reactors with attached biomass. AUDIC [1] and BROCH-DUE [3] show that bacteria attached to a carrier surface are more active than unattached bacteria. Biomass activity is not proportional to its quantity, but increases with biofilm thickness to a specific, critical active thickness, up to 65–150 μm [6]. A total rate of the process is zero order when the biofilm thickness is below the active one. Above this thickness the diffusion of substrates becomes the factor limiting the process rate.

The rate of ammonia oxidation depends greatly on the concentration of this substrate in the bulk solution. The steady-state kinetics of ammonia removal is usually described by the Monod-type equation. Both mathematical analysis and experimental data revealed that at a sufficiently high substrate concentration the reaction rate becomes zero order with respect to this substrate concentration. In such a case, factor other than this substrate concentration becomes the limiting one, for example, the oth-

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er substrate, oxygen. At a sufficiently low substrate concentration, the relationship becomes linear, following the first-order reaction [11].

It is universally accepted that nitrification does not occur at oxygen concentration lower than 0.1–0.2 g O₂/m³ [16]. In the case where oxygen is the reaction-limiting substrate, the concentration of the substrates undergoing nitrification inside the biofilm gradually decreases up to a depth, at which oxygen concentration reaches 0.1 mg O₂/dm³ and then remains constant. An increase of organic carbon or ammonia loading encourages oxygen consumption in biofilm by heterotrophs. As a result, oxygen does not penetrate deep into biofilm which reduces the nitrification rate [2], [3], [11]. This hypothesis is proved by the fact that high concentration of organic substances has no influence on ammonia and nitrites profiles, if oxygen is not a reaction rate-limiting substrate. This also takes place when heterotrophs reach the maximum respiration rate [15].

The aim of this research was to estimate the efficiency and capacity of nitrogen removal in a cascade system with two stages of denitrification, step-feed and moving bed biofilm. The influence of controlled parameters on this process was also studied. In this paper, some results concerning nitrification are discussed.

2. MATERIALS AND METHODS

This research was carried out on a prepared feed wastewater (table 1). Sodium acetate was chosen as the source of carbon. The Kaldnes carriers were used, made of polyethylene with a density ranging from 0.92 kgm⁻³ to 0.96 kgm⁻³. They were shaped like small cylinders, about 9 mm in diameter and 7 mm in height, with a cross inside the cylinder and longitudinal fins on the outside (figure 1). A laboratory set (figure 2) consisted of four reactors (marked as R1, R2, R3 and R4). Each reactor has a 15.4 dm³ volume and was filled with carriers up to 48% of its volume. Denitrification, combined with the oxidizing of carbon compounds, was conducted in the reactors R1 and R3. In R2 and R4, nitrification was carried out. Raw wastewater was pumped into the reactors R1 and R3. The laboratory set operated longer than three months. The biofilm was cultivated longer than three months, prior to this. During the experiment four tests were conducted in order to examine the effect of various factors on the nitrogen removal:

- Test 1 – the recirculation ratio.
- Test 2 – the raw wastewater stream distribution.
- Test 3 – increasing carbon loads.
- Test 4 – increasing nitrogen loads.

Some key parameters are shown in table 2. During the tests, manual grab samples were taken from the effluent of each reactor once or twice a day, 3–5 times a week. The samples were analyzed for N–NH₄⁺, N–NO₂⁻, N–NO₃⁻, soluble COD (SCOD),

suspended solids and total solids. The properties of the biofilm were also investigated and the results published in further material [14].

Table 1

Wastewater composition

Solution	Constituent	Unit	Concentration
I	CH ₃ COONa	mg/dm ³	21–600
		mg O ₂ /dm ³	20–590
II	NH ₄ Cl	mg/dm ³	86–382
		mg N/dm ³	23–100
	NaH ₂ PO ₄	mg /dm ³	125–500
III	NaHCO ₃	mg /dm ³	100–300
		pH	7.0–7.7
IV	FeSO ₄ ×7H ₂ O	mg/dm ³	4.0
		mg Fe ²⁺ /dm ³	1.0
	CuSO ₄ ×5H ₂ O	mg/dm ³	0.12
		mg Cu ²⁺ /dm ³	0.03
	MgSO ₄ ×7H ₂ O	mg/dm ³	100
		mg Mg ²⁺ /dm ³	30
	NaMoO ₄	mg/dm ³	1.9 × 10 ⁻³
		mg Mo ⁷⁺ /dm ³	0.75 × 10 ⁻³
	–	mg Ca ²⁺ /dm ³	75
	EDTA	mg/dm ³	6.6

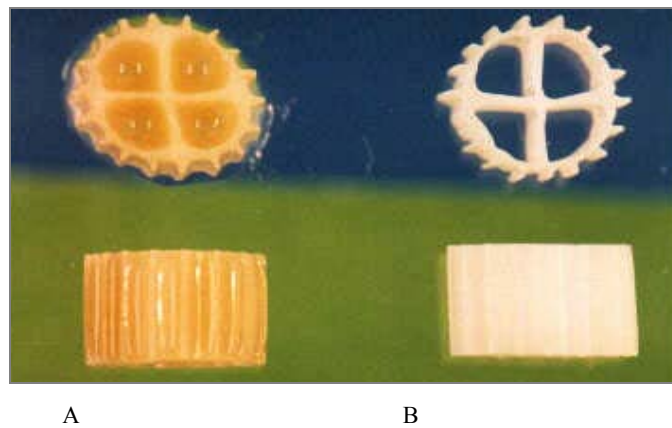


Fig. 1. The Kaldnes carrier:
A – with biomass, B – without biomass

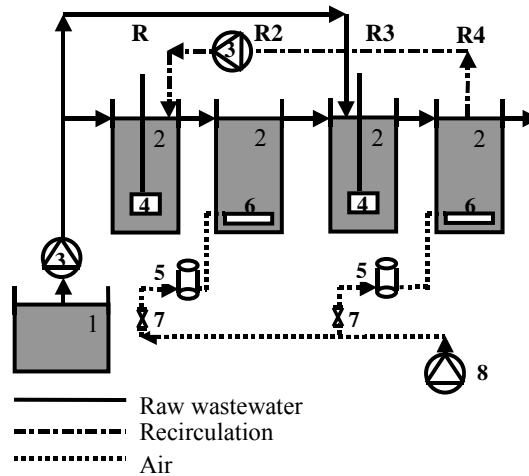


Fig. 2. Laboratory-scale set: 1 – tank with wastewater, 2 – reactor, 3 – peristaltic pump, 4 – stirrer, 5 – air flow-meter, 6 – membrane tube diffuser, 7 – manual valve, 8 – air blower

Table 2

Selected parameters of four tests

Parameter	Test 1			Test 2			Test 3			Test 4		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
Recirculation ratio R [-]	0.22	2.24	0.77	2.13	2.38	2.26	2.13	2.38	2.26	2.68	3.68	3.44
Coefficient of raw wastewater stream distribution Θ [-]	0.46	0.53	0.50	0.50	1.00	0.72	0.50	1.00	0.72	0.60	0.74	0.66
C/N in influent [-]	4.4	5.6	4.9	4.6	5.8	5.2	4.6	5.8	5.2	5.6	9.3	7.3
Dissolved oxygen [$\text{mg O}_2/\text{dm}^3$]	3.9	5.8	5.1	3.9	5.7	5.0	4.2	5.8	4.7	3.9	5.3	4.6
Temperature [$^{\circ}\text{C}$]	18.1	25.5	21.0	23.7	25.6	24.7	21.3	25.4	23.9	21.1	26.0	24.5
pH	7.5	7.8	7.7	7.6	7.9	7.73	7.4	7.8	7.6	7.6	7.9	7.8

3. RESULTS

During Test 1 the recirculation ratio was gradually increased from 0.22 to 2.24 (table 2), but Θ was almost constant. The ammonia nitrogen loading was low – below $0.26 \text{ kg N/m}^3\text{d}$ in both nitrification reactors (table 2), and similar to SCOD loading. At the beginning of the test in reactor R2, the ratio of organic carbon (SCOD) loading to the ammonia nitrogen (N_{NH_4}) loading exceeded 2. Then it was less than 1 (figure 3).

The rate of producing oxidized nitrogen (sum of nitrite and nitrate nitrogen) in reactor R4 was constantly higher than this rate in R2. It increased during the test and reached a maximum value of $0.217 \text{ kg N/m}^3\text{d}$. The efficiency of ammonia nitrogen removal in both reactors fluctuated between 69.2% and 97.4%. Ammonia and oxidized nitrogen concentration gradually decreased in both nitrification reactors (figure 3). At the end of test in R4 reactor, their concentrations were not greater than 0.5 mg N/dm^3 and 15 mg N/dm^3 , respectively.

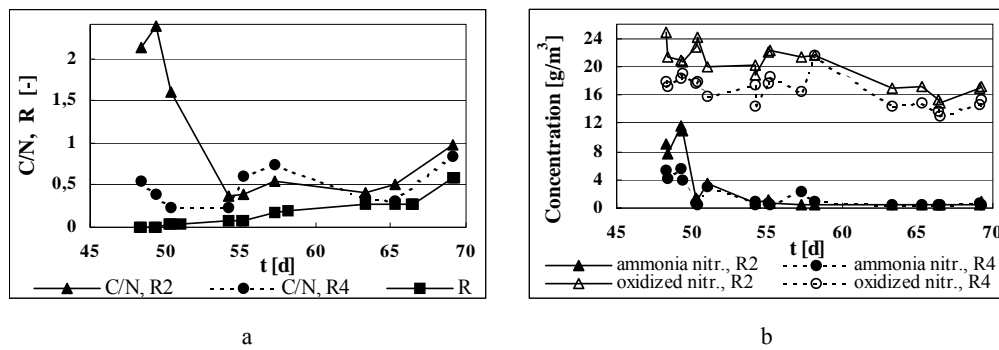


Fig. 3. Changes of recirculation ratio, C/N ratio during Test 1 (a).
Ammonia and oxidized nitrogen concentration during Test 1 (b)

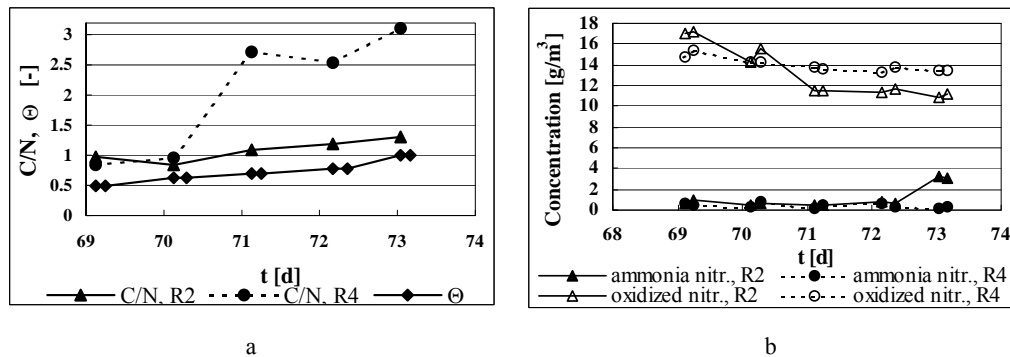


Fig. 4. Changes of coefficient of raw wastewater stream distribution (Θ), C/N ratio during Test 2 (a).
Ammonia and oxidized nitrogen concentration during Test 2 (b)

The coefficient of raw wastewater stream distribution (Θ) changed from 0.5 to 1.0 as the Test 2 was carried out. The ammonia nitrogen loading and organic carbon (SCOD) loading of reactor R2 were permanently rising, while the loading of reactor R4 was decreasing. Ammonia loading reached $0.48 \text{ mg N/dm}^3\text{d}$ in R2. The C/N ratio increased in both reactors, in R2 it reached a value of 1.3 at the end of the test, and in R4 – 3.1 (figure 4). Ammonia nitrogen concentration did not exceed 1 mg

N/dm^3 in both reactors during almost all test. Production rate of nitrite and nitrate nitrogen underwent changes similar to loading changes, and in R2 reached the highest value equal to $0.36 \text{ mg N/dm}^3\text{d}$. The efficiency of ammonia nitrogen removal in R2 demonstrated a downward trend, while in R4 it fluctuated between 82.7% and 94.9% (table 2).

During Test 3 ammonia nitrogen loading of reactor R2 oscillated in a narrow scope. Its arithmetic mean was equal to $0.52 \text{ kg N/m}^3\text{d}$ and was about 50% higher than in R4 (table 2). The loading of organic carbon compounds of reactor R2 permanently rose up to $1.66 \text{ kg O}_2/\text{m}^3\text{d}$, and C/N ratio, to 2.8 (figure 5). The rate of removing oxidized nitrogen decreased during the test by about 50%, from 0.318 to $0.15 \text{ kg N/m}^3\text{d}$. All the time the rate of removing ammonia nitrogen was higher than the rate of producing oxidized nitrogen by about $0.05 \text{ kg N/m}^3\text{d}$.

The loading of reactor R4 with organic carbon compounds was slightly lower, but at the end of the test about 3 times less than in R2. The C/N ratio reached a maximum value equal to 2.25 after 79 days of research (figure 5). The rate of producing oxidized nitrogen was almost equal to the rate of removing ammonia nitrogen and had a tendency to grow. In R4, the concentration of ammonia nitrogen was lower, but the concentration of oxidized nitrogen was higher than in R2. The efficiency of ammonia nitrogen removal in R2 was always poorer than in R4, on average 20%, and reached a low point of 41.2%.

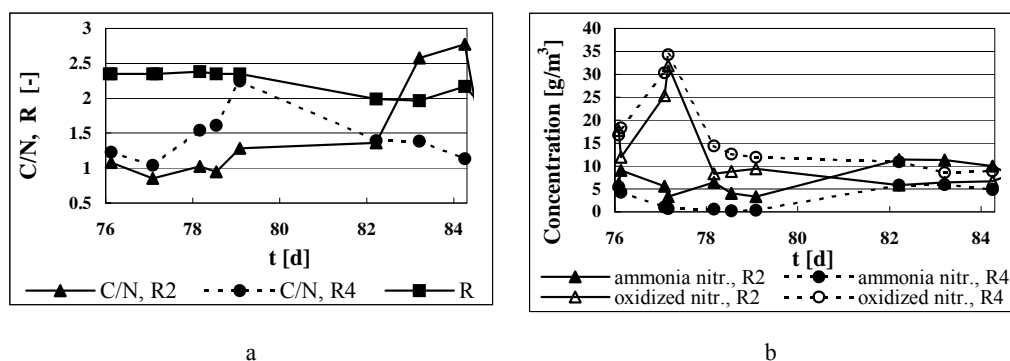


Fig. 5. Changes of C/N ratio, recirculation ratio during Test 3 (a).
Ammonia and oxidized nitrogen concentration during Test 3 (b)

During the Test 4 the loading of the reactor R2 with ammonia nitrogen increased from $0.185 \text{ kg N/m}^3\text{d}$ to $0.847 \text{ kg N/m}^3\text{d}$, in R4 it was only slightly lower than for the most part of the test. In R2, at the beginning of the test, organic carbon loading exceeded $1.5 \text{ kg O}_2/\text{m}^3\text{d}$ and successively dropped to $0.7 \text{ kg O}_2/\text{m}^3\text{d}$. In R4, it fluctuated between 0.5 and $0.8 \text{ kg O}_2/\text{m}^3\text{d}$. The ratio of C/N ranged from 0.96 to 8.2 in R2, while in R4 – to 5.3 (figure 6). In both reactors, the rate of ammonia nitrogen removal

increased, but in R4 it was higher. Production of oxidized nitrogen in R2 varied in the scope from 0.14 to 0.22 kg N/m³d. In the second part of test, it was less than the rate of ammonia nitrogen removal of about 0.1 kg N/m³d. In R4, both parameters differed slightly. Concentration of ammonia nitrogen in R4 was lesser than that in R2. The efficiency of ammonia nitrogen removal in R4 was higher than that in R2 and changed from 43.1% to 92.8%.

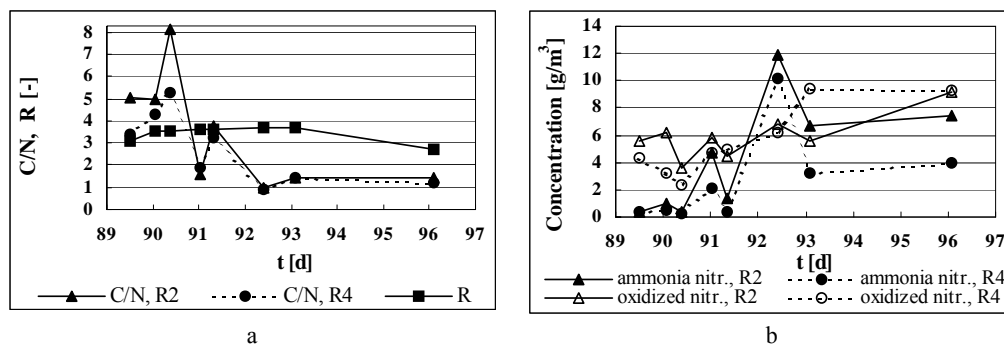


Fig. 6. Changes of C/N ratio, recirculation ratio during Test 4 (a).
Ammonia and oxidized nitrogen concentration during Test 4 (b)

4. DISCUSSION

The highest rate of producing oxidized nitrogen obtained during all the tests was equal to 0.41 kg N-NO_x⁻/m³d (2 g N-NO_x⁻/m²d and 0.53 g N-NO_x⁻/g d.m.o.d) and was observed in R4. In R2, it was usually lower due to a higher SCOD loading. It would be good to take into account that other researchers using systems with Kaldnes carriers obtained similar results [5], [8], [10], but some obtained lower ones [9].

The highest impact on the rate of ammonia nitrogen removal had the loading of ammonia nitrogen. For ammonia nitrogen loading to about 0.36 kg N-NH₄⁺/m³d in R2 and 0.3 kg N-NH₄⁺/m³d in R4, a linear relationship between ammonia nitrogen loading and the rate of its removal was observed (figure 7a, b). The efficiency of ammonia nitrogen removal exceeded 80% (figure 7c, d). Ammonia nitrogen concentrations did not exceed 2 g N-NH₄⁺ (figure 7c, d). These results were obtained at loading of organic carbon to 1.5 kg O₂/m³d in R2, to 0.8 kg O₂/m³d in R4 and oxygen concentration above 5 mg O₂/dm³. This proved that in this range the nitrification rate was the first-order process, limited by lack of ammonia nitrogen compounds.

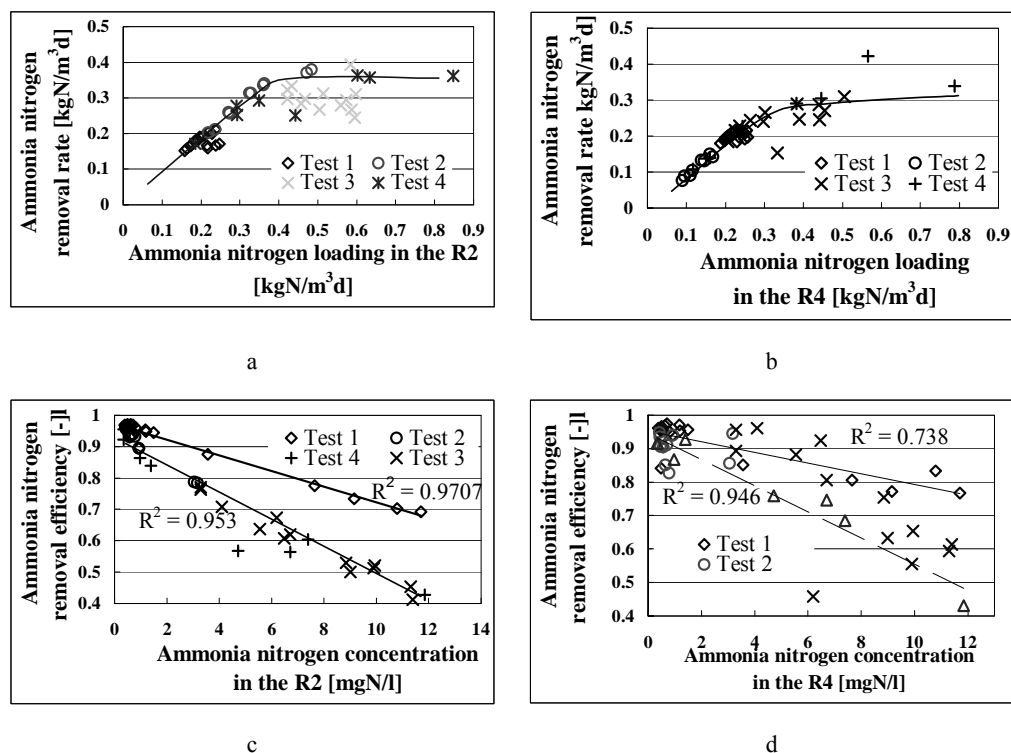


Fig. 7. Relationship between ammonia nitrogen removal rate and ammonia nitrogen loading in R2 (a). Relationship between ammonia nitrogen removal rate and ammonia nitrogen loading in R4 (b). Ammonia nitrogen removal efficiency as a function of ammonia nitrogen concentration in R2 (c). Relationship between ammonia nitrogen removal efficiency and ammonia nitrogen concentration in R4 (d)

For a greater loading of ammonia nitrogen, a decrease in its removal efficiency was visible. A lack of further increase in the rate of ammonia nitrogen removal and a linear relationship between the concentration of N-NH_4^+ in effluent and its removal efficiency were also observed (figure 7a–d). A large scattering of ammonia nitrogen concentration, which occurred for oxygen concentration below $5 \text{ mg O}_2/\text{dm}^3$, showed that in this case, the nitrification was a zero-order process in terms of ammonia nitrogen and was limited by lack of oxygen and other factors. The loading of SCOD, to a smaller extent, affected the nitrification rate (figure 8a). CANZIANI [4] and OKABE [7] found that at $\text{C/N} > 1.5$ nitrification was very slow in spite of a sufficient amount of nitrifiers. In this research, the highest nitrification rates and simultaneously its high efficiency were noticed at $\text{C/N} = 1.3\text{--}1.4$ (figure 8b), during Test 2. OKABE [7] obtained similar rates for lower C/N . This result can be explained by a very small biofilm thickness, below active thickness [14], and hydraulic conditions [12].

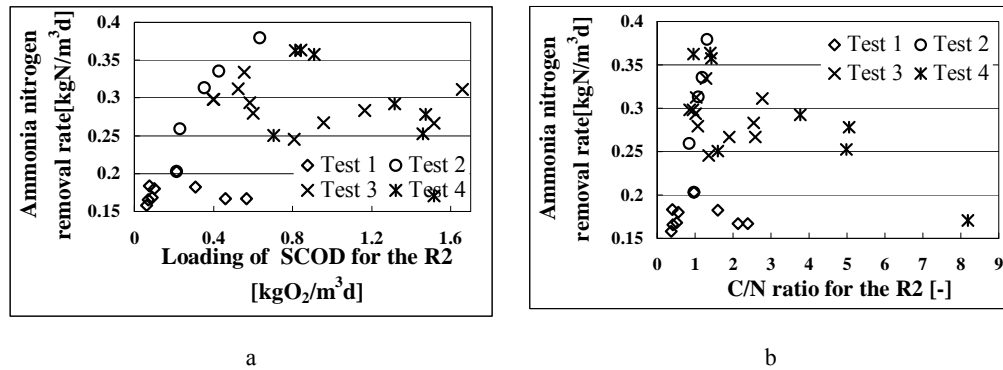


Fig. 8. Relationship between SCOD loading and ammonia nitrogen removal rate in R2 (a). Relationship between C/N ratio and ammonia nitrogen removal rate in R2 (b)

It was worth noting that an increase in the rate of total nitrogen removal was observed at an organic loading above 0.6 kg O₂/m³d and C/N ratio above 1.5 (figure 9). The rate of ammonia nitrogen removal and the efficiency of this process in both reactors were similarly dependent on loading, but underwent changes over time (figures 7 and 8). This resulted from the differences in reactor loading, which caused a dissimilar rate of biofilm development. Despite this, during Test 4 both reactors reached a similar rate of oxidized nitrogen production (table 3). This proves that a similar nitrifier layer expand in both reactors. The efficiency of biodegradation of organic compounds in the first oxygen reactor R2 was larger than that in R4. It was obtained for 1.3 kg O₂/m³d and increased proportionally to the loading (tables 2 and 3).

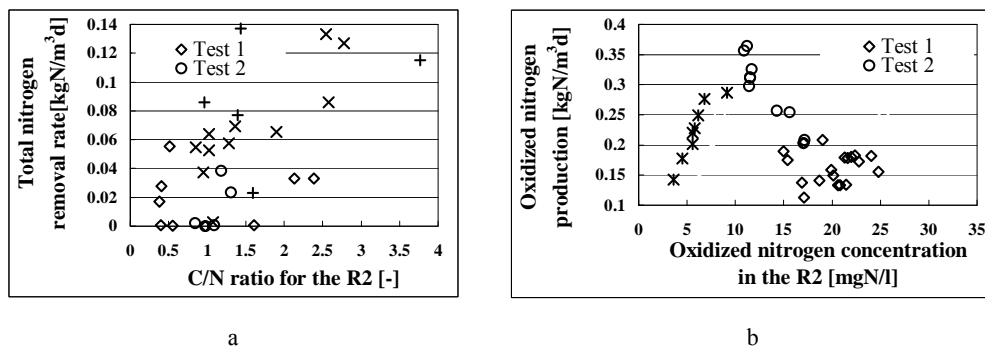


Fig. 9. Influence of C/N ratio on total nitrogen removal rate in R2 (a). Dependence of oxidized nitrogen transformation rate on oxidized nitrogen concentration in R2 (b)

Table 3

Table 4

5. CONCLUSIONS

1. The production rate of oxidized nitrogen compounds in nitrifying reactors with biomass attached to the Kaldnes carriers in cascade system with two-stage denitrification and step-feeding reached $0.41 \text{ kg N-NO}_x^-/\text{m}^3\text{d}$, on average $0.23 \text{ kg N-NO}_x^-/\text{m}^3\text{d}$.

2. Nitrification efficiency exceeding 80% and ammonia nitrogen concentration below 2 g N-NH_4^+ were obtained for ammonia nitrogen loading to about $0.36 \text{ kg N-NH}_4^+/\text{m}^3\text{d}$ and organic carbon loading to $1.5 \text{ kg O}_2/\text{m}^3\text{d}$. This relation proves that the nitrification is the first-order process limited by a shortage of ammonia nitrogen compounds. Linear dependence of ammonia nitrogen loading upon its removal rate under these conditions allows an easy prediction of nitrification effects.

3. For an ammonia nitrogen loading of above $0.36 \text{ kg N-NH}_4^+/\text{m}^3\text{d}$ there is no further increase in the rate of ammonia nitrogen removal, a decrease in nitrification efficiency as well as a linear dependence of ammonia nitrogen concentration in effluent upon its removal efficiency. In this case, nitrification is the zero-order process in terms of ammonia nitrogen and is limited by a lack of oxygen.

4. The C/N ratio, (organic carbon loading (SCOD) to ammonia nitrogen loading ratio) is not a sufficient parameter to predict the efficiency of nitrification process and concentration of ammonia nitrogen in effluent.

5. Insignificant simultaneous denitrification can be observed at organic carbon loading exceeding $0.6 \text{ kg O}_2/\text{m}^3\text{d}$ ($3 \text{ g O}_2/\text{m}^2\text{d}$) and C/N ratio from 1.5 to 4.

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ANALIZA NITRYFIKACJI W KASKADOWYM UKŁADZIE ZE ZŁOŻEM RUCHOMYM

Efektywność procesu usuwania azotu zależy od tego, w jakim stopniu i z jaką szybkością przebiega proces nityfikacji. W reaktorach z biomasą utwierdzoną istotną rolę odgrywają procesy transportu masy. Zasadniczym celem badań była ocena wydajności i efektywności procesu usuwania azotu w układzie kaskadowym z dwustopniową denityfikacją, stopniowym zasilaniem i zastosowaniem złoża ruchomego. Omówiono część wyników dotyczących procesu nityfikacji. Szybkość produkcji związków azotu utlenionego w badanym układzie osiągała $0.41 \text{ kg N-NO}_x^-/\text{m}^3\text{d}$ ($2 \text{ g N-NO}_x^-/\text{m}^2\text{d}$ i $0.53 \text{ g N-NO}_x^-/\text{g s.m.o.d}$). Efektywność nityfikacji przekraczała 80% dla obciążenia azotem amonowym do $0.3 \text{ kg N-NH}_4^+/\text{m}^3\text{d}$, dla większych obciążeń widoczny był stały spadek sprawności procesu.