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# NITRIFICATION ONTO A ROTATING ELECTRO-BIOLOGICAL CONTACTOR

*Joanna Rodziewicz, Urszula Filipkowska*

Department of Environmental Protection Engineering
University of Warmia and Mazury in Olsztyn

K e y w o r d s: electrolysis, nitrification, rotating electro-biological contactor.

A b s t r a c t

The goal of the conducted experiment was to determine the electric current impact on the efficiency of nitrogen compounds oxidation at COD to total Kjeldahl's nitrogen ratio of 20, 10, 5. The experiments were run in bench scale, in a rotating electro-biological contactor (REBC) under both, conventional conditions (i.e. without electric current) and with electric current passage at the following densities: 0.2 A $m^{-2}$, 0.8 A $m^{-2}$, and 1.5 A $m^{-2}$. The cathode comprised stainless steel discs with immobile biofilm, and the anode a stainless steel electrode, submerged in waste water contained in the flow-tank of the contactor. The process of nitrogen oxidation was the most effective with electric current passage at the density of 1.5 A $m^{-2}$ regardless of applied COD/NTK ratio.

## NITRYFIKACJA NA ELEKTROBIOLOGICZNYM ZŁOŻU TARCZOWYM

*Joanna Rodziewicz, Urszula Filipkowska*

Katedra Inżynierii Ochrony Środowiska
Uniwersytet Warmińsko-Mazurski w Olsztynie

S ł o w a k l u c z o w e: elektroliza, nitryfikacja, elektrobiologiczne złoże tarczowe (REBC).

A b s t r a k t

Celem doświadczenia było określenie wpływu przepływu prądu elektrycznego na sprawność utleniania związków azotu gdy stosunek ChZT do azotu ogólnego Kjeldahla wynosił 20, 10 i 5. Badania prowadzono w skali laboratoryjnej na elektrobiologicznym złożu tarczowym (REBC) gdy nie przepływał prąd elektryczny, oraz gdy przepływał prąd elektryczny o gęstości: 0,2 A $m^{-2}$, 0,8 A $m^{-2}$,

Address: Joanna Rodziewicz, University of Warmia and Mazury in Olsztyn, ul. Romana Prawocheńskiego 1, 10-957 Olsztyn, Poland, phone: +48 (89) 523 48 93, e-mail: joanna.rodziewicz@uwm.edu.pl

1,5 A $m^{-2}$. Katodą były tarcze ze stali nierdzewnej z unieruchomioną błoną biologiczną, anodą – elektroda ze stali nierdzewnej, zanurzona w ściekach komory przepływowej złoża. Najefektywniej proces utleniania azotu przebiegał gdy przepływał prąd elektryczny o gęstości 1,5 A $m^{-2}$, niezależnie od stosunku ChZT:NTK.

## Introduction

Biological nitrification and denitrification processes are employed to remove nitrogen from wastewater. Since the requirement for nutrient removal is becoming increasingly stringent, a high efficiency of nitrogen removal is necessary to achieve a low total nitrogen concentration in the effluent. Often, when nitrogen removal fails, it is due to poor nitrification.

Removal of ammonium by biological nitrification using activated sludge system is process that is widely used in the treatment of domestic and industrial wastewater. Nitrification is an obligate aerobic process and is carried out sequentially by ammonia and nitrite oxidizing groups of bacteria, such as *Nitrosomonas* and Nitrobacter nitrifying microorganisms. The nitrifying bacteria are sensitive to changes in temperature, pH, substrate and product concentrations affecting the rate process. Unfortunately, the kinetic of nitrification is slower and more susceptible to environmental conditions than organic matter oxidation by heterotrophs. Generally, simultaneous growth of nitrifiers and heterotrophs in a single reactor leads to low nitrification specific rates due to overwhelming action of heterotrophs, when treating municipal and industrial wastewaters with a high C:N ratio (BERISTAIN-CARDOSO et al. 2009).

The low growth rate of nitrifying bacteria and the relatively poor capacity of activated sludge units to retain nitrifying biomass require large settlers. The most common problem is the apparition of wash out (CAMPOS et al. 2007). For these reasons the activated sludge units can not treat high nitrogen loadings rates. One of the cheapest ways to improve the sludge retention time in immobilization.

As compared with the activated sludge systems, the reactors with immobilized biomass are characterized by a higher concentration of biomass in the reactor, a higher surface area for the biological development of microorganisms, higher hydraulic loads, better stability of treatment, higher rates of pollutants removal, and lower susceptibility to toxic substances (LI et al. 2003, WILDERER 1995). What is more, low investment costs enable carrying out an economical and advanced process of pollutions disposal (BRINKE-SEIFERTH 1999). Microorganisms gain the maximum rate of growth, which in turn facilitates their physiological adaptation and makes the biofilm resistant to rapid changes of the hydraulic load (WOOLARD 1997). In addition, immobiliz-

ation prevents the washing out of slowly-growing nitrifying bacteria that are retained on the carrier irrespective of the hydraulic retention time (LINDEMANN and WIESMANN 2000, TIJHUIS et al. 1995).

The rotating biological contactor (RBC) is an attached growth bioreactor that offers an alternative technology to the conventional activated sludge process. Rotating biological contactors constitute a very unique and superior alternative for biodegradable matter and nitrogen removal on account of their feasibility, simplicity of design and operation, short start-up, low land area requirement, low energy consumption, low operating and maintenance cost and treatment efficiency. More often RBCs have been successfully used to nitrify municipal wastewater and oxide carbon compounds (CORTEZ et al. 2008).

An increasing load of data is being published that point to the possibility of enhancing the nitrification – denitrification processes as a result of electrolytic excitation. The essence of that method is running the processes in an electric field. Thus, the microbial activity is to be facilitated by hydrogen and oxygen produced onto a cathode and anode, respectively (BESCHKOV et al. 2004).

KRZEMIENIEWSKI and RODZIEWICZ (2005) as well as RODZIEWICZ et al. (2011) carried out a study aimed at combining electrochemical processes induced during the passage of electric current in sewage medium with biological processes proceeding on a rotating biological contactor. Technological design of the experiment assumed that the process of nitrogen elimination would occur during electric current passage, since gaseous hydrogen is produced on the cathode's surface during water hydrolysis which is then used as a source of electron donor by autotrophic bacteria in the denitrification process. In the system discussed, processes of nitrification and denitrification proceeded simultaneously owing to the formation of aerobic and anoxic areas. The anoxic medium was generated in deeper areas of the aerobic biofilm due to limited penetration of oxygen.

Even at low DO concentration in the solution, the nitrification rate is very high due to the use of oxygen generated on the anode. Denitrification rate is relatively high at high DO concentrations due to the application of gaseous hydrogen on the inner side of the cathode-biofilm. A higher rate of total nitrogen removal is achieved at lower DO concentrations and higher densities of an electric current. On this ground, one can conclude that the bio-electrochemical process can be applied in nitrification/denitrification due to the creation of stable aerobic and anoxic regions in a single reactor and that it is beneficial compared to the processes carried out separately, because of the reduction of reactor volume and time (WATANABE et al. 2002). Anoxic conditions in the cathode-biofilm are created as a result of DO use along with the use of hydrogen by the aerobic microorganisms not participating in denitrification.

## Materials and Methods

### Characteristics of waste waters

Experiments were carried out in Weinberger model wastewaters (*Woda i ścieki*... PN-87/C-04616/10). The inflowing and treated wastewaters were determined for the following indicators of contamination: concentration of total nitrogen – with the Kjeldahl's method; concentration of ammonia nitrogen – with the colorimetric method; concentration of nitrate nitrogen III and nitrite nitrogen V – with the colorimetric method, chemical oxygen demand – COD; reaction, and temperature of wastewaters and environment – according to the Polish Standard Methods.

Parameters of oxidation of nitrogen compounds by biofilm were determined using computational formulas presented in the work of KRZEMIENIEWSKI and RODZIEWICZ (2005).

## Research station

Investigations were carried out in a rotating biological contactor (RBC) working in a bench scale (Figure 1). The contactor consisted of four sections. Each section was made of packets of disks mounted coaxially on a horizontal shaft 0.42 m in length. Each packet contained eight disks 0.22 m in diameter each. The disks were made of stainless steel. Each section was fixed in a half-round container with a volume of 2 $dm^3$. The disks rotated with the speed of 60 rpm by means of an electric motor.

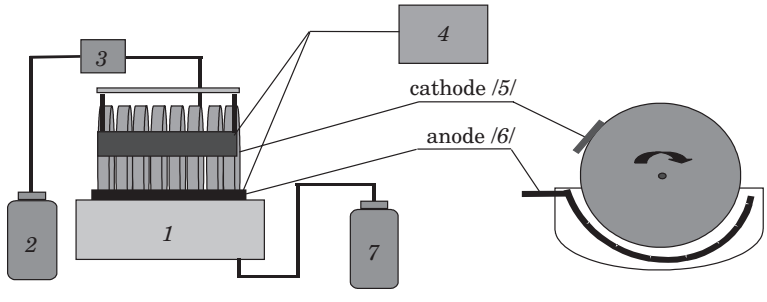



Fig. 1 The scheme of an experimental post: *1* – rotating biological contactor, *2* – tank with untreated waste water, *3* – peristaltic pump, *4* – electric current source, *5* – cathode, *6* – anode, *7* – tank with treated waste water

### Design of kinetic analyses

Kinetic analyses were carried out at COD to total Kjeldahl's nitrogen ratio of 20, 10, 5 and were used as a basis for determining the kinetics of nitrogen compounds oxidation depending on density of the flowing electric current. Samples to be analyzed were collected from a tank of biological contactor in 2.0 h intervals for 10 h, and the last sample was collected after 24 h.

Likewise technological experiments, the kinetic assays were conducted under the flow of electric current with the following densities: 0.0 A $m^{-2}$, 0.2 A $m^{-2}$, 0.8 A $m^{-2}$, and 1.5 A $m^{-2}$.

Results of the kinetic analyses were used to determine reaction order, rate of ammonia nitrogen oxidation. Experimental results obtained were a backbone for formulating a model that was used for the approximation of measuring points of changes in concentrations of oxidized nitrogen.

The rate of ammonia nitrogen oxidation was described by the following equations:

$$C_{\mathrm{Nox}}{}^{t} = (\mathrm{k_{Nox}} \cdot t) + C_{\mathrm{Nox}}{}^{i} \tag{1}$$

where:

$C_{\mathrm{Nox}}{}^{t}$ – concentration of oxidized nitrogen after time $t$ [mg N $L^{-1}$],
$\mathrm{k_{Nox}}$ – constant of the rate of ammonia nitrogen oxidation [mg $L^{-1}$ $h^{-1}$],
$C_{\mathrm{Nox}}{}^{i}$ – initial concentration of oxidized nitrogen [mg N $L^{-1}$].

$$C_{\mathrm{Nox}}{}^{t} = C_{\mathrm{Nox}}{}^{i} \cdot (1 - e^{-k_{Nox} \cdot t}) \tag{2}$$

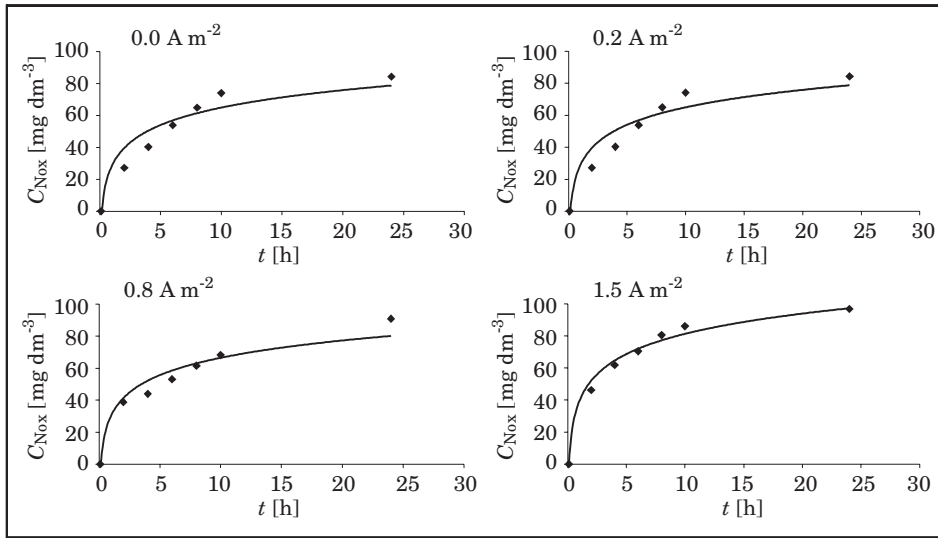
$C_{\mathrm{Nox}}{}^{t}$ – concentration of oxidized nitrogen in the contractor after time $t$ [mg N $L^{-1}$],
$C_{\mathrm{Nox}}{}^{i}$ – initial concentration of oxidized nitrogen [mg N $L^{-1}$],
$\mathrm{k_{Nox}}$ – constant of the rate of ammonia nitrogen oxidation [$h^{-1}$].

Reaction rate constants were determined based on experimental data with the method of non-linear regression using STATISTICA software.

## Results and Discussion

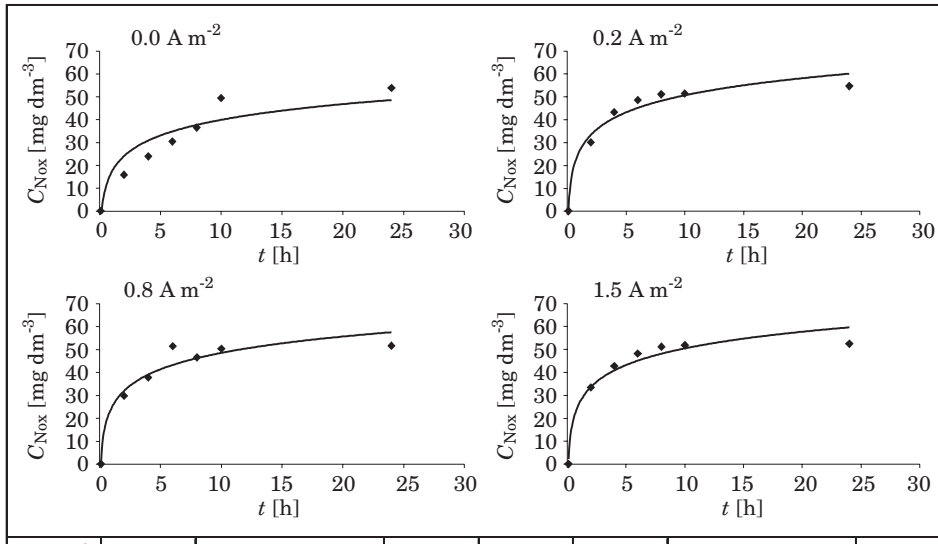
The rate of nitrification was computed based on changes in the concentration of oxidized ammonia nitrogen in the biological contractor at 24-h time of sewage retention.

In all systems, changes in the concentration of oxidized ammonia nitrogen proceeded following the first order reaction.




| $J$ [A m$^{-2}$] | k [h$^{-1}$] | $r$ [mg dm$^{-3}$ h] | $R^2$ | $J$ [A m$^{-2}$] | k [h$^{-1}$] | $r$ [mg dm$^{-3}$ h] | $R^2$ |
|---|---|---|---|---|---|---|---|
| 0.0 | 0.17 | 86.70 | 0.99 | 0.8 | 0.25 | 93.09 | 0.95 |
| 0.2 | 0.17 | 88.35 | 0.99 | 1.5 | 0.27 | 94.86 | 0.99 |

Fig. 2. Changes in the concentration of oxidized ammonia nitrogen ($C_{Nox}$) in time at COD:NTK = 5.0 (the table provides values of rate constant k, initial rate $r$ and conformity coefficient $R^2$)



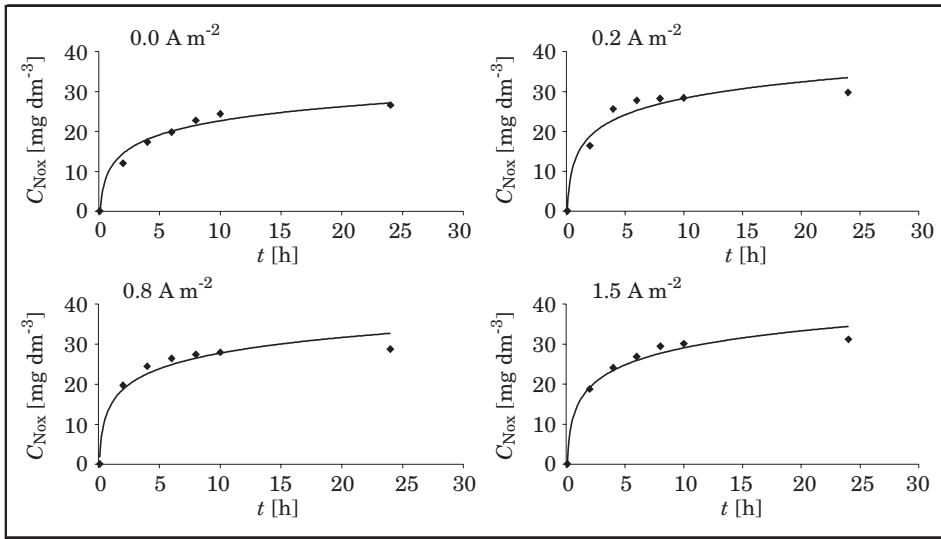

| $J$ [A m$^{-2}$] | k [h$^{-1}$] | $r$ [mg dm$^{-3}$ h] | $R^2$ | $J$ [A m$^{-2}$] | k [h$^{-1}$] | $r$ [mg dm$^{-3}$ h] | $R^2$ |
|---|---|---|---|---|---|---|---|
| 0.0 | 0.23 | 51.24 | 0.97 | 0.8 | 0.41 | 53.44 | 0.98 |
| 0.2 | 0.41 | 51.96 | 0.99 | 1.5 | 0.48 | 56.86 | 0.99 |

Fig. 3. Changes in the concentration of oxidized ammonia nitrogen ($C_{Nox}$) in time at COD:NTK = 10.0 (the table provides values of rate constant k, initial rate $r$ and conformity coefficient $R^2$)

At COD:NTK = 5, the highest value of the constant of ammonia nitrogen oxidation rate k equal to 0.27 $h^{-1}$ was obtained at the flow of electric current with density of 1.5 A $m^{-2}$ (Figure 2). In turn, the lowest oxidation rate constant (0.17) was reported in the conventional system and at the flow of electric current with density of 0.2 A $m^{-2}$. Under conditions of the flow of electric current with density of 0.8 A $m^{-2}$ the value of constant k accounted for 0.25.

At COD:NTK = 10, the highest value of the constant of ammonia nitrogen oxidation rate k equal to 0.48 $h^{-1}$ was obtained at the flow of electric current with density of 1.5 A $m^{-2}$ (Figure 3). In turn, the lowest oxidation rate constant (0.23) was reported in the conventional system. Under conditions of the flow of electric current with densities of 0.2 A $m^{-2}$ and 1.5 A $m^{-2}$ the values of constant k accounted for 0.41.

At COD:NTK = 20, the highest value of the constant of ammonia nitrogen oxidation rate k equal to 0.58 $h^{-1}$ was obtained at the flow of electric current with density of 0.8 A $m^{-2}$ (Figure 4). In turn, the lowest oxidation rate constant (0.27) was reported in the conventional system. Under conditions of the flow of electric current with densities of 0.2 A $m^{-2}$ and 1.5 A $m^{-2}$ the values of constant k accounted for 0.44 and 0.43, respectively.




| $J$ [A $m^{-2}$] | k [$h^{-1}$] | $r$ [mg $dm^{-3}$ h] | $R^2$ | $J$ [A $m^{-2}$] | k [$h^{-1}$] | $r$ [mg $dm^{-3}$ h] | $R^2$ |
|---|---|---|---|---|---|---|---|
| 0.0 | 0.27 | 26.14 | 0.99 | 0.8 | 0.58 | 29.46 | 0.99 |
| 0.2 | 0.44 | 27.93 | 0.99 | 1.5 | 0.47 | 30.37 | 0.99 |

Fig. 4. Changes in the concentration of oxidized ammonia nitrogen ($C_{Nox}$) in time at COD:NTK = 20.0 (the table provides values of rate constant k, initial rate $r$ and conformity coefficient $R^2$)

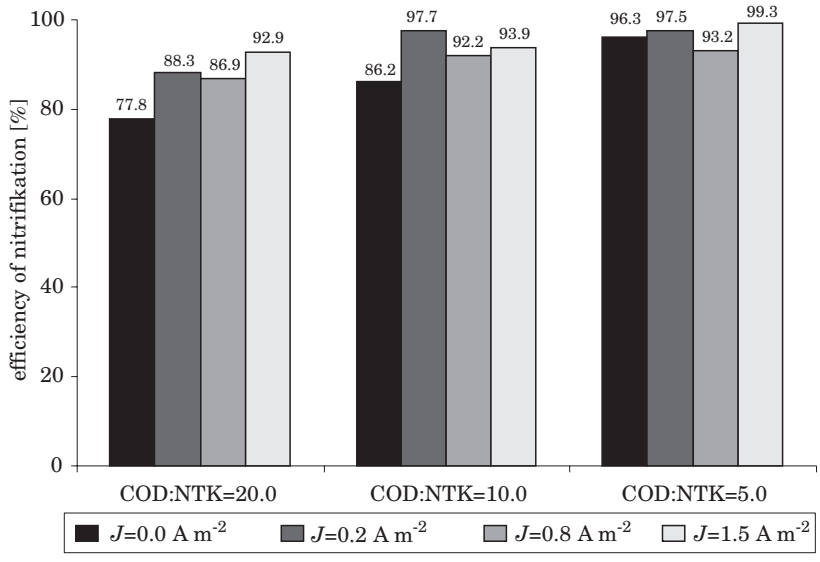



Fig. 5 Efficiency of nitrification onto a rotating electro-biological contactor

In the reported experiment efficiency of nitrification depended on the applied COD:NTK ratio and the flow of electric current. The highest efficiency of nitrification (99.3%) was obtained under conditions of the flow of electric current with density of 1.5 A $m^{-2}$ and at COD:NTK = 5. The lowest efficiency of nitrification, i.e. 77.8%, was observed under conventional conditions and at COD:NTK = 20.

One of more important parameters that determine the efficiency of ammonia nitrogen oxidation is biomass load with organic contaminants. A number of authors point to a dependency of nitrification efficiency on the concentration of biomass immobilized in the reactor. Once investigating nitrifying biomass colonizing pieces of chalk in a fluidized bed, GREEN et al. (2001) reported a higher rate of ammonia nitrogen oxidation at a higher biomass concentration. The higher concentration of biomass restricts diffusion. In turn, HEM et al. (1994) analyzed the effect of organic matter on nitrification efficiency and demonstrated that at a load over 5 g $BOD_7$ $m^{-2}$ $d^{-1}$ the rate of nitrification decreases to values close to zero. At the load ranging from 2 to 3 g $BOD_7$ $m^{-2}$ $d^{-1}$the rate of ammonia nitrogen oxidation fluctuates between 0.3 to 0.8 g N-$NO_x$$m^{-2}$ $d^{-1}$. The results of PATUREAU et al. (1997) showed that the inhibition of nitrifying microorganism activity could be caused by higher organic compound levels in environment. Alike results were reported by PASTORELLI et al. (1997a, 1997b) as well as RUSTEN et al. (1994). According to the authors, the decreasing rate

of ammonia nitrogen oxidation upon the increasing load of organic contaminants is linked with excessive growth of aerobic heterotrophic microorganisms, which results in diminished percentage of nitrifiers in the biomass. The effect of the C:N ratio in sewage on spatial distribution of nitrifiers and heterotrophs in a biofilm was the subject of research of numerous authors (GIESEKE et al. 2001, GIESEKE et al. 2002, OHASI et al. 1995, OKABE et al. 1996, SATOH et al. 2000, VAN LOOSDRECHT et al. 1995). They demonstrated that increasing the C:N ratio in the inflowing sewage leads to the competition for oxygen and ammonia nitrogen between nitrifying and heterotrophic bacteria, which in turn evokes a decrease in the percentage of nitrifiers in the outer aerobic layer of the nitrifying membrane. According to ITOKOWA et al. (2001) nitrate accumulation, lack of ammonium in the effluent and high rate of nitrification were observed when C:N ratio in waste was 2.4 and 3.5.

ØDEGAARD (2000) and ØDEGAARD et al. (1999), who studied changes in a reactor with biomass immobilized on plastic carriers being in motion, demonstrated that at the load higher than 4 g $BOD_7$ $m^{-2}$ $d^{-1}$ the nitrification process required high oxygen concentration, i.e. over 6 mg $O_2$ $L^{-1}$.

The reported experiment was carried out at the COD:NTK ratio of 20 which corresponds to organic contaminants load of 7.0 g COD $m^{-2}$ $d^{-1}$. Similar loading with organic contaminants was applied by KARNCHANAWONG and POLPRASER (1990) in a circulating reactor with immobilized biomass. The COD load used by those authors ranged from 3.56 to 10.16 g $m^{-2}$ $d^{-1}$. The highest efficiency was obtained at the load of 5 g COD $m^{-2}$ $d^{-1}$.

In our study, the flow of electric current turned out to affect both the rate and efficiency of nitrogen compounds removal. Under conventional conditions, the efficiency of nitrification appeared to be the lowest. The application of electric current and increasing its density led to an increase in the efficiency of nitrogen compounds oxidation, which might have been due to the utilization of oxygen generated on the anode by the nitrifiers (VAN LOOSDRECHT et al. 1995).

## Conclusions

In the conducted experiment, the passage of electric current was observed to affect the effectiveness of nitrification and the rate of nitrogen compounds oxidation depending on the value of the COD:NTK ratio applied.

At the high loading of biomass with organic compounds (COD:NTK = 20), the application of an electric current was resulting in an increase in nitrification effectiveness. Under conventional conditions the effectiveness of nitrogen compounds oxidation accounted for 77.8%, whereas under the flow of an electric current with a density of 1.5 A $m^{-2}$ – for nearly 93%.

At COD:NTK = 5 the effectiveness of nitrogen compounds oxidation was similar in all treatment systems.

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