Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.893842

54 (2015) 1903–1911
May

Taylor & Francis
Taylor & Francis Group

Removal of nitrates from processing wastewater by cryoconcentration combined with biological denitrification

Roman Marecik[a], Radosław Dembczyński[a], Wojciech Juzwa[a], Łukasz Chrzanowski[b], Paweł Cyplik[a,*]

[a]*Department of Biotechnology and Food Microbiology, Poznań University of Life Sciences, Wojska Polskiego 48, 60-627 Poznań, Poland Tel. +48 61 8466025; Fax: +48 61 8466003; email: pcyplik@wp.pl*
[b]*Institute of Chemical Technology and Engineering, Poznań University of Technology, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland*

Received 6 July 2013; Accepted 8 February 2014

ABSTRACT

In this study, the treatment of wastewater with a high nitrate content was investigated using the method of cryoconcentration on a pilot scale. The initial nitrate concentration in the treated wastewater was at 1,500 mg N/l. During 40 h of cryoconcentration of the wastewater, 176.6 kg of ice was produced, corresponding to a total process efficiency of 4.42 kg/h of ice. The crystallization temperature decreased from −0.5 to −9°C during the process. The final concentration of nitrates in the concentrated product was at 37 g N/l, and the conductivity was at 158 mS/cm. The conductivity of the water obtained by melting the ice ranged from 0.98 to 1.4 mS/cm. Concentrates with initial nitrate concentrations of 3, 6, and 9 g N/l were then subjected to microbial denitrification. The values of the specific nitrate reduction rates ranged from 43.1 to 49 mg N/gVSS h.

Keywords: Cryoconcentration; Denitrification; Nitrates

1. Introduction

The emission of nitrogen compounds into the environment results in the phenomenon of eutrophication and contributes to a reduction in ecosystem biodiversity. Hence, groundwater is contaminated and human and animal health is put directly at risk. Nitrates contained in potable water and food (vegetables and fruits) may cause methemoglobinemia, dysfunction of the thyroid gland and nervous system and may also be transformed into carcinogenic nitrosamines [1]. The methods for removal of nitrates from potable water and wastewater are based on physicochemical processes, such as ion exchange [2] and membrane processes [3], or biological processes. Microbial denitrification is a respiratory process, during which nitrates act as the final electron acceptors in the respiratory chain. Under anaerobic conditions, the nitrates are reduced to elementary nitrogen. An electron donor is required as a source of energy for the microorganisms. For this purpose, organic compounds such as methanol, ethanol, or acetic acid are often used [4,5].

Technological solutions combining physicochemical and biological methods are also used for removal of nitrates, for example, a combination of ion exchange with biological denitrification of post-regeneration brine [6]. Such processes in many cases demonstrate greater efficiency and effectiveness than single

*Corresponding author.

processes. The development of wastewater treatment technology based on modern separation methods and the introduction of new biological reactors enable reduction in the emission of contaminants to the environment and may even generate waste-free systems [7]. The above-mentioned methods of nitrate removal are those most frequently used for potable water purification or treatment of municipal wastewater. However, industrial wastewater with a very high concentration of nitrates (derived from the production of nitroglycerin, nitroglycol, or fuel additives) poses a problem [8]. The concentration of nitrates in that waste often exceeds 1,500 mg N/l.

The use of the above-mentioned methods for purification of solutions with high nitrate content is often unprofitable (ion exchange) or difficult without adding other substances to the wastewater (biological denitrification).

The cryoconcentration method used in this study is based on the differences between the solidification temperatures of particular solution components. Cryoconcentration, also called crystallization by frost, is a concentration method, which is based on the differences in the freezing points of the components present in a given solution. As a result of cooling the mixture (loss of heat energy), one of the components is frozen, and then, the crystals can be separated and removed from the solution. As a result, the concentration of the remaining components is increased. Water is the most commonly removed component, although this method may also be used for separation of organic compounds. In the first stage of the process, the mixture is cooled to the temperature close to the freezing point value, and then, it is placed in the crystallization chamber. Upon further cooling, the nucleating agents begin to appear in the crystallization chamber, followed by ice crystals, which are then pumped along with the concentrate to the ice separator. The ice separator is typically in a form of a column equipped with a periodically moving piston sieve, which separates the ice from the concentrate. The key concept is to properly wash off the concentrate from the ice. In order to achieve this, some of the ice is melted, and the emerging water is used as a counter current to flush the ice accumulated in the -column. Relatively low amounts of water are needed to carry out this process. The remaining amount of water obtained from the melting of ice is then removed from the cryoconcentration unit [9]. This method is used on a commercial scale for the separation of some organic compounds, such as xylene isomers [10]. It is also used to concentrate sugars, fruit juice, coffee extracts, milk, and whey [11]. Cryoconcentration has also been proposed to facilitate the processes of water desalination and wastewater treatment [12,13].

In the present study, a method of treatment of wastewater with a high content of nitrates is demonstrated, consisting of concentration (cryoconcentration) which generates water and wastewater concentrate, which may be further subjected to microbial denitrification.

2. Material and methods

2.1. Characteristics of wastewater

The nitrate processing wastewater was collected from a Polish explosives production plant. The determined composition of treated wastes was as follows: 1,500 mg N/l, 48 mg/l chlorides, and 720 mg/l sulfates.

2.2. Cryoconcentration of wastewater

Cryoconcentrator Pilot Plant FTC-ISF Freeze Tec (Raamsdonksveer, The Netherlands) was used for wastewater treatment. The device consists of two basic elements: the ice crystallizer and the mechanical washing column (separating column), where separation of the concentrated wastewater from ice takes place (Fig. 1) during the operation of a piston equipped with a sieve. Further upward piston movement results in the compression of the ice crystals and formation of the ice bed. Ice from the upper part of the ice bed is melted and the obtained water is partially used to rinse the concentrate residues off the ice bed; the residual water is continuously discharged outside the installation. The length of the ice bed in the separating column should be constant as a result of the continuous accumulation of ice in the lower part of

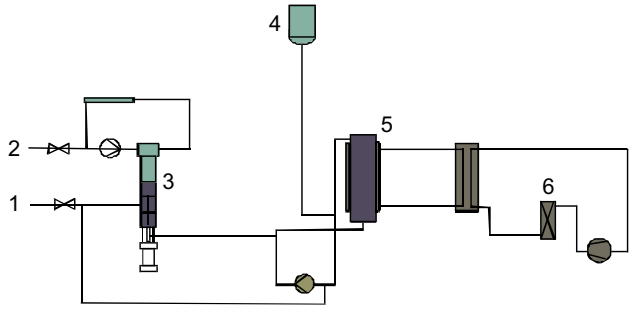

Fig. 1. Diagram of the cryoconcentration system with indirect heat exchange. 1—concentrate, 2—water, 3—mechanical washing column (separating column), 4—feed tank, 5—ice crystallizer, 6—cooling systems.

the column. The concentrated wastewater and purified water (derived from melted ice) are physically separated by the ice bed. Thus, the two liquids do not mix with each other. Therefore, uninterrupted operation of the cryoconcentrator relies on the formation of an ice bed of a stable length in the washing column, whereas maintaining the ice bed at a constant size depends on the efficiency of ice formation in the crystallizer. The velocity of ice crystallization is inversely proportional to the concentration of the concentrated wastewater.

2.3. Microorganisms

Research on concentrate denitrification involving microorganisms isolated from the Carpathian Mountains in Poland has been reported. It revealed a consortium consisting of seven bacterial species, with the closest match to species such as *Pseudomonas stutzeri*, *Alcaligenes xylosoxidans*, *Sphingobacterium* sp., *Comamonadaceae* bacterium, *Citrobacter freundii*, *Sphingobacterium kitahiroshimense* and *Pseudomonas* sp., which were identified by restriction fragment length polymorphism of 16S rRNA gene amplicons and sequencing (Fig. 2). The procedures for isolation and the method of genetic identification were described by Cyplik et al. [14].

2.4. Concentrate denitrification

Denitrification of the concentrate was performed in a BioFlo III bioreactor (New Brunswick Scientific, USA) with a working volume of 5.l, equipped with a pH probe (Ingold). The stirring element was a Rushton turbine-type agitator. The bioreactor tank was filled with 5.l of the wastewater (concentrate). The conditions of the process were as follows: temperature = 22˚C, pH 9.0, and agitation speed = 100 rpm.

2.5. Composition of denitrified wastewater

The wastewater from the first stage of cryoconcentration was subjected to the process of microbial denitrification. Because of the unbalanced composition of the wastewater, the following substances, required to support the denitrifying microorganisms, were added (g/l): KH_2PO_4 2.8, NaCl 0.5, NH_4Cl 1.0, $MgSO_4 \times 7H_2O$ 0.01, $FeSO_4 \times 7H_2O$ 0.001, $MnSO_4 \times 4H_2O$ 0.0005, $ZnCl_2$ 0.00064, $CaCl_2 \times 6H_2O$ 0.0001, $BaCl_2$ 0.00006, $CoSO_4 \times 7H_2O$ 0.000036, $CuSO_4 \times 5H_2O$ 0.000036, H_3BO_3 0.00065, H_2MoO_4 0.005, EDTA 0.001, and HCl 37% 0.0146 ml/l. The carbon source was crude glycerol from biodiesel production (C/N = 3).

2.6. Analytical methods

Determination of nitrate in the brine was conducted with the aid of spectrophotometry ($\lambda = 410$ nm) via reaction with sodium salicylate. Nitrites were also determined with the use of spectrophotometry ($\lambda = 410$ nm) via reaction with sulfanilic acid and 1-naphthylamine (Specord 40, Jena Analytic, Germany) [15]. Conductivity was assessed with the use of a conductometer CP-104 (Elmetron, Poland). Volatile suspended solids were determined using a standard method.

2.7. Denitrification kinetics

The specific nitrate reduction rate and specific zero-order denitrification rate were calculated according to a method described by Foglar et al. [16] and Dhamole et al. [17].

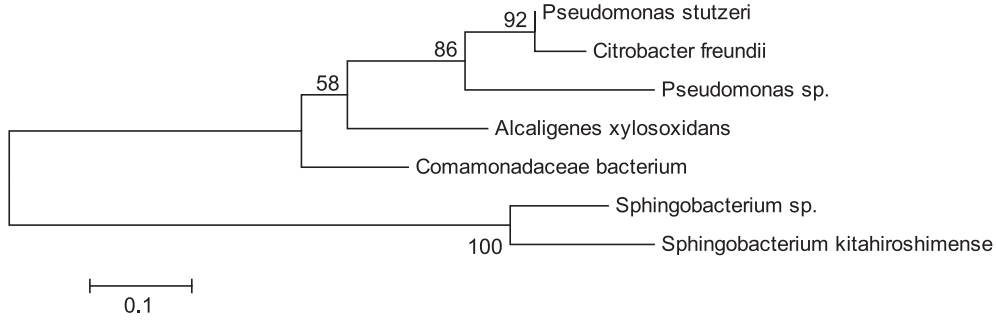

Fig. 2. Phylogenetic tree of the microorganisms involved in the denitrification process.

3. Results and discussion

3.1. Cryoconcentration of the wastewater—the course of the process

The cryoconcentration of the wastewater was conducted in three stages. Different concentrations of the feed solution were applied in each stage (namely 1,500, 9,000, and 27,000 mg N/l). As a result of the increase in concentration, the difference between the feed solution and the concentrate in the cryoconcentrator, the freezing of the washing column piston to the ice bed was more frequently observed. Hence, a given stage was terminated when keeping the operation of the washing column stable became difficult and the risk of destroying the ice bed was serious. The following stage was started with the concentration of the feed solution comparable to the concentration of the concentrate in the previous stage.

3.1.1. Stage 1

Wastewater with a nitrate content of 1,500 mg N/l was continuously gravitationally delivered to the crystallizer chamber from the feed tank placed at the top of the device. The start of the process consisted of initial liquid cooling of the whole system until ice circles were generated in the separating column, which formed the ice bed. At the beginning of cryoconcentrator operation, there is a risk of ice freezing to the crystallizer chamber, so the temperature of the crystallizer-cooling agent was maintained 5˚C below the crystallization temperature. In addition, the duration of the separation cycle (adjusted cycle time) was extended to 200 s in the separating column, which enabled generation of an appropriate amount of ice in the device in order to form the ice bed in the separating column (Table 1). The time required for the formation of the stable ice bed was 3 h. After that time, the product, in the form of purified water, was continuously produced. Maintaining stable operation of the device was essential for the continuity of the process, which ensured the constant formation of ice circles with a thickness of 50–60 mm (time of the separation cycle, adjusted cycle time: 20–40 s). In order to increase the efficiency of ice formation, the temperature of the crystallizer-cooling agent was reduced by 10˚C below the crystallization temperature. This parameter was automatically monitored. In addition, maintaining the appropriate temperature (3–4˚C) of the water used to rinse the ice in the mechanical (separating) column was important for stable operation of the device. Reduction in this temperature below 0˚C could cause freezing of the ice bed to the separating column piston, which could disrupt the operation of the installation due to fragmentation of the ice bed and mixing of the purified water with the wastewater concentrate.

Table 1
Wash column operating parameters

Parameter	Unit	
Adjusted cycle time	s	20–200
Adjusted compression time	s	10–20
Water temperature	˚C	3–4
Washwater pump delay time	s	20
Washfront conductivity	mS/cm	0.1–1.2

Initially, the ice circles formed in the column were 60 mm high, even and homogeneous, with no air spaces inside. After 2 h of operation of the device, nitrate-free water with a conductivity below 0.01 mS was obtained. During this stage, the crystallization temperature of the wastewater decreased from −0.5 to −0.9˚C. The process ran continuously without disruption for 23 h, and 110.3 kg of ice was obtained, which corresponds to an efficiency of 4.8 kg/h of ice (Fig. 3). A constant increase in the concentration of nitrates in the concentrate from the initial value of 1,500 to 9,000 mg N/l was observed, which resulted in an increase in the conductivity of the concentrate to 71.8 mS/cm (Fig. 4). The crystallization temperature decreased to −2.4˚C (Fig. 5).

3.1.2. Stage 2

In the 23rd h of nitrate concentration, phenomena disrupting the operation of the separating column (such as freezing of the separating column piston to the ice bed) prevented further stable operation of the installation. At the same time, the amount of ice being generated decreased, which was manifested in a reduction in the thickness of the ice circles formed to 9 mm. In order to maintain continuity of device operation, the nitrate content of the purified wastewater was increased to 9,000 mg N/l that is to the concentration obtained in the concentrate in the 23rd h. Because of this adjustment, the process ran without any further disruptions until the 36th h. At this time, a total of 156 kg of ice had been obtained; however, the efficiency of the entire process decreased to 4.3 kg/h of ice. This reduction resulted from the decrease in efficiency of the crystallization process during the second stage (efficiency: 3.15 kg/h of ice). During this stage, an increase in the efficiency of concentration was observed, manifesting itself in the increased conductivity of the concentrate to 145 mS/cm. A high concentration of

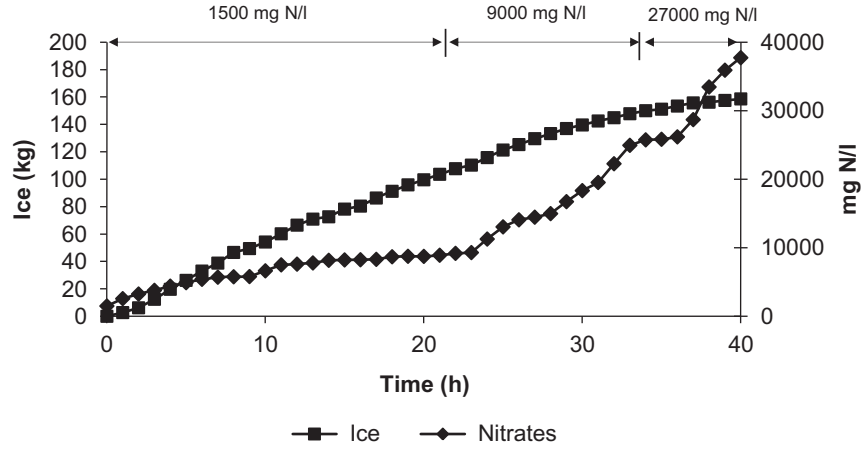

Fig. 3. Amount of ice produced and changes in the nitrate concentration in the concentrate during the process of cryoconcentration.

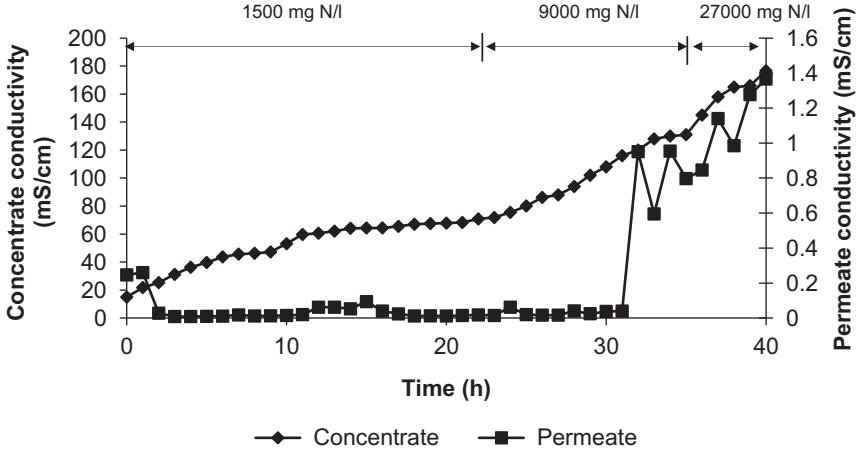

Fig. 4. Changes in the conductivity of the concentrate and water derived from melted ice during the process of cryoconcentration.

nitrates in the concentrate (26 g N/l) caused a decrease in water quality reflected by an increase in the conductivity of the water from the melted ice. In the 32nd h of the process, the conductivity of the purified water was 0.846 mS/cm, which corresponds to the conductivity of potable water. In the second stage of the process, the crystallization temperature decreased from −2.7 to −6.1 °C.

3.1.3. Stage 3

In the 37th h of the process, the nitrate concentration in the feed solution was once again increased, this time to 25 g N/l. The process ran for another 4 h when it was halted as a result of failure of ice generation. The technical parameters of the installation prevented enhancement of the efficiency of ice production by further decreasing the temperature of the ice crystallizer. The minimum temperature of the crystallizer achieved during nitrate concentration was −19 °C. Despite such a low temperature, the amount of ice generated was too low to maintain a stable length of ice bed; the ice bed was not tight and the concentrate permeated through cracks that appeared and mixed with the purified water. As of the 40th h of the process, 176.6 kg of ice had been obtained. Hence, the total efficiency of the process amounted to 4.42 kg/h of ice. The crystallization temperature had decreased to −9 °C. As a result of the concentration process, the final nitrate concentration in the concentrate amounted to 37 g N/h, and the conductivity of the concentrate was at 158 mS/cm. During this stage, the conductivity

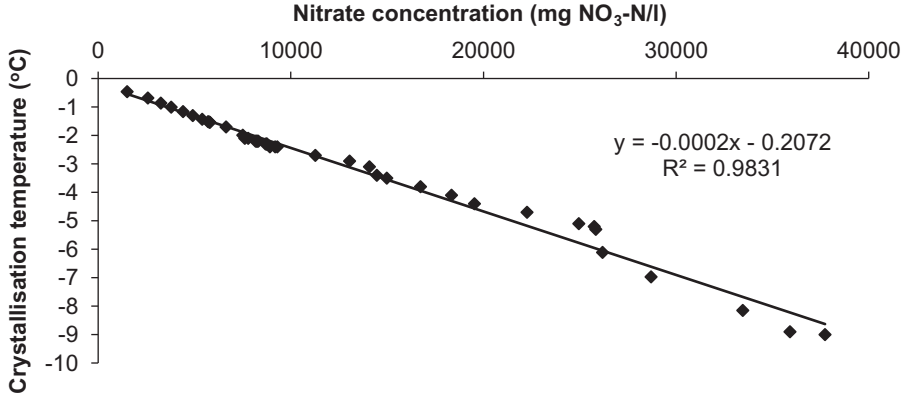

Fig. 5. Changes in the crystallization temperature, which depends on the nitrate concentration in the concentrate.

of the water obtained from the melted ice ranged from 0.98 to 1.4 mS/cm, which corresponded to nitrate concentrations of 25–32 mg N/l.

3.2. Microbial denitrification of the concentrate

The wastewater obtained during the first stage of cryoconcentration was subjected to microbial denitrification. Due to the high concentration of nitrates in the concentrate, the denitrifying microorganisms underwent an adaptation process that consisted of a gradual increase in nitrate concentration from 3 to 9 g N/l (Fig. 6). The acclimatization of microorganisms was based on the denitrification of wastewater with an initial concentration of nitrates equal to 3 g N/l. After the removal of nitrates, the wastewater was changed to fresh wastewater with a concentration of nitrates equal to 6 g N/l, and the biomass was maintained in the bioreactor. Analogically, the same steps were carried out for wastewater with a concentration of nitrates equal to 9 g N/l.

In all cases, an initial biomass concentration of 3 g VSS/l was used. During denitrification, a greater biomass increase and extension of the time required for the total reduction in nitrates, accompanying an increase in the initial concentration of nitrates in the wastewater, was observed. However, the calculated values of specific nitrate reduction rates were not significantly different and ranged from 43.1 to 49 mg N/ gVSS h (Table 2). On the other hand, a decrease in the value of the determined zero-order rate constant for nitrate reduction was clearly notable, caused by an increase in the initial concentration of nitrates in the wastewater and by the inhibiting influence of accumulated nitrites on the process of denitrification (Fig. 7). The accumulation was greatest during denitrification of the wastewater with the initial nitrate concentration at 9 g N/l and amounted to 4 g of nitrite N/l in the

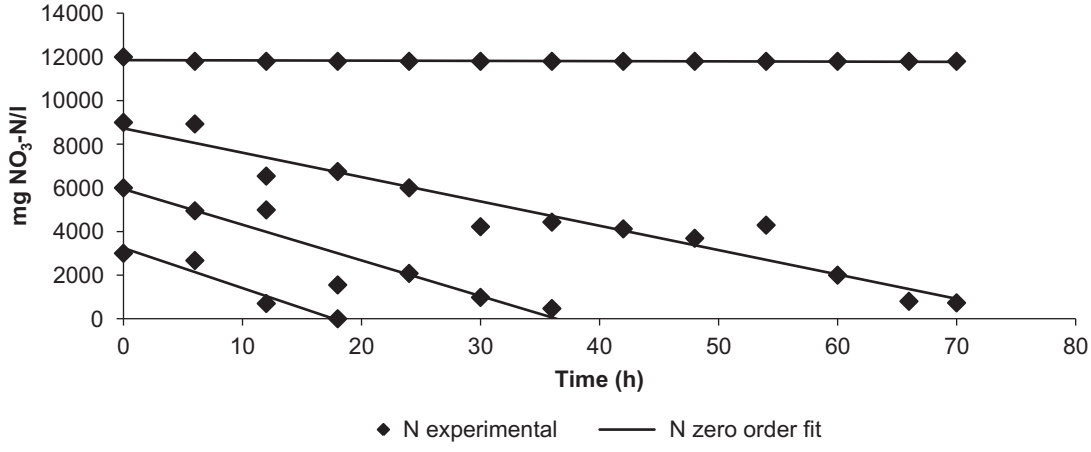

Fig. 6. Experimental and zero-order data fit for nitrate.

Table 2
Values of specific nitrate reduction rate, zero-order rate constant for nitrate reduction, zero-order rate constant for nitrite reduction, nitrate and biomass concentrations for the denitrification process

Parameter				
Initial nitrate concentration	mg N/l	3,000	6,000	9,000
Initial biomass concentration	gVSS/l	3	3	3
Finally biomass concentration	gVSS/l	4.9	8.1	11.4
Max. Nitrate concentration	mg N/l	1,185	2,920	4,000
Efficiency of nitrate removal	%	100	100	100
Specific nitrate reduction rate	mg N/g VSS h	43.1	49.0	44.6
Zero order rate constant for nitrate reduction	mg N/l h	170	159	113
Zero order rate constant for nitrite reduction	mg N/l h	148	133	119

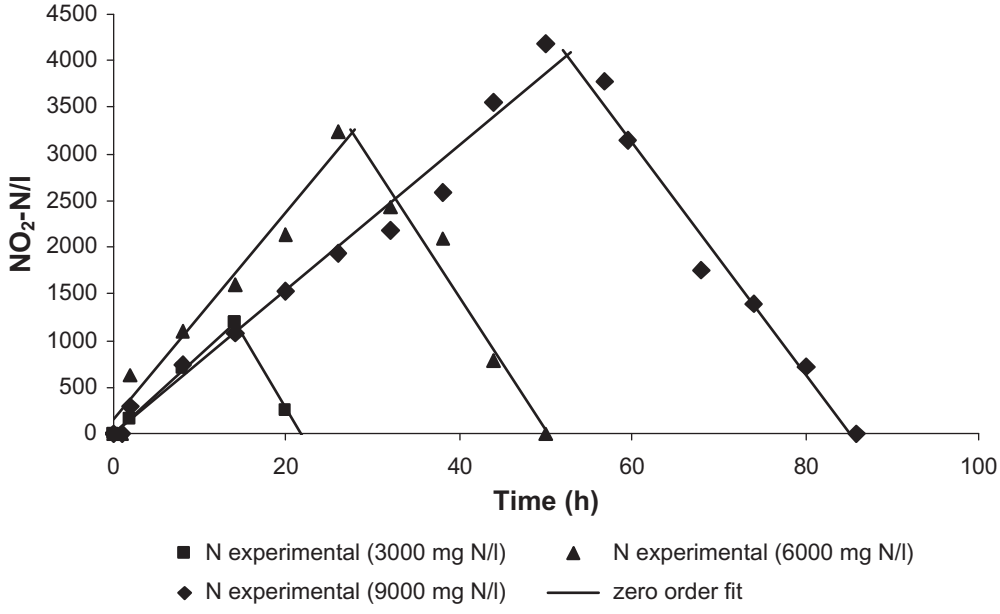

Fig. 7. Experimental and zero-order data fit for nitrite.

49th d of the process. The calculated zero-order rate constants for nitrite reduction were lower than those for nitrate reduction, which explains the growing concentration of nitrites in the wastewater. The increase in the initial nitrate concentration to 12 g N/l turned out to be toxic to the microorganisms and the process was inhibited.

4. Discussion

Previously, methods combining the process of ion exchange and microbial denitrification have been used for removal of nitrates from wastewater [18]. However, such a system has many flaws. It cannot be used for removal of nitrates from highly concentrated solutions because it causes premature column breakthrough of nitrate ions. Application of continuous systems required using at least 3 ion-exchange columns. Due to the use of 5–15% NaCl solutions for resin regeneration, an environmentally hazardous waste (brine) was produced. Apart from chlorides, it contained a high concentration of nitrates that undergo desorption from the ion-exchange column. Denitrification of such a waste using biological methods was difficult because of the high osmotic potential of the solution. In order to solve this problem, 2% NaCl was used as a regenerant. This solution enabled denitrification of the brine using the adapted activated sludge; however, it increased the amount of brine and extended the regeneration time [19]. Denitrification of

brines with higher NaCl concentrations (10–15%) was possible only through the use of halophilic microorganisms (archaeans); however, their specific nitrate reduction rates were low [20].

A solution based on the replacement of ion exchange by a cryoconcentrator enables high-quality water to be obtained from wastewater containing a high concentration of nitrates (1.5 g N/l). Despite relatively infrequent commercial use of cryoconcentration in wastewater management, the process has many merits in comparison with other methods. One of the most important is energy saving. Lower energy consumption during cryoconcentration (in comparison with, e.g. distillation) results from smaller demand for the latent heat of phase transition. In cryoconcentration, the amount of heat (so-called latent heat of crystallization) required to freeze water is only 334 J/g, whereas for evaporation of water the energy consumption increases to 2,257 J/g [21]. The use of cryoconcentration enables recovery of high-quality water and its reuse in a technological process. Such results were not obtained by using reverse osmosis. Purification of solutions containing 1,000 mg N/L via this method did not produce water of quality comparable to that produced via the process of cryoconcentration. The rejection of the membranes used for this purpose is a maximum of 96%. Hence, the concentration of nitrates in the permeate during the purification of wastewater from such solutions amounted to 150 mg N/l [22]. In the case of cryoconcentration of industrial wastewater, the concentrate obtained may also be recycled or incinerated. Moreover, in comparison with ion exchange, no post-recovery waste in the form of brine is produced and the process runs at a low temperature, which additionally protects the device against corrosion [23].

The effect of accumulated nitrites is important in determining the efficiency of the denitrification process [24]. According to previous research, it is ambiguous. Dhamole et al. [17], in their study on denitrification of industrial wastewater with a high content of nitrates (up to 9,000 mg N/l with pH 7.2), did not observe inhibition of the process by nitrites in spite of the fact that their maximum concentration was as high as 6,000 mg N/l. On the other hand, Glass et al. [25] found that the toxic influence of nitrites on activated sludge microorganisms depends on the pH of the wastewater. A concentration of nitrites above 2,000 mg N/l did not affect the process of nitrate reduction when the pH was 8.0. At pH 7.0, the inhibition of the denitrification process by nitrites occurred when 250 mg N/l was added. Specific nitrate reduction rates obtained for the process of concentrate denitrification were typical of denitrification of wastewater with a high concentration of nitrates and have been observed by many authors [16,17,26].

5. Conclusions

Cryoconcentration combined with microbial denitrification provides water free of any pollutants, and the concentrate produced during the process may be used according to requirements, for example for fertilizer production or be denitrified by microorganisms. The microorganisms, once adapted to high concentrations of nitrates, enable the total removal of nitrates from the concentrate.

Acknowledgements

Paweł Cyplik, Roman Marecik, and Łukasz Chrzanowski were financially supported by the Ministry of Science and Higher Education, Poland (Grant No. N N523 419837) years 2009–2012.

References

[1] B. Bottex, J.L.C.M. Dorne, D. Carlander, D. Benford, H. Przyrembel, C. Heppner, J. Kleiner, A. Cockburn, Riskebenefit health assessment of food. Food fortification and nitrate in vegetables, Trends Food Sci. Techol. 19 (2008) 109–115.
[2] Y. Berbar, M. Amara, H. Kerdjoudj, Anion exchange resin applied to a separation between nitrate and chloride ions in the presence of aqueous soluble polyelectrolyte, Desalination 223 (2008) 238–242.
[3] L.A. Richards, M. Vuachère, A.I. Schäfer, Impact of pH on the removal of fluoride, nitrate and boron by nanofiltration/reverse osmosis, Desalination 261 (2010) 331–337.
[4] K.A. Karanasios, I.A. Vasiliadou, S. Pavlou, D.V. Vayenas, Hydrogenotrophic denitrification of potable water: A review, J. Hazard. Mater. 180 (2010) 20–37.
[5] U. Sandhya, D. Banerjee, I.J. Singh, P.K. Wattal, Denitrification of high sodium nitrate bearing effluents using flow-through bioreactor, Desalin. Water Treat. 38 (2012) 52–58.
[6] S.G. Lehman, M. Badruzzaman, S. Adham, D.J. Roberts, D.A. Clifford, Perchlorate and nitrate treatment by ion exchange integrated with biological brine treatment, Water Res. 42 (2008) 969–976.
[7] P. Cyplik, K. Czaczyk, A. Piotrowska-Cyplik, R. Marecik, W. Grajek, Removal of nitrates from brine using *Haloferax mediterranei* archeon, Environ. Prot. Eng. 36 (2010) 5–16.
[8] A. Dario, M. Schroeder, G.S. Nyanhongo, G. Englmayer, G.M. Guebitz, Development of a biodegradable ethylene glycol dinitrate-based explosive, J. Hazard. Mater. 176 (2010) 125–130.
[9] J. Sánchez, E. Hernández, J.M. Auleda, M. Raventós, Freeze concentration of whey in a falling-film based pilot plant: Process and characterization, J. Food Eng. 103 (2011) 147–155.

[10] S. Holt, The role of freeze concentration in waste water disposal, Filtr. Sep. 36 (1999) 34–35.
[11] M. Aider, D. Halleux, Cryoconcentration technology in the bio-food industry: Principles and applications, LWT — Food Sci. Technol. 42 (2009) 679–685.
[12] M.S. Rahman, M. Ahmed, X.D. Chen, Freezingmelting process and desalination: Review of present status and future perospects, Int. J. Nucl. Desalin. 2 (2007) 253–264.
[13] S. Lemmer, R. Klomp, R. Ruemekorf, R. Scholz, Proconcentration of wastewater through the niro freeze concentration process, Chem. Eng. Technol. 24 (2011) 485–488.
[14] P. Cyplik, M.A. Schmidt, A. Szulc, R. Marecik, P. Lisiecki, H.J. Heipieper, M. Owsianiak, M. Vainshtein, Ł. Chrzanowski, Relative quantitative PCR to assess bacterial community dynamics during biodegradation of diesel and biodiesel fuels under various aeration conditions, Bioresour. Technol. 102 (2011) 4347–4352.
[15] W. Hermanowicz, Physicochemical Testing of Water and Sewage. Arkady, Poland, 1999
[16] L. Foglar, F. Briški, L. Sipos, M. Vuković, High nitrate removal from synthetic wastewater with the mixed bacterial culture, Bioresour. Technol. 96 (2005) 879–888.
[17] P.B. Dhamole, R.R. Nair, S.F. D'Souza, S.S. Lele, Denitrification of high strength nitrate waste, Bioresour. Technol. 98 (2007) 247–252.
[18] E.J. McAdam, S.J. Judd, Biological treatment of ion-exchange brine regenerant for re-use: A review, Sep. Purif. Technol. 62 (2009) 264–272.
[19] J.P. Van der Hoek, A.B Griffioen, A. Klapwijk, Biological regeneration of nitrate-loaded anion-exchange resins by denitrifying bacteria, J. Chem. Technol. Biotechnol. 43 (1988) 213–222.
[20] P. Cyplik, W. Grajek, R. Marecik, P. Kroliczak, Effect of macro/micro nutrients and carbon source over the denitrification rate of *Haloferax denitrificans* archaeon, Enzyme Microb. Technol. 40 (2007) 212–220.
[21] K. Nakagawa, S. Maebashi, K. Maeda, Freeze-thawing as a path to concentrate aqueous solution, Sep. Purif. Technol. 73 (2010) 403–408.
[22] J.H. Ahn, K.H. Choo, H.S. Park, Reverse osmosis membrane treatment of acidic etchant wastewater: Effect of neutralization and polyelectrolyte coating on nitrate removal, J. Membr. Sci. 310 (2008) 296–302.
[23] Y.-H. Kim, E.-D. Hwang, W.S. Shin, J.-H. Choi, T.W. Ha, S.J. Choi, Treatments of stainless steel wastewater containing a high concentration of nitrate using reverse osmosis and nanomembranes, Desalination 202 (2007) 286–292.
[24] P. Cyplik, R. Marecik, A. Piotrowska-Cyplik, A. Olejnik, A. Drożdżyńska, Ł. Chrzanowski, Biological denitrification of high nitrate processing wastewaters from explosives production plant, Water Air Soil Pollut. 223 (2012) 1791–1800.
[25] C. Glass, J. Silverstein, Denitrification kinetics of high nitrate concentration water: pH effect on inhibition and nitrite accumulation, Water Res. 32 (1997) 831–839.
[26] W. Huang, B. Zhang, C. Feng, M. Li, J. Zhang, Research trends on nitrate removal: A bibliometric analysis, Desalin. Water Treat. 50 (2012) 67–77.