



Electrodialysis Process to Reduce the Concentration of Nitrates in Waters

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Abstract

Nitrates and nitrites are natural components of the environment and contribute to the nitrogen cycle on Earth. Although nitrogen is essential for life, nitrogen compounds are among the main pollutants in the ecosystem. High concentrations of nitrogen compounds in the groundwater are primarily caused by human activity mostly in the use of chemical fertilizers in agriculture. Common health risks associated with higher concentrations of nitrates give rise to methemoglobin, which negatively affects mainly infants, and the potential formation of carcinogenic nitrosamines. This paper summarizes the results of laboratory tests of electrodialysis to remove nitrates from the model water. For the model solutions we used NaNO_3 and NaNO_2 with NaCl with a concentration of nitrates of approximately 1000 mg/l. The aim of the test was to achieve a concentration of nitrates corresponding to the limit for drinking water, which is 50 mg/l. The tests were carried out in the batch mode, and semi-continuous mode. All the tests have demonstrated the effectiveness of nitrate removal around 90%.

Keywords: electrodialysis, nitrates, water model, batch test, semi-test

Introduction

In recent times, ground water and surface water are contaminated with nitrates mostly due to the common use of fertilizers in agriculture, insufficient treatment of municipal and industrial water and landfilling (Shrimali and Singh, 2001). Higher concentrations of nitrates have been registered in various regions of Czech Republic. Mainly sub-basins of rivers Dyje, Dolní Vltava, Morava and Horní Odra (Český hydrometeorologický ústav, 2015). The pollution by nitrates is a problem of countries like Great Britain, France, Netherlands, Switzerland, Germany, north part of USA and Israel (Elyanow and Persechino, 2012). The various measures are applied in order to improve the situations. According to the Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources or according to the Decree No 252/2004 Coll., on hygienic requirements on drinking water on warm water and on frequency and range of checking drinking water as amended, the total amount of nitrates in drinking water is limited to 50 mg/l.

Nowadays, different methods of nitrates removal from drinking water are known. Mostly used methods are ion exchange, biological denitrification, chemical denitrification and membrane processes such as electrodialysis and reverse osmosis (Rozanská and Wisniewski, 2005). Ion exchange is the most used method in de-

nitrification process for drinking water treatment. The advantage of this method is that nitrate selective resins and also this method can be used for removing multiple contaminants from water. The disadvantages are: high chemical use and brine waste disposal. Biological denitrification reduces nitrates to nitrogen in anaerobic conditions by use of bacteria. Among the advantages are no waste brine and high water recovery. Among the disadvantages are substrate addition and possible sensitivity to environmental conditions. Another method is chemical denitrification usually used when biological method cannot be applied. The advantages are no waste brine and potential for multiple contaminant removal. The disadvantages are pH and temperature dependence and incomplete denitrification (Darby et al., 2012). Membrane processes have recently developed into modern energetically efficient separation methods. They are used for separation of homogenous or heterogeneous solutions (Kolínek, 2013). In our research, electrodialysis method was chosen. The advantages of this method are easy operation, energetically efficient separation without phase change and addition of chemicals, variability of the system (Mega a.s.). In particular, it is used for desalination or salination of water. The aim of this work is to evaluate the maximum degree of nitrate removal from model solution. Electrodialysis parameters for desired degree of nitrate removal have

Tab. 1 Feed solution concentrations

Tab. 1 Stężenia roztworu nadawy

Model Solution		c (NaNO ₃) [g.l ⁻¹]	c (NaCl) [g.l ⁻¹]	c (NO ₃ ⁻) [g.l ⁻¹]	c (Cl ⁻) [g.l ⁻¹]
	NaNO ₃	1.5	-	1.1	-
	NaNO ₃ + NaCl	0.83	0.75	0.61	0.46

Tab. 2 The feed solution volumes

Tab. 2 Objętości roztworu nadawy

Dilute [ml]	Concentrate [ml]
1000	1000
1000	500
5000	500
9500	500

been determined. The next aim was to reduce the volume of waste product (concentrate) and determinate the salination degree of concentrate.

Materials and Methods

Model solution. Model solutions of NaNO₃ and NaNO₃ with NaCl were used in the experimental part.

The concentrations of used solutions are described in Table 1.

Lab-scale electrodyalisis unit. Laboratory electro-dialysis unit P ED (R) - Z/10-1.0 produced by MEGA a.s. in Stráž pod Ralskem was used for the experiments (Mega a. s., Manuál k ED, 2009). The unit equipped from electro-dialysis module; storage reservoirs for diluate, concentrate and electrode solution; centrifugal pumps for dilute, concentrate and electrode circle; rotameters for dilute, concentrate and electrode circle; AC power supply (max. 2 A, 28 V) (Mega a. s., Operační manuál ED, 2009). Electro-dialysis module consists of two electrodes, 10 pairs of anion exchange and cation exchange membranes RALEX and PE spacers. The effective surface area of the membranes in the electro-dialysis module is 1 344 cm² (Hrbáčová, 2014).

Experimental procedure. The system was equilibrated prior to the experiments to achieve uniform flow distribution in the system. The procedure followed in these steps:

- put the specific volume of the model solution into the diluate (D) and concentrate (C) tank;
- 250 ml of electrode solution (Na₂SO₄) put into the electrode (E) tank;
- the circulation flow rate 50-60 l/h and constant voltage of 14 V;
- pH, temperature, conductivity, current and voltage was registered during the test

The test was terminated at maximum degree of desalination when the current reached approximately 0,03 A. In the last step the volumes were measured and the tests were evaluated. To determine achievable reduction of the waste volume (concentrate) different feed volumes were tested. The volumes are described in Table 2.

The degree of desalination was calculated according to:

$$DR = [(c_{Di}^0 - c_{Di}^T)/c_{Di}^0] \cdot 100 [\%],$$

where c_{Di}^0 is the concentration (conductivity) of the diluate at time $t = 0$ and c_{Di}^T is the concentration (conductivity) of the diluate at time t .

The degree of salination was calculated according to:

$$SR = [(c_{Ci}^T - c_{Ci}^0)/c_{Ci}^0] \cdot 100 [\%],$$

where c_{Ci}^0 is the concentration (conductivity) of the concentrate at time $t = 0$ and c_{Ci}^T is the concentration (conductivity) of the concentrate at time t .

Results and Discussion

Model solution NaNO₃

Four different volumes of feed solutions were used (1000 ml : 1000 ml; 1000 ml : 500 ml; 5000 ml : 500 ml; 9500 ml : 500 ml). The tests were terminated when the current value was 0,03 A. For all tests the dependency of the voltage U (V) on time t (min) was registered. The results are summarized in Table 3. From the results we can conclude that the efficiency of NO₃⁻ separation for feed volumes 1000 ml : 1000 ml; 1000 ml : 500 ml; 5000 ml : 500 ml was around 96–99%. The efficiency for the feed volume 9500 ml : 500 ml was

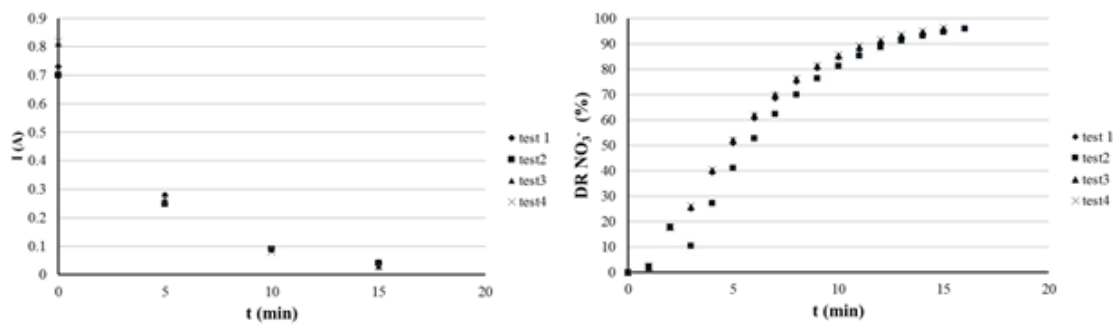


Fig. 1. The current value and desalination degree in time t for feed volume 1000 : 1000 ml
 Rys. 1 Wartość obecna i stopień odsolenia w czasie t dla objętości nadawy 1000 : 1000 ml

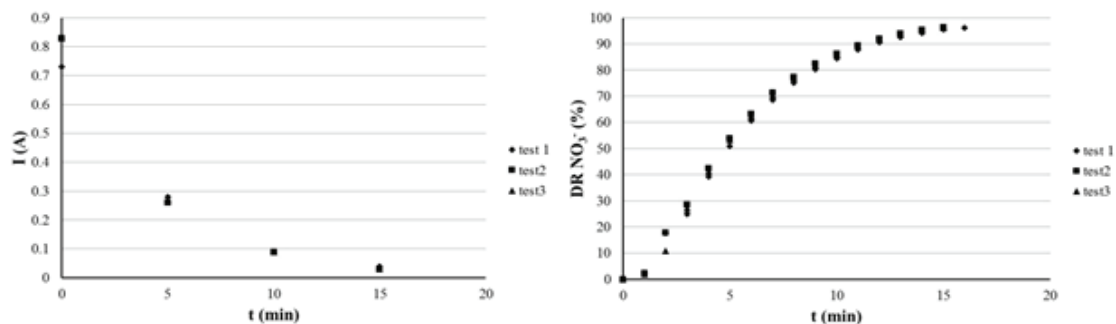


Fig. 2. The current value and desalination degree in time t for feed volume 1000 : 500 ml
 Rys. 2 Wartość obecna i stopień odsolenia w czasie t dla objętości nadawy 1000 : 500 ml

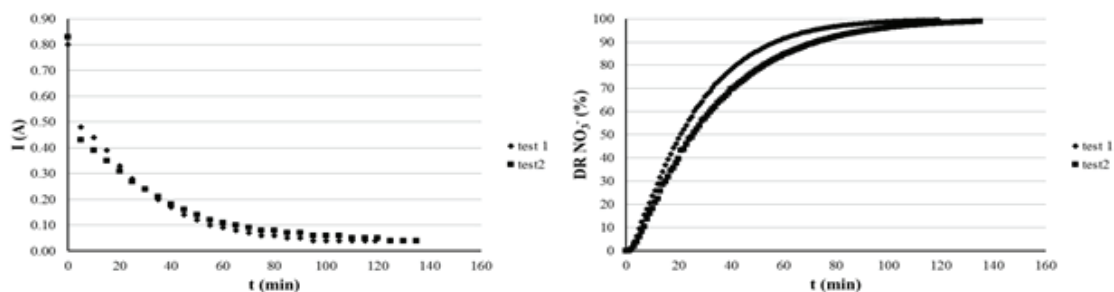


Fig. 3. The current value and desalination degree in time t for feed volume 5000 : 500 ml
 Rys. 3 Wartość obecna i stopień odsolenia w czasie t dla objętości nadawy 5000 : 500 ml

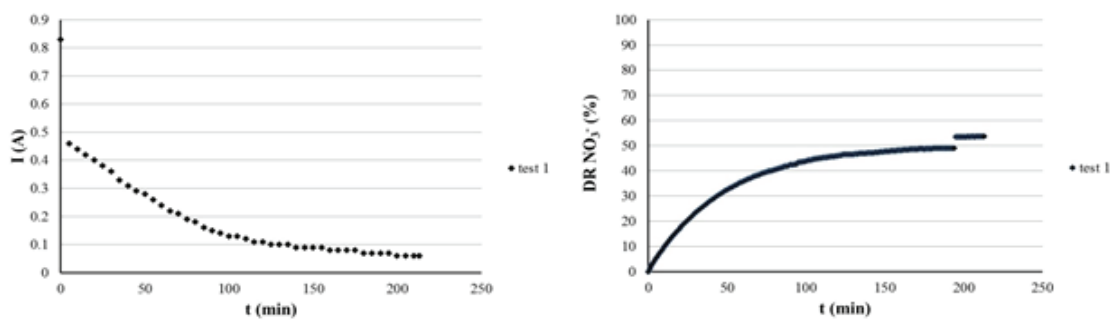


Fig. 4. The current value and desalination degree in time t for feed volume 9500 : 500 ml
 Rys. 4 Wartość obecna i stopień odsolenia w czasie t dla objętości nadawy 9500 : 500 ml

Tab. 3 The product quality

Tab. 3 Jakość produktu

V Feed [ml]	t [min]	Q [l/h]	Water recovery [%]	DR NaNO ₃ [%]	DR NO ₃ ⁻ [%]	SR NaNO ₃ [%]
2000	15	8	50	96.82-97.14	95.27-95.85	80.73-88.89
1500	15	6	66.67	96.98-99.19	95.63-95.92	131.68-147.53
5500	119-135	2.4-2.8	90.90	98.86-99.19	98.26-99.13	685.78-744.17
10000	213	2.8	95	67.03	51.89	1 369.39

Tab. 4. The product quality

Tab. 4 Jakość produktu

V Feed [ml]	t [min]	Q [l/h]	Water recovery [%]	DR NaNO ₃ NaCl [%]	DR NO ₃ ⁻ [%]	SR NaNO ₃ NaCl [%]
1500	20	4.5	66.67	97.39-97.72	97.42-97.75	119.03-171.07
1000	189	3.2	95	96.13	96.17	1 272.00

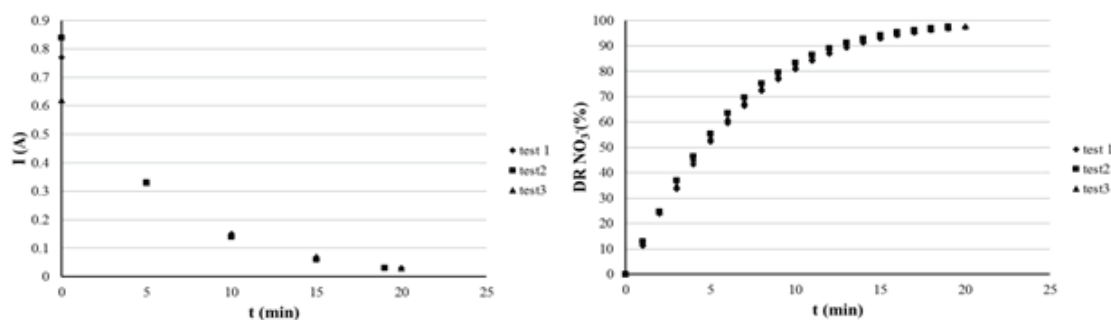


Fig. 5. The current value and desalination degree in time t for feed volume 1000 : 500 ml

Rys. 5 Wartość obecna i stopień odsolenia w czasie t dla objętości nadawy 1000 : 500 ml

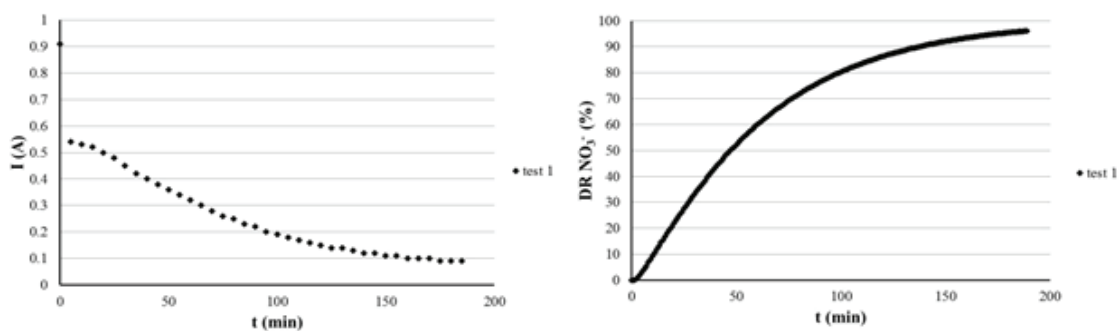


Fig. 6. The current value and desalination degree in time t for feed volume 9500 : 500 ml

Rys. 6 Wartość obecna i stopień odsolenia w czasie t dla objętości nadawy 9500 : 500 ml

around 52%. The test was terminated when the voltage increase probably due to a high concentrate gradient which the system tried to compensate. This negative effect can be solved by increasing the volume of the waste product (concentrate).

Model solution NaNO₃ with NaCl

Two volumes (1000 ml : 500 ml a 9500 ml : 500 ml) were tested. The tests were terminated when the current value was 0,03 A. For all tests the dependency of the voltage U (V) on time t (min) was registered. The results are summarized in Table 4. According to the results we can see the efficiency of NO₃⁻ separation for volumes 1000 ml : 500 ml; 9500 ml : 500 ml was around 96–98%.

Conclusion

This work studies the application of membrane process and electrodialysis for nitrate removal from model water. It was proven that this technology can achieve

high efficiency of NO₃⁻ separation of around 99%. The results meet the limits for nitrates concentrations according to the Decree No 252/2004 Coll. The recovery of the water was around 95% of the total feed volume. For waste product (concentrate) it is good to suggest another degree of treatment by electrodialysis. By this process we can achieve reduction of the total volume of waste brine. In this study the maximum salination degree of concentrate was achieved around 23 g/l NaNO₃. It can be worked with till the maximum degree of salination approximately 900 g/l. This technology can be used for drinking water treatment and for waste water treatment.

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Proces elektrodialýzy w zastosowaniu do redukcji stężenia azotanów w wodzie

Azotany i azotyny są naturalnymi składnikami środowiska i biorą udział w obiegu azotu na Ziemi. Pomimo tego, że azot jest niezbędny do życia, związki azotu występują wśród głównych składników zanieczyszczeń w ekosystemie. Wysokie stężenia związków azotu w wodach gruntowych są spowodowane głównie działalnością ludzką poprzez stosowanie nawozów w rolnictwie. Powszechne zagrożenia zdrowia związane z wyższymi stężeniami azotanów to wzrost poziomu methemoglobiny, która negatywnie wpływa zwłaszcza na niemowlęta, jak również potencjalne tworzenie się rakotwórczych nitrozoamin. W artykule przedstawiono wyniki testów laboratoryjnych elektrodialýzy, przeprowadzanych w celu usunięcia azotanów z wody wzorcowej. Jako modelowe roztwory zastosowano NaNO_3 oraz NaNO_3 z NaCl o stężeniu azotanów na poziomie ok. 1000 mg/l. Celem testu było osiągnięcie stężenia azotanów na poziomie akceptowalnym dla wody pitnej, który wynosi 50 mg/l. Testy zostały przeprowadzone w trybie przedziałowym i pół-ciągłym. Wszystkie testy wskazały efektywność usuwania azotanów na poziomie około 90%.

Słowa klucze: elektrodialýza, azotany, model wodny, test przedziałowy, pół-test