

Removal of troublesome anions from water by means of Donnan dialysis

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Abstract

Donnan dialysis is a simple and one of the most economic membrane processes. The driving force of the process is the chemical potential gradient of components of two solutions separated by a membrane. During Donnan dialysis there is a stoichiometric exchange of ions of the same charge (so called *counter-ions*) through an ion-exchange membrane, and the process ends when Donnan equilibrium is reached. Donnan dialysis can be used in the recovery of valuable metals or their complexes from diluted solutions (e.g. rinse waters after metal plating). Good results were also obtained in the process application for organic acids separation from fermentative solutions. An important field of Donnan dialysis application is undesired ions removal from water. The research has shown that efficient defluoridation and denitrification of drinking water is possible. A new direction for the process is bioreactor with ion-exchange membrane (IEM), where nitrates removed from water are subject to biological denitrification. This paper presents the results of our experiments on selected anions removal from water. Preliminary removal of some ions, especially ‘troublesome’ anions (sulphates and bicarbonates), would enable high degree of water desalination by means of electrodialysis. In the experiments we used Selemon (AMV, DMV) and Neosepta (AFN, AMX) anion-exchange membranes (AEMs). We investigated the effects of salt concentration in the receiving solution, and of volume ratio of the feed and the receiver on the efficiency and on the rate of ions removal. The phenomenon of salt leakage from the receiver to the treated water (that is related to co-ions transport through the membrane) was also analysed. For each of four examined membranes high efficiency of anions removal was obtained: 87–98% removal of nitrates, 94–100% removal of sulphates, whereas bicarbonates were removed with the efficiency of 77–99%. We found out that with higher concentrations of NaCl in the receiving solution (300 and 500 mM), equilibrium concentration of the exchanged ion in the feed was lower. However, with the higher ratio of feed and receiver volumes (4:1), the concentration at the point of Donnan equilibrium was set on higher level. The best transport properties for the examined anions has shown the Neosepta AFN membrane. An average flux of nitrates and sulphates was up to two times higher than with the other membranes, and bicarbonate flux—even three times higher. This membrane also performed greater NaCl leakage from the receiving solution, reaching 0.33 mol/m²h, with the receiver concentration of 500 mM NaCl.

Keywords: Donnan dialysis; Anion-exchange membrane; Anion removal; Salt leakage

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1. Introduction

Some ions present in natural water impede deep desalination by means of membrane techniques—especially with higher concentrations of such ions. It is connected with the possibility of precipitation of troublesome sediments in solutions being concentrated. To avoid scaling, addition of appropriate chemicals to treated water is necessary (e.g. addition of an acid allows to avoid the precipitation of CaCO_3). Removal of troublesome ions by their replacement with a neutral ion, that does not precipitate—even with high concentration—is another solution. One process that enables to achieve such effect is Donnan dialysis.

The process consists in the exchange of ions of the same charge between two solutions separated by an ion-exchange membrane. The driving force of the process is the chemical potential gradient of an electrolyte (usually NaCl or an inorganic acid with relatively high concentration), that causes the transport of counter-ions from the receiving solution to the feeding solution. Because the flux of co-ions in the same direction is impossible, for the electroneutrality of the solutions to be retained, stoichiometrically equal amount of counter-ions should flow from the feed to the receiving solution. The process of ion exchange between solutions lasts until so called Donnan equilibrium is reached, that can be described by the following Eq. 1:

$$\left(\frac{c_{i_r}}{c_{i_f}}\right)^{\frac{1}{z_i}} = K \quad (1)$$

where c_{i_r} and c_{i_f} means the activity of the i -ion in the receiver and in the feed, respectively; z_i stands for the ion charge, and K is constant for all counter-ions present in the system.

In the Donnan dialysis with a cation-exchange membrane, the recovery of valuable metals from diluted solutions is possible, e.g. cobalt and nickel [2], silver and copper [3] or

chromium [4]. The possibilities for the concentration of recovered ions are however limited, because of the phenomenon of osmosis, that becomes more intense when the concentration of the driving cation in the receiving solution is higher [3].

Donnan dialysis with an anion-exchange membrane (AEM) gives interesting possibilities for the process application. The process may be applied to removal of harmful anions from drinking water. A lot of research has been conducted in the field of defluoridation [5–7]. The authors examined different AEMs, and observed that the best effects in the defluoridation can be obtained with the Selemion DSV membrane. The concentration of fluoride was lowered below the upper value allowed in drinking water (1.5 mg/dm^3). The authors observed also that if the receiving solution circulates in a batch mode, the complexation of fluorides is necessary to avoid their backflow to the feeding solution. Aluminium cations may be successfully used for this purpose [6].

Donnan dialysis ensures also high efficiency in other anions removal from water. With the Morgane ADS membrane, nitrates concentration was lowered from 90 to 16 mg/dm^3 , which is below the limiting value for drinking water ($50 \text{ mgNO}_3^-/\text{dm}^3$). It was observed, that the rate and the efficiency of the nitrate removal depends on the NaCl concentration in the receiving solution [8].

An interesting combination of the Donnan dialysis process and a bioreactor was presented in the paper [9]. The nitrates are removed from treated water with use of the mono-anion selective membrane (Neosepta ACS) to the bioreactor, where their biological reduction takes place. It allows to avoid the increase in the nitrate concentration in the receiving solution, and—in effect—the overall nitrate flux is greater than in ‘traditional’ Donnan dialysis. The nitrate concentration in this process was lowered from 150 to

20 mg/dm³, while the conductivity of the treated water was identical to that observed before the process. It is connected with the use of mono-anion selective membrane, that prevents the electrolyte leakage from the receiver.

In our paper we present results of the experiments on selected anions removal from water by means of Donnan dialysis. Preliminary removal of some ions, especially troublesome anions like sulphates and bicarbonates, would enable deep desalination of water during electro dialysis. In the paper we examined the effects of the type of AEM and of selected process parameters on the rate and the efficiency of the Donnan dialysis.

2. Experimental

2.1. Membranes

For the Donnan dialysis process we used four AEMs: Selemion AMV and DMV (Asahi Glass), and Neosepta AFN and AMX (Tokuyama Corp.). The main properties of the membranes are shown in Table 1.

2.2. Donnan dialysis

We prepared one-component solutions containing NaNO₃, Na₂SO₄ or NaHCO₃ with the concentration of 5 mM (the feed). As the receiver we used the NaCl solution with the concentration of 100, 300 or 500 mM.

The process was conducted in the laboratory set-up for dialysis (Geomasep 136), that comprised 20 cell pairs separated with AEMs.

The total working area of membranes was 0.14 m². The feeding solution volumes were 2.5, 5 or 10 dm³, whereas the volume of the receiver was constant and equaled 2.5 dm³. The experiments were conducted with the constant flow of the solutions: the feed—75 dm³/h and the receiver—30 dm³/h. The process was conducted with the recirculation of both solutions (so called batch system), until the equilibrium concentration of the anion being removed was reached in the feed.

During the process we measured the concentration of anions in the feed and in the receiver. The nitrate and sulphate concentration was measured spectrophotometrically with the spectrophotometer DREL2000. The concentration of chlorides and bicarbonates was determined by means of titration (with AgNO₃ or HCl, respectively).

On the basis of the results of all measurements we determined the removal efficiency of the anions and their fluxes from the feed, as well as the fluxes of chlorides entering the feed.

Comparing the average flux of removed anion (from the feed to the receiver) with the average flux of chlorides (from the receiver to the feed) we determined salt leakage from the receiver to the feeding solution.

3. Results

The salt concentration in the receiver has an important influence on the rate and the efficiency of ions removal from the feeding solution. Fig. 1 presents the change in the nitrate concentration during the process of Donnan dialysis with different NaCl concentrations in the receiver. As one may notice, with higher salt concentration in the receiving solution, the ion exchange is faster, and the equilibrium concentration of the ion being removed in the feeding solution is lower. The reason for this phenomenon is the higher

Table 1
Properties of anion-exchange membranes

Parameter	Selemion		Neosepta	
	AMV	DMV	AFN	AMX
Ion-exchange capacity (mmol/g)	1.85	4.70	3.15	1.30
Water content (%)	19.9	40.7	64.8	26.1
Thickness (mm)	0.11	0.14	0.12	0.13–0.14

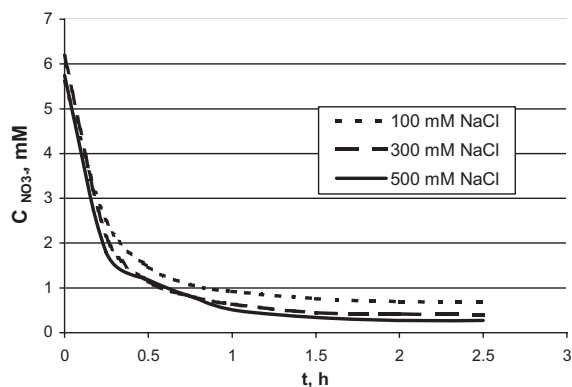


Fig. 1. Decrease in the nitrate concentration in the feed with different NaCl concentration in the receiver (Selemon AMV membranes; $V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$).

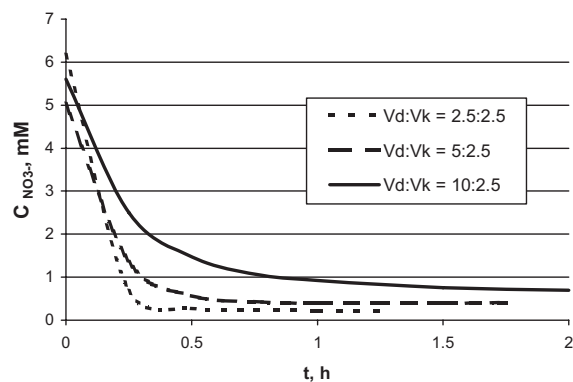


Fig. 2. Decrease in the nitrate concentration in the feed with different volume ratios of the feed and the receiver (Selemon AMV membranes, NaCl concentration in the receiver—100 mM).

concentration gradient of counter-ions (Cl^-) and resulting high counter-ion flux to the feeding solution, that causes an increase in the flux of removed ion (Table 2).

The rate and the efficiency of the Donnan dialysis also depends on the volume ratio of the feed and the receiver. Fig. 2 presents the decrease in the nitrate concentration in the feed with different volume ratios of the solutions. The results show that with the increase of volume ratio of the feed and the receiver, the equilibrium concentration of the exchanged ion increases, as well as time required for its achieving. It should be linked to the higher volume of the feeding solution. Under such conditions (when the volume of the feed is a few times larger than the volume of the receiver), the amount of chloride ions

transferred to the feed is respectively large because of significant dilution of these ions in the feeding solution. In effect, the concentration gradient of Cl^- ions decreases, and at the same time the driving force of the Donnan dialysis becomes weaker. Simultaneously, there is transport of stoichiometrically equal amount of nitrates to the receiver, where these ions are concentrated. In such circumstances, the equilibrium concentration of NO_3^- ions in the receiver is high, as well as the concentration gradient of nitrates, that slows down the process in its final stage. As the result of this phenomenon, the efficiency of ion removal from the feed is lower in the system with greater volume of the feeding solution.

However, one should notice that the increase in the salt concentration counteracts the described phenomenon—because it results in increasing the driving force of the process. Thus, the efficiency of ion removal from the system with higher volume ratio (of the feed and the receiver) can be improved when applying higher salt concentration in the receiver (Fig. 1).

A kind of exchanged ion has also a significant impact on the rate and the efficiency of ion removal in the Donnan dialysis. Fig. 3 presents the change in the concentration of

Table 2

Average nitrate flux from the feeding solution with different NaCl concentration in the receiver (Selemon AMV membranes; $V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$)

	NaCl concentration in the receiver (mM)		
	100	300	500
$J_{av}^{\text{NO}_3}$ mol/m ² ·h	0.139	0.165	0.195

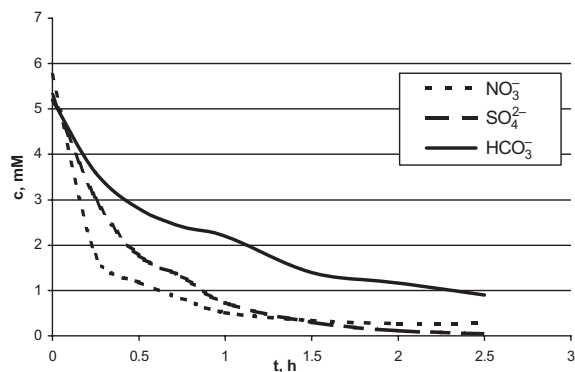


Fig. 3. Decrease in the nitrate, sulphate and bicarbonate concentration in one-component feeding solution (Selecion AMV membranes; $V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$; the NaCl concentration in the receiver—500 mM).

nitrate, sulphate and bicarbonate during the process, in the one-component feeding solution. Ions that are removed with the highest rate are nitrates—the average flux until equilibrium is reached equals $0.195 \text{ mol/m}^2 \cdot \text{h}$. Sulphates are removed a little bit slower—with the average flux of these anions $0.150 \text{ mol/m}^2 \cdot \text{h}$. But in this case the concentration in the state of equilibrium has the lowest value— 0.05 mM . Bicarbonates are removed from the feed with the smallest rate—because of their ionic size—and the average ionic flux equals $0.109 \text{ mol/m}^2 \cdot \text{h}$. At the same time, the equilibrium concentration of bicarbonates is the highest and equals 0.60 mM . Table 3 summarizes the average fluxes of all anions, as well as the efficiencies of their removal under certain process conditions.

The lowest equilibrium concentration achieved with sulphates (which means also the highest removal efficiency) should be linked to the charge of the ion: as a divalent counter-ion sulphates are easily transferred through the membrane.

It was observed that the rate and the efficiency of the ion removal in the Donnan

Table 3
Average ionic flux from the feed and the efficiency of ion removal (Selecion AMV membranes; $V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$; the NaCl concentration in the receiver—500 mM)

	NO_3^-	SO_4^{2-}	HCO_3^-
Average ionic flux ($\text{mol/m}^2 \cdot \text{h}$)	0.195	0.150	0.109
Removal efficiency of anion (%)	95.3	99.0	88.5

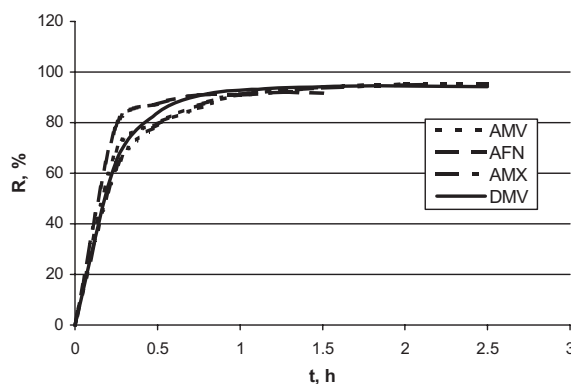


Fig. 4. Nitrate removal with different anion-exchange membranes ($V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$; the NaCl concentration in the receiver—500 mM).

dialysis depends significantly on the properties of an AEM. Fig. 4 presents the efficiency of the nitrate removal with different AEMs. Although process efficiencies for examined membranes are similar, the differences in the duration of the process are observed (i.e. time necessary for achieving the equilibrium concentration of the removed ion). The state of equilibrium is achieved the fastest with the Neosepta AFN membrane—a membrane with relatively high ion-exchange capacity and the highest water content. High ion-exchange capacity increases the flux of counter-ions. On the other hand, high water content (that results from the decrease in the cross-linking of the membrane) facilitates transport of ions. It is worth to mention that the average nitrate flux through the

Neosepta AFN membrane (until equilibrium is set), under certain process conditions, equals $0.333 \text{ mol/m}^2 \cdot \text{h}$ —the value that is 1.5–2 times higher than that with other examined membranes.

Similar observations are true for the process of the sulphate removal (Fig. 5). For each of the examined membranes very high removal efficiencies were obtained (98.4–100%), but the Neosepta AFN membrane yields the fastest equilibrium. The average flux of SO_4^{2-} anions through this membrane equals $0.248 \text{ mol/m}^2 \cdot \text{h}$, which is about 1.5 times higher than that with other AEMs.

The removal of bicarbonate ions is slower and less efficient in comparison with other examined anions (Fig. 6). One may notice, that with the Selemion DMV and the Neosepta AFN membranes time of the process is significantly shorter. It is the result of a high ion-exchange capacity and a high water content of these membranes, that facilitate the transport of large HCO_3^- ions. The average bicarbonate flux through these membranes equals $0.209 \text{ mol/m}^2 \cdot \text{h}$ (Selemion DMV) and $0.228 \text{ mol/m}^2 \cdot \text{h}$ (Neosepta AFN). These values are about 2 times higher than those

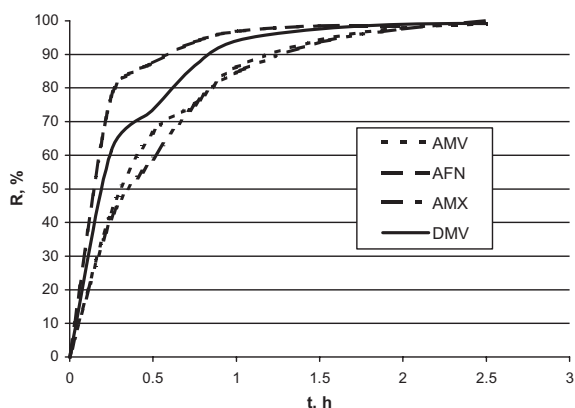


Fig. 5. The sulphate removal with different AEMs ($V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$; the NaCl concentration in the receiver—500 mM).

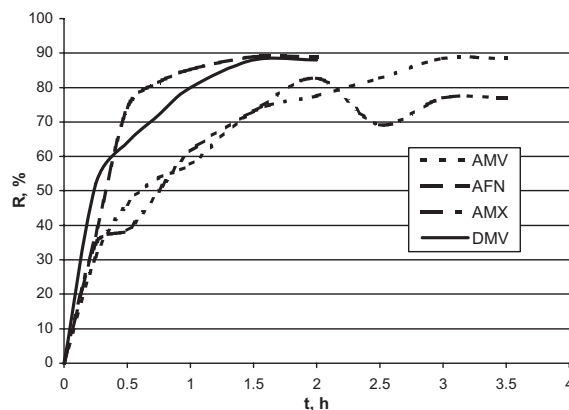


Fig. 6. The bicarbonate removal with different AEMs ($V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$; the NaCl concentration in the receiver—500 mM).

with the Selemion AMV and the Neosepta AMX membranes. Moreover, it should be noticed that with the Neosepta AMX membrane the efficiency of the process is distinctly lower. It is the result of high cross-linking of this membrane (which means lower water content in the membrane). In the effect, the transport of large HCO_3^- ions through this membrane is significantly impeded.

The desirable transport of ions (i.e. chloride transport to the feed and, at the same time, the transport of the removed ion to the receiver) may be accompanied with the salt leakage from the receiver to the feed (Table 4). It can be observed that in the Donnan dialysis with the Selemion AMV and DMV membranes, as well as with the Neosepta AMX membranes, the NaCl leakage to the feeding solution is low. However, with the Neosepta AFN membrane the salt leakage is significantly higher than that with the other membranes. It is probably the result of high water content in the membrane (64.8%, Table 1). This parameter, linked to the low cross-linking of the membrane, makes easier transport through the membrane of not only large counter-ions, but also of co-ions.

Table 4

The NaCl leakage to the feed through different anion-exchange membranes ($V_f:V_r = 10 \text{ dm}^3:2.5 \text{ dm}^3$, the NaCl concentration in the receiver—500 mM)

Anion-exchange membrane	NaCl leakage ($\text{mol/m}^2 \cdot \text{h}$) during the removal of		
	NO_3^-	SO_4^{2-}	HCO_3^-
Selemion AMV	0	0	0.018
Selemion DMV	0.025	0.017	0.035
Neosepta AFN	0.248	0.331	0.218
Neosepta AMX	0.026	0	0.055

In the effect, the Neosepta AFN AEM has the best transport properties, but at the same time, the greatest salt leakage during Donnan dialysis.

4. Conclusions

1. The NaCl concentration in the receiver has a significant influence on the flux of ion removed from the feed, and on the equilibrium concentration of this ion. With the increase of the salt concentration in the receiver, the flux of removed ion increases, which results in shorter time necessary for the process to reach equilibrium. Moreover, the equilibrium concentration of the removed ion in the feed is set on a lower level.

2. With higher volume ratio (the feed and the receiver), the equilibrium concentration of the removed ion is higher, and the time required for its achieving is longer. In order to increase the efficiency of ion removal from the feed (at high volume ratio of the solutions), one should apply respectively high concentration of NaCl in the receiver (here: 500 mM).

3. The flux of the removed ion (that affects the time of the process), and the equilibrium concentration of the ion in the feeding solution (that determines the efficiency of ion removal) depend on the size and on the charge of the ion. Nitrates and sulphates are removed from one-component solutions with the highest rate,

while bicarbonates are transported much slower. The highest efficiency of ion removal was obtained for sulphates (94–100%); the efficiency of the nitrate removal equaled 87–98%, and of the bicarbonate—77–99%.

4. The properties of the AEM (i.e. ion-exchange capacity and water content) significantly influence flux of the removed ion. With the Neosepta AFN membrane (high ion exchange capacity and high water content) we obtained ionic fluxes 1.5–2 times higher than those with other membranes. It also means that the time of the process is about 1.5–2 times shorter.

5. In the process of Donnan dialysis the salt leakage from the receiver to the feed can be observed. The amount of the leakage depends on the properties of the AEM—first of all on the water content in the membrane. The largest salt leakage was observed with the Neosepta AFN membrane ($0.331 \text{ mol/m}^2 \cdot \text{h}$).

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