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DONNAN DIALYSIS – A USEFUL METHOD OF TROUBLESOME ANION REMOVAL FROM WATER

Donnan dialysis with the anion-exchange membrane (Selemion AMV, Asahi Glass) was applied to the removal of troublesome anions (nitrates, sulphates and bicarbonates) from multi-component water solutions. The authors examined the effect of selected parameters on the rate and on the removal efficiency of anions from the feed. It was observed that at a higher salt (NaCl) concentration in the receiver, the ion exchange was faster and the equilibrium concentration of the removed anion in the feed was lower. It was also found that anion species had a decisive effect on the process rate and efficiency: average fluxes of nitrates and sulphates were over two times as high as that of bicarbonates. In turn, the highest removal efficiency (91%) was obtained for sulphates, whereas bicarbonate were removed with the lowest efficiency (37%). Analyzing the effect of temperature on the Donnan dialysis process it was found that with the rising temperature of the solutions (the feed and the receiver) anion transport was accelerated: the average flux of nitrates and sulphates was increased by 50–60% and that of bicarbonates – by over 90%. Simultaneously, bicarbonate removal efficiency increased from 37% (at 17 °C) to 46% (at 37 °C).

1. INTRODUCTION

Surface water often contains ionic components that can be considered as troublesome ions. Anions with a harmful effect on human health (e.g., nitrates) as well as anions that impede deep desalination by means of membrane techniques (sulfates and bicarbonates) belong to such components. Due to the high concentration of the latter anions in a solution being concentrated, precipitation of sediments may occur. The phenomenon (known as *scaling*) causes several negative effects, e.g., a decrease in ionic fluxes, an increase in energy consumption, and membrane exploitation difficulties [1]. To avoid the problems with *scaling*, the addition of appropriate chemicals to the concentrate stream is necessary. When electrodialysis is applied in water desalination, it is also possible to change periodically the polarity of the electrodes (the proc-

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ess is known as *electrodialysis reversal* (EDR) [1]). Another way to avoid *scaling* is by replacing troublesome anions with neutral anions that do not precipitate, even at high concentration. The process that enables us to achieve such an effect is Donnan dialysis with anion-exchange membrane. In this process, an anion-exchange membrane separates two solutions: the feed (containing anions that should be removed) and the receiver (with an electrolyte, usually NaCl, of relatively high concentration). The driving force of the process is the chemical potential gradient of an electrolyte that causes the transport of counter-ions from the receiver 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 a stoichiometrically equal amount of counter-ions should flow from the feed to the receiving solution (figure 1). As a result of the process, previously troublesome anions are replaced with neutral anions (e.g., chlorides) and the water that is going to be desalinated contains only easily soluble salts.

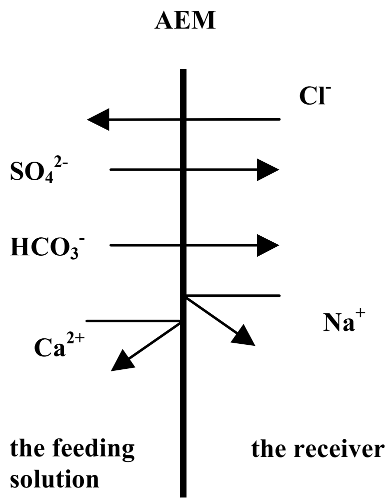


Fig. 1. Removal of troublesome anions from water in Donnan dialysis with anion-exchange membrane (AEM)

Donnan dialysis with an anion-exchange membrane offers a large application potential. The process can be applied in the removal of harmful anions from drinking water. Satisfactory results were obtained in fluoride removal – their concentration was reduced below the admissible value for drinking water (1.5 mg/dm^3) [2]–[4]. Good effects were also achieved in the case of nitrate – the concentration of these ions was lowered to 16 mg/dm^3, i.e., much below the admissible value for drinking water (50 mg/dm^3) [5]. Also the combination of Donnan dialysis with a bioreactor offers interesting possibilities. In this process, nitrates are transported through a mono-anion-selective membrane from treated water to the bioreactor where biological denitrification takes place. In a solution like this, nitrate flux to the receiver increases and a significant drop of the nitrate concentration in the treated water can be achieved (below 0.3 mg/dm^3) [6], [7].

The experiments conducted by WIŚNIEWSKI [8], [9] show that Donnan dialysis with the anion-exchange membrane enables the troublesome anions to be removed from the solution with the efficiency of 78% (sulphates) and 98% (bicarbonates). The change of the ionic composition in the solution increases the salt flux during electrodialysis (by about 20%) and reduces the energy consumption for the salt transport (up to two times compared with raw solution).

In this paper, the authors presented the results of the experiments on the effect of the process parameters (in particular, the effect of the solution temperature) on troublesome anion removal from water by means of Donnan dialysis with the Selemion AMV anion-exchange membrane.

2. EXPERIMENTAL

The process was conducted in the laboratory set-up for dialysis (Goemasep 136) that comprised 20 cell pairs separated from each other with anion-exchange membranes (Selemion AMV). The total working area of the membranes amounted to 0.140 m^2. The main parameters of the membrane are shown in table 1. The volume ratio of the feed to the receiver was 4:1 (10 dm^3 : 2.5 dm^3). The experiments were conducted at the constant flow of the solutions: the feed – 75 dm^3/h and the receiver – 30 dm^3/h. The temperatures of the solutions were: 17, 27 and 37 °C. The process was conducted with the recirculation of both solutions (the so-called *batch system*), until the equilibrium concentration of the anion being removed fastest was reached in the feed.

Table 1

Properties of AMV anion-exchange membrane

Parameter	
Ion-exchange capacity, mmol/g	1.85
Water content, %	19.9
Thickness, mm	0.11

Donnan dialysis was carried out with multi-component solutions containing the following salts: $NaNO_3$, Na_2SO_4, $NaHCO_3$ and NaCl, each of the concentration of 5 $mmol/dm^3$. As the receiver the solution of NaCl was used of the concentration of 100, 300 or 500 $mmol/dm^3$.

During the process the concentration of anions in the feed and in the receiver was measured. The nitrate and sulphate concentration was measured spectrophotometrically with the spectrophotometer DREL 2000. The concentration of chlorides and bicarbonates was determined by means of titration (with $AgNO_3$ and HCl, respectively). On the basis of the measurement results 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 the removed anions with the average flux of chlorides entering the feed allowed the salt leakage from the receiver to the feeding solution to be assessed.

3. RESULTS AND DISCUSSION

The salt concentration in the receiver influenced the removal rate and the final concentration of the ion removed from the feeding solution. Figures 2, 3 and 4 present the concentration decrease and the removal efficiency of nitrate, sulphate and bicarbonate anions, respectively, at different NaCl concentration in the receiver.

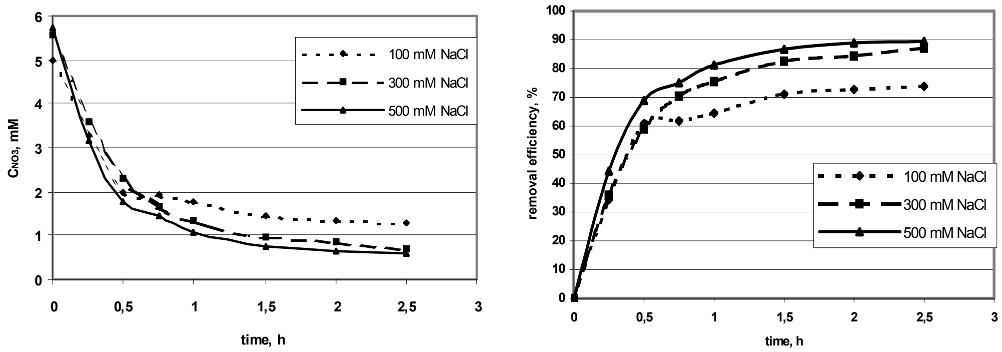


Fig. 2. Concentration decrease and removal efficiency of nitrates during Donnan dialysis at various NaCl concentration in the receiver ($T = 17$ °C)

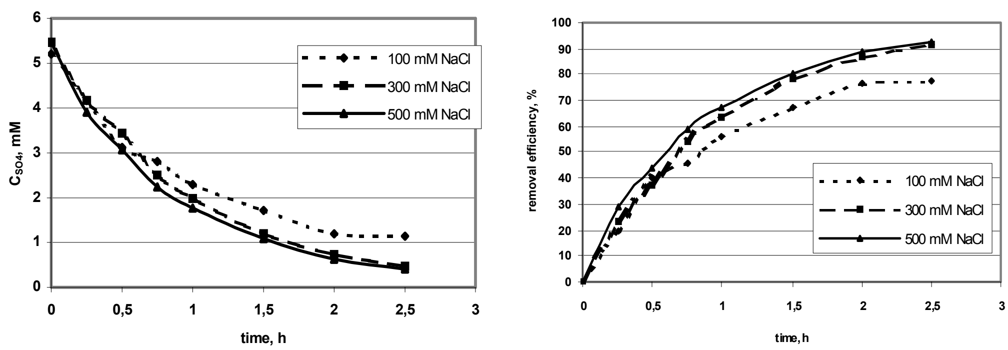


Fig. 3. Concentration decrease and removal efficiency of sulphates during Donnan dialysis at various NaCl concentration in the receiver (T = 17 °C)

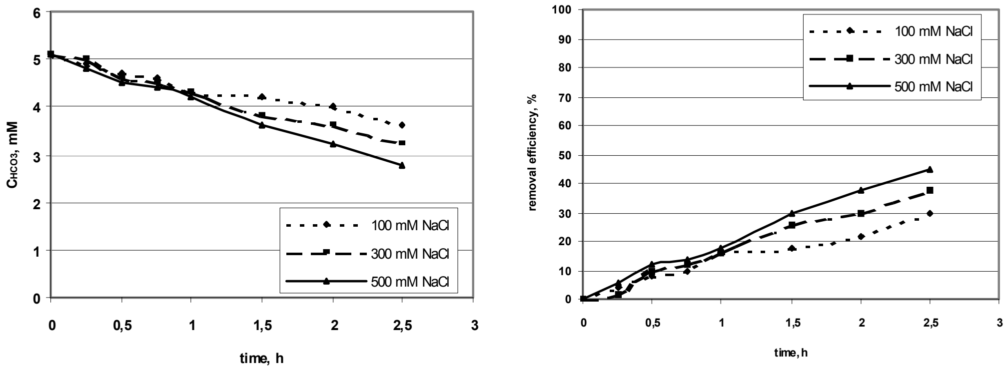


Fig. 4. Concentration decrease and removal efficiency of bicarbonates during Donnan dialysis at various NaCl concentration in the receiver (T = 17 °C)

As may be noticed, at higher salt concentration in the receiving solution, the ion exchange is faster and the final concentration of the ion being removed in the feeding solution is lower. As a result, the process efficiency increases. This phenomenon can be explained by a higher concentration gradient of the driving ion (Cl^-) and the resulting high counter-ion flux to the feeding solution which increases the flux of the removed anion (table 2).

Table 2

Average anion flux from multi-component feeding solution at different NaCl concentration in the receiver (T = 17 °C)

	NaCl concentration in the receiver (mM)		
	100	300	500
$J_{av}^{NO_3}$ mol/m^2·h	0.107	0.139	0.146
$J_{av}^{SO_4}$ mol/m^2·h	0.117	0.142	0.144
$J_{av}^{HCO_3}$ mol/m^2·h	0.049	0.060	0.070

The rate and the efficiency of anion removal during Donnan dialysis depends greatly on the anion species. Figure 5 presents the effect of anion exchange in multi-component solution. It can be seen that the removal of nitrate ions from the feed is the fastest. The average flux of this anion, until its equilibrium concentration is reached, equals 0.139 mol/m^2·h. Sulphates are removed at a comparable rate of 0.142 mol/m^2·h. And the rate of bicarbonate transfer is over two times lower than that of nitrates: the average flux of HCO_3^- ions equals 0.059 mol/m^2·h. The above results can be explained by the difference in the ion size: the radius of hydrated NO_3^- ion is 0.349 nm, the radius of SO_4^{2-} ion equals 0.380 nm, and that of HCO_3^- is the biggest as it exceeds 0.394 nm [10].

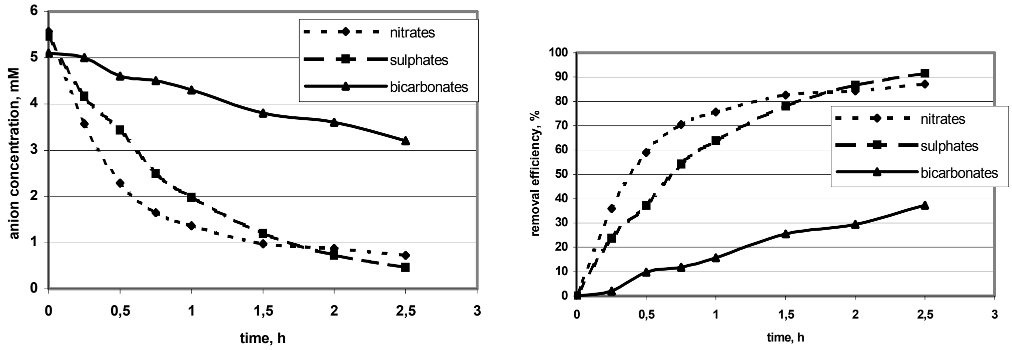
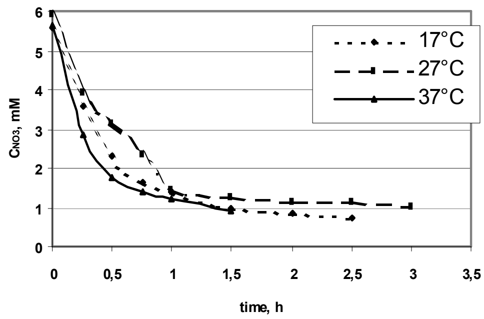


Fig. 5. Concentration decrease and removal efficiency of anions during Donnan dialysis of multi-component solution (C_{NaCl} = 300 mM, T = 17 °C)

It is worth noting that the lowest concentration (and the highest removal efficiency) is achieved for sulphate ions. This is caused by the interaction of these anions (that have higher ionic charge) with positively charged ion-exchange groups of the membrane. As a result, sulphates are removed with higher efficiency than nitrates, despite the fact that the sulphate ion is bigger than the nitrate one.

Analyzing the effect of the solution temperature (the feed and the receiver) on the results of anion exchange it can be found that this parameter does not affect significantly the efficiency of nitrate and sulphate removal: the final concentration of these anions in the feed changes subtly with temperature (figures 6, 7). As a result, the efficiency of nitrate removal is on the level of 82–87% and that of sulphate removal in the range of 82–92%. But the rise in temperature of the solutions accelerates the process of nitrate and sulphate removal.



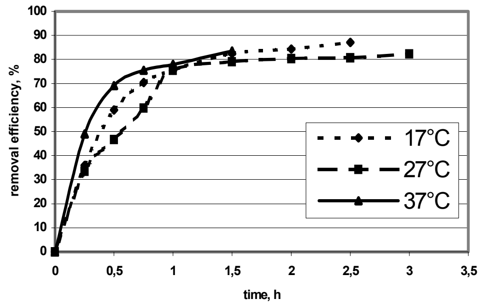


Fig. 6. Concentration decrease and removal efficiency of nitrates during Donnan dialysis at various temperatures (C_{NaCl} = 300 mM)

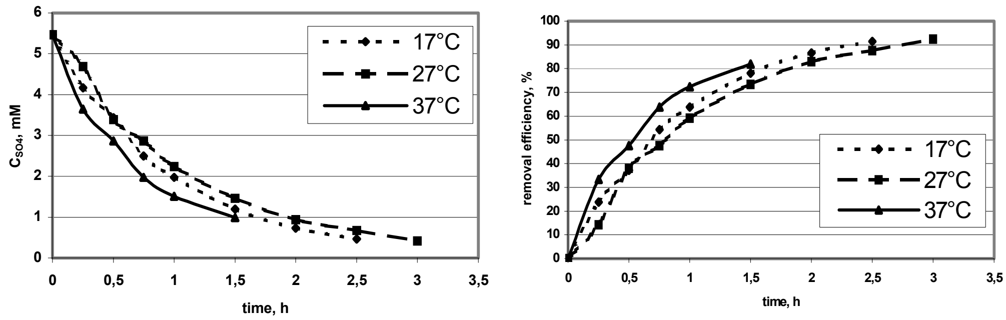


Fig. 7. Concentration decrease and removal efficiency of sulphates during Donnan dialysis at various temperatures (C_{NaCl} = 300 mM)

The average flux of nitrates increases from 0.139 mol/m^2·h (at 17 °C) to 0.223 mol/m^2·h (at 37 °C) and the average flux of sulphates – from 0.142 to 0.213 mol/m^2·h (table 3). Due to the higher transport rate of these anions, the length of the process time (i.e., the time necessary for reaching the equilibrium concentration of the nitrate ions) decreases from 2.5 to 1.5 h. This phenomenon should be linked with a higher chemical potential of the ions (the driving and the removed ones) which increases ion mobility in the solution and in the membrane.

Table 3

Average anion flux from multi-component feeding solution at various temperatures

	Temperature (°C)		
	17	27	37
$J_{\mathrm{av}}^{\mathrm{NO_3}}$, mol/m^2·h	0.139	0.117	0.223
$J_{\mathrm{av}}^{\mathrm{SO_4}}$, mol/m^2·h	0.142	0.120	0.213

$J_{av}^{HCO_3}$, mol/m^2·h	0.059	0.069	0.114

The process of bicarbonate exchange follows another pattern. Because of a large ion size, the mobility of this ion in the anion-exchange membrane is relatively low. According to STRATHMANN [1], the transport rate of ions through a membrane is proportional to their concentration and mobility. In the case of Donnan dialysis, ions that are exchanged for the so-called driving ion are transported against their concentration gradient. And just the concentration gradient is one of the factors influencing the efficiency of the process. Analyzing the data presented in figure 8 it can be seen that at the low temperature (17 °C) the final concentration of bicarbonates in the feed is higher than that of nitrates and sulphates (figures 6, 7). This means that the concentration gradient of bicarbonates in the feed and the receiver is relatively low. That is why, at the higher solution temperature, bicarbonates are more easily transported against their concentration gradient. Moreover, the rise in a temperature increases the mobility of the ions. Due to these phenomena, the concentration of bicarbonates in the membrane increases and this implicates (according to STRATHMANN [1]) the substantial rise of the bicarbonate flux through the membrane: from 0.059 mol/m^2·h at 17 °C to 0.114 mol/m^2·h at 37 °C (table 3). As a result, the bicarbonate concentration in the feed is established on the lower level and the efficiency of the ion removal increases from 37% to 46%.

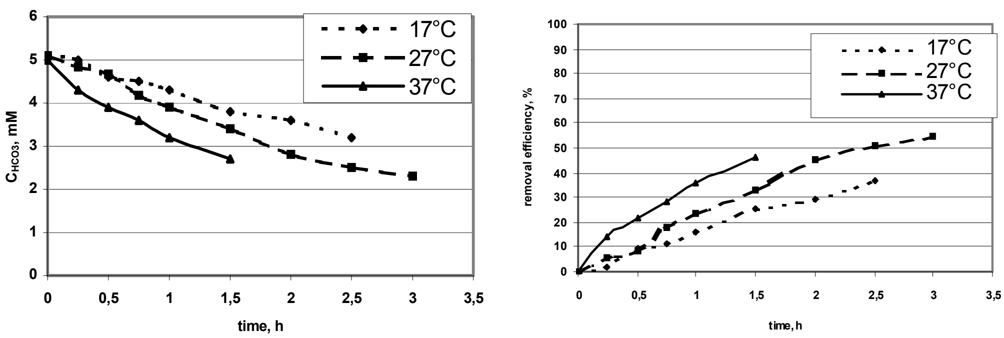


Fig. 8. Concentration decrease and removal efficiency of bicarbonates during Donnan dialysis at various temperatures (C_{NaCl} = 300 mM)

In order to estimate the salt leakage from the receiver to the feed, the total average flux of the removed anions was compared with the average flux of chlorides entering the feed. It was found that for any process studied (conducted at various salt concentration in the receiver and at various temperatures) the salt leakage did not occur. This confirms our previous studies on Donnan dialysis with the Selemion AMV membrane [8].

4. CONCLUSIONS

1. The salt (NaCl) concentration in the receiver has a significant effect on the flux of anions and their removal efficiency from the feed. With an increase in salt concentration, the flux of removed anions increases and the equilibrium concentration in the feed is set on a lower level. As a result, the process efficiency increases.

2. The flux of the removed anions and their removal efficiency depend on the size and on the charge of the ion. Nitrates and sulphates are transported at the highest rate from multi-component solution, whereas the transport of bicarbonates was twice as lower. The highest removal efficiency (at 17 °C), i.e., 91%, was obtained for sulphates, the efficiency of nitrate removal equalled 87% and the process of bicarbonate removal had the lowest efficiency – 37%.

3. The rise in a solution temperature (the feed and the receiver) does not affect significantly the efficiency of nitrate and sulphate removal from the feed, but it accelerates the transport rate of these anions: the average ion fluxes increase by 50–60% when the temperature rises from 17 to 37 °C.

4. The rate and efficiency of bicarbonate removal are considerably affected by the solution temperature. The average bicarbonate flux increases by over 90% and the efficiency of ion removal increases from 37% to 46%, when the solution temperature rises from 17 to 37 °C.

5. In the process of Donnan dialysis with the Selemion AMV membrane, the salt leakage (NaCl) from the receiver to the feed does not occur. This indicates that co-ions (i.e., sodium ions) are efficiently excluded by the ionic groups of the membrane.

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DIALIZA DONNANA – SKUTECZNA METODA USUWANIA UCIĄŻLIWYCH ANIONÓW Z WODY

Zastosowano dializę Donnana z membraną anionowymienną (Selemion AMV, Asahi Glass) do usuwania uciążliwych anionów (azotanów, siarczanów i wodorowęglanów) z wody. Zbadano wpływ wybranych parametrów na szybkość i skuteczność usuwania anionów. Zaobserwowano, że wzrost stężenia soli (NaCl) w roztworze odbierającym przyśpiesza proces wymiany jonów, a stężenie równowagowe usuwanego anionu w roztworze zasilającym jest niższe. Stwierdzono, że rodzaj usuwanego anionu ma duży wpływ na szybkość i skuteczność procesu: średni strumień azotanów i siarczanów jest ponad dwukrotnie większy od średniego strumienia wodorowęglanów. Z kolei najwyższą skuteczność uzyskano w procesie usuwania siarczanów (91%), podczas gdy skuteczność usuwania wodorowęglanów była najniższa i wynosiła 37%. Analizując wpływ temperatury na wymianę jonów w procesie dializy Donnana, stwierdzono, że w wyższej temperaturze roztworów (zasilającego i odbierającego) transport jonów jest szybszy: średni strumień azotanów i siarczanów rośnie o 50–60%, a strumień wodorowęglanów – o ponad 90% (gdy temperatura rośnie z 17 do 37 °C). Jednocześnie skuteczność usuwania wodorowęglanów wzrasta z 37 do 46%.