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Removal of bromide ions from an aqueous solution by Donnan dialysis with anion-exchange membranes

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ABSTRACT

The potential of Donnan dialysis to remove the bromide ions and associated ions (nitrates and bicarbonates) from a model solution was examined, using three anion-exchange membranes (AMEs) differing in their ion-exchange capacity and water content: Selemion AMV, Neosepta AFN and Neosepta ACS. Selemion AMV provided the most advantageous exchange of bromide ions for chloride ions and effectively limited co-ion transport, thus contributing to the lowest salt leakage into the feed observed in this study. The efficiency of bromide exchange ranged from 70 to 78% (for 500 μg Br^-/L) at a salt concentration in the receiver of 100 and 300 mM NaCl, respectively. Anion exchange with Neosepta AFN (characterized by a loose structure) proceeded at a faster rate and provided a slightly lower efficiency of bromide removal (68–70%). The a major advantage that Neosepta AFN offered was the short duration of the process (the time required for achieving minimal bromide concentration in the feed). Nonetheless, the loose membrane structure was responsible for the relatively high salt leakage into the feeding solution. The use of the monoanion-selective membrane Neosepta ACS brought about a concomitant decrease in the rate of anion removal, which extended the time required for obtaining a similar extent of bromide exchange (70–77%). It was observed with all the membranes examined that the rise in the initial concentration of bromides in the feed (from 200 to 1000 μg/L) enhanced the efficiency of their exchange for chloride ions.

Keywords: Bromide; Donnan dialysis; Anion-exchange membrane

1. Introduction

Chemical oxidation of water supplied for human consumption generates a number of disinfection by-products (DBPs), which have become a matter of growing public concern on account of the obvious health implications they carry. Ozonation of water containing bromide ions (Br^-) has the potential to induce the formation of carcinogenic bromate ions (BrO_3^-). The research conducted at the US EPA revealed that for an adult human consuming a 2 L daily portion of water containing 5 μg BrO_3^-/L, the

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Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain lifetime risk of developing a cancer disease is 10^{-4} [1,2]. In this context, the USA and the Member States of the European Union have set the permissible bromate concentration in drinking water to 10 μg/L [3,4]. When Br^- containing water is disinfected with chlorine or chloramines, the bromides enter into reaction with natural organic matter and undergo oxidation to form brominated trihalomethanes (THMs), as well as brominated haloacetic acids (HAAs). The literature contains many references indicating that brominated THMs and brominated HAAs are far more mutagenic and carcinogenic than chlorinated THMs and chlorinated HAAs, and thus pose a greater risk to human health than do their chlorinated analogues [5–7]. That is why the admissible THM concentrations for potable water have been set at 100 and 80 μg/L in the EU and the USA, respectively [3,4]. Moreover, US EPA lawfully regulates the content of five haloacetic acids (HAA5), whose overall concentration cannot exceed 60 μg/L [4].

Bromide ions, which are the precursors of brominated DBPs (bromo-DBPs), constitute a natural component of all types of water, specifically of ground- and surface waters in offshore areas. A natural source of origin for bromides derives from the contact of water with a substrate material (such as soil, where the bromide concentration typically approaches 1 mg Br^-/kg), and also from the intrusion of seawater or ocean water (where the bromide concentration amounts to approximately 65 mg Br^-/L) [8]. But there are also major anthropogenic sources of waterborne bromide ions, e.g. run-offs from roads salted in the winter season, or run-offs resulting from application of brominated pesticides on farmland. In surface water and groundwater, bromide concentrations vary from several to about 800 μg/L. In some instances, the bromide concentration may reach 2 mg/L (the Sea of Galilee, Israel), in others, especially during drought periods, even 4 mg/L (Crete) [8,9]. For those reasons, it is essential to remove the bromide ions from drinking water prior to disinfection to control the brominated DBPs that are being formed.

Among the methods of bromide removal from water, the process of aluminium chloride coagulation deserves particular attention [10]. With a coagulant dose of 15 mg/L, at a pH of raw water amounting to 6, bromides were removed with an efficiency of 87%, which, however, fell to 43% when the pH increased to 8. Attempts have also been made to remove bromides by nanofiltration, coagulation and the hybrid system coagulation–nanofiltration [11]. The results were not very promising, since the hybrid system alone provided bromide removal, which was low, totalling 16 and 18% for the alum coagulant and the ferrous sulphate coagulant, respectively. Efforts have also been reported to remove DBPs precursors by means of the magnetic anion-exchange resin MIEX® [12,13]. However, the extent of bromide removal obtained via this route was relatively low, ranging from 15 to 46%, and depended on the initial bromide concentration and alkalinity of the water being treated. The results of recent investigations reported from Florida [14] demonstrated that the type of the counterion in the MIEX® anion-exchange resin did not significantly affect the removal of bromides, which totalled 61 and 53% for fresh MIEX-HCO_3 and MIEX-Cl resins, respectively. Another finding of those studies was that after a dozen regenerations of the resins, the efficiency of bromide removal declined to about 25% with MIEX-HCO_3 and about 35% with MIEX-Cl.

In the study reported here, bromides were removed from water by the anion-exchange membrane (AME) separation process that is referred to in scientific literature as *Donnan dialysis* [15]. In this process, the AME separates two solutions: the feed (which contains undesired or harmful anions) and the receiver (which is an electrolyte where the driving salt, for example NaCl, occurs at a comparatively high concentration) (Fig. 1). As a result of the anion exchange between two solutions, the anions in the feed, which includes the bromides, are replaced with neutral ones, i.e. chlorides.

The aim of this work here was to investigate the efficiency of the Donnan dialysis process when used for the removal of bromides and associated ions (nitrates and bicarbonates) from aqueous solutions.

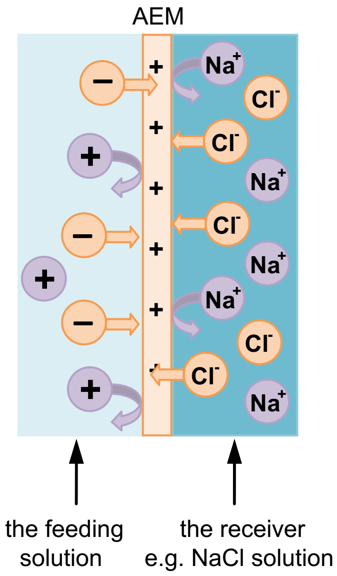

Fig. 1. Donnan dialysis with AEM.

Table 1
Major parameters of the AMEs used in the Donnan dialysis

Parameter	Membrane		
	Selemion AMV	Neosepta AFN	Neosepta ACS
Ion-exchange capacity, mmol/g dry membrane	1.85	2.15	1.72
Water content, %	18.9	47.3	21.7
Thickness, mm	0.11	0.12	0.15

The impact of some process parameters (type of AME, bromide ion concentration in the feed, and salt concentration in the receiver) on the efficiency of the process was considered.

2. Methods

The Donnan dialysis process was conducted using a laboratory dialytic set-up equipped with 20 cell pairs with AMEs, Selemion AMV (Asahi Glass), Neosepta ACS (Tokuyama Corp.) or Neosepta AFN (Tokuyama Corp.). The working area of the membranes was 0.140 m^2. The major parameters of the membranes are shown in Table 1.

The process was carried out with recirculation of the feed and the receiver until the minimum concentration of bromide ions in the feed was obtained. The volume ratio of the feed to the receiver was 4:1 (10 L:2.5 L). In our studies, we used the multi-component feeding solution containing 3 mM of NO_3^-, HCO_3^-, Cl^- and 200, 500 or 1,000 µg Br^-/L. The receiver used in the study was an NaCl solution of varying concentrations: 100, 200 or 300 mM.

Anion concentrations in the feed were measured in the course of the process. The concentration of nitrate and sulphate ions was determined using a DREL 2000 spectrophotometer. The concentration of bicarbonates and chlorides was measured by titration (with HCl and $AgNO_3$, respectively). Bromide concentration was determined using a DIONEX ICS 1000 ion chromatograph equipped with IONPAC AS9-HC analytical column.

3. Results and discussion

3.1. *Influence of membrane type on the efficiency of the process*

At the first stage of the study, we examined how the type of the AME affects the rate and efficiency of bromides and associated ions (nitrates and bicarbonates) removal from a feeding solution, where the Br^- concentration amounts to 500 µg/L. This concentration value corresponds with the values observed in Poland's surface waters, where they range between 400 and 700 µg Br^-/L [8]. The receiver was a 100 mM NaCl solution.

When the Donnan dialysis process was conducted with the Selemion AMV membrane, the efficiencies of bromide exchange and nitrate exchange for chloride ions (driving ions) were similar, amounting to 70 and 74%, respectively (Fig. 2). This is attributable to the size of the ions: the radius of hydrated Br^- amounts to 0.330 nm and does not very much differ from that of NO_3^- which is 0.335 nm [16]. On the other hand, HCO_3^-, which is characterized by the largest size among the investigated ions (0.394 nm), was removed with a relatively low efficiency (45.4%).

Simultaneously, differences were observed in the rate of anion transport across Selemion AMV from the feed to the receiver (Table 2). Thus, nitrates were exchanged for chloride ions at the fastest rate: up to the achievement of minimal bromide concentration in the feed, their flux averaged 0.123 mol/m^2 h. Owing to their large size which inhibits flow through the membrane, bicarbonates were removed at a noticeably slower rate: their flux was half that of nitrates. Bromides were transported at the slowest rate, despite the high efficiency of removal. It is essential to note, however, that the slow transport rate cannot be ascribed to the size of bromides. The underlying cause is the relatively low initial concentration of these ions, which is by nearly three orders of magnitude lower

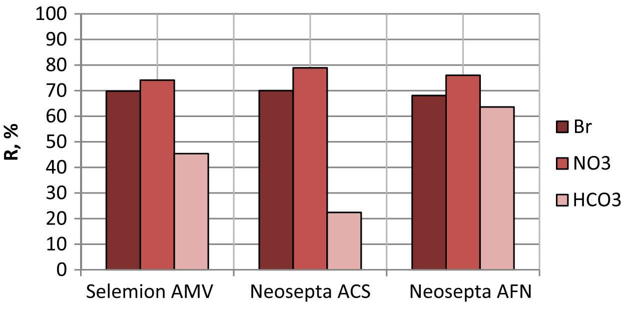

Fig. 2. Efficiency of anion removal from the feed (C_{Br} = 500 µg Br^-/L, C_{NaCl} = 100 mM).

Table 2
Average fluxes of ions transported from the feed to the membranes

Type of membrane	Duration of the process (h)	Average flux of anions (mol/m^2 h)		
		J_{Br}	J_{NO_3}	J_{HCO_3}
		0.214 10^{-3}	0.123	0.072
Neosepta ACS	3.5	0.140 10^{-3}	0.090	0.022
Neosepta AFN	0.75	0.420 10^{-3}	0.264	0.185

compared with the concentrations of the other two counterions (nitrates and bicarbonates). Consequently, the proportion of bromides in the overall flux of anions transported from the feed to the receiver is also low.

Anion exchange carried out with Neosepta ACS produced treatment effects differing from those achieved with Selemion AMV. Owing to the presence of a thin, highly cross-linked layer on its surface, Neosepta ACS possesses monoanion-selective properties [15]. This specific structure exerted an inhibiting effect on the flux of anions (particularly the large-sized ones) across the membrane. As a result, the values obtained for the average fluxes of counterions transferred from the feed to the receiver were significantly lower than those achieved with the standard AME Selemion AMV (Table 2). Hence, to achieve a minimal concentration of bromide ions in the feeding solution, it was necessary to extend the duration of the process (3.5 h). The compact surface layer of Neosepta ACS substantially limited the transport of large-sized anions, i.e. bicarbonates: both rate and efficiency of removal were noticeably lower as compared with the standard Selemion AMV membrane. Average ion flux took more than threefold lower values (Table 2), and the efficiency of HCO_3^- removal was as low as 22.4% (Fig. 2). A similar effect was noted with bromide ions: average flux across Neosepta ACS was observed to be 35% lower than the average flux across Selemion AMV. However, the extended duration of the process enabled the same efficiency of bromide ion removal to be achieved (70%). Owing to the low proportion of bicarbonate ions in the flux of counterions transported across Neosepta ACS to the receiver, the efficiency of nitrate removal was higher (78.9%) than in the case of Selemion AMV (74%).

The use of Neosepta AFN in the Donnan dialysis process provided the highest rate of counterion transport from the feed to the receiver, which is directly attributable to the short duration of the process (0.75 h). Yet, this was concomitant with a slight decrease in the efficiency of bromide ion removal (68%) as compared with Selemion AMV and Neosepta ACS (Fig. 2). Neosepta AFN is characterized by a high ion-exchange capacity and a high water content (Table 1), which accelerates and facilitates counterion transport for the ionic groups of the membrane. The loose structure of Neosepta AFN enables fluxes not only of anions with a small hydrated radius (bromides, nitrates), but also of large-sized anions (bicarbonates). A comparison of the results obtained with the three membranes examined makes it clear that Donnan dialysis involving Neosepta AFN provided the highest HCO_3^- ion flux (Table 2) and the highest efficiency of HCO_3^- ion removal (63.6%, Fig. 2), whereas bromides were removed with a slightly reduced efficiency. The latter should be attributed to the enhanced transport of anions dominating in the feed (and this includes bicarbonates), which is a limiting factor in the exchange of bromide ions for chloride ions.

3.2. Influence of salt concentration in the receiver on the efficiency of the process

The second stage of the study was focused upon determining the impacts of driving ion concentrations in the receiver on the efficiencies of counterion removal from the feed.

We observed that in the processes with Selemion AMV, the increase in salt concentration in the receiver was paralleled by the decrease in the final concentration of anions removed from the feed, which indicated an enhancement in the exchange of these anions for chloride ions. When the NaCl concentration increased from 100 to 300 mM, the removal efficiency rose from 70 to 78% for bromides, from 74 to 83% for nitrates and from 45 to 47% for bicarbonates (Fig. 3). The underlying cause was the rise in the concentration gradient of driving ions (chlorides), which enhanced the chloride ion flux from the receiver to the feeding solution. An appropriately high flux of counterions

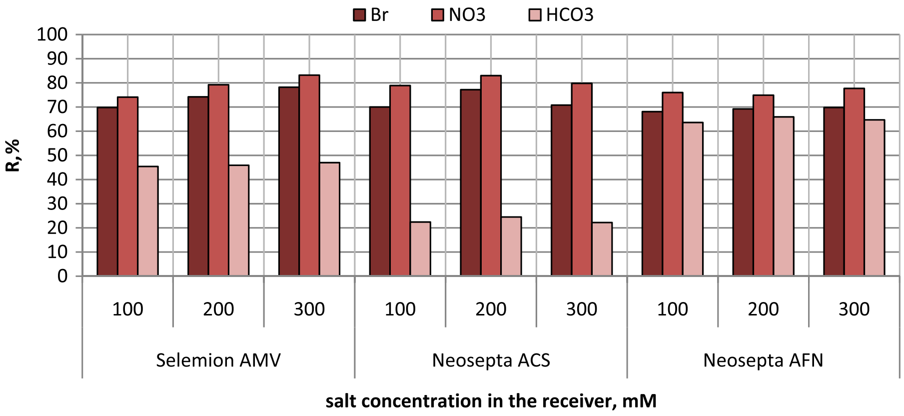

Fig. 3. Efficiency of anion removal from the feed at various salt concentrations in the receiver ($C_{\mathrm{Br}} = 500\,\mu\mathrm{g/L}$).

removed from the feed to the receiver was then formed to maintain the electroneutrality of the solutions. It is essential to notice that the high Cl^- concentration gradient enables the transport of bromides and associated ions to the receiver against their increasing concentration gradient (with the progress of the process). And this suggests the possibility that at an increased salt concentration in the receiver, the final concentration of the anions being removed will decline.

The analysis of salt concentration impact on the anion exchange efficiency observed with Neosepta ACS and AFN demonstrated that the rise in the gradient of driving ion concentration in the receiver did not significantly improve the efficiency of the process. In Donnan dialysis with Neosepta ACS, the rise in NaCl concentration from 100 to 200 mM increased the removal of bromides from 70 to 77%. At the highest salt concentration (300 mM), the efficiency of exchange was only 71%. Similar relations were obtained with associated ions, nitrates and bicarbonates. The explanation for the limited impact of salt concentration in the receiver on the removal of anions from the feed lies in the compact surface structure of Neosepta ACS, which exerts an inhibiting effect on the transport of driving ions (chlorides). Also in the anion exchange process involving Neosepta AFN did the rise in salt concentration from 100 to 300 mM only slightly upgrade the efficiency of removal, which increased from 68 to 70% for bromides, from 76 to 78% for nitrates and from 64 to 65% for bicarbonates. The contributing factor in the poor improvement was the loose structure of Neosepta AFN, which enabled the occurrence of high fluxes of driving ions to the feed and of anions being removed to the receiver, even at the lowest NaCl concentration (100 mM). Thus, in the process with Neosepta AFN, any further rise in the gradient of chloride ion concentration contributes solely to an insignificant increase in the flux of counterions and in the efficiency of their removal from the feed.

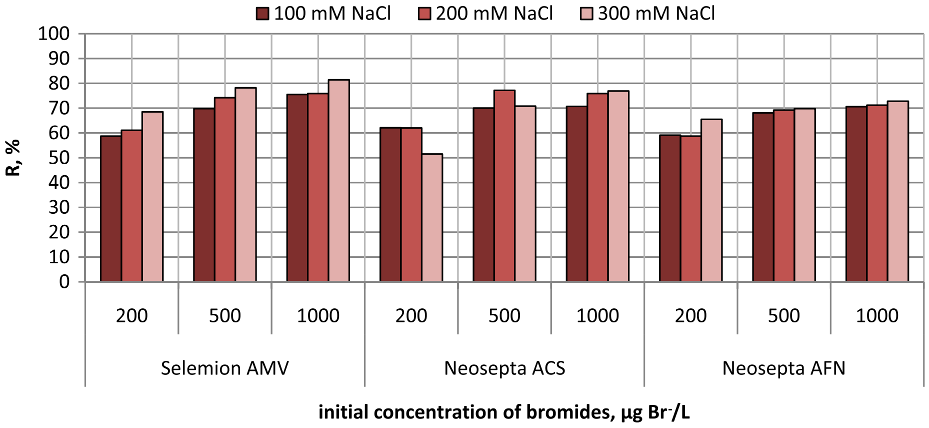

Fig. 4. Efficiencies of bromide ion removal from the feed at various initial concentrations of bromides (200, 500 and 1,000 µg Br^-/L) and various salt concentrations in the receiver (100, 200 and 300 mM NaCl).

Table 3
Salt leakage from the receiver to the feeding solution over the investigated range of bromide ion concentrations (200–1,000 μg/L) in Donnan dialysis with different AMEs and salt concentrations in the receiver

Membrane	NaCl leakage (mol/m^2 h) at salt concentration in the receiver:		
	100 mM	200 mM	300 mM
Selemion AMV	0	0.017–0.034	0.014–0.072
Neosepta ACS	0	0–0.072	0.065–0.170
Neosepta AFN	0–0.050	0.139–0.253	0.321–0.602

3.3. Influence of initial bromide concentration on the efficiency of the process

Since in natural water the bromides occur at diverse concentrations, it seemed worthy of analysing how the concentration of bromide ions in the feed affects the efficiency of their removal in the Donnan dialysis process. It was found that irrespective of the membrane used (Selemion AMV, Neosepta ACS or Neosepta AFN), the increase in the initial concentration of bromides was concomitant with the increase in the efficiency of their exchange for chloride ions (Fig. 4). At the lowest salt concentration in the receiver (100 mM), the rise in the initial concentration of bromides from 200 to 1,000 μg Br$^-$/L augmented the extent of their removal from 59 to 75% with Selemion AMV, from 62 to 71% with Neosepta ACS and from 59 to 71% with Neosepta AFN. At the highest NaCl concentration in the receiver (300 mM), and at the rise in initial bromide concentration from 200 to 1,000 μg Br$^-$/L, the exchange of bromide ions for chloride ions increased from 68 to 81% (Selemion AMV), from 51 to 77% (Neosepta ACS) and from 65 to 73% (Neosepta AFN). The improvement of process efficiency is to be attributed to the higher proportion of bromide ions in the overall quantity of anions in the feeding solution, which in turn heightens the proportion of these ions in the overall flux of counterions transported from the feed to the receiver.

3.4. Assessment of the properties of AMEs in the removal of bromide ions

A comparison of the bromide ion removal efficiencies obtained by the Donnan dialysis with various AMEs has revealed that the type of membrane used does not significantly affect the exchange of bromides for chloride ions. At a salt concentration of 100 mM in the receiver, the efficiency of Br$^-$ removal with the investigated membranes ranged from 59 to 62% (200 μg Br$^-$/L), from 68 to 70% (500 μg Br$^-$/L) and from 71 to 75% (1,000 μg Br$^-$/L). But as already mentioned, differences occurred in the rate of bromide ion transport, which is directly linked with the time of the process required for achieving the minimal Br$^-$ concentration in the feeding solution. This time equals 0.75 h for Neosepta AFN, 1.5 h for Selemion AMV and 3.5 h for Neosepta ACS. When analysing the properties of AMEs with regard to bromide ion removal from a model solution, it is necessary to take into account the extent of NaCl leakage from the receiver to the feed (Table 3). The highest salt leakage was observed with Neosepta AFN. This is to be attributed to the loose structure of this membrane, which facilitates the transport of co-ions (Na$^+$ ions) from the receiver to the feeding solution. In this way not only chloride anions but also sodium cations enter the solution being treated, contributing to a rise in salinity. Selemion AMV and Neosepta ACS have more compact structures (as indicated by the low water content of both the membranes, Table 1), which limits the co-ion flux from the receiver.

In sum, among the membranes examined, Selemion AMV provided the best treatment effects in Donnan dialysis: a highly efficient exchange of bromides for chloride ions at a relatively low salt leakage from the receiver to the feeding solution.

4. Conclusions

- Selemion AMV displays the most advantageous properties in the exchange of bromides for chloride ions. With this membrane the efficiency of bromide removal varied from 59 to 75% at a comparatively low salt concentration in the receiver amounting to 100 mM NaCl. The increase in NaCl concentration to 300 mM enhanced the efficiency of bromide removal, which ranged between 68 and 81%. Selemion AMV also provided the lowest salt leakage from the receiver to the solution being treated.
- In the anion-exchange process involving Neosepta AFN, which is a membrane with a loose structure, anions are removed from the solution at a rate twice to three times as high as the rates observed with the other membranes, and at a relatively high salt leakage from the receiver to the feed. On account of an enhanced HCO_3^- ion flux, a lower

efficiency of bromide ion removal was obtained (compared with Selemion AMV), which varied from 59 to 71% (at NaCl concentration in the receiver of 100 mM). Further increase in NaCl concentration only slightly improved the exchange of bromides for chloride ions.

- When the anion-exchange process involves Neosepta ACS, a membrane with a compact surface structure, the rate of anion removal from the solution decreases twofold to threefold, which requires that the duration of the process should be extended (3.5 h), as compared with Selemion AMV (1.5 h) and Neosepta AFN (0.75 h). The efficiency of bromide ion removal in this process varied between 62 and 71% at an NaCl concentration in the receiver of 100 mM.

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