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Removal of harmful anions from water in the anion-exchange membrane process

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ABSTRACT

When water contains bromide ions (Br^-), ozonation favours the formation of bromates (BrO_3^-) classified as ions with carcinogenic implications for human organisms. The permissible concentration of bromates in drinking water for the European Union and United States is now 10 μg/l. We proposed the anion-exchange membrane separation process referred to in the literature as Donnan dialysis for the removal of bromides or bromates from water. As a result of anion exchange between two solutions separated with an anion-exchange membrane, harmful anions are replaced with neutral ones, i.e., chlorides. The process was performed in a laboratory dialytic set-up comprising 20 cell pairs with anion-exchange membranes, Selemion AMV or Neosepta ACS. The feed was natural water enriched with bromides (500 μg/l) or bromates (100 μg/l); the receiver was an NaCl solution (100 mM). As for bromides, Selemion AMV and Neosepta ACS provided similar removal efficiency: 86% and 90%, respectively. As for the other anions, removal efficiency depended on the membrane type. With Selemion AMV, sulphate and bicarbonate removal totaled 76% and 70%, respectively; with Neosepta ACS, sulphate ions were rejected almost entirely (removal efficiency, 3%), and bicarbonates were rejected partly (removal efficiency, 43% and below). The process is also an efficient method of bromate removal. With both membranes the exchange of bromates was high (93% (AMV) and 97% (ACS)). The exchange of associated anions (sulphates and bicarbonates) depended on the membrane type. Upon termination of the process, the concentration of bromates was reduced to a level much below 10 μg/l.

Keywords: Bromide; Bromate; Bicarbonate; Sulphate; Donnan dialysis; Anion-exchange; Anion-exchange membrane

1. Introduction

Bromide ions are ubiquitous both in surface water and groundwater, where their concentrations were found to range between several and approx. 800 μg/l, although in some instances they reached a level as high as 2 mg/l (e.g., in the Sea of Galilee, Israel) [1]. Bromides come from natural sources (contact of the water with the water base material; intrusion of sea water, where bromide concentration approaches 65 mg/l) and anthropogenic sources (run-off from road salting in the winter season; run-off from agricultural operations entailing brominated pesticides). There is evidence that the presence of bromides in drinking water has no implications for human health [2]; but if the water being disinfected by chlorination contains bromides, this leads to the formation of harmful disinfection by-products (DBP). During water disinfection with chlorine, bromides undergo oxidation to hypobromous acid (HOBr), which reacts with natural organic matter (NOM) to form brominated trihalomethanes (THM) [1]. Being even more harmful than their chlorinated analogues, brominated THM have obvious

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carcinogenic implications for human organisms. That is why their permissible concentrations defined for potable water in the European Union and the United States are very strict [2].

If use is made of ozone for water disinfection, the bromides that are present in the water oxidize to form hypobromite ions (OBr^-), which are further oxidized to form bromates (BrO_3^-) [3]. The research conducted by the US EPA has revealed that for an adult human who consumes everyday 2 l of potable water containing 5 μg of BrO_3^- per litre, the lifetime risk of developing cancer is 10^{-4} [4,5]. As a result, the permissible concentration of bromates for drinking water in the USA and the EU Member States is now 10 μg/l [5]. The same value has recently been recommended by the World Health Organization [6].

These data corroborate the necessity of removing either bromide ions (as harmful DBP precursors) or bromate ions from the water that serves for drinking purposes. The literature contains many references to the methods used for bromide removal. Of these, the process of aluminium chloride coagulation deserves particular mention. With an aluminium chloride coagulant dose of 15 mg/l, Ge et al. removed bromides from raw water (which additionally contained humic acids) with the efficiency of 87%. They have, however, made the observation that the presence of humic acids reduces the efficiency of bromide removal [7]. Boyer and Singer tested a magnetic ion-exchange resin (MIEX®) for the removal of DBP precursors (NOM and bromides) [8]. They have concluded that even though the potential of THM formation was remarkably reduced, the concentration of Br^- ions decreased only slightly (from 240 to 200 μg/l). The efficiency of nanofiltration in removing NOM and bromides from water was examined by Chellam [9], who found that the promising NOM removal was paralleled by a poor retention of bromides, which ranged between 3 and 10%. In consequence, the concentrations of brominated THM in the water being chlorinated increased.

Of the various methods by which bromates are removed from drinking water, adsorption onto granular activated carbon (GAC) has come to the forefront [10,11]. It has, however, been observed that the efficiency of the process decreased notably during the transition of the fresh GAC to the biologically active carbon (BAC), which considerably reduced the quantity of the functional groups available on the carbon surface [10]. It has furthermore been observed that the reduction of bromates decreased due to NOM adsorption onto the carbon surface [11].

The efficiency of bromate removal achieved with other methods reported in the literature was less promising. In the process of aluminum sulphate coagulation, bromates were removed from water with 26% efficiency at a comparatively high coagulant dose (100 mg/l) [12]. The extent of bromate removal attained in the process of UV irradiation was solely 19% [13]. The highest removal efficiencies for bromates were achieved using membrane processes. With electrodialysis reversal and reverse osmosis the extent of removal amounted to 64% and 96% [14]. It is essential to note, however, that the concomitant high degree of desalination is a drawback to both the processes when the mineralization of the water being treated is low.

In the study reported on here bromides and bromates were removed from water by the anion-exchange membrane separation process referred to in scientific literature as Donnan dialysis [15]. In this process the anion-exchange membrane 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 comparatively high concentration). As a result of the anion exchange between two solutions, the anions in the feed, which includes bromides or bromates, are replaced with neutral ones, i.e., chlorides.

Donnan dialysis with anion-exchange membrane is used mostly for the removal of harmful anions, such as fluorides and nitrates from drinking water. It was proved, that Donnan dialysis enabled the efficient removal of fluorides [16] and nitrates [17] from water. As a result of the process, the concentration of these ions was lowered below the values allowed in the drinking water. The process was also applied for the removal of troublesome anions (sulfates and bicarbonates) from water before electrodialytic desalination [18]. It was observed that the changed ionic composition of the solution brought about the increase of the salt flux during electrodialysis and reduced energy consumption for the salt transport.

2. Methods

The Donnan dialysis process was conducted using a laboratory dialytic set-up equipped with 20 cell pairs with anion-exchange membranes, Selemion AMV (Asahi Glass) or Neosepta ACS (Tokuyama Corp.). Major parameters of the membranes are listed in Table 1.

Table 1
Selected parameters of the anion-exchange membranes used in Donnan dialysis

Parameter	Membrane	
	AMV	ACS
Ion-exchange capacity, mmol/g	1.85	1.40
Water content, %	19.9	20.0
Thickness, mm	0.11	0.15

The working area of the membrane was 0.140 m^2. The process was performed with recirculation of the feed and the receiver until the equilibrium concentration of bromide (or bromate) ions in the feed was attained. The volume ratio of the feed to the receiver was 4:1 (10 l : 2.5 l).

The feed was natural water enriched with bromide or bromate salt, where total anion concentration, bromide ion concentration and bromate ion concentration amounted to 3.7 mM, 500 μg/l and 100 μg/l, respectively. The receiver was an NaCl solution of a concentration of 100 mM.

Anion concentrations in the feed were measured in the course of the process. The concentration of nitrate ions was determined using a DREL 2000 spectrophotometer. The concentration of bicarbonates and chlorides was established by titration (with HCl and $AgNO_3$, respectively). Bromide ion concentration was measured using a DIONEX ICS 1000 ion-chromatograph equipped with IONPAC AS9-HC analytical column. Bromate concentration was determined photometrically with 3,3′-dimethylnaftidin and iodine [19], using a UV mini 1240 spectrophotometer (Shimadzu) and 50 mm glass cuvettes. Sample absorbance was measured at the wavelength of 550 nm.

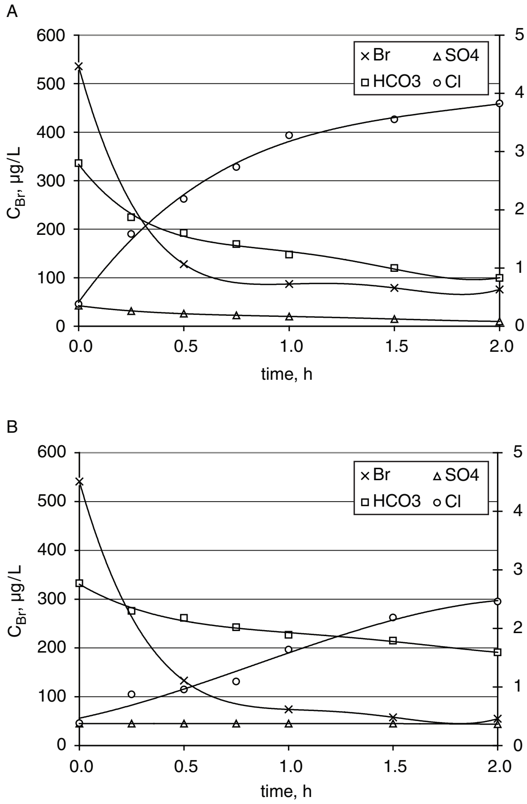

Fig. 1. Anion exchange in water containing bromides when use is made of Selemion AMV (A) and Neosepta ACS (B).

3. Results

3.1. Removal of bromides from water

The course and efficiency of the anion-exchange process involving the two membrane types are depicted in Figs.1 and 2. As can be seen, there is only a slight difference in the extent of bromide removal between Selemion AMV and Neosepta ACS (86 and 90%, respectively). This does not hold true, however, for the removal of the associated anions.

In the process with the Selemion AMV membrane, sulphates and bicarbonates were exchanged for chloride ions with the efficiency of 76 and 70%, respectively, whereas in the process with the Neosepta ACS membrane, SO_4^{2-} ions were retained in the water almost completely (97%), so their exchange for chloride ions approached 3%. Neosepta ACS was also found to largely limit the transport of bicarbonates, which were exchanged for chloride ions with the efficiency of 43%.

The compact surface structure of Neosepta ACS also influenced the ion removal rate. The average fluxes of the anions being removed by the two anion-exchange membranes (until the bromide ions in the feed achieved the minimal concentration) are compiled in Table 2. As shown by these values, the rate of anion removal from water depends largely on the membrane structure. Sulphates and bicarbonates are ions of similar size, as can be inferred from the radius of the hydrated SO_4^{2-} ion and that of the HCO_3^- ion amounting to 0.379 nm and 0.394 nm, respectively [20]. The compact structure of the Neosepta ACS surface visibly limits the flux of the ions mentioned, so their exchange for chloride ions is far less effective than when use is made of Selemion AMV. The above effect slightly increases the rate of bromide ion transport across the Neosepta ACS membrane.

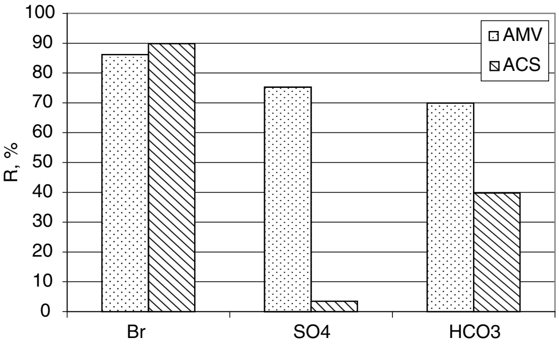

Fig. 2. Removal of bromides and associated anions from water during processes involving different anion-exchange membranes.

Table 2
Average fluxes of bromides and associated anions across the two membranes tested

Membrane	J_{Br}	J_{SO_4}	J_{HCO_3}
	mol/m^{2}h		
Selemion AMV	0.209×10^{-3}	0.010	0.073
Neosepta ACS	0.219×10^{-3}	0.002	0.048

As can be inferred from the data in Table 2, the flux of Br^- ions across the anion-exchange membrane is several times weaker than the flux of HCO_3^- ions. Nevertheless, this finding cannot be attributed to the size of the ion; with its radius of 0.330 nm, the hydrated bromide ion is the smallest among the anions that occur in the water being analyzed [20]. The slow rate of the transport of bromides is due to their very low concentration in the water (by three orders of magnitude lower as compared to the concentration of bicarbonates), and that is why the proportion of bromides in the flux of the counterions transported from the feed to the receiver is low.

3.2. Removal of bromates

Fig. 3 depicts the variations of anion concentrations in natural water containing bromate ions. When Donnan dialysis was carried out with Selemion AMV, the efficiency with which the anions were exchanged for chloride ions was very high: 93% for bromates and sulphates, and 80% for bicarbonates (Fig. 4).

When use was made of Neosepta ACS, the retention of sulphates was almost complete (97%), which means that their exchange for chloride ions was very poor (3%). HCO_3^- ions reached a higher extent of exchange for Cl^- ions (47%), as they were retained by the membrane only partly (Fig. 4). It was due to the significantly limited transport of the associated anions (SO_4^{2-}, HCO_3^-) across Neosepta ACS that the exchange of bromates for chlorides with this membrane was more efficient than with Selemion AMV (97% and 93%, respectively). It is essential to note that upon termination of the process with either of the two membranes the concentrations of bromates in the treated water were reduced to values lower than 10 μg/L, which is the permissible value established for potable water.

The structure of the membranes tested had also a strong influence on the rate of anion removal from water. The compact surface structure of Neosepta ACS slowed down significantly the flux of large ions (Table 3), and consequently reduced the efficiency of exchange (particularly that of sulphates) for chloride ions. At the same time, the limited flux of large ions was the underlying cause of the rise in the flux of the bromate ions, which is indicative of an increase in the efficiency of their removal (Fig. 4).

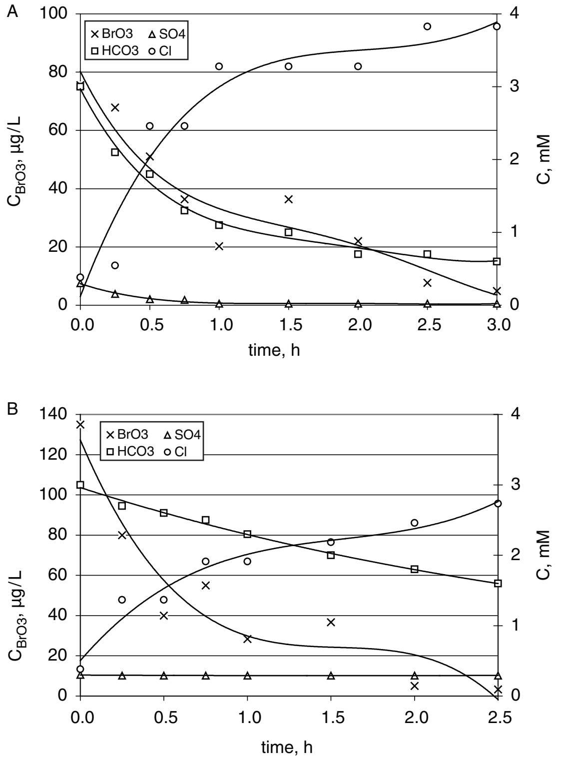

Fig. 3. Anion exchange in bromate containing water, obtained with Selemion AMV (A) and Neosepta ACS (B).

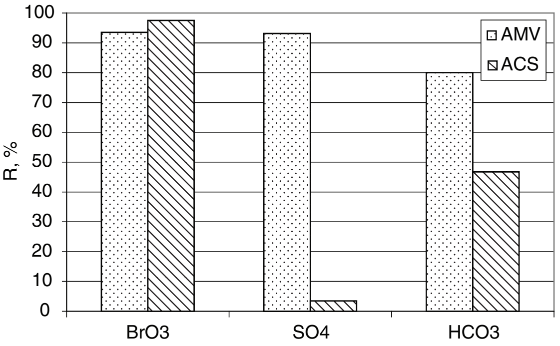

Fig. 4. Removal of bromates and associated anions from water during processes involving different anion-exchange membranes.

Bromate flux across the anion-exchange membrane (Selemion AMV or Neosepta ACS) is by an order of magnitude smaller than bromide flux. This should be attributed to a larger size of the bromate ion, as the radius of the hydrated BrO_3^- amounts to 0.351 nm, while that of the hydrated Br^- ion – to 0.330 nm [20]. Furthermore, the initial concentration of bromates in the water was one-fifth the initial concentration of bromides, so the proportion of bromates in the flux of the anions transported from the feed to the receiver was lower accordingly.

Table 3
Average flux of bromates and associated anions across the two membranes tested

Membrane	J_{BrO_3}	J_{SO_4}	J_{HCO_3}
	mol/m²h		
Selemion AMV	0.013×10^{-3}	0.020	0.057
Neosepta ACS	0.029×10^{-3}	0.0005	0.041

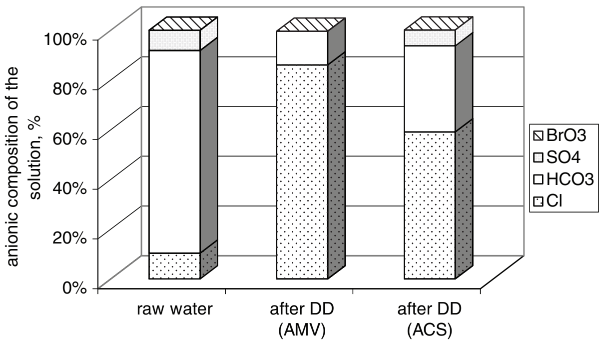

Fig. 5. Ionic composition of raw water and water after anion-exchange with Selemion AMV and Neosepta ACS.

The exchange of anions between the receiver and the solution accounts for the change in the ionic composition of the water being treated. The data in Fig. 5 demonstrate that the Cl^- ion is the main anion in the water treated by Donnan dialysis with an anion-exchange membrane. The proportion of the Cl^- ion in the total amount of anions depends on the type of the anion-exchange membrane used. Thus, when Donnan dialysis is conducted with a standard anion-exchange membrane (Selemion AMV), this proportion is large (84.8 %), owing to the high efficiency of anion-exchange in this process. In the Donnan dialysis process, however, where use is made of a mono-anion-selective membrane (Neosepta ACS), the proportion of the Cl^- ion is noticeably smaller (58.3%), which is attributable to the much poorer exchange of the anions for chloride ions.

4. Conclusions

1. The anion-exchange membrane separation process is an efficient method for the removal of bromide ions or bromate ions from water. The type of the anion-exchange membrane does not significantly affect the removal of bromide or bromate ions, but its influence on the removal of the associated anions is considerable.
2. The anion-exchange process conducted with the Selemion AMV membrane provides efficient removal of bromides or bromates (86% and 93%, respectively) at a relatively low NaCl concentration in the receiver (100 mM). There is a concomitant exchange of other anions (sulphates and bicarbonates) for chloride ions.
3. Compared to the anion-exchange process with Selemion AMV, the process entailing Neosepta ACS provides a higher efficiency of bromide or bromate removal (90% and 97%, respectively) at high retention of the associated anions, specifically sulphates.
4. Regardless of whether the anion-exchange process is performed with the Selemion AMV or Neosepta ACS membrane, the concentration of carcinogenic bromates can be reduced to a level below the permissible value established for potable water (10 μg/l).

Acknowledgements

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