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Removal of bromate and associated anions from water by Donnan dialysis with anion-exchange membrane

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ABSTRACT

Ozone is considered as a strongest oxidizer and disinfectant applied in drinking water treatment. If the water to be ozonated contains bromides, this will lead to the formation of bromates, ions with potential carcinogenic implications to human organisms. We proposed Donnan dialysis process with an anion-exchange membrane to remove bromate ions from water. The rate and efficiency of anion removal (BrO_3^-, SO_4^{2-}, HCO_3^-) from the natural water were examined with the use of two types of anion-exchange membranes: Selemion AMV and Neosepta ACS and with the use of varying salt concentration in the receiver: 50, 100 or 200 mM NaCl. Bromate ions were removed from natural water with 90% efficiency in the process with the Neosepta ACS (of a highly cross-linked surface layer) when salt concentration in the receiver equalled 100 mM NaCl. The application of the Selemion AMV yielded similar efficiency of bromate removal (94%) but NaCl concentration in the receiver had to be twice as high as with Neosepta ACS (200 mM). However, Neosepta ACS rejected bicarbonates ranged between 35 and 53% and almost entirely rejected sulphates (in 97%). In turn, the Selemion AMV enabled flow of sulphates (93% of removal) and bicarbonates (ranged from 60 to 87% of removal).

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

1. Introduction

In many countries ozone is widely used for drinking water disinfection [1]. The growing interest in ozone as a water disinfectant is attributable to its capacity for limiting the formation of some halogen disinfection by-products and for deactivating some of the microorganisms that are resistant to chlorine (e.g., *Cryptosporidium parvum*) [2]. However, during ozonation one of the natural water components, namely bromides (Br^-), undergoes oxidation to form bromates (BrO_3^-), which have potential carcinogenic implications to human organisms [1–3].

The concentration of bromate ions in the water after ozonation depends on the concentration of bromide ions in the raw water. Tyrovola and Diamadopoulos [3] have observed that at a low initial concentration of Br^- ions, 160 μg/dm^3, the concentration of bromates in the ozonated water may exceed 30 μg/dm^3 (at ozone dose and contact time sufficient for providing minimum 99% deactivation of *Cryptosporidium oocytes*). They also found that when the concentration of bromides in raw water was high, approaching 600 μg/dm^3, the concentration of bromates in ozonated water might be as high as 80 μg/dm^3.

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The simplified reactions presented below describe the formation of bromates during ozonation [1]:

$$O_3 + Br^- \rightarrow O_2 + OBr^-$$

$$O_3 + OBr^- \rightarrow 2O_2 + Br^-$$

$$2O_3 + OBr^- \rightarrow 2O_2 + BrO_3^-$$

In the presence of ozone, bromide (Br^-) oxidizes to form the hypobromite ion (OBr^-). Hypobromite is further oxidized to form bromate (BrO_3^-).

Based on the US EPA report, Wagner et al. inform that the risk of developing a cancer disease is 10^{-4} and 10^{-5} when the concentration of bromates in drinking water totals 5 µg/dm^3 and 0.5 µg/dm^3, respectively [4]. This means that among those who consume 2 dm^3/d of potable water where bromates occur at the two concentrations mentioned, one consumer out of 10,000 and 100,000, respectively, will probably develop cancer [5]. That is why the permissible concentration of bromates in drinking water established for the European Union and the United States is now 10 µg/dm^3 [6]. The same value has recently been defined as permissible also by the World Health Organization [7].

Amongst the various methods for bromate removal from water after ozonation, preference is given to adsorption onto granular activated carbon (GAC) [8–11]. It has been reported [8] that in the adsorption process, on the GAC surface, the BrO_3^- ion was reduced to the OBr^- ion and then to the Br^- ion. The efficiency of reduction, which initially exceeded 60%, deteriorated over time, owing to the gradual transformation of the GAC bed into a biological activated carbon (BAC) bed, and on the BAC bed bromates were not reduced to bromides [8].

Investigations have also been reported into the applicability of other processes to the removal of bromates from water. Thus, during alum coagulation bromates were removed with the efficiency of 26% at a relatively high coagulant dose, which equalled 100 mg/dm^3 [12]. UV irradiation produced bromate removal of 19% at UV fluence ten times as high as the UV fluence for drinking water disinfection [13]. The application of some membrane processes for bromate removal was found to be promising. In reverse osmosis bromate retention reached 96%, although in electrodialysis reversal the efficiency of bromate removal was 64% [14]. It is essential to note that in reverse osmosis and electrodialysis processes dissolved salts are removed with high efficiency (98%), which, however, is not desirable when water mineralization is low.

The aim of our study was to use Donnan dialysis with anion-exchange membranes for the removal of bromates from water. In the Donnan dialysis process, the anion-exchange membrane separates two solutions: the feed (containing anions that have to be removed) and the receiver (an electrolyte with relatively high concentration of the driving anion, e.g., NaCl). The driving force of the process is the chemical potential gradient of the components on both sides of the membrane. The gradient of the chemical potential induces counter-ion (anion) flow from the receiver to the feed. In order to maintain the electroneutrality of both solutions, an equal amount of counter-ions is transported in the opposite direction, from the feed to the receiver (Fig. 1). Since the anion-exchange membrane prevents the flow of co-ions (cations), the ionic composition of the water undergoes changes; the previously troublesome anions (e.g., bromates) are replaced with neutral anions from the receiver (e.g., chlorides) [15]:

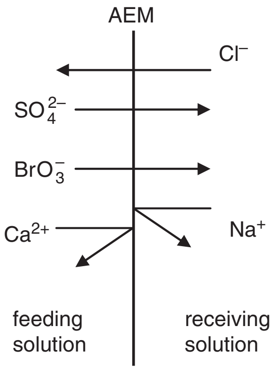

Fig. 1. Donnan dialysis with anion-exchange membrane (AEM).

In this paper, the authors demonstrated how the type of anion-exchange membrane and the varying salt concentration in the receiver influence the efficiency and rate with which bromate and associated anions are removed from natural water of low mineralization in the Donnan dialysis process.

2. Methods

The Donnan dialysis process was conducted in a laboratory dialytic set-up equipped with 20 cell pairs with anion-exchange membranes separated by spacers (thickness of the spacer was 0.5 mm). The working area of the membranes was 0.140 m^2. Two types of AEMs were examined: Selemion AMV and Neosepta ACS. Table 1 includes the major parameters of the anion-exchange membranes used in our experiments.

The process was conducted with recirculation of both solutions (feed and receiver) until the equilibrium concentration of bromate ions in the feeding solution was obtained. The volume ratio of the feed and the receiver was 4:1 (10 dm^3: 2.5 dm^3). The feed was natural water (pH = 5.6, conductivity = 106 µS/cm, 3 mM HCO_3^-, 0.38 mM Cl^-, 0.3 mM SO_4^{2-}) enriched with $NaBrO_3$ (the concentration of bromate ions amounting to 200 µg BrO_3^-/dm^3). The receiver used in the experiments was an NaCl solution of varying concentration: 50, 100 or 200 mM.

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

Parameter	Membrane	
	AMV [16]	ACS [17]
Ion-exchange capacity, mmol/g dry membrane	1.85	1.40
Water content, %	19.9	20.0
Thickness, mm	0.11	0.15

During Donnan dialysis anion concentrations were measured in the feed. The concentration of bicarbonates and chlorides was measured by titration with HCl and $AgNO_3$, respectively. The concentration of sulphate ions was determined using a DREL 2000 spectrophotometer. Bromate concentration was measured photometrically using 3,3′-dimethylnaftidin and iodine with a UV mini 1240 spectrophotometer (Shimadzu) and 50 mm glass cuvettes [18]. Sample absorbance was measured at the wavelength of 550 nm. Each ion concentration was measured twice. The mean measurement error did not exceed 10%.

3. Results and discussion

Fig. 2 shows the efficiency of bromate removal from natural water at various NaCl concentrations in the receiving solution.

It was observed that when the Donnan dialysis process involved Selemion AMV, the increase in salt concentration in the receiver accounted for a gradual rise in the efficiency of bromate removal from the feeding solution. As shown by the bars in Fig. 2, bromate ions were removed with the efficiency of 68.8% (the final bromate concentration in the treated water was 58.9 µg BrO_3^-/dm^3) at the salt concentration in the receiver of 50 mM NaCl. When salt concentration increased to 200 mM NaCl, the efficiency of bromate ion removal rose to 94% (13.3 µg BrO_3^-/dm^3).

During Donnan dialysis with Neosepta ACS the greatest differences in bromate removal efficiency were observed when salt concentration in the receiver rose from 50 to 100 mM NaCl. With an NaCl concentration of 50 mM, the efficiency of bromate removal amounted to 74.7%, and rose to the value of 90%, when salt concentration was increased to 100 mM. It means that final bromate concentration in the treated water was reduced to 53.7 µg BrO_3^-/dm^3 and 15.8 µg BrO_3^-/dm^3, respectively. Further increase in salt concentration did not significantly change the efficiency of the process. Hence there is no need to increase the salt concentration in the receiver to 200 mM NaCl, when use is made of Neosepta ACS, because similar effects can be obtained using a receiving solution with a lower salt concentration (100 mM NaCl). It is worth noting that the results of our research are comparable with those obtained by Matos at all [19]. In the ion exchange membrane bioreactor (ICMB) with ACS membrane, they decreased bromate concentration in the treated water below 20 µg BrO_3^-/dm^3 (at the initial concentration equal to 200 µg BrO_3^-/dm^3).

The rate of bromate ion removal from the feeding solution was found to be slightly higher for Neosepta ACS than Selemion AMV (Fig. 3). The average flux of bromate ions (for attaining the equilibrium concentration of this ion in the feed) approached 0.029×10^{-3} and 0.032×10^{-3} mol/m²h, for Selemion AMV and Neosepta ACS, respectively (at NaCl concentration of 100 mM). The rate of bromate removal influenced the duration of the process. Thus, a longer time was required to achieve

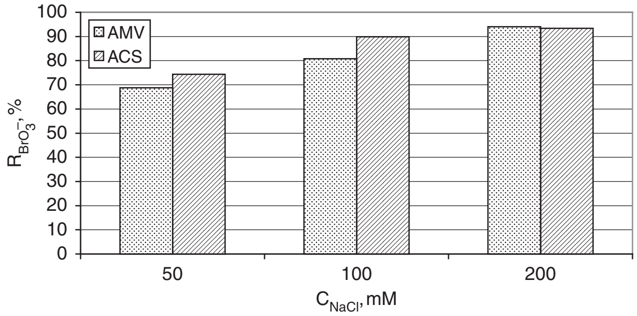

Fig. 2. Efficiency of bromate removal from natural water at various NaCl concentrations in the receiver.

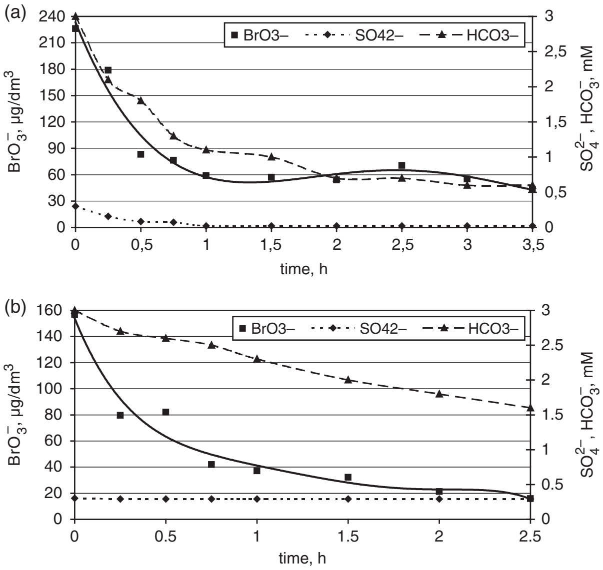

Fig. 3. Decrease in anion concentration: (a) in the process with Selemion AMV; (b) in the process with Neosepta ACS (C_{NaCl} = 100 mM).

the equilibrium state of BrO_3^- ions when Selemion AMV was used. The duration of the process entailing Selemion AMV for attaining the equilibrium concentration of BrO_3^- ions amounted to 3.5 h (Fig. 3a), whereas with Neosepta ACS - to 2.5 h only (Fig. 3b). It means that to achieve the minimum concentration of bromate ions in the treated water it is required to circulate the both solutions (the feed and the receiver). The system is well known in literature as a batch system. Time of the anion-exchange process can be, obviously, shortened when total area of the membranes are higher.

As shown by these plots, the two membranes differ in the rates with which the associated anions (sulphates and bicarbonates) were removed from the feeding solution (Fig. 3). Until the minimum concentration of bicarbonate ions was achieved, the average flux equalled 0.057 mol/m^{2}h for Selemion AMV and 0.041 mol/m^{2}h for Neosepta ACS. Sulphates were transported at a significantly slower rate: the average flux of SO_4^{2-} ions required to achieve the minimum concentration amounted to 0.020 mol/m^{2}h and 0.003 mol/m^{2}h for Selemion AMV and Neosepta ACS, respectively. This is attributable to the difference in the membrane structure. Selemion AMV, which has a loose surface structure and a higher ion-exchange capacity (Table 1), facilitates the transport of large ions (HCO_3^-) and multivalence ions (SO_4^{2-}). That is why the removal efficiencies were high: that of sulphate ions amounted to 93% (the final sulphate concentration in the treated water was 0.02 mM SO_4^{2-}) and that of bicarbonate ions ranged from 60 to 87% (the final bicarbonate concentration ranged from 1.2 to 0.4 mM HCO_3^-) when salt concentration in the receiver varied between 50 and 200 mM (Fig. 4a). Owing to the large share of SO_4^{2-} and HCO_3^- ions in the total flux of the counterions transported from the feed to the receiver, the efficiency of BrO_3^- ion removal was lower as compared with Neosepta ACS (Fig. 4).

Donnan dialysis with Neosepta ACS produced different removal efficiencies. Neosepta ACS, a mono-anion-selective membrane, has a highly cross-linked layer on its surface, which obstructs the flow of large counterions (sulphates and bicarbonates) across the membrane. As a result, sulphate ions were almost entirely retained, since the efficiency of their removal was only 3% (the final sulphate concentration in the treated water was 0.29 mM SO_4^{2-}) (Fig. 4b). The retention of bicarbonate ions ranged from 40 to 53% (the final bicarbonate concentration was 1.2 and 1.6 mM HCO_3^-, respectively) at salt concentration in the receiver varying between 50 and 100 mM NaCl. As a result, bromate ions were removed with high efficiency, because sulphates and bicarbonates (effectively blocked by the membrane) were the only competitors for BrO_3^- ions.

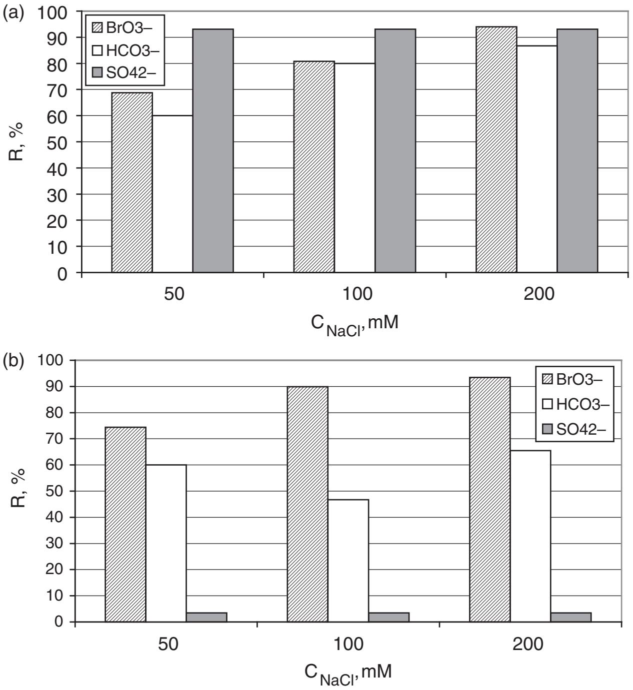

Fig. 4. Efficiency of anion removal from natural water at various NaCl concentrations in the receiver: (a) in the process with Selemion AMV; (b) in the process with Neosepta ACS.

To recapitulate, Donnan dialysis with Neosepta ACS provides 90% removal of bromates at the salt concentration in the receiver of 100 mM. To achieve a similar removal efficiency for BrO_3^- ions (94%) with Selemion AMV, it is necessary to increase the salt concentration in the receiver to 200 mM. However, considering the costs involved in receiver preparation, it is advisable to make use of Neosepta ACS, since this membrane has the capacity for obstructing a significant quantity of bicarbonate ions (53% of retention), whose presence in drinking water is highly desirable (especially at low degree of mineralization).

In spite of the high efficiency of bromate removal obtained with both Neosepta ACS and Selemion AMV, the concentration of BrO_3^- ions cannot be reduced to 10 µg BrO_3^-/dm^3, which is the permissible value for drinking water. It is therefore recommended that the natural water where high concentrations of BrO_3^- ions still persist after treatment by Donnan dialysis be made subject to adsorption on granular activated carbon (GAC). There is probability that the concentration of bromates will then fall below the permissible value [8].

As a result of anion exchange, the ionic composition of natural water changes noticeably (Fig. 5). After Donnan dialysis with Selemion AMV, the molar percent of chloride ions increased from 10.4 to 86%, whereas that of the remaining anions decreased as follows: bicarbonates

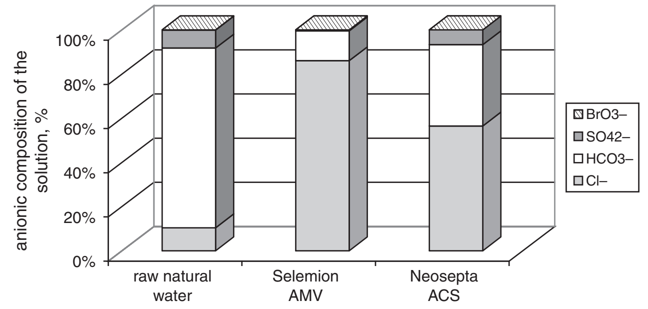

Fig. 5. Ionic composition of raw natural water and natural water after Donnan dialysis with Selemion AMV and Neosepta ACS (C_{NaCl} = 100 mM).

from 81.4 to 13.5%; sulphates from 8.2 to 0.5%, and bromates from 0.04 to 0.008%. With Neosepta ACS, the molar percent of chloride ions increased from 10.4 to 56.5%, whereas that of the other anions decreased according to the following pattern: bicarbonates from 81.4 to 36.8%; sulphates from 8.2 to 6.7%, and bromates from 0.04 to 0.003%.

In every instance the molar percent of chlorides was significantly higher when Donnan dialysis was performed with Selemion AMV (86%) than Neosepta ACS (56%). Obviously, this is attributable to the high efficiency with which the anions in the feeding solution are exchanged for Cl^- ions when use is made of Selemion AMV.

4. Conclusions

i. Bromate ions were removed from natural water with 90% efficiency (bromate concentration in the treated water was 16 μg/dm^3) when Donnan dialysis involved Neosepta ACS, an anion-exchange membrane with a tight surface layer, and when salt concentration in the receiver was 100 mM NaCl. Further increase in salt concentration only slightly increased the efficiency of bromate removal.

ii. With Selemion AMV, the efficiency of bromate removal in Donnan dialysis was similar (94%, bromate concentration in the treated water was 13 μg/dm^3) but NaCl concentration in the receiving solution had to be twice as high as with Neosepta ACS (200 mM).

iii. Neosepta ACS provided a high extent of retention in the case of large anions (sulphates and bicarbonates). This is of particular importance when the mineralization of the water being treated is low. Sulphates were almost entirely blocked by the membrane, so the efficiency of their removal was as low as 3%. Bicarbonates were blocked to a smaller extent, and the efficiency of their removal was 47% (at the salt concentration in the receiver amounting to 100 mM NaCl).

iv. Donnan dialysis provided high efficiency of bromate removal from natural water with high initial BrO_3^- concentration (200 μg/dm^3), regardless of whether Neosepta ACS or Selemion AMV was applied. In spite of this, the concentration of BrO_3^- ions could not be reduced to 10 μg BrO_3^-/dm^3, which is the permissible value for drinking water.

v. When high concentrations of BrO_3^- ions still persist in the treated water, it is recommended that Donnan dialysis be followed by adsorption on granular activated carbon (GAC). There is probability that the concentration of bromates will then fall below the permissible value.

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