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Removal of bromate ions from water in the processes with ion-exchange membranes

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ABSTRACT

In this paper effects of bromates and accompanying anions removal from water in the processes with the use of ion-exchange membranes, like Donnan dialysis (DD) and electrodialysis (ED), have been analyzed. Also the suitability of electrodialytically recovered NaCl solution for removing bromates from water in the process of Donnan dialysis has been checked. The process of Donnan dialysis with the anion-exchange membrane (Selemion AMV, Neosepta ACS) makes it possible to remove efficiently the bromate ions from natural water with a relatively low concentration of salt in the receiving solution (100 mM NaCl). Mono-anion-selective membrane (Neosepta ACS) applied in the process of Donnan dialysis is particularly useful for removing bromates from water with a domineering participation of large anions: bicarbonates and sulfates. Electrodialysis with the use of AMX/CMX membranes allows to remove bromates from water efficiently, together with a high efficiency of removing residual anions: bicarbonates, chlorides and sulfates. Electrodialysis with the ACS/CMX membranes, where the ACS membrane is a mono-anion-selective one, allows to reach a similar effect of removing bromates, bicarbonates, and chlorides, whereas sulfates are effectively retained by the ACS membrane. The process of electrodialysis with the ACS/CMX membranes makes it possible to recover efficiently NaCl from the spent receiving solution after the Donnan dialysis. Reuse of the regenerated salt solution (as a receiving solution in the process of Donnan dialysis) makes it possible to reach high efficiency of bromates removal.

1. Introduction

Ozone is an effective oxidizer and disinfector commonly used in water treatment in order to obtain drinkable water. Ozone may be applied in water treatment plants for different purposes, among which the most important are: preliminary disinfection, taste control, limitation of creating trihalomethanes (THM) and haloacetic acids (HAA), as well as enhancing coagulation [1,2]. In water treatment plants which apply preliminary ozonization of water it is necessary to use an additional disinfectant (mostly chlorine) in order to prevent the deficiency of residual disinfectant in the water supply system [2]. As a result of dosing chlorine into water, disinfection by-products (THM, HAA) come into being, however, preliminary ozonization leads to decrease of concentration of THM and HAA in cleaned water due to the degradation of precursors of these compounds by ozone [1,2].

In the process of ozonization of water containing bromide ions which occur commonly in natural waters, bromate ions are formed [3]. These ions come into being in the process of multistage oxidation of bromides by molecular ozone and/or by hydroxyl radicals [4,5]. Bromide ion is oxidized by ozone to the hypobromus acid (HOBr), being in equilibrium with the hypobromite ion (OBr^-) which in a subsequent reaction with ozone creates the bromite ion (BrO_2^-), afterwards the latter is oxidized by ozone to the bromate ion (BrO_3^-). Bromide ion may also react with the hydroxyl radical ($^{\cdot}OH$), creating the bromine radical ($Br^{\cdot}$), and the latter is further oxidized by ozone creating the intermediate radical $BrO^{\cdot}$, and as a final result the ion BrO_2^-. The last stage is oxidation of this ion by ozone to the ion BrO_3^-.

Final concentration of the bromates in water after ozonization depends among others on the concentrations of bromides and on pH of water: the higher pH the greater concentration of the hypobromite ion, and thus greater probability of creating the bromates. The concentration of the bromates also depends on the ozone dosage used for disinfection [6]. The data presented in the paper [7] indicate that as a result of ozonation of water with relatively low concentration of bromides (160 μg/L), the concentration of bromates in water reaches 30 μg BrO_3^-/L (assuming the ozone dosage and contact time necessary for 99% deactivation of *Cryptosporidium* oocysts).

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Bromates are ions with carcinogenic impact on the human body. According to the data of USEPA [8], the risk of developing a cancer disease is 10^{-4} at the concentration of bromates in drinking water of 5 μg BrO_3^-/L and 10^{-5} at the concentration of bromates of 0.5 μg BrO_3^-/L. That means that in the group of adults who consume 2 L/d of water with a determined concentration of bromates, one person per 10,000 or one person per 100,000 may fall ill with cancer [9]. Therefore, admissible concentration of bromates in drinking water in EU countries and in the USA is now of 10 μg/L [10,11]. The same value is recommended by WHO [12].

The result of the above mentioned data is a necessity of removing bromate ions from drinking water. In the group of methods applied for this target it is necessary to mention, first of all, adsorption on the granular activated carbon [13,14]. In this process bromate ion (BrO_3^-) is reduced on the surface of the activated carbon to the bromide ion (Br^-). Initial efficiency of bromate adsorption reaches 65%, however, in the course of time it significantly decreased as a result of gradual development of the biofilm on the surface of the activated carbon [13]. Decrease in efficiency of the bromates removal in the process of adsorption on the activated carbon may be also caused by adsorption of natural organic compounds on the sorbent surface [14].

High removal efficiency of bromates (up to 96%) has been achieved in the process of adsorption on granular ferric hydroxide [15]. High efficiency was also observed in a hybrid process coagulation-nanofiltration [16]. Ferrous sulfate applied in this process reduces completely bromates to bromides whereas obtained ferric hydroxide efficiently removes humic acids and residual bromates. Good effects in removing bromate ions from water have been also achieved using pressure-driven membrane processes. In the process of reverse osmosis 96% of bromates was removed [17] and in the process of nanofiltration – 89% [9].

In this paper we analyzed effects of bromates and accompanying anions removal from water in the processes with the use of ion-exchange membranes, like Donnan dialysis (DD) and electrodialysis (ED). Application of these processes may result in higher removal efficiencies comparing to the current methods – bromate concentration in the treated water could be decreased bellow the admissible value, i.e. 10 μg/L. Moreover, the above mentioned processes allow to reach high water recovery. In the process of Donnan dialysis the high concentration gradient of driving ions (usually – chloride ions) causes the transport of these ions from the receiver through the anion-exchange membrane to the treated water which results in an equivalent, adversely directed anion flow [18]. This way the harmful or troublesome anions present in water are replaced by neutral ions i.e. chlorides. The principle of this process is presented in Fig. 1.

Donnan dialysis has been applied effectively in removing harmful anions, like fluorides [19] and nitrates [20], from water. In the process of removing fluoride ions from water, an adsorbent in the form of Al_2O_3 has been additionally used in order to bind F^- ions transferred from treated water to the receiver, which makes it possible to maintain concentration of fluorides in produced water below the admissible value for drinking water (1.5 mg F^-/L) [19]. On the other hand, in order to remove nitrates from water membrane bioreactor has been used. In such a case two processes occur: transfer of harmful ions (NO_3^-, ClO_4^-) from treated water to the receiver (Donnan dialysis) and subsequently biological reduction of these ions in the receiver chamber to the harmless products (N_2, Cl^-). In this integrated process the concentration of nitrates in treated water has been decreased significantly below the admissible value for drinking water (50 mg NO_3^-/L) [20].

Electrodialysis is an electro-membrane process in which constant electric field causes the transfer of ionic ingredients of water through alternately arranged anion- and cation-exchange membranes. The result of this process are two streams of water with different concentration of ions: the desalted stream (diluate) and the concentrated stream (concentrate) [18]. In this paper the process of electrodialysis is applied for two reasons: to remove bromates from the water and to recover salt (NaCl) from the waste receiver after the process of Donnan dialysis. Also the suitability of the recovered sodium chloride solution for removing bromates from water in the process of Donnan dialysis has been checked. The principle of the electrodialytic recovery of NaCl from the waste solution has been presented in Fig. 2.

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 (ASTOM Corp.). Some major parameters of the membranes are listed in Table 1.

The working area of the membrane amounted to 0.140 m^2. The process was performed with recirculation of the feed and the receiver until the minimum concentration of bromate ions in the feed was attained (at the time 2.5–3.0 h). The volume ratio of the feed to the receiver was 4:1 (10 L:2.5 L). The feed was natural water (its composition is shown in Table 2) enriched with bromate salt (100 μg BrO_3^-/L). The receiver was a NaCl solution with concentrations of 50, 100 or 200 mM.

Electrodialysis was conducted in the laboratory set-up Goemasep 136, which contained 15 cell pairs with Neosepta AMX/CMX or ACS/CMX membranes (Table 1). The working surface

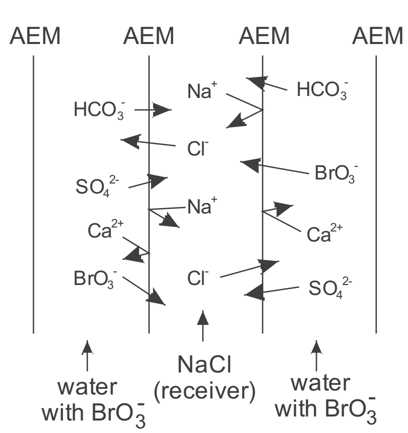

Fig. 1. The idea of Donnan dialysis process with anion-exchange membranes (AEM).

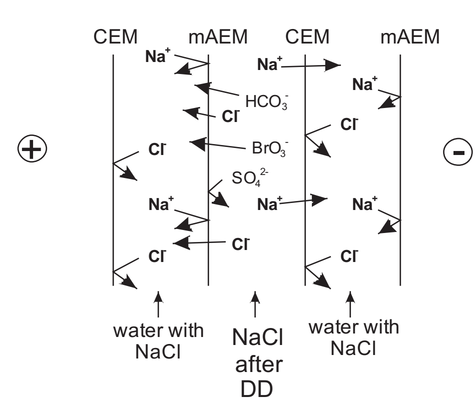

Fig. 2. The idea of electrodialysis process with mono-anion-exchange membrane (mAEM) for NaCl recovery from DD waste receiver.