V.I. Vernadskii Institute
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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE

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CHAPTER 10

PECULIARITIES OF REMOVAL OF NATURAL WATER MICROCOMPONENTS WITHIN THE PROCESS OF MEMBRANE DESALINATION (THE CASES OF ARSENIC, BORON, AND MANGANESE)

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Abstract. *The removal of microcomponents during electrodialysis down to the norms of drinking water has been established to require deeper desalination than that provided by traditional techniques (0.2-0.3 g/dm^3). The concentration range, within which the growth of the coefficient of microcomponent retention by nanofiltration and reverse osmosis membranes is observed, is individual for each component and depends on the nature of the membrane.*

Keywords: *microcomponents, natural water, removal, membrane desalination*

Introduction. Over recent decades membrane methods such as reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED) have gained wide practical use in the process of desalination of brackish ground- and marine waters as well as the treatment of wastewater and polluted water resources. The intensification of the use of membrane desalination methods and the diversity of natural waters in terms of chemical composition make it urgent to study the behavior of a number of microcomponents within membrane processing. In particular, it is necessary to remove As, B, and Mn, concentration of which in ground- and surface water often exceeds the standards for drinking water due to both natural and anthropogenic intake. A number of modern studies [1-3] has established the carcinogenic and genotoxic effect of arsenic, the gonadotoxic and embryotoxic effects of boron, the neurological, general toxic, embryotoxic and mutagenic effects of manganese. Therefore these microcomponents components are among the priority toxicological indicators of water quality. The analysis of scientific literature shows that it is difficult to remove As, B, and Mn down to the level that corresponds to the quality of drinking water.

Experimental. The model solutions containing microcomponents (arsenic, boron, manganese) were used in the processes of electrodialysis, nanofiltration and reverse osmosis. Ion exchange MK-40 and MA-40 (Schekinoazot, Russia) were applied to electrodialysis, OPMN-P nanofiltration membrane (Vladipor, Russia) and ESPA-1 reverse osmosis membrane (Hydranautics, USA) were used for baromembrane separation. The feed solution was supplied to the desalination chambers in a circulating mode in the process of electrodialysis, and a dead-end cell was used for baromembrane processes.

Results and discussion. The dependence of the degree of electrodialytic manganese removal on the degree of solution desalination differs significantly from the curves obtained for borate- and arsenate-ions (Figure 10.1). The main amount of manganese is removed from water down to 30% of initial content. In the case of boron and arsenic, intensive electromigration is observed only with an increase in the desalination degree up to 82.9 and 90.0%, respectively (with a decrease of value of the total salinity of dialysate down to ≈1.0 and 0.5 g/dm^3).

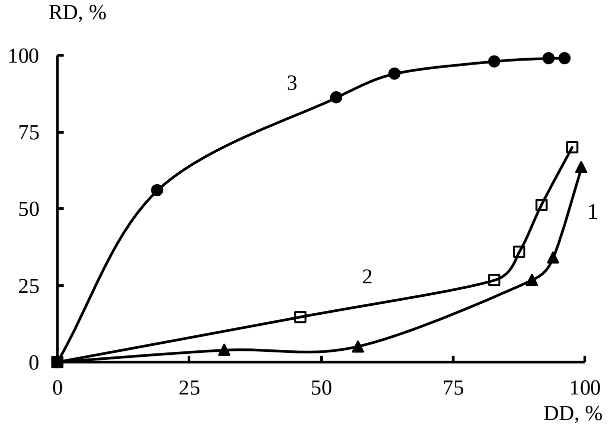

Fig. 10.1. *The dependence of the degree of arsenicic (1), boron (2) and manganese (3) removal on the degree of the model solution desalination in the process of electrodialysis using MC-40 and MA-40 membranes.*
The model solution contained 0,1 mg/dm^3 As(V), 5,85 g/dm^3 NaCl (1); 1,6 mg/dm^3 B, 8,5 g/dm^3 NaCl (2); 5,0 mg/dm^3 Mn(II), 11,7 g/dm^3 NaCl (3).

The results obtained during desalination of boron- and arsenic-containing waters can be explained by analyzing the following equation:

$$\bar{t}_1 = \frac{\bar{C}_1\bar{U}_1}{\bar{C}_1\bar{U}_1 + \bar{C}_2\bar{U}_2} \qquad (10.1)$$

where $\bar{C}_1$, $\bar{C}_2$, $\bar{U}_1$, $\bar{U}_2$ are the concentration and mobility of the micro- and macrocomponents in the membrane respectively. Indeed, as the equation (10.1) suggests, the transport number of $\bar{t}_1$ microcomponent in the membrane can reach high values only with the concentration of the macrocomponent decreasing significantly.

In the case of electrodialytic desalination of a model manganese-containing solution, the removal of manganese is intensive already at the initial stages of desalination. This is explained by selectivity of the MK-40 cation exchange membrane towards double-charged cations, which reduces the competing effect of the macrocomponent (Na^+) on the transport of manganese ions. The presence of Ca^{2+} and Mg^{2+} cations has been shown to have a competing effect on the electromigration of Mn^{2+}, but this effect slightly affects the rate of manganese removal.

Taking into account that the maximum allowable concentration (MAC) of arsenic in drinking water is very low (10 μg/dm^3), obviously it is problematic to achieve this value in the process of electrodialysis, since it requires almost complete desalination of the solution.

In the case of electrodialytic treatment of manganese-containing solutions (owing to the selectivity of the cationic membrane to Mn^{2+} ions), the concentration of manganese decreases to the MAC, when the total salinity of the dialysate reduces down to 0.2-0.3 g/dm^3. This is despite the fact that the maximum permissible concentration of manganese in drinking water is also fairly low and reaches 50 μg/dm^3.

The boron concentration in dialysate also reduced down to the MAC with the reducing salinity of dialysate down to 0.2-0.3 g/dm^3, despite the fact that the rates of removal of borate and arsenate anions are close to each other. Obviously, this is due to the fact that the limit for boron content in drinking water is less stringent (500 μg/dm^3) than the one for the content of manganese and arsenic.

The analysis can be used to predict the prospects for removing other microcomponents of natural and waste water by electrodialysis down to the standards for drinking water. This analysis has to take into consideration the MAC magnitudes for any microcomponent and the shape of the kinetic curve of its removal during desalination.

The retention coefficient of borate-anion (pH 11) by ESPA-1 reverse osmosis membrane has been established to be bot higher than 93% within the range of boron concentration of 1.2-20.0 mg/dm^3 (Figure 10.2). The increase in boron retention is observed within the concentration range of 1.2-2.0 mg/dm^3, which is explained on the basis of capillary-filtration model of the selective permeability of reverse osmosis membranes.

The arsenate-anion retention coefficient for ESPA-1 reverse osmosis membrane and OPMN-P nanofiltration membrane reaches 95-99% within the wide range of pH, operating pressure, concentration and nature of background electrolyte with a permeate recovery of up to 90% (Table 10.1). The coefficient of arsenate retention by OPMN-P nanofiltration membrane increases within the range of arsenate concentrations of 50-100 μg/dm^3, whereas the arsenate retention coefficient is constant and reaches 99% in this concentration range using ESPA-1 reverse osmosis membrane.

The reliable data on the radius of the hydrated ion $HAsO_4^{2-}$ (as well as its heat of hydration) are absent. However, the diffusion coefficients of arsenate-ion and other ions, which are typical for water, are compared. Besides, they stress correlation between the diffusion coefficient of ion and its hydrated radius [4, 5].

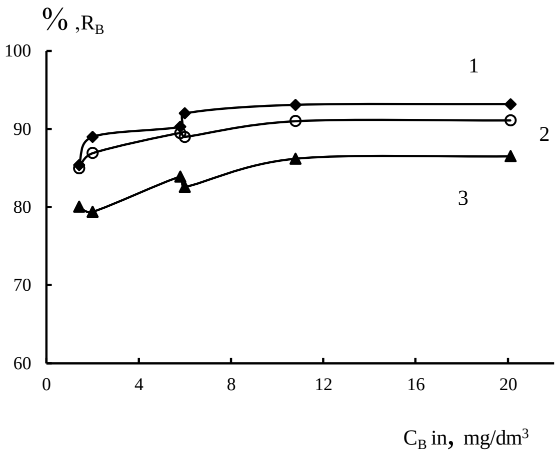

Fig. 10.2. *The coefficients of boron retention using ESPA-1 membrane at different boron concentrations in the initial solution and 25 (1), 50 (2), 75% (3) permeate recovery. The model solution contained 1,0 g/dm^3 NaCl; pH – 11,0; P – 3,0 MPa; T – 18-20 ^{o}C.*

Table 10.1. Removal of As(V) compounds using OPMN-P nanofiltration membrane at different operating pressure and permeate recovery

Permeate recovery, %	**0.5 MPa**			**1.0 MPa**			**1.5 MPa**		
	C_{As}perm, µg/dm^3	**R,%**	**J, dm^3/ m^2·h**	**C_{As}perm, µg/dm^3**	**R,%**	**J, dm^3/ m^2·h**	**C_{As}perm, µg/dm^3**	**R,%**	**J, dm^3/ m^2·h**
25	1.5	98.3	15.2	-	-	28.5	2.6	97.1	40.5
50	1.8	98.0	15.1	1.8	98.0	27.8	2.5	97.2	39.8
75	1.6	98.2	15.1	1.9	97.9	27.7	2.4	97.3	39.8
90	2.2	97.5	14.9	2.3	97.4	27.1	2.9	96.7	39.1

Note. The solution contained 90 µg/dm^3 As(V) and 1 g/dm^3 NaCl; pH 7,5; T=15-16 ºC.

Table 10.2 shows that the diffusion coefficient of the anions in the solution decreases within the following series: Cl^{-}> HCO^{3-}> SO_4^{2-}> $HAsO_4^{2-}$. The coefficient of ion retention by the NF membranes increases within this series as well: SO_4^{2-}> HCO_3^{-}> Cl^{-}.

Table 10.2. The heat of hydration (ΔH) and diffusion coefficient (D) of anions typical for natural waters [4, 5]

Ion	**$Cl^–$**	**$HCO_3^–$**	**$SO_4^{2–}$**	**$HAsO_4^{2–}$**
ΔH, kJ/mol	351	381	1109	-
D·10^9, m^2/s	2,030	1,185	1,065	0,323

Conclusions. Electrodialytic removal of microcomponents of manganese, boron, arsenic down to the standards for drinking water requires a deeper procedure of water desalination (0.2-0.3 g/dm^3) comparing with traditional desalination. This is caused by the competing influence of macrocomponents on the process as well as low MAC of microcomponents in water. It has been proposed to forecast the prospects of removal of microcomponents from natural and waste waters by electrodialysis to the standards for drinking water based on the analysis of the kinetic peculiarities of the microelement removal from water in the process of electromembrane desalination and the value of its MAC.

Increase of the concentration of a microelement (boron and arsenic) improves its retention by reverse osmosis and nanofiltration membranes. However, the concentration range, within which this growth is observed, is individual for each component and depends on the nature of the membrane. The obtained results correspond to the capillary-filtration model of selective permeability of reverse osmosis membranes.

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ОСОБЛИВОСТІ ВИДАЛЕННЯ МІКРОКОМПОНЕНТІВ ПРИРОДНИХ ВОД У ПРОЦЕСАХ МЕМБРАННОГО ОПРІСНЕННЯ (НА ПРИКЛАДІ АРСЕНА, БОРУ, МАРГАНЦЮ)

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Резюме. *Встановлено, що видалення мікрокомпонентів в процесі електродіалізу до норм питного водопостачання вимагає більш глибокого знесолення води (0,2-0,3 г/дм^3), аніж за традиційного опріснення. Інтервал концентрацій, в якому спостерігається зростання коефіцієнта затримки мікрокомпонента нанофільтраційними та зворотноосмотичними мембранами, для кожного компонента є індивідуальним і залежить від природи мембрани.*

Ключові слова: *мікрокомпоненти, природні води, видалення, мембранне опріснення*