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ENVIRONMENTAL PROTECTION: FROM SORBENTS TO MEMBRANES



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ENVIRONMENTAL PROTECTION: FROM SORBENTS TO MEMBRANES

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Коллективна монографія «Environmental Protection: from Sorbents to Membranes» - під ред. проф. Н. Кабай, докт. хім. наук Ю. С. Дзязько, проф. М. Арда, докт. хім. наук К.О. Каздобіна - 108 с.

Коллективна монографія включає статті за матеріалами українсько-турецького семінару, який було проведено 11 листопада 2016 р. на базі Інституту загальної та неорганічної хімії ім. В. І. Вернадського НАН України за участю фахівців Егейського університету (Турецька республіка) та за підтримки Відділення хімії НАН України, Відділу міжнародних зв'язків НАН України, а також Наукової та Технічної дослідної Ради Турецької республіки TÜBİTAK. У монографії наведено результати досліджень, які направлені на вилучення токсичних і цінних компонентів із розчинів техногенного та природного походження, зокрема з біологічних рідин, із застосуванням сорбційних та мембранних методів. Результати робіт можуть бути застосовані у водопідготовці, хімічній, фармацевтичній, харчовій промисловості. Особливу увагу приділено синтезу нових матеріалів для процесів розділення та впливу структури цих матеріалів на їх функціональні властивості: проникну здатність, електропровідність, каталітичну спроможність тощо.

Монографія є корисною для фахівців в області мембранних та сорбційних технологій, а також для студентів вищих навчальних закладів.

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REMOVAL OF As(V) COMPOUNDS FROM WATER USING OPMN-P NANOFILTRATION MEMBRANE

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Abstract. *High efficiency of removal of As(V) compounds from water with nanofiltration technique was shown. OPMN-P nanofiltration membrane was involved to investigations, which were performed within a wide range of pH, concentration of background electrolyte, operating pressure and permeate recovery (25-90%). The rejection has been found to reach 93-98%. As shown, the membrane is promising for water purification from arsenic, the maximal contaminant level is 10 $\mu\text{g}/\text{dm}^3$. As(III) has to be oxidized preliminarily down to As(V) using photocatalysis.*

Keywords: *arsenate, removal, drinking water, nanofiltration, membrane.*

Introduction. Arsenic compounds are often found in natural waters, owing to both natural factors and human impact. However, the content of As-containing ions in water sources can be higher than the maximal allowable concentration. Thus, the development of efficient and low-cost methods for the removal of these toxic impurities is an important task.

It has been shown earlier, that reverse osmosis (RO) involving ESPA-1 membrane provides high efficiency of water purification from As(V) compounds [1].

Since the operating pressure of nanofiltration (NF) is lower than that for RO, the energy costs of NF is 21% lower. Additionally, higher output at lower operating pressure is achieved. Thus, a possibility of NF application to removal of As(V) compounds from water solutions has to be considered. The purpose of this work was to research the NF process, which involves OPMN-P nanofiltration membrane (Vladipor, RF). This type of membranes is available in the market, they are often used in Ukraine.

Experimental. The effect of pressure, permeate recovery, temperature, pH and composition of the feeding solution on As(V) rejection was studied. OPMN-P membrane was used. Model solutions contained 100 $\mu\text{g}/\text{dm}^3$ As(V), 1-3 g/dm^3 NaCl (1-3 g/dm^3 Na_2SO_4). The solution pH was varied.

Results and discussion. As shown from Table 1, no significant effect of operating pressure within the range of 0.5-1.5 MPa on As(V) removal can be found, when the temperature was kept at 15-16° C. The rejection coefficient, *R*, decreased from 97.8 to 97.1%, the permeate recovery was 90 %.

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Table 1. Removal of As(V) Compounds Using OPMN-P Nanofiltration Membrane at Different Operating Pressure and $T = 15-16^{\circ}\text{C}$. Modeling Solution Contained Initially $100\ \mu\text{g}/\text{dm}^3$ As(V), $1\ \text{g}/\text{dm}^3$ NaCl, the pH Was 7.5

Permeate recovery, %	0.5 MPa			1.0 MPa			1.5 MPa		
	$C_{\text{As,perm}}$, $\mu\text{g}/\text{dm}^3$	R_{As} , %	J , $\text{dm}^3/(\text{m}^2\cdot\text{h})$	$C_{\text{As,perm}}$, $\mu\text{g}/\text{dm}^3$	R_{As} , %	J , $\text{dm}^3/(\text{m}^2\cdot\text{h})$	$C_{\text{As,perm}}$, $\mu\text{g}/\text{dm}^3$	R_{As} , %	J , $\text{dm}^3/(\text{m}^2\cdot\text{h})$
25	1.5	98.5	15.2	-	-	28.5	2.6	97.4	40.5
50	1.8	98.2	15.1	1.8	98.2	27.8	2.5	97.5	39.8
75	1.6	98.4	15.1	1.9	98.1	27.7	2.4	97.6	39.8
90	2.2	97.8	14.9	2.3	97.7	27.1	2.9	97.1	39.1

However, the rejection coefficient for As(V) reduces significantly, when the pressure increases to 1,5 MPa at $20-22^{\circ}\text{C}$ (Table 2). This may be caused by growing influence of concentration polarization on the process. When the temperature increases, the output (J) of the OPMN-P membrane shows a growth (Tables 1, 2).

Table 2 Removal of As(V) Compounds Using OPMN-P Nanofiltration Membrane at $20-22^{\circ}\text{C}$ and under Different Pressure. Modeling Solution Contained Initially $100\ \mu\text{g}/\text{dm}^3$ As(V), $1\ \text{g}/\text{dm}^3$ NaCl, the pH Was 7.8

Permeate recovery, %	0,75 MPa			1,0 MPa			1,5 MPa		
	$C_{\text{As, perm}}$, $\mu\text{g}/\text{dm}^3$	R_{As} , %	J , $\text{dm}^3/(\text{m}^2\cdot\text{h})$	$C_{\text{As, perm}}$, $\mu\text{g}/\text{dm}^3$	R_{As} , %	J , $\text{dm}^3/(\text{m}^2\cdot\text{h})$	$C_{\text{As,perm}}$, $\mu\text{g}/\text{dm}^3$	R_{As} , %	J , $\text{dm}^3/(\text{m}^2\cdot\text{h})$
25	1.2	98.8	24.5	1.7	98.3	31.7	14.0	86.0	40.9
50	1.5	98.5	24.3	1.9	98.1	31.7	16.5	83.5	40.6
75	2.5	97.5	24.3	3.2	96.8	31.7	17.2	82.8	40.5
90	2.8	97.2	24.1	3.3	96.7	31.2	18.9	81.1	40.5

The effect of increase of the permeate recovery from 25 to 90% on As(V) removal is inconsiderable. Nevertheless, the rejection of sodium chloride decreases from 55.1 to 30.4% ($P = 1.0\ \text{MPa}$, $T = 22^{\circ}\text{C}$).

Table 3 shows that the change of the pH within the range of 4.0-9.3 does not affect As(V) rejection. Slightly higher rejection of arsenate (99,7-99,8%) at pH of 4.0-4.9 is probably due to lower temperature of the process (the research at these pH values was performed at $12-13^{\circ}\text{C}$, the separation processes at the pH of 5.9-9.3 was carried out at $15-16^{\circ}\text{C}$).

According to [2], As(V) rejection by NF270 and TFC-SR-2 nanofiltration membranes increases dramatically (from 51-54% to 89%) with the pH growth from 4.0 to 6.7. Further increasing of the pH (up to pH 10) causes insignificant change of As(V) rejection (91-93%). These data are in agreement with of [3], where the similar effect is reported for N30F and NE90 nanofiltration membranes. It is noted in [2], that the similar dependence of As(V) rejection on pH is observed only for the membrane with a relatively large pore sizes. These membranes reject As mainly according to the charge repulsion mechanism.

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When the solution pH increases, monovalent arsenate anions transform into divalent one (a sharp transition at pH 6-7), which causes the improvement of arsenic rejection by negatively charged membranes. Membranes with much smaller pore sizes (e.g, NF70 membrane) reject As mainly due to the steric factor (size exclusion), thus, with the change of pH the As(V) rejection of such membranes virtually remains the same [2].

Table 3: Effect of pH and Permeate Recovery on Rejection of As(V) compounds with OPMN-P Nanofiltration Membrane. $P = 1.0$ MPa, $T = 12-16^{\circ}\text{C}$. Modeling Solution Contained $100 \mu\text{g}/\text{dm}^3$ As(V) and $1 \text{ g}/\text{dm}^3$ NaCl

pH	Permeate recovery, %							
	25		50		75		90	
	$C_{\text{As, perm}}, \mu\text{g}/\text{dm}^3$	$R_{\text{As}}, \%$	$C_{\text{As, perm}}, \mu\text{g}/\text{dm}^3$	$R_{\text{As}}, \%$	$C_{\text{As, perm}}, \mu\text{g}/\text{dm}^3$	$R_{\text{As}}, \%$	$C_{\text{As, perm}}, \mu\text{g}/\text{dm}^3$	$R_{\text{As}}, \%$
4.0	0.3	99.7	0.3	99.7	0.4	99.6	-	-
4.9	0.2	99.8	0.5	99.5	0.5	99.5	1.0	99.0
5.9	1.7	98.3	2.1	97.9	2.4	97.6	2.8	97.2
6.9	1.8	98.2	1.9	98.1	2.0	98.0	2.3	97.7
9.3	2.4	97.6	2.5	97.5	2.6	97.4	2.8	97.2

Comparison of the results obtained by the author and other researchers shows domination of steric factor for NF of As(V)-containing solutions using OPMN-P membrane. Nature of background electrolyte (NaCl or Na_2SO_4) and increasing in its concentrations up to $3 \text{ g}/\text{dm}^3$ slightly affect As(V) rejection.

The results of NF treatment of ground water are shown in Table. 4. As(V) compounds (Na_3AsO_4) were added preliminarily to natural water.

Table 4. Rejection of As(V) Compounds with OPMN-P Nanofiltration Membrane. Ground Water Is from Artesian Well (Kyiv, Irpenska str., 76) was treated. $P=1$ MPa, $T=16-17^{\circ}\text{C}$.

Permeate recovery, %	$C_{\text{As(V), feed}}, \mu\text{g}/\text{dm}^3$							
	116				220			
	$C_{\text{As, perm}}, \mu\text{g}/\text{dm}^3$	$R_{\text{As}}, \%$	$R_{\text{salt}}, \%$	$J, \text{dm}^3/(\text{m}^2 \cdot \text{h})$	$C_{\text{As, perm}}, \mu\text{g}/\text{dm}^3$	$R_{\text{As}}, \%$	$R_{\text{salt}}, \%$	$J, \text{dm}^3/(\text{m}^2 \cdot \text{h})$
25	4.9	95.8	85.6	84.3	4.1	98.1	85.4	75.7
50	6.5	94.4	84.3	82.4	6.9	96.9	83.8	74.2
75	7.0	94.0	81.9	79.8	8.4	96.2	81.7	74.1
90	7.7	93.3	79.7	77.8	9.4	95.7	79.3	72.9

As seen from Table 4, the rejection coefficient of As(V) compounds is 93.3 and 95.7%, when the concentration of these components in the feeding solution was 116 and $220 \text{ mg}/\text{dm}^3$ respectively (the permeate recovery was 90%). This gives a possibility to obtain permeate, in which the content of As corresponds to standards for drinking water.

Conclusions. NF processes, which involve OPMN-P membrane allow us to reach high efficiency of removal of As(V) compounds from water. The process can be performed within a wide ranges of the solution pH, concentration of background electrolyte and pressure at 90% permeate recovery. The membrane is promising for purification of water from arsenic compounds (including the As (III) with its previous photocatalytic oxidation [1]), concentration of the toxic component decreases down to the maximal allowable level of 10 µg/dm³.

References

1. Babak Yu.V., Melnik L.A., Goncharuk V.V. Removal of arsenic compounds from natural waters using a hybrid system (photocatalysis-reverse osmosis) // Journal of Water Chemistry and Technology. 2014. Volume 36. P. 296-302.
2. Fang J., Deng B. Arsenic rejection by nanofiltration membranes: effect of operating parameters and model analysis // Environmental Engineering Science. 2014. V. 31. P. 495-506.
3. Nguyen C.M., Bang S., Cho J., Kim K.-W. Performance and mechanism of arsenic removal from water by a nanofiltration membrane // Desalination. 2009. V. 245. P. 82-94.

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ВИДАЛЕННЯ As(V) ІЗ ВОДИ МЕТОДОМ НАНОФІЛЬТРАЦІЇ З ВИКОРИСТАННЯМ МЕМБРАНИ ОПМН-П

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Резюме. Показано високу ефективність затримки сполук As(V) нанофільтраційною мембраною ОПМН-П в широкому діапазоні рН розчину, концентрації фонового електроліту, робочого тиску при ступені відбору пермеату до 90%. Вказана мембрана є перспективною для очистки води від сполук арсену до гранично допустимої концентрації 10 мкг/дм³ (в тому числі і від As(III)) при попередньому його фотокаталітичному окисненні.

Ключові слова: арсенати, видалення, питна вода, нанофільтрація, мембрана