

ARSENIC, ZINC AND MAGNESIUM ION REMOVAL FROM WATER BY NANOFILTRATION, MODELLING OF REJECTIONS

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The drinking water sources in some parts of Hungary are highly contaminated with arsenic. The recent arsenic removal technologies use chemical treatment combined with filtration, adsorption etc. Nanofiltration, which is a relatively new area of membrane filtration, could be suitable for removing arsenic from well water, and in addition it does not require chemical pretreatment.

The nanofiltration membranes remove the bivalent ions, therefore the removal of trivalent and pentavalent forms of arsenic could be presumed too. In our measurements the possibility of the nanofiltration of typical bivalent ions (Zn, Mg) and As (tri- and pentavalent forms) were examined and compared using model solutions. Because of the surprisingly low rejection of As(III) two oxidation agents (KMnO₄ and H₂O₂) were applied to gain removable As(V). On the base of measurements regression equations were developed to calculate the individual ion - rejection.

The experimental investigations proved that additive ions in the solution do not influence the individual rejection of a metal ion in this range of concentrations. The joint removal of Zn, Mg, As(III) and As(V) ions from South - Hungarian well water could be well estimated on the base of our regression equations.

Keywords: Arsenic removal, bivalent ion removal, membrane filtration, nanofiltration

Introduction

Nanofiltration is a relatively new membrane filtration procedure. At the end of the last decade Eriksson [1] wrote that an interesting hybrid membrane area was found, which was suitable to retain multivalent ion and it is similar to both ultrafiltration and reverse osmosis. Even in the middle of the 90's the nanofiltration was not categorised obviously, it was not mentioned at all (Bilstad [2]), or referred by another name (Ujang and Anderson in 1996 called it as membrane softener [3]).

The recently valid Hungarian standard relating to drinking water (MSZ 450/1-1989) permits maximum 50 mg/l arsenic. Most of the arsenic-contaminated wells of Southern Hungary contain four times higher arsenic as it is permitted in the standard. In fact it is not only a Hungarian problem. It causes also great difficulties in the Vojvodina region (Yugoslavia) and concerning this problem Janic at al carried out measurements [4].

Directives of the European Community dealing with drinking water (98/83/EC) valid from 1998 allows 10 mg/l arsenic. As a condition of accession to European Union, Hungarian authority should apply this value too.

Wayapa [5] made measurements on membrane filtration of arsenic, but he rather examined reverse osmosis. Brandhuber and Gary [6] carried out pilot plant experiments with nanofiltration of arsenic from drinking

water. Hagemeyer and Gimbel [7] modelled the salt rejection of nanofiltration membranes. Charles [8] removed As(V) ions by different nanofiltration membranes with high efficiency.

On the basis of the results of measurements a full scale nanofiltration equipment was established in Paris for water treatment (Ventesque et al. [9]).

Numerous researches have studied the arsenic, as the source of soiling material spreading in water and ground, as well. Chen et al. [10] have investigated the consequences of illness caused by arsenic species in Taiwan. The different kind of the species of arsenic are poisonous in different levels. Mester, Woller and Fodor [11, 12] studied the possibilities of measuring the arsenic species.

Experimental

Nanofiltration equipment used for the measurements is shown in Fig. 1. The model solution (distilled water with metal ions) was poured into the feeding vessel (1). A high pressure piston pump (2) circulated the liquid on the surface of the membrane (3). In some cases the permeate was led back to the feeding vessel, in other cases it was discharged from the system. The retentate remained in the feeding vessel. The recirculation flow rate was set up by an adjusting-device, which was on the

pump cabinet (5), the values were measured by rotameter (7). The pressure was regulated by a setting valve (4). The temperature of the solution was kept constant by using a built-in water cooler (10). A pH meter (type HI 8314) controlled the pH of the solution.

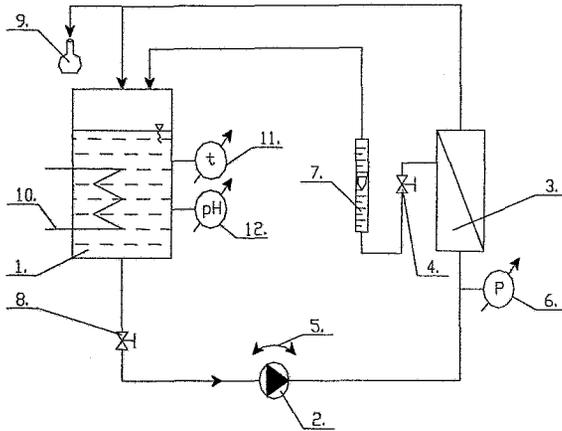


Fig. 1. Laboratory nanofiltration apparatus

1. Feed vessel, 2. Pump, 3. Membrane modul, 4. Pressure valve, 5. Recycle valve, 6. Pressure gauge, 7. Rotameter, 8. Stopcock, 9. Sampling, 10. Heat exchanger, 11. Thermometer, 12. pH meter.

Before and after the experiments the equipment was rinsed over by circulating distilled water for 10-10 minutes. The clean water flux and the salt rejection of the membrane were checked after each cleaning procedure.

Round shaped flat sheet membranes were used with an active surface of $2 \times 180 \text{ cm}^2$. The parameters of the chosen membranes are collected in Table 1.

In the model-experiments the concentration of the As, or Zn, or Mg ions of the feed solution were equal with that of the average well-water doses. The concentrations are shown in Table 2.

Table 2. Amounts of the dosed metals

Ion	Concentration	Form
As	0,2 mg/L	As ₂ O ₃
Zn	0,6 mg/L	ZnSO ₄
Mg	60 mg/L	MgSO ₄

The As in the well water appears mostly in As(III) and partly in As(V) form. Using oxidating agent in a proper excess all the As ions can be regarded as As(V) ions. As oxidising agent potassium permanganate and hydrogen peroxide were used.

The experiments were carried out under different temperatures, pressures and pH values (Table 3). The

concentration of As, Zn and Mg ions in the feed, permeate and concentrate was measured by ICP (Inductive Coupled Plasma) method.

Table 3. Operational parameters and levels

Operational parameters	
Temperature	10 °C
	20 °C
	30 °C
Transmembrane pressure drop	5 bar
	10 bar
	15 bar
pH	5,00
	7,00
	9,00

Results

Results on UTC-60 membrane and models

The rejection of different ions did not depend on the pressure in the measured range. An increase in the temperature decreased while in the pH increased the rejection.

Rejection of arsenic in functions of temperature and pH are plotted in Fig. 2 and 3, as examples. The comparison of the two figures shows that the rejection of the arsenic without oxidation is 2 - 3 times lower than that of the oxidised form.

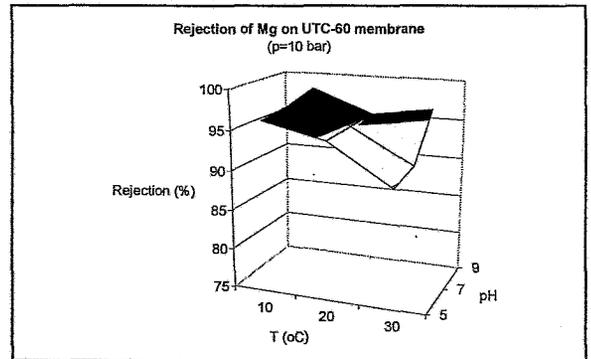


Fig. 2. Rejection of As (III) on UTC-60 membrane

Arsenic without oxidation is four times more sensitive to a change in the operation parameters than that of oxidized arsenic. Decreasing the hydrogen ion concentration with one unit the rejection of As(III) increases by 4%, and that of oxidised arsenic, the As(V), by 1 %. Considering the influence of the temperature the same difference can be observed: the temperature coefficient of As(III) in the regression equations is four

Table 1. Characteristics of the examined membranes

Membrane Type	Membrane producer	NaCl Rejection [%]	Pure water flux [L/m ² h]	Operational parameters		
				p [bar]	T [°C]	pH
UTC - 60	Toray/Ropur	55	55	15	35	3-11
DESAL - 5	Desalination Systems	50	58	41	50	4-11

times higher than that of the oxidised arsenic.

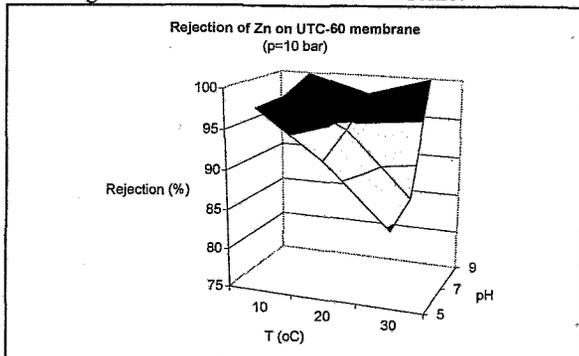


Fig. 3. Rejection of As (V) on UTC-60 membrane

Dependence of the rejection of an individual ion on pH and temperature can be well described with a linear regression equation:

$$R = A + B \times T + C \times \text{pH}, \%$$

Coefficients of the equations are summarised in Table 4. A validity domain of the formula is the measured domain: $T = 10 \text{ - } 300\text{C}$, $\text{pH} = 5 - 9$, and feed concentration according to Table 2.

Table 4. Coefficients of regression functions fit onto the rejections of UTC 60 membrane

Name of ion	A/constant	B/temperature	C/pH	R ²
As(III)	15,140	-0,865	4,060	0,937
As(V)	85,601	-0,185	1,060	0,988
Zn	87,880	-0,263	1,474	0,978
Mg	94,362	-0,142	0,499	0,996

Results on Desal D 5 membrane and models

On Desal D5 membrane similar results were obtained as on UTC-60 membrane.

Rejection of Zn and Mg ions is shown in Fig. 4. and 5, as examples.

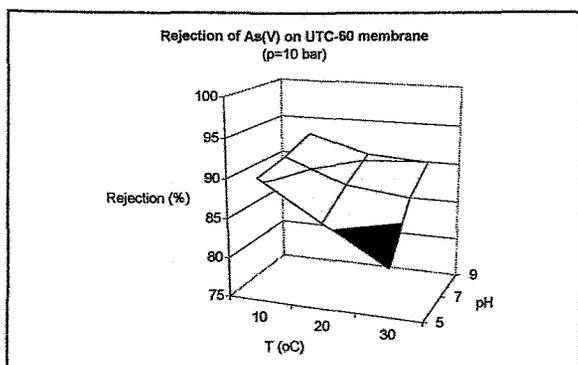


Fig. 4. Rejection of Zn on Desal D5 membrane

Experiments carried out with arsenic, Zn and Mg ions show the same influence of operational parameters (pressure, pH and temperature) on the rejection. Values of rejection in the case of Mg ion exceed 90% at all adjustment of experimental parameters. Rejection of Zn

depends more sensitively on temperature and pH than that of Mg. When the decrease of Mg is undesirable, the hardness of water can be increased by additive Mg salts.

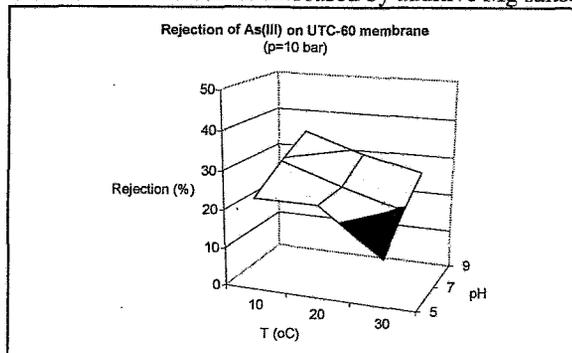


Fig. 5. Rejection of Mg on Desal D5 membrane

Dependence of the rejection of individual ions on the pH and temperature could be described with a linear regression equation:

$$R = D + E \times T + F \times \text{pH}, \%$$

Coefficients of the equations are summarised in Table 5. The validity domain of the formula is the measured domain: $T = 10 - 300\text{C}$, $\text{pH} = 5 - 9$, and feed concentration according to Table 2.

Table 5. Coefficients of regression functions fit onto the rejections of Desal D5 membrane

Ion	D/constant	E/temperature	F/pH	R ²
As(III)	15,170	-0,818	4,296	0,986
As(V)	93,169	-0,097	0,625	0,988
Zn	86,440	-0,230	1,784	0,957
Mg	94,980	-0,218	0,694	0,996

Model of permeate flux

The permeate flux was slightly influenced by the ion content in the measured low concentration range. Measured fluxes are shown in Fig. 6.

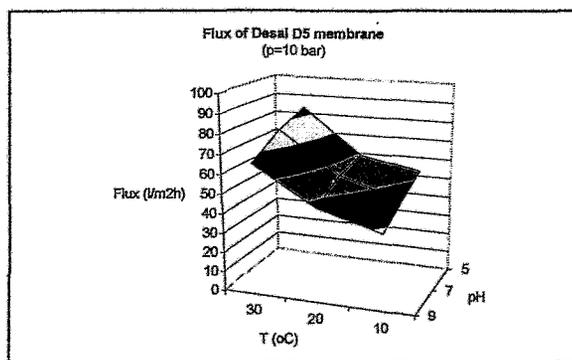


Fig. 6. Permeate flux of Desal D5 membrane

The permeate flux can be described as a ratio of transmembrane pressure drop and the sum of resistance of the membrane and the boundary layer. In case of model solution the boundary layer can be neglected,

therefore the flux is:

$$J = \Delta P / R_M$$

On the base of the measured data, the resistance of membranes was described by a two-variable linear equation:

$$R_M = G + H \cdot T + K \cdot \text{pH}$$

The coefficients are summarised in Table 6. The validity of the expression is the measured range: $T = 10 - 300^\circ\text{C}$, $\text{pH} = 5 - 9$ and feed concentration according to Table 2.

Table 6. Coefficients of regression functions fit onto the membrane resistance

Membrane	G/constant	H/temperature	K/pH	R^2
UTC 60	0,199	-0,00435	0,0055	0,947
Desal D5	0,193	-0,00458	0,0110	0,976

If there is an increase in the temperature, the membrane resistance decreases, and consequently, the flux increases. Similar influence of the temperature was observed by Bilstad [2] in the case of ultrafiltration. The influence of the pH is the opposite on the above parameters.

Joint retention of ions from well water

Measurements with model solutions indicated that the retention of a metal ion in the measured range was not influenced by the presence of another ion or ions.

Table 7. Ion content in well water from South - Hungary

Ion	Concentration
As	214 $\mu\text{g/L}$
Zn	0,6 mg/L
Mg	15,8 mg/L

These results made possible the estimation of the retention of the investigated metal ions using well water. The referring data of the well water are shown in Table 7.

Ion retention calculated from the regression equation was compared with measured retention on Desal D5 membrane using well water. The results are collected in Table 8. The deviations from the measured results are very low, we think it is supposed that there was no component/material in the well water which could significantly influence the individual retention of the investigated metal ions.

The diverse rejection behaviour of As(III) and As(V) was observed in case of well water too. Without oxidation only 25 - 30 % of arsenic ions could be filtered out, which show the high proportion of As(III) besides As(V). After oxidation the As(V) was very well rejected as it was observed using other nanofiltration membranes, too (Gergely et al [13], Békássy-Molnár et

al [14]).

Table 8. Measured and calculated rejections using well water, Desal D5 membrane

Ion	T[$^\circ\text{C}$]	pH	Rejection %	
			Measured	Calculated
As without oxidation	20	6,5	47,0	-
As after oxidation by KMnO_4	20	6,5	94,82	95,29
Zn	20	6,5	91,16	93,43
Mg	20	6,5	93,86	95,13

Conclusions

The UTC-60 and the Desal D5 nanofiltration membranes rejected from model solutions the bivalent Zn and Mg ions with a high efficiency: 85 - 95 %. The rejection of non-oxidized As (mostly trivalent ions) was surprisingly low: 15 - 35 %. The oxidized As, which is in As(V) form could be filtered out with very high efficiency: 80 - 95 %. There was no influence of oxidising agent on the rejection of arsenic.

The influence of transmembrane pressure drop on the rejection could be neglected in the measured range, while the temperature and pH had an influence on the rejection.

The membrane resistance slightly decreased with an increase in the temperature, while it slightly increased with an increase in the pH.

The individual rejection of Zn, Mg and As ions and the membrane resistance were described by linear regressions in function of temperature and pH.

Experimental results proved that additive ion/s in the solution did not influence the individual rejection in the measured range, therefore As, Zn, and Mg rejection from well water could be estimated on the base of regression equations.

Even if the well water has very high As concentration (200 mg/L) with proper membrane and operation parameters (low temperature, neutral pH) the EC regulation relating to As concentration in drinking water ($\leq 10 \text{ mg/L}$) could be reached in one nanofiltration step. In case of need, the total hardness of the filtered water can be increased by additive lime.

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SYMBOLS

A,B,C,D,E,F,G,H,K	- constants
cP	- ion concentration in the permeate, mg/L
cR	- ion concentration in the retentate, mg/L

J	- permeate flux, L/(m ² h)	rejection of nanofiltration membranes for ternary ion mixtures and for single salts at different pH values. <i>Desalination</i> 117, 247-256, 1998.
R	- rejection, $R = (cR - cP)/cR \times 100, \%$	
RM	- resistance of membrane, L/(m ² h bar)	8. CHARLES P.: Elimination de certains micropollutans relargues par les sediments. Proceedings of 79. Congres Assotiation Generale des Hygienistes & Techniciens Municipaux (AGHTM), Budapest, 275-289, 1999.
R2	- square of correlation coefficient	9. VENTESQUE C., TURNER G., BABLON G.: Nanofiltration from prototype to full scale AWWA 89 (10) 65, 1997
DP	- transmembrane pressure drop, bar	10. CHEN S-L. DZENG, S.R. YANG, M-H. CHLU, K.H. SHLEH, G.-M. WAL, C.M.: <i>Env. Sci. Techn.</i> , 1994, 28 (5) 877
T	- temperature, 0C	11. MESTER Z., WOLLER A., FODOR P. <i>Microchem. J.</i> , 1996, 54, 184

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