



Szent István University

# Arsenic removal from drinking water by nanofiltration

Doktoral (PhD) thesis, new scientific results

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## **INTRODUCTION AND OBJECTIVES**

Drinking water contaminated with arsenic causes significant problem at some regions of Hungary. The effect of arsenic on human organism has been known for a long time, but the solving of the real problem was started only in the 80's. The standard, which was prepared at that time, allows 50 µg/L arsenic in the drinking water in Hungary.

The European guideline issued at the end of 1998 determined the maximum level of arsenic in drinking water at 10µg/L. The European Union (EU) gives ten years transition period to adopt the strict regulations. Hungary must adopt this 10µg/L limit after accession to the EU.

The arsenic and its compounds are well known as carcinogenic substances, the permanent, great arsenic intake causes poisoning. Nevertheless the arsenic is considered as an essential trace element too. At the same time arsenic belongs to frequently appearing microelements in water, coming from deep-layer waters, so it has geological origin.

The literary data published up to now referring that nanofiltration belonging into membrane filtration group can be suitable for removing ions with two and three valences as well, depending the characters of the ion and the type of the membrane.

In the theses the possibility of adaptation of nanofiltration known as the most up to date method for reducing the arsenic content of drinking water was investigated. This technology is careful of environment, its deploy costs are relatively low and the arising waste materials are insignificant.

The goals of the experiments were investigation of six different membranes representing the whole nano-filtration area and comparison of their properties in order to see their capability of arsenic retention. The effects of some technical (recirculation volume flow, trans-membrane pressure) and environmental parameters onto arsenic retention as well as the influence of different oxidation status of arsenic onto filtering properties were examined. Beyond retention the flux of the retentate was measured systematically to get to know the influence of above mentioned factors onto flux.

Both the retentions and the filtering performances were specified and described numerically by setting up regression equations. Flux experiments presented an opportunity for precise observation and description of one of the interesting phenomenon (spectacular flux attribute that derives from reverse osmosis but applicable for nanofiltration too) of membrane filtration, and setting up a descriptive model and determining its coefficient relating to drinking water.

During setting up the model the events (changing of concentration, polarisation layer thickness) which took place at the wall of the membrane placed into the equipment functioning at our department were examined.

During my experiments first model solutions, than later real well water were used. It was investigated weather the result experienced at model solutions are valid in the case of well waters too.

In the course of well water experiments the opportunity of examining further cation retention's and of comparing these retention's raised.

The results of these thesis's on the one hand give the possibility of planning an arsenic removing equipment, on the other hand present a method in that case when environmental circumstances of the water source are significantly different from the arsenic contaminated water source wells of southern Hungary.

## **MATERIALS AND METHODS**

The feed solution was put into the 10 L feed tank. The recycle flow was set up by regulator between 200–400 L/h, and measured by rotameter. The inlet pressure was fixed with valve between 5–15 bar. The temperature of the feed tank was controlled by heat exchanger connected with a thermostat. The measured temperature range was between 10-30 °C. The surface of the membrane was 360 cm<sup>2</sup>.

Before and after each measurement the apparatus was flushed by distilled water. The salt rejection of the membranes was checked before every measurement and compared with the rejection data of the producer. If the salt rejection was less than expected (the membrane was presumably damaged), then a new membrane was installed.

In the case of model experiments the feed solution was distilled water, in each run only one type of ion was added. Mg, Zn or As ions were put into the water, as much as it is the average value in the Hungarian drinking water:

Mg: 60 mg/L  
 Zn: 6 mg/L  
 As: 0,2 mg/L

In the case of well water experiments the feed was ground water from South-Hungary, with higher As content than the EU Standard.

The parameters of the investigated nanofiltration membranes are collected in Table 1.

Table 1: Characteristics of the investigated membranes

Membran Type	Membran Producer	NaCl Rejection <sup>x</sup> (%)	Pure water flux <sup>x</sup> (L/m <sup>2</sup> h)	Recommended max. operating limits		
				p (bar)	t (°C)	pH
K 5	KÉKI Hungary	5	120	40	80	2-11
K 21	KÉKI Hungary	21	80	40	80	2-11
Desal 5	Desalination Systems	50	58	40	50	4-11
NF 45	DOW / Filmtec	55	55	15	60	1-11.5
UTC 60	Toray / Ropur	55	55	15	35	3-11
TFC 4921S	Fluid Systems	85	45	24	45	4-11

<sup>x</sup> Membrane producer's data at max. recommended pressure and 25°C

The concentration of metal and other ions in the feed, permeate and retentate were analysed by ICP and AAS techniques.

## RESULTS AND DISCUSSION

### Model solution

In the first step the whole nanofiltration spectrum/range has been checked. The As (III) ion rejection was below 45% on every membrane, which is a surprisingly low value. To remove As (III) from drinking water the As (III) have to be oxidised to As (V).

The most suitable nanofiltration membranes were those, where the salt rejection was between 45 and 60 %, because in these case the flux is fairly high, and the As rejection is over 85%.

The influence of operation parameters (pH, pressure and temperature) on the permeate flux and on the rejection of all ion was calculated (on 95 % significance level) using SPSS 7.2. program. The results for UTC–60 and Desal D-5 were summarised in previous publication.

In the case of UTC–60 membrane the influence of pH, pressure and temperature was significant. To check the significance of the above 3 parameters on the rejection was calculated using 108 measurements. The pressure had no significant influence on the

rejection. The permeate flux for Desal D-5 membrane is significantly influenced by pH, pressure and temperature, while the rejection of all ions was not influenced by the pressure (on the base of 81 measurements).

## **Well water**

### ***Results with Desal D-5 membrane***

Water with high As content without treatment with oxidation by  $\text{KMnO}_4$  and with  $\text{H}_2\text{O}_2$  was filtered. This way the As rejection was 90-95 %. The Desal membrane decreases the Mn content with 80-90 %.

The water hardness was determined on the basis of Ca, and Mg ions. Mg ion was rejected between 90-95 %, and Ca ion was rejected between 70-75 %, which means that the nanofiltered water became too soft. The Na and K rejection was 55-65 %. The Zn rejection was 90-95 %, while the rejection of Si was the lowest, 10-20 %.

The permeate flux on Desal membrane is obviously strongly influenced by the pressure and slightly by the recycle rate. The average permeate flow rate is acceptable. Range is between 20-90  $\text{L/m}^2\text{h}$ .

### ***Results with NF-45 membrane***

Long time concentration (semi-batch experiment) of high As content well water was measured. The feed was well water without any treatment and with oxidation by  $\text{KMnO}_4$ .

The As concentration in retentate and permeate in function of time. The recycle rate influenced the permeate concentration. The As concentration was kept below the EU limit of 10  $\mu\text{g/L}$  As although the yield was 80 % at the end of experiment.

The permeate flux of this membrane slightly decreased in function of time or permeate yield from 35 to 25  $\text{L/m}^2\text{h}$ .

## **New scientific results**

1. On the basis of measurements using laboratory membrane filter equipment, model solutions with different nanofilter membranes and different operational parameters it was determined that nanofilters can only retain As (III) ions at 10-40 percents. This small retention ability can be improved neither by the reduction of the pore size of the filter nor by changing the operational parameters at the 50-200  $\mu\text{g/L}$  range which is typical of the Hungarian well-waters contaminated with arsenic. The operational parameter ranges are the followings:  $5 < p < 15$ ,  $5 < \text{pH} < 9$ ,  $10^\circ\text{C} < T < 30^\circ\text{C}$ .

2. By conversion As (III) ion into As (V) ion, the arsenic retention grows dramatically. Retention of the As (V) ions can achieve the 90-95 % efficiency (it can be filtered by those nanofiltermembranes which can characterised higher than 45 % NaCl retention, NF50, Desal D5, UTC-60 for example). These statements are valid under the circumstances described at point 1.

3. When as an oxidizing agent  $\text{KMnO}_4$  or  $\text{H}_2\text{O}_2$  is used in excess, the total arsenic content of water can be converted in the form of As(V) ion, which removal by nano-filtration is practically independent of the oxidizing agent. It refers to the reason of arsenic retention is not the adsorption of particular manganese-oxide crystals, formed during the oxidation by potassium permanganate.

4. Those membranes that retained NaCl over 21% are able to retain ions with two valences (e.g.: Mg, Zn) more than the tree valences arsenic. Nano-filtration parallel with arsenic removal is suitable for iron and manganese removal as well. It radically decreases the total hardness off the water; in some cases we get excessively soft water after nano-filtration. I set up an order describing the retention (nano filtration) of typical cations situated in real well water.

$$\mathbf{R(B)} < \mathbf{R(Si)} < \mathbf{R(Na)} < \mathbf{R(K)} < \mathbf{R(Ca)} < \mathbf{R(Ba)} < \mathbf{R(Sr)} < \mathbf{R(Zn)} < \mathbf{R(Mg)}$$

5. Statements concerning UTC 60 membrane retention.

Describing the different ions retentions (R(%)), the following type of regression equation was set:

$$R(\%) = A + B \cdot (T) + C \cdot (pH)$$

Name of ion	A/constant	B/temperature	C/pH
As(III)	15,27	-0,85	4,08
As(V)	85,60	-0,19	1,06
Zn	87,88	-0,26	1,47
Mg	94,36	-0,14	0,50

There was no effect experienced on to retention of the given ion by presence of different ions. Validity of the equations:  $5 \leq pH \leq 9$ ,  $10^\circ C \leq T \leq 30^\circ C$

As(III):	0,2 mg/L	$\leq$	$W_1$	$\leq$	20 mg/L
As(V):	0,2 mg/L	$\leq$	$W_1$	$\leq$	20 mg/L
Zn:	0,6 mg/L	$\leq$	$W_1$	$\leq$	60 mg/L
Mg:	6 mg/L	$\leq$	$W_1$	$\leq$	600 mg/L

6. Statements concern Desal D5 membrane retention.

Describing the different ions retentions (R(%)), the following type of regression equation was set as well:

$$R(\%) = A + B \cdot (T) + C \cdot (pH)$$

Name of ion	A/constant	B/temperature	C/pH
As(III)	15,17	-0,82	4,30
As(V)	93,17	-0,10	0,63
Zn	86,44	-0,23	1,78
Mg	94,98	-0,22	0,69

There was also no effect experienced on to retention of the given ion by presence of different ions.

Validity of the equations:  $5 \leq pH \leq 9$ ,  $10^\circ C \leq T \leq 30^\circ C$

As(III):	0,2 mg/L	$\leq$	$W_1$	$\leq$	20 mg/L
As(V):	0,2 mg/L	$\leq$	$W_1$	$\leq$	20 mg/L
Zn:	0,6 mg/L	$\leq$	$W_1$	$\leq$	60 mg/L

$$\underline{\text{Mg: } 6 \text{ mg/L} \leq W_1 \leq 600 \text{ mg/L}}$$

7. Experiments carried out with high arsenic content well water verify that retention of arsenic and two valences ions can be calculated well on the basis of regression equations set up as a result of experiments using model solutions. The reason is that the individual retention of the examined ion is practically not influenced by the presence of difference ions at the measured concentration range. This way, applying nanofiltration to decreasing As, Mg and Zn content of well water contaminated with arsenic can be precisely (<2%) estimated in advance, using my results.

#### 8. Pure water flux of the membranes

The flux (flow-density of the permeate volume) is described as a quotient of pressure loss of trans-membrane and resistance of a membrane:

$$Jp = \frac{\Delta P}{R_M}$$

The resistance of membranes ( $R_M$  (bar·m<sup>2</sup>·h/L)) was described by the following regression equation:

$$R_M = D + E \cdot (T) + F \cdot (\text{pH})$$

Name of membrane	D/constant	E/temperature	F/pH
UTC 60	0,199	-0,00435	0,0055
Desal D5	0,193	-0,00485	0,011

Validity of the equations:  $5 \leq \text{pH} \leq 7$ ,  $10^\circ\text{C} \leq T \leq 30^\circ\text{C}$

9. In case of arsenic containing well water because of concentration growth at the wall of the membrane, calculation of the flux was corrected by osmotic pressure model (Rautenbach), which is typical to nanofiltration. The advantage of the Rautenbach model that it is not necessary to measure additionally the resistance of the polarization layer, which appears during filtering process. This model set up strict correlation between the filtering performance and the flow and hydrodynamic conditions.

On the basis of my experimental results the value of the motive power modification factor (a) in the osmotic pressure model was determined at drinking water filtration process (a=2,64 bar/g/L).

In case of small ion concentration ( $W_2=8 \cdot 10^{-3}$  %) in drinking water the linear Van't Hoff correlation is valid. So exponent "n" in equation  $\Pi_w = a \cdot W_2^n$  can be considered one (n=1).

#### 10. Constants determined for nanofiltering equipment

The thickness of the polarization layer can be determines as a ratio of the diffusion constant and the mass transfer coefficient.

Degree of polarization of the concentration can be calculated as the exponential power (e) of the ratio of the flow-density of the permeate volume and the mass transfer factor.

On the grounds of flow and geometric conditions of the universal membrane filtering equipment (DDS Lab 20 (Denmark)) the mass transfer factor, the polarization layer thickness and the concentration polarization was determined for the filtration of arsenic contaminated water of South-Transdanubian region:

Recirculation volume flow	Mass transfer factor	Thickness of polarization layer	Polarization of concentration
300 l/h	$6,68 \cdot 10^{-5}$ m/s	3,24 $\mu\text{m}$	1,1
400 l/h	$7,33 \cdot 10^{-5}$ m/s	2.02 $\mu\text{m}$	1,05

## CONSEQUENCES AND PROPOSALS

Nano-filtration both technologically and economically is suitable procedure for treatment of arsenic contaminated drinking waters.

In case of treatment of extremely soft well waters, water should be harden back by adding Mg and Ca salts.

During the procedure minimal amount of wastewater is produced. Because of it, I suggest to perform further concentration and handling experiments with the wastewater.

In the interest of enlarging and optimisation of the efficiency of the procedure the further investigation of the cleaning technology of the nanofilter equipment contaminated with arsenic and survey of additives that prevent deposit formation of arsenic content mud are such an areas, which offer economical advantages in the future.

## PUBLICATIONS

### *1.1 Articles*

#### *Articles - with IF:*

1. K. Manninger, **S. Gergely**, E. Békássy-Molnár, Gy. Vatai and M. Kállay: Pretreatment effect on the quality of white and red wines using cross-flow ceramic membrane filtration. **Acta Alimentaria** 27 (4), p. 377-387, **1998**. (Impact Factor: 0,400)

10 pont

2. **S. Gergely**, E. Bekassy-Molnar, G. Vatai: Wine production design by multiobjective optimization. **Journal of Food Engineering**. Közlésre elfogadva: **Paper 00/1130**, 2000 (Impact Factor: 0,611)

10 pont

3. **S. Gergely**, Gy.Vatai, E. Bekassy-Molnar: Arsenic, magnesium and zinc ion removal from water by nanofiltration. **Hungarian Journal of Industrial Chemistry**, **29**, p. 21-25, **2001** (Impact Factor: 0,250)

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*Article in Hungarian language:*

4. **S. Gergely**: A szőlő beszállításától a membránszűrésig. **Magyar Szőlő és Borgazdaság**. Melléklet 1999. április. 6. Oldal, **1999**

2 pont

*1.2 Book, chapter of book:*

5. **S. Gergely**, P. Téglásy, Z. Formanek,: Az élelmiszeripar napjainkban Magyarországon. **Könyv fejezet**: Higiénia. G-Mentor Kiadó, **2001**

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*1.3 Conference proceedings:*

6. **S. Gergely**, E. Bekassy-Molnar, G. Vatai and P. Biacs: Membrane filtration as a promising technology for arsenic and heavy metal ion removal from drinking water sources. International **Symposium on Energy and Food Industry**. Budapest 1998. Sept.15-16, p. 220-225, **1998**

5 pont

7. **S. Gergely**, K. Manninger, M. Kállay, Gy. Vatai, E. Békassyné-Molnár: Characterisation of quality parameters of wines by regression analysis. **Műszaki Kémiai Napok '97**, Book of Abstracts, p. 52., Veszprém 1997.

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8. **S. Gergely**, Sz. Major, Gy. Vatai, E. Békassyné-Molnár: Influence of operation parameters on the metal ion retention of nanofiltration membranes. **Műszaki Kémiai Napok '98**, Book of Abstracts, p. 95., Veszprém 1998.

2 pont

9. **S. Gergely**, Cs. Szántó, K. Manninger, M. Kállay, Gy. Vatai Gy., E. Békassyné-Molnár: Borszűrés modellezése és az optimális minőségi paraméterek meghatározása. (Modeling of wine filtration and determination of optimal quality parameters.) VIII. Országos Membrántechnikai Konferencia. Előadás összefoglaló 4. oldal, Nyergesújfalu 1997.

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10. **S. Gergely**, Gy. Vatai, E. Békassyné-Molnár: Elimination of Pollutants from drinking water by nanofiltration. **Balaton Symposium '97**, Book of Abstracts, p. 86., Siófok 1997.



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11. **S. Gergely**, Cs. Szántó, K. Manninger, M. Kállay, Gy. Vatai, E. Békassyné-Molnár: Modelling and optimization of wine membrane filtration on ceramic membranes. Balaton Symposium '97, Book of Abstracts, p. 195., Siófok 1997.

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12. **S. Gergely**, Gy. Vatai, E. Békassyné-Molnár, B. Czukor: Ivóvíz tisztítási kísérletek nanoszűrőssel. (Experimental drinking water treatment using nanofiltration.) VIII. Országos Membrántechnikai Konferencia. Előadás összefoglaló 6. oldal, Nyergesújfalu 1997.

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13. **S. Gergely**, Sz. Major, Gy. Vatai, E. Békassyné-Molnár, B. Czukor, J.-P. Duguet: Arsenic removal from drinking water by nanofiltration. CHISA '98. No 0375, Praha, 1998

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14. C. Szanto, **S. Gergely**, Gy. Vatai, E. Békassyné-Molnár: Wine production design by multiobjective optimization. EURO-Membrane 99 Int. Congr. Book of abstracts, Vol.2., p. 311-312 , Leuven. 1999.

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15. **S. Gergely**, Gy. Vatai, E. Békassyné-Molnár, J.-P. Duguet: Arsenic and bivalent cation removal from drinking water by nanofiltration. EURO-Membrane 99 Int. Congr. Book of abstracts, Vol.2., p. 240, Leuven. 1999.

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### *3. Participation in R+D projects*

#### *3.1 Participantion in Hungarian scientific- and R+D projects:*

16. OTKA T 026140: Ivóvíz és nagy tisztaságú vizek előállítása membránszeparációval. (Drinking water and high quality water producing with membrane separation.) 2000.

1 pont

#### *3.2 Participation in international scientific – and R+D projects:*

17. Report on „Use of nanofiltration membranes for the removal of heavy metal pollutants from drinking water.” Nemzetközi K+F pályázat a Lyonnaise des Eaux, Franciaország támogatásával. 1998

3 pont

18. Report on „Influence of oxidazing agent on the rejection of As (V) and impact of joint oxidation of Fe, Mn and As on membrane performances.” Nemzetközi K+F pályázat a Lyonnaise des Eaux, Franciaország támogatásával. 1999

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