

Effect of operating conditions in removal of arsenic from water by nanofiltration membrane

Hugo Saitúa^a, Mercedes Campderrós^a, Soledad Cerutti^b, Antonio Pérez Padilla^{*a}

^a*Instituto de Investigaciones en Tecnología Química (INTEQUI), ^bArea de Química Analítica, Departamento de Química, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis (CONICET), C.C. 290, Chacabuco 915, 5700 San Luis, Argentina*
Fax +54 (2652) 426711; e-mail: apadilla@unsl.edu.ar

Received 1 September 2003; accepted: 4 August 2004

Abstract

The removal of arsenic from synthetic waters and surface water by nanofiltration (NF) membrane was investigated. In synthetic solutions, arsenic rejection experiments included variation of arsenic retentate concentration, transmembrane pressure, crossflow velocity and temperature. Arsenic rejection increased with arsenic retentate concentration. Arsenic was removed 93–99% from synthetic feed waters containing between 100 and 382 µg/L As V, resulting in permeate arsenic concentrations of about 5 µg/L. Under studied conditions, arsenic rejection was independent of transmembrane pressure, crossflow velocity and temperature. In surface water, the mean rejection of As V was 95% while the rejection of sulfate was 97%. The co-occurrence of dissolved inorganics does not significantly influence arsenic rejection. The mean concentration of As in collected permeated was 8 µg/L. The mean rejection of TDS, total hardness and conductivity were 75, 88 and 75% respectively.

Keywords: Arsenic removal; Drinking water; Nanofiltration (NF); Operating conditions

1. Introduction

The United States Environmental Protection Agency (USEPA) maximum contaminant level (MCL), for arsenic was 50 ppb (µg/L) over

50 years ago. The arsenic MCL was lowered to 10 µg/L in a rule promulgated on January 22, 2001. Data had been under review by the USEPA for several years prior to issuing the new standard and seek an independent review of the science behind the standard and the cost as-

* Corresponding author

sociated with implementing the new rule. The USEPA indicated that they believe that the arsenic standard needs to be revised and lowered below the current 50 µg/L level, but that they need to review if it is necessary to set the standard as low as 10 µg/L. The World Health Organization (WHO) has established a provisional arsenic limit of 10 µg/L because of the epidemiological evidence of arsenic carcinogenicity [1–4]. In Argentina, some of the drinking water sources contain more than this value [5,6]. The concern over arsenic is especially severe because of the number of surface and groundwater systems that exceed the arsenic MCL.

Various technologies such as coagulation, filtration, lime softening, activated alumina, anion exchange, reverse osmosis have been studied to determine efficacy of arsenic removal [7]. Reverse osmosis has been identified as a best available technology for arsenic removal, but economic studies have shown it to be the most costly [8–9].

Developments in membrane technology have produced nanofiltration (NF) membranes with higher selectivity and increased water flux at much lower operating pressure. In addition, because arsenic is typically present in natural waters as a divalent oxyanion (HAsO_4^{2-}) [9–12], there has been much interest in the use of NF membranes which are known to be quite effective at removing divalent ions.

A limited number of studies have been performed to examine the removal of arsenic by NF membranes [9,13–16]. The results show that NF processes are effective for the removal of arsenic. Removal however depends upon operating parameters, membrane properties and the characteristics of the source water.

In this work experiments were performed using a NF module to determine the efficacy of As V retention from a synthetic solution under various operating conditions such as solution concentration, concentration factor (CF), transmembrane pressure, recovery, crossflow velocity and temperature. Finally, experiments were

performed to determine the removal of arsenic from surface water.

2. Materials and methods

2.1. Standards and reagents

All salt solutions were prepared fresh using reagent-grade chemicals dissolved in pure water. The arsenate, As V, standard was prepared from sodium salt heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Mallinckrodt®), dissolved in pure water. Sodium bicarbonate solutions were prepared from NaHCO_3 (Fluka®).

2.2. NF membrane module

The NF membrane module is spiral wound thin film composite polyamide membrane (192-NF 300) manufactured by Osmonic Inc. The molecular weight cut off 180 Da. The NF membrane module is enclosed in an OSMO® 19E-HR 500-ECN-membrane housing. Each element is 2×39 in and has an active membrane surface of 1.5 m².

2.3. NF unit description

The unit used for carrying out NF experiments is reported in Fig. 1. It was equipped with a feed and permeate container, a pressure vessel containing the membrane module, a circulation and pressurization pump with a security valve two pressure gauges, a thermometer for temperature measurement in the circulation reservoir, a tap water heat exchanger for temperature control, two flow-meters on permeate and retentate exit pipers.

2.4. Sample analysis

Arsenic standard solution was prepared by appropriate dilutions of a 1000 mg/L stock solution (Merck) immediately before use.

A 0.6% (w/v) sodium borohydride solution (Aldrich Chemical Co.) was prepared in 0.5% (w/v) sodium hydroxide solution and was filtered through Whatman No. 42 filter paper to remove undissolved solids.

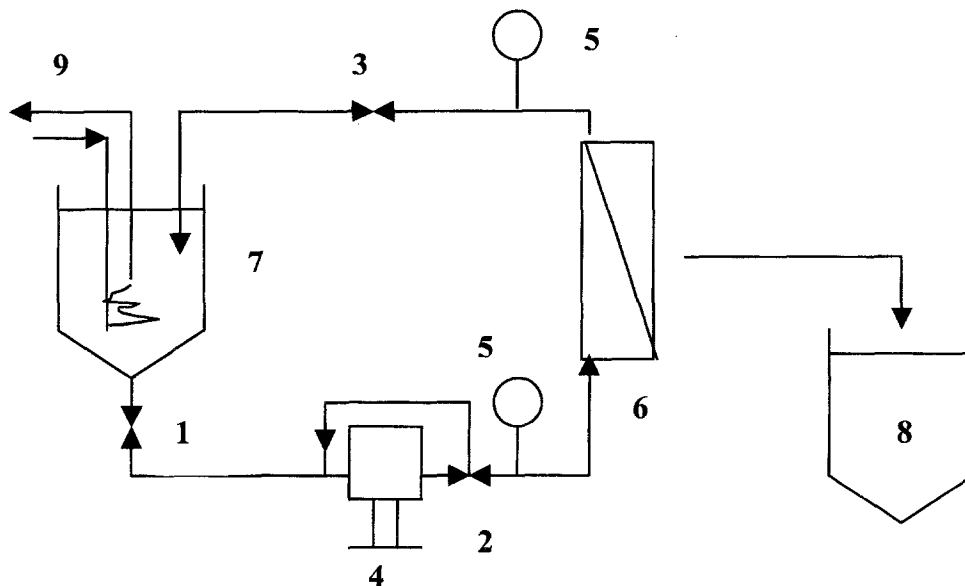


Fig. 1. Schematic experimental unit for NF; 1,2,3: valves; 4: pump, 5: pressure gauge, 6: membrane module; 7: feed tank; 8: permeate tank, 9: water bath.

The measurements were performed with a sequential inductively coupled plasma spectrometer [BAIRD (Bedford, MA, USA) ICP 2070]. The 1m-Czerny Turner monochromator had a holographic grating with $1800 \text{ grooves mm}^{-1}$. The hydride unit used was a PS Analytical LTD Hydride Generator and the flow speeds of the reagents were controlled by a Watson-Marlow 303X peristaltic pump.

pH readings were made in accordance with SM 4500-H⁺ on an Orion 720A. A three-point calibration (pH 4, 7 and 10) with Beckman Instruments Inc., traceable pH buffers was performed daily. Between tests, the pH probe was kept wet in KCl solution.

The conductivity was measured by handheld Cole Parmer Instrument Company Model 1-19820-10 conductivity meter. On a daily basis, the monitor was calibrated with standard solutions from the manufacturer.

3. Experimental methods

In this research, the experiment has been divided into two parts. The first part deals with

the study on the performance of the rejection of As V from synthetic solution by NF membrane as a function of arsenic concentration in the retentate, concentration factor, transmembrane pressure, crossflow velocity and temperature. The second part reports the results of arsenic retention in natural surface water.

3.1. NF test with synthetic solution

For the first part of the research, As V separation tests were all conducted in the presence of $10^{-3} \text{ M NaHCO}_3$ to simulate the alkalinity and pH of natural waters. It should be noted that in most natural waters, arsenic is present only in the divalent form of arsenate (HAsO_4^{2-}) [9–12].

Concentration of As was increased step-by-step operating in a closed system simulating a real operation for obtaining the membrane behavior with increasing concentration in the retentate. Initial concentration was equal to $100 \mu\text{g/L}$ in an initial volume of 20 L. These tests were carried out at pressure of 724 kPa and a temperature of 25°C , with full recycle of

both permeate and retentate for 4 h to stabilize the membrane. Samples of permeate and retentate were drawn every hour to check if stability was reached. After that 5 L of permeate were collected followed by stabilization for 1 h, samples of permeate and retentate were collected, this cycle was repeated three times for a total of 6 samples. The total volume of collected permeate was 15 L, the permeate flux during the run was practically constant (11.08 $\mu\text{m/s}$) with increasing the concentration factor to 4. The crossflow velocity was kept in 18.11 cm/s.

In the study on the effect of transmembrane pressure on As V rejection, the pH solution was adjusted to 8.1–8.2 and the temperature was of 25°C. The crossflow velocity was of 18.11 cm/s. The transmembrane pressure was varied in the range of 310–724 kPa. In the study on the effect of crossflow velocity on As V rejection, the experiment was done at 724 kPa. The crossflow velocity was varied in the range of 8.4–18.11 cm/s. Previously the effect of crossflow velocity on transmembrane pressure in pure water was studied. The study of the effect of temperature on rejection of As V and permeate flux were done at transmembrane pressure of 724 kPa, varying temperature from 10–25°C. The crossflow velocity was 18.11 cm/s.

It must be observed that in all runs, samples were withdrawn from the return pipe of the retentate in the recirculation batch. Owing to water permeation in the membrane module the retentate concentration is always greater than the initial and that one in the recirculation batch.

3.2. Nanofiltration test with surface water

For the second part of the research 24 L of surface water were collected, contaminated and submitted to NF membrane modules. The tests were carried out by recycling permeate and retentate for 4 h before switching the operating mode for permeate collection. The initial volume was reduced at 9 L by means of permeate

Table 1

Retentate and permeate concentration of As V in the time

Time, h	CF	Retentate conc., $\mu\text{g/l}$	Permeate conc. ¹ $\mu\text{g/l}$	Rejection, %
1	1	108.40	5.63	95
2	1	110.07	7.68	93
3	1	96.03	6.16	94
4	1	97.01	6.72	93
5	1.33	114.88	< 5	96
6	2	159.73	< 5	98
7	4	382.58	< 5	99

¹The minimum detection limit for arsenic measurements by ICP-OES is of 5 $\mu\text{g/L}$.

drawing. The concentration factor was 2.66 so retentate concentration increased with the time. The experiment was conducted at a crossflow velocity of 18.11 cm/s, a transmembrane pressure of 724 kPa and a temperature of 25°C.

4. Results

4.1. NF test with synthetic solution

4.1.1. Effect of As retentate concentration on the rejection of As V

Table 1 shows the separation of As V in the time. The permeate arsenic concentrations were all lower than MCL. Concentration values, measured in the collected permeate were of 6.23 $\mu\text{g/L}$. At the end of the run an easy washing with pure water for 2 h was sufficient to restore the initial flux. The effectiveness of washing was confirmed by analysis of samples drawn after the washing that showed a total arsenic absence.

Fig. 2 shows the rejection of As V as a function of As retentate concentration. The rejection of As V, increases as the retentate As concentration increases. The transport of As V through the membrane does not increase proportionally with increasing retentate concentration and consequently the retention of As V species increases.

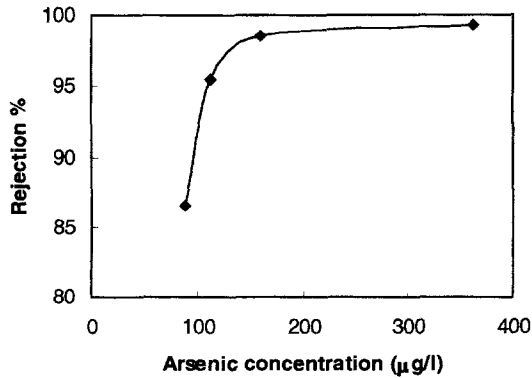


Fig. 2. Effect of retentate arsenic concentration on the removal of As V in the presence of 10^{-3} M, NaHCO_3 to simulate alkalinity and pH of natural waters; crossflow velocity: 18.11 cm/s; pH: 8.1–8.2 and temperature: 25°C.

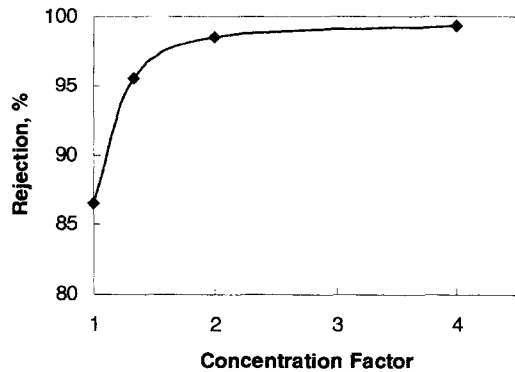


Fig. 3. Effect of concentration factor on the removal of As V in the presence of 10^{-3} M, NaHCO_3 to simulate alkalinity and pH of natural waters; crossflow velocity: 18.11 cm/s; pH: 8.1–8.2 and temperature: 25°C.

Fig. 3 shows the separation of As V as a function of CF. As CF is increased, the rejection of As V increases exponentially. The permeate flux was practically constant proving that the membrane was not significantly fouled.

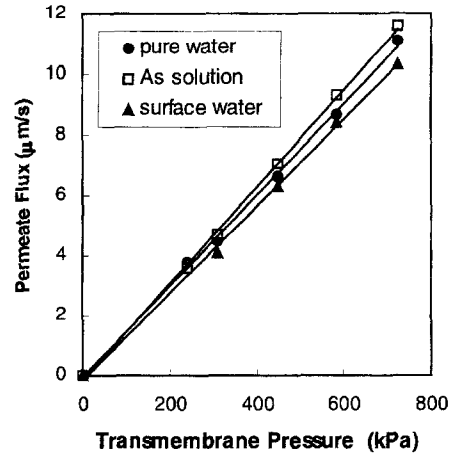


Fig. 4. Fluxes of 3 types of feed waters; crossflow velocity: 18.11 cm/s; temperature: 25°C.

4.1.2. Effect of transmembrane pressure on rejection of As V and permeate flux.

The permeate fluxes of pure water, synthetic solution and surface water were investigated as a function of transmembrane pressure under steady state after 4 h. The results are shown in Fig. 4. It was found that the fluxes increase with transmembrane pressure. The permeate fluxes obtained at a transmembrane pressure of 724 kPa were 11.56, 11.08 and 10.34 $\mu\text{m/s}$ for pure water, synthetic solution and surface water respectively.

The separation of As V as a function of transmembrane pressure after the filtrate time of 4 h is showed in Fig. 5. The rejection of As V seemed not to be sensitive to the change in operating transmembrane pressure from 310–724 kPa. The results suggest that the solute permeate flux seems independent of the water flux. The range of water recoveries was 5.6–15%. The formula used to calculate percentage water recovery was as follows:

$$\% \text{ water recovery} = 100 (Q_p/Q_f) \quad (1)$$

where Q_f : feed water flow rate and Q_p : permeate flow rate.

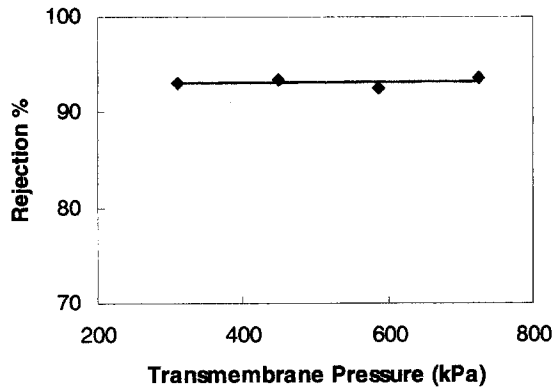


Fig. 5. Effect of transmembrane pressure on the removal of As V in the presence of 10^{-3} M, NaHCO_3 to simulate alkalinity and pH of natural waters; crossflow velocity: 18.11 cm/s; pH: 8.1–8.2 and temperature: 25°C.

4.1.3. Effect of crossflow velocity on the rejection of As V and permeate flux

The effect of crossflow velocity on permeate flux and rejection of As V are shown in Fig. 6. The flux and the rejection As V were not affected by changing crossflow velocity in the range of 8.40–18.11 cm/s.

It is well known that increasing crossflow velocity increases both the mass coefficient across the concentration polarization boundary layer and the degree of mixing near the membrane surface, thereby reducing both the accumulation of a gel layer on the membrane surface and the fouled membrane resistance [17–18]. Hence the effect of crossflow velocity on membrane performance was investigated. The state of turbulence in the spiral-wound module is not too clear. The velocity on the feed channel is calculated by dividing the feed flow rate by cross-sectional area. The cross-sectional area is $a \times b$ for slits where a is the width of the flat sheet minus the glued portion, and b is the channel (spacer) height. On that basis, the crossflow velocity in spiral-wound units are superficial velocities, since the volume

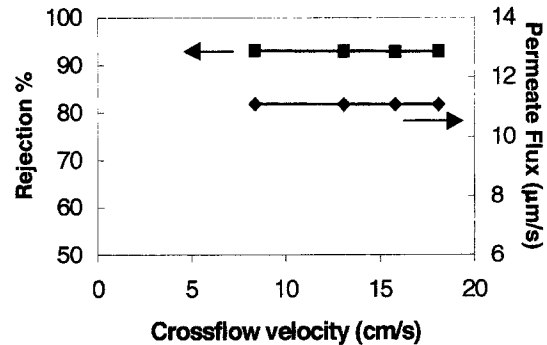


Fig. 6. Effect of crossflow velocity: on the removal of As V and permeate flux in the presence of 10^{-3} M, NaHCO_3 to simulate alkalinity and pH of natural waters; temperature: 25°C; pH: 8.1–8.2.

occupied by mesh-like spacer in the feed channels is neglected. The crossflow velocity between 8.40 and 18.11 cm/s, corresponding to Reynolds numbers of 128–275. Technically, this is the laminar flow region, but the additional turbulence contributed by the spacers, which can be substantial should also be taken into account [19].

The state of turbulence can be determined by the nature of relationship between transmembrane pressure (ΔP) and flow rate (Q_f) in the feed channel. The general relationship between these two quantities is: $\Delta P = f(Q_f)^n$, with $n = 1$ for laminar flow and $n = 1.5$ – 1.9 for turbulent flow. To determine the state of turbulence a series of experiments with pure water was carried out at cross flow velocity between 8.40 and 18.11 cm/s ($T = 25^\circ\text{C}$). Data were well fitted by the following correlation:

$$\Delta P = 4.73 (Q_f)^{1.62} \quad (2)$$

The n value of 1.62 indicates that the system is working in the turbulent flow regimen. Fig. 6 confirms that a turbulent flow is produced in the range of operating conditions considered here.

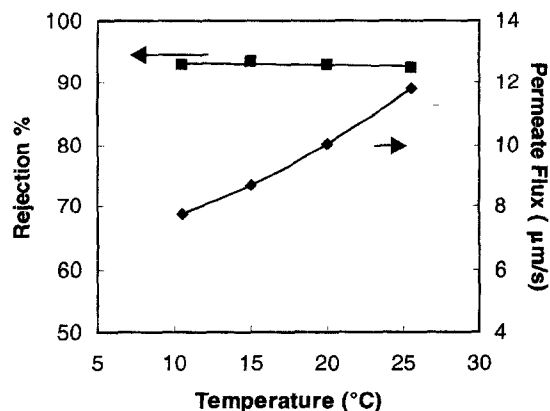


Fig. 7. Effect of temperature on the removal of As V and permeate flux in the presence of 10^{-3} M, NaHCO_3 to simulate alkalinity and pH of natural waters; cross-flow velocity: 18.11 cm/s; pH: 8.1–8.2.

4.1.4. Effect of temperature on the rejection of As V and permeate flux

The effect of temperature on permeate flux and rejection As V is shown in Fig. 7. The permeate flux increased with increasing temperature apparently. The rejection of As V seemed not to be sensitive to the change in operating temperature.

4.1.5. Arsenic mass balance

In order to examine possible retention of arsenic within the module a mass balance for arsenic was carried out. The mass balance was calculated by the following expression:

$$C_f V_f = C_r V_r + C_p V_p \quad (3)$$

where V_f is the initial feed volume; V_r retentate volume; V_p , permeate volume, C_f feed concentration, C_r retentate concentration and C_p permeate concentration.

If all of the arsenic present in the feed water exited the membrane module, then the sum of mass in the retentate and permeate waters should be equal to mass of arsenic in the feed water. The difference or possible retention of arsenic in the system was calculated by subtracting the

arsenic measured in the retentate and permeate waters from the feed water. The mass balances show that the total arsenic entering the system was higher than the mass of total arsenic existing in the system. The amount of total arsenic unaccounted in the mass balance represents approximately 8% of the initial quantity of arsenic.

The unaccounted total arsenic in the mass balances may be a result of several factors, including sample collection method, laboratory variation and retention of arsenic within the module. Given the consistent “loss” of arsenic in the mass balance calculation in all the runs, it is suspected that some arsenic is being retained within the membrane module. Some of the arsenic is most likely being trapped in the membrane and the membrane is acting as a filter to remove and retain this material.

4.2. NF test with surface water

Surface water was taken from The Volcán River near the University of San Luis. One hundred $\mu\text{g/L}$ of arsenate was added because the original surface water is not contaminated by arsenic.

Table 2 provides a summary of parameters dates in the feed, retentate and permeate streams. The mean rejection of As V is about 96% while sulfate rejection is higher (97%), the rejection of TDS is 75% and the total hardness is 88%. Global ionic rejection, as indicated by conductivity measurements, was the 75%.

5. Conclusion

Experiments were performed to evaluate the ability of NF-300 membrane module to remove As V from synthetic solution and surface water. In synthetic solutions, the results clearly show that the NF-300 membrane consistently reduced the arsenic concentration in the permeate at values that are below the current and proposed arsenic MCL (50 and 10 $\mu\text{g/L}$). The rejection of As V by the NF-300 membrane was found to be between 93–99% for retentate arsenic concen-

Table 2
Sample analysis in NF test using surface water

Parameter	Feed	Collected permeated	Final retentate
pH	8.45	8.28	8.14
Total dissolved solids ^a , mg/L	525	233	914
Conductivity, $\mu\text{S}/\text{cm}$	859	394	1569
Total hardness ^b , mg/L as CaCO_3	276	68.1	573
Arsenic, $\mu\text{g}/\text{L}$	100	8	240.3
Sulfate ^c , mg/L	225	18	550
Chloride ^d , mg/L	24	23.4	24.8

^a SM 2540 C; ^b SM 2340 C; ^c SM 4500 SO_4^{2-} E; ^d SM 4500 Cl^- B

tration in the range of 100 and 382 $\mu\text{g}/\text{L}$, resulting in permeate arsenic concentrations of about 5 $\mu\text{g}/\text{L}$.

Operating under the defined conditions in this test, the rejection of As V was independent of transmembrane pressure, crossflow velocity and temperature.

The mass balance shows “loss” of arsenic in the system. The importance of recognizing the possible retention of arsenic within the membrane is that fouling of membranes is a primary cause of high maintenance cost.

Application of NF-300 membrane to surface water showed that the co-occurrence of dissolved inorganics do not significantly have influence on the rejection of As V. A concentration factor of 2.66 was applied. The mean rejection of As V was 95% while the rejection of sulfate was 97%. The membrane also reduced the concentrations of TDS and total hardness.

Because arsenic in surface waters is typically in the form of As V, low pressure, NF-300 membrane can be used to treat surface waters with unacceptable arsenic concentrations.

References

- [1] F.W. Pontius, J. AWWA, 90(3) (1998) 38.
- [2] F.W. Pontius, J. AWWA, 87(4) (1995) 38.
- [3] E.M. Vrijenhoek and J.J. Waypa, Desalination, 130 (2000) 165.
- [4] NSF International, Environmental Technology Verification Report: Removal of arsenic in drinking water: Prepared for USEPA, August, 2001.

- [5] J.A. Castro, Acta Bioqca. Clínica Latinoam., 16 (1982) 3–17.
- [6] J.C. Luján, Pan. Am. J. Public Health, 5 (2001) 9.
- [7] International Consultants Inc. and Malcolm Pirnie Inc., Technologies and Cost for Removal of Arsenic from Drinking Water, Prepared for USEPA, April, 1999.
- [8] M.M. Frey, D.M. Owen, Z.K. Chowdhury, R.S. Raucher and M.A. Edwards, J. AWWA, 90(3) (1998) 89.
- [9] J.J. Waypa, M. Elimelech and J.G. Hering, J. AWWA, 89(10) (1997) 102.
- [10] P. Brandhuber and G. Amy, Desalination, 117 (1998) 1.
- [11] J.G. Hering and M. Elimelech, Project 953-93, AWWARF Final Report, No. 90706, 1996.
- [12] J.G. Hering P.Y. Chen, J.A. Wilkie and M. Elimelech, J. Environ. Eng., 123 (1997) 800.
- [13] T. Urase, J. Oh and K. Yamamoto, Desalination, 117 (1998) 11.
- [14] M.A. Thompson and Z.K. Chowdhury, Proc. AWWA Annual Conference, San Antonio, TX, 1998.
- [15] S.D. Chang, in: Critical Issues in Water and Wastewater Treatment, ASCE, Boulder, CO, 1994.
- [16] Malcolm Pirnie Inc, Arsenic Removal Pilot-Scale Studies: Prepared for USEPA Office of Ground Water and Drinking Water, 1992.
- [17] M. Cheryan, ed., Ultrafiltration and Microfiltration Handbook, Technomic, Lancaster, PA, 1998.
- [18] R. Noble and S.A. Stern, eds., Membrane Separations Technology: Principles and Applications, Elsevier, Amsterdam, 1995.
- [19] M. Cheryan and B.H. Chiang, in: Food Process Engineering, Vol. 1B, McKenna, ed., Appl. Sci. Pub., London, UK, 1984.