

Experimental Investigation of Nanofiltration Process for the Separation of Complex Aqueous Electrolyte Mixtures

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The era of membrane technology began in 1960s as a viable alternative to the more conventional separation techniques (distillation, extraction and evaporation processes) and can carry out separations that are difficult by other means. For these reasons membranes are becoming increasingly important in food and dairy industries for a variety of desalting, purification, concentration and other separations. Most of the previous work done on NF process is at room temperature and low pressures. The novelty of this work lies in the high pressure and high temperature applications in connection with our previous work mentioned in the reference section. This work focuses on the experimental study of nanofiltration (NF) process for the separation of binary, ternary and quaternary aqueous mixtures of different salts at a starting concentration of 0.25 w% of each, whether single or in a mixture form. The experiments proved that NF process is capable of separating different ions from solution. The evaluation of the data revealed that the rejection of divalent cations and anions was greater than 96 % in most of the cases.

1. Introduction

The chemical and process industry is governed by environmental legislation to reduce the number of toxic solvents, reagents and effluents used in processes to minimize the industrial waste which is potentially harmful to the environment. The need to meet more stringent legislation has led to the search for alternative for additional separation techniques (Timmer, 2001). The advancement in the research related to development and application of membrane separation processes is one of the most significant achievement in chemical, environmental and biological process engineering (Lyshevski, 2014). A membrane can be defined as a selective barrier that permits the passage of certain species (called permeate) in a fluid. Solute particles are (partially) retained depending on the properties like size, shape and charge. The four pressure driven membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). NF is an intermediate process between RO and UF with pore radius of about 0.5 to 2 nm, molecular weight cut off between 200 to 1,000 Dalton and operating pressure between 5 to 40 bar. NF is advantageous in different aspects such as it can be operated at low pressure, gives high permeate flux, retention of multivalent salts and organic solutes, low investment and operation and maintenance costs. In comparison with UF and RO, NF has always been a difficult process to define and to predict (Li et al., 2008). Transport mechanisms in nanofiltration membranes are generally described in terms of: convection, diffusion and electromigration for electrolyte systems (Szymczyk et al., 2003). In literature, for mathematical modelling purposes, the NF membranes are typically characterised by the pore radius, effective membrane charge density and effective membrane thickness to porosity ratio (Bowen et al., 1997).

2. Materials and method

In this work the separation performance of NF for aqueous solutions of single inorganic electrolytes (NaCl, MgCl₂·6H₂O, Na₂SO₄ and MgSO₄) and different combinations of them to form ternary and quaternary ionic systems has been studied experimentally. The experiments were conducted on a lab-scale cross-flow membrane unit OS-MC-01 from Osmota with effective membrane area of 0.008 m². A negatively charged NF

membrane (MPF-34) from Koch Membrane was used. It has a typical operating temperature range of 40 to 70 °C, a pressure range of 14 to 35 bar and a pH range of 0 to 14. All the experiments were performed in recirculation mode. The retentate was made to flow back to the feed tank to see the effect of increasing concentration on permeate flux and rejection. The process conditions for all the experiments were 32 bar, 60 °C, feed flowrate of 2.5 L/min and starting feed concentration of 0.25 w% of each electrolyte whether single or in a mixture form. The feed flow rate is high with respect to compact membrane module design resulting in crossflow velocities of more than 1.3 m/s. In addition, feed solutions are reasonably dilute, viscosities are low, and – as an advantage of this process – operating pressures are moderate to high. Specific fluxes are moderate and so the concentration polarization phenomenon is anticipated not to have a very profound effect on the separation performance of the NF membrane in most of the cases. The permeate weight was measured gravimetrically with an electrical balance in specified intervals to calculate the permeate flux. Pure water permeability was tested before and after each experiment at 32 bar, 2.5 L/min and 30 °C. The cleaning of the membrane was done accordingly as per manufacturer’s instructions. The flow diagram of the process is shown in Figure 1.

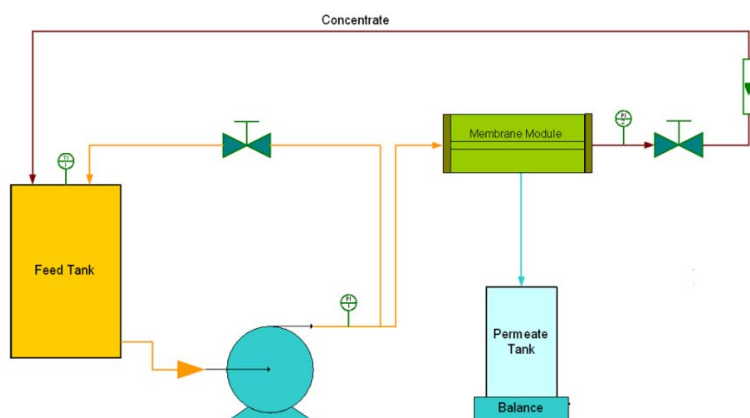


Figure 1: Experimental setup

The concentrations of dissolved solutes in the feed and permeate samples collected during the experiments were detectable by conductivity ~ concentration calibration curves for single electrolytes, while the individual concentrations of anions and cations for single and mixtures of electrolytes were analysed on Dionex 5000+ ion chromatography system.

3. Results and discussion

3.1 Separation of binary ion system

3.1.1 NaCl

The negatively charged NF membrane attracts the cations and repels the anions. This effect is known as Donnan effect. At lower concentration, the rejection of Na⁺ in NaCl was high (82 %). As the concentration was increased, the rejection started to decline (78 %) as shown in Figure 2(a) where the effect of concentration polarization is negligible but the rejection of Na⁺ and Cl⁻ ions of the same concentration of NaCl solution in the presence of sucrose (13 to 25 °Bx) has been reported to be decreased to almost zero (Samee et al., 2016) due to strong effect of concentration polarization on transport phenomenon. At higher concentration, the effect of steric hindrance was also negligible due to shielding of charged solutes (Wang et al., 1995). To keep the electroneutrality condition the Cl⁻ ion follows the same rejection behaviour presented in Figure 2(c). It was also inferred that at lower concentration, the adsorption of Cl⁻ ions at the membrane surface is negligible and at higher concentration, more chloride ions will get adsorbed (Schaep et al., 1999) for negatively charged membrane. Cl⁻ ions adsorption is prevalent on the membrane, with respect to sodium adsorption, since anions show lower hydration radii than cations (Takagi et al., 1990).

3.1.2 Na₂SO₄

Na⁺ ions presented a very high rejection (96 to 98 %) in Na₂SO₄ solution shown by Figure 2(a) with increasing trend as concentration of the solution increases followed by SO₄²⁻ shown in Figure 2(d). Since SO₄²⁻ ions cannot

permeate due to strong electrostatic exclusion so Na^+ were rejected accordingly to maintain zero current density.

3.1.3 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

In $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution, Mg^{2+} showed a slightly increase in rejection from 96 to 98 % shown in Figure 2(b) upon the increase of concentration. This behaviour has also been observed by other researchers (Bandini et al., 2003). As the concentration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ increases, more Mg^{2+} will be attracted to the surface and shield the membrane and results in positive charge. Charge reversion at the surface can also be expected like positive charge density in this case. The interfacial precipitation of the metal hydroxide which occurs at a lower pH value than the bulk lead to adsorption phenomenon (Labbez et al., 2003). The adsorption is influenced by the charge and dielectric constant. It was also explained that at higher concentration, pore shrinking can be expected (Hunter, 1981). Cl^- ions followed the same pattern to keep the electroneutrality presented in Figure 2(c).

3.1.4 MgSO_4

In MgSO_4 solution, since the SO_4^{2-} ions show a strong electrostatic exclusion so the rejection of SO_4^{2-} ions was more than 98 % as shown in Figure 2(d). Mg^{2+} ions followed the same rejection trend to keep zero current density condition as presented in Figure 2(b).

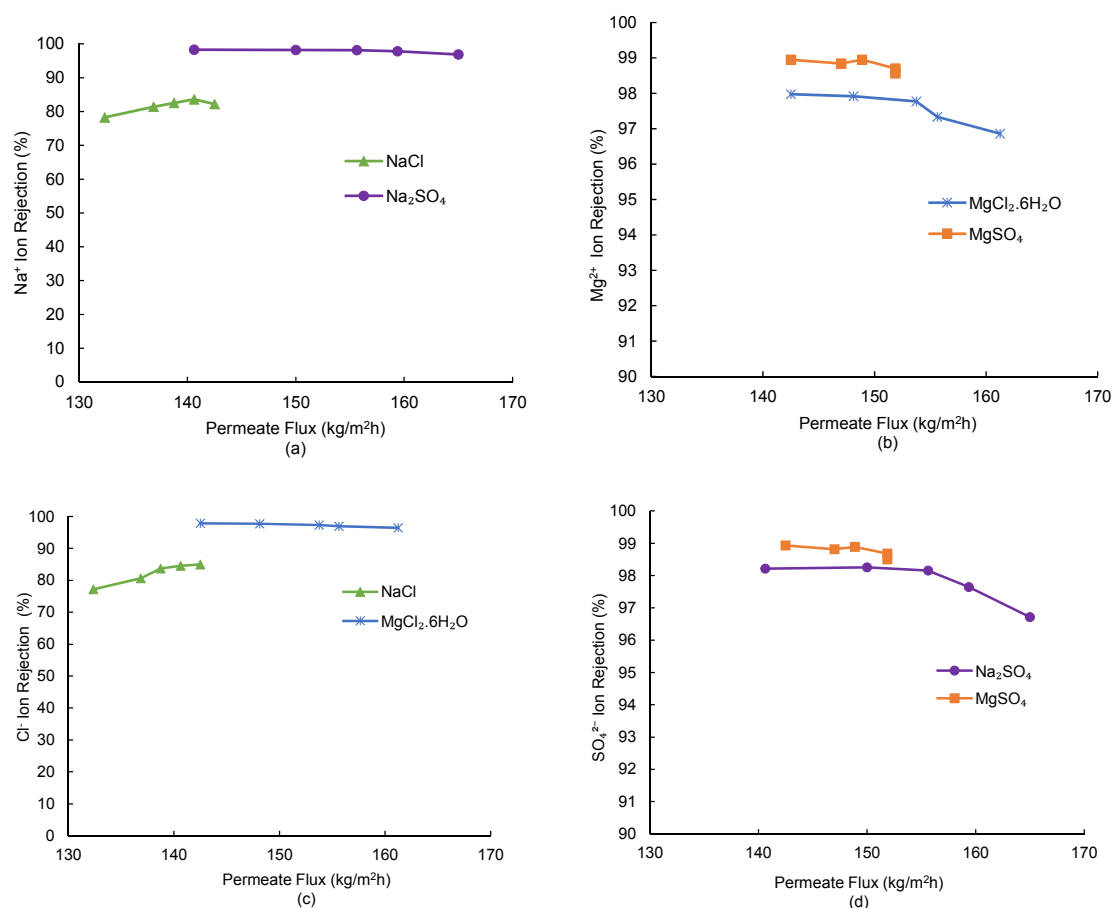


Figure 2: Rejection of cations and anions as a function of permeate flux in binary ion system

3.2 Separation of ternary ion systems

3.2.1 $\text{NaCl} + \text{Na}_2\text{SO}_4$

In this ternary ionic system the rejection of SO_4^{2-} ions remained in the range of 98 to 99 % owing to its large size and strong electrostatic exclusions between divalent SO_4^{2-} ions and negative membrane charge as depicted in Figure 3(d). The retention of Na^+ ions was decreased from 89 to 82 % as shown in Figure 3(a) and

is strongly dependent on the highly rejected SO_4^{2-} ions due to the electroneutrality condition. Here the concentration polarization has an appreciable effect on rejection mechanism. With increasing feed concentration the ionic concentration increases in the polarization layer. Na^+ ions contributed to shield the membrane charge to offer Cl^- ions a reduced electrostatic exclusion from the membrane. Also SO_4^{2-} gave a pull to monovalent co-ion (Cl^-) to permeate more to keep the electroneutrality condition. So the rejection of monovalent co-ion Cl^- decreases more (80 to 59 %), as shown in Figure 3(c) and could show negative retention under certain conditions. Negative retention of Cl^- ions has been observed by (Bowen et al., 1996) at lower molar ratios in the same mixture and also by (Szoke et al., 2002) at certain pH range of feed solution. Another study by (Samee et al., 2016) with the same feed concentration of salts as that of this experiment but additionally in the presence of sucrose (13 to 25 °Bx) has elucidated the negative rejection of Cl^- ions (up to -46 %) caused by enhanced concentration polarization effect on transport phenomena. Hereby, the driving force due to the electroneutrality was higher than the concentration gradient driving force.

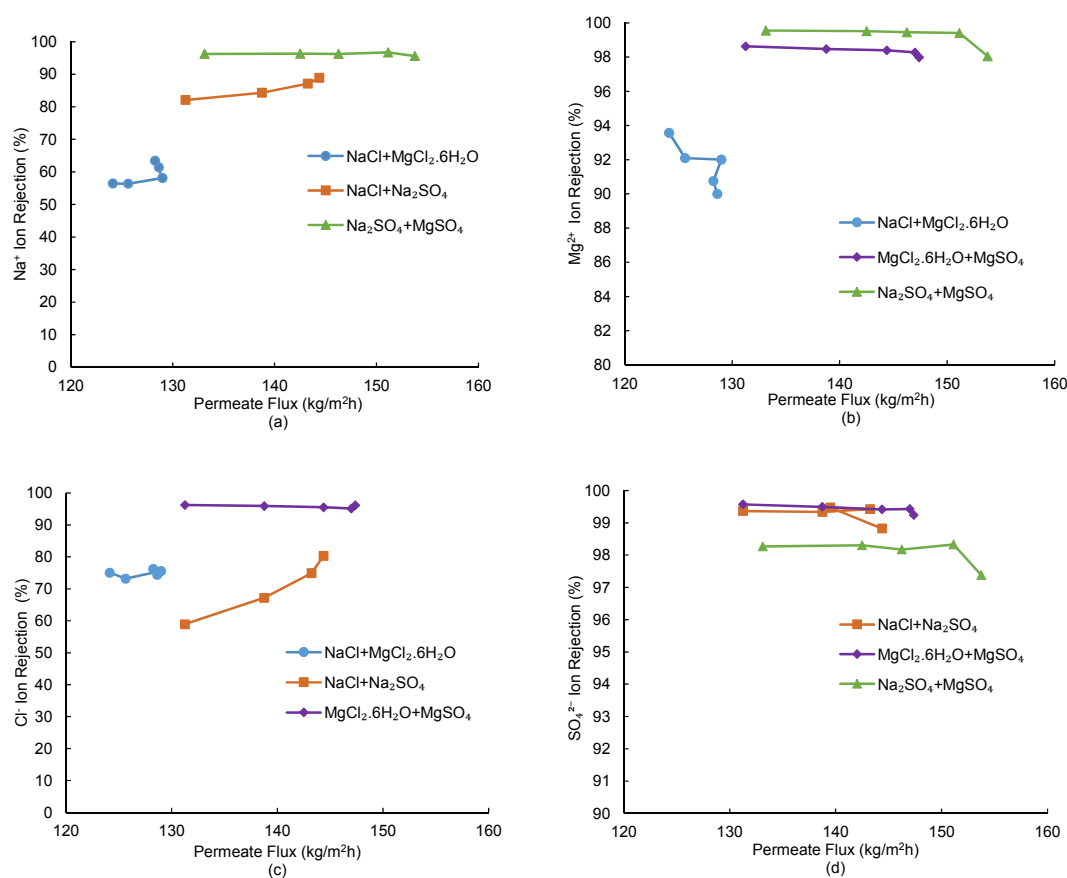


Figure 3: Rejection of cations and anions as a function of permeate flux in ternary ion system

3.2.2 NaCl+MgCl₂.6H₂O

In this ternary ionic mixture the monovalent counter ion Na^+ in the presence of divalent counter ion Mg^{2+} showed the same behaviour as Cl^- ion in $\text{NaCl}+\text{Na}_2\text{SO}_4$. The rejection of Na^+ ion was minimum amongst all the ions due to its lower molar ratio and decreased from 61 to 56 % shown in Figure 3(a). Here the effect of concentration polarization is not very profound as the rejections were not decreased appreciably but Na^+ ion has been reported to show negative retention (up to 21 %) in a mixture of $\text{NaCl}+\text{MgCl}_2.6\text{H}_2\text{O}$ with the same feed concentration as used in this experiment in the presence of sucrose (13 to 24 °Bx) due to strong effect of concentration polarization as mentioned by (Samee et al., 2016). Although Mg^{2+} ion has higher stokes radius than SO_4^{2-} ion, rejections obtained were lower than SO_4^{2-} ion rejections presented in the previous section. This can be attributed to the positive charge of Mg^{2+} ions and strong electrostatic exclusion between SO_4^{2-} ions and

membrane. The rejection of Mg^{2+} and Cl^- were 90 to 93 % and 74 to 75 % as shown in Figure 3(b) and 3(c) respectively.

3.2.3 $Na_2SO_4+MgSO_4$

In this mixture, high rejections of all the ions were observed. In contrast to Mg^{2+} ion possessing larger stokes radius, Na^+ ion with relatively smaller stokes radius will permeate through the membrane. Nevertheless due to electroneutrality condition SO_4^{2-} ions should pass through the membrane as well, which was mostly hindered by electrostatic exclusion and due to relatively large size of this ion. Consequently, the Na^+ permeation was hindered as well to represent a high rejection greater than 95 % as shown in Figure 3(a). The rejections of Mg^{2+} ions and SO_4^{2-} ions were greater than 98 % and 97 % as shown in Figure 3(b) and 3(d) respectively.

3.2.4 $MgCl_2.6H_2O+MgSO_4$

In this ternary ionic mixture the high rejections of the ions were observed which were greater than 95 % for Cl^- ions as shown in Figure 3(c) and 98 % for and Mg^{2+} and SO_4^{2-} ions as shown in Figure 3(b) and 3(d) respectively.

3.3 Separation of quaternary ion systems

3.3.1 $NaCl+MgSO_4$

In this quaternary ion system Na^+ ions permeated (52 to 71 %) with Cl^- ions (70 to 72 %) as shown in Figure 4(a) and 4(c), whilst Mg^{2+} ions were rejected with SO_4^{2-} ions at higher values greater than 96 % as shown in Figure 4(b) and 4(d) respectively. In addition, it is observed that divalent Mg^{2+} ion worsens the permeation of Cl^- ion in comparison to the ternary $NaCl+Na_2SO_4$ system where the rejection decreased from 80 to 59 %. It is difficult to attain a high performance separation in such systems. Nevertheless, it is possible to partly separate $NaCl$ from $MgSO_4$ at relatively high concentrations.

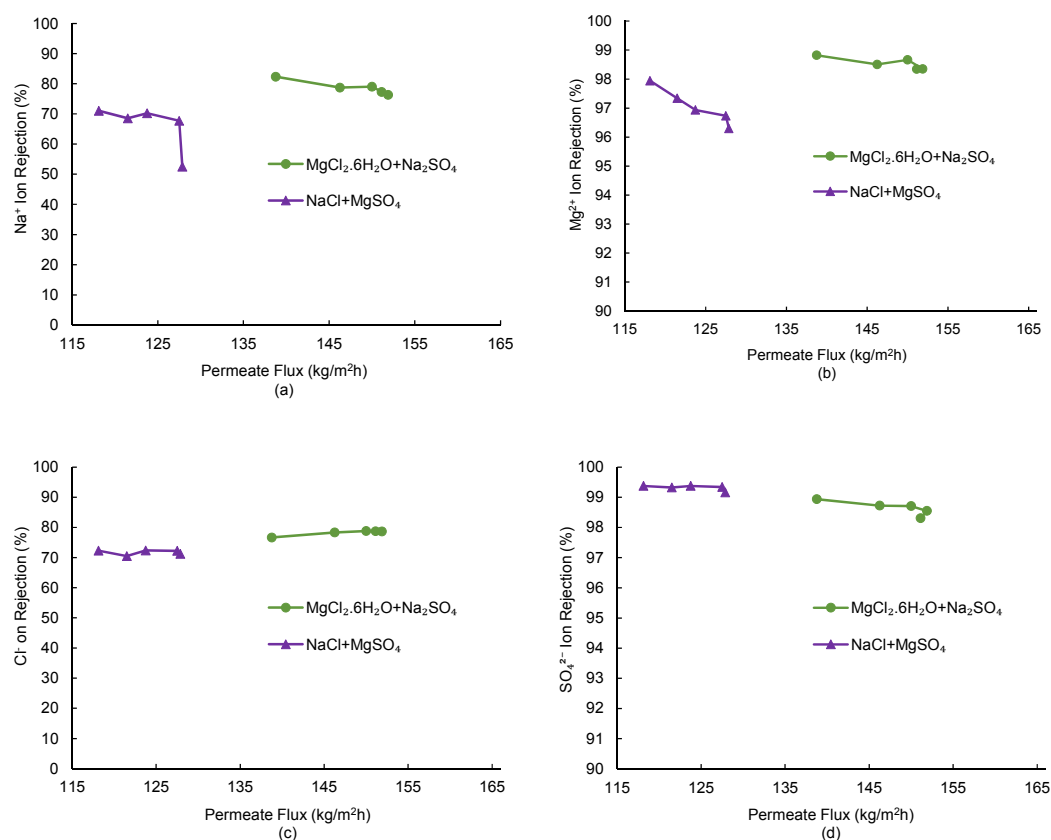


Figure 4: Rejection of cations and anions as a function of permeate flux in quaternary ion system

3.3.2 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$

It was observed that in this quaternary ionic system the divalent ions were better rejected than monovalent ions. The rejections of Mg^{2+} ion and SO_4^{2-} ion were greater than 98 % as shown in Figure 4(b) and 4(d) respectively. Cl^- ion permeated with Na^+ ion to keep the electroneutrality condition as elucidated in Figure 4(a) and 4(c) with rejections in the range of 76 to 82 % without any considerable effect of concentration polarization.

4. Conclusions

SO_4^{2-} as a divalent co-ion, showed strong electrostatic exclusion from membrane and resulting in a very high rejection. In addition, due to the zero current density at steady state, counter-ions Mg^{2+} was rejected as well. Monovalent ions Na^+ and Cl^- showed less rejection than divalent ions and could show negative rejection under certain conditions. Monovalent ions were permeated together to keep the electroneutrality condition. Concentration polarization may have significant effects on rejection phenomenon especially in case of concentrated solutions. In summary, the experimental study of NF separation performance for complex electrolyte mixtures is beneficial in lieu of process prediction, effective development and optimisation.

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References

- Bandini S., Vezzani V., 2003, Nanofiltration Modeling: The Role of Dielectric Exclusion in Membrane Characterization, *Chemical Engineering Science*, 58, 3303-3326.
- Bowen W.R., Mukhtar H., 1996, Characterization and Prediction of Separation Performance of Nanofiltration Membranes, *Journal of Membrane Science*, 112, 263-274.
- Bowen W.R., Mohammad A.W., Hilal N., 1997, Characterisation of Nanofiltration Membranes for Predictive Purposes - Use of Salts, Uncharged Solutes and Atomic Force Microscopy, *Journal of Membrane Science*, 12, 91-105.
- Hunter R.J., 1981, *Zeta Potential in Colloid Science: Principles and Application*, Academic Press, London, UK.
- Lyshevski S.E., 2014, *Dekker Encyclopedia of Nanoscience and Nanotechnology*, 3rd ed., CRC Press, Boca Raton, USA.
- Labbez C., Fievet P., Thomas F., Szymczyk A., Vidonne A., Foissy A., 2003, Evaluation of the "DSPM" Model in a Titania Membrane: Measurements of Charged and Uncharged Solute Retention, Electro-kinetic Charge, Pore Size and Water Permeability, *Journal of Colloid and Interface Science*, 262, 200-211.
- Li N.N., Fane A.G., Winston W.S., Matsuura T., 2008, *Advanced Membrane Technology and Applications*, Wiley-Blackwell, Oxford, UK.
- Samee M.A., Elgohary A., Harasek M., Friedl A., 2016, Experimental Investigation of Nanofiltration Process for the Separation of Complex Sugar Mixtures Containing Mono- and Multivalent Salts, *Chemical Engineering Transactions*, 52, 799-804.
- Schaep J., Vandecasteele C., Mohammad A.W., Bowen W.R., 1999, Analysis of the Salt Retention of Nanofiltration Membranes Using the Donnan Steric Partitioning Pore Model, *Separation Science and Technology*, 34, 3009-3030.
- Szymczyk A., Labbez C., Fievet P., Vidonne A., Foissy A., Pagetti., 2003, Contribution of Convection, Diffusion and Migration to Electrolyte Transport Through Nanofiltration Membranes, *Advances in Colloid and Interface Science*, 103, 77-94.
- Szoke S., Patzay G., Weiser L., 2002, Characteristics of Thin-film Nanofiltration Membranes at Various pH-Values, *Desalination*, 150, 123-129
- Takagi R., Nakagaki M., 1990, Theoretical Study of the Effect of Ion Adsorption on Membrane Potential and Its Application to Collodion Membranes, *Journal of Membrane Science*, 53, 19-35.
- Timmer J. M., 2001, *Properties of Nanofiltration Membranes: Model Development and Industrial Application*, PhD thesis, Technische Universiteit Eindhoven, Netherlands.
- Wang X. L., Tsuru T., Togoh M., Nakao S., Kimura S., 1995, Evaluation of Pore Structure and Electrical Properties of Nanofiltration Membranes, *Journal of Chemical Engineering of Japan*, 28, 186-192.